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Original

Availability:
This version is available http://hdl.handle.net/11390/1142421 since 2019-01-03T12:25:04Z

Publisher:

Published
DOI:10.1007/s10973-018-7408-3

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12 October 2024

Thermodynamics of sorption of platinum on superparamagnetic nanoparticles functionalized with mercapto groups.

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Abstract.
The adsorption of Pt(IV) by iron oxide (Fe_3O_4) superparamagnetic nanoparticles (SPION) functionalized with 3-mercaptopropionic acid (3-MPA) is investigated by means of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and isothermal titration calorimetry (ITC). Experimental ICP data are better fitted by Langmuir rather than Freundlich isotherms. The whole thermodynamic parameters and maximum loading capacity for the adsorption process of Pt(IV) on the functionalized SPION nanoparticles (SPION@3-MPA) are obtained. The process is enthalpy-driven while entropy is largely unfavourable suggesting that some other interaction should be present in addition to the electrostatic ones with the coverage surface. When compared to other thiol-functionalized materials, the SPION@3-MPA can be considered an interesting adsorbent for Pt(IV), especially with respect to the short contact time evidenced.

Introduction

The special properties displayed by platinum such as chemical inertness, high corrosion resistance, high melting temperature determine the large range of application of the metal [1]. Platinum finds application in the manufacturing of electronic and electrical devices, catalysts, jewelry, biomedical devices, fuel cell production, plating and coatings, and many more products. Because of the increasing demand for platinum in various industries, and the limited natural resources available, the recovery of the metal from aqueous solutions is economically attractive. Also the treatment of hospital liquid waste containing CPC (Cancerostatic Platinum Compounds) compounds originated has become

a growing topic in the last decade, since the dispersion in sewage water of such mutagenic compounds is highly undesirable.

The methods for the recovery of platinum from aqueous solutions include precipitation, co-precipitation, liquid–liquid extraction, and adsorption [2,3].

Among these methods, adsorption technology has proven to be one of the best techniques for metal wastewater treatment because it offers flexibility in design and operation [4]. Furthermore, since this process is often reversible, adsorbed species can be recovered by suitable desorption process and the material regenerated for its re-use.

Nanoparticles attracted much attention for metal ion recovery from water because of their high surface area to volume ratio, fast reaction kinetics, the possibility to be chemically modified on their surface [4–6]. These materials can be then separated from the liquid samples with relatively simple methods. Among them, nanosized metal oxides demonstrated to be promising materials for metal removal from wastewaters [4,6,7]. As an example, in several recent studies functionalized materials have been used as adsorbents for platinum(IV) in aqueous solution [8].

Recently, Super Paramagnetic Iron Oxide Nanoparticles (SPION), received special attention for their low toxicity, low cost and easy recovery from aqueous media by magnetic separation [4,9,10]. In addition, iron is one of the widespread elements in the earth and easily accessible [11], rendering the material a low-cost adsorbent which is a requisite for wastewaters treatment. It is also important to develop protection strategies to stabilize the magnetic nanoparticles against their degradation, such as core-shell, which are also used for functionalization of the adsorbent material for selective application. Hence, if the surface of magnetite is coated with an compound containing a thiol or amino group, the removal of metals should be enhanced enabling, in addition, the magnetic separation of the adsorbent from the solution [8,12–16].

In this work, the adsorption of Pt(IV) on iron oxide (Fe_3O_4) SPION functionalized with 3-mercaptopropionic acid (SPION@MPA) is studied by means of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) technique in parallel with Isothermal Titration Calorimetry (ITC). The aim is to investigate the efficiency of the nano-adsorbent but also to gain parameters on the thermodynamic of adsorption of Pt(IV) by functionalized SPION@MPA.

The organic ligand 3-MPA has been selected as promising ligand for surface functionalization of magnetite nanoparticles. It contains a carboxyl group, which facilitates the coating with iron oxide due to the high affinity of the carboxyl group

towards iron [7], whereas the additional thiol group has shown good adsorption properties for noble-metal ions and some other metals [8,12–16].

The use of calorimetry is a novel approach used here to quantify an adsorption process from aqueous solution to solid phase. Indeed, this technique was widely used by our group mainly to characterize chemical equilibria processes in aqueous or non-aqueous solutions [17–26]. Meanwhile, a few number of ITC applications in adsorption studies are found in the recent literature [27–30], being the enthalpy associated to desorption process usually calculated indirectly by van't Hoff equation [31,32]. Nevertheless, many studies revealed serious discrepancies between enthalpy values calculated from van't Hoff equation and obtained directly from ITC and, evidencing large uncertainties associated to the former method [33–36]. On the contrary, ITC analysis provides independent and robust thermodynamic parameters, which allows to gain information of specificity of functionalization towards metal ions adsorption and about the possible nature of the interactions at play between the surface and the anionic ligand.

Experimental

Material preparation

All reagents used in the experiment were analytical grade and used without further purification. Ammonium hydroxide (NH_4OH), hydrochloric acid (HCl), Iron (II) chloride ($FeCl_2 \cdot 4H_2O$), Iron (III) chloride ($FeCl_3 \cdot 6H_2O$) and 3-mercaptopropionic acid (3-MPA) were purchased from Sigma-Aldrich.

The metal stock solution was prepared by dissolving hydrogen hexachloroplatinate (IV) hydrate (Aldrich) in HCl solutions prepared in milliQ water.

Iron oxide nanoparticles were synthesized by a co-precipitation method, as described elsewhere [15,16,37].

The SPION were functionalized with 3-MPA (SPION@3-MPA) by ligand addition method [15]. A known amount of synthesized SPION was suspended in water acidified with HNO_3 to pH = 2.0, to have the surface charged positively (pH_{pzc} of the SPION = 6.8) [38]. Then, 10mL of SPION suspension were stirred for 24h in N_2 atmosphere, with a solution of the 3-MPA 150 mM in toluene. After phase separation using magnetic decantation, the particles were washed with ethanol, dried at room temperature and stored in dry box in N_2 atmosphere. The nanoparticles were characterized as previously described in ref. [15] by means of BET (Micromeritics Tristar 3000 gas adsorption analyzer), FT-IR and thermogravimetry (Q500 TGA, TA Instruments). The pH_{pzc} of

SPION@3-MPA was determined following the published methodology [39]. The overall results on the characterization of the SPION@3-MPA resulted to be in good agreement with ref. [15].

Adsorption studies

The adsorption experiments for Pt(IV) were performed at 298 ±1K by suspending 5mg of SPION@3-MPA to 10mL solutions containing the metal ion in the 0.1-1.0 mM concentration range. The pH of the solution was adjusted at pH = 3.0 with HCl where the main Pt(IV) species should be $PtCl_6^{2-}$ and $PtCl_5(H_2O)^-$ complex [8,37,40]. The pH value was chosen in order to avoid the hydrolysis of chloro-complex of Pt(IV) (at pH > 3.5) [41] and the eventual dissolution of magnetic particles (at pH < 2).

The suspension was sonicated during 30 min and then allowed 2 hours in contact, due to a relatively low kinetic of adsorption of Pt(IV). In preliminary experiments the contact time necessary between nanoparticles and Pt(IV) was found to be about 100 minutes, as no significant variation of adsorption % was observed after that time. The magnetic adsorbent was separated from the aqueous phase and the Pt(IV) concentration in the filtered solution was determined by ICP-OES (Varian VISTA-MPX CCD Simultaneous ICP-OES). Iron content was also determined to control the particle dissolution, which did not occur in our experimental conditions.

Adsorption data were fitted by the Langmuir and Freundlich isotherms, as it has been demonstrated that such models better fit the adsorption from solutions [42]. These models are expressed by eq. 2 and eq. 3 respectively [43]:

$$C_{ads} = \frac{Q_{\max} b C_e}{1 + b C_e} \qquad (2)$$

C_e = solute equilibrium concentration (M), C_{ads}= solute adsorbed at equilibrium (mol g^{-1}), $Q_{\max}$ = maximum quantity of solute adsorbed per gram of adsorbent (mol g^{-1}) and b = Langmuir constant (M^{-1}).

$$C_{ads} = K_f C_e^{\frac{1}{n}} \qquad (3)$$

K_f = Freundlich constant (($L \cdot mmol^{-1}\ g^{-1})^{1/n}$), n = adsorption intensity, C_e = equilibrium concentration of adsorbate (M), C_{ads} = amount of Pt adsorbed at equilibrium (mol g^{-1}).

Isothermal Titration Calorimetry (ITC)

A TAMIII isothermal microcalorimeter (TA Instruments) connected with an automatic titration syringe was used to measure the heat of adsorption of the Pt(IV) metal ion on SPION@3-MPA. The titration cell was filled with a solution at pH = 3.0 (adjusted by HCl) in which ~0.5g L^{-1} SPION@3-MPA were dispersed. The suspension was stirred continuously at 120rpm. The cell content was titrated with 14 additions of 14µL of 5mM metal ion solution. A delay time of 2 hours between consecutive injections, because of Pt(IV) slow kinetics. The reference cell was filled with 0.7 mL of MilliQ water.

The values of b and Q_{max} obtained by the fit of the Langmuir isotherm obtained from ICP-OES data, have been used as input data in eq. 4 to calculate C_e for each titrant addition by numerically solving eq. 2 with the same experimental conditions as the calorimetric titrations [44,45]. Then, the ΔH_{ads} (kJ mol^{-1}) value has been calculated to best fit the experimental heat according to the isotherm (eq. 4):

$$q_{cum} = \frac{Q_{max} b C_e}{1 + b C_e} \Delta H_{ads} \qquad (4)$$

q_{cum} = total heat involved at each titrant addition per gram of SPION@3-MPA (kJ g^{-1}). Dilution heat (q_{dil}) was also determined to correct the total heat measured (q_{meas}) by the instrument. Thus $q_{cum} = (q_{meas} - q_{dil})/w$ represents only the heat involved on the adsorption reaction. Data fitting and statistical analysis of the results has been done with the MS-Excel Solverstat and EST tools [46,47].

Results and discussion

The adsorption data have been fitted with Langmuir and Freundlich isotherms, and the obtained parameters are summarized in Table 1, while the experimental points and calculated curves are reported in Figure 2. The best fit is obtained with the Langmuir isotherm as evident from the significantly higher quality of the fit (higher R^2, Table 1 and Figure 2), indicating the presence of a homogeneous adsorption by the formation of a monolayer adsorbate on the adsorbent surface.

The calorimetric titration of the SPION@3-MPA suspension is shown in Figure 3a, while the experimental and calculated q_{cu} values are reported in Figure 3b as obtained by using eq. 4. The corresponding ΔH_{ads} is reported in Table 2 together with the calculated entropy values. A strong exothermic effect (ΔH_{ads}= -50 kJ mol^{-1}) is associated to the process together with a high negative entropy value ($T\Delta S_{ads}$= - 18.2 kJ mol^{-1}), as calculated by

the ΔG value obtained from b value (ΔG_{ads}= -31.8 kJ mol^{-1}) in Table 1. In a recent work [48], negative enthalpy and entropy values were obtained for the interaction of Cr(VI) with a nanocomposite adsorbent based on grafted Fe_3O_4/poly(methylmethacrylate) (ΔH= -97.5kJ mol^{-1} ΔS= -320 J $mol^{-1}K^{-1}$).

The low solvation of anions in water, as compared to cations,[49] should partially account for the thermodynamic values relative to Pt(IV) adsorption, but also some concomitant effects at probably at play.

Indeed, the adsorption mechanism could be due to the *i)* coordination on thiol group in a pendant fashion or in combination with vicinal hydroxyl groups and *ii)* electrostatic attraction between charges of opposite sign. In our experimental conditions Pt(IV) is in anionic form and the adsorbent surface is positively charged so electrostatic interactions are certainly possible. Nevertheless, also some interaction with the thiol groups could be present. In any case, the fact that the anionic $PtCl_6^{2-}$ species is poorly solvated could be responsible of the negative ΔS: in this case the loss of degrees of freedom of the adsorbate prevails on the desolvation processes regarding the solute and the surface.

The adsorption efficiency of the SPION@3-MPA towards Pt(IV) (0.31mmol g^{-1}) is poorer with respect to other adsorbents as evidenced from the comparison with data reported in Table 2[50–52], but higher with respect to the adsorption capacity shown by magnetic cellulose functionalized with thiol and amine[8].

It is to underline that materials that reported a better efficiency than SPION@3-MPA, also showed a significant higher amount of sulphur present in the adsorbent (Table 2), which is related to the quantity of immobilized 3-MPA. This is a decisive factor for the sorbent ability of the material and, in addition, some aggregation present on our adsorbent could be responsible of the lower efficiency. Despite that, SPION@3-MPA presents promising low contact time, which is a key parameter to be faced for possible applications.

Conclusions

The present work presents a complete thermodynamic characterization of the adsorption of Pt(IV) by SPION functionalized with the ligand 3-MPA in acidic aqueous solution.

The Langmuir isotherm better fits experimental data providing the apparent stability constant and the maximun loading capacity. Direct calorimetric data show that the process is enthalpy-driven while entropy is largely unfavourable. If compared to other thiol-

functionalized materials, the SPION@3-MPA can be considered an interesting adsorbent for Pt(IV) mainly with respect to the short contact time evidenced.

Acknowledgments.

The research leading to these results has received funding from the European Community's H2020 Programme H2020-MSCA-RISE 2017 under the project *RECOPHARMA* with grant agreement nº 778266.

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Figures

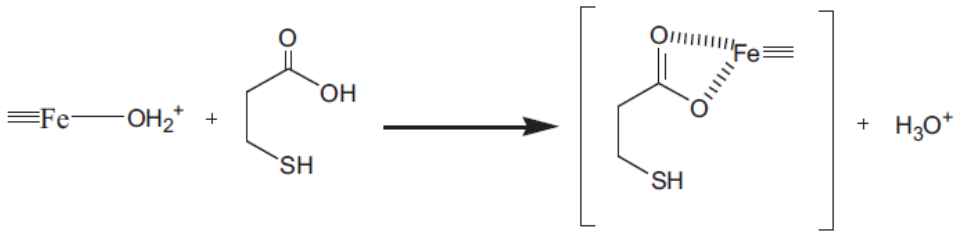

Figure 1. Functionalization mechanism of 3-MPA on SPION (=Fe) surface.

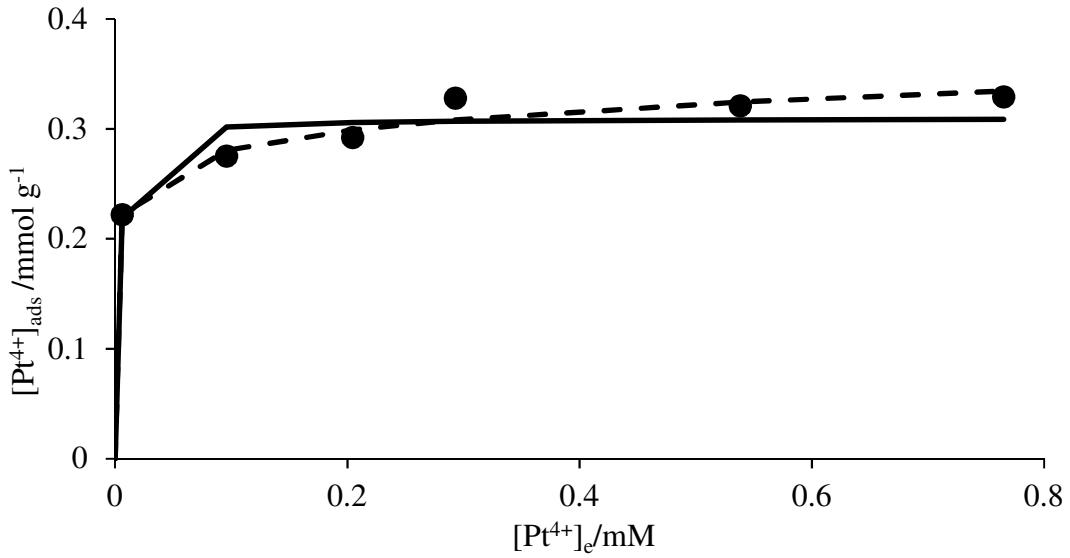

Figure 2. Adsorption isotherms showing the experimental data fitted with Langmuir (solid line) and Freundlich (dashed line) models. In the batch experiments, 5mg of the SPION@3-MPA were added to 10mL of the metal solutions, with a metal concentration varying from 0.1 to 1.0mM.

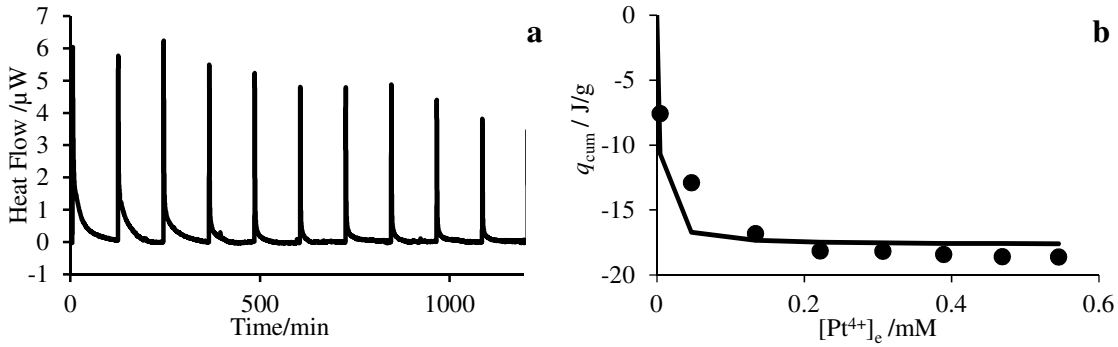

Figure 3. Calorimetric titrations plots corresponding to the addition of Pt(IV) solution to 0.7mL of 0.5g L^{-1} SPION@3-MPA suspension (a), and experimental calorimetric data (points) fitted with eq. 4 (line) for Pt(IV) adsorption process (b).

Tables

	Langmuir equation				Freundlich equation		
	Q_{max} (mol g^{-1})	b (M^{-1})	log b	R^2	n	K_f (L $mmol^{-1}$ g^{-1})	R^2
Pt(IV)	0.00031 ±0.00001	368483 ±129319	5.6 ±0.3	0.997	12 ±2	0.342 ±0.008	0.951

Table 1. Langmuir and Freundlich isotherm parameters for Pt(IV) by SPION@3-MPA at pH=3.0

Adsorbent	S % (mmol g^{-1})	Initial M^{n+} (mM)	Adsorbent dosage (g L^{-1})	pH	Temp. (K)	Contact time (h)	Adsorption capacity (mmol g^{-1})	*b* (M^{-1})	ΔH_{ads} (kJ mol^{-1})	$T\Delta S_{ads}$ (kJ mol^{-1})	Ref.
Magnetic cellulose functionalized with thiol and amine	-	0.03-0.25 (5-50 mg L^{-1})	0.04 g	2.0	318	1	0.21 (40.48mg g^{-1})	212641 (1.09L mg^{-1})	-	-	[8]
Thiolated mesoporous silicas	2.4 (7.59%)	-	1.0	2.0	298	48	1.19 (232.6mg g^{-1})	2898948 (14.86L mg^{-1})	-	-	[50]
Straw-SH	2.71 (8.70%)	-	-	1.0	room	24	1.95 (380mg g^{-1})	-	Exothermic	-	[51]
Thiol functionalized mesoporous silica	-	0.5 – 4	1.0	1.0	299	-	4.4 (861.9mg g^{-1})	-	-	-	[52]
SPION@3-MPA	1.4	0.1 - 1.0	0.5	3.0	298	2[a]	0.31 ±0.01	368483 ±129319	-50 ±2	-18.2	This work

Table 2. Parameters of Pt(IV) adsorption for several thiol-functionalized adsorbents. In parentheses, the original values in the cited references are reported. [a]Delay time between metal solution additions.