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"Environmental and Energy Engineering Sciences"

Cycle (XXXIII)

Dissertation Title

"Advanced oxidation processes (AOPs) for the treatment of liquid wastes"

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Dedication

I dedicate this research to my Mother, Father, Sister and Teachers who have always encouraged and supported me to strive for knowledge.

Contents

Abstract

Advanced oxidation processes (AOPs) are very efficient technologies for wastewater treatment. The main objective of this study is to develop new, sustainable and cost effective AOPs for the treatment of liquid wastes. Heterogeneous Fenton like oxidation has been chosen as the model AOP for the treatment of liquid wastes due to ease of operation, recyclability of the catalyst, cost effectiveness and above all high organic removals. The development of a sustainable heterogeneous catalyst is a challenging task and requires a perfect combination of a metal over an appropriate support.

First, a range of metallic catalysts supported over ZrO_2, CeO_2 and ZrO_2-CeO_2 are prepared by wet impregnation method, characterized by standard techniques and tested for their activities in oxidation process, using aqueous solution of ibuprofen (IBP) as model pollutant. Iron and copper-based catalysts supported over ZrO_2 achieved maximum degradation and mineralization of IBP. Moreover, the oxidation pathway confirmed that they do not form more toxic metabolites than that of the parent molecule.

Second, the catalyst Cu/ZrO_2 is used for the oxidation of model pollutant IBP and heterogeneous Fenton process is optimized by investigating the favorable conditions of pH, catalyst dose, H_2O_2 dose and temperature. The optimized process was employed for the treatment of landfill leachate and analogous results with similar process efficacy were obtained. The Fenton process removed 65 and 92% of the total dissolved organic carbon (TDOC) from landfill leachate in a single-step and two-step processes, respectively. The developed catalyst is efficient for the removal of adsorbable organic halogens (AOX) and is also recyclable without losing activity. The qualitative abatement of organics is determined through proton nuclear magnetic resonance (^1H NMR) analysis which revealed that the oxidation of leachate significantly degraded the organics.

Third, to further enhance the efficacy of the Fenton process, a series of Fe/ZrO_2 and Cu/ZrO_2 catalysts with varying metal loadings are prepared and their activities are investigated in terms of IBP mineralization. The optimum metal loading for both type of catalysts is 7.5% but Fe/ZrO_2 achieves maximum activity (80%) at pH 3 while Cu/ZrO_2 affords maximum activity (70%) at pH 5. Moreover, both type of catalysts with 7.5% metal loading undergo minimal leaching at optimum conditions which are lower than the European Union directives for release in wastewater. However, Fe/ZrO_2 requires higher catalyst doses and loses its activity when recycled due to complex formation with the degradation products. On the other hand, lower doses of Cu/ ZrO_2 achieve higher and stable IBP mineralization upon recycling.

Fourth, a series of Fe and Cu bimetallic catalysts are prepared to induce better redox cycle in the catalyst composites. These catalysts are very active within the pH range of 3 and 4. The extent of bimetallic activity is governed by the limiting metal while the excess metal component also

exhibits monometallic behavior. Among the developed catalysts 5Cu/5Fe not only displays the highest TOC abatement (82%) under optimum conditions but also sustains minimum metal loses. Moreover, the bimetallic catalysts with balanced metal loadings are better able to yield stable activities upon recycling.

Finally, iron slag is employed for the treatment of leachate because it contains iron species that can catalyze the heterogeneous Fenton process. Characterization of iron slag revealed that it contains iron in the form of metal oxides which are suitable as heterogeneous catalyst. Iron slag mineralized 75% of organics present in leachate under optimum conditions; pH 3, catalyst dose – 1g/L and reaction temperature 70 °C. This is very important from a circular economy perspective because a solid waste (iron slag) that is produced in huge quantities can be effectively used as a catalyst for the treatment of highly polluted liquid wastes.

Chapter 1

A brief introduction of advanced oxidation processes (AOPs)

1.1. Introduction

Water pollution is a serious threat towards the management of sustainable water sources [1-3]. The immense population growth triggering vast expansion in industrial and agricultural activities have turned the water pollution, an even serious concern among the scientific communities [4]. Water pollution occurs when one or more substances that will modify the water in negative way are discharged into it [5]. These undesired substances can adversely affect the end users and also to the environment [6]. Water contamination can arise from water to water, air to water and soil to water. Some of the main sources of water contamination are highlighted in the Figure 1.1 [7].

The principal pollutants being released by these sources are organic, inorganic and microbial. Organic pollutants include personal care products, pharmaceuticals, pesticides, herbicides, petroleum products and detergents. Inorganic pollutants typically comprise of chemical wastes, heavy metals, solids and fertilizers while microbial pollutants include bacteria, viruses and protozoa [8]. However, in this study we have only focused on the processes which specifically targets the removal of organic pollutants.

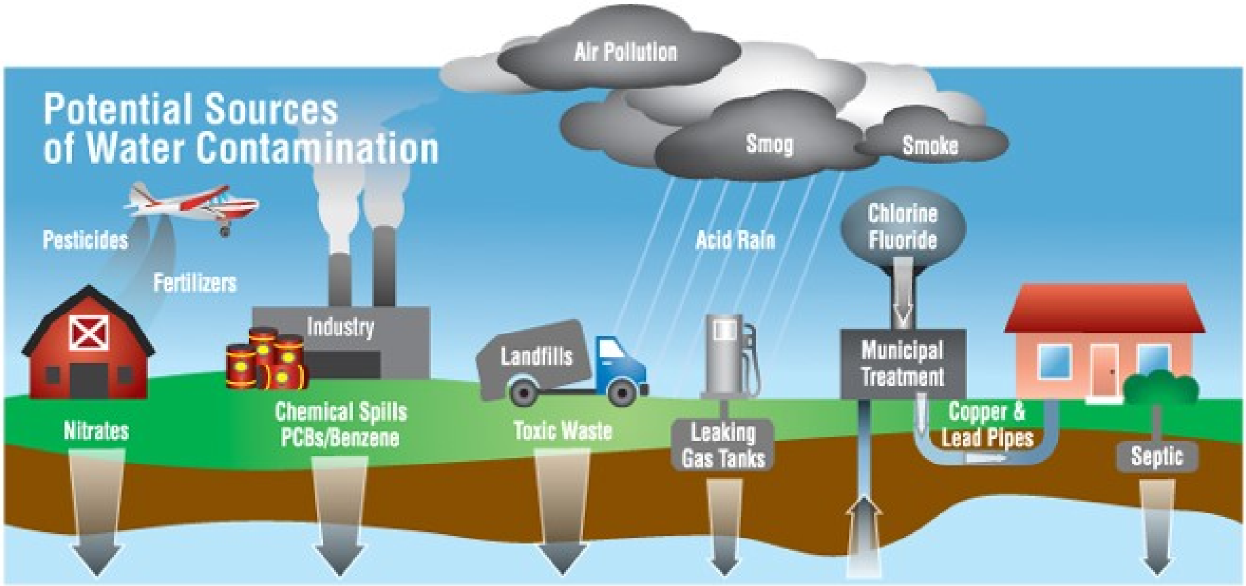

Figure 1.1: Sources of water pollution [7]

1.2. Wastewater treatment processes

All kinds of water pollutants have their specific adverse environmental impacts and treated employing a range of processes. However, organic compounds are considered the most problematic because not only they can persistently remain in their original released form but may also change into more toxic metabolites [9]. There are numerous wastewater treatment processes but these processes can be broadly classified into three types namely (Figure 1.2): physical, biological and chemical [10, 11].

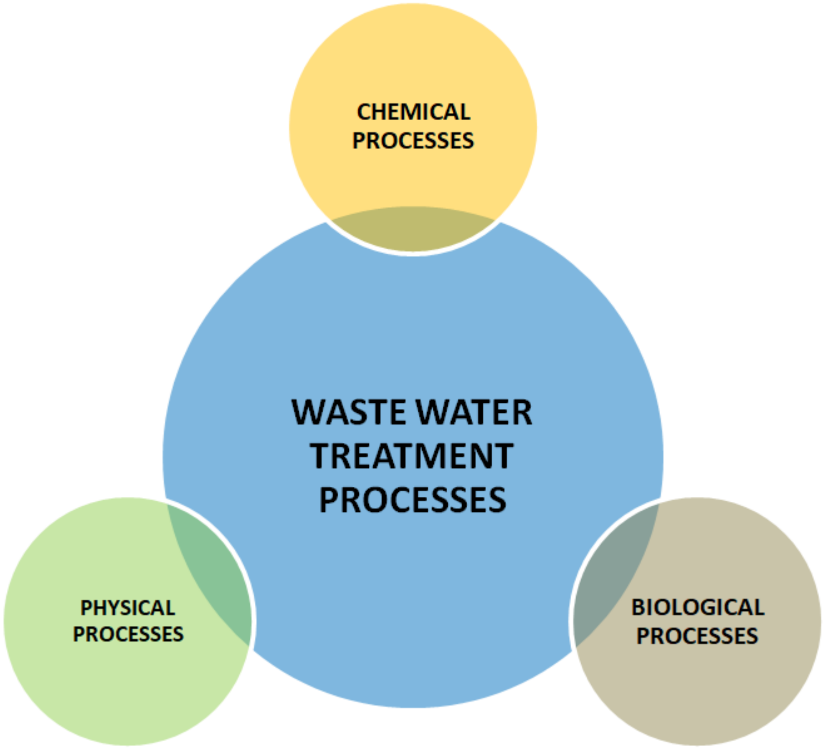

Figure 1.2: Main wastewater treatment processes

1.2.1. Physical processes

These processes employ the concept that the pollutants can be separated from the aqueous phase either through physical or mechanical means. The typical physical processes being used for wastewater treatment include filtration, absorption, sedimentation and membrane filtration. However, all these processes are mostly effective for the removal of inorganic pollutants. Moreover, these processes have another underlying limitation that the separated concentrated stream needs further processing such as dewatering and disposal which may give rise to other serious environmental implications [5].

1.2.2. Biological processes

These wastewater treatment processes rely on microorganisms for the elimination of organic compounds. There are two types of biological processes i.e. aerobic and anaerobic [12]. These processes are somewhat efficient, only if the organic loading in the wastewater streams is low and is mainly originated from domestic sources. Activated sludge process has been used on industrial scales for the organic abatement for wastewater streams. However, these processes cannot be used for the removal of organics, originating from industrial sources due to their higher molecular weights, complexity and recalcitrant nature. Similarly, the efficacy of these processes is very limited for the remediation of emerging organic pollutants such as pharmaceuticals and personal care products [13-16]. Moreover, it is also likely that the recalcitrant organic compounds are transformed into metabolites which are even more persistent and toxic than the parent compounds [9].

1.2.3. Chemical processes

A range of chemical processes are available such as neutralization, adsorption, chemical coagulation and flocculation; all of them employ specific chemicals depending upon the type of targeted pollutants. However, a new class of chemical processes i.e. advanced oxidation processes (AOPs) have gain tremendous amount of interest from the scientific and industrial communities due to their remarkable salient features regarding the abatement of organic pollutants [17]. All AOPs essentially rely on the generation of hydroxyl radicals (OH•) through different means [18], which in turn attack the organic compounds and either transform them into smaller (easily biodegradable organics) or completely mineralize them into carbon dioxide and water [19-22]. The theme of this research is to harness scalable AOPs for the treatment of wastewaters/liquid wastes and here we briefly explain the main characteristics of these processes.

1.3. Advanced oxidation processes (AOPs)

All the processes which lead towards the intentional generation of hydroxyl radicals (OH•) through any means are generally defined as Advanced oxidation processes (AOPs). The enormous environmental stress caused by the release of large amounts of emerging organic pollutants into the water bodies have forced the scientists working in the area of water treatment, to develop new and innovative AOPs by employing different mechanisms. Although, numerous AOPs have been reported by researchers but these can be broadly classified into five categories as shown in Figure 1.3 [23-25]. These processes are discussed one by one in the following paragraphs.

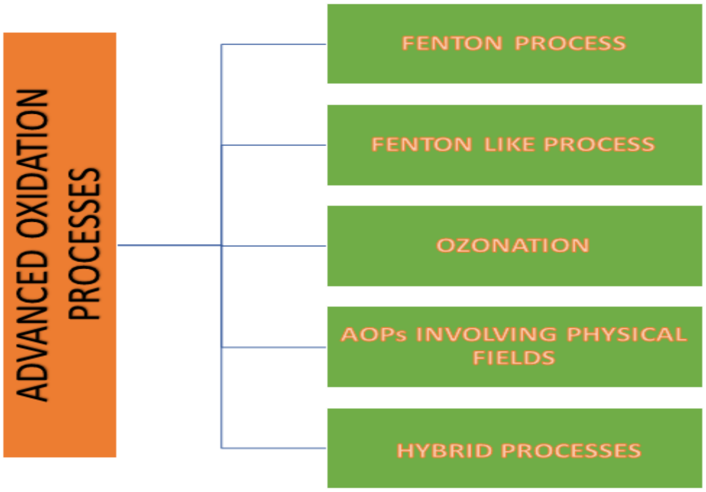

Figure 1.3: Broad classification of advanced oxidation processes (AOPs)

1.3.1. Fenton process

"The process which employs any chemical as a source of Fe(II) along with hydrogen peroxide as Fenton reagent for the generation of hydroxyl radicals (OH•) is termed as Fenton process [26]." Fenton reagent was developed by Henry John Horstman Fenton in 1890 [27]. The process using ferrous ions and H_2O_2 produces very reactive (OH•) species at ambient conditions which are non-selective for the abatement of organic compounds [28-30].

but Here, for the sake of simplicity, only the key Fenton reaction is presented (Eq. 1) [31] (for a complete report on the full set of reactions involved in the Fenton process, please refer to our review [13]). The OH• reacts with organics and converts them into organic radicals which undergo a series of oxidation reactions to yield secondary and tertiary metabolites (Eq.2) [32].

$$Fe^{+2} + H_2O_2 \longrightarrow 2Fe^{+3} + OH\bullet + OH^- \qquad (Eq.1)$$

$$RH + OH\bullet \longrightarrow H_2O + R \longrightarrow \text{Oxidation} \qquad (Eq.2)$$

The Fenton process is a homogeneous phase reaction and iron ions continuously change from ferrous to ferric and vice versa [33]. The Fenton process is the very first and the most fundamental process which laid out the foundation of advanced oxidation processes and have found industrial scale application for the treatment of wastewaters. A schematic overview of the Fenton process is shown in Figure 1.4. As evident from the process diagram, pH control in the Fenton process is critical, not only to achieve high process efficacy but also to minimize the loss of homogeneous catalyst as iron sludge [13].

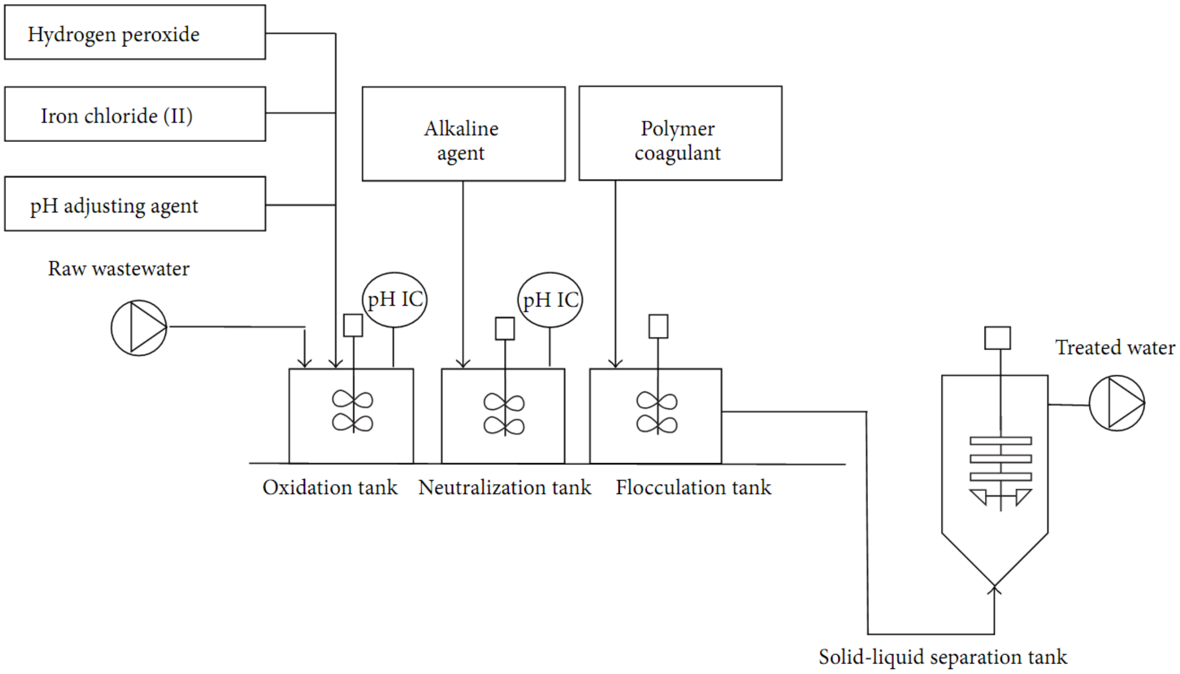

Figure 1.4: Industrial layout of the conventional Fenton process

1.3.2. Fenton like process

"Fenton like processes are those processes in which either Fe^{+3} or other metallic ions but excluding Fe^{+2} react with the H_2O_2 for the generation of OH• radicals [17]." Fenton like process, as the name suggests is mainly originated from the Fenton process because the ferric ions (Fe^{+3}) in the Fenton process may also react with the H_2O_2 and generate OH• radicals and this reaction is termed as Fenton like reaction (Eq.3) [34].

$$Fe^{+3} + H_2O_2 \longrightarrow Fe\text{-}OOH^{+2} + H^+ \qquad \text{(Eq.3)}$$

Unlike the conventional Fenton process, the Fenton like processes incorporates heterogenous phase reactions for the generation of OH• radicals. The concept of replicating Fenton process but with new and better characteristics has encouraged the research community to develop Fenton like processes. The potential of developing such processes by employing other transition metals is not only gigantic but also promising in a sense that tailor made processes can be developed, keeping in view of the nature of the organics to be dealt with. Moreover, the limitations of traditional Fenton process such as acidic pH, generation of large volumes of residual sludge and non-recyclability of the catalyst can be conveniently addressed [35]. The notable transition metals which have been harnessed for the development of Fenton like processes are: copper, manganese, silver, cerium, nickel, zinc, chromium, cobalt and ruthenium [36, 37]. Generally, the metallic oxides act as the heterogeneous catalysts and often these are supported over a support material [13].

1.3.3. Ozonation

Ozone has long been used for the disinfection of water/wastewater [38]. "The ozone based AOPs are the processes in which ozone is used as a primary source for the generation of OH• radicals [39]." An essential component of ozone-based process is the ozonator which generally harnesses electrical energy and ambient air to produce ozone. In this type of AOP, hydroxyl radicals are indirectly generated which involves two reactions i.e. production of H_2O_2 and then its decomposition into OH• radicals (Eq. 4 and 5) [40].

$$O_3 + H_2O \longrightarrow O_2 + H_2O_2 \qquad \text{(Eq.4)}$$

$$H_2O_2 \longrightarrow 2OH\bullet \qquad \text{(Eq.5)}$$

Ozone based process is different than the other AOPs in a way that it specifically targets only electron rich organic compounds such as those containing double bonds and aromatic rings etc. [41]. The targeted approach of this process is very helpful for the treatment of selective pollutants and thus can be useful to reduce the energy inputs. Moreover, this process is handy when the treatment objective is either to integrate the ozone process with the biological process or the intention is to conserve the useful resources in the treated effluent. However, ozone-based processes cannot be implemented for the treatment of wastewaters where the aim of the treatment is the complete or maximum removal of organic pollutants [42].

1.3.4. AOPs based on physical fields

“The processes which employ physical fields within the aqueous phase and corresponding chemical and physical processes are induced which either directly or indirectly target the pollutants in the wastewater through the generation of reactive oxidizing species, are collectively termed as physical field AOPs [43, 44].” Some of these processes are briefly described here.

1.3.4.1. Electrochemical AOPs

Electrochemical AOPs typically works by employing electrodes which act as point sources of OH• radicals [45-47]. These radicals are generated via O_2 evolution from water oxidation without the addition of any chemicals [48]. Although, electrochemical AOPs are considered eco-friendly for the removal of organics but the reactivity range of OH• radicals generated in these processes is very limited (1 µm) with respect to the electrode because these radicals are generated onto the electrode surface [49]. As the diffusion of OH• radicals in the aqueous phase is restricted and that is why electrochemical AOPs cannot yield very high process efficacies [38]. Electrochemical AOPs are energy intensive processes and special attention must be paid to the energy cost while assessing the overall cost of such processes [38].

1.3.4.2. Microwave assisted AOPs

These processes utilize high energy microwave irradiations (300 MHz – 300 GHz) for the degradation of organics in wastewaters [50]. However, these processes are generally used along with the oxidants to speed up the organic removal process [51]. Microwaves can elevate reaction rates by inducing targeted heating of the contaminants by means of internal molecular vibrations [38]. However, most of the microwave irradiations are merely converted into heat energy and there is an additional requirement to install cooling devices to remove the excess heat from the treated effluent [38].

1.3.4.3. Ultrasound assisted AOPs

These AOPs work on the principle that the introduction of ultrasonic waves (20 – 500 KHz) in the wastewater will produce micro bubbles. These micro bubbles will rapidly form and collapse (cavitation phenomenon) and during this process, high temperature and pressure will be induced that aid in the generation of hydroxyl radicals that will ultimately target the organic pollutants [52]. A coupling effect of thermal decomposition and oxidation by free radicals is mainly responsible for the organic abatement in these AOPs [53]. However, these processes have only been implemented on lab scale and also the electric efficacy of ultrasonic processes is very low and that is why these processes are often integrated with other AOPs [54, 55].

1.3.4.4. UV-based AOPs

“All the oxidation processes which use ultraviolet irradiations for the organic abatement are classified as UV-based AOPs .” The UV light is either generated from the mercury lamps or from the light emitting diode (LED) lamps [56]. The monochromatic UV light emitted from the source lamps (257.3 nm) is harnessed to remove organics from wastewaters [57]. UV-based AOPs can remove the organic pollutants by working on the principle that when the organic compounds high energy UV light directly from the source, it can cause the destruction of chemical bonds and subsequent breakdown of the contaminants. However, some organic pollutants cannot be efficiently degraded by UV irradiation alone and the addition of the oxidant is necessary for improved organic removal [58, 59].

1.3.5. Hybrid AOPs

“These processes can be defined as those processes which utilizes two or more individual AOPs together for the removal of organic compounds from wastewaters [38].” This approach is either employed when the overall efficacy of the AOP needs to be increased or when a wide range of organic compounds are present in wastewater and a single process is inadequate for the abatement of all types of organic compounds. The combination of AOPs increases the generation of reactive oxidizing species and ultimately, an enhanced wastewater treatment efficacy is attained.

1.4. Conclusion

There is a great variety of advanced oxidation processes (AOPs) which have been successfully employed and proven efficient for the removal of organic contaminants from wastewaters. Not only that, but there is still space for the development of even new AOPs. However, the application of each individual AOP, basically depends upon the availability of input chemicals, energy and overall cost of the process. Moreover, selection of individual AOPs can also be made based on the treatment requirements. Among all the AOPs, heterogeneous Fenton like process has all the features deemed fit for any process, to sustainably scale up wastewater treatment.

In this thesis we have focused on the heterogeneous Fenton process. We started with the development of iron and copper-based catalysts supported on zirconia for the treatment of model solutions (based on ibuprofen) and then went on to study the degradation capacity for real liquid waste (landfill leachate).

The final aim of this experimental research is to develop new AOPs on lab scale with the futuristic approach of implementation on pilot and industrial scales.

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Chapter-2

Analytical and characterization techniques

2.1. Introduction

The progress in science heavily relies on the sophisticated techniques used for the analysis and characterization of materials. It is especially true in the field of chemical engineering where characterization of materials is critical to better control, optimize and develop new processes. The processes involving catalysts and liquid streams, require precise monitoring of the characteristics of these materials. Moreover, these techniques are also essential to comprehend the in-depth mechanism of catalytic processes [1]. The treatment of wastewater streams is becoming a challenge these days due to the release of new and emerging organic pollutants. Moreover, wastewater treatment is a difficult task because environmental regulatory authorities have enforced very stringent guidelines. In order to meet these guidelines, new and innovative wastewater treatment processes are being introduced. Advanced oxidation processes (AOPs) have gain high acceptability among the researchers for the treatment of wastewaters. These processes rely on the generation of reactive oxidizing species for the organic abatement. Among AOPs, heterogenous Fenton like process which employ a catalyst along with the oxidant, have shown bright prospects in the field of wastewater treatment due to high efficacies and the scalability point of view [2]. Typically, wastewater effluents are described based on their chemical oxygen demand (COD), total organic carbon (TOC), and heavy metals. The wastewater treatment through heterogenous Fenton like process, requires the harnessing of additional techniques for the characterization of catalysts to monitor their stabilities. The efficacy of the heterogenous Fenton process cannot be examined without the application of recommended analytical techniques. In this chapter we have discussed some main analytical techniques for the characterization of solid catalyst and wastewaters.

2.2. BET Surface Area

Surface area is a very important aspect of a catalyst to monitor its activity and stability, [3]. It is the total surface area of the solid sample and is comprised of external as well as the area contributed by internal pores. It is measured in square meters per gram of dry sample. Though, higher exposed surface area in the heterogenous Fenton process is advantageous due to increased number of active sites but very high surface area of the catalyst may also make it prone to enhanced leaching [4]. Generally, catalyst surface area is determined by exposing it to a gas adsorption and the corresponding adsorbed gas is the indication of the total surface area. Total surface area also helps us to determine how much active metal is needed to completely cover the support material by forming a monolayer over it [5]. There are different methods used to measure surface area and each method can yield different results. Most methods are based on the isothermal adsorption of nitrogen. We measured the surface area of the catalysts using the Brunauer, Emmett and Teller (B.E.T.) method and it can be illustrated with Eq. 1.

$$\frac{1}{W\left[\left(\frac{P_0}{P}\right)-1\right]}=\frac{1}{W_mC}+\frac{C-1}{W_mC}\frac{P}{P_0} \qquad \text{(Eq. 1)}$$

Where, W is the weight of nitrogen adsorbed at a given P/P_o (P is the pressure nitrogen adsorbed and P_0 is the saturation pressure), W_m the weight of gas to give monolayer coverage and C, a constant that is related to the heat of adsorption. A linear relationship between $1/W[(P_o/P)-1]$ and P/P_o is required to obtain the quantity of nitrogen adsorbed. Catalyst samples are pre-treated to remove any contaminants adsorbed during the atmospheric exposure and cooled in vacuum to cryogenic temperature. An adsorbent (typically nitrogen) is added in controlled increments and after each increment, the pressure is allowed to reach equilibrium and the quantity of the gas adsorbed is calculated. The gas volume adsorbed at each pressure (at one constant temperature) defines an adsorption isotherm, from which the quantity of gas required to form a monolayer over the external surface of the solid and its pores is determined. With the area covered by each adsorbed gas molecule known, the surface area can also be calculated.

2.3. X-Ray Diffraction (XRD)

Solid catalysts are mostly crystalline in nature and XRD analysis can give us an insight regarding the nature of crystals, concentration of each type of crystals and also the size of the crystals [1]. A beam of X-rays is directed towards the analyte and upon reflection, the scattered rays give important information regarding the crystalline structure of the solid material [6]. The X-ray diffraction pattern returning from a material depends upon its crystal structure. Crystal atoms are arranged in regular patterns, while X-rays are electromagnetic radiation. Crystal atoms scatter incident X-rays, primarily through interaction with the atoms' electrons. The elastic scattering of electrons produces a regular array of spherical waves. Generally, these waves cancel each other out through destructive interference, however, they add constructively in a few specific directions, as determined by Bragg's law (Eq. 2 and Figure 2.1).

$$2d\sin\theta = n\lambda \qquad \text{(Eq. 2)}$$

Where d is the spacing between diffracting planes, θ is the incident angle, n is an integer, and λ is the beam wavelength. The number and position in terms of 2θ, of the reflection peaks depend on the cell parameters, crystal class, lattice type and wavelength used to collect data, while peak intensity depends on the type of present atoms and their position [7].

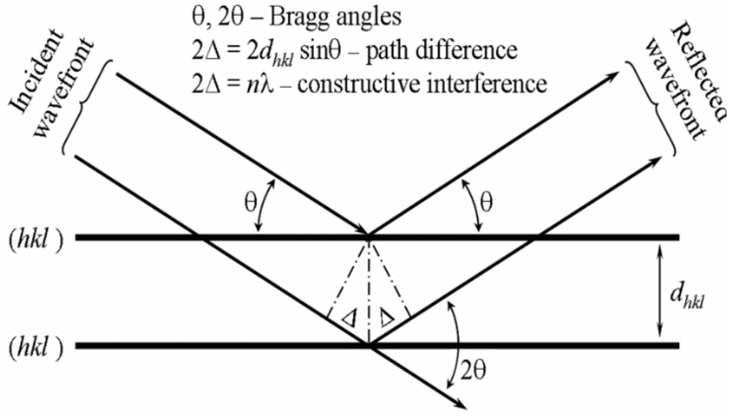

Figure 2.1: Illustration of Bragg's law

2.4. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM), technique is very useful to understand the surface properties of the solid catalysts such as texture, homogeneity and composition. This technique employs a focused beam of electrons to produce a high-resolution image which reveals the solid surface features. The signals coming from the interactions of the sample and electrons reveal the external morphology of the sample (texture), crystalline structure, chemical composition and also the specific orientation of the materials which formulate the sample [8]. Generally, SEM data is collected over a selected area of the sample surface and a two-dimensional image is generated that displays the spatial changes in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining of chemical compositions (using EDS) [8, 9].

2.5. Temperature Programmed Reduction (TPR)

Temperature programmed reduction (TPR) is a powerful technique to analyse the reduction properties of catalysts [3, 10]. Heterogenous Fenton process involves redox reactions and consequently the reduction behaviour of the materials gives us a very good overview regarding the catalytic activity of solid catalysts. This technique consists in heating the catalyst with a linear temperature ramp in a flow of hydrogen while monitoring the hydrogen consumption. Moreover, the amount of the reducible species in the catalyst and their degree of reduction can be derived from the integrated hydrogen consumption. The results obtained by TPR experiments are correlated to the redox activity of the investigated solid samples.

2.6. Inductivity Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES)

This analytical technique is not only useful for the determination of heavy metals in aqueous samples to comply with the environmental regulation but is equally useful to monitor the exact metal loadings in a solid catalyst through acid solubilization process. Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP- AES) is an emission spectrophotometric technique, exploiting the fact that excited electrons emit energy at a given wavelength as they return to ground state after excitation by high temperature Argon Plasma [11]. This technique works on a principal that all elements emit energy only at specific wavelengths which is related to their atomic character. When the electrons come back from excited state to the ground state, a unique energy transfer occurs depending upon the electronic configuration of the orbitals of elements. [11]. The energy transfer is inversely proportional to the wavelength of electromagnetic radiation which is given by (Eq. 4) and hence the wavelength of light emitted is also unique.

$$E = hc/ \lambda \qquad \text{(Eq. 4)}$$

where, h is Planck's constant, c the velocity of light and λ is wavelength

Although all elements emit energy at multiple wavelengths but generally, only a single wavelength is chosen for individual elements. The intensity of the emitted energy at the specific wavelength is proportional to the amount (concentration) of that element in the sample being analyzed. Thus, the intensities of the different wavelengths obtained from the sample being analyzed and comparing these with the standard reference, the quantity of the elements present in the sample is determined. The wavelengths used in AES ranges from the upper part of the vacuum ultraviolet (160 nm) to the limit of visible light (800 nm). As borosilicate glass absorbs light below 310 nm and oxygen in air absorbs light below 200 nm, optical lenses and prisms are generally fabricated from quartz glass and optical paths are evacuated or filled by a non-absorbing gas such as Argon [11, 12]. Generally, a calibration curve is obtained using an ICP 23-element standard solutions which are prepared in 5% HNO_3. Yttrium (Y) is used as an internal standard. The method detection limit (MDL) is calculated as 3 s/m (s = Standard deviation of 10 replicate blanks and m = slope of the calibration curve for each element).

2.7. Total Organic Carbon (TOC)

TOC has become an important parameter used to monitor overall levels of organic compounds present. This has happened despite the lack of any direct quantitative correlation between total organic carbon and the total concentration of organic compounds present and reflects the importance of having an easy-to-measure, general indicator of the approximate level of organic contamination [13].

A typical analysis for total carbon (TC) measures both the total organic carbon (TOC) present and the complementing total inorganic carbon (TIC), the latter representing the amount of non-organic carbon, like carbon in carbonate minerals. Subtracting the inorganic carbon from the total carbon yields TOC.

TOC methods use either high temperature (typically 680 to 950°C) with catalysts and oxygen or air, or lower temperatures (<100°C) with ultraviolet irradiation and/or one or more chemical oxidants and catalysts to convert organic carbon into carbon dioxide. The CO_2 may be purged from the sample, dried, and transferred via carrier gas to a nondispersive infrared analyzer (NDIR) or coulometric titrator. Alternatively, CO_2 may be separated from the sample via a CO_2-selective membrane into high-purity water, where the increase in conductivity corresponds to the amount of CO_2 passing through the membrane.

The methods and instruments used to measure TOC analyze fractions of total carbon (TC) and measure TOC via two or more determinations. These fractions of total carbon are defined as:

- inorganic carbon (IC)—carbonate, bicarbonate, and dissolved CO_2;
- total organic carbon (TOC)—all carbon atoms covalently bonded in organic molecules;
- dissolved organic carbon (DOC)—the fraction of TOC that passes through a 0.45-µm-pore-diameter filter;

- suspended organic carbon (also called particulate organic carbon)—the fraction of TOC retained by a 0.45-µm filter;

- purgeable organic carbon (also called volatile organic carbon)—the fraction of TOC removed from an aqueous solution via gas stripping under specified conditions; and

- nonpurgeable organic carbon (NPOC)—the fraction of TOC not removed by gas stripping. In most cases, inorganic carbon is purged and not "determined," in which case only NPOC is determined and purgeable organic carbon is assumed to be negligible.

Since all TOC analyzers only actually measure total carbon, TOC analysis always requires some accounting for the inorganic carbon that is always present. One analysis technique involves a two-stage process commonly referred to as TC-IC. It measures the amount of inorganic carbon (IC) evolved from an acidified aliquot of a sample and also the amount of total carbon (TC) present in the sample. TOC is calculated by subtraction of the IC value from the TC of the sample. Another variant employs acidification of the sample to evolve carbon dioxide and measuring it as inorganic carbon (IC), then oxidizing and measuring the remaining non-purgeable organic carbon (NPOC). This is called TIC-NPOC analysis. A more common method directly measures TOC in the sample by again acidifying the sample to a pH value of two or less to release the IC gas but in this case to the air not for measurement. The remaining non-purgeable CO_2 gas (NPOC) contained in the liquid aliquot is then oxidized releasing the gases. These gases are then sent to the detector for measurement.

2.8. Chemical Oxygen Demand (COD)

The chemical oxygen demand (COD) measures the amount of oxygen required to fully oxidize all organic compounds into carbon dioxide and water in a sample of surface water or wastewater. It is commonly expressed in mass of oxygen consumed over volume of solution (mg O_2/l) This method is the most widely used method to estimate the organic loading of wastewater samples [14]. The COD analysis works on the principle that the organic compounds in aqueous phase can be oxidized into CO_2 and H_2O using strong oxidizing agents ($K_2Cr_2O_7$) in acidic solution (H_2SO_4) under condition of heat (Eq. 5). Silver sulfate is used as a catalyst and mercuric sulfate is added to remove chloride interference.

A known excess amount of the oxidant is added to the sample. Once oxidation is complete, the concentration of organics in the sample is calculated by measuring the amount of oxidant remaining in the solution. by titration with ferrous ammonium sulphate, which allows the determination of the consumed oxygen equivalents.

$$C_aH_bO_c + dCr_2O_7\_2 + 8dH^+ \xrightarrow{heat} 2dCr^{3+} + aCO_2 + (b+8d)/2H_2\mathrm{O} \qquad \text{(Eq. 5)}$$

d = 2a/3 + b/6 - c/3

For a faster determination, most laboratories prefer using COD tests in tubes, thereby minimizing costs and chemical disposal. The reagent vials contain premeasured solutions of sulfuric acid and potassium dichromate. To perform the COD determination, the analyst simply adds sample to the vial and then heated it for two hours at 150 °C in a standard digestor block. Once digestion is completed, results are obtained using a photometer. Usually, built-in COD methods and calibrations on proprietary instrument can be used without the need for a new calibration.

2.9. Ultraviolet – Visible Spectroscopy (UV-VIS)

Ultraviolet-Visible Spectroscopy (UV-Vis) can help in monitoring the colored organic compounds present in wastewaters. Moreover, during wastewater treatment processes, when color changes from dark to light, indicates about the extent of organic abatement depending upon the intensity of color left after treatment. UV-Vis spectroscopy is a type of absorption spectroscopy in which light of ultra-violet to visible regions (200-700 nm) is absorbed by the molecules in the aqueous sample which results in the excitation of the electrons from the ground state to higher energy state. The absorption of light by these chemical compounds produces a unique spectrum which can be correlated for the identification of the compounds [15]. Generally, aqueous sample along with a reference sample is subjected to UV-Vis source and a comparison between the absorptions give an indication regarding the organic abatement [16].

2.10. Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance (NMR) is a very sophisticated analytical technique, generally used for the identification of organic compounds. It can be exploited to track the organic profiles during the heterogenous Fenton process for wastewater treatment. This can also be used to examine which particular organic compounds are readily oxidizable and the organic compounds which show persistence towards Fenton like oxidation.

The nuclear magnetic resonance (NMR) works on the principle that all nuclei are electrically charged and many of them have spins as well. When an external magnetic field is applied then it is possible that energy is transferred from the base level to the higher energy level. This energy transfer takes place at a wavelength that corresponds to radio frequencies and when the spin returns to its base level, energy is emitted at the same frequency. The signal that matches this transfer is measured in many ways and processed in order to yield an NMR spectrum for the nucleus concerned [17].

The samples are placed in a magnetic field and the NMR signal is produced by the excitation of the nuclei with the aid of radio waves into nuclear magnetic resonance and is finally detected the help of sensitive radio receivers. The intramolecular magnetic field around an atom in a molecule changes the resonance frequency, thus giving access to details of the electronic structure of a molecule and its individual functional groups [18]. As the fields are unique or highly characteristic to individual compounds, NMR spectroscopy is the definitive method to identify monomolecular organic compounds. Besides identification, NMR spectroscopy provides detailed information about the structure, dynamics, reaction state, and chemical environment of molecules. The most common types of NMR are proton and carbon-13 NMR spectroscopy, but it is applicable to any kind of sample that contains nuclei possessing spin [19, 20].

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Chapter-3

Catalytic activity of metals in heterogeneous Fenton-like oxidation of wastewater contaminants: a review

Sajid Hussain, Eleonora Aneggi, Daniele Goi, Environmental Chemistry Letters (2021), https://doi.org/10.1007/s10311-021-01185-z

Abstract

Innovations in water technology are fundamental in finding solutions to the nowadays challenges: climate change, resource shortages, emerging contaminants, urbanization, sustainable development, and demographic changes. Nowadays the use of conventional wastewater processes is becoming increasingly challenging mainly due to the presence of biorecalcitrant organic matter. Liquid waste can be produced by all sectors of society including wastewater from industrial processes and they can be divided into subgroups depending on their nature and their toxicological risk. Therefore, an emerging technology is needed to deal with these highly concentrated and toxic non-biodegradable pollutants. Advanced oxidation processes such as Fenton, Fenton-like and hybrid processes have been successfully employed for the treatment of different types of wastewaters and liquid waste.

In this article we have comprehensively reviewed the application of some metallic catalyst- H_2O_2 systems in heterogeneous Fenton process. Each metallic catalyst- H_2O_2 system has unique redox cycle which is greatly influenced by an intrinsic factor such as oxidation states of the metal involved in the redox cycle and the most important extrinsic factor like pH of the aqueous phase. The metallic catalysts of iron and cerium form stable complexes with oxidation products and H_2O_2, therefore their activities are hindered. Copper only forms transitory complexes with oxidation products and its catalytic activity is easily restored during the continuous redox cycle while silver and manganese do not form complexes at all. The extent to which metallic catalysts can oxidize (mineralize/degrade) organics is of the order manganese > copper > iron > silver > cerium. The conclusive practicality of employing various metals in heterogeneous Fenton oxidation follow the sequence copper > manganese > iron > silver > cerium.

Keywords: Fenton process, heterogeneous, catalyst, H_2O_2, oxidation, wastewater treatment, AOP

3.1. Introduction

Over the past few decades, the massive industrialization and urbanization has triggered an enormous stress on the environment. Water being the fundamental pillar of the environment has been affected the most and numerous organic pollutants are being detected in ground and surface waters. Water contamination has raised an alarm for the scientific community because it has serious consequences for the humans as well as to the eco system [1]. To safeguard standard quality, it is crucial to carefully manage this precious resource, especially in the face of the current challenges: climate change, population growth, urbanization, and pollution. Innovations in water technology are fundamental in finding solutions to these essential issues. A key feature is the pollution of anthropogenic origin constantly introduced in the environment [2]. Nowadays, more than 700 emerging pollutants, their metabolites and transformation products, are present in the European aquatic environment. The list of emerging compounds and chemicals is significantly large and continuously growing with the introduction of new commercial compounds, disposal of chemicals and further identification of new molecules that includes pharmaceuticals and personal care products (PPCPs), pesticides, endocrine-disrupting chemicals (EDCs), industrial chemicals, surfactants and antibiotic resistant bacteria [3]. Conventional treatment processes (sedimentation and biological treatment) are not capable of removing these micropollutants and thus innovative technologies are required [4-10].

Advanced oxidation processes (AOPs), have been proven effective when it comes to deal with persistent organic pollutants [11-18]. AOPs are the processes which generates temporary species, fundamentally hydroxyl radicals ($OH^{\bullet}$) which attack the targeted pollutants and oxidize them [19-22]. The key features which make AOPs superior to other processes is their ability to be operated near ambient conditions, non-selective nature of $OH^{\bullet}$ radicals and conversion of pollutants into nontoxic products such as CO_2 and H_2O [23]. AOPs can also be integrated with existing biological processes as a pre-treatment strategy for the treatment of heavily polluted wastewater streams [24].

There are several types of AOPs based on the mechanism of $OH^{\bullet}$ generation. For instance, classical Fenton reaction, heterogeneous Fenton like reaction, processes which employ any of these physical fields such as electrical, microwave, ultraviolet and ultrasonic etc. [25-29]. Since, AOPs involving physical fields have not been widely adopted by the industry yet for a reliable wastewater treatment due to high energy and capital cost. Therefore, in this article we will first briefly discus Fenton reaction and finally, focus on heterogeneous Fenton like reaction (Figure 3.1) because the classical Fenton reaction which is currently in place for wastewater treatment, lacks processing and economic sustainability.

3.2. Homogeneous Fenton Reaction

The Fenton reaction was developed by Henry John Horstman Fenton in 1890 [30, 31]. The Fenton reagent comprising of ferrous ions and an oxidant H_2O_2 yields transitory but extremely reactive species i.e. hydroxyl radicals which have remarkable oxidizing capability [23, 32-34]. Although, the Fenton's reagent was discovered 100 years ago but it was not applied for the abatement of toxic organic pollutants until 1960 [35].It is critically important to comprehend the mechanism of Fenton reaction where ferrous (II) iron is mixed with H_2O_2, hydroxyl radicals are generated through the following chain initiation (Eq. 1) [36] and chain termination (Eq. 2) reactions [37, 38]. The ferric (III) iron may also react with H_2O_2 and decompose it through the reaction outlined in (Eq. 3),and this particular reaction is referred as Fenton like reaction [39]. A series of other reactions involved in the Fenton process are outlined here (Eq. 4-7)[23, 40].

$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^{\bullet} + OH^{-}$ (Eq. 1)
$Fe^{+2} + OH\cdot \rightarrow OH^{-} + Fe^{+3}$ (Eq. 2)
$Fe^{+3} + H_2O_2 \leftrightarrow Fe\text{-}OOH^{+2} + H^{+}$ (Eq. 3)
$Fe\text{-}OOH^{+2} \rightarrow HO_2^{\bullet} + Fe^{+2}$ (Eq. 4)
$Fe^{+2} + HO_2^{\bullet} \rightarrow Fe^{+3} + HO_2^{-}$ (Eq. 5)
$Fe^{+3} + HO_2^{\bullet} \rightarrow Fe^{+2} + O_2 + H^{+}$ (Eq. 6)
$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$ (Eq. 7)

Instead of looking into all these complex reactions, Walling [41] proposed a simplified version of Fenton reaction (Eq. 8) [42].

$Fe^{+2} + H_2O_2 + 2H^{+} \rightarrow 2\,Fe^{+3} + 2H_2O_2$ (Eq. 8)

The $OH^{\bullet}$ reacts with organics and convert them into organic radicals which undergo a series of oxidation reactions to yield secondary and tertiary metabolites (Eq. 9) [43, 44].

$RH + OH^{\bullet} \rightarrow H_2O + R^{\bullet} \rightarrow \text{Oxidation}$ (Eq. 9)

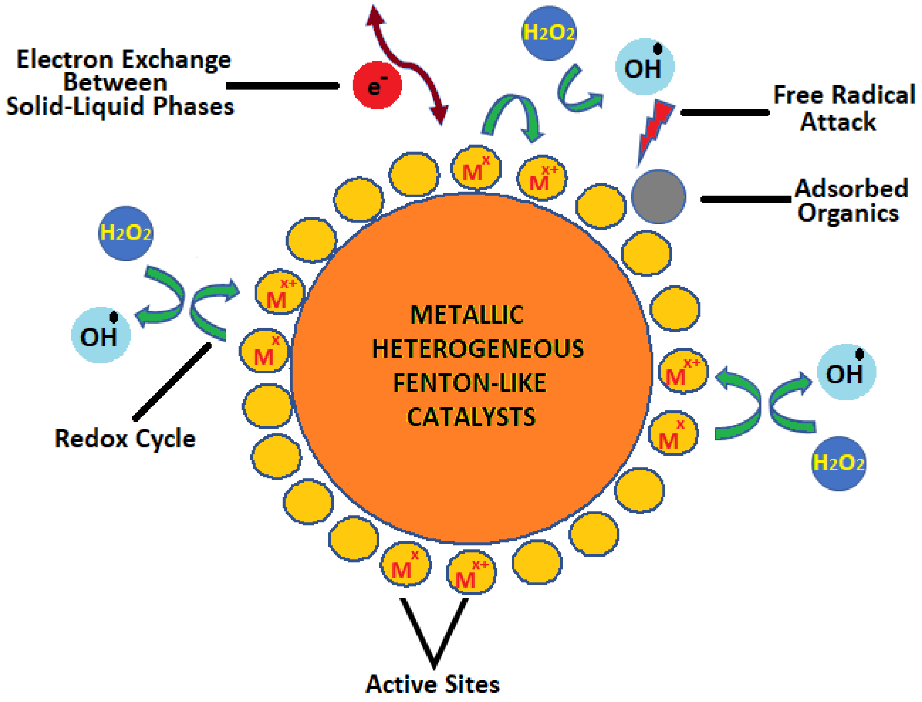

Figure 3.1: Heterogeneous Fenton like oxidation process

Homogeneous Fenton reaction essentially involves three processing steps: dissolution of the catalyst [45], OH• radical generation and finally the oxidation of organics (Figure 3.2). Since, Fenton reaction is mainly dependent on the extent of dissolution of iron catalyst and this is the reason for which Fenton reaction does not afford good efficacy near neutral pH conditions. To improve the efficiency of the process, the pH of the aqueous medium has to be shifted towards acidic conditions which favors the dissolution of the catalyst. Almost all researchers have concluded that acidic conditions near pH-3 afford the best efficiency for Fenton process [46-50]. Apart from conducive pH conditions, there are several other factors which may influence the dissolution of the catalyst and can be explained using Noyes–Whitney equation (Eq. 10) [51, 52].

$$\frac{dW}{dt} = \frac{DA\,(Cs - C)}{L} \qquad (Eq. 10)$$

Where,

$\frac{dW}{dt} = Rate\ of\ catalyst\ dissolution$
A = Surface area of the catalyst
C = Concentration of the solid catalyst in the bulk dissolution medium
Cs = Concentration of the solid catalyst in the diffusion layer surrounding the solid
D = Diffusion coefficient
L = Diffusion layer thickness

This equation clearly suggests that catalyst surface area plays a critical role and is proportional to the rate of dissolution of the catalyst. Further, larger quantities of catalyst also enhance the solubility of solid due to higher concentration gradient between liquid and solid phases. Moreover, the characteristics of dissolving medium i.e. wastewater also govern the solubility of catalyst. It is also important to note that the nature of the iron catalyst may also affect the dissolution rate.

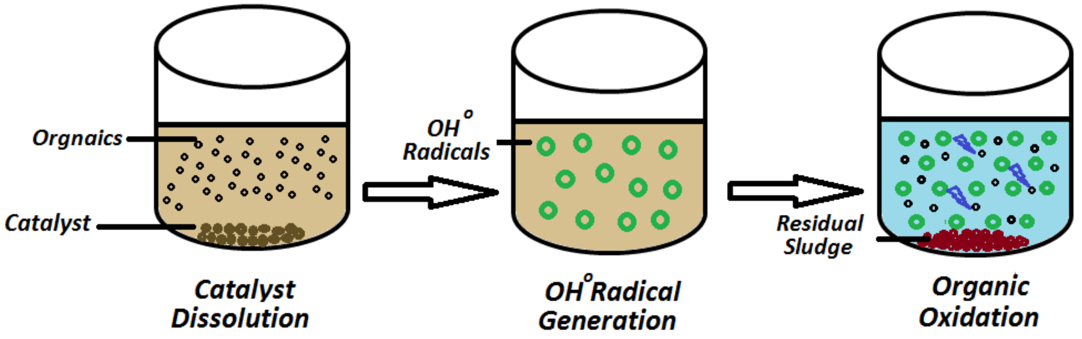

Figure 3.2: Homogeneous Fenton process. Homogeneous Fenton reaction essentially involves three processing steps: dissolution of the catalyst, OH● radical generation and the oxidation of organics.

Once the catalyst is dissolved, the Fe^{+2} ions start producing $OH^{\bullet}$ radicals from the oxidant. The rate of $OH^{\bullet}$ radicals mainly depend on the concentrations of both the catalyst and the oxidant. However, excess amounts of either of these entities beyond optimal conditions may also trigger a scavenging effect which may hinder the process efficiency (Eq.11 & 12)[53, 54].

$$Fe^{2+} + OH\bullet \longrightarrow Fe^{3+} + OH^{-} \qquad \text{(Eq. 11)}$$
$$H_2O_2 + OH\bullet \longrightarrow HO_2\bullet + H_2O \qquad \text{(Eq.12)}$$

Therefore, to avoid the adverse effects of scavenging phenomenon, Fenton process must be optimized with respect to catalyst and oxidant doses.

The transitory $OH^{\bullet}$ radicals then attack on the organic molecules and abstract one of their hydrogen atoms and turns them into $R^{\bullet}$ which ultimately undergoes series of oxidation reaction to yield secondary and tertiary products, ideally H_2O and CO_2. Since, organics must go through the oxidation process and consequently, the nature of the organics not only affects the extent of oxidation but also the quality of the finally treated wastewater. Therefore, hydrocarbons with stable and high molecular weights tend to yield relatively stable radicals which are difficult to oxidize. Another factor which hinder their oxidation is their poor solubility in the aqueous medium because homogeneous Fenton reaction must take place in the solution phase. The order of stability and consequently the difficulty posed by organic pollutants to undergo oxidation is illustrated in Figure 3.3 [55].

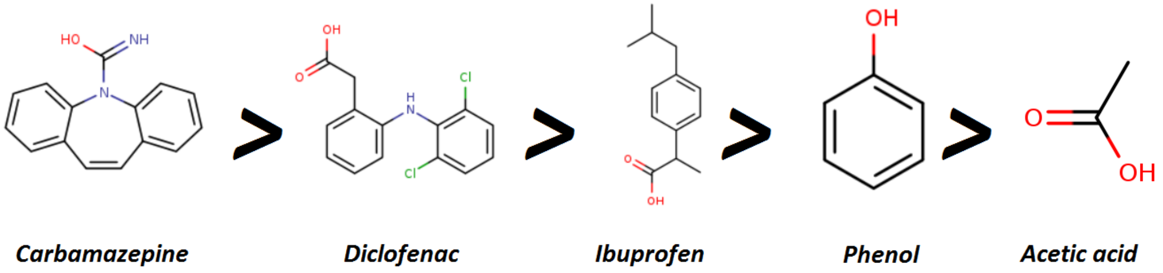

Figure 3.3: Order of organic pollutants stability towards oxidation

3.2.1. Limitations of Fenton process

Fenton process has many advantages such as processing of wastewater at ambient conditions, high reaction rate between H_2O_2 & Fe (II) [56], nontoxic reagents, and convenience of integration with existing treatment facilities [57]. Moreover, Fenton process has been successfully employed for the treatment of numerous industrial wastewaters [47-49, 58-60]. However, homogeneous Fenton reaction is only feasible when pH is lower than 4 because the interconversion of Fe^{+2} and Fe^{+3} maximizes the process efficiency [61]. When pH exceeds 4 then Fe^{+3} is converted into ferric hydroxide sludge and part of the catalyst is lost and hence efficacy of the Fenton reaction declines [62]. The rigid acidic conditions require constant addition of chemicals before and after wastewater treatment and thus leading the process towards economic non feasibility. Besides, handling and disposal of solid sludge incurs additional costs. Moreover, the newly formed sludge may also serve as an absorbent for the pollutants in the wastewater and hence giving rise to another environmental hazard. Furthermore, recycling of the iron sludge is also not feasible.

3.3. Heterogeneous Fenton like Reaction

Fenton like reaction is established when Fe^{+2} is either replaced with Fe^{+3} or other transition metal ions in the Fenton reagent system [63]. Although heterogeneous Fenton like reaction also co-exists within homogeneous Fenton reaction but it is limited because of the narrow pH range and quickly dissipates once favorable conditions are inverted [64]. Heterogeneous Fenton like reaction can be successfully used to overcome the processing and economic constraints associated with homogeneous Fenton reaction such as high input of chemicals, catalyst loss and large amount of sludge generation [65, 66]. In heterogeneous Fenton reaction, the Fe^{+3} is principally used in the non-soluble form either harnessing naturally occurring minerals such as magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), hematite (α-Fe_2O_3) and pyrite (FeS_2) [67, 68] or impregnating it over suitable supports to afford extended surface area [69-72].

Heterogeneous Fenton process is altogether different when compared with homogeneous Fenton process because adsorption is mainly responsible for determining the efficiency of the process. There are three steps involved in heterogeneous Fenton process; adsorption of organics over the catalyst surface, in situ generation and attack of $OH^{\bullet}$ radicals on organics [73] and finally desorption of oxidation products from catalyst surface Figure 3.4. In order to explain the driving force of adsorption in heterogeneous Fenton oxidation, Langmuir equation can be used (Eq. 13).

$$\frac{Ce}{Qe} = \frac{1}{QmKl} + \frac{Ce}{Qm} \qquad \text{(Eq. 13)}$$

Where

C_e = Equilibrium concentration of organics

Q_e = Equilibrium monolayer adsorption capacity

Q_m = Complete monolayer adsorption capacity

K_l = Langmuir adsorption constant

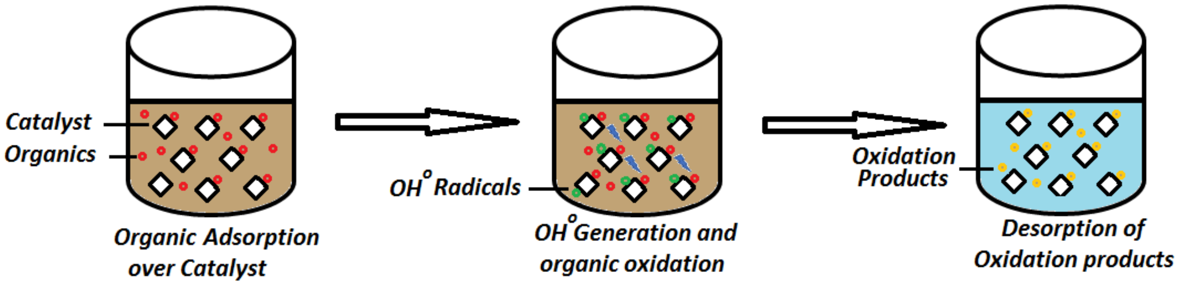

Figure 3.4: Heterogeneous Fenton process. Heterogeneous Fenton reaction essentially involves three processing steps: adsorption of organics over the catalyst surface, OH● radicals generation through active sites on the catalyst surface and oxidation of the organics, desorption of the oxidation products from the catalysts surface.

The equation clearly suggests that the rate of adsorption predominantly depends upon the monolayer adsorption capacity of the solid catalyst. This further suggests that when higher surface area of the catalyst is exposed in the aqueous medium, results a higher organic adsorption [74]. Although, multilayer adsorption may also exist, but it only happens when organics are present in very high concentrations. Once the organics are adsorbed onto catalyst surface, $OH^{\bullet}$ radicals are generated through active sites on the catalyst surface and start oxidizing the organics. The oxidation products either undergo further oxidation or desorb from the catalysts surface, completing the heterogeneous catalytic cycle.

Originally, heterogeneous Fenton process was developed by harnessing iron (Fe^{+3}) to overcome the disadvantages of homogeneous Fenton process, mitigating several processing constraints such as reduced sludge generation, lower chemical input, and hence lower cost. However, pH optimization and control remain the major defect in the process because in order to afford high efficiency, acidic conditions are favorable but in doing so metal ions start coming off from the catalyst surface. Leaching of the active metal from the catalyst surface inevitably results in lowering the catalytic activity, turning the process less sustainable. Therefore, many researchers have been striving to employ various metals including iron to develop heterogeneous catalysts with enhanced stability without compromising the acceptable activity threshold. Now, we will discuss frequently used metals for the development of heterogeneous catalyst for Fenton oxidation and critically analyze their performance in terms of activity and stability. Specifically, we will focus on iron, cerium, copper, manganese, and silver catalysts.

Iron-based catalysts have been mainly discussed because the main idea of the Fenton and Fenton-like processes originated using iron-containing materials. This is the only metal which forms stable complexes with the degradation products. Copper-based materials have been considered due to the redox cycle that is very similar to that of iron. Moreover, unlike iron, copper forms temporary complexes with the degradation products. Silver has been chosen because its unique redox cycle involving elemental Ag and Ag^{+}. Cerium has been taken into consideration because this is the only metal when employed in Fenton like oxidation process, forms complexes with the oxidant. Manganese has been included in the review because it offers two separate redox cycles depending upon the nature of manganese-based material.

3.4. Role of metals in heterogeneous Fenton like oxidation

3.4.1. Considerations for development of sustainable catalyst

The fundamental prerequisites to develop a sustainable heterogeneous catalyst for Fenton oxidation are high activity and stability. In order to achieve these features in a catalyst, it is essential that the metal used for catalyst development can exist in multiple oxidation states due to its higher capacity to transform H_2O_2 into $OH^{\bullet}$ radicals [2]. Moreover, all these oxidation states ought to be stable over a wide range of pH to avoid the loss of catalyst though leaching. Another aspect which must be considered is the resistance of the metallic species towards hydration forces / non soluble nature of the metallic ions. Apart from these requirements, the metal entities must have the potential to transform pollutants into terminal oxidation products i.e. CO_2 and H_2O.

3.4.2. Iron

The abundant and cost-effective availability of iron is the prime reason due to which researchers are still focused to develop heterogeneous catalysts by employing this metal [67]. Another reason for harnessing this metal is its high activity in Fenton process and familiarity with reaction mechanism [56]. Iron based heterogeneous catalysts are still the most widely used catalysts in Fenton like process and many researchers have reported their findings which are presented in Table 1.1. Iron can exhibit its heterogeneous catalytic features cycling between Fe^{3+} and Fe^{2+} [40, 75, 76]; some researchers have also proposed high-valent iron species such as ferryl (Fe^{+4}) but these species only exist in basic conditions [73, 77, 78].

3.4.2.1. Controlling parameters

The nature of the iron-based catalyst is the governing parameter which dictates rest of the factors for optimal performance of the catalyst in Fenton process because coordination of the iron species in different catalytic environments is inherently different; the nature of the catalyst predominantly regulates the optimization of the parameters in Fenton process [79]. For example, there is a marked difference of optimal pH between $BiFeO_3$ and zero valent iron (Table 1.1). Likewise, similar iron-based catalysts such as nanoparticle iron and zerovalent iron yield maximum activity at identical pH conditions.

Other parameters such as pH, catalyst dose, oxidant dose, temperature, reaction time and pollutant type will strongly affect the efficiency of the Fenton process. The most critical parameter for iron based heterogeneous catalysis is the pH of the wastewater. Acidic pH conditions yield higher activity of the process because part of the iron species is lost into the solution phase and may contribute towards improving efficiency of the process through partial homogeneous Fenton reaction [109]. However, this will also cause substantial metal loss from catalyst surface and turning the catalyst less active in subsequent cycles. Moreover, acidic pH conditions of the aqueous solutions are adjusted by the addition of HCl or H_2SO_4 and this will increase the concentration of SO_4^{2-} and Cl^- ions, which are known as inhibitors for the generation of $OH^\bullet$ radicals, thus adversely affect the overall process efficacy [115].

Another important parameter is the catalyst dose and the associated surface area of the catalyst. Generally, higher catalyst loadings favor the efficacy of the Fenton process especially when iron-based heterogeneous catalysts are used but beyond a certain point it may also negatively impact the efficacy due to scavenging effect i.e. consumption of $OH^\bullet$ radicals by the catalyst itself [105, 112]. Since, heterogeneous Fenton process is a surface phenomenon and higher surface area of the catalyst will increase the effectiveness of the catalyst. However, extended surface area of iron-based catalysts may subject them to strong hydration forces especially in acidic conditions and ultimately resulting the increase of metal loss [84].

Obviously, oxidant dose is also critical when it comes to achieve optimal efficiency in Fenton process. However, it has been observed that when iron-based catalysts are used, only a small excess of oxidant is required to obtain maximum pollutant abatement [84, 112]. It is also worth mentioning that the type of the pollutants will not only regulate the extent of oxidation but also the degree to which oxidation objectives are achieved i.e. whether a mere degradation of the organics is required, or a complete mineralization is the primary objective.

Table 3.1: Iron based heterogeneous catalysts

Catalyst composition	Catalyst dose (g/l)	H_2O_2 dose (mM/l)	pH	T (°C)	Target compound	Degradation (%)	Mineralization (%)	REF
Fe(III)AspSiW	0.2	20	6.5	25(30 min)	4-chlorophenol	100	85	[80]
Fe_3O_4 Nanoparticle	0.1	1	3	25(30 min)	Methylene blue	100	77	[81]
Fe_0/Fe_3O_4	3	300	6	25(2h)	Methylene blue	100	75	[82]
Nanoparticle iron	0.5	3.0	3	30 (1 h)	4-chloro-3-methyl phenol	99	63	[83]
Iron over activated carbon	0.1	6	3	30 (24 h)	azo dye Orange II	100	60	[84]
Fe-Lap-RD	1	60	3	25(30 min)	Ciprofloxacin	100	57	[85]
Zero valent iron	1	128	3	20 (8 min)	4-chlorophenol	100	-	[86]
$Fe_3O_4/\gamma\ Al_2O_3$	1	44	3	50(3h)	4-chlorophenol	100	-	[87]
				50(2h)	2,4-dichlorophenol	100	-	
				50(1h)	2,4,6-trichlorophenol	100	-	
GO- Fe_3O_4	0.2	22	3	25(3h)	Acid Orange 7	100	-	[88]
Fe_3O_4/CeO_2	2	30	3	30(2h)	4-Chlorophenol	100	-	[89]
FeNi/C-300	1	100	7	25(1 h)	Methylene blue	100	-	[90]
Fe/saponite clay	0.07	13	3	40(4h)	Azo dye	100	-	[91]
Fe/clinoptilolite	5	3	3	25(1h)	phenol	100	-	[92]
Quartz/Goethite	0.1	58	5	20(30 min)	Methyl red	100	-	[93]
Fe/Faujasite Y zeolite	1	7	5.5	20 (4h)	Phenol	100	-	[94]
Fe_2O_3	20	24	2.5	25(2h)	Drimarene	99	-	[95]
Fe-Zeolite Y	2.5	16	2.5	30(1h)	Acid red I	99	-	[96]
Fe Clay	5	8	3	30(3h)	Reactive blue 4	99	-	[97]
Amorphous FeOOH	2.5	15.8	7	1.5 h	Methyl orange	99	-	[98]
Fe-Al Clay	0.3	4	4	30(3h)	Phenol	99	-	[99]
Fe_0–Fe_3O_4–RGO	0.1	0.8	3	25 (1 h)	Methylene Blue	98	-	[100]
AC-FeOOH	1	10	7	30(4h)	Azo dye	98	-	[101]
Fe/ZSM-5	1	267	3.5	60(2h)	Reactive red	97	-	[102]
Fedpa/SiO_2	0.87	4.5	8	25(2h)	2,4-dichlorophenol	95	-	[103]
$FeVO_4$	0.5	15	6.1	25(1h)	Methyl orange II	94.7	-	[104]
Fe_2O_3 Over CeO_2	1	640	9.6	27 (7 h)	methylene blue	94	-	[105]
Fe_2O_3-MWCNTs	0.5	15	3.5	25(30 min)	Acid orange II	94	-	[106]
$Fe_2(MoO_4)_3$	1.4	18	3	30(1h)	Acid orange II	94	-	[107]
Fe^{II}@MIL-100(Fe)	1	40	3	25 (5 h)	methylene blue	91	-	[108]
$LaFeO_3$ and $BiFeO_3$	0.1	26	5	40	phenol	90	-	[109]
NZVI/CD particles	1	60	3.5	25(1 h)	Amoxicillin	90	-	[110]
SCFA	10	5	3	30 (1.5 h)	p-nitrophenol	90	-	[111]
FeS	0.5	10	4.5	50 (5 h)	of 2,4-dichlorophenoxyacetic acid	88	-	[112]
Zero valent iron	0.5	6.6	3	30(20 min)	Amoxicillin	86.5	-	[113]
Fe/ZSM-5	0.2	8.35	4	60 (2 h)	Acetic acid	-	50.5	[114]

A key characteristic of the Fenton like process carried out by iron-based catalysts is their ability to degrade wide range of organics [86]. Further, iron-based catalysts afford high reaction rates in terms of organic degradation, but rate of mineralization is far slower due to two possible reasons. First, the oxidation products do not desorb from catalyst surface; second, due to their inability to generate in-situ R• radicals from secondary oxidation products because Fe^{+3} forms very stable complexes with oxidation products, and ultimately inhibit the oxidation of degraded products Figure 3.5 [116-118].

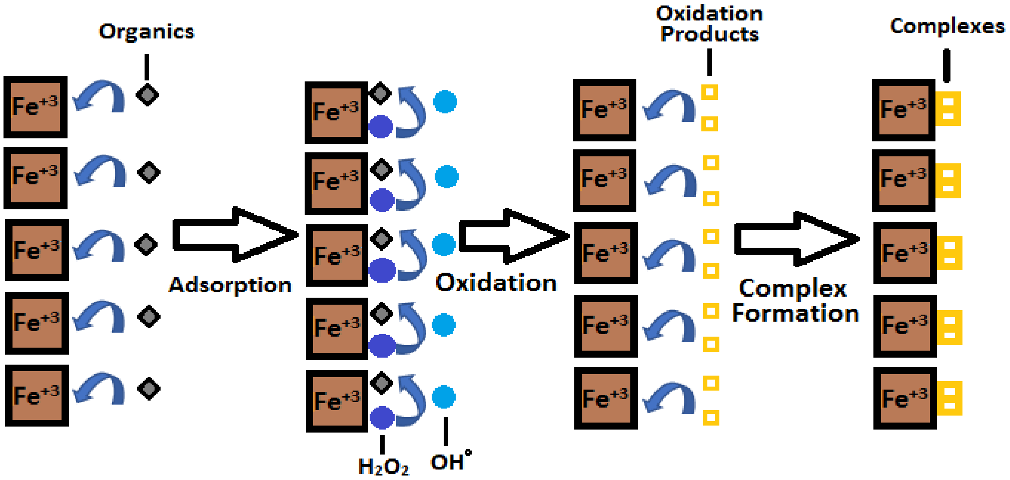

Figure 3.5: Complex formation of iron with oxidation products. The organics are adsorbed over the catalyst surface where they are oxidized by the iron-based catalyst. After the oxidation, the formation of very stable complexes between Fe^{3+} and oxidation products, inhibits the desorption of the reaction products

3.4.3. Copper

Copper is the second most used transition metal in heterogeneous Fenton process because of several characteristics such as inexpensive, abundant availability, non-toxic nature, and high activity. Another feature which has attracted the attention of research community is its similar redox behavior like iron. There are two oxidation states of copper i.e. cuprous (Cu^+) and cupric (Cu^{+2}) which can react with H_2O_2 to form OH• radicals [2]. However, copper has a distinct property which makes it even a better catalytic entity when compared with iron, its ability to form temporary complexes with oxidation products and rapid interconversion of Cu^+ into Cu^{+2} and vice versa [119]. The oxidation products do not form permanent complexes with copper and hence the active sites remain available for continuous catalytic cycle (Figure 3.6). Therefore, copper not only offers better redox cycle, but it is also active in the mineralization of organics. Several researchers have employed copper in variable forms as heterogeneous catalyst in Fenton process (Table 3.2).

3.4.3.1. Controlling parameters

The principal feature of copper-based heterogeneous catalysts is their potential to perform well over a broad pH range, especially near neutral pH conditions. However, the optimal pH conditions depend upon the nature of the catalyst and its corresponding value of point of zero charge. Unlike iron catalysts, acidic conditions not only reduce the overall activity of these materials but also amplify the loss of metal from catalyst surface. Moreover, copper-based catalysts do not offer catalytic activity through homogeneous phase. Another advantage of copper over iron is its ability to afford better catalytic activities with lower catalyst dose because it possesses superior redox cycle and extended catalyst stability. Further, heterogeneous catalysis carried out by copper made catalysts is much faster. However, optimal catalyst dose ought to be determined experimentally and any additional amount of catalyst will bear strong scavenging effects and ultimately process efficiency will decline.

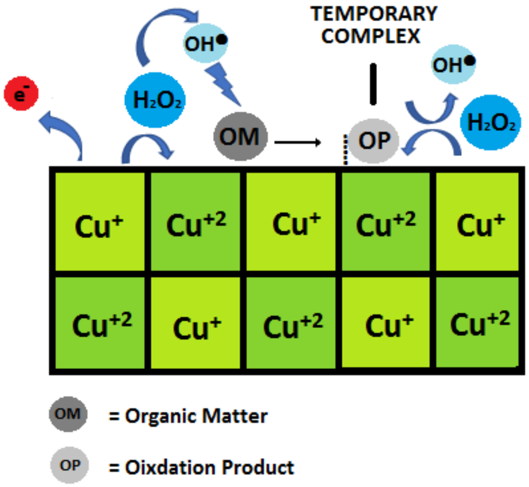

Figure 3.6: Complex formation of copper with oxidation products. The oxidation products do not form permanent complexes with copper and hence the active sites remain available for continuous catalytic cycle

Copper-based catalysts have a serious disadvantage concerning oxidant dose, a fairly large excess of oxidant is required to obtain optimal pollutant abatement because molecular oxygen disturbs the redox cycle of copper and part of the oxidant is lost in the process. The large excess of H_2O_2 not only increases the cost of the Fenton process but also make it susceptible to severe scavenging effect caused by the oxidant itself for $OH^\bullet$ radicals [139, 140].

Contrary to iron, the activity of the copper-based catalysts is greatly influenced by variations in the reaction temperature. Higher reaction temperature favors the rate as well efficiency of the Fenton process because the energy required by the organics and H_2O_2 to form oxidation products is supplied through an elevation in temperature[53, 141]. However, beyond a certain point, temperature may also negatively impact the process efficiency due to the formation of undesirable stable oxidation products, loss of active sites through hydration forces and decomposition of oxidant into useless species.

Table 3.2: copper-based heterogeneous catalysts

Catalyst composition	Catayst dose (g/l)	H_2O_2 dose (mM/l)	pH	T (°C)	Target compound	Degradation (%)	Mineralization (%)	REF
5Cu/ZrO_2	0.25	32	5	70 (2 h)	Ibuprofen	100	53	[120]
CuFe/ZSM-5	0.15	40	3.5	50(2h)	Rhodamine 6G	100	51.8	[121]
Copper slag	2.49	4.7	3	30 (4h)	Phenol	100	50	[122]
$CuFe_2O_4$/rGO	0.6	660	7	25(4h)	Phenol	100	-	[123]
copper-doped mesoporous silica	0.4	10	5	30 (2h)	Ibuprofen	100	-	[119]
Cu/SiO_2	0.035 Cu	29	-	60(1h)	Rhodamine B	100	-	[124]
Cu(I) doped nano-Fe_3O_4	0.1	10	6	25 (2h)	Carbamazepine	100	-	[125]
Cu-Fe_3O_4@SiO_2	1 (0.2 cu-fe)	15	5	25 (2h)	Acetaminophen	100	-	[126]
$CuFeO_2$ Microparticles	1	20	5	30(2h)	Bisphenol	99.2	85	[127]
CuO over CeO_2	1	640	9.6	27 (7 h)	Methylene blue	99	-	[105]
Cobalt–copper oxalate nanofibers	0.1	380	5	30 (5h)	Congo Red	99	-	[128]
Cu–$CuFe_2O_4$/SiO_2	0.2	250	7	25 (2h)	Methylene blue	98	-	[129]
CuO/SiO_2 hollow sphere	6	34	3.5	60(2 h)	acid scarlet 3R	97	-	[130]
$Co_{0.5}$-$Cu_{0.5}O$	0.1	380	9	30(5h)	Congo red	95	-	[131]
7.5 CuY	1	200	5	60(4 h)	Congo red	93.58	79.52	[132]
CuFe-MC-1-800	0.3	30	3	25 (1 h)	Bisphenol	93	66.3	[133]
					Imidacloprid	--	94.3	
					Methylene Blue	--	95.4	
					2,4,6-trichlorophenol	--	93.5	
					Methyl orange	--	86.9	
					Phenol	--	83.7	
					Benzoic Acid	--	81.4	
					Ketoprofen	--	77.8	
mesoporousCu/TUD-1	0.1	90	3.5	25(3h)	Bisphenol	90.4	-	[134]
Cu^{2+}/Al_2O_3, Cu^{2+}/ZrO_2	1	300	6.8	30 (5h)	bromophenol blue	90	-	[135]
CuO nanoparticles	0.1	800	6	25(4 h)	Enrofloxacin	90	-	[136]
CuO/Al_2O_3	0.2	40	5.5	21 (2h)	Reactive black 5	90	-	[137]
Fe-Cu/Al_2O_3	1.5	49	4	40(2h)	Phenol	-	80	[138]

Cu-based catalysts have a main disadvantage which is the high excess of H_2O_2 requirement for maintaining the catalytic activity. This disadvantage has often been mitigated by employing a bimetallic composite of copper with iron and other transition metals. However, iron has been used more frequently and various studies have shown promising results in this regard. The induction of two metals not only enhances the catalytic activity but also increases the stability of the catalytic composite because of superior redox cycle (Figure 3.7). Tian et.al. have summarized the redox mechanism of bimetallic redox cycle using a single equation (Eq. 14) [142].

$$Fe^{3+} + Cu^{+} \rightarrow Fe^{2+} + Cu^{2+} \qquad (\text{Eq. } 14)$$

Fe^{3+} is reduced to Fe^{2+} while Cu^{+} is oxidized to Cu^{2+}, favoring the oxidation of organic matter.

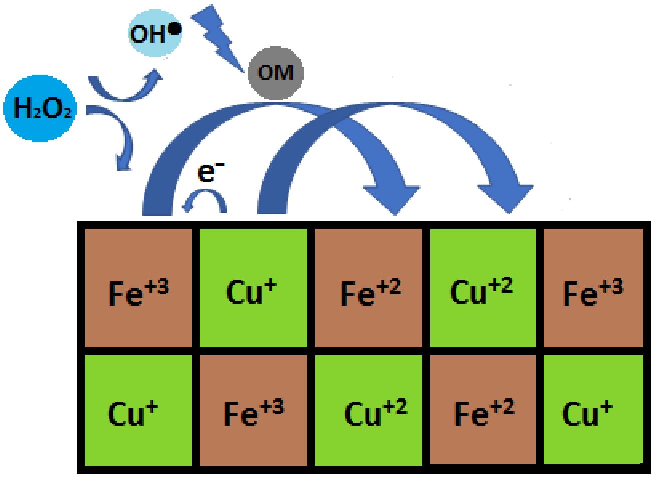

Figure 3.7: Redox cycle of copper and iron bimetallic composite. Fe^{3+} is reduced to Fe^{2+} while Cu^{+} is oxidized to Cu^{2+}, favoring the oxidation of organics.

3.4.4. Silver

The main drive to use silver as a catalyst in Fenton like process is its proven ability to oxidize organics such as methanol [143], ethylene [144], methane and volatile organic compounds [145]. He et.al. reported the use of silver nanoparticles for the generation of $OH^{\bullet}$ from H_2O_2 [146]. Until now silver has not been widely studied as a heterogeneous Fenton catalyst (Table 3.3).

Table 3.3: silver-based heterogeneous catalysts used in Fenton like processes

Catalyst composition	Catayst dose (g/l)	H_2O_2 dose (mM/l)	pH	T (°C)	Target compound	Degradation (%)	Mineralization (%)	REF
NZVI-Ag	0.025	5.3	3	25 (1.5 h)	4- cholorophenol	100	80	[147]
Ag/CeO_2	0.01	63	2	70 (2 h)	phenol	100	-	[148]
Silver nanoparticles	0.010	0.4	4	25 (8 h)	bisphenol	100	-	[149]
Silver nanoparticles	0.01	0.4	4	25 (8 h)	17a-ethinyl estradiol	100	-	[149]

3.4.4.1. Controlling parameters

In the context of Fenton like oxidation, silver can exist in two oxidation forms i.e. Ag^{0} and Ag^{+1} depending upon the pH conditions of the aqueous medium, therefore, pH is the most crucial parameter [150]. Under acidic conditions, bare silver will tend to dissolve in the water phase and will transform H_2O_2 into $OH^{\bullet}$ radicals through homogeneous phase. However, basic conditions will shift the redox reaction in the opposite direction and instead of $OH^{\bullet}$ radical generation, O_2 is produced through heterogenous phase reaction (Figure 3.8). Keeping in view of these facts, silver can efficiently be used as heterogeneous catalyst when pH conditions are either neutral or basic. However, the unfavorable redox reactions will suppress the catalytic activity while the conditions become basic as suggested by Weaver and Frederikse (Eq.15 & 16) [151]. Additionally, basic conditions may activate the agglomeration of the catalyst particles, reducing surface area and diminishing the activity [149]. Moreover, with the progress of Fenton reaction, the degradation products being predominantly acidic will acidify the aqueous medium and silver will start leaching out from the solid surface.

$$2Ag + H_2O_2 \rightarrow 2Ag^+ + 2OH^- \qquad (\text{ Eq. } 15\text{ })$$
$$2Ag^+ + OH^- + HO_2^- \rightarrow 2Ag + O_2 + H_2O \qquad (\text{ Eq. } 16\text{ })$$

These drawbacks associated with silver can be averted by incorporating an appropriate support material such as ceria, zirconia etc. The integration of silver on supports with oxygen storage capacity will not only enhance its activity but also strengthen the catalytic structure because of dual redox cycle, one responsible for activity and the other for stability (Figure 3.8). Moreover, surface area is also increased manifolds by the introduction of supports which will ultimately increase the activity of the catalyst. Further, the catalyst can afford viable activities through broader pH range due to dual redox cycle.

The oxidant dose directly affects the silver catalyzed heterogeneous Fenton process; however, only a small excess of stochiometric oxidant dose is sufficient to achieve optimal efficacy. Further, a large excess of oxidant dose ought to be avoided because it can either cause scavenging effect or lower the pH and hence catalytic activity is subdued [149]. The most prominent feature of silver formed catalysts is that they can afford equivalent process efficacies with minimal catalyst loadings.

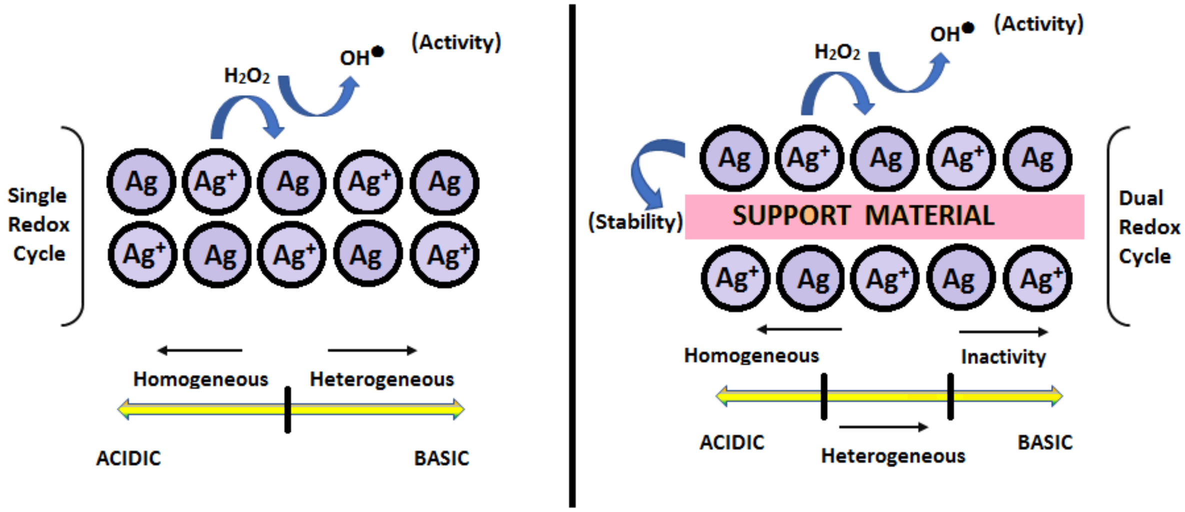

Figure 3.8: Activity of bare and supported silver catalysts under variable pH conditions. Bare silver interacts with H_2O_2 forming $OH^\bullet$ radicals through homogeneous phase. The integration of silver on supports enhances its activity and strengthens the stability.

3.4.5. Cerium

Cerium is a rare earth metal from lanthanide group which has been widely employed in wet air oxidation and water gas shift reactions [152]. Owing to its oxidation properties cerium can conveniently produce $OH^\bullet$ from H_2O_2 due to exhibition of two oxidation states i.e. +3 and +4. Heckert et al. used cerium based heterogeneous catalysts for the production of $OH^\bullet$ from H_2O_2

through the mechanism outlined in Eq. 17 and 18 [153]. It is important to note that cerous (Ce^{+3}) is a strong reducing agent while ceric (Ce^{4+}) is a strong oxidizing agent. Since, these two ions can interchange quite easily, offering a good redox cycle which is critical for heterogeneous Fenton like oxidation [154]. A list of studies employing cerium in Fenton like oxidation is presented in Table 3.4.

$$Ce^{3+} + H_2O_2 \rightarrow Ce^{4+} + HO^{\bullet} + HO^{-} \qquad \text{(Eq. 17)}$$
$$Ce^{4+} + H_2O_2 \rightarrow Ce^{3+} + HO_2^{\bullet} + H^{+} \qquad \text{(Eq. 18)}$$

Table 3.4: Cerium-based catalysts employed in heterogeneous Fenton like oxidation

Catalyst composition	**Catayst dose (g/l)**	**H_2O_2 dose (mM/l)**	**pH**	**T (°C)**	**Target compound**	**Degradation (%)**	**Mineralization (%)**	**REF**
CeO_2-$LaCuO_3$	0.4	12.5	7	25 (6 h)	Bisphenol	99.85	72.44	[159]
Ce-Cu composite oxide	1	-	4	50 (2h)	2,4-Dichlorophenol	99.5	82	[160]
Fe_3O_4/CeO_2	2	30	2	30 (1.5 h)	2,4,6-trichlorophenol	99	65	[161]
CeO_2	0.5	10	-	25 (8 h)	Acid orange7	98	-	[155]
Ce-Cu composite oxide	1	-	4	50(2h)	4- Chlorophenol	95	88	[160]
CexCuOy	0.1	50	5	25 (1h)	Fluconazole	94	-	[162]
CeO_2	1	18	-	25 (5 h)	Acid orange7	90	-	[156]
Fe^0 / CeO_2	0.1	100	5.8	26 (1 h)	tetracycline	90	-	[163]
$FeCeO_x$	1.5	80	5	35 (2.5)	rhodamine B	90	-	[164]
CeO_2	1.5	60	3	22 (2 h)	Orange II	85	-	[165]
Fe_2O_3-CeO_2	0.5	8	3	45 (2h)	Sulfamerazine	70	-	[166]
CeO_2	1.5	116	3	22 (2 h)	Acid Green	60	-	[165]

3.4.5.1 Controlling parameters

Unlike other metals, the favorable redox cycle of cerium in aqueous environments is very much dependent on the pH of the medium. Therefore, pH of the polluted water is the most critical parameter which governs the activity of cerium catalyst. Under basic conditions, H_2O_2 forms very stable peroxide like species (OOH^{-}) with cerium [155] and these species do not decompose even at neutral pH conditions, thus no $OH^{\bullet}$ radicals are generated at all because the redox cycle between Ce^{4+}/ Ce^{3+} is completely blocked [156-158]. On the contrary, when acidic conditions are available, the H^{+} ions attack the cerium-peroxide complex and redox cycle is unblocked which yields $OH^{\bullet}$ radicals (Figure 3.9). However, it is important to note that the cerium-peroxide complex will form under both conditions and will only decompose when acidic conditions are applied.

Apart from using an experimentally determined optimal dose of oxidant, it is also crucial to use it in a suitable processing fashion which favors the Fenton oxidation i.e. oxidant should never be pre-mixed with the cerium catalyst because it is highly likely that it will block the catalytic activity [158]. Therefore, it is viable to employ the oxidant as a last processing step so that part of the cerium catalyst sites is pre-occupied by the organics and partly by cerium-peroxide complexes. Further, higher oxidant dose will only intensify the blockage of catalytic activity of cerium. The cerium-peroxide complexes are either reverted by acidic conditions or by applying very high temperatures ~300°C [167, 168]. Since, an increase in temperature is beneficial in reversing the cerium-peroxide complex which triggers the redox cycle Ce^{4+}/ Ce^{3+} and therefore, any elevation in temperature would certainly enhance the heterogeneous activity of cerium catalyst [168].

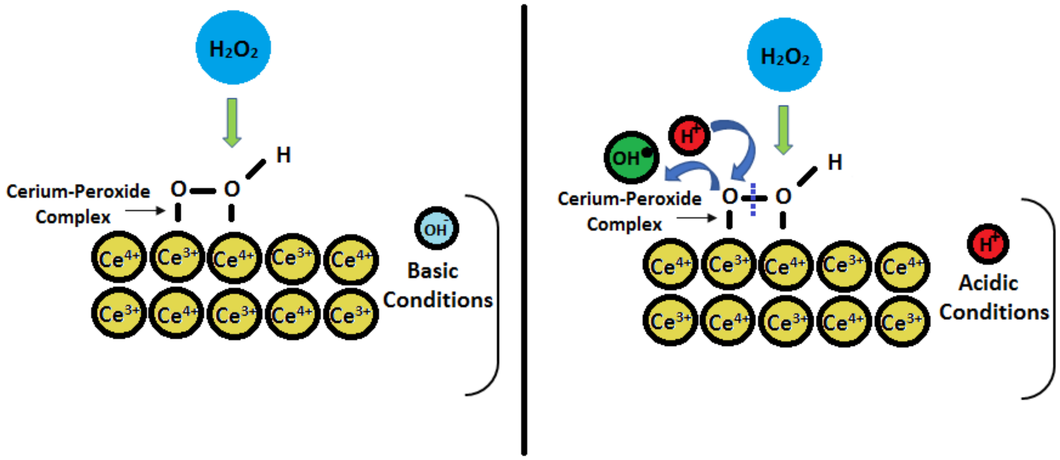

Figure 3.9: Cerium reactions with H_2O_2 under acidic and basic conditions. Under basic conditions, H_2O_2 forms very stable peroxide like species (OOH^-) with cerium inhibiting $OH^\bullet$ radicals generation, while in acidic conditions, H^+ ions attack the cerium-peroxide complex with and $OH^\bullet$ radicals generation

3.4.6. Manganese

Manganese is a transition metal, which is abundantly available, with low toxicity and not very expensive, and exists in multiple oxidation states [169]. Manganese offers structural flexibility in its metallic oxides while exhibiting the favorable oxidation states [170]. However, Mn^{+2} and Mn^{+4} are the only suitable oxidation states while considering heterogeneous Fenton like oxidation as reported in many studies (Table 3.5) [171]. It is important to mention that manganese transforms H_2O_2 into $OH^\bullet$ radicals by undergoing through a transitional intermediate i.e. Mn^{+3} [172-174], thus possessing a unique redox cycles depending upon the type of oxide and an electron is exchanged between the substrate and the solution (Figure 3.10) [175].

3.4.6.1 Controlling parameters

The most critical parameter which dictates the efficacy of manganese catalyzed Fenton oxidation is the pH of the aqueous medium because the pH conditions changes altogether when MnO_2 and Mn_3O_4 are used (Figure 3.10). When Mn_3O_4 is employed, the reaction is favored by a basic environment (Eq. 19 and 20), though neutral conditions are applied for practical reasons.

$$Mn^{+2} + H_2O_2 \rightarrow Mn^{3+} + HO^\bullet + HO^- \qquad (Eq. 19)$$
$$Mn^{+3} + H_2O_2 \rightarrow Mn^{+2} + HO_2^\bullet + H^+ \qquad (Eq. 20)$$

Conversely, MnO_2 requires acidic conditions to drive the redox cycle towards Mn^{+3} generation which in turn transform H_2O_2 into $OH^\bullet$ radicals (Eq.21 and 22). Additionally, precise control of the pH is also essential because adsorption of organics over the catalyst surface is influenced by it [185]. Moreover, the oxidation pathway of organics as well as stability of the catalyst heavily relies on the pH.

$$Mn^{+4} + H_2O_2 \rightarrow Mn^{3+} + HO_2^{\bullet} + H^{+} \qquad \text{(Eq. 21)}$$
$$Mn^{+3} + H_2O_2 \rightarrow Mn^{+4} + HO^{\bullet} + OH^{-} \qquad \text{(Eq. 22)}$$

Table 3.5: manganese-based heterogeneous catalysts used in Fenton like oxidation

Catalyst composition	Catayst dose (g/l)	H_2O_2 dose (mM/l)	pH	T (°C)	Target compound	Degradation (%)	Mineralization (%)	REF
Mn_3O_4 / Silicate	0.4	97	6	25 (4 h)	Methylene blue	100	81	[176]
Fe/Mn-MOF-71	0.064	600	6.2	35 (3h)	Phenol	100	-	[177]
MnO_2-MWCNT	0.2	300	6	25 (3 h)	reactive blue 19	99	-	[178]
MnO_2	0.1	1450	6.1	25(0.3 h)	Methylene blue	99	-	[179]
Mn_3O_4–FeS_2/Fe_2O_3	0.3	5	2.8	25 (1 h)	Orange II	99	-	[180]
Fe-Mn oxide hollow fiber membrane	-	22	9	25	Methylene blue	97	-	[181]
Diatomite/Manganese silicate	0.3	30	-	30(1 h)	Malachite green	93	-	[182]
Mn/Ti-HMS	1	10	7	25 (2 h)	Methylene blue	63.9	-	[183]
Mesoporous MnO_x	1	20	3	20 (1 h)	Norfloxacin(NFX)	60	-	[184]
Mn/Ti-HMS	1	10	7	25 (2 h)	Rhodamine B	49.7	-	[183]

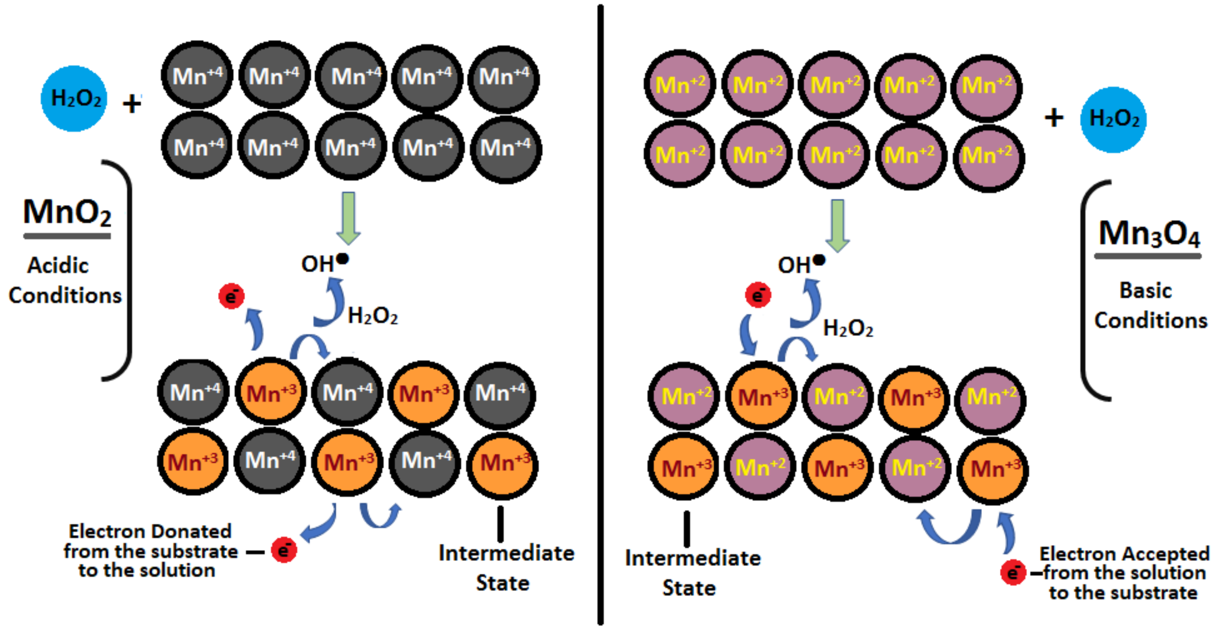

Figure 3.10: Redox cycles of MnO_2 and Mn_3O_4 under feasible conditions. Manganese transforms H_2O_2 into $OH^{\bullet}$ radicals by undergoing through a transitional intermediate i.e. Mn^{+3}

In case of manganese-based catalysts, another parameter which greatly influences their performance in Fenton like process is their morphology [179, 186]. For instance, MnO_2 can exist in four crystalline structures i.e. α- MnO_2, β-MnO_2, γ-MnO_2, δ-MnO_2. Since, all of them have different surface areas and extent of crystallinity, thus exhibiting variable catalytic activities in heterogeneous Fenton process [187]. γ-MnO_2 affords maximum activity because of well-formed morphology and high surface area while δ-MnO_2 is the least active because it is an amorphous solid with minimum surface area [179]. Kim et.al. also explained that different morphologies of MnO_2 have different magnetic moments, indicating that these oxides exhibit mixed oxidation states [179].

H_2O_2 dose has a direct impact on the efficacy of manganese driven Fenton like process because more oxidant is available for $OH^\bullet$ radical generation. However, an optimal oxidant dose has always to be determined experimentally because excess dose may give rise to scavenging effect which negatively affects the process efficiency. Moreover, any excessive oxidant dose may also disturb the pH balance of the solution which may suppress the activity of the catalyst [188]. Similarly, increasing the manganese catalyst loading also increases the overall efficiency of the Fenton process due to increase in the number of active sites through which $OH^\bullet$ radicals are generated, and organics are attacked. However, beyond a certain point surplus catalyst starts moderating the potency of the process due to scavenging effect and aggregation of the material which reduces the exposed active sites of the catalyst. In accordance with Arrhenius law, a rise in temperature elevates the activity of manganese catalyst because lower amount of activation energy is required for product formation [187].

3.5. Conclusion

The inborn limitations of classical Fenton process such as large volumes of sludge and stringent pH prerequisites can easily reverted by adapting heterogeneous Fenton like approach, either employing iron or other metallic systems. The choice of an appropriate metal not only offers milder pH conditions but also greatly enhances the efficacy of the Fenton process by providing alternate and better redox cycle. In this review we have discussed different metals and their suitability in Fenton process, considering all the processing factors (Figure 3.11). Iron based catalysts require severe acidic conditions, high catalyst doses and they form stable complexes with oxidation products and complete mineralization of organics is difficult to achieve. However, these catalysts can bear optimum activities with minimal H_2O_2 excess and the energy required to produce oxidizing species is the lowest amongst the discussed metals. Although, silver-based catalysts require less excess H_2O_2, low catalyst loadings for optimal performance but a poor redox cycle coupled with susceptibility towards leaching, limit their application in Fenton process unless a proper support is employed. Cerium based catalysts form very stable complexes with the oxidant and can only be broken if stringent acidic conditions are applied. Besides, they require the highest catalyst loadings and excess H_2O_2. Copper and manganese both possess superior redox cycles, require feasible catalyst loadings, excess H_2O_2, and can afford optimum activities under flexible pH conditions and they have the ability to completely mineralize the organics.

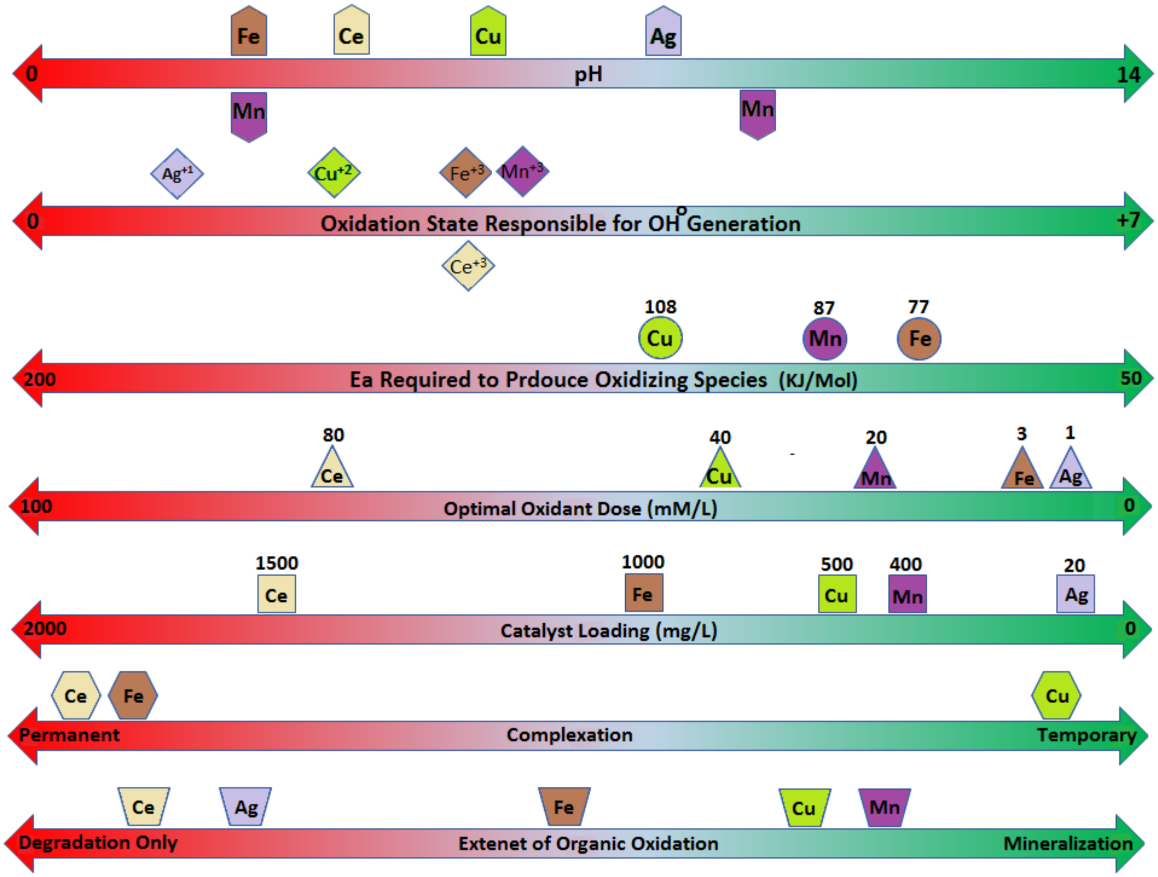

Figure 3.11: Comparative analysis of metals in heterogeneous Fenton like oxidation. Several processing factors are considered for metal suitability in Fenton process

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Chapter-4

Enhanced ibuprofen removal by heterogeneous-Fenton process over Cu/ZrO_2 and Fe/ZrO_2 catalysts

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Abstract

The aim of this work is to develop new heterogeneous catalysts for the mineralization of Ibuprofen, a pharmaceutical compound commonly found in wastewaters, using a Fenton like process. Iron and Copper catalysts supported over zirconia, eventually doped with strontium were developed. Structural and morphological properties of the materials were investigated by conventional techniques and Fenton-like reactions were carried out in a batch system. Copper/iron-doped zirconia samples exhibited a promising activity in terms of Ibuprofen degradation and mineralization. The best catalyst, copper supported over zirconia, achieves an almost complete degradation of ibuprofen (98%) with 50% of mineralization. Optimization of the reaction variables (oxidant dose, pH, catalyst loading and temperature) led to increased process efficiency. Moreover, these catalysts do not produce toxic metabolites which is important when considering the degradation of water pollutants. The present study highlights the potential of iron/copper supported catalysts for the removal of organic compounds in wastewaters via heterogeneous Fenton-like process.

Keywords: Ibuprofen, Mineralization, Heterogeneous catalysis, Fenton like process, Advanced Oxidation Processes.

4.1. Introduction

In recent years there has been a great progress in the wastewater treatment technologies, to develop increasingly effective techniques against pollutants due to an increasing demand for clean water sources [1-3]. Various strategies, including water treatment, recovery and reuse, have been effectively developed along the years. An increasing attention is paid to the "emerging micropollutants", i.e. those pollutants present at very low concentrations, (µg/L or ng/L) and not yet regulated but which are extremely dangerous for the safeguard of the water body; these include pharmaceuticals and personal care products (PPCPs). There are many pharmaceutical compounds present in the wastewater that include different categories, such as anti-inflammatory and analgesic drugs, antibiotics, anti-epileptics, hormones, etc.; their extensive use has led to an increased concentration in surface and ground waters [4-6] with the consequence that a number of these pollutants have also been detected in drinking water [7-10]. Conventional treatments, based mainly on sedimentation and biological treatment, are not effective ~~in~~ for their removal and it is therefore necessary to adopt advanced oxidation techniques (AOPs) for their treatment [11-17].

AOP treatments are widely used for the removal of refractory compounds in liquid waste; many studies have been done on model molecules such as phenol, drugs or dyes [15, 18-26] while in other cases the efficiency has been evaluated on real and complex matrices such as landfill leachate [13, 27-33]. The Fenton method is one of the most interesting AOPs and it is a very attractive method due to its feasibility, performance and cost [34-48]. AOP techniques include several processes such as photo-catalytic oxidation (PCO), Fenton/photo-Fenton, wet air oxidation (WAO), catalytic wet air oxidation (CWAO) and ozonation [49]. Some of them operates at room temperature, others need high temperatures and pressures, while each technique has different cost-benefits evaluation.

The advantage of the heterogeneous Fenton process is mainly based on the possibility of recovery and reuse of the catalyst. On the other hand, the process requires temperatures around 60-80 °C for an optimal efficiency, which is higher than that required in the homogeneous Fenton process, that operates at room temperature. However, in the overall evaluation, it must be considered the higher operating cost of the homogeneous reaction due to a limited optimum pH (around pH 3) and the difficulties in recycling the homogeneous catalyst with production of high quantities of sludge that must be treated [34, 38], thus balancing the requirements of higher temperatures typical of the heterogeneous Fenton process [50].

Ibuprofen (IBP) is a non-steroidal, anti-inflammatory drug which is widely used for the treatment of fever, migraine, and muscle pains [51, 52]. It is released along with its metabolites into the environment either by domestic or industrial routes. IBP and its metabolites are very persistent and have severe impacts on humans and aquatic environment [7, 9, 10, 53, 54]. Since, the conventional biological treatment plants are unable to completely remove Ibuprofen from wastewater, advanced oxidation processes are required for the treatment of emerging and non-biodegradable pollutants [55]. A number of studies have been performed regarding the abatement of IBP by employing advanced oxidation processes (AOPs) such as Fenton and Fenton-like oxidation, photocatalysis, electrolysis, sonolyisis and ozonation [49, 56-72]. Since some of the metabolites are even more toxic than IBP itself [73, 74], it is essential to devise a process which either completely mineralize IBP or mineralize it to the maximum extent; further, the metabolites produced during the process must be less toxic, compared to the parent IBP molecules. Summarizing, the decision to use ibuprofen as a model molecule in the heterogeneous Fenton process with Cu and Fe-based catalysts supported over zirconia is due to its severe environmental impact and large diffusion with many studies in literature related to its abatement.

Recently we have investigated the activity of transition (Cu or Fe) and alkaline-earth (Sr) metal-doped catalysts supported on ceria or zirconia for the NOx-assisted oxidation of diesel particulate and we have found that they are promising oxidation materials [75]. In this work we have prepared similar catalysts but using different calcination temperature of the material after the synthesis. The aim of the study is to develop novel catalysts for the full mineralization of IBP using a Fenton-like heterogenous process. Iron and copper catalysts supported over zirconia were prepared and investigated in the conversion/mineralization of IBP by heterogeneous Fenton reaction. Further, the catalytic reaction has been optimized by varying catalyst loading, pH, reaction temperature and oxidant dose.

4.2. Experimental

4.2.1. Catalyst preparation and characterization

A series of 5 wt % Cu (or Fe) catalysts eventually doped with Sr (10 wt %) was prepared. ZrO_2 support was prepared by calcination of zirconium hydroxides (Mel Chemicals, Manchester, UK) at 500 °C for 3 h. Then, aqueous solutions with appropriate amounts of Cu (copper (II) nitrate hemi (pentahydrate), Sigma Aldrich, Saint Louis, MO, USA), Fe (Iron (III) nitrate nonahydrate, Sigma Aldrich), and/or Sr (strontium nitrate, Strem chemicals, Newburyport, MA, USA) were added by incipient wetness impregnation, and dried overnight at 100 °C. Copper and iron materials were synthesized by a single impregnation step, while for materials containing Sr, two successive impregnation steps have been applied. After drying, the samples were finally calcined at 500 °C for 3 h. Textural characteristics of all fresh samples were measured according to the BET method by nitrogen adsorption at −196 °C, using a Tristar 3000 gas adsorption analyser (Micromeritics). Structural features of the catalysts were characterized by X-ray diffraction (XRD). XRD profiles were recorded on a Philips X'Pert diffractometer (equipped with a real time multiple strip detector) operated at 40kV and 40mA using Ni-filtered Cu-K⍰ radiation. Spectra were collected using a step size of 0.02° and a counting time of 40s per angular abscissa in the range 20°-80°. The Philips X'Pert HighScore software was used for phase identification.

4.2.2. Catalytic activity measurements

Aqueous solutions of ibuprofen (10 mg/L) were prepared dissolving ibuprofen sodium salt, $C_{13}H_{17}O_2Na$ (Sigma-Aldrich) in ultra-pure water. Fenton-like reaction was carried out, in a three neck round bottom flask with reflux to avoid evaporation phenomena, under continuous stirring. The experiments were conducted for 2 hours at 70 °C using 200 mL of IBP solution loaded with 250 mg/L catalyst and 25 ml/L (3%) H_2O_2(Sigma-Aldrich), with a contaminant/oxidant ratio of $1.8*10^{-3}$ in order to work under conditions that are not limited by the quantity of oxidant in solution. After addition of all the reagents the pH of the solution was ca. 5. The reactants were introduced into the reactor in sequence, first the catalyst and then the hydrogen peroxide; the reaction starts with the addition of H_2O_2 and is carried on for two hours under ambient pressure. The treated samples were filtered using a 0.2 µm syringe filters and IBP mineralization and degradation were analyzed. On selected catalysts, the oxidation process was optimized evaluating the effect of catalyst dose (250, 500 and 750 mg/L), hydrogen peroxide, (12.5, 25 and 37.5 ml/L), temperature (50,70 and 90ºC) and pH (3, 5 and 7, acidifying the sample with hydrochloric acid (Sigma Aldrich) or basifying the sample with sodium hydroxide (Sigma Aldrich)). In order to observe the mineralization of IBP, the total organic carbon (TOC) of treated samples was analyzed using a TOC-VCPN, Shimadzu analyzer.

The carbon content of samples was analyzed by Shimadzu TOC analyzer (V-Series) with auto sampler. First, the standard solutions with known concentrations of 2.5, 5.0, 10.0 20.0 mg C/l were prepared using potassium hydrogen phthalate stock solution. A calibration curve was obtained by analyzing the standard samples, and after each analysis the injection syringe was auto sparged with 2M HCl. The samples were analyzed without dilution and using the same calibration curve to determine TOC present in each sample.

Further, to monitor the extent of IBP degradation, aqueous samples were analyzed with Orbitrap Liquid Chromatography Mass Spectrometry (LC-MS) (ARPA, Udine, Italy). LC separation was performed on a Dionex Ultimate-3000 System (Thermo Fisher Scientific). Reversed-phase gradient separation was obtained by an Hypersil GOLD column (50 x 2.1 mm, 1.9 µm; Thermo Scientific). The column flow rate was set at 0.3 mL/min and the injection volume was 100 µL. The mobile phases were an aqueous solution of ammonium acetate 5mmol/L (A) and methanol (B); analytical grade ammonium acetate was purchased by Fluka, while analytical grade methanol was purchased by Carlo Erba. The following gradient steps were used: 2% B, increased to 98% after 7,5 min ad held for 1,5 min and returned to 2% at 11 min. Mass spectrometric detection was carried out by a Q Exactive mass spectrometer (Thermo Fisher Scientific) operated in negative electrospray ionization (ESI(-)) mode. The further mass parameters used were: probe heater, 350 °C; capillary temperature, 350 °C; auxiliary gas flow rate, 12 arb; sheat gas flow rate, 44 arb; spray voltage, 3.4 kV; S-lens RF kevel, 55; automatic gain control target 1x 10^6; maximum injection time, auto; scan range. m/z 100-350; mass resolution, 70000 full width at half maximum (m/z 200). Data were acquired in full scan mode, the mass extraction window was ±5ppm. The target ion for the ibuprofen quantitation was 205.12340 m/z; ibuprofen standard was purchased by Dr. Ehrenstofer. The sample was injected without preparation.

Orbitrap LC-MS analysis is also important to monitor the degradation products in order to evaluate the formation of more toxic metabolites during the oxidation process.

The stability of the most promising catalyst over several repeated reaction cycles was carried out. After each catalytic test, the catalyst has been filtered on 0,45 µm polycarbonate membrane filters, recovered from the filter and directly used in another catalytic test, without any regeneration or treatment. Further, every time the catalyst was reused, a fresh IBP solution of 10 mg/L concentration was used.

4.3. Results and discussion

4.3.1. Textural and structural characterization

Composition and BET surface area of the materials are reported in Table 4.1. The addition of Cu or Fe does not strongly affect the surface area (53 vs 64 m^2/g), while addition of Sr impacts more heavily on the textural properties due to the addition of a larger proportion of low surface area material (10%) which negatively affect the overall available surface area (35-40 vs 64 m^2/g).

Table 4.1: Composition and surface area of investigated samples.

Sample	Composition[a]	Specific Surface Area (m^2/g)
Zr	ZrO_2	64
ZrCu	Cu(5%)/ZrO_2	55
ZrFe	Fe(5%)/ZrO_2	53
ZrSr	Sr(10%)/ZrO_2	40
ZrSrCu	Cu(5%)-Sr(10%)/ZrO_2	36
ZrSrFe	Fe(5%)-Sr(10%)/ZrO_2	35

[a]: Composition derives from the amount of metals added during the preparation of the catalysts.

The structural features of the zirconia-based materials were analysed by powder X-ray diffraction (XRD). Materials show the simultaneous presence of tetragonal (space group P42/nmc; main reflection at 30,2°) and monoclinic ZrO_2(space group P121/c1, main reflection at 28,2°) while no evidence for any copper or iron phase was found (Figure 4.1), suggesting that Fe or Cu are homogeneously dispersed on the surface, as confirmed by SEM analysis (Figure S1 and S2).
Strontium doped materials exhibit reflections characteristic of the formation of $SrZrO_3$ (30,8°, 44,0° and 64,1°). In addition, $SrCO_3$ phase was detected (@ 25, 1 and 25,8°) for Sr impregnated materials (ZSr, ZrSrFe, and ZrSrCu) and it may occur as a consequence of the exposure of the catalysts to ambient air conditions; indeed, the basic oxides such as the oxides of alkaline-earth elements are readily carbonated when exposed in air [76, 77].

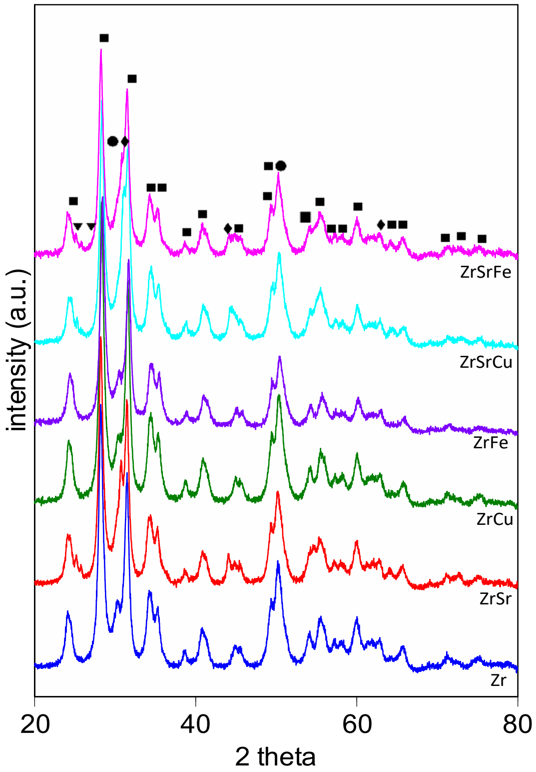

Figure 4.1: XRD profile of zirconia-based materials (ZrO_2 monoclinic, ■; ZrO_2 tetragonal, ●; $SrZrO_3$ ♦; $SrCO_3$ ▼).

4.3.2. Reduction Behaviour

Temperature-programmed reduction experiments with H_2 (H_2-TPR) have been carried out on all samples in order to characterize the reduction behaviour of the materials (Figure 4.2). For pure zirconia, a TPR feature of a typical "non-reducible" support was found while, the ZrSr show peak centred at around 750 °C, correlated with the desorption of carbonate species.

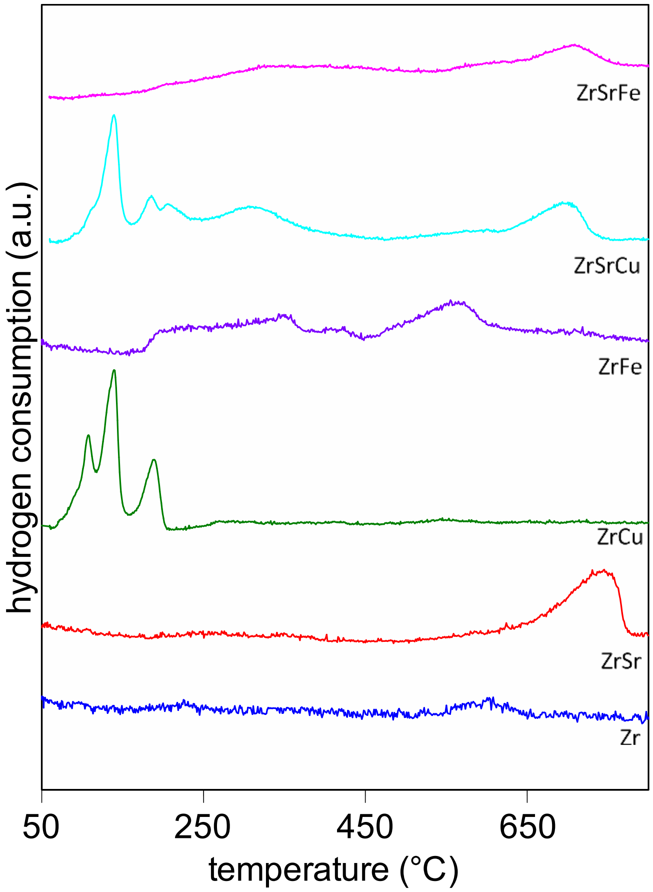

Figure 4.2: H_2-TPR profile of zirconia-based materials

ZrFe reduction profile shows two peaks, one very broad between 250 and 350 °C, the other narrower centred at about 550 °C that could be correlated to the existence of free Fe_2O_3 on the zirconia surface. It is commonly known that Fe_2O_3 is reduced in two steps, first to Fe_3O_4 and then to Fe [78]. The addition of Sr induces a broadening of the peak (between 200 and 500 °C) and the appearance of a high-temperature peak (approximately 700 °C) correlated to the desorption of carbonates [75, 79]. TPR profile of ZrCu exhibits three main reduction peaks at 110, 140 and 190 °C due to the reduction of copper species. The presence of three peaks suggests the existence of different types of Cu-phase over zirconia, strongly or weakly CuO interacting with the support and highly dispersed copper oxide, in agreement with other studies [80-82]. Specifically, the peak at higher temperature could be due to the reduction of crystalline CuO, while the peaks at lower temperature can be ascribed to the reduction in two steps of highly dispersed Cu^{2+} to Cu^0.

The addition of Sr does not significantly affect the H_2-TPR profile. As observed for ZrSrFe, there is the appearance of a peak at high temperature due to the desorption of carbonates. In the low temperature area peaks correlated to the reduction of the CuO-phases are still clearly visible but show a different intensity, indicating a different dispersion and a different interaction with ZrO_2.

4.3.3. Catalytic activity

Heterogeneous Fenton process was investigated on different zirconia-based catalysts performing reactions at 70 °C for 2hours. Two different series of data were analysed: the mineralization (as TOC abatement) and the degradation of IBP. It is important to evaluate both processes because the catalyst could degrade IBP to secondary compounds without a complete conversion to CO_2 and H_2O. The mineralization is calculated on the basis of TOC values before and after the reaction ($TOC_{in} - TOC_{out}/TOC_{in}$) and indicates the fraction of IBP that is completely oxidized to CO_2 and H_2O (equation 1) while the degradation is calculated on the amount of IBP before and after the reaction ($[IBP]_{in} - [IBP]_{out}/[IBP]_{in}$) from Orbitrap LC-MS analysis (see as an example Figure S3) and indicates the fraction of IBP that has been oxidized to secondary molecules (also including CO_2 and H_2O).

$$C_{13}H_{18}O_2 + 33H_2O_2 \rightarrow 13CO_2 + 42H_2O \qquad \text{(Eq. 1)}$$

It is critical to also estimate the adsorption effect of the materials for two reasons: a) the aim of the process is the mineralization of IBP and not only its removal by mere adsorption; b) the adsorption over the material surface may cause the deactivation of the catalyst, either by blocking the active sites or by poisoning the catalyst. To this aim, TOC removal over the catalysts have been investigated in the absence of H_2O_2 and is reported in Figure 4.3.

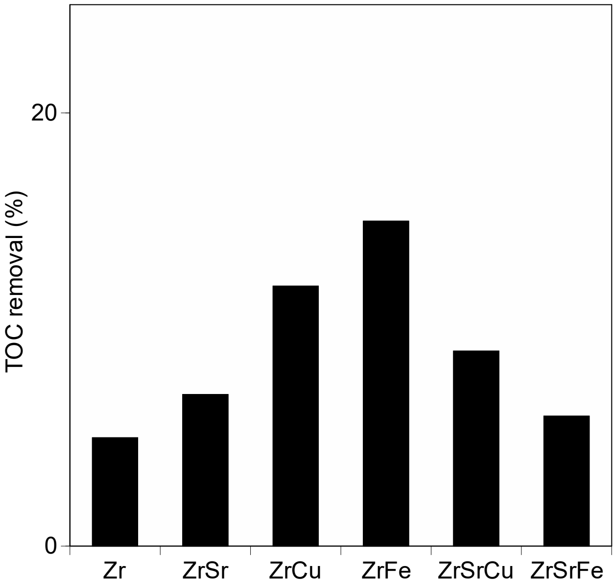

Figure 4.3: TOC removal over catalysts (reaction condition: 70 °C, IBP conc. 10 mg/L, catalyst dose 250 mg/L and reaction time 2 h).

Removal of ibuprofen under these conditions can be related to its adsorption over the catalyst surface and to the oxidation activity of the catalyst without H_2O_2. It has been observed that Zr and ZrSr reveal very low oxidation/adsorption capacity, i.e. ca. 5-7% of TOC removal, while the TOC removal increases to 12 and 15% for ZrCu and ZrFe, respectively, indicating a higher affinity between IBP molecules and the catalyst. However, the co-impregnation of Cu and Fe with Sr reduced the oxidation/adsorption capacities of the catalysts to ca. 9 and 6% for ZrCuSr and ZrFeSr, respectively which can be explained by the reduced surface area of the catalysts, as shown in Table 1. Summarizing, IBP conversion was negligible over zirconia catalyst in the absence of H_2O_2 and therefore it is possible to exclude any oxidation activity of the catalyst under these conditions and to exclude any important adsorption effects of the pollutant on the catalyst surface.

Preliminary blank tests were also carried out in order to verify the activity in the absence of catalyst. As reported in Figure 4.4, in the absence of catalyst and H_2O_2 the conversion of IBP, due only to the thermal treatment at 70°C, is small, ca. 20% but only ca. 2% is completely mineralized. Using hydrogen peroxide increases IBP degradation to 60%, however, its mineralization is around 16%, indicating that the oxidant can induce the formation of by-products but is not able to achieve an important abatement of the pollutant. When the Fenton-like process is performed over zirconia-based catalysts, an improvement in the mineralization/degradation was achieved (Figure 4.4).

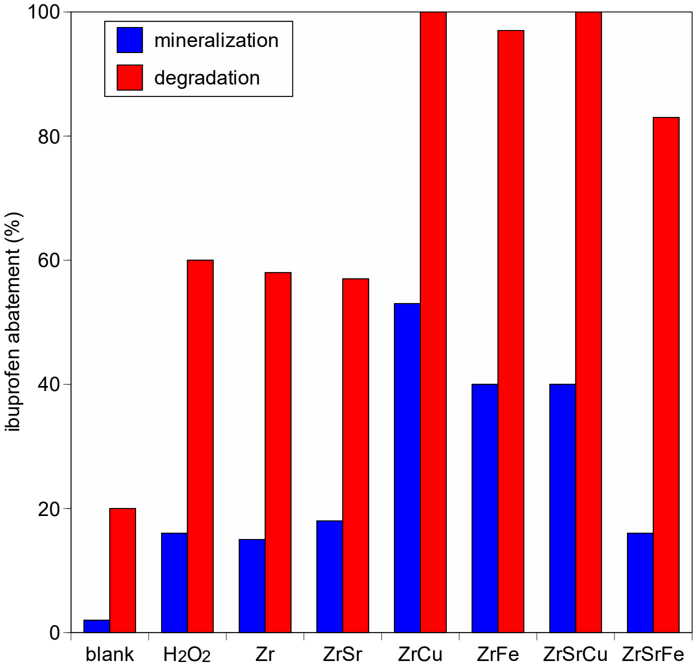

Figure 4.4: degradation and mineralization of IBP (reaction condition: 70 °C, catalyst dose 250 mg/L, pH 5, H_2O_2 dose (3%) 25 ml/L, IBP conc. 10 mg/L and reaction time 2 h). The experiment indicates as "blank" has been performed without oxidant and without catalyst.

Bare zirconia is not active for the degradation of the pollutant in Fenton-like process and the addition of Sr does not significantly modify the activity. When iron or copper are introduced in the formulation, an almost complete degradation of IBP is achieved-with a mineralization of 40% and 53% respectively for ZrFe and for ZrCu. The higher activity of ZrCu could be correlated to its reduction properties. Indeed, copper-based materials display better reduction at low temperature and this capability can be correlated to an enhanced IBP degradation under mild conditions. The presence of diverse species of CuO differently related to the support, as disclosed by H_2-TPR experiments, allow an enhanced removal of ibuprofen for ZrCu catalyst. Addition of Sr on ZrCu does not significantly affect the activity, just a slight decrease is observed, while on ZrFe the mineralization of IBP is dramatically reduced. The degradation of the activity for the ZrFeSr catalyst could be probably related to a lower reducibility of the material at low temperature, as discussed in the previous section.

ZrFe and ZrCu catalysts have proved to be among the most active in the literature, as shown in Table 4.2, with an almost complete degradation of IBP (97 and 100% respectively) and a mineralization of 40 and 53%, respectively.

Table 4.2: Comparison with literature results.

IBP amount (mg/L)	H_2O_2 dose (mM)	Catalyst dose[*] (mg/L)	Catalyst	Reaction	T (°C)	pH	Degradation (%)	Mineralization (%)	Ref
10	24,5	12,5	Cu/ZrO_2	Het.	70	5	100	53	This study
20	6,4	7,5	$FeSO_4$	Hom.+US	25	2,6	100	40	[69]
20	6,4	7,5	$FeSO_4$	Hom.	25	2,6	100	10	[69]
10	10	50	γ-Cu–Al_2O_3	Het.	r.t.	7	98	63	[83]
10	24,5	12,5	Fe/ZrO_2	Het.	70	5[#]	97	40	This study
50	3,5	430	$FeSO_4$	Hom.+UV	r.t.	-	93	90	[84]
20	6,4	163	Fe-MFI zeolite	Het.	25	3,3[#]	88	27	[87]
10	/	5	$FeSO_4$	Hom.+O_3	r.t.	6,5	85	3	[88]
10	/	5	Fe(OH)O goethite	Het.+O_3	r.t.	6,5	80	30	[88]
180	0,32	67	$FeSO_4$	Hom.+UV	30	6,25	80	40	[85]
60	8,9	25,2	$FeSO_4$	Hom.	20	3	80	15	[86]
10	/	5	Zervo valent iron	Het. O_3	r.t.	6,5	79	41	[88]
180	0,32	67	$FeSO_4$	Hom.	30	6,25	60	10	[85]

[*] in terms of metal concentration ([Fe] or [Cu])

[#] experiments were carried out without any pH adjustment (pH obtained after the addition of the catalyst).

Similar degradation but with higher mineralization than those obtained in this study were reported by Lyu et. l. [83] and Monteiro et al. [84]. In this last study, they obtained a mineralization of 90% through a photo-Fenton process, in which the synergistic effect of ultraviolet (UV) radiation and the presence of a homogeneous catalyst ($FeSO_4$) was utilized.

Indeed, the homogeneous process alone is not efficient in the mineralization reaching a 10-15% in ibuprofen reduction, independently on the pH, and on the catalyst and oxidant dose [69, 85, 86], while the degradation is strictly dependent over pH (100% is achieved with pH 2,6 while only 60% is obtained for pH 6,25). To increase the activity in the homogeneous treatment it is necessary to combine it with a second technology like ultrasound (US) [69] or ultraviolet (UV) radiation [84, 85]. In the heterogeneous process Lyu et al. [83] obtained a mineralization of about 60%, working with higher amount of catalyst compared to that used in this study. Degradation lower than 90% and mineralization in the range 25-40% were also obtained with high catalyst [87] or by exploiting a a synergic action by catalytic ozonation mechanism [88] or UV radiation [85].

As previously detailed, it is of fundamental importance evaluate not only the IBP degradation (conversion of IBP into other compounds) but also its mineralization (TOC decrease correlated to the complete oxidation into CO_2 and H_2O); indeed, the reaction could degrade IBP forming secondary compounds and the nature of these compounds is crucial in the evaluation of the process.

Orbitrap LC-MS analysis was used to quantify the IBP conversion and to identify some of the more important degradation products. A number of by-products of IBP can be more toxic than IBP itself such as dihydroxy ibuprofen, 1-(4-Isobutylphenyl)-1-ethanol and 4-isobutylacetophenone [89-91], therefore, presence of any of these metabolites may lead to a higher toxicity of treated sample. Preliminary Orbitrap LC-MS analysis has confirmed that none of these metabolites are present in the samples, when treated with zirconia-based catalyst, while they are detectable when treatment with only H_2O_2 (without catalyst) is performed. This is a very important result because it is of fundamental importance to degrade IBP into less toxic compounds. Moreover, LC-MS analysis, not detecting any degradation compound that still contains the phenyl group, suggests that the used catalysts are able to open the ring and therefore produce degradation by-products that are less recalcitrant and less toxic than the starting molecule. Summarizing ZrFe, ZrCu and ZrSrCu show to be very promising catalysts for IBP degradation; indeed, they almost completely degrade the pollutant (more than 97%) achieving a mineralization higher than 40%, avoiding the production of more recalcitrant or toxic degradation molecules. Focusing on these three formulations, the effect of reaction parameters was investigated.

In order to investigate the effect of temperature on IBP abatement, aqueous solutions have been treated at different temperatures (50, 70, and 90 °C) and the results are presented in Figure 4.5A. It is obvious that the reaction temperature is of fundamental importance in the mineralization of IBP and an increase in the reaction temperature significantly enhanced IBP removal. At 50 °C ZrCu, ZrFe and ZrSrCu afford 43, 17 and 30% abatement of IBP, respectively. When reaction temperature is increased from 50 to 70^{o}C, the most significant change is observed with Zr5Fe, where IBP mineralization has increased from 17 to 40%. Similarly, IBP abatement with Zr5Cu and Zr10Sr5Cu has also increased from 43 to 53% and 30 to 40%, respectively. When the temperature is further increased from 70 to 90 °C, percentage of IBP abatement was once again increased. The maximum IBP abatement has been obtained while using ZrCu. The lower catalytic activity observed at 50 °C, is not due to the unavailability of oxidant (we work in large excess of H_2O_2) but is related to the influence of the temperature on the formation of radical species at this temperature. Indeed, H_2O_2 utilization efficiency also increases by increasing the reaction temperature, i.e. at higher temperature the reaction rate between hydrogen peroxide and the catalyst increases, thus enhancing the rate of generation of oxidizing OH free radicals [92]. In addition to a higher conversion rate of oxidant into OH radicals, increasing the temperature favours the reaction between the IBP and the free OH radicals and improves the removal of pollutants [93, 94].

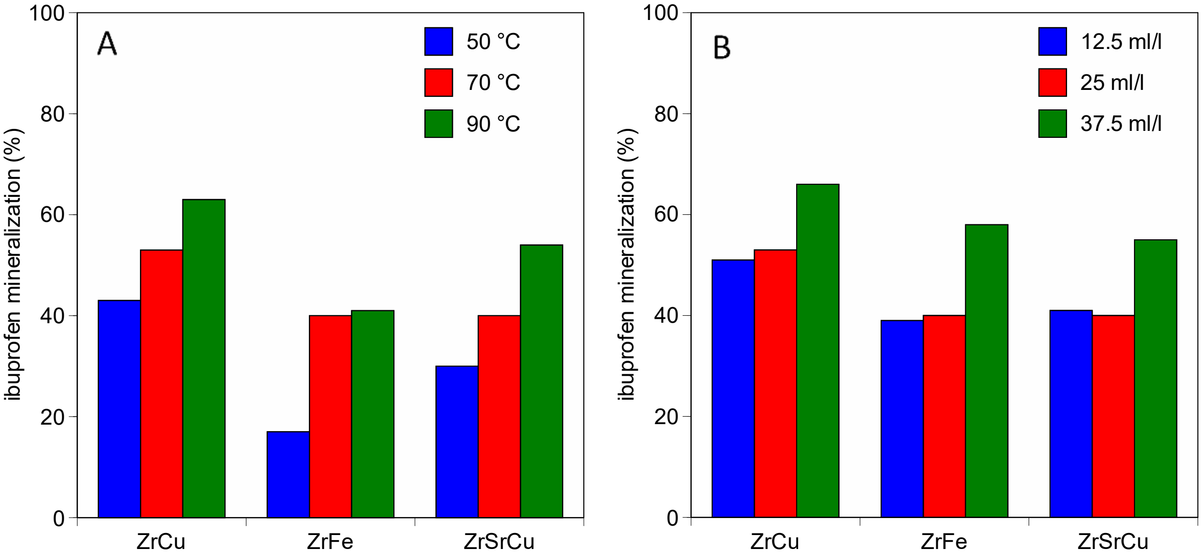

Figure 4.5: A, effect of temperature on IBP mineralization (reaction condition: catalyst dose 250 mg/L, pH 5, H_2O_2 dose (3%) 25 ml/L, IBP conc. 10 mg/L and reaction time of 2 h); B, influence of the amount of H_2O_2 (3%) on IBP removal (reaction condition: 70 °C with catalyst dose 250 mg/L, pH 5, IBP conc. 10 mg/L and reaction time of 2 h.

H_2O_2 is the primary source of OH radicals, generated by catalysts; therefore, oxidant dose is the key parameter in Fenton like processes. To examine the effect of oxidant towards IBP mineralization, varying oxidant doses have been employed and the results are illustrated in Figure 4.5B. The results indicate that when oxidant dose of 12.5 ml/L is used, the overall IBP abatements are 51% with ZrCu, 39% with ZrFe and 41% with ZrSrCu. An increase in the oxidant dose from 12.5 to 25 ml/L slightly altered the IBP mineralization. However, when oxidant dose is further increased from 25 to 37.5 ml/L, IBP abatements have markedly increased from 53 to 66% with ZrCu, from 40 to 58% with ZrFe, and 40 to 55% with ZrSrCu. These results suggest that when oxidant dose is increased from 12.5 to 25 ml/L, the increase in the generation of OH radical, is negligible. It is possible that the added oxidant is rapidly decomposed and does not add much free radical into the aqueous system to enhance process efficiency. However, further addition of the oxidant i.e. 37.5 ml/L generates sufficiently higher amount of free radicals which markedly increases the IBP mineralization.

An optimized catalyst dose must be found experimentally because a too low amount is not enough to obtain good catalytic activity, while too large amounts may negatively affect the reaction as well as make the process economically non feasible. In order to investigate the effect of catalyst loading on IBP mineralization, catalyst doses of 250, 500, and 750 mg/L are used, and the results are presented in Figure 4.6A. Increasing the catalyst dose from 250 to500 mg/L slightly affects the abatement of IBP. These results indicate that a higher catalyst dose caused generation of higher number of free radicals, which in turn increased the process efficiency. However, further increase in the catalyst dose from 500 to 750 mg/L does not significantly affect IBP mineralization when ZrCu and ZrFe are employed but negatively affect the activity over ZrSrCu. These results suggest that further increase in catalyst loading started to cause scavenging effect i.e. catalyst started to consume the generated free radicals in the system, giving rise to lower process efficiency [38].

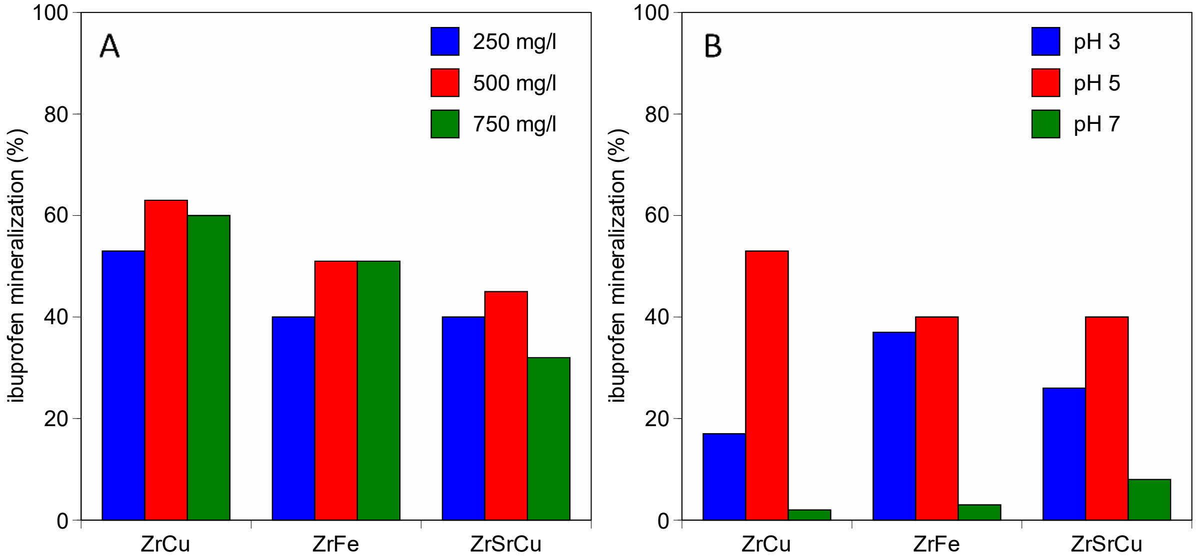

Figure 4.6: A, Effect of catalyst dose on IBP mineralization (reaction condition: 70 °C, pH 5, H_2O_2 dose (3%) 25 ml/L, IBP conc. 10 mg/L and reaction time of 2 h); B, influence of pH on IBP mineralization (reaction condition: 70 °C, catalyst dose 250 mg/L, H_2O_2 dose (3%) 25 ml/L, IBP conc. 10 mg/L and reaction time of 2 h) at 70 °C, oxidant dose 25 ml/L, pH 5, IBP conc. 10 mg/L, and reaction time of 2 h.

One of the most critical parameters in Fenton like processes is pH because it governs the activity of the catalyst. Although, many research studies suggest that Fenton like processes yield better results at lower pH [95, 96], the optimum values of pH can vary depending upon the nature of catalyst and pollutants as well and needs to be determined experimentally [97, 98]. In order to investigate the effect of pH on IBP mineralization, aqueous solutions are treated at pH 7, 5, and 3 respectively and the corresponding results are presented in Figure 4.6B. As evident from the graphical illustration, IBP mineralization at neutral pH is almost negligible with each catalyst. However, when pH of aqueous solution is maintained at 5, each catalyst afforded maximum IBP mineralization. These results suggest that all the employed catalysts are more active under mild acidic conditions i.e. pH 5. When pH is further decreased from 5 to 3, the mineralization of IBP is declined. It is possible that at lower pH, the active sites/metal ions of the catalyst are lost by leaching, leading towards the lowering of activity [99]. Thus, it can be deduced that the catalytic activity is predominantly, by means of active sites rather than its dissolution in the aqueous media [38].

ZrCu was the most promising catalyst and its stability over several repeated reaction cycles was carried out (Figure 4.7 and S4). No significant variation of ibuprofen mineralization was observed in four cycles confirming the stability of the materials over several reaction cycles. The average low Cu concentration in the output streams (0,02 mmol/l) reveals the good stability of ZrCu catalyst against leaching of active components. This confirms the high attractiveness of copper systems supported on zirconia for the removal of ibuprofen from liquid waste.

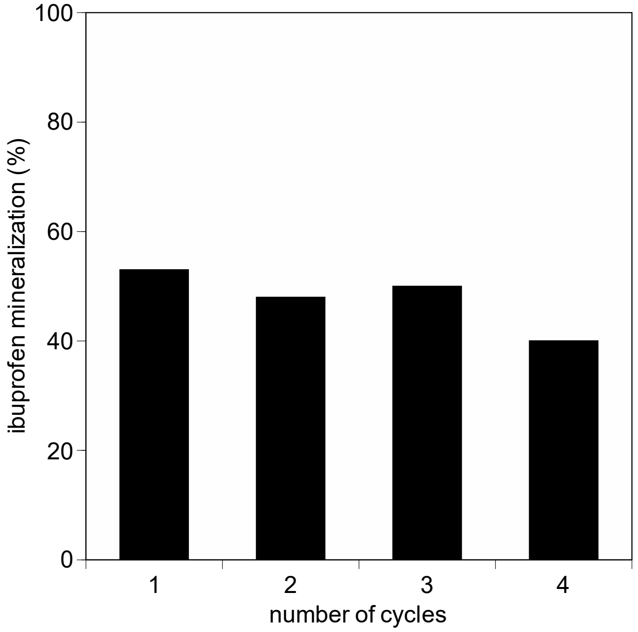

Figure 4.7: Effect of catalyst recycling on IBP mineralization (reaction condition: 70°C, oxidant dose 25 ml/L, pH 5, catalyst dose 250 mg/L, IBP conc. 10 mg/L and reaction time of 2 h)

4.4. Conclusions

Our study shows that the heterogeneous Fenton process over copper or iron catalysts could be successfully used in the treatment of ibuprofen from liquid waste. Promising results were obtained with ZrCu catalysts with an almost complete degradation of the ibuprofen and a 50% of mineralization. The higher activity of ZrCu is related to the presence of several CuO species. Orbitrap LC-MS analysis evidenced that the zirconia-based materials are able to degrade the parent molecule opening the ring and therefore inducing the degradation into less recalcitrant and less toxic compounds.

Acknowledgements: The authors thank Stefano De Martin, Director of ARPA FVG and Dr. Maria Lekka (University of Udine) for SEM analysis.

Supplementary Data

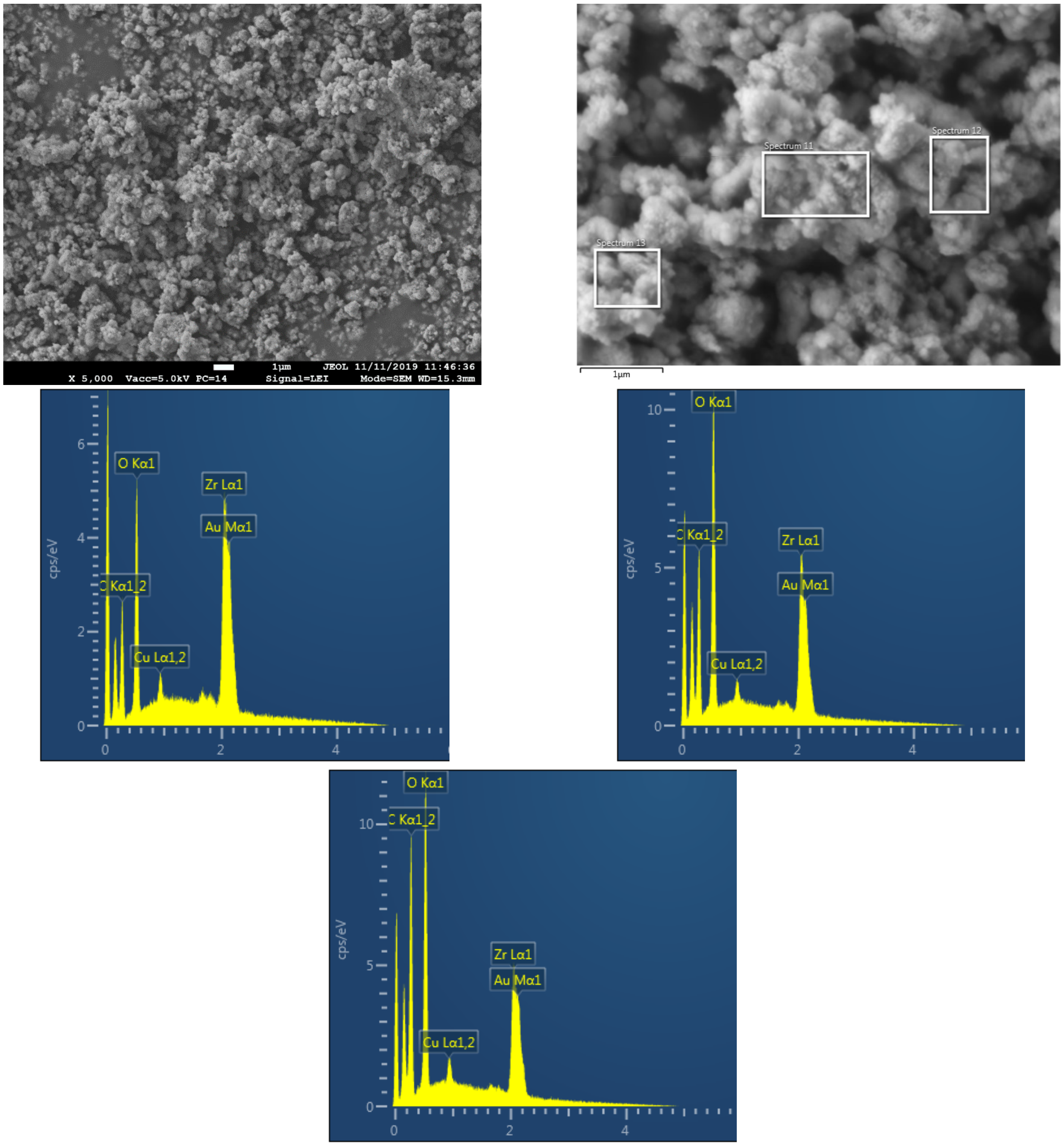

Figure S1: SEM images and EDXS for ZrCu

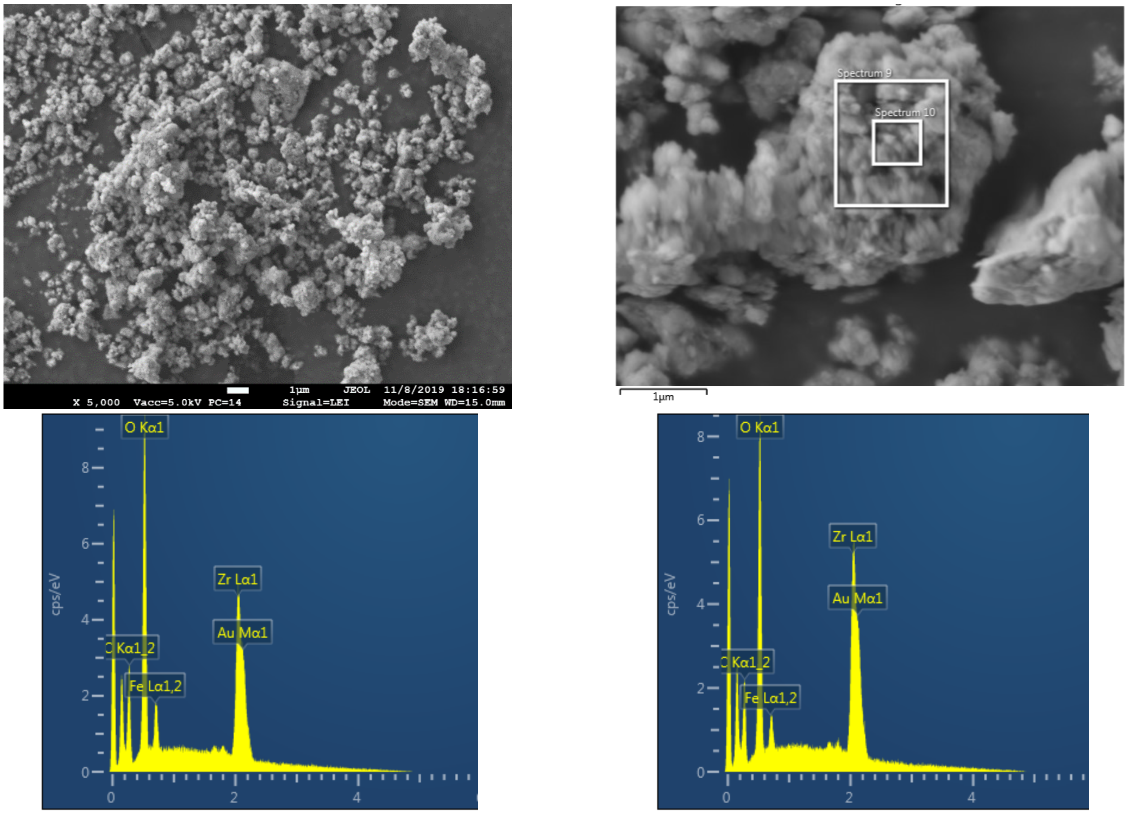

Figure S2: SEM images and EDXS for ZrFe

SEM images for ZrCu and ZrFe. Materials show a very similar morphology and evidenced, in agreement with XRD results, a homogeneous dispersion of the metal (Cu or Fe) over the zirconia support.

The powders morphology has been observed by Field Emission Scanning Electron Microscopy (JEOL model JSM-7610FPlus). The specimens have been coated by a thin gold layer by spattering prior the observations. The observations have been performed in secondary electron mode using an acceleration voltage of 5KeV. The chemical composition was determined by Energy Dispersive X-ray Spectroscopy- EDXS (Oxford Instruments X-Max 20) analysis using a Quant Standardization of 5keV.

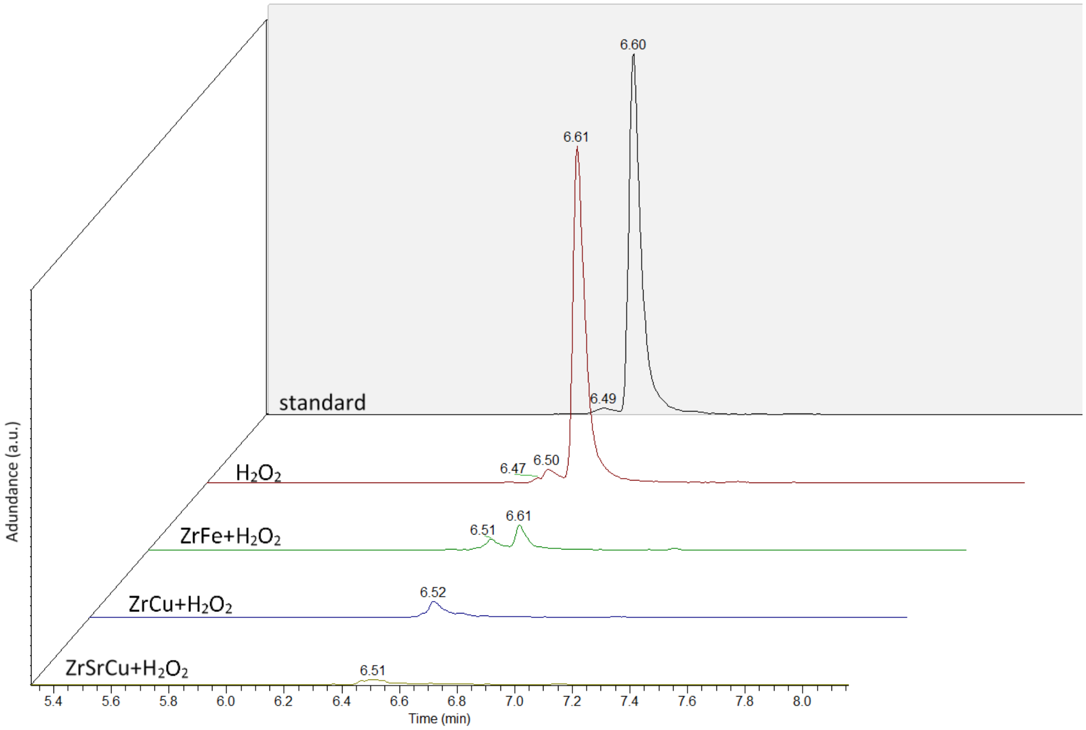

Figure S3: LC-MS Orbitrap chromatograms (reaction condition: 70 °C, catalyst dose 250 mg/L, pH 5, H_2O_2 dose (3%) 25 ml/L, IBP conc. 10 mg/L and reaction time 2 h). The experiment indicates as H_2O_2 has been performed without catalyst.

LC-MS Orbitrap chromatograms. The peak at retention time 6.60 minutes is due to the presence of ibuprofen. When Fenton process over zirconia-based catalysts has performed an almost complete removal of ibuprofen is observed.

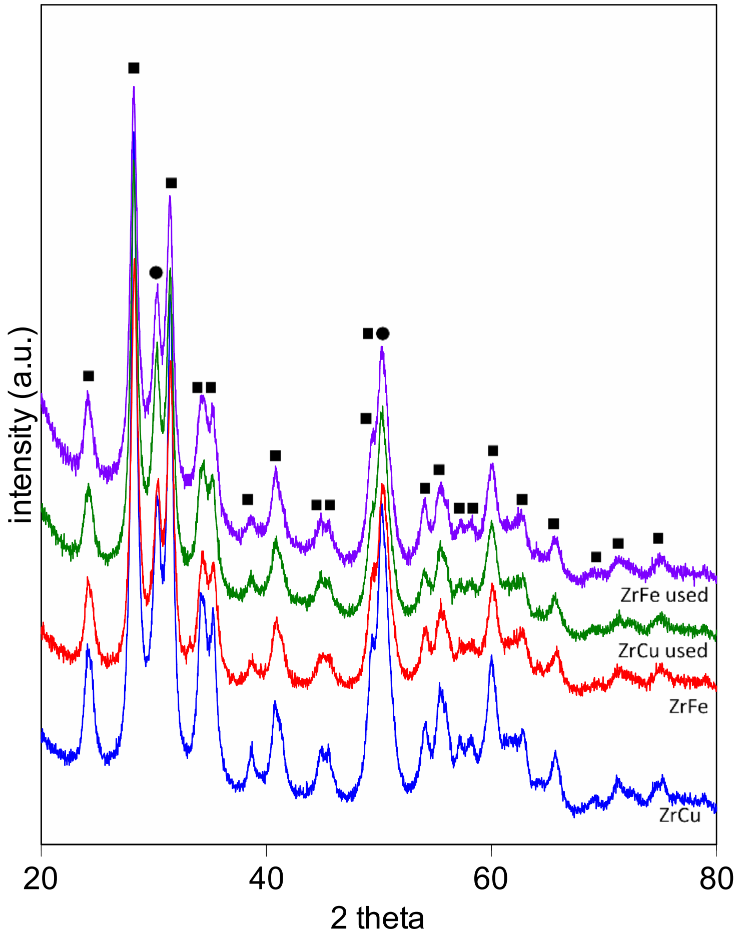

Figure S4: XRD profile for ZrCu and ZrFe (ZrO$_2$ monoclinic, ■; ZrO$_2$ tetragonal, ●)

XRD profiles for ZrCu and ZrFe. Materials (before and after four cycles of reaction) show the simultaneous presence of tetragonal (space group P42/nmc; main reflection at 30,2°) and monoclinic ZrO$_2$ (space group P121/c1, main reflection at 28,2°) while no evidence for any copper or iron phase was found. XRD profiles for catalysts before and after reaction do not show any significant difference, confirming the stability of the materials over several reaction cycles.

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Chapter-5

Treatment of landfill leachate through heterogeneous Fenton like oxidation using copper supported over zirconia and qualitative monitoring of the organic abatement with H^1 NMR spectroscopy

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Abstract

This study encompasses the treatment of landfill leachate through heterogeneous Fenton like oxidation process using ZrCu catalyst. The catalyst is prepared using incipient wetness impregnation method and is characterized using conventional techniques. The maximum abatement, 65% in terms of total dissolved organic carbon (TDOC), is obtained at optimal conditions of pH 5, 200 mg/L of catalyst, 30 ml/L of H_2O_2 and reaction temperature of 70 °C. The activity of the catalyst is almost stable under optimal reaction conditions, as proved by recycle tests. AOS (average oxidation state) and COS (carbon oxidation state) parameters has been used for the evaluation of the degree of oxidation of the process, obtaining some insight about the formation of oxidized intermediates and the total oxidation (mineralization) of the leachate during the reaction. The qualitative abatement of various organic compounds is determined through proton nuclear magnetic resonance (^{1}H NMR) analysis. Heterogeneous Fenton process also removes 63% of the absorbable organic halogens (AOX) from the leachate and significantly reduced the toxicity as disclosed in bioassay risk assessment tests. The Fenton-like treatment over ZrCu catalyst achieve not only depollution but also detoxification of landfill leachate. A two-step oxidation process enhances the overall performance of the reaction from 65 to 92% in terms of TDOC reduction confirming the promising activity of ZrCu for the treatment of liquid waste.

Keywords

Landfill, wastewater, AOP, Catalytic Treatment, Fenton like, Oxidation

5.1. Introduction

Landfill is the most widely adopted method for the disposal of solid wastes. Approximately, 95% of the world's solid waste is discarded in landfills [1, 2]. Over the period of time, the solids in the landfills undergo through physiochemical and biological processes and landfill leachate, a heavily polluted wastewater [2, 3] is produced when rainwater runs through these sites [4]. Consequently, leachate has become a serious environmental concern because it contaminates both soil and groundwater [5]. The concentration and composition of this liquid waste, typically depends on the site and the age of the landfill [6]. Leachate can be classified into three types based on chemical oxygen demand (COD) values: young (>10,000 mg/L) , intermediate (4000 – 10,000 mg/L) and old (<4000 mg/L) [2, 7]. Generally, landfill leachate consists of contaminants such as organics, inorganics, nitrogen/ammonia, heavy metals etc. [3]. It can only be treated using conventional biological treatment process if the leachate is not very old [8]. However, biological treatments are often unable to treat leachate because of the heavy organic loading and the presence of very stable and high molecular weight organics [9]. Therefore, treatment of leachate requires intensive physical and chemical processes in order to comply with the stringent environmental regulations [2, 10].

Advanced oxidation processes (AOPs) are among the most effective treatment methods for the abatement of refractory pollutants and thus can be applied for the treatment of leachate [11-13] because these processes have been successfully employed for the treatment of different types of wastewaters [3, 14-16]. These processes typically rely on the generation of highly reactive hydroxyl radicals ($OH^{\bullet}$), which in turn attack the organics and degrade them [17]. Since $OH^{\bullet}$ is the second strongest oxidizing species with respect to oxidation potential (Table 5.1), it is extremely effective for the abatement of organics.

Table 5.1: Oxidation potential of some oxidizing agents

Type of Oxidant	Oxidation Potential (E^0) (V)
Fluorine	3.06
Hydroxyl Radical	2.80
Oxygen (Atomic)	2.42
Ozone	2.08
Hydrogen Peroxide	1.78
Hypochlorite	1.49
Chlorine	1.36
Oxygen (Molecular)	1.23

There are various types of AOPs such as Fenton, Fenton like, ozonation, electrochemical, photochemical etc. but in principle, all these processes are essentially the same due to similar oxidation mechanism. However, the effectiveness of these processes depends upon their ability to generate oxidizing species. The conventional Fenton process is the most widely used AOP because of its simplicity and economic feasibility, however, there are several drawbacks associated with this process. For instance, the process is ineffective when it comes to degrade complex organics and high activity of the process is only achievable when strict acidic conditions are applied [19]. Moreover, it generates large volumes of residual sludge which needs to be disposed, creating another environmental and economic problem [20, 21]. Similarly, other AOPs employing physical fields are neither economically feasible due to high energy input nor have the potential to be scaled up on industrial levels [22]. That is why, a modified Fenton process generally referred as Fenton-like process employing Fe^{3+} in place of Fe^{2+}, remains the most viable solution for the treatment of wastewater because it produces less solid sludge, catalyst can be recycled and these features make this process feasible in terms of scalability and economics [22, 23].

However, there is a growing need for the development of new catalysts with extended recyclability, improved activity and selectivity which can ultimately be employed in Fenton-like process. The organic abatement efficiency of a Fenton-like process can substantially be enhanced by replacing Fe^{+3} with other transition metals as a catalytic source [23-27]. One good replacement is copper impregnated over appropriate supports. There are several advantages of employing copper such as high catalytic activity, non-toxicity, abundant availability and lower price compared with other reactive transition metals [25, 27, 28]. Moreover, copper has an additional advantage that it can also be employed in an integrated process i.e. photo-Fenton process [28]. Furthermore, the mechanism of $OH^{\bullet}$ generation from Cu^{+} and Cu^{+2} is similar to the conventional Fenton process (Eq. 1 and 2)[25, 29]:

$$Cu + H_2O_2 \longrightarrow Cu^{+} + HO_2 + OH^{-} \qquad \text{(Eq. 1)}$$

$$Cu^{+} + H_2O_2 \longrightarrow Cu^{2+} + HO^{\bullet} + HO^{-} \qquad \text{(Eq. 2)}$$

Additionally, unlike iron, copper does not form stable complexes with oxidation products of organics and by employing copper, consequently, it is absolutely possible to completely mineralize the pollutants into water and CO_2 [27, 30, 31]. Moreover, copper catalyzed Fenton like process is also able to afford high catalytic activities, particularly near neutral pH conditions[30]. It is worth mentioning that although supports do not directly participate in catalytic activity, but selection of an appropriate support not only enhances the activity but also increases the stability of the catalyst. It is particularly true in heterogeneous Fenton-like reactions where leaching of the catalyst causes a reduction in catalytic performance [13]. Therefore, appropriate supports are desirable which offer strong bonding with the catalyst, inhibit the loss of the catalyst and prevent the transformation of heterogeneous reaction into homogeneous one [25]. Keeping in view of the favorable catalytic characteristics of copper for Fenton like oxidation many researchers employed various supports to enhance the stability and activity of the copper based catalysts such as alumina [32], calcium phosphate [33], zeolites [34], activated carbon [35], birnessite (δ-MnO_2) [12], montmorillonite [36], mesoporous SBA-15 [37], graphene [38], polymers [39], perlite [40], mixed supports [41] etc.

In this study we have employed copper supported over zirconia as a heterogeneous catalyst for the treatment of landfill leachate because it showed promising catalytic results in Fenton like oxidation while working with model aqueous solutions of Ibuprofen [42]. The activity of the catalyst is investigated in terms of total dissolved organic carbon (TDOC) and chemical oxygen demand (COD) because these parameters are widely studied by the industry and academia [43]. TDOC results indicate the amount of organics in the raw leachate that are mineralized during the treatment, while COD give us important information about the degradation of the compounds into more oxidized molecules. Moreover, COD-TOC relationship, before and after treatment, provides some insight on the formation of organic intermediates during the oxidation reaction.

The efficacy of chemical oxidation of Fenton-like process and the state of oxidation can be interpreted by means of combination of TOC, COD and their relationship. When organics are treated by Fenton reaction partial or ultimate degradation can be achieve. In partial degradation parent compounds are degraded into more oxidize intermediates with improvement of the biodegradability and reduction of the toxicity. When ultimate degradation occurs, organics are complete oxidized into carbon dioxide, water and other inorganics. The various degradation stages are followed by means of COD (degree of oxidation), while TOC provides an insight regarding the total mineralization. If mineralization is achieved during Fenton reaction, TOC decreases but if only partial oxidation occurs it remains constant with a decrease of the COD [43]. Additionally, the AOX content analysis of the leachate before and after treatment has been performed which is also another parameter used to monitor the quality of the effluent. AOX parameter indicates the content of organics binding some elements from the group of halogens; these substances are potentially toxic, especially for aquatic ecosystems, and their contents in landfill leachate should be carefully monitored [44-48].

A study on the effects of leachate on unicellular green algae was carried out under controlled laboratory conditions to evaluate the toxicity after Fenton treatment. These results indicate a detoxification of the liquid waste after Fenton treatment, suggesting that the process can completely mineralize a part of the organic compounds and partially degrade other pollutants into less toxic molecules.

In order to optimize the efficacy of the Fenton like process, several operating parameters such as pH, catalyst dose, oxidant dose, temperature, and reaction time have been studied and their corresponding effects on pollutant abatement are discussed. Moreover, the catalytic activity has also been investigated after subsequent/multiple recycles of the catalyst. Furthermore, a two-step oxidation process is also carried out to enhance the overall process efficiency so that the finally treated leachate is conveniently integrated with existing biological treatment facilities. For the first time, we have utilized ^{1}H NMR spectroscopic analysis to monitor the qualitative abatement of organics from landfill leachate. The final aim of this study is the development of an innovative catalyst for Fenton-like process to achieve, by tuning the degradation pathway through less toxic byproducts, not only depollution but also detoxification of landfill leachate.

5.2. Materials and methods

5.2.1. Materials

Landfill Leachate samples were collected from landfill site situated in Friuli Venezia Giulia, Italy. The leachate samples were collected in polyethylene bottles and were preserved at 4 °C and the characterization was carried out following the Standard Methods for the Examination of Water and Wastewater [49]. Copper doped catalyst (5 wt. %) was prepared by incipient wetness impregnation of ZrO_2 (MEL Chemicals) with an aqueous solution of copper (II) nitrate hemi pentahydrate (Sigma Aldrich), and dried overnight at 100 °C. After drying, the sample was finally calcined at 500°C for 3 h.

5.2.2. Treatment of Landfill Leachate

The suspended solids from landfill leachate were removed by centrifugation at 5000 rpm for an hour using Eppendorf Centrifuge 5804 R, followed by filtration through a 0.45 µm membrane filter. The pH of the leachate samples was adjusted by the addition of HCl/NaOH/H_2SO_4 (Sigma Aldrich), and an optimum pH for maximum catalytic activity was experimentally determined before conducting the standard experiments. The leachate samples (100 ml) loaded with 200 mg/L of ZrCu catalyst were heated at 70 ˚C under continuous stirring conditions of 500 rpm, using a STEM Omni multistage reaction station (Electrothermal) with a provision of reflux. Finally, 30 ml/L of 3% H_2O_2 was added into the reaction system and the Fenton like oxidation reaction was carried out for 150 minutes and the samples were collected after every 30 minutes of time interval to observe the periodic catalytic activity. Further, the oxidation process was optimized evaluating the effects of catalyst dose (100, 200 and 300 mg/L), hydrogen peroxide 3% (30, 40 and 50 ml/L), temperature (60, 70 and 80^{o}C) and pH (3, 5 and 8). To observe the catalytic activity of the recycled catalyst, it was recovered and reused without any modification. A two-step Fenton process was performed by employing fresh catalyst in each oxidation step. The treated samples were centrifuged at 5000 rpm using Eppendorf Centrifuge 5804 R for 10 minutes and the supernatant solutions were collected in vials for TDOC analysis.

5.2.3. Catalytic activity measurements

5.2.3.1. TDOC analysis

Total dissolved organic carbon (TDOC) was used instead of Total organic carbon (TOC), because the suspended organic matter in leachate may affect the oxidation process. These disturbances were mainly arising due to the deposition of suspended particles over catalyst surface, hindering its activity and also due to the miscalculation of the oxidant dose, needed to degrade pollutants from leachate. Keeping in view of these processing constraints and to precisely monitor the activity of the catalyst with varying parameters, TDOC has been chosen as standard process parameter. In order to observe the mineralization of organics in the leachate, the TDOC of the treated samples was analyzed using a TOC-VCPN, Shimadzu analyzer (V-Series) with an auto sampler. First, the standard solutions with known concentrations of 2.5, 5.0, 10.0, 20.0 and 50.0 mg C/l were prepared using potassium hydrogen phthalate stock solution. A calibration curve was obtained by analyzing the standard samples, and after each analysis the injection syringe was auto sparged with 2M HCl. The samples were analyzed without dilution and using the same calibration curve to determine TDOC present in each sample. The TDOC removal efficiencies were determined using Eq. 3:

$$\text{TDOC removal efficiency } (\%) = \frac{TDOC_i - TDOC_f}{TDOC_i} * 100 \qquad \text{(Eq. 3)}$$

Several experiments were also carried out to verify the reproducibility of our activity measurements and the errors resulted to be within 3%.

5.2.3.2. *COD analysis*

To determine the chemical oxygen demand (COD) of samples, 2 ml of distilled-deionized water (blank reference) and leachate samples were separately added into COD testing kits. These testing kits were thoroughly shaken and subjected to heating at 150 °C for 2 hours using HACH COD reactor. Later, these vials were cooled down to room temperature and the COD values were measured using) PC MULTIDirect SN 05835 photo spectrophotometer. The COD removal efficiencies are calculated using Eq. 4:

$$\text{COD removal efficiency } (\%) = \frac{COD_i - COD_f}{COD_i} * 100 \qquad \text{(Eq. 4)}$$

Several experiments were also carried out to verify the reproducibility of our activity measurements and the errors resulted to be within 10%.

5.2.3.3. COD/TOC analysis

In order to evaluate the degradation/mineralization degree of our treatment, AOS (average oxidation state) and COS (carbon oxidation state) are calculated by means of equation 5 and 6 [50].

$$AOS = 4 - 1.5\frac{COD}{TOC} \qquad \text{(Eq. 5)}$$

$$COS = 4 - 1.5\frac{COD}{TOC_0} \qquad \text{(Eq. 6)}$$

COD and TOC are expressed in mg/l; TOC_0 is the TOC value at the beginning of the process (TOC of raw leachate).

AOS give an insight into the composition of organic matter, indeed increases along the process when more oxidized intermediates are formed during the reaction. COS, instead gives information about the oxidation of organic matter: low COS value indicates the presence of rather reduces organic compounds, while higher values are related with strong mineralization and generation of highly oxidized intermediates. Summarizing, AOS is associated to partial oxidation and formation of oxidized intermediates, while COS is related to total oxidation (mineralization) of the leachate.

5.2.3.4. AOX analysis

In order to measure the concentration of adsorbable organic halogens (AOX), the leachate samples were first diluted 1/100 times with distilled-deionized water and mixed with 1 g/L of activated carbon. To purge the chlorides coming from inorganic sources, 1 ml of 0.1 M solution of $Na_2S_2O_3$ was added into the solution and the mixture was subjected to shaking at 180 rpm/m using KS 501 D Shaker (IKA-Werke GmbH & Co. KG) for 1 hour. The thoroughly mixed solution was then filtered through 0.2 µm cellulose acetate membrane filter, followed by washing of the filter cake with 0.5 M $NaNO_3$ solution to eliminate any residual inorganic sourced chlorides. The membrane filter carrying activated carbon was inserted into Euroglass AOX sampler and the concentration of AOX was measured. Several experiments were also carried out to verify the reproducibility of our measurements and the errors resulted to be within 5%.

5.2.3.5. ICP and UV-Vis spectrophotometric analysis

The concentration of heavy metals in landfill leachate was determined with US EPA 3051 method using Inductivity Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES vista pro.) First, a calibration curve was obtained using an ICP 23-element standard solutions which were prepared in 5% HNO_3. Yttrium (Y) was used as an internal standard. The method detection limit (MDL) was calculated as 3 s/m (s = Standard deviation of 10 replicate blanks and m = slope of the calibration curve for each element).

UV-Vis analysis of samples is carried out using Shimadzu 2600i spectrophotometer and absorbance was measured from 200 to 700 nm, in a quartz cell with a path of 1 cm.

5.2.3.6. ^{1}H NMR spectroscopic analysis

A volume of 200 µl of raw and treated landfill leachate samples were separately dissolved in 800 µl of D_2O followed by thorough mixing. The samples were subjected to ^{1}H NMR analysis using (Bruker Avance 400 MHz NMR spectrometer). The qualitative efficacy in the organic abatements over the Fenton like process is determined by analyzing the resonance signals in the spectra of landfill leachate before and after treatment.

5.2.3.7. Toxicity test on a single-celled green algae culture

The algal growth inhibition test with Raphidocelis subcapitata was performed in a 24-well plate following the OECD 201 guideline and ISO 8692: 2012.

An aliquot of cryofrozen algae (1 million / vial) was taken from the biobank and cultured in BG-11 medium at 25 ± 1 ° C in an incubator in the presence of light. Before use in the ecotoxicological test, the algae were kept in line for 2 weeks with bi-weekly renewal of the culture medium to allow the exponential growth of the algal population. After 14 days, the response of the algal population to potassium dichromate in the range 0.1-3.2 mg / L was evaluated as an indicator of the suitability of the culture for use in the toxicity test.

Once the desired sensitivity was reached, the algal growth inhibition assay was performed. The algae (10,000 cells / mL) were inoculated into the wells of the multiwell plate containing dilutions of the leachate as it is or treated in previously oxygenated reconstituted standard water (ISO Algal Freshwater). The reconstituted standard water was used as a negative control while the potassium dichromate (range 0.1-3.2 mg / L) was used as a positive control to check algal sensitivity during the test.

The multiwell plate was then incubated at 23 ° C for 72 hours in the presence of light and under dynamic shaking (tilting shaker, 90 rpm).

At the end of the exposure period, the algal growth in each well was determined as the change in the number of algae with respect to time 0 (inoculum) by means of an automatic counter TC20, selecting a dimensional gate between 4 and 10 microns.

5.3. Results and discussion

All the catalytic tests have been carried out after the removal of the suspended solids from landfill leachate by centrifugation. Suspend solid has been removed because we would like to focus on dissolved organics that represents the more recalcitrant compounds in landfill leachate. Moreover, we would like to investigate the intrinsic activity of our catalyst and suspended solids could interfere with the catalyst, masking its efficiency by blocking its active sites. The characteristics of leachate selected to test oxidative Fenton-like process are presented in Table 5.2. The raw landfill leachate can be classified as an intermediate-age leachate with a COD value of 8700 mg/L and a pH of 8.5. The pH of young leachate is less than 6.5 while it progressively increases with the aging of the leachate [10]. The concentration of heavy metal ions is quite low, which is in agreement with landfill leachate in the intermediate phase; indeed, the increasing in the pH induces a decreasing solubility of many metal ions.

Table 5.2: Characteristics of landfill leachate

Parameters	Value
pH	8.5
Chlorine	80 mg/L
Hardness ($CaCO_3$)	360 mg/L
COD	8700 mg/L
TOC	970 mg/L
AOX	13 mg/L
Total Nitrogen (TN)	1.94 g/L
Color	Dark brown
Al	5 mg/L
Ca	38.2 mg/L
Cr	0.7 mg/L
Fe	2.7 mg/L
Mn	0.1 mg/L
Mg	55.8 mg/L
Ni	0.4 mg/L
Zn	0.3 mg/L

Textural, structural and redox characteristics of the catalyst have already been reported [42]. The surface area is 55 m^2/g, the material is composed by tetragonal (space group P42/nmc) and monoclinic (space group P121/c1) zirconia and copper is homogeneously dispersed on the surface of the support. Characterization of the redox properties of the catalyst indicates a high reducibility of the materials at low temperature (three reduction peaks at 110, 140 and 190 °C) and the presence of different types of Cu-phase over zirconia: highly dispersed copper oxide and CuO interacting with the support [42] .

Heterogeneous Fenton process was investigated on ZrCu catalyst performing reactions at 70 °C for 150 minutes. The process has been optimized over several variables such as pH, catalyst and H_2O_2 dose, reaction temperature and their effect on the catalytic reaction has been investigated. The catalytic activity was followed by TDOC abatement. It is of fundamental importance to evaluate the adsorption capacity of the material because the aim of the process is the degradation of organics in landfill leachate and not only their removal by mere adsorption; moreover, the adsorption of organics over the surface could deactivate the catalyst, by poisoning it or by blocking its active sites.

Preliminary blank tests were also carried out. Landfill leachate conversion was negligible (7 % of TDOC abatement) over ZrCu catalyst in the absence of H_2O_2 at 70 °C and therefore it is possible to exclude any important adsorption phenomena of the organics over the catalyst surface and any oxidation activity of the catalyst under these conditions. surface. Similar outcome was found with the use of H_2O_2 in the absence of catalyst at 70 °C, with negligible values of conversion (10% of TDOC abatement).

5.3.1. Effect of pH

The pH of the aqueous medium is the most critical parameter which governs the efficacy of the Fenton like process. An optimum pH is always required which facilitates the catalyst to generate maximum $OH^{\bullet}$ radicals from the oxidant. Therefore, it is essential to experimentally determine the optimum pH for an enhanced performance of the catalyst. In order to illustrate the performance of the catalyst at different pH values, TDOC and COD results have been presented in Figure 5.1.

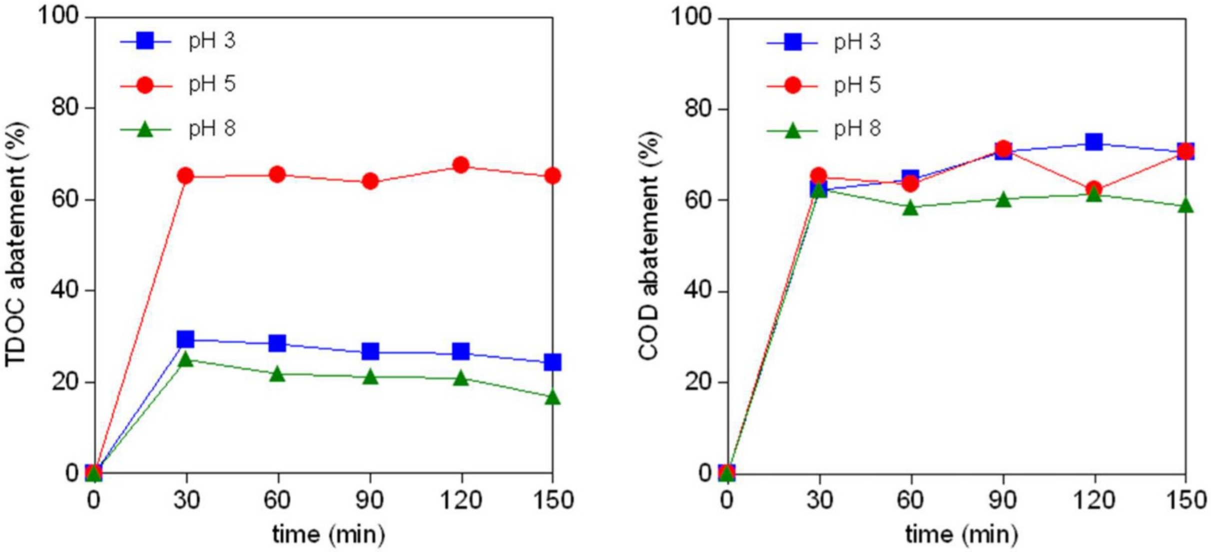


Figure 5.1: TDOC and COD abatements with variable pH (reaction condition: 70 °C, catalyst dose 200 mg/L, H_2O_2 dose 30 ml/L (3%) and reaction time 150 min)

When leachate is processed at lower pH (pH 3) the TDOC removal is only around 30%. This indicates that the employed pH is too acidic for the catalyst to produce maximum amount of $OH^{\bullet}$ from the oxidant. Instead of forming beneficial oxidizing species, the oxidant may have formed oxonium ions and, consequently, a lower organic mitigation was afforded [6]. When landfill leachate is treated at pH 5 the highest TDOC reduction has been achieved (66%) in early 30 minutes and later, the catalytic activity stabilized. This is explained by Choina et.al. [51] suggesting that the activity of a catalysts in Fenton like oxidation reaches to its maximum when the process is run at pH values which conform to its point of zero charge (PZC) . Since, the practically determined PZC of CuO is 6 [52] and that of ZrO_2 is 5.5 [53] pH 5 is very near to PZC of the catalytic system and should be the optimal pH for the maximum removal of organics from landfill leachate. However, when the heterogeneous Fenton reactions are carried out at pH 8, the TDOC removal is markedly decreased to 25% and this is due to the fact that H_2O_2 tend to decompose into water and oxygen at higher pH [54, 55] and consequently, a lower mineralization activity of the organics in the leachate is obtained.

While TDOC shows higher activity at pH 5, COD abatement is almost independent over the pH, achieving around 65% of removal for all the pH conditions, after 30 minutes of reaction. This phenomenon suggests that complete oxidation of organics occurs at pH 5 while at pH 3 and 8 both partial and complete oxidations occur.

Consequently, pH 5 results the best condition in order to mineralize the organics in the leachate, while lower or higher pH mainly induce degradation with formation of more oxidized intermediates. However, in all the conditions a better biodegradability of the landfill leachate could be obtained by Fenton-like process over ZrCu.

COS (Table 5.3) calculated by means of eq. 6 increases from -9.5 for raw leachate to 0 after Fenton oxidation at pH 3 and 5 and to -1.5 for reaction at pH 8, indicating a strong oxidation of organic matter for all pH conditions, although, oxidation is more pronounced at pH 3 and 5. AOS, calculated by means of Eq. 5 at the beginning of the reaction is -9.5. After reaction at pH 3 and 8 increases to -1.4 and -2.6, respectively confirming the degradation into more oxidized intermediates, while at pH 5 is -7.5 suggesting that the complete oxidation of the organics into CO_2 (mineralization) is prevalent.

Table 5.3: AOS and COS values calculate by Eq. 6 and 7.

Process Conditions	AOS	COS
	pH	
pH 3	-1.4	0
pH 5	-7.5	0
pH 8	-2.6	-1.5
	temperature	
60 °C	-1.6	0
70°C	-7.5	0
80 °C	-4.7	0.5
	catalyst dose	
100 mg/L	-3.3	0.4
200 mg/L	-7.5	0
300 mg/L	-2.7	0.8
	recyle	
1st use	-7.5	0
2nd use	-4.0	0.6
3rd use	-1.4	1.7
4th use	-0.2	1.6

5.3.2. Effect of temperature

A sufficient amount of thermal energy is required to cross the energy barrier for the transformation of pollutants into desired products i.e. H_2O and CO_2 [56]. An increase in the reaction temperature significantly enhanced the leachate abatement in terms of TDOC (Figure 5.2). At 60 °C only 27% of the TDOC removal efficiency is observed, clearly suggesting that the employed temperature is not sufficient to enable the reactants for crossing the activation energy barrier and thus the TDOC abatement is modest [56]. When the reaction temperature is increased from 60 to 70 ° C, the catalytic activity is boosted with a 65% reduction of TDOC after 30 minutes of reaction, while further increase in temperature from 70 to 80 °C does not enhances the process efficacy [57-59]. Although, higher temperatures yield higher rates of $OH^{\bullet}$ radical generation but the rate of wasteful utilization of these radicals (side reactions) also increases which negatively affects the productivity of the process [60]. Moreover, higher temperatures may also increase the desorption of organics from the catalyst surface and consequently a lower removal of organics is afforded [61].

The COD abatements at 70 and 80 °C after 30 minutes are 65 and 71% respectively and there is only a slight increase in COD with extended reaction times. On the contrary, at 60 °C there is no observable COD abatement until 60 minutes suggesting that the temperature significantly affects the reaction rate and at low temperature a longer induction time is needed to start the reaction. COS values suggests that for all the investigated temperatures a significant oxidation of organics is obtained over ZrCu catalyst; COS increases from -9.5 to 0 at 60 and 70 °C and +0.5 at 80 °C. The analysis of AOS indicates that at 60 °C the formation of highly oxidized intermediates is more pronounced (higher value of AOS, -1.6), while at 70 °C the mineralization prevails (lower AOS -7,5). At 80 °C an intermediate value of AOS is found (- 4.7) indicating a balance between partial and total oxidation.

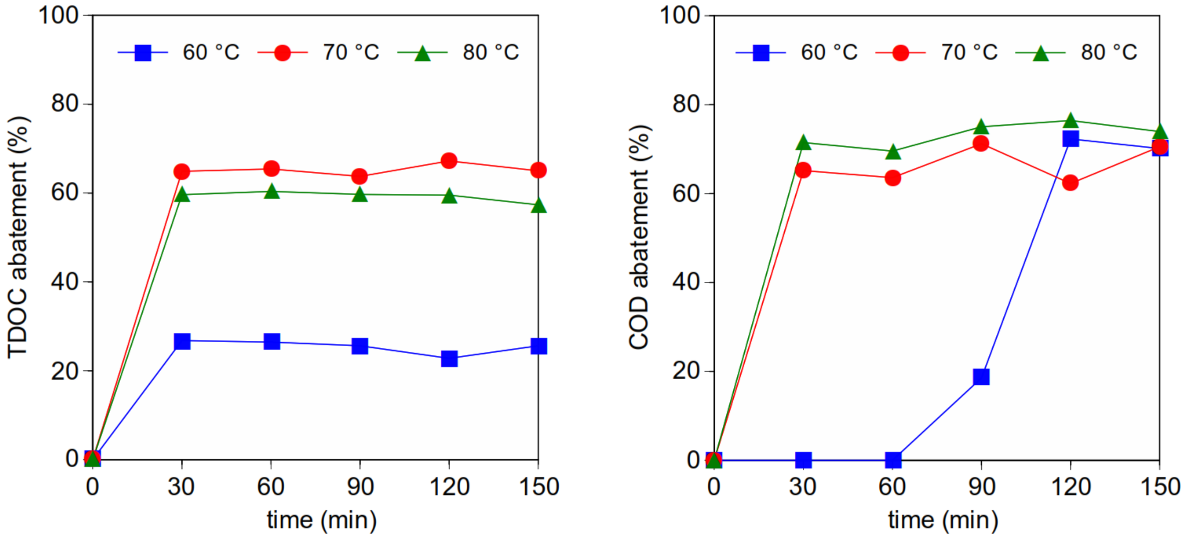


Figure 5.2: Effect of temperature on TDOC and COD abatements efficiencies (reaction condition: pH 5, catalyst dose 200 mg/L, H_2O_2 dose 30 ml/L (3%) and reaction time 150 min)

5.3.3. Effect of catalyst dose

An optimized catalyst dose not only maximizes the process efficiency but is also critically important to control the economics of the Fenton like process [62]. The effect of variable catalyst doses on TDOC removal efficiencies (Figure 5.3) evidenced that 200 mg/L is the optimum concentration. These results suggest that neither a lower nor does a higher catalyst dose favors the Fenton like oxidation process for the organic mineralization [8]. Too little catalyst amount does not possess sufficiently high number of active sites to generate enough $OH^{\bullet}$ radicals from the oxidant and thus cannot yield reasonable process efficacy. On the other hand, a catalyst concentration higher than the optimal may cause the scavenging effect i.e. the free hydroxyl radicals are consumed by the catalyst itself and thus a decrease in the organic abatement [6, 63-65]. COD abatements after 150 minutes are almost independent on the amount of the catalyst used for the reaction. When 100 mg/L of catalyst is used, the reduction of COD starts with a long delay compared to the other concentrations, indeed, 50% of COD abatement is reached only after 90 minutes of reaction, while with 200 and 300 mg/L such removals are already observed after 30 minutes. However, after 90 minutes the removal effect is similar for all the catalysts dose used, suggesting that the amount of catalyst has a key role on the reaction rate but not on the overall activity. The comparison between AOS and COS indicates that for 200 mg/L of catalyst a maximum degree of mineralization is obtained (AOS -7.5), while for 100 and 300 mg/L a certain degree of partial oxidation occurs (AOS -3.3 and -2.7, respectively).

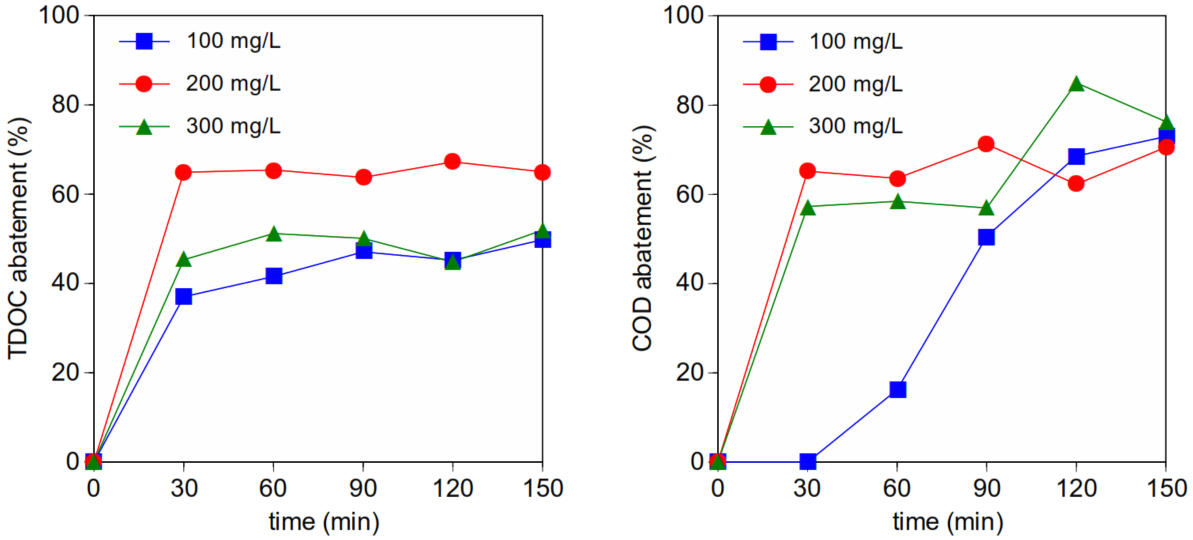


Figure 5.3: Effect of catalyst dose on TDOC and COD removal efficiencies (reaction condition: 70 °C, pH 5, H_2O_2 dose 30 ml/L (3%) and reaction time 150 min)

5.3.4. Effect of oxidant dose

An optimized oxidant dose is not only critical to afford maximum process efficacy but also lowers the processing cost associated with wastewater treatment and must be experimentally determined [64, 66]. The effect of oxidant dose on the process efficiency in terms of TDOC abatement is depicted in Figure 5.4.

When heterogeneous Fenton process is carried out using the optimal dose of oxidant i.e. 30 ml/L, the TDOC removal efficiency is 65% in early 30 minutes and additional reaction times did not increase the process efficiency significantly. However, when the oxidant doses are increased to 40 and 50 ml/L, the observed TDOC abatements remained almost the same. These results suggest that the excess amounts of H_2O_2 scavenged part of the extra generated $OH^\bullet$ radicals and, consequently, no additional organic abatement could be achieved [67, 68]. Due to the interference of hydrogen peroxide on the COD test, COD analysis for high H_2O_2 dose has not been performed.

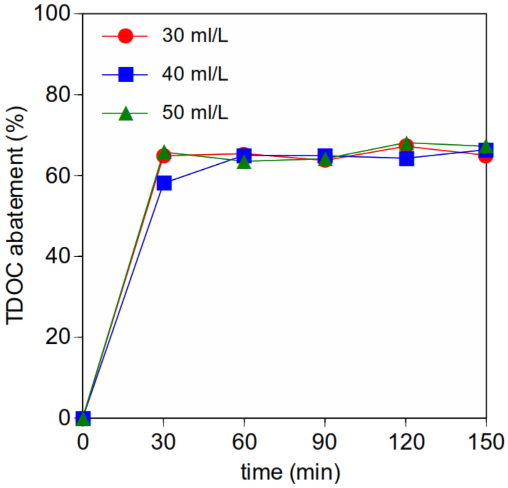


Figure 5.4: Dependence of process efficiency on oxidant dose (reaction condition: 70 °C, pH 5, catalyst dose 200 mg/L and reaction time 150 min)

5.3.5. Catalytic activity after recycling

Recyclable nature of the catalyst in Fenton like process is considered as a valuable aspect to achieve the goal of environmental and economic sustainability [6]. In order to investigate the reusability of the catalyst, the recovered catalyst was used as it is for the treatment of fresh leachate samples, keeping rest of the process conditions same. The effect of catalyst recycling on process potency is outlined in Figure 5.5. The freshly employed catalyst afforded 65% of TDOC abatement in first 30 minutes and later the process efficacy reached a plateau. In the 2nd and 3rd application of the recovered catalyst, the TDOC abatements have slightly decreased to around 58% within half an hour and subsequently outlining no significant variation in the process efficiency. However, in the 4th employment, the TDOC removal efficiency in the first 30 minutes has markedly dropped to 33% and it gradually but moderately increased to 43% at the end of the Fenton reaction. This slight decline in the process efficiency could probably due to two phenomena [54, 69]; on one side the leaching of copper from the catalyst surface (ca. 8% in every cycle), on the other the deposition of the organics over the surface which may have blocked the active sites.

When the fresh catalyst is employed in heterogeneous Fenton process, the COD removal in 30 minutes is 65% and there is no notable fluctuation in the COD abatement until the end of the oxidation reaction. The second and third employment of the catalyst yielded, respectively, 75% and 83% of COD abatement. A comparison of TOC and COD results suggests that in the second and third cycles the catalyst achieved a slightly lower degree of mineralization (ca. 58%) but is still able to induce a partial oxidation of organics in the landfill leachate, lowering the toxicity and increasing the biodegradability. In the fourth cycle the COD is negligible in first 30 minutes, increased to 36% in the first 60 minutes and finally, at the end of the oxidation reaction it reached to 82%. These results indicate that the catalyst was still active but it required a longer induction time to start the reaction.

COS values (≥ 0 for all the cycles) indicate that the high oxidation degree of the landfill leachate over ZrCu is maintained over several cycles, while a progressively increase of AOS suggests a modification on the ratios between total and partial oxidation of parent molecules. After recycling, the catalyst activity is lower in terms of mineralization but is improved in terms of partial oxidation, indicating that ZrCu is still active and is a very promising catalyst for Fenton-like oxidation of landfill leachate.

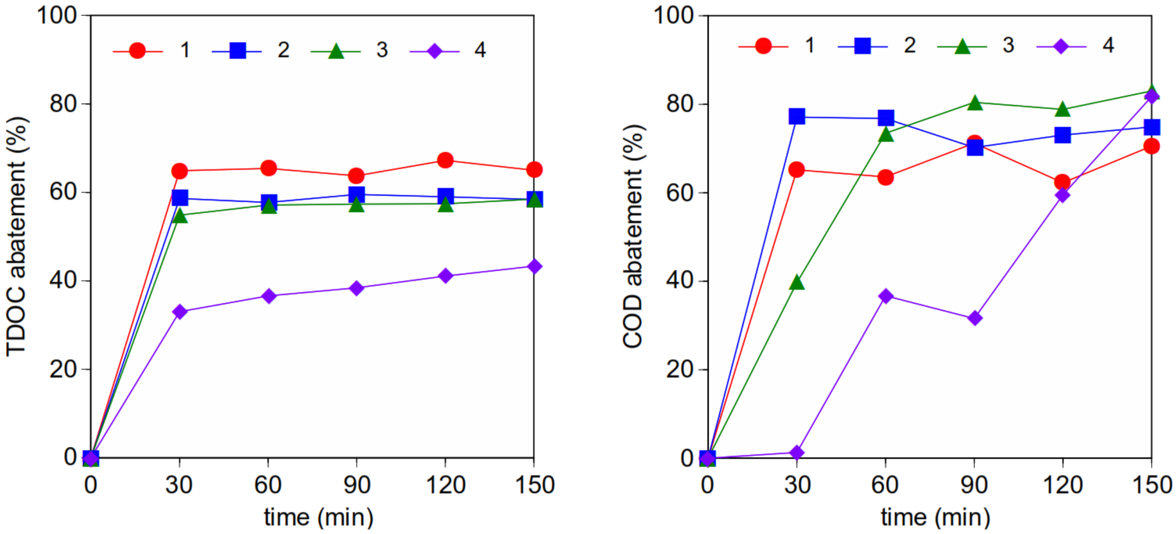
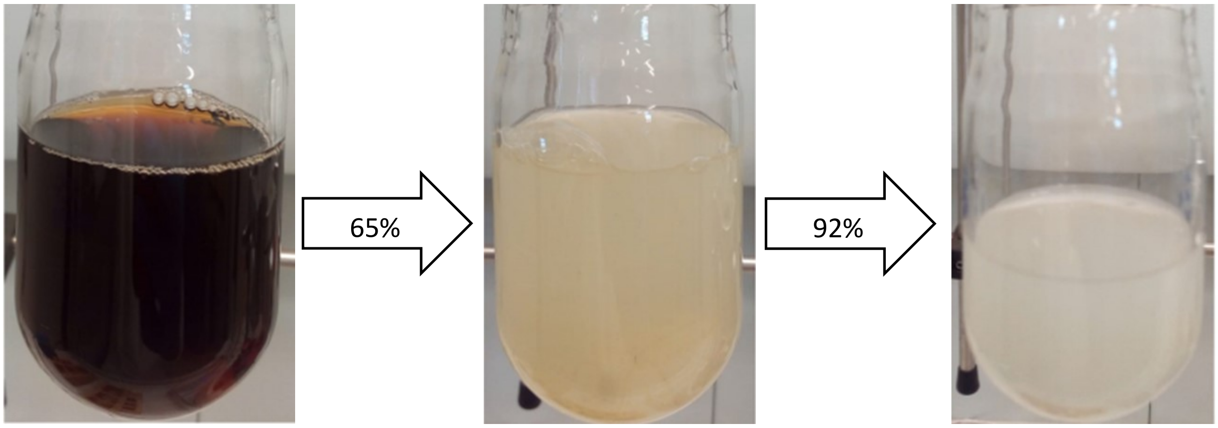


Figure 5.5: Effect of catalyst recycle on TDOC and COD abatements (reaction condition: 70 °C, pH 5, catalyst dose 200 mg/L, H_2O_2 dose 30 ml/L (3%) and reaction time 150 min)

5.3.6. Two-step Fenton like oxidation

Landfill leachate is a heavily polluted wastewater and it is possible that a single step treatment of the wastewater stream is not suitable to be integrated with the existing wastewater treatment facilities. A two-step oxidation is also necessary to monitor the extent of catalytic abatement of organics i.e. whether the catalyst is able to further abate the organics or the maximum threshold of Fenton like activity has been reached in the first step and the catalyst is unable to further degrade the secondary and tertiary organic metabolites. This is also very important because it gives us an insight regarding the potentiality of the catalyst to completely mineralize all sort of organics in the Fenton like process. Therefore, to increase the overall removal efficiency of the Fenton like oxidation and enhance the mineralization / biodegradability of the treated stream, a second oxidation step has also been performed with standard operating conditions (Figure 5.6). It has been observed that, when a two-step Fenton like process is carried out, 92% of the TDOC have been removed from the leachate. The results clearly suggest that the developed catalyst have the potential to reach nearly complete abatement of the organics through a series of simultaneous oxidation reactions depending upon the initial organic loading coming in the wastewater stream. Moreover, the leftover organics are likely to be small molecular weight carboxylic acids and which can easily be treated through the biological processes. Therefore, a two-step oxidation process is highly feasible to enhance the biodegradability of the effluent followed by an integration and treatment through sewage treatment plants.



before treatment 1st treatment 2nd treatment

Figure 5.6: TDOC removal efficiency after 1st and 2nd treatments

5.3.7. Detection and abatement of aromatics

Benzene with varying functional groups and number of rings, being the fundamental aromatic compound has found its application over a broad range of domestic and industrial chemicals. For example, benzene ring containing ingredients are present in the household detergents and dishwashing liquid soaps. Moreover, benzene ring is also the essential and fundamental building block of numerous dyes, coating materials and pharmaceuticals and therefore when solids either containing or bearing such residual compounds are disposed in landfills, finally find their way to the aqueous phase. The concentration of aromatic compounds in wastewater is the main criterion for estimating the overall toxicity because these compounds are very persistent and have proven toxicological data, and that is why any treatment which can reduce their concentration would definitely reduce the final toxicity of the effluent. Landfill leachate is a very complex liquid waste and a comprehensive compound based compositional analysis is very hard to perform. Therefore, to broadly estimate the aromatics content before and after the Fenton like oxidation will surely enable us to predict the reduction in overall toxicity of the effluent. Two different techniques, ^{1}H NMR spectroscopic analysis and UV-vis spectroscopy, have been used for the evaluation of aromatic compounds in the leachate before and after treatment.

5.3.7.1. ^{1}H NMR spectroscopy

^{1}H NMR spectroscopic analysis not only provides the insight regarding the nature of the organic compounds present in the leachate but is equally useful to understand the qualitative efficacy of the Fenton like oxidation. To better comprehend the nature of organics in landfill leachate and monitor the qualitative abatement of organics due to Fenton treatment, both samples have been subjected to ^1H NMR analysis. The ^1H NMR spectrum of the leachate (Figure 7) can be divided into three major resonance areas: the 0 -3.0 ppm area, where alkylic chains and aliphatic compounds absorb, the 3.0-6.0 ppm area, typical for compounds bearing groups such as -OH, -NH_2, alkyl halides and alkenes and, finally the 6.0-9.0 ppm region characteristic for resonances of aromatics compounds. The ^1H NMR spectrum of the treated leachate shows that the Fenton-like process affects all these three resonance regions leading to a significant simplification of the spectrum. As can be seen, the initial complex mixture is now reduced to a mixture of a small number of compounds, some of which can be tentatively recognized, based on the chemical shift, as acetic acid (2.1 ppm), acetone (2.3 ppm), and formic acid (8.3 ppm). These outcomes indicate that the oxidation process significantly affects the overall organic removal efficiency and specifically is very active in the degradation of aromatics compounds, indeed in the region 6.0-9.0 ppm resonance signals are dramatically decreases after treatment.

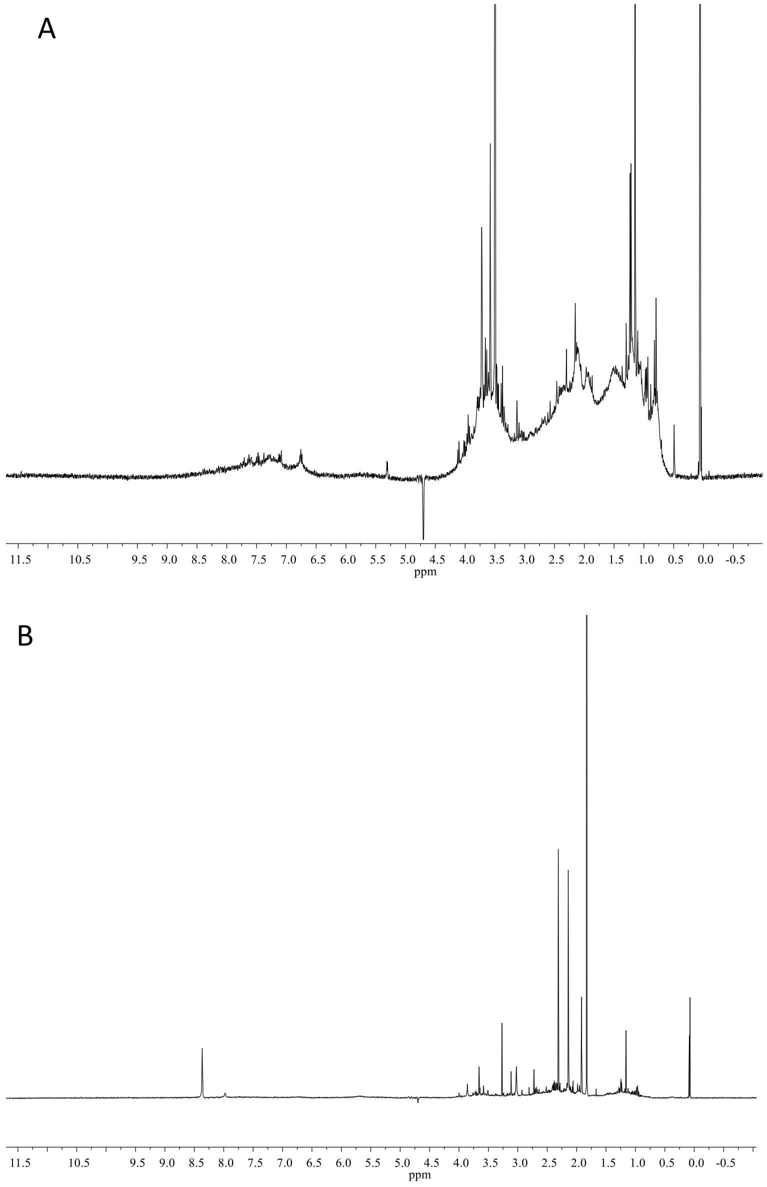


Figure 5.7: ^{1}H NMR spectrum of raw and treated landfill leachate

5.3.7.2. UV-Vis spectroscopy

To further observe the extent of qualitative abatement of organics in general and aromatics in particular, landfill leachate samples have been analyzed using UV-Visible spectrophotometer and results are presented in Figure 5.8. Each wavelength on the spectra corresponds to the concentration of a particular organic specie especially in the range from 220 to 270 nm where most of the aromatics exhibit their maximum absorptions [70]. It is quite visible that the heterogeneous Fenton like oxidation has markedly reduced the concentrations of organics compounds which can be observed in terms of substantial reduction in absorptions.

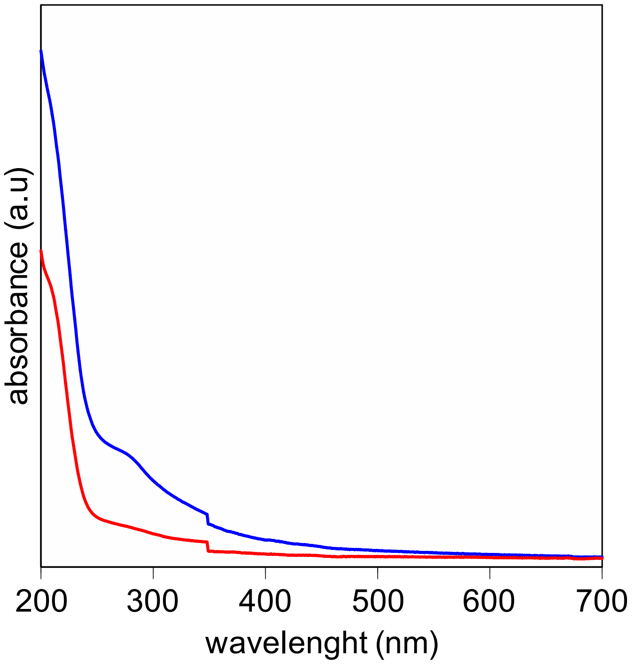


Figure 5.8: UV-Vis spectrum of leachate before and after treatment

5.3.8. AOX abatement

The adsorbable organic halogens (AOX) are one of the most persistent organic pollutants and their concentration must be controlled in wastewater streams due to adverse environmental impacts [71, 72]. These pollutants can be removed from wastewater through chemical [73, 74] and adsorptive [75, 76] processes. Many countries have set a limit for the AOX concentration in wastewater streams through their environmental legislations, and consequently, it is essential to analyze the concentration of AOX in the leachate before and after treatment [77, 78]. In order to investigate the AOX loading in leachate and the extent of abatement through Fenton like oxidation process, the samples have been subjected to AOX analysis and the results are outlined in Figure 5.9.

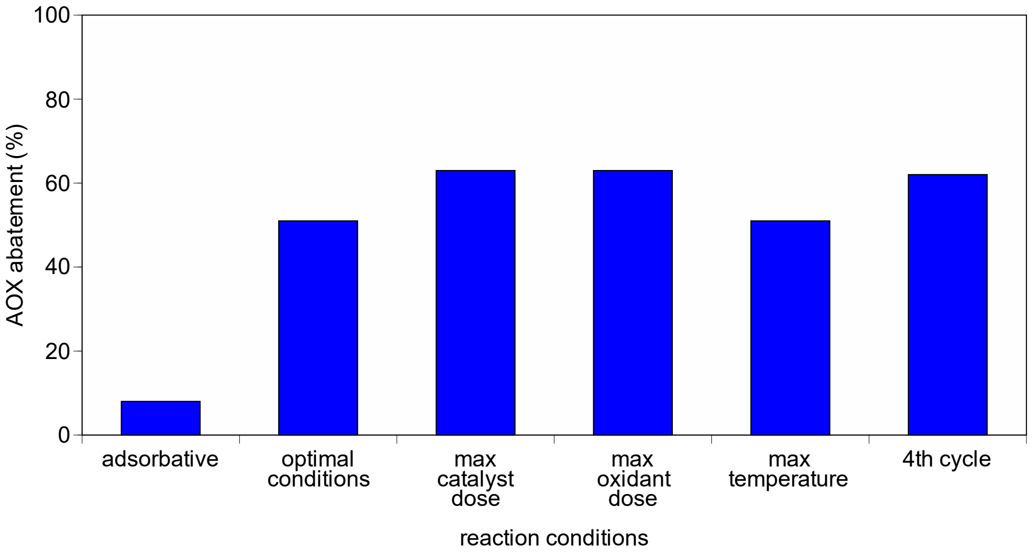


Figure 5.9: AOX abatements with variable process conditions. (Standard conditions: 70 °C, pH 5, catalyst dose 200 mg/L, H_2O_2 dose 30 ml/L (3%) and reaction time 150 min; max catalyst dose 300 mg/L; max oxidant dose 50 ml/L; max temperature 80°C).

The adsorptive removal of AOX is investigated by using three different doses of activated carbon i.e. from 1 to 2 g/L. However, despite the increase in the adsorbent doses, AOX abatements did not increased beyond 6-8%, indicating that the adsorptive removal of AOX is limited [79]. The Fenton-like process over ZrCu carried out in conventional conditions (reaction condition: 70 °C, pH 5, catalyst dose 200 mg/L, H_2O_2 dose 30 ml/L (3%) and reaction time 150 min) has been able to reduce 51% of AOX from leachate. However, when the leachate is treated using higher catalyst dose, i.e. 300 mg/L, the AOX removal efficacy has increased to 63%. This increase in AOX abatement can be attributed to an enhanced oxidative and adsorptive removal, associated with additional catalyst dose. Similarly, when excess amount of oxidant dose is employed i.e. 50 ml/L, the AOX removal efficiency also rose to 63%. This increase in the AOX abatement is due to the induction of higher number of free radicals which in turn better oxidized the halogenated organic compounds. However, an elevation in temperature i.e. 80 °C did not increase the AOX abatement significantly which suggests that it does not have any impact over the oxidative removal of AOX. Further, these results also suggest that rise in temperature does not aid in AOX removal through volatilization process. If we analyze the effect on AOX abatement after reuse of the catalyst, we observe that ZrCu is active even after three recycles (the 4th employment of the catalyst afforded 62% of the AOX abatement).

The promising activity of ZrCu on landfill leachate degradation could be associated to its high reduction capacity at low temperature. As shown in a previous study, diverse CuO species are homogeneously dispersed over zirconia; these high reducible species can abate organics in landfill leachate through a radical mechanism which is often proposed in the literature for similar catalytic systems [80, 81].

5.3.9. Bioassays for toxicological risk assessment

A study on the effects of leachate on unicellular green algae was carried out under controlled laboratory conditions. The study evaluated the toxicity of leachate pre- and post-mineralization treatment as effects inhibiting the proliferation of a population of unicellular freshwater green algae, used for years as a model organism of algae and of the trophic level of producers (plants, algae, photosynthetic bacteria) in ecotoxicity studies for the aquatic environment [82].

In the present study, the antiproliferative effects of 2 leachate samples (leachate as it is and after Fenton treatment) on the algal population of R. subcapitata were investigated. The samples were studied in concentrations from 0.1 to 20% volume / volume, by directly diluting the samples with standard reconstituted water. It was not necessary to modify the pH of the samples as they had values compatible with the survival of the algae (between 8.1 and 8.4). The results of the study are reported in Table 5.4 relating to biomass and growth rate. The study showed that the leachate as it is a very toxic sample and that the maximum effect is reached already at the dilution of 0.5% while at 0.1, the lowest point tested, an inhibition of about 15% is obtained compared to the control. The inhibitory effect of 50% is obtained at an estimated concentration of 0.17% by evaluating the biomass and at 0.49% by evaluating the growth rate. The Fenton treatment substantially changes the toxicity of the leachate, indeed the sample after treatment is significantly less toxic. The inhibitory effect of 50% is obtained at an estimated concentration of 0.80% considering the biomass and 3.25% considering the growth rate.

Table 5.4: Algal growth inhibition test. The results are normalized on the control and the analysis based on the change in algal density (biomass) and growth rate.

Sample	**% leachate v/v**	**Biomass**		**Growth rate**	
		% CTR	% STD	% CTR	% STD
Before treatment	0	100.00	4.80	100	0.99
	0.1	83.52	1.95	96.49	0.47
	0.5	4.43	1.11	38.56	12.39
After treatment[a]	0	100.00	4.80	100	0.99
	0.1	89.64	5.10	97.85	1.14
	0.5	79.67	10.57	95.44	2.75
	1	28.99	2.73	75.69	2.56
	2.5	20.59	1.22	69.03	1.69
	5	3.74	0.12	35.61	1.71

[a] reaction conditions: 70 °C, pH 5, catalyst dose 200 mg/L, H_2O_2 dose 30 ml/L (3%) and reaction time 150 min

5.4. Conclusion

This study investigates the activity of copper supported zirconia catalyst for the treatment of landfill leachate in Fenton like reaction. In addition to the investigation of process variables, the evaluation of the degradation/mineralization degree of our treatment has been performed by means of AOS (average oxidation state) and COS (carbon oxidation state) parameters. These indicators are extremely important in the monitoring of the degree of oxidation and for each investigated variable, the ratios between total and partial oxidation of parent molecules has been obtained. ZrCu is a very promising heterogeneous Fenton catalyst and is able to reduce 65% of the TDOC from a heavily polluted landfill leachate in a single step oxidation. While a two-step Fenton process is further able to reduce the organic loadings to 92%, thus making the final effluent more suitable for treatment through sewage wastewater treatment plants. The good stability of ZrCu catalyst under reaction conditions, as proved by recycle tests, confirms the high attractiveness of copper systems supported on zirconia for the treatment of liquid waste. When optimal process conditions are applied, the complete oxidation of the organics into CO_2 (mineralization) is prevailing on the partial oxidation into intermediates compounds. Moreover, this study has also successfully suggested a new way of monitoring the qualitative performance of Fenton reaction using H^1 NMR. The developed catalyst is also very active for the abatement of AOX compounds and a 63% removal has been obtained. The findings of this study are equally useful for academia as well as to the industry and this process can be extended for the treatment of other heavily polluted wastewater streams.

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Chapter-6

Iron and copper-based catalysts for Fenton like oxidation of ibuprofen

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Abstract

In this study, a series of iron and copper-based catalysts with varying metal loadings are prepared by wet impregnation over zirconia support and tested as catalyst for the treatment of ibuprofen with a Fenton-like process. The textural and morphological properties of catalysts are analyzed by standard techniques. Both iron and copper-based catalysts when loaded with 7.5% of metal affords maximum activities of 80 and 70%, respectively under optimum conditions. Besides, iron and copper catalysts with optimum metal loadings only lose 1.67% (0.3 mg/L) of iron and 6.2% (0.9 mg/L) of copper during oxidation process. Further, all the Fe/ZrO_2 catalysts exhibit better activities at pH 3 while Cu/ZrO_2 catalysts better perform at pH 5. Iron-based catalysts drastically lost their activities when recycled and the activity of 7.5%Fe/ZrO_2 catalyst decreased from 80 to 38% in the 3rd recycle. Unlike iron, Cu-based catalysts maintain their high activity even after 3 recycles. The findings of this study outline that the developed iron-based catalysts are better suited for single run applications while copper-based catalysts possess extended stabilities without losing activities. Copper-based catalysts are very promising materials with enhanced catalytic activity and high stability for the degradation of ibuprofen over Fenton-like process.

Keywords: Fenton like oxidation, heterogeneous catalysis, metal loading, ibuprofen, wastewater treatment

6.1. Introduction

The environmental stress on water bodies is growing due to the addition of a large number of pollutants coming from multidimensional sources [1]. There is an increasing demand for the development of sustainable processes which are able to completely eliminate the pollutants into fundamental chemical entities such as water and carbon dioxide [2, 3]. Advanced oxidation processes (AOPs), a new class of chemical processes have shown great prospects and have successfully been employed for the treatment of a wide range of wastewater streams. These processes generate very strong oxidizing species such as hydroxyl radicals (OH•) which attack the pollutants and degrade them [4]. The OH• radicals have very high oxidation potential and can degrade wide range of organics [5, 6]. Among AOPs, Fenton process is the most widely employed process for the treatment of wastewaters due to its simplicity, low cost, and very high oxidation rates [4, 7, 8]. However, it has two serious limitations such as the process requires fairly strict acidic conditions (pH 3 - 3.5) and large volumes of residual sludge is produced during the process which creates another processing and environmental challenge [9, 10]. The limitations of the homogeneous Fenton process can be easily averted using heterogeneous Fenton like process in which iron and other metals are supported/bonded over different metal oxide materials [11-14]. In this way, not only it is possible to reduce the metal loading in Fenton process but the catalyst can be easily recovered and reused in subsequent cycles, thus making the process more sustainable [15-17]. Furthermore, heterogeneous catalysts can also afford better catalytic activities over a wide range of pH [11].

The development of highly active and stable heterogeneous catalysts is a multiplex challenge because it involves several key steps such as finding the right metal as a catalyzing source in Fenton process, impregnation of the optimal amount of metal over the appropriate support, catalyst characterization followed by activity analysis and finally the investigation of the catalyst stability [18-20]. An optimized metal loading is critical for the maximum catalytic activity and stability because it provides complete and efficient redox cycle. In this study, we have developed a number of iron and copper-based catalysts with variable metal loadings using zirconia as a supporting material and their catalytic activities have been investigated using a model pollutant ibuprofen (IBP). The effect of metal loadings on catalytic activity and stability has been investigated in conjunction with variable processing conditions of pH, temperature, catalyst, and oxidant doses.

6.2. Experimental

6.2.1. Catalyst preparation

A series of Cu (or Fe) catalysts (5, 7,5 and 10%) over ZrO2 support was prepared. ZrO2 was prepared by calcination of zirconium hydroxides (Mel Chemicals, Manchester, UK) at 500 °C for 3 h. Then, aqueous solutions with appropriate amounts of Cu (copper (II) nitrate hemi (pentahydrate), Sigma Aldrich, Saint Louis, MO, USA), Fe (Iron (III) nitrate nonahydrate, Sigma Aldrich), were added by incipient wetness impregnation, and dried overnight at 100 °C, then the samples were calcined at 500 °C for 3 h. Textural characteristics were measured according to the BET method by nitrogen adsorption at −196 °C, using a Tristar 3000 gas adsorption analyzer (Micromeritics). Structural features of the catalysts were characterized by X-ray diffraction (XRD). XRD profiles were recorded on a Philips X'Pert diffractometer (equipped with a real time multiple strip detector) operated at 40 kV and 40 mA using Ni-filtered Cu-Kα radiation. Spectra were collected using a step size of 0.02° and a counting time of 20 s per angular abscissa in the range 20°- 80°. The Philips X'Pert HighScore software was used for phase identification.

6.2.2. Catalytic activity experiments

Aqueous solutions of ibuprofen (10 mg/L) were prepared dissolving ibuprofen sodium salt, $C_{13}H_{17}O_2Na$ (Sigma-Aldrich) in ultra-pure water. Ibuprofen samples (100 ml) loaded with 200 mg/L of individual catalysts were heated at 70˚C under continuous stirring conditions of 500 RPM, using an Omni multistage reaction station with a provision of reflux. The Fenton like reaction was carried out for 150 minutes and the treated samples were centrifuged at 5000 rpm using Eppendorf Centrifuge 5804 R, followed by filtration through a 0.45 µm membrane filters. The oxidation process was optimized evaluating the effects of catalyst dose (200, 300 and 400 mg/L), hydrogen peroxide, (20, 30 and 40 ml/L), temperature (60,70 and 80 °C) and pH (3,5 and 8, acidifying the sample with hydrochloric acid (Sigma Aldrich) or basifying the sample with sodium hydroxide (Sigma Aldrich)). The mineralization of IBP, the total organic carbon (TOC) of treated samples was analyzed using a TOC-VCPN, Shimadzu analyzer(V-Series) with auto sampler. First, the standard solutions with known concentrations of 2.5, 5.0, 10.0 20.0 mg C/l were prepared using potassium hydrogen phthalate stock solution. A calibration curve was obtained by analyzing the standard samples, and after each analysis the injection syringe was auto sparged with 2M HCl. The samples were analyzed without dilution and using the same calibration curve to determine TOC present in each sample. The TOC removal efficiencies were determined using Eq.1. Moreover, TOC and IBP mineralization have been used interchangeably in this study.

$$\text{TOC removal efficiency (\%)} = \frac{\text{TOC}_\text{i}\text{-TOC}_\text{f}}{\text{TOC}_\text{i}} * 100 \qquad \text{(Eq.1)}$$

Several experiments were also carried out to verify the reproducibility of our activity measurements and the errors resulted to be within 3%.

6.2.3. *ICP analysis for metal leaching*

The leaching of iron and copper during heterogeneous Fenton process was determined with US EPA 3051 method using Inductivity Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES vista pro.) First, a calibration curve was obtained using an ICP 23-element standard solutions which were prepared in 5% HNO_3. Yttrium (Y) was used as an internal standard. The method detection limit (MDL) was calculated as 3 s/m.

Where;

s = Standard deviation of 10 replicate blanks

m = slope of the calibration curve for each element

The percentages of metal loss were calculated using the following Eq.2.

$$\text{Metal leaching }(\%) = [1\text{-}(\frac{M_i - M_f}{M_i})]*100 \qquad \text{(Eq.2)}$$

Where,

M_i = Initially introduced metal weight (mg)

M_f = Finally left metal weight at the end of Fenton process (mg)

6.3. Results and discussion

6.3.1. Catalyst characterization

Composition and BET surface area of the materials are reported in Table 6.1. The addition of Cu or Fe does not strongly affect the surface area of pure zirconia (64 m^2/g) with a maximum decrease to 59 m^2/g for copper and 54 m^2/g for iron-based materials

Table 6.1. Composition and surface area of investigated samples.

Sample	Composition	Surface Area (m^2/g)
Zr5Cu	Cu(5%)/ZrO_2	59
Zr7.5Cu	Cu(7.5%)/ZrO_2	60
Zr10Cu	Cu(10%)/ZrO_2	59
Zr5Fe	Fe(5%)/ZrO_2	55
Zr7.5Fe	Fe(7.5%)/ZrO_2	55
Zr10Fe	Fe(10%)/ZrO_2	54

The structural features of the zirconia-based materials were analysed by powder X-ray diffraction (XRD). Materials show the simultaneous presence of tetragonal (space group P42/nmc; main reflection at 30,2°) and monoclinic ZrO_2 (space group P121/c1, main reflection at 28,2°). No evidence for any copper phase was found (Figure 6.1), suggesting that Cu are homogeneously dispersed on the surface, while iron-based materials exhibit reflections characteristic of the formation of Fe_2O_3 (33,2°) when iron concentration is higher than 7.5%.

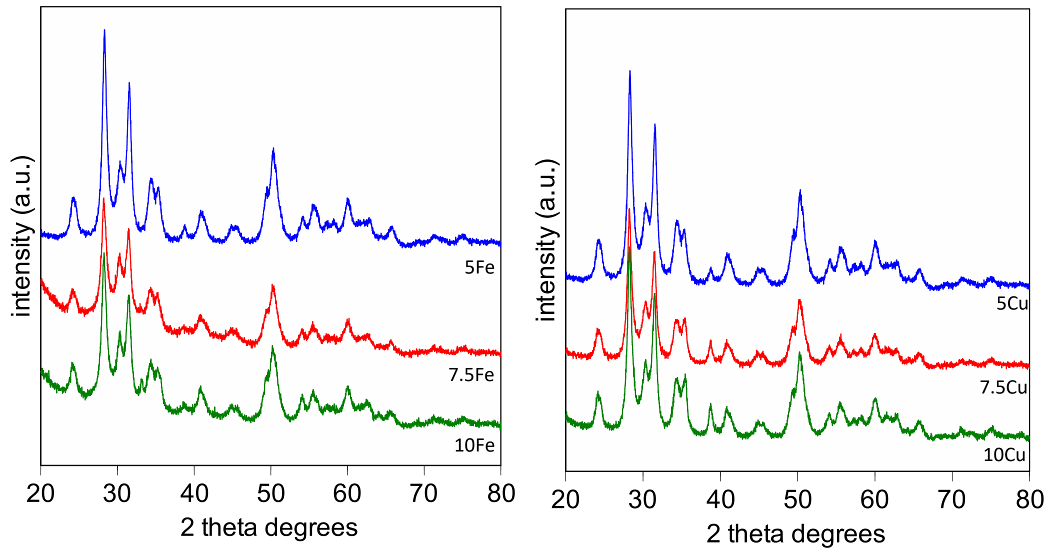

Figure 6.1: XRD profile of zirconia-based materials

6.3.2. Effect of pH on catalytic activity and stability

The pH of the aqueous phase is the most critical parameter in heterogeneous Fenton like process because the employed catalyst can only exhibit maximum activity through a single optimal pH [11]. In order to observe the effect of pH on the catalytic performance of iron and copper-based catalysts with variable loadings, Fenton like oxidation was performed at three pH conditions and the results are presented in the Figure 6.2. The aqueous solution of IBP has a pH of 5, then we tested the catalytic activity under acidic (pH 3) and basic (pH 8) conditions [21-23]. For all the catalysts the highest IBP abatement has been achieved in early 30 minutes, then the catalytic activity is almost maintained.

If we look into the results, it is evident that the optimal pH for all the iron-based catalysts is 3 and the optimal pH for all the copper-based catalysts is 5. This confirms that the nature of the heterogeneous catalyst determines the favorable pH conditions. Moreover, it also indicates that the optimal pH of any catalyst in heterogeneous Fenton process is always near its point of zero charge (PZC) [24] and the catalytic activity progressively decreases moving away from this value. It is worth mentioning that under optimized conditions of pH, the catalytic activity of Zr7.5Fe catalyst is slightly higher than Zr7.5Cu. It is likely that under more acidic conditions, the lost iron ions triggered a homogeneous Fenton process and thus yielded a slightly better catalytic activity. On the other hand, the leached copper ions should form $Cu(OH)_2$ which is inactive for the oxidation of organics and ultimately, the solely responsible heterogeneous phase reaction afforded a bit lower TOC abatement.

The best metal loading for both iron and copper catalysts is 7.5% because under the favorable conditions of pH, both the catalysts with such loading afforded the highest IBP mineralization, 76 and 70%, respectively. On the contrary, catalysts with 5% iron and copper loadings mineralized only 65 and 62% IBP. Similarly, when the zirconia supports are charged with 10% of iron and copper, the TOC abatements declined. These results indicate that 5% metal loading is not enough to cover the entire surface area of the supporting material and thus a defective and incomplete redox cycle would reduce the catalytic activity of Fenton process. On the contrary, 10% metal loading seems excessive because IBP mineralization either remained the same or decreased. This suggests that once, the supporting material is entirely covered by the monolayer of the metal, the additional metal loading starts forming a binary layer over the catalyst surface and competing redox cycles may result in lessening of the process efficacy Figure 6.3 [25].

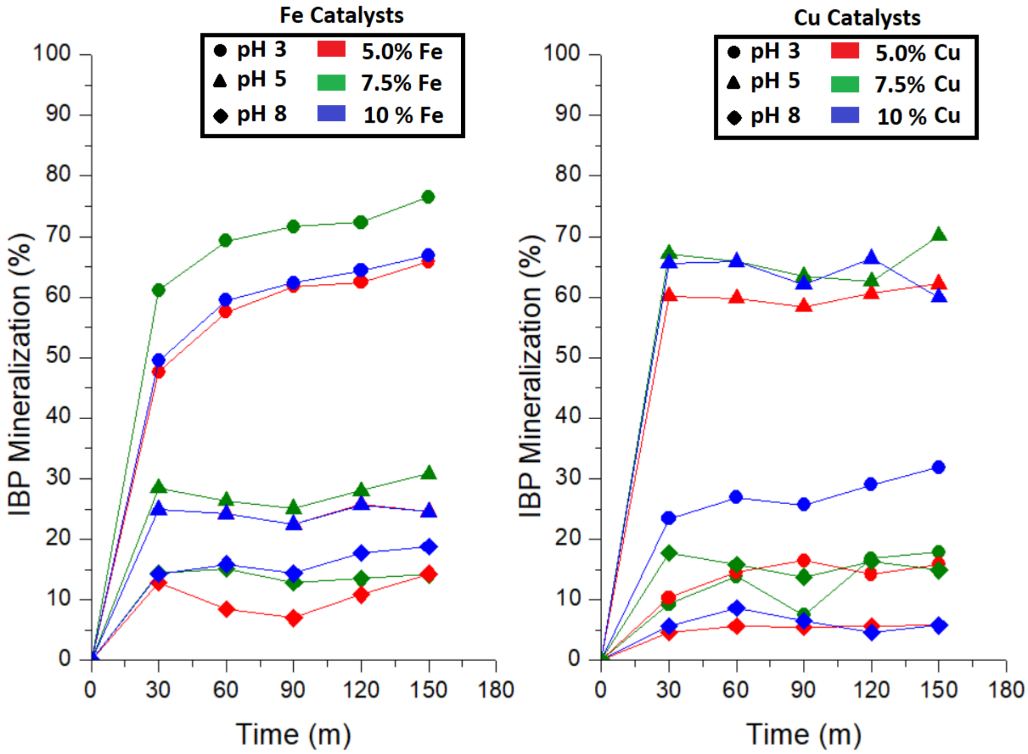

Figure 6.2: Effect of pH on the catalytic activity of iron and copper catalysts (reaction condition: 70 °C, catalyst dose 200 mg/L, H_2O_2 dose (3 %) 30 ml/L, IBP conc. 10 mg/Land reaction time 150 min).

Apart from fairly high activity, the stability of the heterogeneous catalyst is also of paramount importance because if the catalyst keeps losing the impregnated metal then it will not only suppress the recyclability of the catalyst but also make the Fenton process non-environment friendly. The leaching of iron and copper at variable pH conditions during the Fenton process has been determined using Eq.2 and the results are presented in the Table 6.2. It is quite visible from the results that all the iron-based catalysts are very stable under all pH conditions. The order of iron leaching at variable pH conditions is pH 3 > pH 8 > pH 5. Besides, it has been observed that the iron-based catalyst with 7.5% loading has undergone through minimum iron loss i.e. 1.67% (0.3 mg) and this iron loss is way below the regulations of European Union directives on the maximum limits of metals allowed to be released in the treated water [26]. On the other hand, copper-based catalysts are very unstable under acidic conditions i.e. pH 3 and 57 - 86% copper was lost after Fenton process. However, when the pH condition is shifted to 5, the copper leaching reduced 10 times. Moreover, at optimum pH 5 the catalyst with 7.5% loading has lost the minimum copper ca. 6.5% (0.9 mg) which is again below the guidelines of Environmental Protection agency (EPA) [27]. These results stipulate that the heterogeneous Fenton process which employs copper-based catalysts must be carried out at mild acidic to near neutral pH conditions to avoid heavy metal leaching [28]. It also indicates that, the optimal loading of a metal over the catalyst support strongly enhances the catalyst stability by incorporating complete metal-metal and metal-support interactions. On the other hand, catalysts with either lower or higher metal loadings are susceptible to metal leaching either due to the absence of metal-metal interactions or due to the absence of metal-support interactions Figure 6.4. However, the higher catalyst stabilities of iron-based catalysts compared with their peer copper catalysts suggests that iron have stronger bonding with the zirconia support and this higher stability enabled it to afford higher IBP mineralization as well. Another reason for the enhanced stability of iron-based catalysts is due to the fact that they form stable complexes with organics/oxidation products, enabling them to stay intact with the support [29].

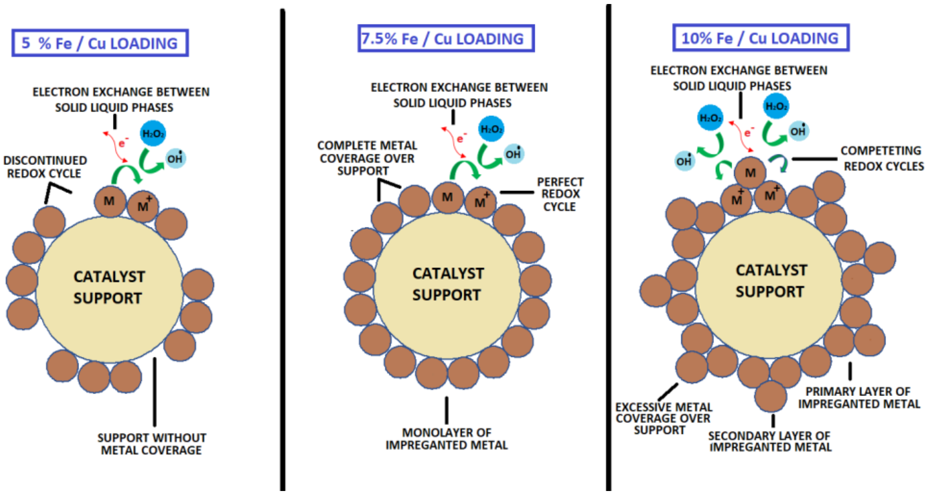

Figure 6.3: Schematic depiction of variable metal loadings and the corresponding support coverage

Table 6.2: Leaching of iron and copper from catalysts under variable conditions of pH

Catalyst	**pH 3**		**pH 5**		**pH 8**	
	Metal loss (%)	**Metal loss (mg)**	**Metal loss (%)**	**Metal loss (mg)**	**Metal loss (%)**	**Metal loss (mg)**
5%Fe	5.3	0.53	0.6	0.06	3.3	0.33
7.5%Fe	1.67	0.3	0.2	0.1	1.53	0.2
10%Fe	2.5	0.5	0.25	0.1	0.7	0.1
5%Cu	86.4	8.64	8.8	0.88	12.2	1.22
7.5%Cu	73.4	6.5	6.2	0.9	5.6	0.8
10%Cu	57.5	12	3	0.6	0.25	0.1

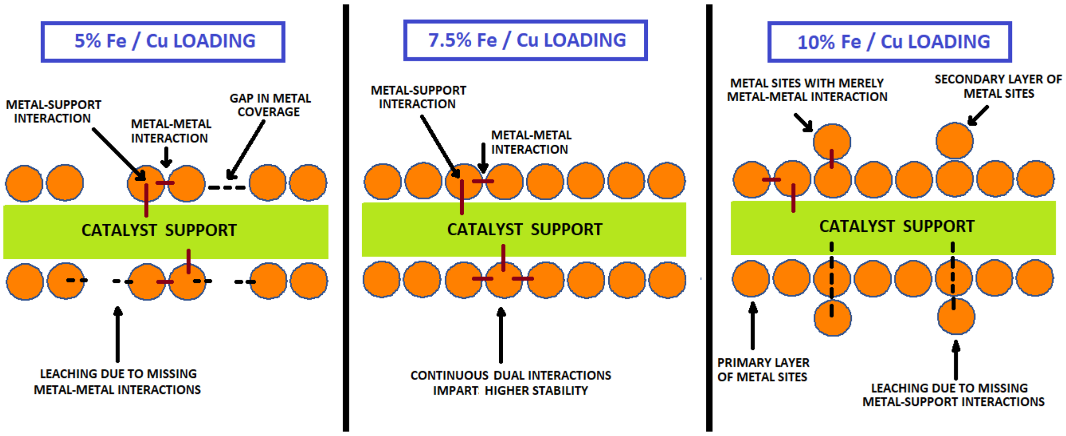

Figure 6.4: Effect of percentage metal loading on catalyst stability

6.3.3. Effect of catalyst dose on catalytic activity and stability

The active sites of the heterogeneous catalyst are mainly responsible for the generation of OH• radicals from the oxidant. To monitor the effect of variable metal loadings coupled with varying catalyst doses, the heterogeneous Fenton oxidation reactions were performed, and the results are presented in the Figure 6.5.

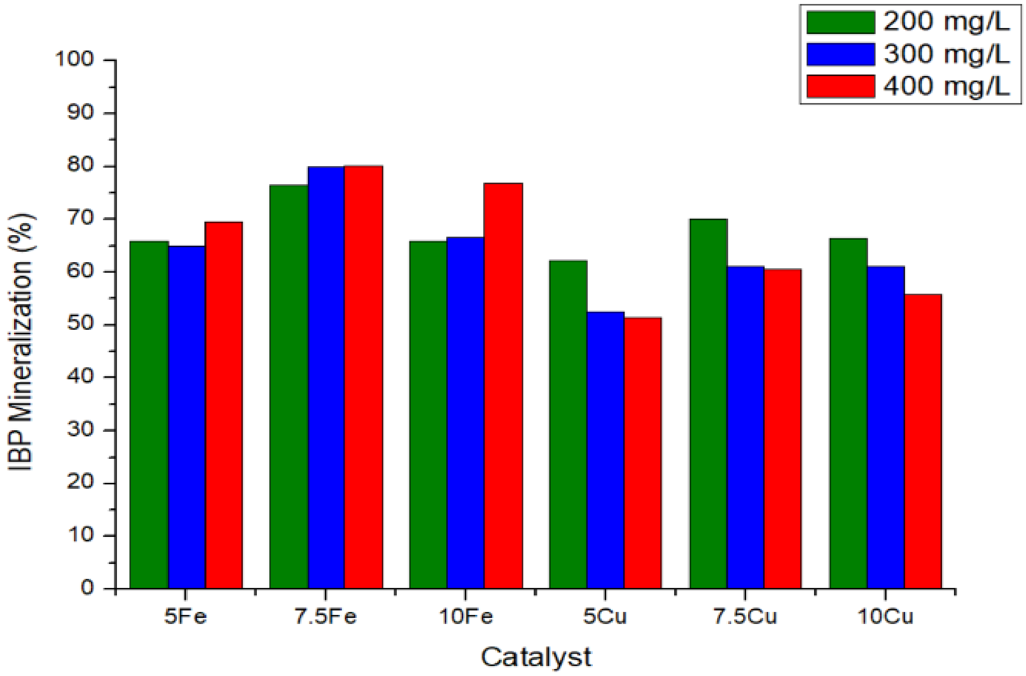

Figure 6.5: Effect of catalyst dose on the catalytic activity of iron and copper catalysts (reaction condition: 70 °C, H_2O_2 dose (3 %) 30 ml/L, pH 3 (Fe catalysts) or pH 5 (Cu catalysts), IBP conc. 10 mg/Land reaction time 150 min).

It is important to mention that the variation in the metal loading is the key factor to determine the total number of active sites through which the oxidant is converted into free OH• radicals. While the catalyst dose serves merely as a multiplier to the total number of active sites offered by the catalyst with certain metal loading and is illustrated using (Eq.3).

$$N = W_c[S^*M_l] \qquad \text{(Eq.3)}$$

Where;

N = Total number of active sites

W_c = Catalyst dose employed in the reaction

S = Active sites per unit weight of the catalyst

M_l = Metal loading (%)

When the catalyst dose (W_c) of 5%Fe catalyst is increased from 200 to 400 mg/L in Fenton process, the IBP mineralization increases from 65 to 69%. Zr5Cu has lower number of active sites (S) due to the insufficient metal coverage over the support and increasing the W_c will increase the total number of active sites and ultimately raise the catalytic activities. Similarly, when Zr7.5Fe catalyst is used and the W_c is increased from 200 to 400 mg/L, the TOC abatements increased from 76 to 80%. These results are in compliance with Eq.3 and indicate that 7.5%Fe loaded catalyst has the maximum number of active sites per unit weight of the catalyst and increasing the catalyst dose elevates the total sum of active sites (N) participating in the Fenton reaction and thus higher TOC abatements are obtained [2, 30]. It is also likely that 200 mg/L of Zr7.5Fe catalyst incorporated optimum number of active sites in the reaction system and the additional active sites by increasing W_c may have induced a scavenging effect [31] but counter balanced by the reciprocating homogeneous phase reaction, maintaining a higher oxidation potency. On the contrary, when 200 and 300 mg/L of 10%Fe are engaged in the Fenton oxidation, the IBP degradation declined to 65 and 66% respectively but substantially increased to 76% when W_c is increased to 400 mg/L. These results suggest that the compound active sites exposed in Zr10Fe catalyst are reduced because the primary layer of iron species is blocked by the secondary layer and that is why lower catalytic activities have been observed with lower catalyst doses. However, when the W_c is increased to 400 mg/L, N substantially grew leading to higher TOC abatement.

Unlike iron, when 200 mg/L of 5%Cu catalyst is employed for Fenton oxidation, the observed IBP mineralization is 62%. Strangely, when the W_c of 300 and 400 mg/L are used, the TOC removal efficacies dropped to 52 and 51%. Similarly, 200 mg/L of Zr7.5Cu catalyst mineralized 70% of IBP but higher catalyst doses negatively impacted the process efficacy. On the other hand, 200 mg/L of 10%Cu catalyst afforded 66% of TOC removal and further increase in the catalyst dose resulted in the form of decreasing activity. These results suggest that the total number of active sites (N) provided by the excess amounts of all the copper-based catalysts are higher than the optimum number of active sites to procure maximum catalytic activity and additional active sites caused very strong scavenging effects and thus reduced the overall catalyst performances.

Metal leaching from the catalyst surface can also be explained using Eq.3 because the total number of active sites exposed in the aqueous phase are proportional to the amount of metal loss. The losses of iron and copper from different catalysts during Fenton process are measured and are reported in Table 6.3. It has been observed that the iron-based catalysts with 5 and 10% metal loadings have lost higher amounts of iron during Fenton oxidation and these loses slightly increased when higher W_c are employed. On the contrary, 7.5%Fe loaded catalyst has lost minimum aggregate of iron and the higher W_c minutely increased the metal leaching. On the other hand, higher metal leaching has been observed when copper-based catalysts with 5 and 10% loadings are employed in Fenton process and these loses further increased when W_c is increased. However, 7.5% copper loaded catalyst showed higher stability and elevation in W_c also did not increase the metal leaching. These results indicate that the large number of active sites which are poorly dispersed over the catalyst support have higher tendency to be lost during the heterogeneous Fenton reaction. On the other hand, equal number of active sites which are exposed from a catalyst with better metal dispersion over the support will remain intact and ultimately metal leaching would be reduced. However, excess amounts of W_c will always induce higher concentration gradient of metal species between the solid - liquid phases [4] and thus higher metal loses are observed Figure 6.6.

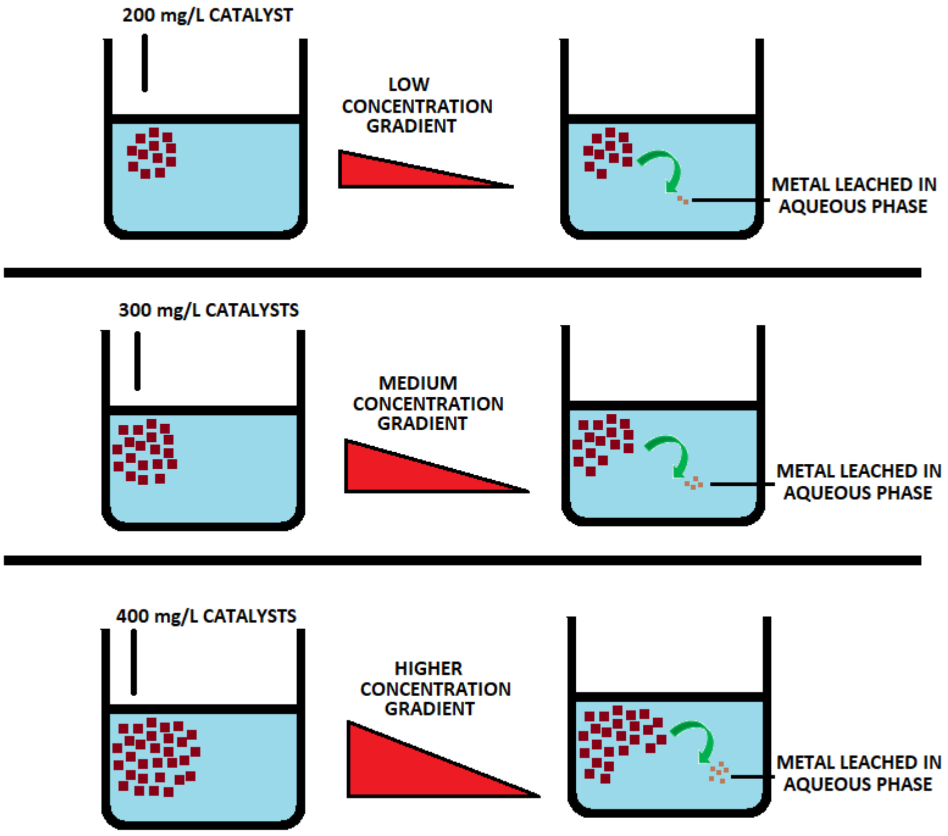

Figure 6.6: Effect of catalyst dose on metal leaching as a function of concentration gradient

Table 6.3: Metallic leaching with varying catalyst doses in heterogeneous Fenton reaction

Catalyst	200 mg/L		300 mg/L		400 mg/L	
	Metal loss (%)	Metal loss (mg)	Metal loss (%)	Metal loss (mg)	Metal loss (%)	Metal loss (mg)
5%Fe	5.3	0.53	4.4	0.66	4.75	0.95
7.5%Fe	1.67	0.3	1.56	0.4	2	0.6
10%Fe	2.5	0.5	3.07	0.9	3.13	1.3
5%Cu	8.8	0.88	1.73	0.26	10.15	2.03
7.5%Cu	6.2	0.9	9.33	1.4	9.6	1.4
10%Cu	3	0.6	4.83	1.5	3.8	1.5

6.3.4. Effect of oxidant dose on catalytic activity and stability

H_2O_2 is the source of OH• radicals and the optimal concentration of the oxidant will not only reduce the chemical cost but also enhance the efficacy of the Fenton process. The effect of variable oxidant doses on the IBP mineralization with different catalysts is experimentally measured and is summarized in Figure 6.7.

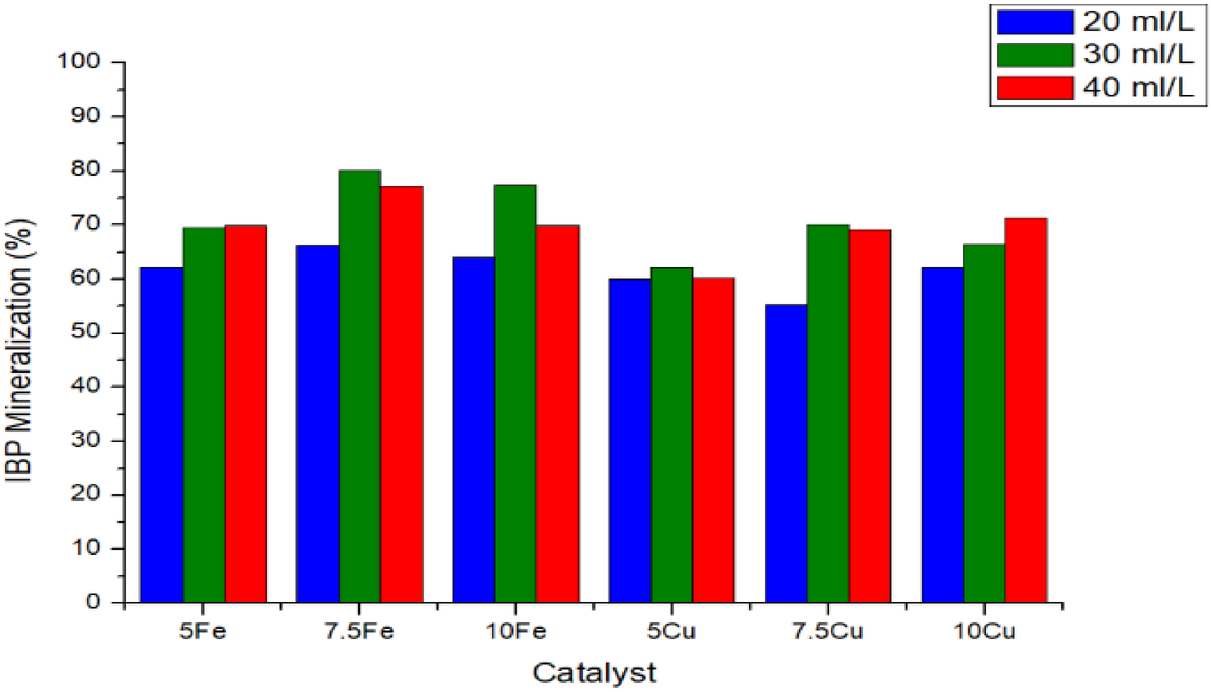

Figure 6.7: Effect of H_2O_2 dose (3%) on the catalytic activity of iron and copper catalysts (reaction condition: 70 °C, IBP conc. 10 mg/L, reaction time 150 min, pH 3 and 400 mg/L of catalyst dose for Fe catalysts and pH 5 200 mg/L of catalyst dose for Cu catalysts)

For all the catalysts, 20ml/L of oxidant dose induced the lower activity. In general, the best activity is obtained for 30 ml/l of H_2O_2, while a further increase to 40 ml/l does not affect the activity. These results demonstrate that 20 ml/L of the oxidant dose is insufficient to generate enough OH• radicals to afford high IBP mineralization. It seems that 30 ml/L of H_2O_2 is the optimal oxidant dose and generated maximum amount of OH• radicals which in turn subsided the highest amount of IBP. It also indicates that, the prime catalyst to oxidant ratio is obtained when 7.5% metal loaded catalysts are used along with 30 ml/L of H_2O_2 because higher IBP mineralization is obtained under these conditions. On the contrary, 40 ml/L of H_2O_2 is excessive and the surplus amount of the oxidant may have caused scavenging effect due to which efficacy of the Fenton process dropped [32, 33]. Moreover, when excess amount of oxidant is employed in the Fenton process, radicals with low oxidation potential are generated and ultimately oxidation efficiency drops [34]. It is worth mentioning that the iron-based catalysts have better capacity to transform the oxidant into OH• radicals when compared with their counterpart copper-based catalysts and is in agreement with previous studies [35, 36].

The metal leaching from different catalysts with varying doses of the oxidant has been studied and the results are outlined in Table 6.4. It is visible from the results that the metal leaching from iron bearing catalysts with varying H_2O_2 doses increases in the following order; 30 ml/L > 20 ml/L > 40 ml/L. Moreover, the 7.5% iron loaded catalyst has endured minimal metal loses with fluctuating doses of the oxidant. Similarly, copper bearing catalysts have shown parallel metal loses when oxidant doses are changed in heterogeneous Fenton process and the metal leaching increased in the sequence; 30 ml/L > 40 ml/L > 20 ml/L but the overall loses are higher when compared with iron-based catalysts. The minimal copper losses (0.9 mg) are observed when 30 ml/L of H_2O_2 is employed together with 7.5% copper loaded catalyst. Again, these results suggest that the catalyst which is loaded with the optimal amount of metal on the support, will offer higher stability under varying processing conditions like oxidant dose. Moreover, it also stipulates that when the catalyst: oxidant ratio is shifted away from the optimal ratio, catalyst will experience higher metal leaching. Furthermore, copper-based catalysts lose higher amount of metal under non optimal doses of the oxidant because the disproportionate amounts H_2O_2 will turn the pH of the solution more acidic and ultimately metal leaching would soar. Besides, the mineralization products or intermediates also shift the aqueous phase to more acidic pH due to which copper bearing catalysts experience additional metal leaching [37].

Table 6.4: Metallic leaching with varying oxidant doses in heterogeneous Fenton reaction

Catalyst	**20 ml/L**		**30 ml/L**		**40 ml/L**	
	Metal loss (%)	**Metal loss (mg)**	**Metal loss (%)**	**Metal loss (mg)**	**Metal loss (%)**	**Metal loss (mg)**
5 Fe	5.9	0.59	5.3	0.53	9.9	0.99
7.5 Fe	0.66	0.1	1.67	0.3	2.33	0.4
10 Fe	5.1	1	2.5	0.5	5.5	1.1
5 Cu	25.8	2.58	8.8	0.88	11.1	1.11
7.5 Cu	4.89	1.1	6.2	0.9	4.27	1.3
10 Cu	6.5	1.3	3	0.6	6.2	1.2

6.3.5. Effect of temperature on catalytic activity and stability

The rate of OH• generation from the oxidant is greatly influenced by the reaction temperature and in turn affects the overall efficacy of the heterogeneous Fenton process [38, 39]. In order to observe the effect of temperature on the activities of different catalysts, the Fenton process has been carried out at three different temperatures and results are outlined in Figure 6.8.

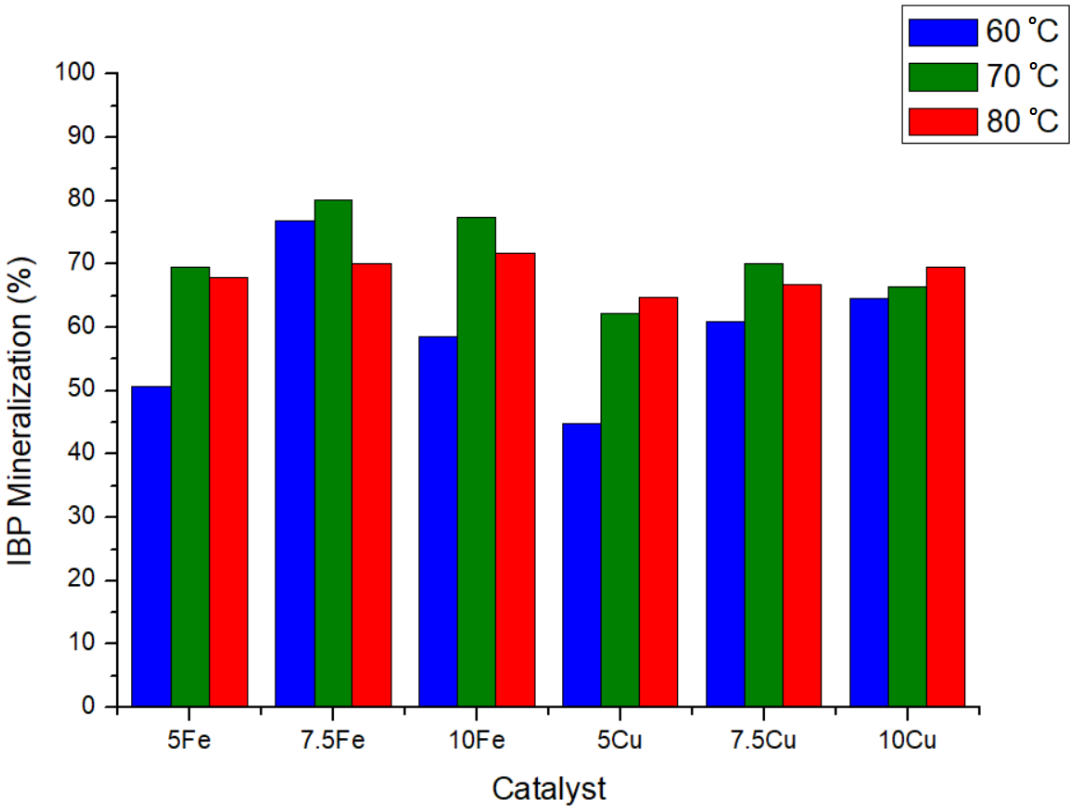

Figure 6.8: Effect of temperature on the catalytic activity of iron and copper catalysts (reaction condition: H_2O_2 dose (3%) 30 ml/L, IBP conc. 10 mg/L, reaction time 150 min, pH 3 and 400 mg/L of catalyst dose for Fe catalysts and pH 5 200 mg/L of catalyst dose for Cu catalysts)

Zr5Fe and Zr10Fe afforded 50 and 58% IBP mineralization at 60 °C and when the temperature is increased to 70 °C, IBP abatements rose sharply to 69 and 77% respectively. However, further increase in the reaction temperature i.e. 80 °C slightly reduced the IBP mineralization to 67 and 71%. While working with 7.5Fe, as the temperature increases from 60 to 70 °C the TOC abatement did not increase substantially i.e. 76 to 80% but further increase in the temperature negatively impacted the catalytic performance and efficacy of the Fenton process dropped to 70%. It is important to mention that the catalyst with optimal iron loading has yielded better activities even at lower reaction temperature. Contrary, Zr5Cu and Zr10Cu have shown linear catalytic activities with rising temperature and IBP degradation increased from 44 to 64% and 64 to 69%, respectively. However, when 7.5Cu is utilized in Fenton process the IBP mineralization first increased until 70 °C but further increase in temperature caused a slight decline in the activity. These results indicate that the rate of OH• radical generation from the oxidant at 60 °C is relatively low and induces lower degradation of IBP. As the temperature increases, the rate of OH• radical generation increases [40] but beyond 70 °C the wasteful utilization of free radicals increases and thus overall process efficiency declines. It is also likely that at 80 °C the equilibrium of adsorption/desorption is disturbed and poor adsorption of IBP molecules onto the catalyst surface has resulted the lower TOC abatement. Moreover, at 80 °C higher amount of the oxidant is decomposed into water and oxygen and reduced quantity of free radicals negatively affects the process efficacy [41, 42].

In order to monitor the stability of catalysts, the loss of metal from each catalyst during the Fenton process is experimentally determined and is summarized in Table 6.5. The results clearly depict that the stability of both iron and copper catalysts loaded with 7.5% metal have increased when temperature is increased from 60 to 80 °C and metal loses are below the limits suggested by EPA [27]. It indicates that the catalysts with optimum metal loadings can withstand any reaction temperature without being prone to substantial metal leaching due to their superior bonding with the support material. On the contrary, when 5Fe and 5Cu are employed in heterogeneous oxidation process, they undergo severe metallic loses and the order of metal leaching at different temperatures is 60 °C > 80 °C > 70 °C. Similar but less severe metal loses has been observed with 10% metal loaded catalysts. These results indicate that the catalysts with excessive metal loading have higher stability than those with insufficient metal charge because they only experience leaching from the secondary layer of metal sites which is loosely attached to the support

Table 6.5: Metallic leaching with varying temperatures in heterogeneous Fenton reaction

	60 °C		**70 °C**		**80 °C**	
Catalyst	**Metal loss (%)**	**Metal loss (mg)**	**Metal loss (%)**	**Metal loss (mg)**	**Metal loss (%)**	**Metal loss (mg)**
5 Fe	15.5	1.55	5.3	0.53	9.9	0.46
7.5 Fe	9	1.4	1.67	0.3	1.73	0.3
10 Fe	4.2	0.8	2.5	0.5	5.5	0.3
5 Cu	10.7	1.07	8.8	0.88	11.1	1.36
7.5 Cu	9.93	1.5	6.2	0.9	4.27	0.8
10 Cu	6.25	1.3	3	0.6	6.2	0.9

6.3.6. Effect of recycling on catalytic activity and stability

The reusability of the catalyst without losing its activity in any process and particularly in heterogeneous Fenton process is of paramount importance because it reduces the cost of the chemicals and eliminates the post treatment costs such as separation of the lost catalyst from the aqueous phase [43]. To monitor the activity of the catalysts in subsequent applications, all the catalysts were recycled thrice without any modification and the results are graphically presented in Figure 6.9. Since metallic leaching has a direct impact on the catalyst activity in the following cycles and therefore, these results are outlined in Table 6.6 and are discussed together with the activity.

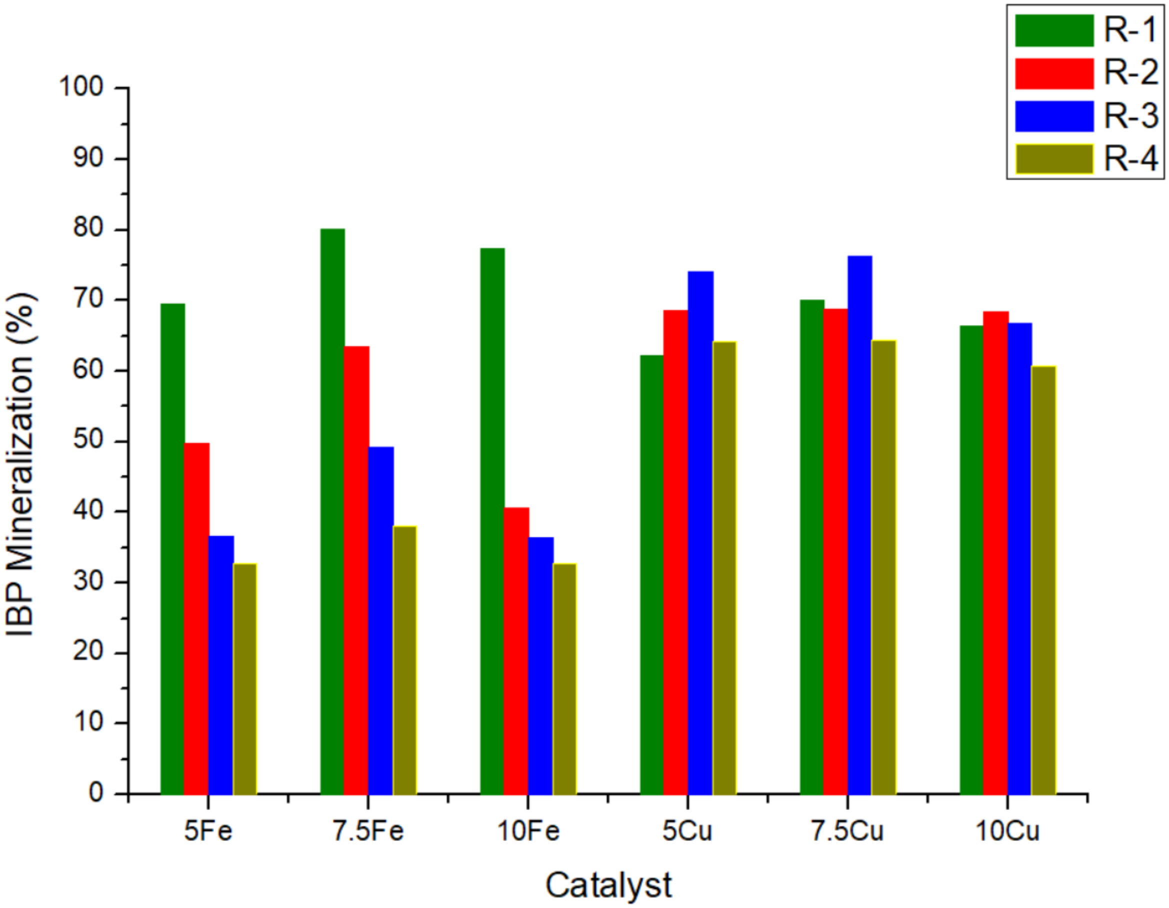

Figure 6.9: Effect of catalyst recycling on IBP mineralization (reaction condition: 70 °C, H_2O_2 dose (3%) 30 ml/L, IBP conc. 10 mg/L, reaction time 150 min, pH 3 and 400 mg/L of catalyst dose for Fe catalysts and pH 5, 200 mg/L of catalyst dose for Cu catalysts)

If we look into the activity profile of Zr5Fe, the IBP mineralization sharply decreased from 69 to 49% after 1st recycle and continuously decreased to 32% in the 3rd recycle. Similarly, Zr7.5Fe afforded 80% TOC abatement when freshly employed and after 3rd recycle only mineralize 38% of IBP. Likewise, Zr10Fe lost more than 50% of its activity after 3rd recycle. However, when we look into the metallic loses of all the iron-based catalysts separately, these loses are not more than 15% in all the three recycles. These results affirm that the iron-based catalysts do not lose their activities primarily due the metallic leaching, but due to the formation of very stable complexes with the degradation products of the pollutant [44] which deactivate them (Figure 6.10). On the other hand, catalytic activity of the 5Cu gradually increased from 62 to 74% after 2nd recycling of the catalyst and then declined to 64% in the 3rd recycle. Although, substantial metallic sites were lost in each cycle especially in the 2nd employment of the catalyst, but sustained activities indicate that the optimal catalyst dose is perhaps a little lower than the employed one. When Zr7.5Cu is used in Fenton process, the IBP mineralization almost remained the same in the first two employments of the catalyst i.e.70%. However, IBP abatement increased to 76% after the 2nd recycle and dropped again to 64% in the final recycle. While working with 10Cu, uniform TOC abatements i.e. 66% were obtained until first two recycles but in the 3rd recycle it slightly reduced to 60%. Moreover, Zr7.5Cu and 10Cu lost negligible amounts of their sites in each cycle. These results stipulate that the developed copper-based catalysts yield very stable performances in the heterogeneous Fenton process and do not lose activity upon losing small fraction of active sites. It also suggests that copper-based catalysts do not form any sort of complexes either with the parent organic molecule or its metabolites and the afforded TOC abatements are entirely achieved through Fenton oxidation [44].

Table 6.6: Metallic leaching in each employment of catalyst in heterogeneous Fenton reaction

	1st Run		2nd Run		3rd Run		4th Run	
Catalyst	**Metal loss (%)**	**Metal loss (mg)**	**Metal loss (%)**	**Metal loss (mg)**	**Metal loss (%)**	**Metal loss (mg)**	**Metal loss (%)**	**Metal loss (mg)**
5 Fe	5.3	0.53	9.5	0.95	4.2	0.42	3.6	0.36
7.5 Fe	1.67	0.3	2	0.3	3.27	0.5	1.53	0.2
10 Fe	2.5	0.5	2.95	0.6	1.5	0.3	1.15	0.2
5 Cu	8.8	0.88	22.6	2.26	9.9	0.99	7.2	0.72
7.5 Cu	6.2	0.9	2.27	0.3	2.33	0.4	2	0.3
10 Cu	3	0.6	2	0.4	1.15	0.2	1.65	0.3

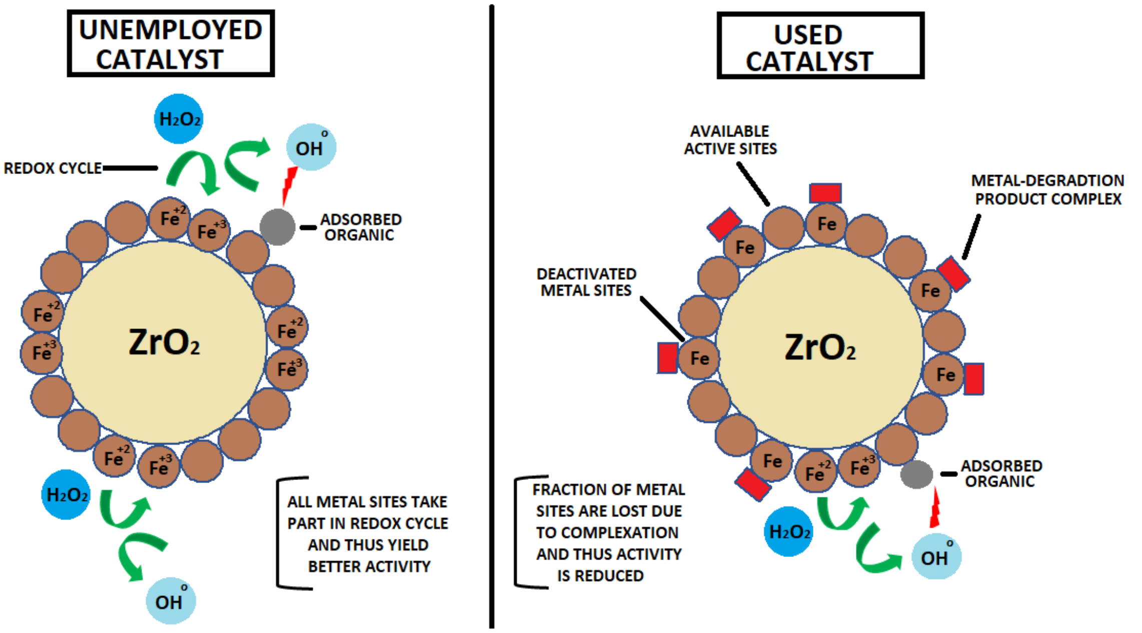

Figure 6.10: Depiction of catalytic activities of fresh and used iron catalysts in heterogeneous Fenton process

6.4. Conclusion

This study has shown that the developed catalysts with 7.5% iron and copper loadings over zirconia support possess very high and promising activities for IBP mineralization in heterogeneous Fenton process. Although both type of catalysts has same supporting material, iron loaded catalysts afford better activities at pH 3 while optimal pH for copper-based catalysts is 5. Further, the catalysts with optimal metal loadings of 7.5% are very stable under all processing conditions of Fenton process and metal loses are below the guidelines laid out by the environmental protection agency. However, iron-based catalysts though afford better activities, but they lose their activities substantially when recycled. On the other hand, copper-based catalyst though yield slightly lower TOC abatements, but they afford stable activities in the subsequent cycles of Fenton process making them better than their counterpart iron peers. The results obtained therefore, highlight how the copper-based catalysts are extremely promising in terms of activity and stability in Fenton-like treatments.

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Chapter-7

Effects of metal loading and reaction conditions on the oxidative removal efficiency of ibuprofen in the heterogeneous Fenton process over Fe-Cu bimetallic catalysts

Sajid Hussain, Eleonora Aneggi, Daniele Goi, to be submitted

Abstract

In this study, a series of bimetallic catalysts, Cu/Fe supported over ZrO_2 are prepared by wetness impregnation and characterized by standard techniques. All bimetallic catalysts afford high mineralization of ibuprofen within the pH range of 3 – 4. The extent of bimetallic catalytic activity is governed by the limiting metal component while part of the excess metal component also exhibits monometallic behavior. Among the developed catalysts, 5%Cu-5%Fe/ZrO_2 with equal proportions of both metals not only displays the highest TOC abatement (82%) under optimum conditions but also sustains minimum loses of copper and iron. Optimization of the reaction variables (oxidant dose, pH, catalyst loading and temperature) led to increased process efficiency. The recycling of bimetallic catalysts reveals that only 5%Cu-5%Fe/ZrO_2 system is able to provide sustainable activity in heterogenous Fenton process while rest of the catalysts experienced substantial activity loss. The present study highlights the potential of bimetallic Cu/Fe supported catalysts for the removal of organic compounds in wastewaters via heterogeneous Fenton-like process.

Keywords: Fenton like oxidation, heterogeneous catalysis, metal loading, bimetallic catalyst, ibuprofen, wastewater treatment

7.1. Introduction

Water contamination has become a very serious challenge due to the release of large number of refractory pollutants into water bodies [1-3]. Global environmental protection agencies have progressively enforced very stringent guidelines to safeguard ground and surface waters [4]. The conventional biological processes are not capable to eliminate these persistent organic pollutants from water streams [5]. Advanced oxidation processes (AOPs) especially Fenton process is very effective for the abatement of refractory organics due the utilization of highly reactive and non-selective hydroxyl radicals (OH•) [6, 7]. Although, the homogeneous Fenton process is very simple, efficient, and cost effective but it produces large volumes of residual sludge which needs to be processed and disposed of, creating another environmental challenge [8, 9]. Moreover, the process is only efficient under acidic pH conditions i.e. pH 3 and this induces additional chemical costs [10, 11]. These drawbacks can be overcome by employing heterogenous Fenton process because it does not produce sludge, catalyst is easily separated from the liquid stream and can be reused [12, 13]. However, iron-based heterogeneous catalysts still require acidic conditions to achieve high process efficacies and catalysts become more susceptible to higher amounts of metal leaching [14]. Moreover, iron tend to form complexes with oxidation products in heterogeneous Fenton process and consequently deactivation of the catalyst.

On the contrary, the heterogenous catalysts employing other transition metals such as copper afford fairly good catalytic performance in Fenton process and also have the capacity to be recycled multiple times without losing their activities [15]. However, the efficacy of copper-based catalysts is lower than that of iron-based catalysts. Further, copper-based catalysts require higher excess stoichiometric amounts of the oxidant to yield better activities. Further, these catalysts require relatively high activation energies to produce OH• radicals, and in turn the overall operational cost of the Fenton process can increase [16, 17]. Although, monometallic heterogeneous catalysts afford very high catalytic activities, the limitations such as narrow working pH, metallic leaching and complexation drive the researchers for the development of new and more active heterogenous catalysts. Keeping in view of the narrow working optimal pH offered by monometallic catalysts in Fenton process, the optimization of the process is itself a great challenge because the slightest disturbance in the pH of the aqueous solution may significantly reduce the process efficacy. Bimetallic catalysts employing two transition metals over an appropriate support may eliminate all these limitations and it is also possible to further enhance the efficiency of the heterogeneous Fenton process [18].

In this study we have developed different bimetallic catalysts based on iron and copper supported over zirconia support. The effects of total metal loading and iron/copper ratio on catalytic activity have been investigated under varying process conditions of pH, catalyst dose, H_2O_2 dose and temperature. Moreover, catalytic performances of all these catalysts have been observed after recycling. Furthermore, the metal loses from these catalysts under different conditions have also been monitored.

7.2. Experimental

7.2.1. Catalyst preparation

A series of bimetallic catalysts with varying wt % (Cu + Fe) supported over ZrO_2 were prepared. ZrO_2 support was prepared by calcination of zirconium hydroxides (Mel Chemicals, Manchester, UK) at 500 °C for 3 h. Then, aqueous solutions with appropriate amounts of Cu (copper (II) nitrate hemi (pentahydrate), Sigma Aldrich, Saint Louis, MO, USA), and Fe (Iron (III) nitrate nonahydrate, Sigma Aldrich), were added in a single step by incipient wetness impregnation and were dried overnight at 100 °C. After drying, the samples were finally calcined at 500 °C for 3 h. Textural characteristics of all fresh samples were measured according to the BET method by nitrogen adsorption at −196 °C, using a Tristar 3000 gas adsorption analyser (Micromeritics). Structural features of the catalysts were characterized by X-ray diffraction (XRD). XRD profiles were recorded on a Philips X'Pert diffractometer (equipped with a real time multiple strip detector) operated at 40 kV and 40 mA using Ni-filtered Cu-Kα radiation. Spectra were collected using a step size of 0.02° and a counting time of 20 s per angular abscissa in the range 20°-80°. The Philips X'Pert HighScore software was used for phase identification.

7.2.2. Catalytic activity experiments

Aqueous solutions of ibuprofen, IBP (10 mg/L) were prepared dissolving ibuprofen sodium salt, $C_{13}H_{17}O_2Na$ (Sigma-Aldrich) in ultra-pure water. Ibuprofen samples (100 ml) loaded with 200 mg/L of individual catalysts were heated at 70 ˚C under continuous stirring conditions of 500 RPM, using an Omni multistage reaction station with a provision of reflux. The Fenton like reaction was carried out for 150 minutes and the treated samples were centrifuged at 5000 rpm using Eppendorf Centrifuge 5804 R, followed by filtration through a 0.45 µm membrane filters. The oxidation process was optimized evaluating the effects of catalyst dose (200, 300 and 400 mg/L), hydrogen peroxide, (20, 30 and 40 ml/L), temperature (60,70 and 80 °C) and pH (3 - 8, acidifying the sample with hydrochloric acid (Sigma Aldrich) or basifying the sample with sodium hydroxide (Sigma Aldrich)). The mineralization of IBP, the total organic carbon (TOC) of treated samples was analyzed using a TOC-VCPN, Shimadzu analyzer(V-Series) with auto sampler. First, the standard solutions with known concentrations of 2.5, 5.0, 10.0 20.0 mg C/l were prepared using potassium hydrogen phthalate stock solution. A calibration curve was obtained by analyzing the standard samples, and after each analysis the injection syringe was auto sparged with 2M HCl. The samples were analyzed without dilution and using the same calibration curve to determine TOC present in each sample. The TOC removal efficiencies were determined using Eq.1. Moreover, TOC and IBP mineralization have been used interchangeably in this study.

$$\text{TOC removal efficiency (\%)} = \frac{\text{TOC}_\text{i}\text{-TOC}_\text{f}}{\text{TOC}_\text{i}} * 100 \qquad \text{(Eq.1)}$$

Several experiments were also carried out to verify the reproducibility of our activity measurements and the errors resulted to be within 3%.

7.2.3. ICP analysis for metal leaching

The leaching of iron and copper from bimetallic catalysts during the heterogeneous Fenton process was determined with US EPA 3051 method using Inductivity Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES vista pro.) First, a calibration curve was obtained using an ICP 23-element standard solutions which were prepared in 5% HNO_3. Yttrium (Y) was used as an internal standard. The method detection limit (MDL) was calculated as 3 s/m.

Where;

s = Standard deviation of 10 replicate blanks
m = slope of the calibration curve for each element

The percentages of metal loss were calculated using the following Eq.2.

$$\text{Metal leaching}\ (\%) = [1\text{-}(\frac{M_i - M_f}{M_i})]*100 \qquad \text{(Eq.2)}$$

Where,

M_i = Initially introduced metal weight (mg)

M_f = Finally left metal weight at the end of Fenton process (mg)

7.3. Results and discussion

7.3.1. Catalyst characterization

Composition and BET surface area of the materials are reported in Table 7.1. The addition of Cu or Fe does not strongly affect the surface area of pure zirconia (64 m^2/g) with a maximum decrease to 59 m^2/g for copper and 54 m^2/g for iron-based materials.

Table 7.1: Composition and surface area of investigated samples

Sample	Composition	Surface Area (m^2/g)
2.5Cu/2.5Fe	Cu(2.5%)-Fe(2.5%)/ZrO_2	59
2.5Cu/5Fe	Cu(2.5%)-Fe(5%)//ZrO_2	55
5Cu/2.5Fe	Cu(5%)-Fe(2.5%)/ZrO_2	59
5Cu/5Fe	Cu(5%)-Fe(5%)/ZrO_2	55

The structural features of the zirconia-based materials were analysed by powder X-ray diffraction (XRD). Materials show the simultaneous presence of tetragonal (space group P42/nmc; main reflection at 30,2°) and monoclinic ZrO_2 (space group P121/c1, main reflection at 28,2°) while no evidence for any copper or iron phase was found suggesting that Cu and Fe are homogeneously dispersed on the surface (Figure 7.1)

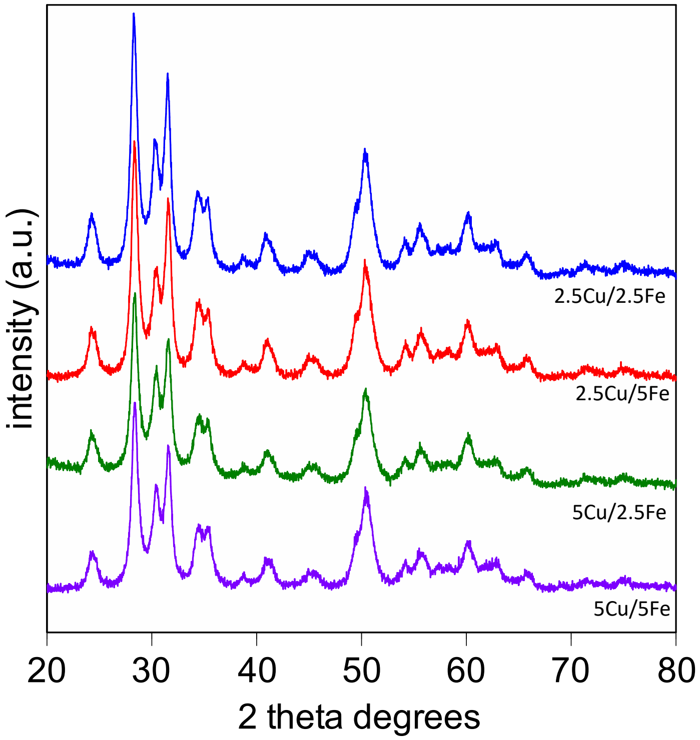

Figure 7.1: XRD profiles of the investigated samples

7.3.2. Effect of pH

The pH of the aqueous solution is the most critical parameter in heterogeneous Fenton process because the catalyst can only produce maximum amount of OH• radicals from the oxidant within a specific range of pH conditions and in turn yield higher catalytic activity [19]. To precisely investigate the activities of bimetallic catalysts, the oxidation reactions were performed over a broader pH range and results are presented in Figure 7.2. For all the materials the highest IBP abatement has been achieved in early 30 minutes and later, the catalytic activity is maintained.

All bimetallic catalysts have shown very high and stable abatements of IBP (~75%) within the pH range of 3 – 4. It indicates that the point of zero charge (PZC) of bimetallic catalysts, conforms to these conditions of pH and small variation in catalyst composition does not significantly affects it [20]. Moreover, this is a very important result because unlike monometallic catalysts, these catalysts have a wider window of optimal pH through which they can achieve maximum TOC removals [5, 21]. Further, bimetallic catalysts offer improved redox cycle due to the interfacial electron transfers between Fe^{+3}/Fe^{+2} and Cu^{+2}/Cu^{+} Figure 7.3 [22]. However, when the Fenton process is carried out at pH 5, the IBP abatement declined substantially to ~60% suggesting that the frequency of redox reactions involving the decomposition of H_2O_2 into OH• radicals is reduced, negatively affecting the efficacy of the Fenton process. The TOC abatements are dramatically reduced to ~20 and 10 % when operating pH is changed respectively to 6 and 8.

These results indicate that when the heterogeneous Fenton process employing bimetallic catalysts is operated under near neutral to basic conditions, the oxidant starts decomposing into oxygen and water and thus efficiency is suppressed [23]. Summarizing, pH 4 let to achieve maximum TOC abatements, with a relatively less acidic condition compared to pH 3 and is advantageous not only to reduce the chemical costs but also favorable to minimize metal leaching. Therefore, the optimization of the other variables has been performed at pH 4.

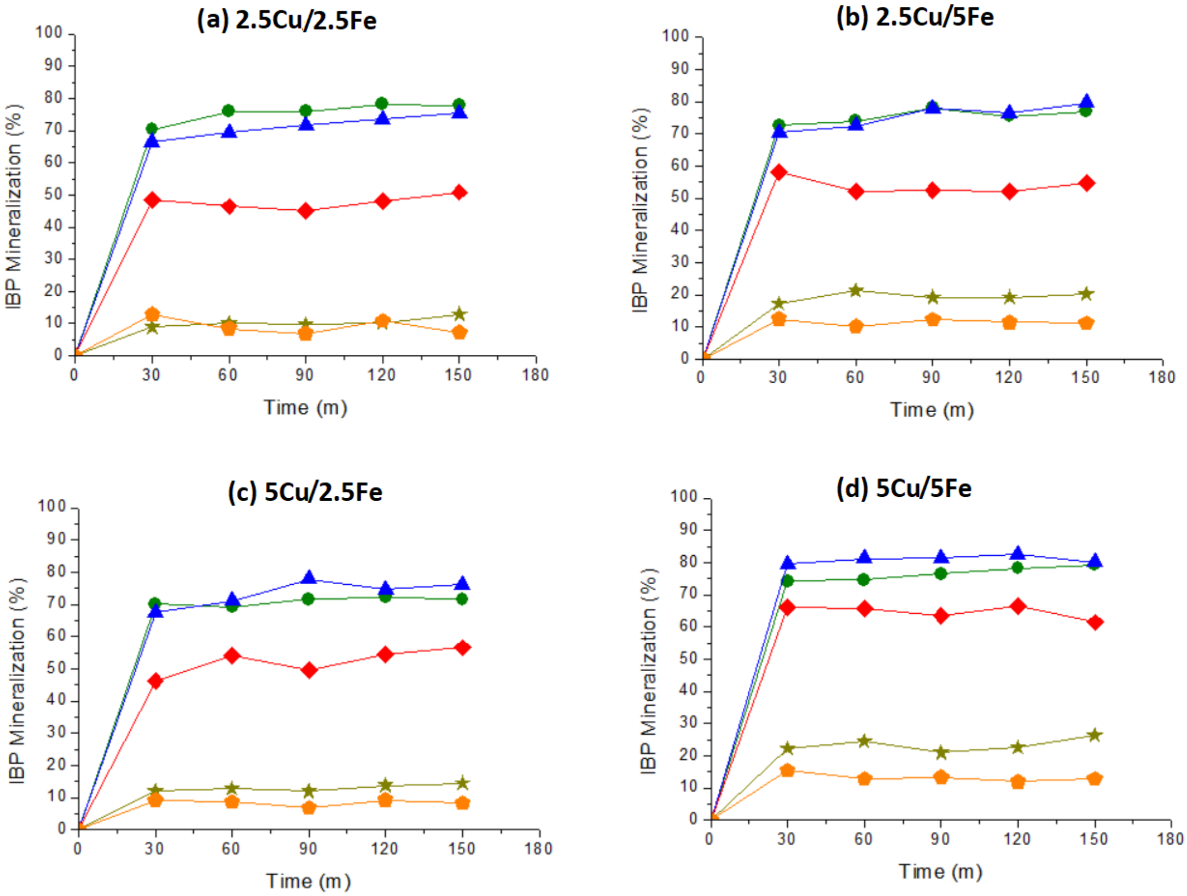

Figure 7.2: Effect of pH on the IBP mineralization by bimetallic catalysts: (reaction condition: catalyst dose - 200 mg/L, H_2O_2 dose (3%) - 30 ml/L, Temperature -70 °C, and reaction time - 150 minutes, pH 3 – o, pH 4 – Δ, pH 5 – □, pH 6 – ✡, pH 8 - ⌂)

It is important to note that the ratios of iron and copper in the bimetallic samples also governs the extent/fraction to which these catalysts can exercise bimetallic redox cycle. For instance, the 2.5Cu/5Fe catalyst can only exhibit the characteristics of bimetallic catalyst through 50% of its sites because the total fraction of the limiting metal component is 0.5 while rest of the material will exhibit the characteristics of monometallic iron catalyst Figure 7.4. On the other hand, 5Cu/2.5Fe catalyst will display 50% of its activity as bimetallic while the rest of the 50% as monometallic copper catalyst. Unlike the other catalysts discussed above, 2.5Cu/2.5Fe and 5Cu/5Fe can express the features of a perfect bimetallic catalysts because both metals are charged onto the supporting material in equal proportions. These adjustments in the ratios of the two metallic parts not only aid in building robust and highly active catalysts but also reduce the overall cost of the catalyst.

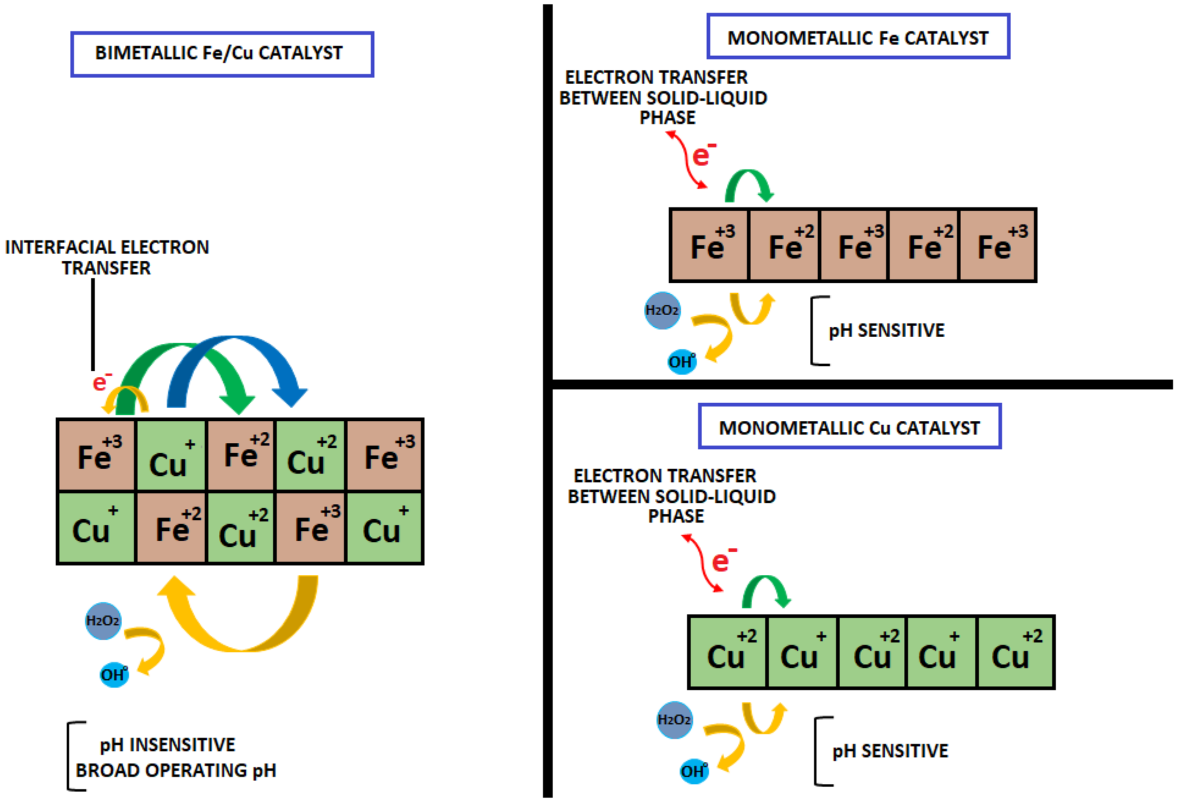

Figure 7.3: Comparison of redox cycles of monometallic and bimetallic catalysts

The stabilities of all these bimetallic catalysts have been examined at pH 3 and 4 because they afforded maximum activities under these conditions and results are presented in the Table 7.2. The results clearly suggest that iron leaching from the bimetallic catalysts is substantially lower than copper and negligibly changes with varying the pH, indicating stronger bonding of iron atoms with the support material. On the other hand, copper leaching is significantly reduced at pH 4 which stipulates that the stability of copper atoms is strongly affected under acidic conditions. These results also suggest that when iron and copper are used in equal proportions it induces greater stability in the bimetallic catalysts. It is worth mentioning that none of the catalysts at pH 4 exceeded the maximum limits set by European Union for the amount of iron and copper in treated water [22].

Table 7.2: Metallic leaching from bimetallic catalysts with varying pH (reaction condition: catalyst dose – 200 mg/L, H_2O_2 dose (3%) – 30 ml/L, temperature – 70 °C and reaction time – 150 minutes)

Catalyst	pH 3				pH 4			
	Cu Loss (%)	Cu Loss (mg)	Fe Loss (%)	Fe Loss (mg)	Cu Loss (%)	Cu Loss (mg)	Fe Loss (%)	Fe Loss (mg)
2.5Cu/2.5Fe	10.75	0.43	3.2	0.16	6.75	0.27	3	0.15
2.5Cu/5Fe	18.6	0.93	1.1	0.11	17.6	0.88	2.2	0.11
5Cu/2.5Fe	13.2	1.32	4.4	0.22	7.2	0.72	2.4	0.12
5Cu/5Fe	6.27	0.62	1.4	0.14	4.9	0.49	3.4	0.34

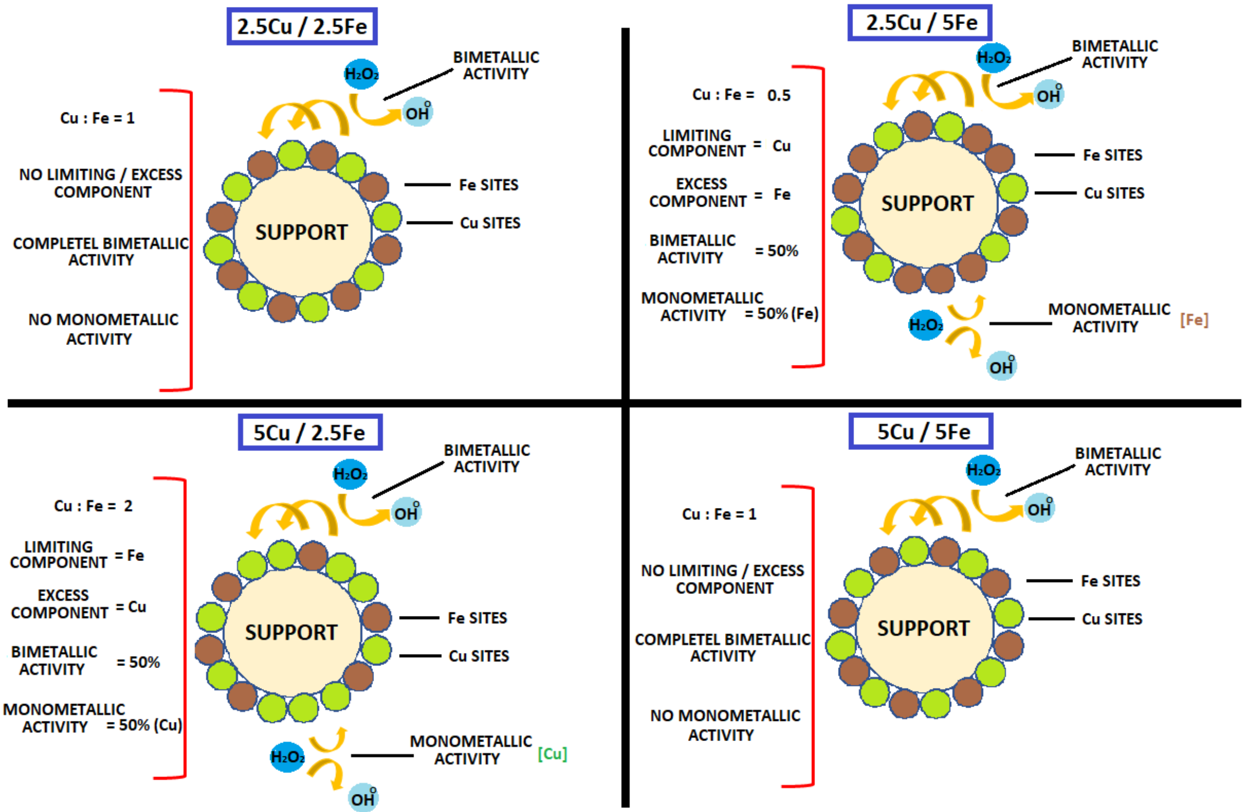

Figure 7.4: The extent of bimetallic and monometallic catalytic activity of the employed catalysts

7.3.3. Effect of catalyst dose

Generally, increasing the catalyst dose increases the efficacy of the Fenton process but the optimum catalyst dose ought to be determined experimentally to maintain the economic feasibility of the process [24]. To observe the influence of the catalyst dose on the overall efficacy of the oxidation process, variable catalyst doses of bimetallic catalysts have been employed and resulted are shown in Figure 7.5. The IBP mineralization slightly increased from 75 to 79% when the catalyst dose of 2.5Cu/2.5Fe is increased from 200 to 300 mg/L and further increase did not improved the IBP mineralization. The 2.5Cu/2.5Fe catalyst has the minimum metal loading on the support and the corresponding number of active sites are also low, therefore, increasing the catalyst dose will increase the total number of active sites which can take part in oxidation process and thus, process efficacy will increase. Similar results have been observed while working with 2.5Cu/5Fe and 5Cu/2.5Fe. These results clearly indicate that the optimal catalyst dose is 200 mg/L to achieve maximum catalytic activity and a further increase does not significantly improve the removal of IBP [22]. Although increasing the catalyst dose would increase the total number of active sites, but excess metal sites may also negatively affect the catalytic activity due to the scavenging effect [25]. However, for 5Cu/5Fe, when 200 mg/L are used, 80% of TOC removal is achieved, but a further increase in catalyst dose to 300 mg/L and 400 mg/l, induced a significant decrease in the TOC removal to 60 and 55%, respectively. These results exhibit that the optimum catalyst dose of the 5Cu/5Fe bimetallic catalyst is 200 mg/L and additional catalyst doses will induce very strong scavenging effect with dramatically reduction of the catalyst performance [26].

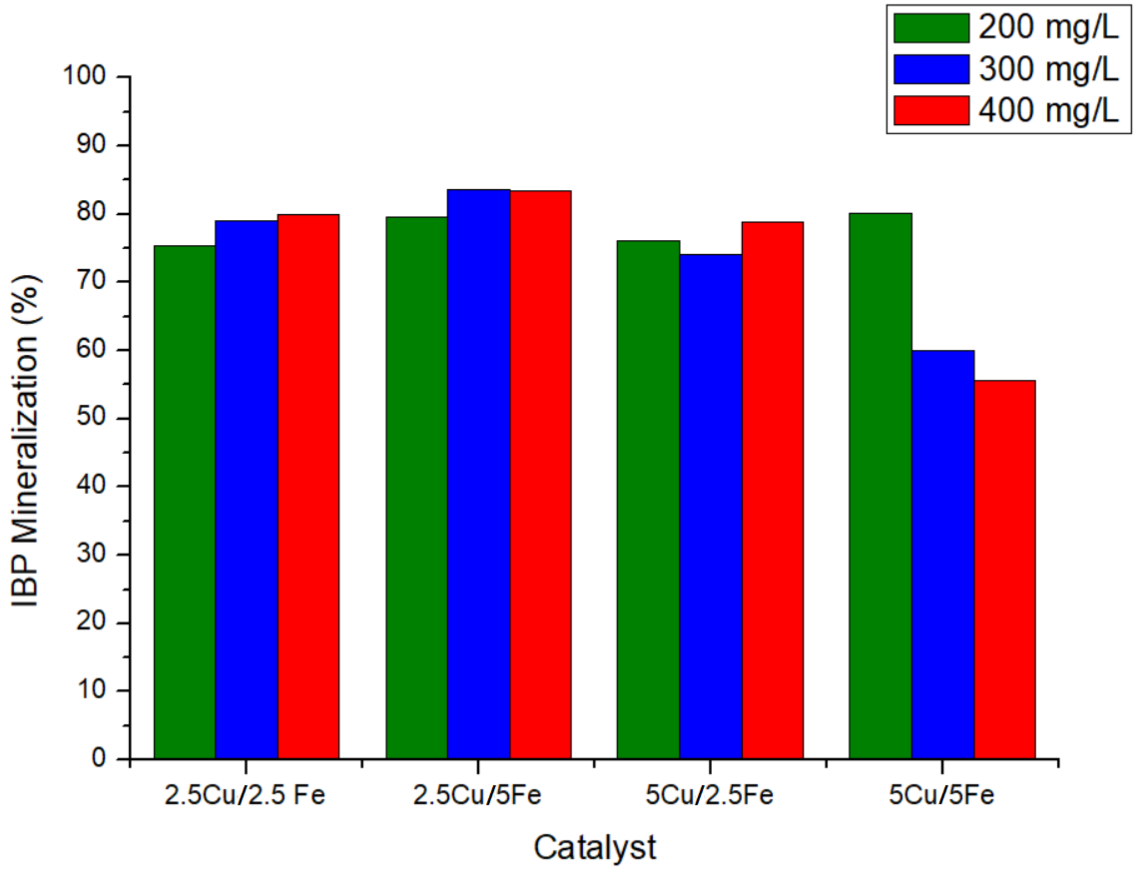

Figure 7.5: Effect of catalyst dose on the IBP mineralization by bimetallic catalysts (reaction condition: pH 4, H_2O_2 dose (3%) - 30 ml/L, Temperature -70 °C, and reaction time - 150 minutes)

The effect of an increased catalyst dose on leaching of iron and copper from the bimetallic catalysts has been investigated and results are presented in Table 7.3. The results clearly demonstrate that copper is more susceptible to leaching, especially when the employed catalyst has disproportionate amounts of iron and copper. Moreover, the results also stipulate that increasing the catalyst dose beyond optimal value would increase the metallic leaching due to higher concentration gradient between solid and liquid phases.

Table 7.3: Metallic leaching from bimetallic catalysts with varying catalyst doses (reaction condition: pH 4, H_2O_2 dose (3%) – 30 ml/L, temperature - 70 °C and reaction time – 150 minutes)

Catalyst	**200 mg/L**				**300 mg/L**				**400 mg/L**			
	Cu loss (%)	**Cu loss (mg)**	**Fe loss (%)**	**Fe loss (mg)**	**Cu loss (%)**	**Cu loss (mg)**	**Fe loss (%)**	**Fe loss (mg)**	**Cu loss (%)**	**Cu loss (mg)**	**Fe loss (%)**	**Fe loss (mg)**
2.5Cu/2.5Fe	6.75	0.27	3	0.15	7.17	0.43	8.67	0.65	6.88	0.55	5.5	0.55
2.5Cu/5Fe	17.6	0.88	2.2	0.11	13.6	1.02	1.5	0.3	12.40	1.24	1.47	0.44
5Cu/2.5Fe	7.2	0.72	2.4	0.12	8.6	1.29	5.47	0.41	6.55	1.31	4.60	0.46
5Cu/5Fe	4.9	0.49	3.4	0.34	5.2	0.78	2.35	0.47	4.87	0.97	1.47	0.44

7.3.4. Effect of oxidant dose

In heterogeneous Fenton process, H_2O_2 is the source of OH• free radicals and controlling the oxidant dose may help in optimizing the process efficacy. The removal efficacy of IBP using bimetallic catalysts as a function of H_2O_2 dose is shown in Figure 7.6**.** The bimetallic catalyst 2.5Cu/2.5Fe only mineralized 53% of IBP when 20 ml/L H_2O_2 is used in the oxidation process. However, when the oxidant doses are increased to 30 and 40 ml/L, the IBP abatement sharply increased to 75 and 77% respectively. These outcomes clearly suggest that a catalyst with low metal loadings would require higher oxidant doses to acquire higher TOC abatements.

On the other hand, while working with 2.5Cu/5Fe and 5Cu/2.5Fe, almost stable TOC abatements have been obtained despite varying the oxidant doses [24]. These results indicate that the catalysts with sufficient metal loadings can afford optimal activities with minimum oxidant doses i.e. 20 ml/L because the utilization efficacy of the oxidant is enhanced due to the bimetallic and monometallic redox cycles [27]. Moreover, excess oxidant doses may generate higher amounts of the free radicals but the self-scavenging of OH• radicals by the H_2O_2 (Eq. 3 and 4) may inhibit the increment in the process efficacy [28].

$$H_2O_2 + \bullet OH \longrightarrow H_2O + \bullet OOH \qquad (Eq.3)$$

$$\bullet OOH + \bullet OH \longrightarrow H_2O + O_2 \qquad (Eq.4)$$

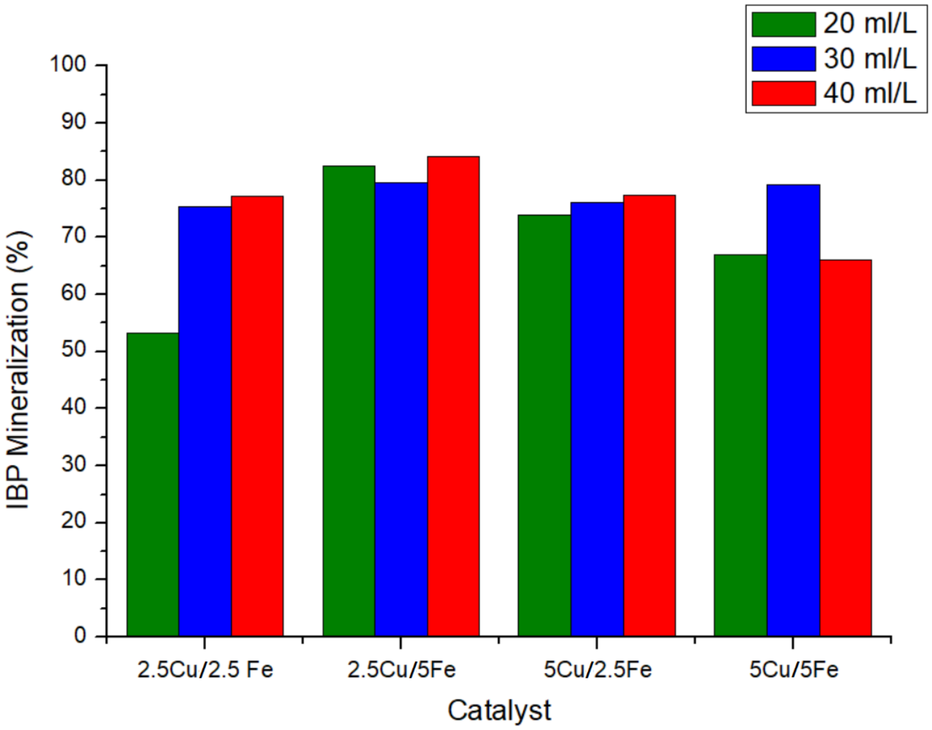

Figure 7.6: Effect of H_2O_2 dose on the IBP mineralization by bimetallic catalysts: (reaction condition: pH 4, catalyst dose – 200mg/L, temperature -70 °C, and reaction time - 150 minutes)

The bimetallic catalyst 5Cu/5Fe achieved 67% of IBP removal when 20 ml/L of H_2O_2 is used while 30 ml/L of the oxidant increased the removal efficacy to 80%. However, further increasing the oxidant dose to 40 ml/L adversely affected the process and removal of IBP declined to 66%. These results suggest that the catalyst with proportionate loadings of iron and copper, offering a perfect bimetallic redox cycle would require a specific optimum oxidant dose to yield maximum organic abatement.

To monitor the stability of bimetallic catalysts under varying conditions of the oxidant dose, the losses of iron and copper have been measured and results are shown in the Table 7.4. 5Cu/5Fe and 2.5Cu/2.5Fe have experienced lower amounts of metallic leaching but higher oxidant doses i.e. 40 ml/L slightly increases the metallic losses. This can be attributed to the lowering of the pH by an increased amount of H_2O_2 in the aqueous solution. Similar but slightly higher metal losses have been observed from 2.5Cu/5Fe and 5Cu/2.5Fe catalysts and these losses linearly increased with the increasing doses of oxidant. These results are very important to focus on the varying conditions of the oxidant within which these bimetallic catalysts not only achieve maximum organic abatements but also meet the regulations laid out by the environmental regulators [29, 30].

Table 7.4: Metallic leaching from bimetallic catalysts with varying H_2O_2 doses (reaction condition: pH 4, catalyst dose – 200 mg/L, temperature - 70 °C and reaction time – 150 minutes)

Catalyst	20 ml/L				30 ml/L				40 ml/L			
	Cu loss (%)	**Cu loss (mg)**	**Fe loss (%)**	**Fe loss (mg)**	**Cu loss (%)**	**Cu loss (mg)**	**Fe loss (%)**	**Fe loss (mg)**	**Cu loss (%)**	**Cu loss (mg)**	**Fe loss (%)**	**Fe loss (mg)**
2.5Cu/2.5Fe	8	0.32	10.2	0.51	6.75	0.27	3	0.15	12	0.48	15	0.75
2.5Cu/5Fe	11.6	0.58	4.10	0.41	17.6	0.88	2.2	0.11	12.2	0.61	2.9	0.29
5Cu/2.5Fe	8.5	0.85	8.2	0.41	7.2	0.72	2.4	0.12	14.4	1.44	9.4	0.47
5Cu/5Fe	4.6	0.46	1.7	0.17	4.9	0.49	3.4	0.34	9.1	0.91	1.8	0.18

7.3.5. Effect of temperature

The influence of temperature on the performance of bimetallic catalysts as a function of IBP removal is shown in Figure 7.7. The catalysts 2.5Cu/2.5Fe and 5Cu/2.5Fe managed to remove 64 and 65% of IBP from aqueous solution at 60°C. When the temperature is elevated to 70 °C, the removal efficacy increased to 75 and 76% respectively but further elevation of temperature resulted in negligible increase in IBP abatement. These results suggest that the TOC abatements of bimetallic catalysts with 2.5% of Fe increase proportionally with rising temperature until 70 °C and beyond this temperature the process potency does not rise notably. This also suggests that the rate of OH radical generation linearly increases with rising temperature but at 80 °C, the oxidant also starts to decompose thermally and thus adversely affecting IBP abatement [24]. On the other hand, 2.5Cu/5Fe eliminated 77and 79% of IBP at 60 and 70 °C, respectively and at 80 °C, the IBP degradation notably increased to 85%. These results indicate that the catalyst with higher iron content than copper yield better activities at higher temperatures. 5Cu/5Fe showed relatively poor performance at 60 °C because only 54% of IBP is removed. However, the IBP removal sharply soared to 80% at 70 °C but additional thermal energy provided through elevated temperature of 80 °C negatively impacted the Fenton process and IBP removal declined to 70%. These results propose that 60 °C does not add sufficient thermal energy into the aqueous phase to activate the generation of large number of free OH• radicals from the oxidant and thus yielding poor activity [31]. Similarly, higher temperature i.e. 80 °C is also seems unfavorable, either due to the thermal decomposition of H_2O_2 into water and oxygen and to the waste of oxidant due to side reactions [32].

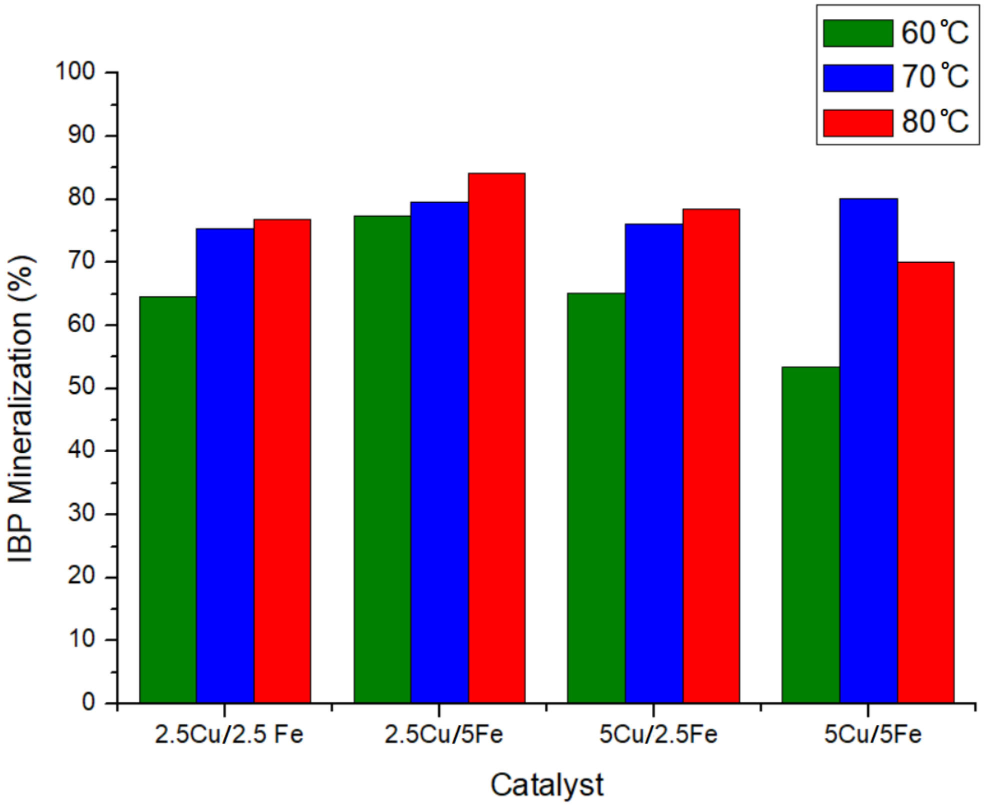

Figure 7.7: Effect of temperature on the IBP mineralization by bimetallic catalysts (reaction condition: pH 4 , catalyst dose – 200 mg/L, H_2O_2 dose(3%) – 30ml/L and reaction time - 150 minutes)

The influence of different reaction temperatures on the metallic leaching from the bimetallic catalysts is summarized in Table 7.5.

Table 7.5: Metallic leaching from bimetallic catalysts with varying temperatures (reaction condition: pH 4, catalyst dose – 200 mg/L, H_2O_2 dose(3%) – 30ml/L and reaction time – 150 minutes)

	60 °C				**70 °C**				**80 °C**			
Catalyst	**Cu loss (%)**	**Cu loss (mg)**	**Fe loss (%)**	**Fe loss (mg)**	**Cu loss (%)**	**Cu loss (mg)**	**Fe loss (%)**	**Fe loss (mg)**	**Cu loss (%)**	**Cu loss (mg)**	**Fe loss (%)**	**Fe loss (mg)**
2.5Cu/2.5Fe	9.5	0.38	7	0.35	6.75	0.27	3	0.15	11.25	0.45	4.4	0.22
2.5Cu/5Fe	16.4	0.82	8.6	0.86	17.6	0.88	2.2	0.11	17.8	0.89	2.6	0.26
5Cu/2.5Fe	11.3	1.13	5	0.25	7.2	0.72	2.4	0.12	11.8	1.18	2.6	0.13
5Cu/5Fe	5.7	0.57	2.10	0.21	4.9	0.49	3.4	0.34	6.4	0.64	1	0.10

The generalized order of metallic losses with varying temperatures is; 80 °C > 60 °C > 70 °C. Surprisingly, bimetallic catalysts endured higher loses of iron and copper at 60 °C when compared with the loses at 70 °C. These results clearly indicate that the bimetallic catalysts manifest higher stabilities at optimal reaction temperature i.e. 70 °C due to better and continuous redox reactions between the two metals. On the other hand, the solvent forces would increase with increasing temperature, making the catalysts more susceptible for metallic leaching. It has also been observed that the catalysts with proportionate amounts of copper and iron i.e. 5Cu/5Fe and 2.5Cu/2.5Fe are less prone to leaching compared with other catalysts having disproportionate amounts of copper and iron.

7.3.6.Recycling of the catalyst

The recyclable nature of the catalyst without losing activity is one of the most important aspect for a heterogenous catalyst. The bimetallic catalysts were recovered and reused without any modification or post treatment and results are presented in Figure 7.8.

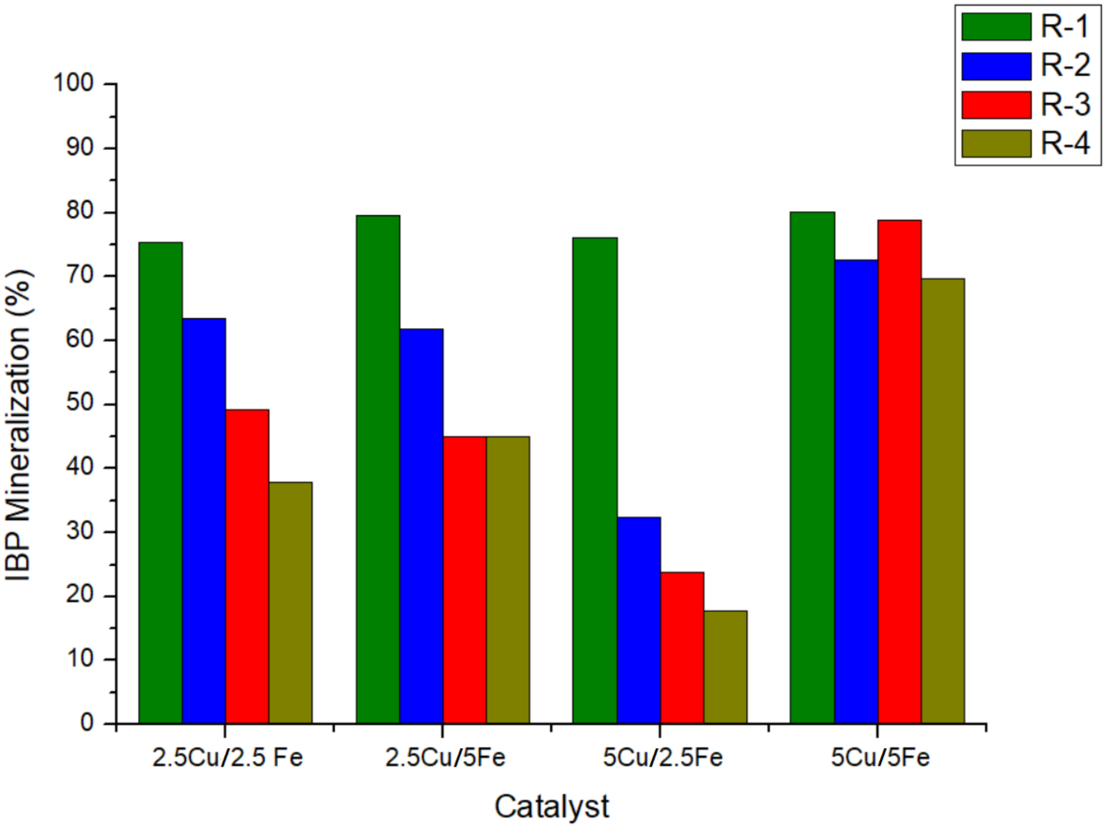

Figure 7.8: Effect of recycling on the IBP mineralization by bimetallic catalysts (reaction condition: pH 4 , catalyst dose – 200 mg/L, H_2O_2 dose(3%) – 30ml/L, temperature – 70 °C and reaction time - 150 minutes)

Since metallic leaching has a direct impact on the catalyst activity in the following cycles this behavior has been investigated and the results are outlined in Table 7.6. The freshly employed 2.5Cu/2.5Fe mineralized 75% IBP and the ibuprofen abatements substantially and gradually declined to 63, 49 and 38% in the 2nd, 3rd and 4th application of the catalyst, respectively. Similar results have been observed with 2.5Cu/5Fe and 45% IBP is removed in the 4th employment. A different situation was found for 5Cu/2.5Fe catalyst that showed a dramatically reduction of the degradation capacity, from 76 to 17% when the catalyst is reused in the 4th cycle. On the contrary, the catalytic activity of 5Cu/5Fe it is not dramatically affected by several recycles, indeed the IBP removal shift from 80 % in the first cycle to 72, 78and 70% respectively in the 2nd, 3rd, and 4th cycles. These results suggest that while in the first cycle all the bimetallic catalysts show similar IBP abatement (70-75%), after recycling, 5Cu/5Fe appears to be the more stable material with a ibuprofen degradation in the range 70-80%.

For all the materials, the metal loses resulted to be more important in the first use of the catalyst and they are reduced in the following cycles.

5Cu/5Fe has equal loadings of iron and copper and all the metal sites are acting through bimetallic redox reactions achieving very high activity. Moreover, only those iron and copper sites that are loosely bonded to the support are lost from 5Cu/5Fe in the 1st employment, indeed these loses became negligible in the following cycles and the activity has remained very high.

Table 7.6: Metallic leaching from bimetallic catalysts in each cycle (reaction condition: pH 4, catalyst dose – 200 mg/L, H_2O_2 dose(3%) – 30ml/L, temperature – 70 °C and reaction time – 150 minutes)

Catalyst	**R-1 (Fresh catalyst)**				**R-2**				**R-3**				**R-4**			
	Cu loss (%)	**Cu loss (mg)**	**Fe loss (%)**	**Fe loss (mg)**	**Cu loss (%)**	**Cu loss (mg)**	**Fe loss (%)**	**Fe loss (mg)**	**Cu loss (%)**	**Cu loss (mg)**	**Fe loss (%)**	**Fe loss (mg)**	**Cu loss (%)**	**Cu loss (mg)**	**Fe loss (%)**	**Fe loss (mg)**
2.5Cu/2.5Fe	6.75	0.27	3	0.15	1.25	0.05	9	0.45	0.75	0.03	5.2	0.26	1	0.04	3.4	0.17
2.5Cu/5Fe	17.6	0.88	2.2	0.11	1.85	0.06	3	0.3	0.92	0.03	2.8	0.28	1.23	0.04	3.5	0.35
5Cu/2.5Fe	7.2	0.72	2.4	0.12	1	0.1	8.8	0.44	0.4	0.04	5	0.25	0.3	0.03	2.6	0.13
5Cu/5Fe	4.9	0.49	3.4	0.34	1.11	0.11	2.9	0.29	1.6	0.16	1.4	0.14	0.9	0.09	2.6	0.26

7.4. Conclusion

This study highlighted the promising activities of a series of Cu-Fe/ZrO_2 bimetallic catalysts for ibuprofen degradation in heterogeneous Fenton process. The developed catalysts exhibited maximum IBP mineralization through a relatively wider window of pH 3-4, eliminating the typical constraint associated with monometallic catalysts. The catalytic activity is strictly correlated to the copper to iron ratio. This is a very important result because finding the right composition of the two metals in the bimetallic catalyst is not only critical to achieve better catalytic activities but is equally important to maintain their stabilities. It has been observed that 5Cu/5Cu exhibited very high and stable activities in several cycles with minimal inputs of chemicals (catalyst and H_2O_2 dose) and energy (i.e. temperature).

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Chapter-8

Application of iron slag as a heterogeneous Fenton like catalyst for the treatment of landfill leachate, a step towards sustainable circular economy

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Abstract

Sustainable industrial processes are essential for better economic growths and for the conservation of the environment. In this study we have employed iron slag as a heterogeneous Fenton like catalyst for the treatment of landfill leachate to implement the concept of “sustainable circular economy”. The textural, morphological, and elemental characteristics of iron slag are observed using standard techniques. Iron slag mainly contains iron in the form of various metal oxides. We found that Fenton like process is optimal when 1g/L of iron slag and 40 ml/L of oxidant is used at pH 3. Experimental results reveal that the optimized Fenton like oxidation process is able to remove 75% of the organics from the leachate. Our study highlighted that iron slag is a very promising material as a heterogeneous Fenton like catalyst for the treatment of heavily polluted wastewater streams. These results are extremely important from a circular economy perspective, because solid waste (iron slag) that is produced in huge quantities can be effectively used as a catalyst in a highly polluted liquid waste treatment process.

Keywords

Iron slag, Landfill leachate, Fenton like oxidation, Water treatment, waste minimization

8.1. Introduction

The large amounts of non-biodegradable and non-recyclable solid waste end up in landfills worldwide every year [1]. However, landfills produce large volumes of leachate when rainwater runs through these sites. The characteristics of leachate may vary depending upon the leachate age, landfill site, solid waste, and climate [2, 3]. Landfill leachate is a very complex liquid waste mainly consisting of refractory organics, heavy metals, ammoniacal nitrogen and chlorides [4-6]. Discharge of untreated landfill leachate may cause serious environmental pollution of soil and water bodies [7, 8]. Therefore, stringent legislation prohibit the direct discharge of leachate either to the sewage treatment plant or to the environment and a rigorous treatment of leachate is mandatory to meet the environmental guidelines [2, 5, 9].

Biological treatment of landfill leachate would be an ideal process considering its simplicity and economic feasibility. However, the biological processes can only treat biodegradable fraction of organics in the leachate which is negligible and ultimately making these processes unfit for its treatment [10-12]. On the other hand, physical processes merely offer separation of the pollutants and afterwards a highly concentrated polluted stream must be dealt with, giving rise to another environmental hazard [13, 14]. In last few decades, advanced oxidation processes (AOPs) have gain enormous acceptability among the research community for the treatment of liquid wastes due to their ability to mineralize of organics and to enhance the biodegradability of treated liquid wastes [15]. All AOPs are essentially based on a core mechanism of organic abatement through generation and utilization of hydroxyl radicals. In the last decades Fenton reaction employing Fe(II) as catalyst along with an oxidant, has gain special attention due to high process efficiency, simplicity and non-toxic reagents [5, 15-17]. However, there are some unavoidable limitations of this process such as severe acidic conditions and generation of large volumes of iron sludge which eventually needs to be separated from liquid and finally be disposed, creating another environmental problem [18, 19].

In order to mitigate the processing constraints of homogeneous Fenton reaction, heterogenous Fenton like process harnessing Fe(III) or other transition metals as catalyst has successfully been employed for the treatment of a range of liquid wastes [20-31]. Fenton like process is better than the traditional Fenton reaction but preparation of heterogenous catalysts requires additional resources and effort [32, 33]. Moreover, overall cost for the treatment of liquid waste also increases, making the process less feasible. Furthermore, during the Fenton like process, catalysts may get deactivated, poisoned and lose activity due to metallic leaching. From sustainability point of view, it is critical that such materials are readily available, cost effective and reduce the overall environmental stress [34].

Iron slag is a solid waste material produced during the steel making process [35]. Every year, millions of tons of iron slag is produced and only part of it, manages to find its way to industrial applications such as cement production in the form of "Argillaceous Material" [36]. Sometimes, iron slag is also used in soil to enhance the soil fertility. However, disposal of large volumes of metallic solid waste may disturb the environmental balance of soil and groundwater. Since, iron slag is rich in iron content and therefore, can be employed as a heterogeneous catalyst for the treatment of liquid wastes. This concept of employing solid waste for the treatment of liquid waste is very important for achieving the goals of sustainable growth and waste minimization. In recent years, iron slag has been mainly used for the removal of heavy metals [37], phosphate [38], dyes [39] and model pollutants from wastewaters [40].

In light of our knowledge, this study is the first attempt to utilize iron slag for the treatment of landfill leachate. In this research we have investigated the catalytic ability of iron slag as a heterogenous Fenton like catalyst for the treatment of a complex liquid waste such as leachate under variable conditions of iron slag dose, pH, temperature, and oxidant dose. Moreover, iron slag is also recycled to monitor the catalytic activity in the following employment.

8.2. Experimental

8.2.1. Materials

Iron slag used in this study as Fenton like catalyst is produced in a steelworks in the Friuli-Venezia Giulia region (North-East of Italy); the leachate used in this research was drawn from an aged landfill near the city of Udine (northeast Italy). All the chemicals used in the present study, 30% H_2O_2, NaOH and H_2SO_4 are from Sigma Aldrich.

8.2.2. Methods

8.2.2.1. Textural and morphological characterization

Textural characteristics of iron slag were measured according to the BET method by nitrogen adsorption at −196 °C, using a Tristar 3000 gas adsorption analyser (Micromeritics). Structural features were characterized by X-ray diffraction (XRD). XRD profiles were recorded on a Philips X'Pert diffractometer (equipped with a real time multiple strip detector) operated at 40 kV and 40 mA using Ni-filtered Cu-Kα radiation. Spectra were collected using a step size of 0.02° and a counting time of 20 s per angular abscissa in the range 20°-80°. The Philips X'Pert HighScore software was used for phase identification.

The powders morphology has been observed by Field Emission Scanning Electron Microscopy (JEOL model JSM-7610FPlus). The specimens have been coated by a thin gold layer by spattering prior the observations. The observations have been performed in secondary electron mode using an acceleration voltage of 5KeV. The chemical composition was determined by Energy Dispersive X-ray Spectroscopy- EDXS (Oxford Instruments X-Max 20) analysis using a Quant Standardization of 5keV.

8.2.2.2. Adsorption tests

First iron slag is grinded and sieved into four different particle sizes namely raw, 350, 200 and 100 microns. Second, iron slag was added into the landfill leachate, stirred for 2 hours at room temperature as well as at 70 °C to observe the adsorption behaviors. Moreover, iron slag was washed with distilled water and acidic distilled water to monitor the change in TOC values.

8.2.2.3. Fenton like oxidation

The suspended solids from landfill leachate were removed by centrifugation at 5000 rpm for an hour using Eppendorf Centrifuge 5804 R, followed by filtration through a 0.45 µm membrane filter. The pH of the leachate samples was adjusted by the addition of NaOH / H_2SO_4 (Sigma Aldrich), and an optimum pH for maximum catalytic activity was experimentally determined before conducting the standard experiments. The leachate samples (100 ml) loaded with 1g/L of iron slag with variable particle sizes were heated at 70 ˚C under continuous stirring conditions of 500 RPM, using an Omni multistage reaction station with a provision of reflux. Finally, 30 ml/L H_2O_2 was added into the reaction system and the Fenton like oxidation reaction was carried out for 150 minutes and samples were collected after every 30 minutes of time interval to observe the catalytic activity dependence over time. Further, the oxidation process was optimized evaluating the effect of catalyst dose (0.1 - 2 g/L), hydrogen peroxide (10 - 60 ml/L), temperature (20 – 70 °C), iron slag particle size (50 – 350 µm) and pH (2 - 9). Catalytic activity of recycled iron slag was also investigated, and the percentage of residual hydrogen peroxide was determined in each cycle. The treated samples were centrifuged at 5000 rpm using Eppendorf Centrifuge 5804 R for 10 minutes and the supernatant solutions were collected in vials for TOC analysis.

8.2.2.4.Microwave irradiated acid solubilization of iron slag

First, 0.3 g of iron slag in triplicates was directly transferred into Teflon tubes followed by the addition of 8ml of HNO_3 and 2ml of HCl. The samples were heated at 185 °C using microwave irradiation for 1 h. The samples were left to cool and later transferred to a glass flask and volume was increased to 20 ml by the addition of ultrapure water. The samples were left to stabilize for 24 h. The stabilized samples were filtered through 0.20 µm PTFE filters and were diluted 1:10 using ultrapure water.

8.2.2.5. TOC analysis

The organic content of the raw leachate and treated samples was analyzed using a TOC-VCPN, Shimadzu analyzer (V-Series) with an auto sampler. First, the standard solutions with known concentrations of 2.5, 5.0, 10.0, and 20.0 mg C/l were prepared using potassium hydrogen phthalate stock solution. A calibration curve was obtained by analyzing the standard samples, and after each analysis the injection syringe was auto sparged with 2M HCl. The samples were analyzed without dilution and using the same calibration curve to determine TDOC present in each sample. Several experiments were also carried out to verify the reproducibility of our activity measurements and the errors resulted to be within 3%.

8.2.2.6. ICP analysis

The metallic composition of iron slag and concentration of heavy metals in landfill leachate was determined with US EPA 3051 method using Inductivity Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES vista pro.) First, a calibration curve was obtained by using an ICP 23-element standard solutions which were prepared in 5% HNO_3. Yttrium (Y) was used as an internal standard. The method detection limit (MDL) was calculated as 3 s/m.

Where;

s = Standard deviation of 10 replicate blanks

m = slope of the calibration curve for each element

8.3. Results and discussion

8.3.1. Characterization of iron slag

Surface area measurements on the different fractions (100, 200, 350 µm and raw sample) evidenced that iron slag is a non-porous material; for all the fractions an almost zero surface area was found, in agreement with SEM analysis. The structural features of the iron slag (Figure 8.1) were analyzed by powder X-ray diffraction (XRD). Although the XRD measurements are very disturbed due to the fluorescence due to the high amount of iron in the samples, all the fraction of the materials shows the simultaneous presence of wuestite (FeO, main reflection at 41,7°), hematite (Fe_2O_3, main reflection at 33,2°) and magnetite (Fe_3O_4, main reflection at 35,2°). Reflections are more intense for the fraction with lower particle size, probably due to the higher number of particles per unit of weight

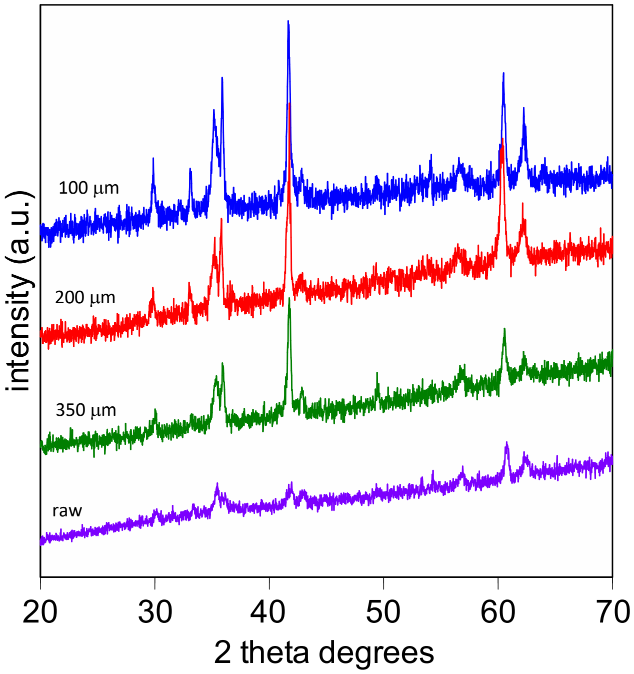

Figure 8.1: XRD profiles of the investigate samples

The SEM analysis of raw iron slag depicted a rather homogeneous morphology with the presence of little and scattered solid clusters on the solid surface. On the contrary, the iron slag after application in Fenton like oxidation revealed a more heterogenous morphology with numerous cavities on the solid surface indicating that part of the solid composite has been lost during the oxidation reaction Figure 8.2. The appearance of cavities after Fenton like oxidation is probably due to the loss of aluminum, magnesium, and calcium silicates [40].

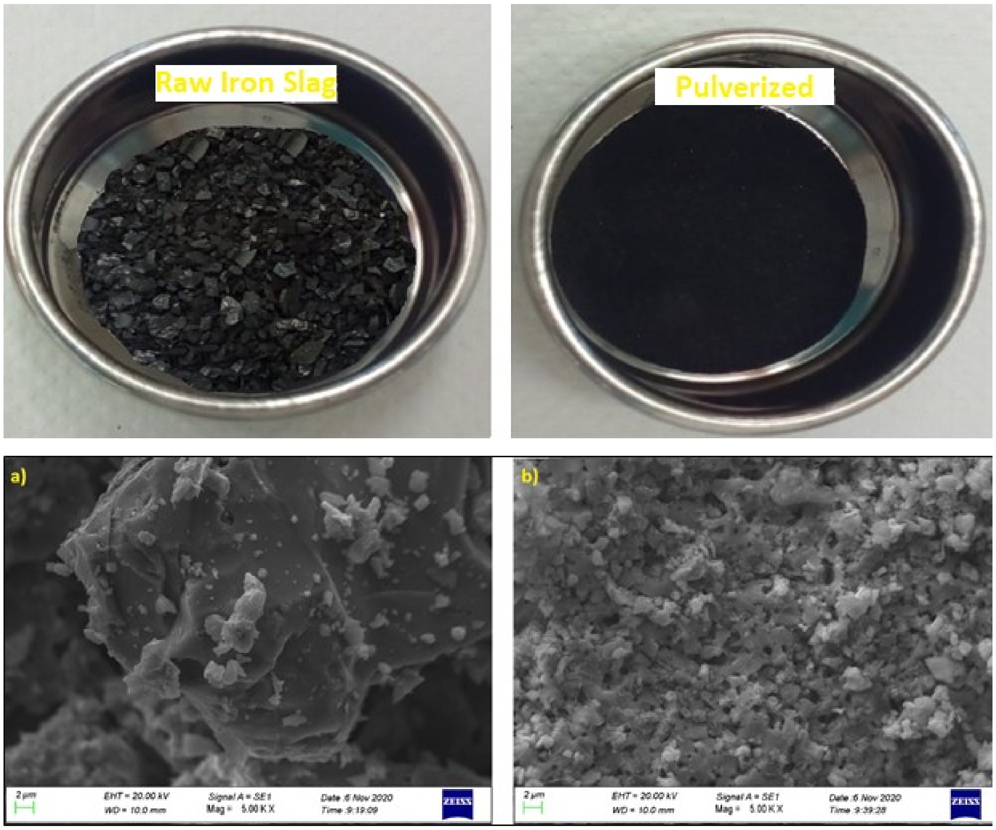

Figure 8.2: Raw, pulverized, and SEM micrographs (5k x magnification) of iron slag (a) before (b) after application in Fenton like oxidation

The elemental composition of iron slag was determined by EDX analysis and is shown in Table 8.1. The metallic composition of iron slag has been obtained through acid solubilization followed by microwave irradiation and finally ICP analysis of the extract. Fe and Mn are the main components of the iron slag (Table 8.2).

Table 8.1: Elemental composition of iron slag measured through EDX

Element	Fe (%)	Mn (%)	C (%)	O (%)	Si (%)	Al (%)	Ca (%)	Mg (%)
Before	12.8-68	2.6-13.8	3-22.2	3.2-38.8	0-3.5	0-1.7	0-0.8	0-1.7
After	14.7	13.8	---	14.7	0.5	0	0	0

Table 8.2: Metallic composition of iron slag obtained by microwave irradiated acid solubilization

Element	Fe (%)	Mn(%)	Mg(%)	Cr(%)	Ni(%)	K(%)	Cu(%)	Ca(%)	Al(%)	Co(%)
Max	81.20	17.16	2.13	1.6	0.31	0.18	0.29	0.28	0.08	0.03
Min	79.82	15.59	0.27	0.7	0.22	0.02	0.14	0.08	0.04	0.02

8.3.2. Effect of adsorption

Preliminary blank tests were also carried out. Landfill leachate conversion was negligible (9 % of TDOC abatement) over iron slag in the absence of catalyst when H_2O_2 was used at 70 °C. In the absence of the catalyst, the Fenton reaction cannot take place and the TOC abatement is definitely low. This is in agreement with the metallic composition of landfill leachate (obtained by ICP analysis) that evidenced a very low amount of Iron (Table 8.3). This amount is not enough to catalyse the homogeneous reaction and in order to degrade the organic loading, a heterogeneous catalyst is need.

Table 8.3: Metallic composition of leachate before and after treatment

Leachate	Fe (mg/L)	Mn (mg/L)	Mg (mg/L)	Cr (mg/L)	Ni (mg/L)	K (mg/L)	Cu (mg/L)	Ca (mg/L)
Pure	1.93	0.05	53.2	0.55	0.3	1379	0.06	33.3

It is critically important that the iron slag has some adsorption capacity so that the Fenton like oxidation may take place at the solid interface. However, the dissolved matter must not possess high adsorption capacity because it may block active sites through which oxidation of organics is carried out. The adsorption capacity of iron slag for TOC removal from landfill leachate is investigated at 25 and 70 °C by employing four different particle sizes namely, raw, 100, 200, and 350 microns and results are presented in Figure 8.3.

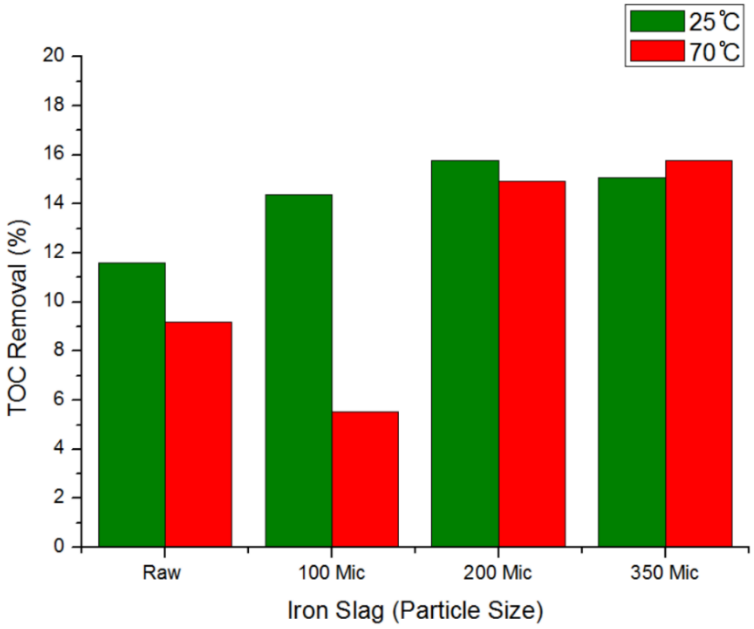

Figure 8.3: Effect of particle size and temperature over adsorptive removal of TOC

It is evident that regardless of the temperature, 25 or 70 °C, the variation in the particle size slightly impacts the adsorption behavior of iron slag as the TOC removal is almost the same i.e.

in the narrow range of 5-15%. These results indicate that, iron slag has a very little capacity to remove organics through adsorption and TOC is mainly removed through heterogeneous Fenton like oxidation. This behavior is directly related to the very low surface area of the samples.

8.3.4. Effect of iron slag particle size

The size of the iron slag particles can significantly influence the efficacy of the Fenton like oxidation. Therefore, variable particle sizes of iron slag have been employed separately to examine their effect on overall oxidation efficiency and results are presented in Table 8.4. Initially, when iron slag with very fine particle size i.e. 50 µm is used, only 50% of the TOC has been abated. On the contrary, when particle size is doubled i.e 100 µm, the efficacy of the Fenton like oxidation is increased to 75%. When larger particle sizes, from 150 µm to raw iron slag are employed, the organic abatement progressively declined from 67 to 51% respectively.

Table 8.4: Effect of iron slag particle size and catalyst dose on TOC abatement efficiencies (reaction condition: pH 3, catalyst dose – 1 g/L, H_2O_2 dose – 40 ml/L (3%), temperature – 70 °C and reaction time – 150 min)

Particle size (µm)	TOC abatement (%)	Catalyst dose (mg/L)[a]	TOC abatement (%)
50	49.51	0.1	32.86
100	75.08	0.2	41
150	67	0.5	62.82
200	63	0.75	58.6
250	62.5	1	75.08
300	56	1.5	69.9
350	53	1.75	70.33
raw	51.21	2	68.21

[a]: experiments have been carried out over iron slag with particle size of 100 µm.

These results indicate that although in the 50 mm fraction, the number of particles per unit of weight is much higher, there is a tendency to form agglomerates with consequent lower process efficiency [41] Figure 8.4. This agglomeration behavior of the fine particles may also become prominent when the liquid phase imparts wettability to the particles. However, an optimal size distribution of particles, i.e. 100 µm, minimizes the probability of agglomeration, exposing maximum of its active sites (higher number of particles per unit of weight) and thus yielding better catalytic activity. On the other hand, further enlargement of particles may have better suppressed the agglomeration phenomenon, but the number of particle per unit of weight progressively decreases, resulting in continuous decline of the TOC abatements [42].

8.3.5. Effect of iron slag dose

Although, iron slag is an industrial waste and optimization of the catalyst dose is critically important not only to afford maximum process efficacy but also to minimize the overall cost of the Fenton like oxidation. In order to investigate the optimal catalyst loading, variable iron slag doses have been employed for the treatment of landfill leachate and results are illustrated in Table 8.4. It is evident that working with smaller catalyst doses i.e. 0.1 and 0.2 g/L rendered only 32 and 41% of TOC abatements respectively.

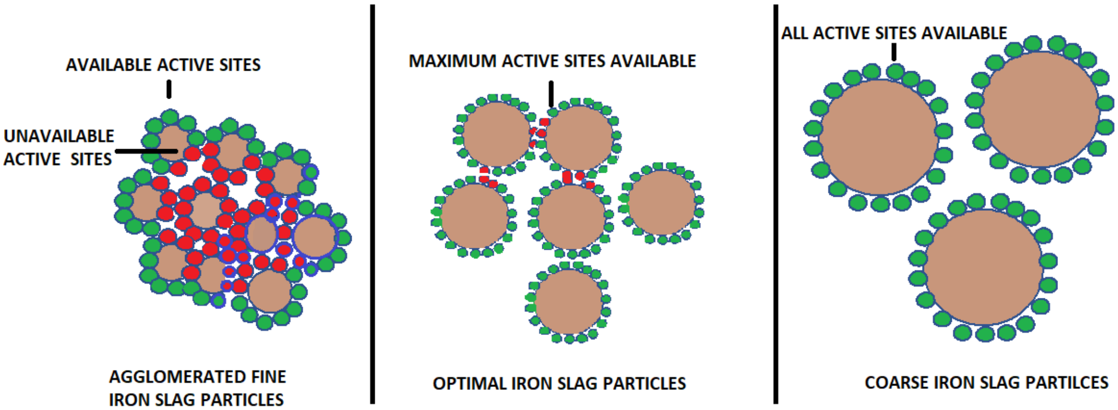

Figure 8.4: Agglomeration behavior of various particle sizes of iron slag

These results indicate that the iron slag loadings are too little to decompose all the oxidant into OH• because there are only few active sites available for OH• generation [43]. Further, when iron slag loadings are further increased until 1 g/L, Fenton like oxidation yielded 75% of TOC reduction. This suggests that it is of fundamental importance working with the optimal H_2O_2/catalyst ratio to achieve higher leachate degradation; i.e. when an optimal ratio is used, the oxidant is converted into useful hydroxyl radicals and thus the highest TOC abatement is achieved. Another reason for the increased catalytic activity with rising catalyst dose is the dual phase reaction because part of the Fe is leached out into the aqueous phase, contributing towards homogeneous Fenton reaction [40]. A further increase in catalyst does not produce an increase in catalytic activity. For doses above 1 g/L a slight decrease in activity is observed due to a scavenging effect of the OH• radicals Figure 8.5 [44, 45].

8.3.6. Effect of pH

An optimal pH is not only necessary to achieve higher catalytic activity in heterogeneous Fenton reaction but also equally important to transform maximum amount of the oxidant into hydroxyl radicals [5]. Moreover, heterogeneous catalysts afford better activities when oxidation reactions are performed at a pH which conforms to the point of zero charge (PZC) of the catalyst [46]. Furthermore, the loss of the active sites from the catalyst surface is also minimal when Fenton like reaction is carried out at optimum pH conditions. In order to monitor the effect of pH on TOC abatement from leachate, iron slag is used at variable pH conditions and the results are presented in Figure 8.6.

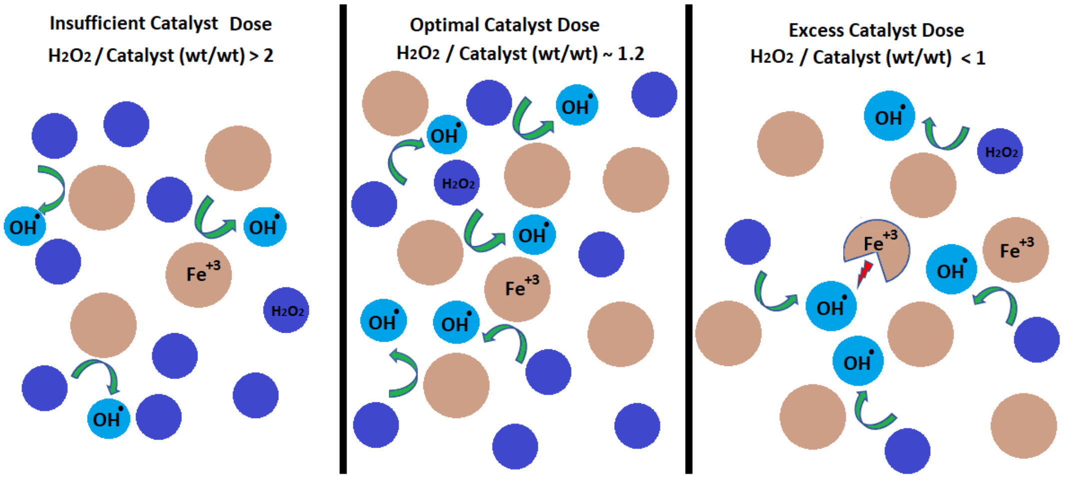

Figure 8.5: Variable iron slag doses and effective utilization of H_2O_2

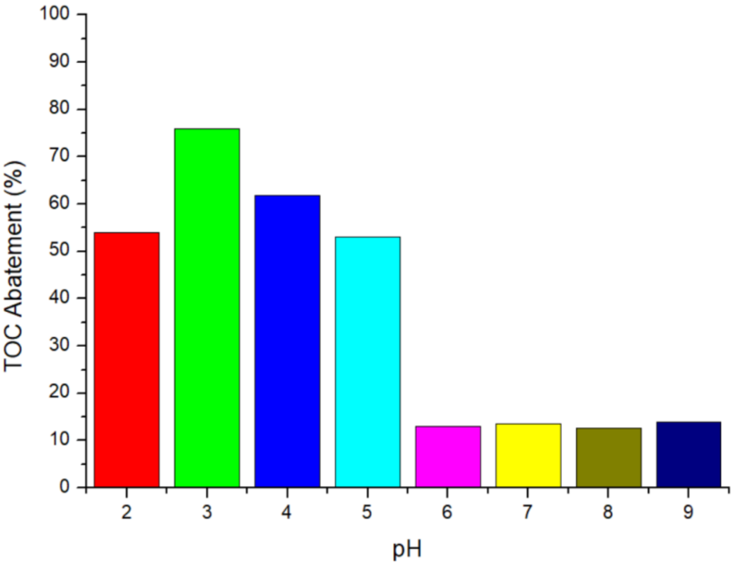

Figure 8.6: Effect of pH on TOC abatement efficiencies (reaction condition: iron slag particle size – 100 µm, catalyst dose - 1 g/L, H_2O_2 dose – 40 ml/L (3%), temperature – 70 °C and reaction time – 150 min)

When Fenton like reaction is performed under very strong acidic conditions of pH 2, only 54% of the TOC has been abated. Further, when the pH of the leachate is adjusted to 3, the TOC removal efficacy is markedly increased to 75% which is in accordance with the previous findings [47, 48]. These results clearly suggest that the rate of OH• generation and the oxidation potential(E) of OH• are optimal at pH 3 and consequently the extent of organic abatement is maximum. On the other hand, very strong acidic conditions may adversely impact the Fenton like oxidation due to a number of reasons such as the suppression of heterogeneous reaction between Fe and H_2O_2, lower rate of OH• generation, generation of oxonium ions instead of OH• and scavenging of generated OH• by H^+ ions [49] as shown in Figure 8.7.

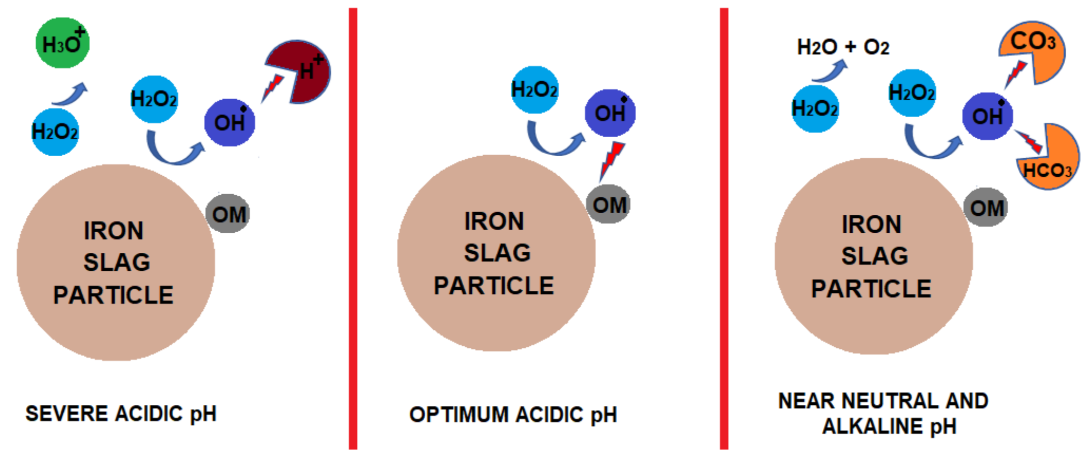

Figure 8.7: Effect of pH on transformation and utilization of oxidant

As the operating pH is shifted towards milder acidic conditions i.e. 4 and 5, the oxidation potency of Fenton process starts to decline and TOC abatements are reduced to 61 and 53%. Again, this can be attributed to the slower rate of OH• generation and reduction in the oxidation potential of OH• because oxidation potential varies from E_0=2.8 to E_{14}=1.95 depending upon the solution pH [50]. However, when near neutral to alkaline conditions i.e. pH 6 to 8 are employed in the Fenton like reaction, the TOC removal dropped sharply to 12-14%. It indicates that Fenton like oxidation is inhibited under neutral and alkaline conditions because the carbonates and bicarbonates in the leachate starts to scavenge the OH• and ultimately the oxidation of organics is hindered [51]. Moreover, the transformation of the oxidant into useful radicals is also diminished because it decomposes into water and oxygen (Figure 8.7).

8.3.7. Effect of oxidant dose

The oxidant is the source of the OH• and an optimum dose is not only critical for the maximum organic abatement but also equally important to minimize the cost of the Fenton like process. To observe the influence of H_2O_2 dose on the organic mineralization, variable oxidant doses have been used keeping rest of the conditions identical and results are presented in Figure8.8. Working with a minimal oxidant dose, i.e. 10 ml/L, a mineralization 46% of the organics from the leachate has been obtained. Further increasing the oxidant dose from 20 to 40 ml/L enhanced the TOC abatement from 50 to 75%, respectively. However, when oxidant dose is increased beyond 40ml/L, the increase in organic degradation is reduced. These results indicate that an increase in the oxidant dose increases the generation of OH• [52] but an excess amount may also enhance the scavenging effect caused by the oxidant itself [53]. Self-scavenging effect, i.e. the reaction between the oxidant and the OH•, produces HO_2• radicals (Eq.2) which have low oxidation potential and ultimately the efficacy of the Fenton like process does not magnify as intended by increasing the oxidant dose [54].

$$H_2O_2 + OH\bullet \longrightarrow HO_2\bullet + H_2O \qquad \text{(Eq.2)}$$

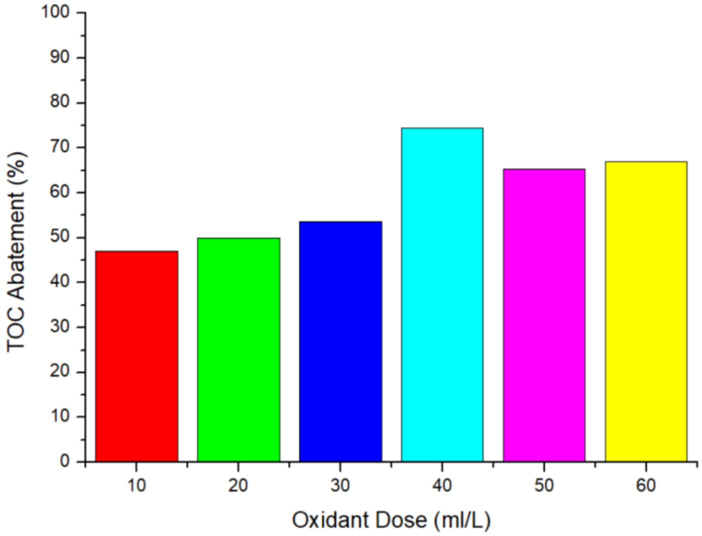

Figure 8.8: Effect of oxidant dose on TOC abatement efficiencies (reaction condition: pH 3, iron slag particle size – 100 µm, catalyst dose – 1 g/L, temperature – 70 °C and reaction time – 150 min)

When the best reaction conditions are used, the reduction of the organic loading in the landfill leachate is very high, as can also be observed by the difference in color before and after the reaction (Figure 8.9).

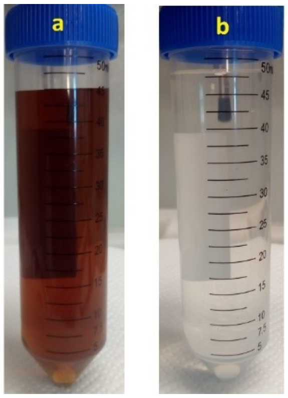

Figure 8.9: Landfill leachate before(a) and after (b) Fenton like oxidation employing iron slag

The reaction is very fast and occurs in the first 30 minutes with a TOC reduction of more than 75%, after which the reaction remains stable Figure 8.10.

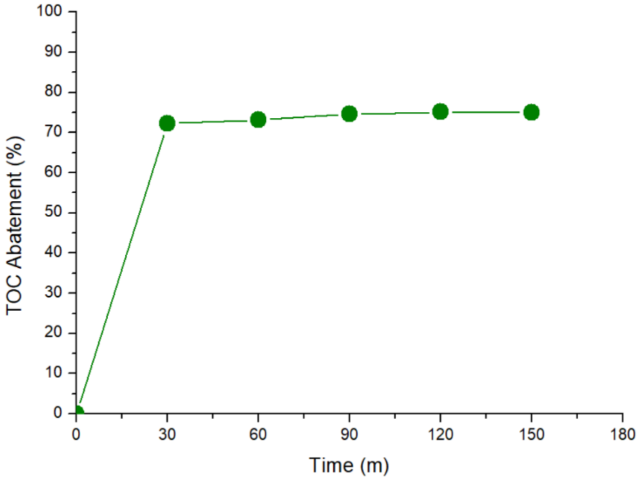

Figure 8.10: TOC abatement as a function of time (reaction condition: pH 3, iron slag particle size – 100 µm, catalyst dose – 1 g/L, H_2O_2 dose – 40 ml/L (3%) and temperature – 70 °C).

8.3.8. Effect of temperature

Generally, a minimum amount of activation energy is always required in Fenton like oxidation reactions to produce the oxidizing species i.e. OH• which in turn attack the organics in leachate. To observe the effect of temperature on the extent of Fenton like oxidation, has carried out at several temperatures and results are outlined in Figure 8.11.

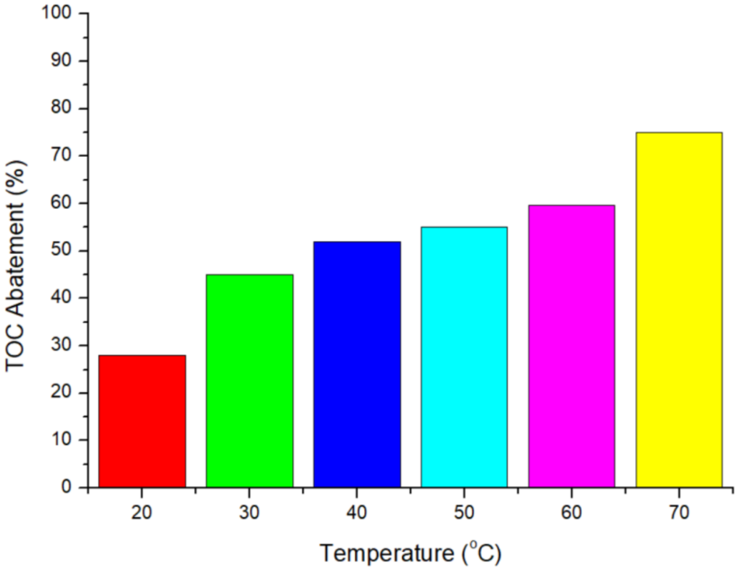

Figure 8.11: Effect of temperature on TOC abatement efficiencies (reaction condition: pH 3, iron slag particle size – 100 µm, catalyst dose – 1 g/L, H_2O_2 dose – 40 ml/L (3%) and reaction time – 150 min)

When leachate is treated at 20 °C, only 28% of the organics are mineralized. A progressively increase in process efficacies has been observed while stepwise increasing the reaction temperatures from 30 to 70 °C. These results indicate that when higher reaction temperature is employed, higher amount of energy is available for the transformation of oxidant into oxidizing species [55, 56] and thus a higher abatement of organics is obtained [57] which is in agreement with the Arrhenius law [58].

8.3.9. Iron slag recycling

Although, iron slag is a solid waste, but its recycling is critically important for several reasons such as waste minimization, controlling the transportation costs and for overall sustainability of the Fenton like process. To better understand the recyclable nature of the iron slag, it is recovered and reused without modification in subsequent Fenton like oxidation reactions and results are presented in the form TOC abatement and residual H_2O_2 in Figure 8.12.

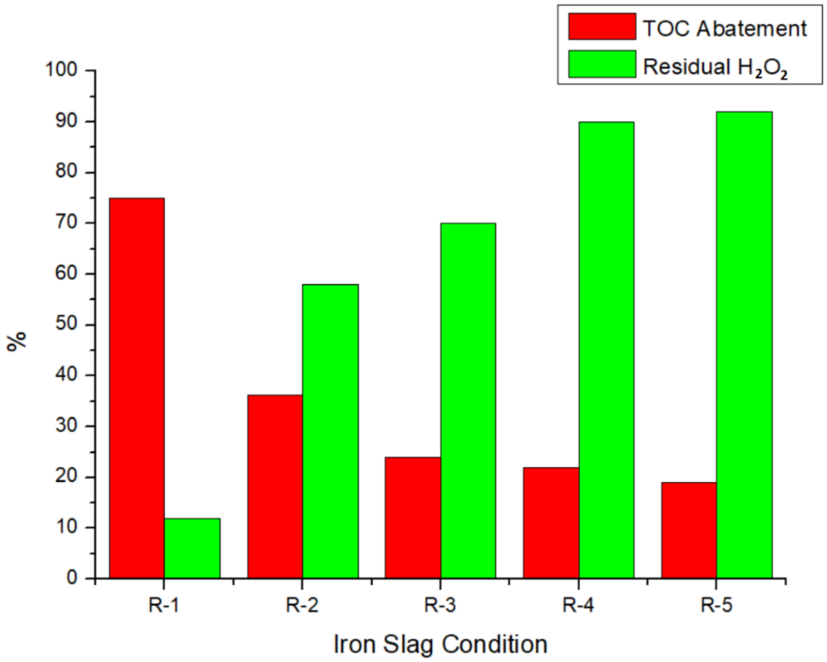

Figure 8.12: Effect of iron slag recycling on TOC abatement efficiencies and H_2O_2 utilization (reaction condition: pH 3, iron slag particle size –100 µm, catalyst dose – 1 g/L, H_2O_2 dose – 40 ml/L (3%), temperature – 70 °C and reaction time – 150 min).

It has been noticed that the freshly employed iron slag afforded maximum TOC abatement of 75%. Moreover, only 12% of the employed H_2O_2 was found at the end of the reaction. The TOC abatement sharply dropped to 36% in the 2nd application of the iron slag and 58% of the oxidant remained intact. Similarly, the catalytic ability of iron slag was progressively decreased after every recycle and in the 5th application only 19% of the TOC was removed while 92% of the H_2O_2 persisted at the end of Fenton like oxidation. These results clearly suggest that fresh iron slag is more active in the formation of OH• radicals, yielding higher process efficacy. The loss of activity after use is closely related to the morphology change observed with SEM analysis and the progressively loss of iron. As noted above, after reaction the iron slag showed a more heterogeneous morphology with numerous cavities on the solid surface (Figure 8.2) indicating that part of the solid composite has been lost during the oxidation reaction (iron leaching). In addition, it is important to consider also the tendency of iron catalysts to form stable complexes with the degradation products [59, 60] and the mere deposition of organics and inorganics onto the iron slag particles, that can hinder its catalytic ability Figure 8.13. Since the number of available active sites keep on decreasing in every cycle, the degree to which H_2O_2 can form OH• also decreases, and ultimately reducing the efficiency of the Fenton like process.

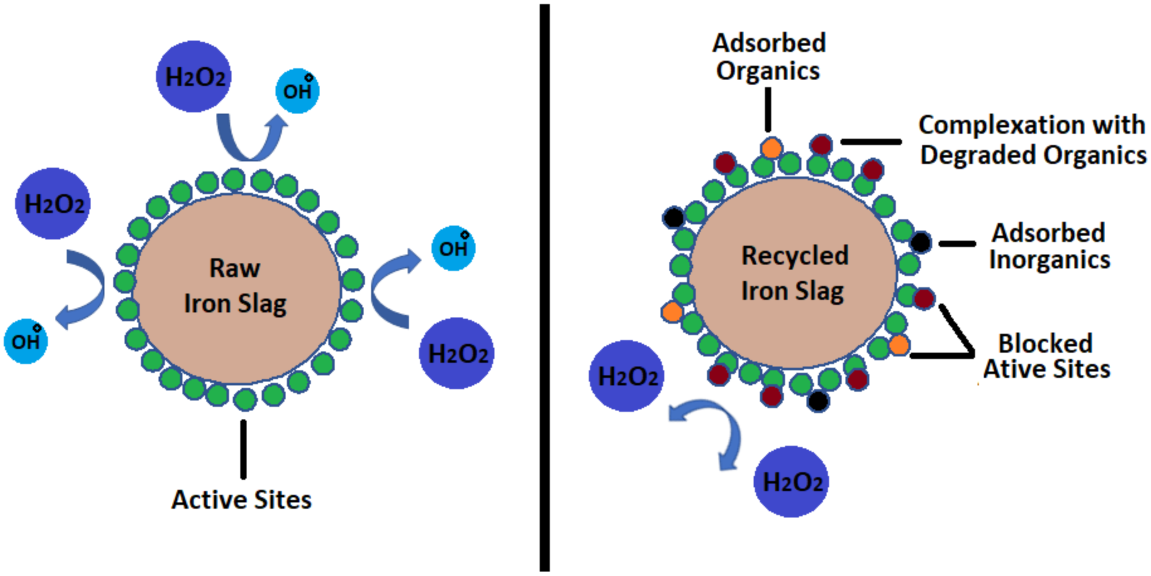

Figure 8.13: Catalytic inactivity of iron slag after recycling

8.4. Conclusion

This study has shown very promising results regarding the employment of iron slag as heterogeneous Fenton like catalyst for the treatment of an extremely polluted liquid waste. The oxidation process over iron slag is optimal when oxidant and catalyst are used in 1.2:1 ratio under acidic conditions (pH 3) and 70 °C of temperature. At optimum conditions iron slag successfully removed nearly 70% of the recalcitrant organic loading from landfill leachate.

These results are extremely important from a circular economy perspective, because solid waste (iron slag) that is produced in huge quantities can be effectively used as a catalyst in a highly polluted liquid waste treatment process. Precisely in the light of this vision of reusing a waste, deactivation after a single use is not to be seen as a problem; in fact, the available quantities of iron slag are extremely high and the fact that their cost is zero, being a waste, makes the process advantageous even without recovery and subsequent reuse. These results highlight the oxidation capacity of iron slag for the abatement of organics and opens new prospects for the low-cost treatment of diverse wastewater streams.

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Chapter-9

Conclusions

The main objective of this PhD program was to develop sustainable advanced oxidation processes (AOPs) which have the potential to completely abate a wide range of persistent organics, present in complex liquid wastes. Among the AOPs, Fenton like oxidation employing heterogeneous catalysts has several advantages over other processes due to operational and economic feasibility. In this thesis, iron and copper-based catalysts supported over zirconium have been developed. These materials are innovative and promising catalysts for their application in Fenton like process because they have the capacity to completely mineralize the organic pollutants into water and carbon dioxide. This aspect of our developed Fenton like process is very important because complete abatement of organics from aqueous phase ensures the reduction in environmental stress on the receiving bodies. This is also critical because a partial degradation of organics may trigger the release of toxic metabolites into the aquatic environment, endangering the well-being of the end users.

The newly developed heterogeneous Fenton process is first examined by treating synthetic aqueous solution of a model pollutant ibuprofen which has a fairly large, stable, and complex molecular structure. This practice is of paramount importance because it enabled us to monitor the extent to which Fenton process can oxidize the pollutant. It also aided in revealing and exploiting the operating parameters through which efficacy of the process is increased. Furthermore, the optimized Fenton process was employed for the treatment of a very complex landfill leachate and very promising results were obtained indicating that the developed process can be used for the treatment of other liquid streams. Moreover, the proton magnetic resonance spectroscopy has been used for the first time to qualitatively monitor the shifting nature of organic compounds when subjected to Fenton like oxidation and this analytical technique can be very beneficial for the analysis of the oxidation pathways of organics during Fenton process.

The intrinsic nature of the heterogeneous Fenton relies mainly on the nature of the catalyst and the correlating pH while extrinsic behavior of the process is controlled through operating conditions such as catalyst dose, temperature, and H_2O_2 dose. In this work, we developed numerous heterogeneous Fenton like processes by changing the intrinsic nature of the catalyst i.e. preparing the catalysts with variable loadings of iron, copper, and iron/copper. It has been observed that the favorable operating pH for iron-based catalysts is 3, for copper-based materials is 5 and bimetallic catalysts achieve optimum activities through a relatively wider pH range (3 - 4). Moreover, metal leaching is not only monitored during the recycling of the catalysts but also with the variation in each operating parameter. The results indicate that the copper-based monometallic catalysts experience higher metal loses compared with iron-based monometallic catalysts. On the other hand, the metal leaching of both iron and copper is fairly reduced for bimetallic catalysts which suggest that the introduction of two types of metals impart higher stability to the catalysts in aqueous phase environments. However, it is worth to mention that all types of catalysts experience higher metal losses if the pH is lower than the optimal one. Moreover, excess catalyst dosses also intensify the metal leaching and therefore, these parameters should be precisely controlled and monitored to maintain the sustainability of developed Fenton Process.

Finally, instead of merely relying on the synthetic catalysts, it is important to look for readily available solids and solid wastes which can catalyze the Fenton process. Iron slag was selected as a heterogeneous catalyst because it contains a very high fraction of iron content revealed by EDX, ICP and a number of iron species revealed through XRD analysis, which can conveniently generate free radicals from the oxidant and in turn degrade the pollutants. The oxidation of landfill leachate using iron slag showed very high organic removals, an immensely useful insight regarding the catalytic ability of a solid waste which is abundantly available and can find its way for the treatment of liquid wastes without any prior treatment. This breakthrough can help us to move forward to achieve the goal of a circular economy and sustainable environment. Moreover, it can also lay the foundation for other researchers to seek for similar materials with the prospects of application in heterogeneous Fenton process.

The commulative output of this PhD program is very comprehensive because the program was not only focussed on the development of new heterogeneous Fenton like processes employing synthetic catalysts but also encompassed the utilization of waste solid materials as heterogeneous catalysts. In future, our objective would be to devise mechanisms to scale up the heterogeneous Fenton processes keeping in view of the nature of catalysts i.e. synthetic or waste solid. The synthetic catalysts are planned to be employed in Fenton process in a way that minimizes the processing and economic constraints. The impellers with their blades loaded with the developed catalysts are envisioned to be employed in pilot scale heterogeneous Fenton like process and the efficacy of the process would be monitored along with the investiagtion of the process parameters. However, scaling up such processes and precisely controlling all the parameters involed, require resources and time. Therefore, such efforts are part of our future research plans.

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