



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

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Abstract

Innovations in water technology are needed to solve challenges of climate change, resource shortages, emerging contaminants, urbanization, sustainable development and demographic changes. In particular, conventional techniques of wastewater treatment are limited by the presence of poorly biodegradable organic matter. Alternatively, recent Fenton, Fenton-like and hybrid processes appear successful for cleaning of different types of liquid wastewaters. Here, we review the application of metallic catalyst-H₂O₂ systems in the heterogeneous Fenton process. Each metallic catalyst-H₂O₂ system has unique redox properties due to metal oxidation state. Solution pH is a major influencing factor. Catalysts made of iron and cerium form stable complexes with oxidation products and H₂O₂, thus resulting in reduced activities. Copper forms transitory complexes with oxidation products, but copper catalytic activity is restored during the reaction. Silver and manganese do not form complexes. The catalyst performance for degradation and mineralization decreases in the order: manganese, copper, iron, silver, cerium, yet the easiness of practical application decreases in the order: copper, manganese, iron, silver, cerium.

Keywords Fenton process · Heterogeneous · Catalyst · H₂O₂ · Oxidation · Wastewater treatment · AOP

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 ecosystem (Kolpin et al. 2002). 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 (Bokare and Choi 2014). 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 (Gavrilescu et al. 2015). Conventional treatment processes (sedimentation and biological treatment) are not capable of removing these micropollutants, and thus innovative technologies are required (Chan et al. 2009; Glassmeyer et al. 2005; Gogate and Pandit 2004; Kasprzyk-Hordern et al. 2008; Kim et al. 2007; Metz and Ingold 2014; Quinn et al. 2008).

Advanced oxidation processes (AOPs), have been proven effective when it comes to deal with persistent organic pollutants (Andreozzi et al. 1999; Bello and Raman 2019; Boczkaj and Fernandes 2017; Glaze and Kang 1989; Mousset and Dionysiou 2020; Rueda Márquez et al. 2018; Salimi et al. 2017; Wang and Zhuan 2020). These processes generate temporary species, fundamentally hydroxyl radicals (OH[•]) which attack the targeted pollutants and oxidize them (Fakhru'l-Razi et al. 2009; Ioannou et al. 2015; Shahidi et al.

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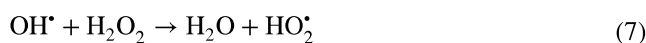
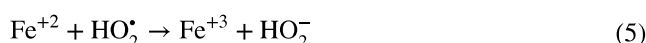
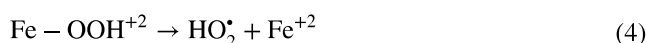
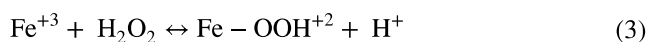
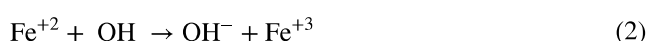
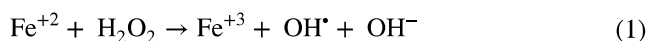
2015; Tiya-Djowe et al. 2016). The key features which make these processes superior to other processes are their ability to be operated near ambient conditions, nonselective nature of OH^\bullet radicals and conversion of pollutants into nontoxic products such as CO_2 and H_2O (Neyens and Baeyens 2003). Advanced oxidation processes can also be integrated with existing biological processes as a pretreatment strategy for the treatment of heavily polluted wastewater streams (Oller et al. 2011).

There are several types of advanced oxidation processes 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 (Comminellis et al. 2008; John and Shaik 2015; Lahkimi et al. 2007; Paramo-Vargas et al. 2016; Rayaroth et al. 2016). Advanced oxidation processes 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 discuss Fenton reaction and finally focus on heterogeneous Fenton-like reaction (Fig. 1) because the classical Fenton reaction which is currently in place for wastewater treatment lacks processing and economic sustainability.

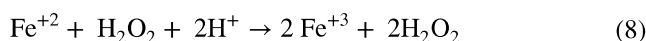
Homogeneous Fenton reaction

The Fenton reaction was developed by Henry John Horstman Fenton in 1890 (Barbusiński 2009; Fenton 1894). 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 (Goldstein et al. 1993; Jain et al. 2018; Navalon et al. 2011; Neyens and Baeyens 2003). Although the Fenton's reagent was discovered 100 years ago, it was not applied for

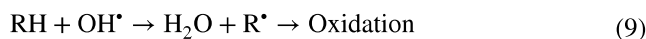
the abatement of toxic organic pollutants until 1960 (Huang et al. 1993). It is critically important to comprehend the mechanism of Fenton reaction where ferrous (II) iron is mixed with H_2O_2 , hydroxyl radicals are generated through the following chain initiation (Eq. 1) (Barhoumi et al. 2017) and chain termination (Eq. 2) reactions (Buxton et al. 1988; Rigg et al. 1954). 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 (Walling and Goosen 1973). A series of other reactions involved in the Fenton process are outlined here (Eqs. 4–7) (Feng et al. 2013; Neyens and Baeyens 2003).



Instead of looking into all these complex reactions, Walling (Walling 1975) proposed a simplified version of Fenton reaction (Eq. 8) (Dhakshinamoorthy et al. 2012):



The OH^\bullet reacts with organics and converts them into organic radicals which undergo a series of oxidation reactions to yield secondary and tertiary metabolites (Eq. 9) (Nidheesh 2015; Nidheesh et al. 2013):



Homogeneous Fenton reaction essentially involves three processing steps: dissolution of the catalyst (de la Plata et al. 2010), OH^\bullet radical generation and finally the oxidation of organics (Fig. 2). 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 at near-neutral pH conditions. To improve the efficiency of the process, the pH of the aqueous medium has to be shifted toward 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 (Aziz and Daud 2012; Bautista et al. 2008; Deng

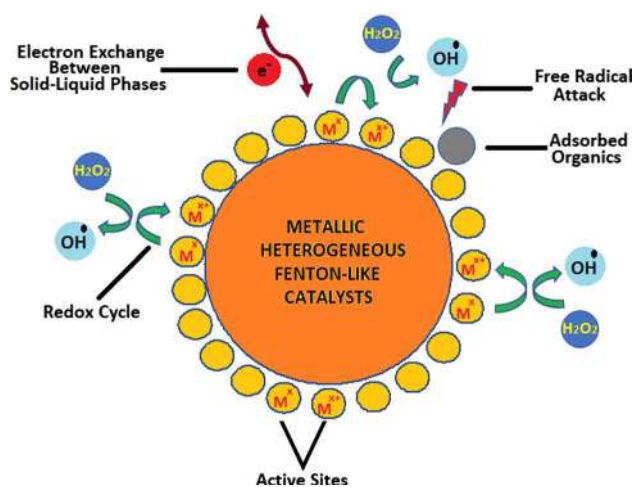
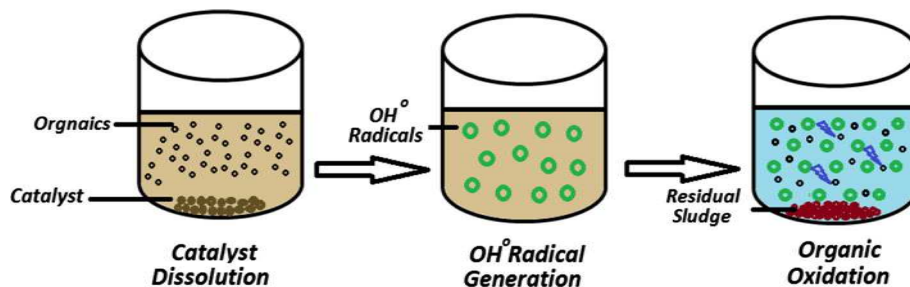


Fig. 1 Heterogeneous Fenton-like oxidation process

Fig. 2 Homogeneous Fenton process. Homogeneous Fenton reaction involves three processing steps: dissolution of the catalyst, OH[•] radical generation and the oxidation of organics



and Englehardt 2006; Lucas and Peres 2009; Umar et al. 2010). 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) (Noyes and Whitney 1897; Otsuka et al. 2007):

$$\frac{dW}{dt} = \frac{DA(C_s - C)}{L}$$

where

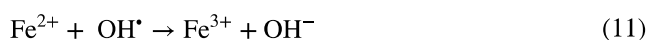
$\frac{dW}{dt}$ is rate of catalyst dissolution

A is surface area of the catalyst, C is concentration of the solid catalyst in the bulk dissolution medium, C_s is concentration of the solid catalyst in the diffusion layer surrounding the solid, D is diffusion coefficient, L is 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.

Once the catalyst is dissolved, the Fe²⁺ ions start producing OH[•] radicals from the oxidant. The rate of OH[•] radicals mainly depends 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 (Eqs. 11 and 12) (Aşçı 2013; Nasuha et al. 2016):



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

The transitory OH[•] radicals then attack on the organic molecules and abstract one of their hydrogen atoms and turn them into R[•] which ultimately undergoes a series of oxidation reactions to yield secondary and tertiary products, ideally H₂O and CO₂. 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 hinders 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 are illustrated in Fig. 3 (Perathoner and Centi 2005).

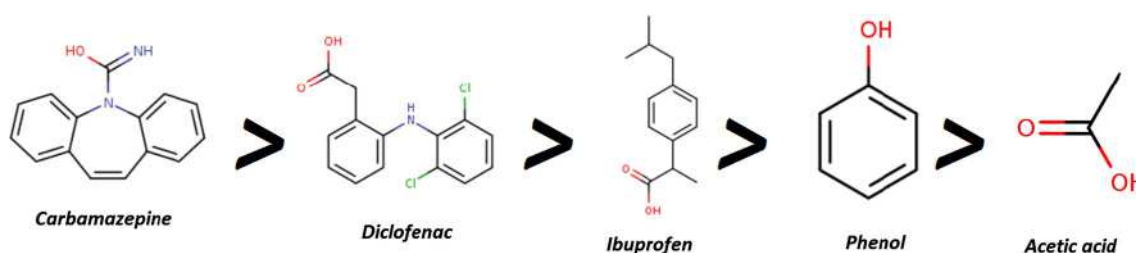


Fig. 3 Order of organic pollutants stability toward oxidation (most stable left)

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) (Pouran et al. 2014), nontoxic reagents and convenience of integration with existing treatment facilities (Brillas et al. 2009). Moreover, Fenton process has been successfully employed for the treatment of numerous industrial wastewaters (Aziz and Daud 2012; Deng and Englehardt 2006; Lucas and Peres 2009; Mosteo et al. 2007; Soares et al. 2014; Wang et al. 2016). 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 (Tang et al. 2019). When pH exceeds 4, Fe^{+3} is converted into ferric hydroxide sludge and part of the catalyst is lost and hence efficacy of the Fenton reaction declines (Garrido-Ramírez et al. 2010). The rigid acidic conditions require constant addition of chemicals before and after wastewater treatment and thus lead the process toward economic nonfeasibility. Besides, handling and disposal of solid sludge incur additional costs. Moreover, the newly formed sludge may also serve as an absorbent for the pollutants in the wastewater and hence give rise to another environmental hazard. Furthermore, recycling of the iron sludge is also not feasible.

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 (Wang et al. 2016). Although heterogeneous Fenton-like reaction also coexists within homogeneous Fenton reaction, it is limited because of the narrow pH range and quickly dissipates once favorable conditions are inverted (Caudo et al. 2006). 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 (Centi et al. 2000; Navalon et al. 2010). In heterogeneous Fenton reaction, the Fe^{+3} is principally used in the nonsoluble form either harnessing

naturally occurring minerals such as magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), hematite ($\alpha\text{-Fe}_2\text{O}_3$) and pyrite (FeS_2) (Feng et al. 2012; Pereira et al. 2012) or impregnating it over suitable supports to afford extended surface area (Flores et al. 2008; Gumy et al. 2005; Muthuvel and Swaminathan 2008; Xue et al. 2009).

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 (He et al. 2016) and finally desorption of oxidation products from catalyst surface (Fig. 4). In order to explain the driving force of adsorption in heterogeneous Fenton oxidation, Langmuir equation can be used (Eq. 13):

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (13)$$

where C_e is equilibrium concentration of organics, Q_e is equilibrium monolayer adsorption capacity, Q_m is complete monolayer adsorption capacity, K_L is Langmuir adsorption constant.

The equation clearly suggests that the rate of adsorption predominantly depends upon the monolayer adsorption capacity of the solid catalyst. This further suggests that higher surface area of the catalyst is exposed in the aqueous medium, resulting in a higher organic adsorption (Geçgel et al. 2015). Although multilayer adsorption may also exist, 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

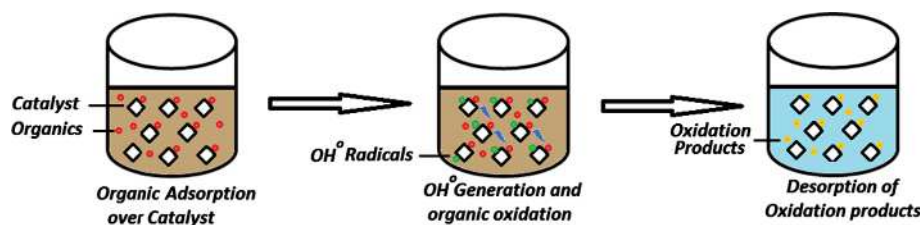


Fig. 4 Heterogeneous Fenton process. Heterogeneous Fenton reaction essentially involves three processing steps: adsorption of organics over the catalyst surface, OH^\bullet radicals generation through active sites

on the catalyst surface and oxidation of the organics, desorption of the oxidation products from the catalysts surface

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 of 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.

Role of metals in heterogeneous Fenton-like oxidation

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 (Bokare and Choi 2014). Moreover, all these oxidation states ought to be stable over a wide range of pH to avoid the loss of catalyst through leaching. Another aspect which must be considered is the resistance of the metallic species toward hydration forces/nonsoluble 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 .

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 (Pereira et al. 2012). Another reason for harnessing this metal is its high activity in Fenton process and familiarity with reaction mechanism (Pouran et al. 2014). 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. Iron can exhibit its heterogeneous catalytic features cycling between Fe^{3+} and Fe^{2+} (Feng et al. 2013; Hartmann et al. 2010; Rusevova et al. 2012); some researchers have also proposed high-valent iron species such as ferryl (Fe^{4+}) but these species only exist in basic conditions (Gonzalez-Olmos et al. 2011; He et al. 2016; Luo et al. 2010).

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 (Wang et al. 2013). For example, there is a marked difference of optimal pH between BiFeO_3 and zerovalent iron (Table 1). Likewise, similar iron-based catalysts such as nanoparticle iron and zerovalent iron yield maximum activity at identical pH conditions.

The parameters 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 toward improving efficiency of the process through partial homogeneous Fenton reaction (Rusevova et al. 2014). However, this will also cause substantial metal loss from catalyst surface and turn 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 affecting the overall process efficacy (Lin et al. 2015).

Another important parameters are the catalyst dose and the associated surface area of the catalyst. Generally, higher catalyst loadings favor the efficacy of the Fenton process,

Table 1 Iron-based heterogeneous catalysts

Catalyst composition	Catalyst dose (g/l)	H ₂ O ₂ dose (mM/l)	pH	T (°C) (time)	Target compound	Degradation (%)	Mineralization (%)	References
Fe(III)AspSiW	0.2	20	6.5	25 (30 min)	4-chlorophenol	100	85	(Chen et al. 2015a)
Fe ₃ O ₄ Nanoparticle	0.1	1	3	25 (30 min)	Methylene blue	100	77	(Wei et al. 2020)
Fe ₀ /Fe ₃ O ₄	3	300	6	25 (2 h)	Methylene blue	100	75	(Costa et al. 2008)
Iron over activated carbon	0.1	6	3	30 (24 h)	Azo dye orange II	100	60	(Duarte et al. 2012)
Fe-Lap-RD	1	60	3	25 (30 min)	Ciprofloxacin	100	57	(Bobu et al. 2008)
Zerovalent iron	1	128	3	20 (8 min)	4-chlorophenol	100	–	(Zhou et al. 2008)
Fe ₃ O ₄ /γ Al ₂ O ₃	1	44	3	50 (3 h) 50 (2 h) 50 (1 h)	4-chlorophenol 2,4-dichlorophenol 2,4,6-trichlorophenol	100 100 100	–	(Munoz et al. 2013)
GO/ Fe ₃ O ₄	0.2	22	3	25 (3 h)	Acid Orange 7	100	–	(Zubir et al. 2014)
Fe ₃ O ₄ /CeO ₂	2	30	3	30 (2 h)	4-Chlorophenol	100	–	(Xu and Wang 2012)
FeNi/C-300	1	100	7	25 (1 h)	Methylene blue	100	–	(Li et al. 2020)
Fe/saponite clay	0.07	13	3	40 (4 h)	Azo dye	100	–	(Herney-Ramirez et al. 2008)
Fe/clinoptilolite	5	3	3	25 (1 h)	Phenol	100	–	(Bayat et al. 2012)
Quartz/goethite	0.1	58	5	20 (30 min)	Methyl red	100	–	(Hanna et al. 2008)
Fe/Faujasite Y zeolite	1	7	5.5	20 (4 h)	Phenol	100	–	(Ayoub et al. 2018)
Nanoparticle iron	0.5	3.0	3	30 (1 h)	4-Chloro-3-methyl phenol	99	63	(Xu and Wang 2011)
Fe ₂ O ₃	20	24	2.5	25 (2 h)	Drimarene	99	–	(Araujo et al. 2011)
Fe-Zeolite Y	2.5	16	2.5	30 (1 h)	Acid red I	99	–	(Hassan and Hameed 2011b)
Fe Clay	5	8	3	30 (3 h)	Reactive blue 4	99	–	(Hassan and Hameed 2011a)
Amorphous FeOOH	2.5	15.8	7	1.5 h	Methyl orange	99	–	(Li and Zhang 2010)
Fe-Al Clay	0.3	4	4	30 (3 h)	Phenol	99	–	(Luo et al. 2009)
Fe ₀ -Fe ₃ O ₄ -RGO	0.1	0.8	3	25 (1 h)	Methylene Blue	98	–	(Yang et al. 2015)
AC-FeOOH	1	10	7	30 (4 h)	Azo dye	98	–	(Wu et al. 2013)
Fe/ZSM-5	1	267	3.5	60 (2 h)	Reactive red	97	–	(Yaman et al. 2013)
Fedpa/SiO ₂	0.87	4.5	8	25 (2 h)	2,4-dichlorophenol	95	–	(Jin et al. 2020)
FeVO ₄	0.5	15	6.1	25 (1 h)	Methyl orange II	94.7	–	(Deng et al. 2008)
Fe ₂ O ₃ Over CeO ₂	1	640	9.6	27 (7 h)	Methylene blue	94	–	(Divya and Renuka 2015)
Fe ₂ O ₃ -MWCNTs	0.5	15	3.5	25 (30 min)	Acid orange II	94	–	(Deng et al. 2012)
Fe ₂ (MoO ₄) ₃	1.4	18	3	30 (1 h)	Acid orange II	94	–	(Tian et al. 2011)
Fe ^{II} @MIL-100(Fe)	1	40	3	25 (5 h)	Methylene blue	91	–	(Lv et al. 2015)
LaFeO ₃ and BiFeO ₃	0.1	26	5	40	Phenol	90	–	(Rusevova et al. 2014)
NZVI/CD particles	1	60	3.5	25 (1 h)	Amoxicillin	90	–	(Pirsaheb et al. 2019)
SCFA	10	5	3	30 (1.5 h)	p-nitrophenol	90	–	(Wang et al. 2018)
FeS	0.5	10	4.5	50 (5 h)	2,4-Dichlorophenoxy-acetic acid	88	–	(Chen et al. 2015b)
Zero valent iron	0.5	6.6	3	30 (20 min)	Amoxicillin	86.5	–	(Zha et al. 2014)
Fe/ZSM-5	0.2	8.35	4	60 (2 h)	Acetic acid	–	50.5	(Cihanoglu et al. 2015)

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• radicals by the catalyst itself (Chen et al. 2015b; Divya

and Renuka 2015). 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 result in the increase in metal loss (Duarte et al. 2012).

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 (Chen et al. 2015b; Duarte et al. 2012). It is also worth mentioning that the type of the pollutants will regulate not only 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.

A key characteristic of the Fenton-like process carried out by iron-based catalysts is their ability to degrade wide range of organics (Zhou et al. 2008). 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^\bullet radicals from secondary oxidation products because Fe^{+3} forms very stable complexes with oxidation products and ultimately inhibits the oxidation of degraded products as shown in Fig. 5 (Salazar et al. 2012; Sirés et al. 2006; Vindedahl et al. 2016).

Copper

Copper is the second most used transition metal in heterogeneous Fenton process because of several characteristics such as inexpensiveness, abundant availability, nontoxic 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^\bullet radicals (Bokare and Choi 2014). 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 (Lyu et al. 2015). The oxidation products do not form permanent complexes with copper, and hence the active sites remain available for continuous catalytic cycle (Fig. 6). Therefore, copper not only offers better redox cycle, but is also active in the mineralization of organics. Several researchers have employed copper in variable forms as heterogeneous catalyst in Fenton process (Table 2).

Controlling parameters

The principal feature of copper-based heterogeneous catalysts is their potential to perform well over a broad pH range, especially at 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

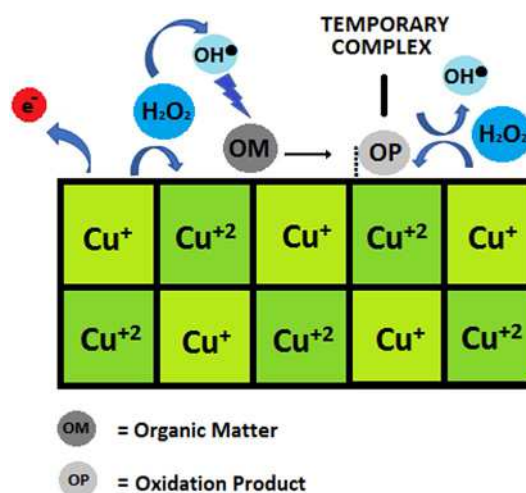


Fig. 6 Complex formation of copper with oxidation products. The oxidation products do not form permanent complexes with copper, and hence the active sites remain available for continuous catalytic cycle

Fig. 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

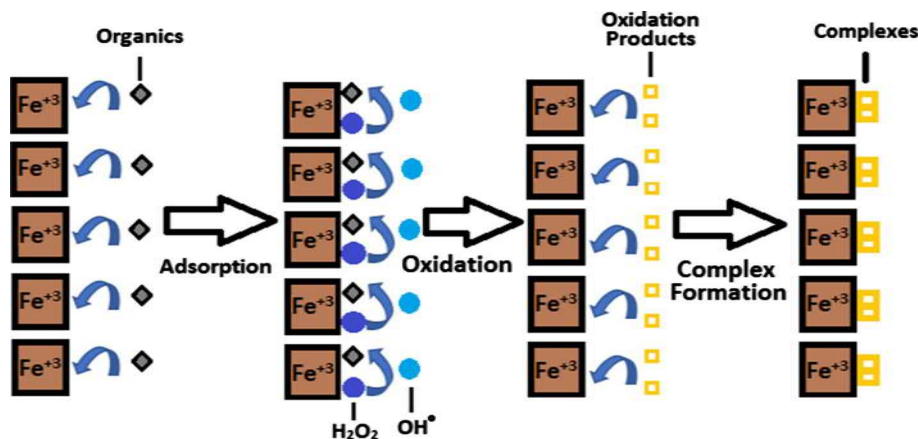


Table 2 Copper-based heterogeneous catalysts

Catalyst composition	Catalyst dose (g/l)	H ₂ O ₂ dose (mM/l)	pH	T (°C) (time)	Target compound	Degradation (%)	Mineralization (%)	References
5Cu/ZrO ₂	0.25	32	5	70 (2 h)	Ibuprofen	100	53	(Hussain et al. 2020)
CuFe/ZSM-5	0.15	40	3.5	50 (2 h)	Rhodamine 6G	100	51.8	(Dükkancı et al. 2010)
Copper slag	2.49	4.7	3	30 (4 h)	Phenol	100	50	(Huanosta-Gutiérrez et al. 2012)
CuFe ₂ O ₄ /rGO	0.6	660	7	25 (4 h)	Phenol	100	–	(Othman et al. 2019)
Copper-doped mesoporous silica	0.4	10	5	30 (2 h)	Ibuprofen	100	–	(Lyu et al. 2015)
Cu/SiO ₂	0.035 Cu	29	–	60 (1 h)	Rhodamine B	100	–	(Sun et al. 2019)
Cu(I)-doped nano-Fe ₃ O ₄	0.1	10	6	25 (2 h)	Carbamazepine	100	–	(Yang et al. 2019)
Cu-Fe ₃ O ₄ @SiO ₂	1 (0.2 cu-fe)	15	5	25 (2 h)	Acetaminophen	100	–	(Do et al. 2018)
CuFeO ₂ Microparticles	1	20	5	30 (2 h)	Bisphenol	99.2	85	(Zhang et al. 2014)
CuO over CeO ₂	1	640	9.6	27 (7 h)	Methylene blue	99	–	(Divya and Renuka 2015)
Cobalt–copper oxalate nanofibers	0.1	380	5	30 (5 h)	Congo Red	99	–	(Shen et al. 2017)
Cu–CuFe ₂ O ₄ /SiO ₂	0.2	250	7	25 (2 h)	Methylene blue	98	–	(Wu et al. 2020)
CuO/SiO ₂ hollow sphere	6	34	3.5	60 (2 h)	acid scarlet 3R	97	–	(Xie et al. 2015)
Co _{0.5} -Cu _{0.5} O	0.1	380	9	30 (5 h)	Congo red	95	–	(Shen et al. 2015)
7.5 CuY	1	200	5	60 (4 h)	Congo red	93.58	79.52	(Singh et al. 2016)
CuFe-MC-1–800	0.3	30	3	25 (1 h)	Bisphenol	93	66.3	(Wang et al. 2015)
					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	
Mesoporous Cu/TUD-1	0.1	90	3.5	25 (3 h)	Bisphenol	90.4	–	(Pachamuthu et al. 2017)
Cu ²⁺ /Al ₂ O ₃ , Cu ²⁺ /ZrO ₂	1	300	6.8	30 (5 h)	Bromophenol blue	90	–	(Salem 2000)
CuO nanoparticles	0.1	800	6	25 (4 h)	Enrofloxacin	90	–	(Fink et al. 2012)
CuO/Al ₂ O ₃	0.2	40	5.5	21 (2 h)	Reactive black 5	90	–	(Bradu et al. 2010)
Fe-Cu/Al ₂ O ₃	1.5	49	4	40 (2 h)	Phenol	–	80	(Xia et al. 2011)

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.

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 H₂O₂ not only increases the cost of the Fenton process but

also makes it susceptible to severe scavenging effect caused by the oxidant itself for OH^\bullet radicals (Bali and Karagözoğlu 2007; Miles and Brezonik 1981).

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 as 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 (Konstantinou and Albanis 2004; Nasuha et al. 2016). 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.

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

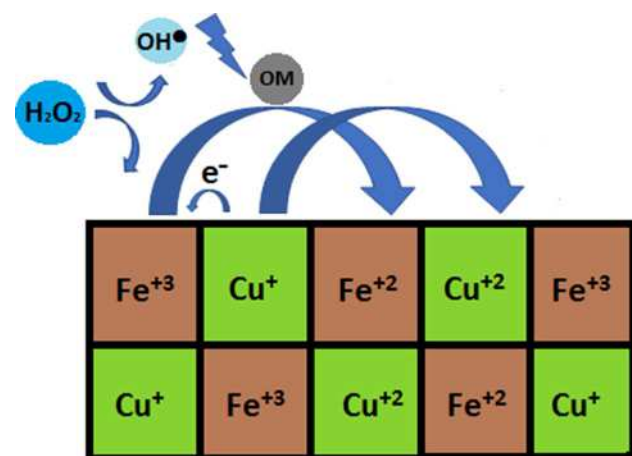
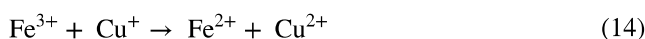


Fig. 7 Redox cycle of copper and iron bimetallic composite. Fe^{3+} is reduced to Fe^{2+} , while Cu^+ is oxidized to Cu^{2+} , favoring the oxidation of organics

(Fig. 7). Tian et al. have summarized the redox mechanism of bimetallic redox cycle using a single equation (Eq. 14) (Tian et al. 2017):



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

Silver

The main drive to use silver as a catalyst in Fenton-like process is its proven ability to oxidize organics such as methanol (Kundakovic and Flytzani-Stephanopoulos 1999), ethylene (Mao and Vannice 1995), methane and volatile organic compounds (Qu et al. 2005). He et al. reported the use of silver nanoparticles for the generation of OH^\bullet from H_2O_2 (He et al. 2012). Until now, silver has not been widely studied as a heterogeneous Fenton catalyst (Table 3).

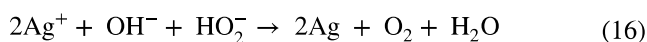
Controlling parameters

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 (Saeed et al. 2018). 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 heterogeneous phase reaction (Fig. 7). 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, and 16) (Weaver and Frederikse 1977). Additionally, basic conditions may activate the agglomeration of the catalyst particles, reducing surface area and diminishing the activity (Park et al. 2017). Moreover, with the progress of Fenton reaction, the degradation products

Table 3 Silver-based heterogeneous catalysts used in Fenton-like processes

Catalyst composition	Catalyst dose (g/l)	H_2O_2 dose (mM/l)	pH	T (°C) (time)	Target compound	Degradation (%)	Mineralization (%)	References
NZVI-Ag	0.025	5.3	3	25 (1.5 h)	4-Chlorophenol	100	80	(Barreto-Rodrigues et al. 2017)
Ag/CeO ₂	0.01	63	2	70 (2 h)	Phenol	100	–	(Aneggi et al. 2017)
Silver nanoparticles	0.010	0.4	4	25 (8 h)	Bisphenol	100	–	(Park et al. 2017)
Silver nanoparticles	0.01	0.4	4	25 (8 h)	17 α -ethinyl estradiol	100	–	(Park et al. 2017)

being predominantly acidic will acidify the aqueous medium and silver will start leaching out from the solid surface:



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 (Fig. 8). Moreover, surface area is also increased manifold 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 stoichiometric 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 (Park et al. 2017). The most prominent feature of silver formed catalysts is that they can afford equivalent process efficacies with minimal catalyst loadings.

Cerium

Cerium is a rare earth metal from lanthanide group which has been widely employed in wet air oxidation and water gas shift reactions (Aneggi et al. 2016; Trovarelli et al. 1999). 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 (Heckert et al. 2008b). It is important to note that cerous (Ce^{+3}) is a strong reducing agent, while ceric (Ce^{4+}) is a strong oxidizing agent. These two ions can interchange quite easily, offering a good redox cycle which is critical for heterogeneous Fenton like oxidation (Aneggi et al. 2012; Rossi et al. 2012). A list of studies employing cerium in Fenton-like oxidation is presented in Table 4.



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 (Chen et al. 2012) 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 $\text{Ce}^{4+}/\text{Ce}^{3+}$ is completely blocked (Cai et al. 2010; Heckert et al. 2008a; Ji et al. 2010). 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 (Fig. 9). However, it is important to note that the cerium-peroxide complex will

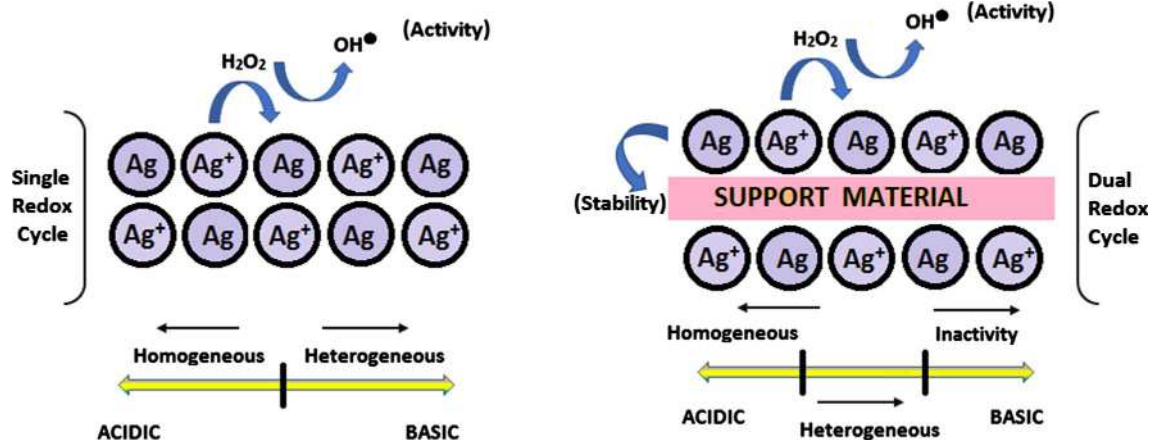
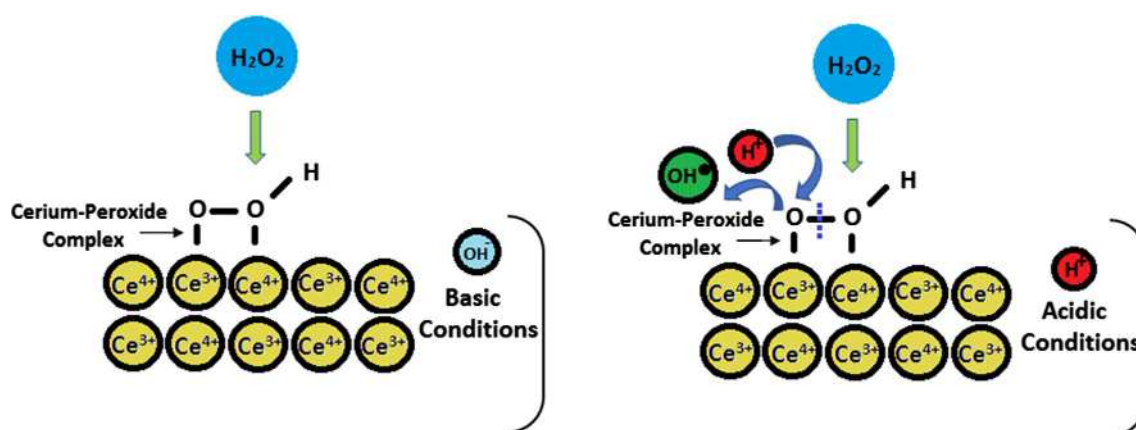


Fig. 8 Activity of bare and supported silver catalysts under variable pH conditions. Bare silver interacts with H_2O_2 forming OH^\bullet radicals through homogeneous phase. The integration of silver on supports enhances its activity and strengthens the stability

Table 4 Cerium-based catalysts employed in heterogeneous Fenton-like oxidation

Catalyst composition	Catalyst dose (g/l)	H ₂ O ₂ dose (mM/l)	pH	T (°C) (time)	Target compound	Degradation (%)	Mineralization (%)	References
CeO ₂ -LaCuO ₃	0.4	12.5	7	25 (6 h)	Bisphenol	99.85	72.44	(Hammouda et al. 2017)
Ce-Cu composite oxide	1	–	4	50 (2 h)	2,4- Dichlorophenol	99.5	82	(Xie et al. 2020)
Fe ₃ O ₄ /CeO ₂	2	30	2	30 (1.5 h)	2,4,6-trichlorophenol	99	65	(Xu and Wang 2015)
CeO ₂	0.5	10	–	25 (8 h)	Acid orange7	98	–	(Chen et al. 2012)
Ce-Cu composite oxide	1	–	4	50 (2 h)	4- Chlorophenol	95	88	(Xie et al. 2020)
Ce _x CuO _y	0.1	50	5	25 (1 h)	Fluconazole	94	–	(Zhang et al. 2020b)
CeO ₂	1	18	–	25 (5 h)	Acid orange7	90	–	(Ji et al. 2010)
Fe ⁰ /CeO ₂	0.1	100	5.8	26 (1 h)	tetracycline	90	–	(Zhang et al. 2019)
FeCeO _x	1.5	80	5	35 (2.5 h)	Rhodamine B	90	–	(Zhang et al. 2020a)
CeO ₂	1.5	60	3	22 (2 h)	Orange II	85	–	(Hamoud et al. 2017)
Fe ₂ O ₃ -CeO ₂	0.5	8	3	45 (2 h)	Sulfamerazine	70	–	(Gao et al. 2019)
CeO ₂	1.5	116	3	22 (2 h)	Acid Green	60	–	(Hamoud et al. 2017)

**Fig. 9** Cerium reactions with H₂O₂ under acidic and basic conditions. Under basic conditions, H₂O₂ forms very stable peroxide-like species (OOH⁻) with cerium inhibiting OH[•] radicals generation, while in

acidic conditions, H⁺ ions attack the cerium-peroxide complex with OH[•] radicals generation

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 premixed with the cerium catalyst because it is highly likely that it will block the catalytic activity (Heckert et al. 2008a). Therefore, it is viable to employ the oxidant as a last processing step so that part of the cerium catalyst sites is preoccupied 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 reverted by acidic conditions or either by applying very high temperatures ~ 300 °C (Ferrizz et al. 2001; Liu et al. 2009). Since an increase in temperature is beneficial in reversing

the cerium-peroxide complex which triggers the redox cycle Ce⁴⁺/Ce³⁺, any elevation in temperature would certainly enhance the heterogeneous activity of cerium catalyst (Ferrizz et al. 2001).

Manganese

Manganese is a transition metal, which is abundantly available, has low toxicity, is not very expensive, and exists in multiple oxidation states (Ren et al. 2012). Manganese offers structural flexibility in its metallic oxides while exhibiting the favorable oxidation states (Birkner et al. 2013). However, Mn⁺² and Mn⁺⁴ are the only suitable oxidation states while considering heterogeneous Fenton-like oxidation as reported in many studies (Table 5) (Robinson et al. 2013). It is important to mention that manganese transforms H₂O₂ into OH[•]

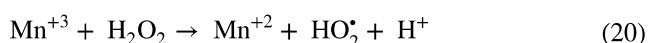
Table 5 Manganese-based heterogeneous catalysts used in Fenton-like oxidation

Catalyst composition	Catalyst dose (g/l)	H ₂ O ₂ dose (mM/l)	pH	T (°C) (time)	Target compound	Degradation (%)	Mineralization (%)	References
Mn ₃ O ₄ /silicate	0.4	97	6	25 (4 h)	Methylene blue	100	81	(Tušar et al. 2012)
Fe/Mn-MOF-71	0.064	600	6.2	35 (3 h)	Phenol	100	–	(Sun et al. 2017)
MnO ₂ -MWCNT	0.2	300	6	25 (3 h)	reactive blue 19	99	–	(Fathy et al. 2013)
MnO ₂	0.1	1450	6.1	25(0.3 h)	Methylene blue	99	–	(Kim et al. 2017)
Mn ₃ O ₄ -FeS ₂ /Fe ₂ O ₃	0.3	5	2.8	25 (1 h)	Orange II	99	–	(Xu et al. 2020)
Fe–Mn oxide hollow fiber membrane	-	22	9	25	Methylene blue	97	–	(Xu et al. 2019)
Diatomite/Manganese silicate	0.3	30	-	30(1 h)	Malachite green	93	–	(Jiang et al. 2018)
Mn/Ti-HMS	1	10	7	25 (2 h)	Methylene blue	63.9	–	(Song et al. 2016)
Mesoporous MnO _x	1	20	3	20 (1 h)	Norfloracin(NFX)	60	–	(Minghao et al. 2013)
Mn/Ti-HMS	1	10	7	25 (2 h)	Rhodamine B	49.7	–	(Song et al. 2016)

radicals by undergoing through a transitional intermediate, i.e., Mn⁺³ (Rhadfi et al. 2010; Sigel 2000; Watts et al. 2005), thus possessing a unique redox cycles depending upon the type of oxide, and an electron is exchanged between the substrate and the solution (Fig. 10) (Parida et al. 2005).

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 change altogether when MnO₂ and Mn₃O₄ are used (Fig. 10). When Mn₃O₄ is employed, the reaction is favored by a basic environment (Eqs. 19 and 20), though neutral conditions are applied for practical reasons:

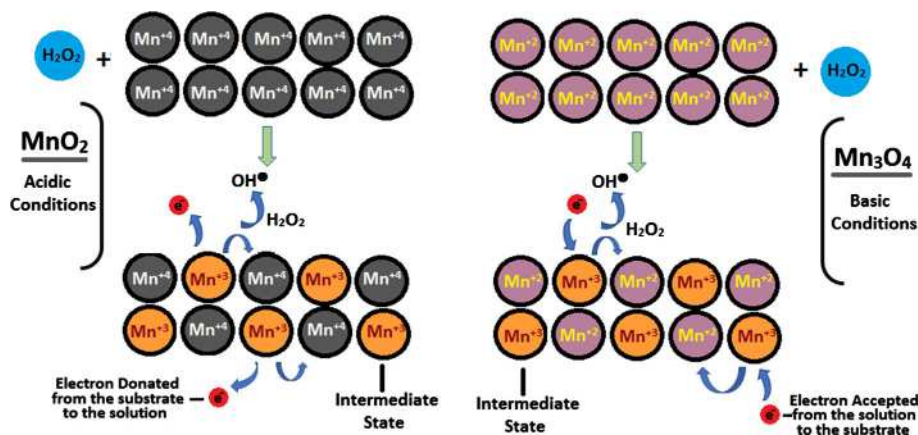


Conversely, MnO₂ requires acidic conditions to drive the redox cycle toward Mn⁺³ generation which in turn transforms H₂O₂ into OH[•] radicals (Eqs. 21 and 22). Additionally, precise control of the pH is also essential because adsorption of organics over the catalyst surface is influenced by it (Zhao et al. 2013). Moreover, the oxidation pathway of organics as well as stability of the catalyst heavily relies on the pH:



In the case of manganese-based catalysts, another parameter which greatly influences their performance in Fenton-like process is their morphology (Hermanek et al. 2007; Kim et al. 2017). For instance, MnO₂ can exist in four crystalline structures, i.e., α-MnO₂, β-MnO₂, γ-MnO₂, δ-MnO₂. All of them have different surface areas and extents of crystallinity, thus exhibiting variable

Fig. 10 Redox cycles of MnO₂ and Mn₃O₄ under feasible conditions. Manganese transforms H₂O₂ into OH[•] radicals by undergoing through a transitional intermediate, i.e., Mn⁺³



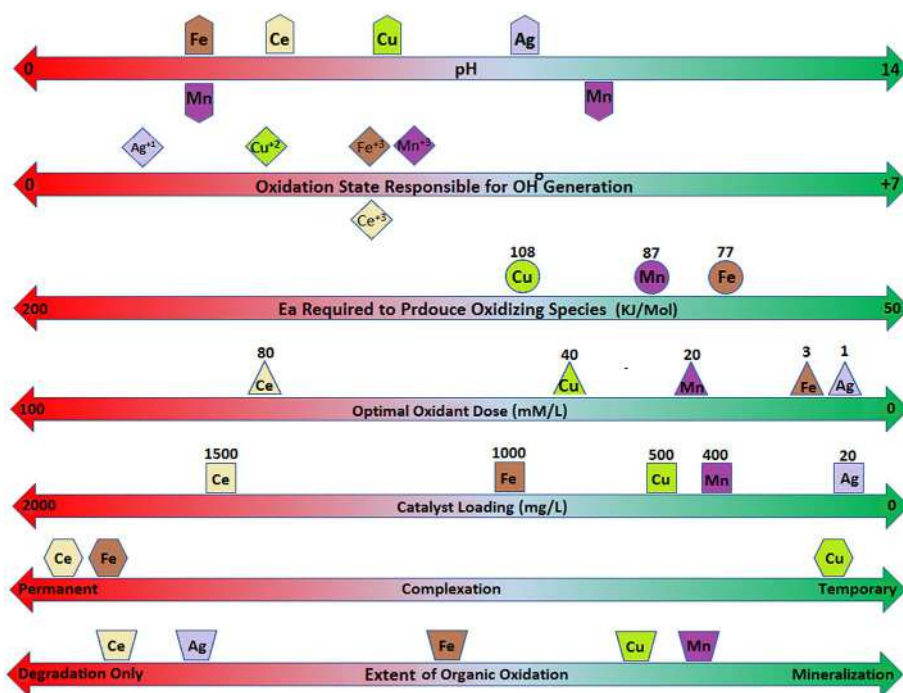
catalytic activities in heterogeneous Fenton process (Xiao et al. 2010). γ - MnO_2 affords maximum activity because of well-formed morphology and high surface area, while δ - MnO_2 is the least active because it is an amorphous solid with minimum surface area (Kim et al. 2017). Kim et al. also explained that different morphologies of MnO_2 have different magnetic moments, indicating that these oxides exhibit mixed oxidation states (Kim et al. 2017).

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 (Molina et al. 2006). 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 (Xiao et al. 2010).

Conclusion

The inborn limitations of classical Fenton process such as large volumes of sludge and stringent pH prerequisites can be easily reverted by adapting heterogeneous Fenton-like approach, employing either 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 (Fig. 11). Iron-based catalysts require severe acidic conditions, high catalyst doses, 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 among the discussed metals. Although silver-based catalysts require less excess H_2O_2 , low catalyst loadings for optimal performance, a poor redox cycle coupled with susceptibility toward leaching limits 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.

Fig. 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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Compliance with ethical standards

Conflicts of interest The authors declare that they have no competing interests.

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