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Exploring arsenic adsorption at low concentration onto modified leonardite

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Abstract

The removal of As(V) from aqueous solutions by leonardite loaded with ferric ions (Fe-leonardite) has been investigated. The influence of pH, contact time and arsenate concentration on the adsorption process were evaluated. Batch kinetic studies showed that equilibrium time was reached at 24 h of contact time. Equilibrium data obtained with low initial arsenate concentrations (10-400 ppb) were fitted to both Langmuir and Freundlich models and the maximum adsorption capacity was estimated to be 322 µg g^{-1}. Arsenic sorption was evaluated in continuous mode to reproduce industrial applications and to determine the conditions where the process was controlled by either mass transfer or reaction rate. A maximum sorption capacity of 905 µg g^{-1} was obtained in continuous experiments. These results indicate that Fe-leonardite is a great potential material for removing arsenate at low initial concentrations from contaminated water.

Keywords. Arsenic, sorption, leonardite, iron-coated sorbent, column test

1. Introduction

Arsenic is ubiquitous in the Earth's crust and it ranks 20th among the elements in abundance. It has been known for centuries as a toxic element. In this sense, chronic arsenic toxicity results in multisystem disease. The International Agency for Research on Cancer (IARC) classifies arsenic as a Group 1 carcinogen (carcinogenic to humans) (IARC 2004). Drinking water can be an important source of arsenic exposure when arsenic occurs naturally in arsenic-rich rocks through which the water has percolated. This happens in some areas of the United States, Argentina, Chile, Mexico, China, Hungary, West Bengal (India), Bangladesh and Vietnam (Smedley and Kinniburgh 2002). However, high concentrations of arsenic in the environment are mainly due to anthropological activities such as mining, petroleum refining, sewage sludge disposal, agricultural chemicals production, ceramic manufacturing industries and coal fly ash emissions.

Because of its high toxicity, contents of arsenic in drinking water supplies are regulated in many countries. In 2001, the Environmental Protection Agency (EPA) lowered the threshold for acceptable arsenic levels in drinking water from 50 ppb to 10 ppb. 10 ppb is also the accepted standard adopted by both the World Health Organization (WHO) and the European Union (EU) (Official Journal of the European Union 1998).

The toxicity of arsenic strongly depends on its oxidation state. Arsenic in aqueous solutions exists in two inorganic forms: arsenate As(V) or arsenite As(III). The oxidation state depends on the redox environment in the water system (Bhattacharya et al. 2007). Arsenate is more prevalent in oxygenated surface water or oxidized conditions while arsenite is more likely to occur in anaerobic or mildly reducing conditions.

The common physico-chemical processes used for arsenic removal can be classified on the basis of the separation mechanisms involved: coagulation-precipitation, ion exchange, membrane processes and adsorption technologies. Much work has been done on arsenic removal through adsorption because this method is cost-effective and simple to operate (USEPA 2002). The effectiveness of adsorption-based methods depends, primarily, on the adsorbent used. So far, various adsorbents either from natural and synthetic origin have been developed for arsenic removal. These include modified activated carbons, agricultural and industrial by-products, clay minerals, and biosorbents (Mohan and Pittman 2007). Among these adsorbents, natural materials containing iron (Gang et al. 2010; Guo et al. 2007; Vaughan and Reed 2005) and modified adsorbents loaded with iron species (Dong et al. 2009; Gang et al. 2010; Vaughan and Reed 2005; Zhang and Itoh 2005; Zouboulis and Katsoyiannis 2002) are particularly efficient to remove arsenic from contaminated water. It appears that electrostatic interaction, surface complexation and specific adsorption are the most important mechanisms for arsenic removal by iron loaded materials. It is known the role of metal ions in bridging the complexation of anions with humic substances. Recently spectroscopic evidences for ternary complex formation between arsenate, ferric ion and humic acid has been described (Mikutta and Kretzschmar 2011).

Leonardite is a low-cost material which has shown a great ability to remove heavy metals (Lao et al. 2005; Solé et al. 2003; Zeledón-Toruño et al. 2005) from aqueous solutions. Leonardite is an immature coal with high humic acids content. Humic acids contain oxygen functional groups (carboxyl, phenol and hydroxyl) which permit to bind metal cations (Livens 1991). According to the stated above, the aim of this work was to develop a material suitable for removing arsenic from water environmentally acceptable, cost-effective, and simple to setup. In the present study, the potential of a leonardite previously coated with Fe(III) ions for the removal of arsenic from aqueous solutions has been investigated. Sorption experiments were conducted at very low arsenic concentrations (ppb range) in order to simulate the sorption behaviour of the contaminant in actual polluted water (Smedley and Kinniburgh 2002).

2. Materials and Methods

2.1. Adsorbent and Chemicals

The leonardite used in this study was supplied by "Sociedad Española de Acidos Húmicos, S.A". (SEPHU®, Zaragoza, Spain). This material was sieved to a grain size of 0.09–0.2 mm before being used in the adsorption experiments. The physical-chemical characteristics of the leonardite were determined in a previous work (Z. C. Zeledón-Toruño et al. 2007).

A stock solution of As(V) was prepared from $Na_2HAsO_4.7H_2O$ (Panreac Química S.A., Barcelona, Spain) at 100 mg L^{-1} concentration. Working solutions for experiments were freshly prepared from this stock solution. Acid solution (0.1 M HNO_3) and base solution (0.1 M NaOH) were used for pH adjustment. Solutions of Fe(III) were prepared from $FeCl_3.6H_2O$ (Scharlau Chemie, S.A, Barcelona, Spain). All chemicals used in the experiments were AR-grade.

2.2. Leonardite impregnation with Fe (III) ions

Preliminary batch experiments were carried out in order to establish the maximum load capacity of iron onto leonardite. 0.1g of leonardite were added to 250 mL Erlenmeyer flasks containing 100 mL of Fe(III) solutions (5-250 ppm). After shaking in a magnetic stirrer during 24 hours, the mixtures were filtered and the filtrate was analysed for the remaining Fe(III) content determination.

Impregnation of leonardite by Fe(III) was carried out on a fixed-bed column using laboratory-scale adsorption columns (Icogamma Plus syringes) of 1 cm diameter and 5.5 cm length. The column was loaded with 5 g of raw leonardite. The sorbent material was firstly rinsed with distilled water and then, a 500 ppm $FeCl_3$ solution was passed through the bed at a 0.4 mL min $^{-1}$ constant flow during 24 h. The obtained material was dried in an oven at 100 °C for 3 h.

2.3. Analytical methods

Fe(III) ions were analysed by UV-Vis spectroscopy previous reduction of Fe(III) into Fe(II) and formation of the coloured complex Fe(II)-Phenantroline which absorbs at 510 nm. As concentrations were determined using an atomic absorption spectrophotometer (Thermo Electron Corporation, model Solaar

S2) coupled to a hydride generator (model VP 100). Potassium iodide (10% m/v) and ascorbic acid (10% m/v) were used for the pre-treatment samples (As(V) reduction into As(III)) while sodium borohydride was used to analyze the arsenic through the production of volatile arsines.

Surface topology and local chemical composition of the raw and the iron-loaded leonardite were examined by scanning electron microscopy (FEI Quanta 200) and Energy Dispersive X-ray (EDS Genesis).

2.4. Arsenate adsorption experiments

2.4.1. Batch experiments

The effect of pH solution on the As adsorption onto Fe-leonardite was studied among the pH range 2.0 to 10.0. For this, 0.1 g of Fe-leonardite were added to 100 mL of 100 ppb As(V) solutions placed in conical flasks. Initial pH was adjusted by HNO_3 or NaOH 0.1 M addition. After agitation with a magnetic stirrer (SBS) for 24 h at 25°C and filtering through a 0.45 µm Millipore Cellulose filter, the remaining arsenic concentration was determined. The amount of arsenic adsorbed was calculated from the difference between the initial and final arsenic concentration.

To evaluate the influence of contact time on adsorption process, 0.1 g of Fe-leonardite were added to 100 mL of 400 ppb As(V) placed in several conical flasks. Samples were taken at various contact times among 15 minutes and 48 hours.

The adsorption capacity of Fe-leonardite for As was obtained using different initial As(V) concentrations (from 10 to 400 ppb) and keeping a constant dose of Fe-leonardite (1g L^{-1}) following the same procedure described above. All the adsorption tests were performed in duplicate.

In order to check the stability of Fe(III) ions retained onto leonardite, Fe(III) concentration was measured after arsenate sorption experiments in all the solutions. In all cases, Fe(III) dissolved concentrations measured after a 24-h contact time was below 0.2 ppm and this concentration was independent on the initial arsenic concentration.

2.4.2. Column experiments

Column adsorption experiments were carried out on fixed-bed column using laboratory-scale adsorption columns (Icogamma Plus syringes) of 1 cm diameter and 5.5 cm length. The column was equipped with a bottom filtration device of glass wood to prevent the escape of the adsorbent during the process. Columns were filled with 5 g of Fe-leonardite. A peristaltic pump delivered an aqueous solution

containing 1 mg L^{-1} As(V) upwards through the column at a fixed flow rate of 0.4 mL min^{-1}. The current

flow rate and the initial concentration of arsenic were set on the basis of the previous batch experiments

results. A fraction collector (Gilson, model FC 203B) was used to collect the different fractions every 20

minutes. Arsenic concentration in each fraction of the effluent was determined as described above.

3. Results and discussion

3.1. Fe-leonardite preparation and characterization

Figure 1 shows the amount of Fe(III) retained by the adsorbent (mg Fe g^{-1} leonardite) versus Fe(III)

concentration in the equilibrium from various initial concentrations among 5-250 ppm. From these data it

can be established that the maximum adsorption capacity is approximately 60 mg Fe (III) /g leonardite.

Based on this value, the impregnation of leonardite was subsequently performed.

Scanning electron micrographs of the raw material and the iron loaded material (Fe-leonardite) are

shown in Figure 2. No significant surface topology changes were evidenced when comparing the

micrographs of both, untreated and treated material. However, the EDS spectra of Fe-treated and untreated

leonardite (Fig 2) showed that the intensity of the peak corresponding to iron increases significantly after

treatment while the peak of calcium decreases. The approximate concentration of iron in Fe-leonardite,

obtained from the spectra, was about 5%. This result was in accordance to those obtained by chemical

analysis of the raw material (1.87 % Ca and 0.98 % Fe) and Fe-leonardite (0.08 % Ca and 5.98 % Fe) and

it suggests that ionic exchange between these two ions may be the mechanism of Fe loading.

3.2. Batch adsorption experiments

3.2.1.pH effect

The protonation degree of arsenate oxyanions depends greatly on pH. Arsenic is commonly present

as negatively charged ions, $H_2AsO_4^-$ or $HAsO_4^{2-}$, within the pH range of natural water. H_3AsO_4 or their fully

deprotonated form AsO_4^{3-} anion may only exist at extreme acid or alkaline pH (pH<2 and pH>10) respectively (Figure 3). Therefore, As adsorption onto Fe-leonardite was studied at a pH range 2-10 in order to determine the optimum pH for the adsorption process. The predominance of the anionic species ($H_2AsO_4^-$ or $HAsO_4^{2-}$) in the pH range studied did not significantly affects As removal efficiency. In this sense, As adsorbed was higher than 96% independently of initial pH at the studied range (Figure 3).

There are different findings described in the bibliography about the effect of pH on arsenic adsorption. According to the literature, the pH effect on arsenic adsorption depends on the type of adsorbent and can not always be explained by arsenic chemical speciation at different pH values. Our results agree with those of Gu et al.(2005), who reported that pH had no obvious effect on As removal from pH 4.4-9.0 in their adsorption study of arsenic on GAC-based iron-containing adsorbents.

In some published works, using other iron-containing sorbents, it has been documented that an increase in the pH values results in a decrease of arsenate adsorption. Vaughan and Reed (2005) reported that As(V) adsorption was highest at low pH values and decreased with increasing pH. Dupont et al. (2007) observed the same pH dependence in a study of arsenic sorption on lignocellulosic substrate loaded with ferric ion. These authors stated that the decrease of arsenate adsorption when the pH increases from 3 to 8 was due to the decrease of the electrostatic attraction between the positively charged surface groups ($FeOH_2^+$) and the anionic arsenate species ($H_2AsO_4^-$ and $HAsO_4^{2-}$) which hinders the formation of surface complexes.

Increasing arsenic sorption with increasing pH has been also described in other works. Payne and Abdel-Fattha (2005) determined arsenate adsorption by iron-treated activated carbon and iron–treated zeolites in the pH interval 2.0–12.0. The % of arsenate sorption by Fe modified activated carbon was enhanced when the pH increased, being most effectively adsorbed in the pH interval 8.0–11.0 (at this pH range the predominant arsenic specie is $HAsO_4^{2-}$). However, Muñoz et al. (2002) studied arsenate removal by Fe(III)-loaded sponges in the pH range 1-12 and found that the best As(V) adsorption corresponded quite well with the predominance pH range of $H_2AsO_4^-$ (from pH 3 to pH 7).

3.2.2. Effect of contact time

The effect of contact time on the uptake of As by Fe-leonardite was studied at 400 ppb concentration. The results are showed in Figure 4. As can be observed, the removal of arsenic was rapid in the first four hours when the decrease of the As concentrations is steepest; more than 50% of the initial arsenic was removed in this time period. This fact might be attributed to the quickly utilisation of most of the available adsorbing sites on the adsorbent surface during this time. The same behaviour has been already observed by other authors (Dupont et al. 2007; Zhang et al. 2004) when using iron-based or iron-loaded adsorption materials. After this initial phase, the adsorption of arsenic was slower and a quasi-steady state was observed after a contact time of 24 hours, so this time was fixed as the equilibrium time for further adsorption tests. Dupont et al.(2007) and Kim et al.(2006) found the same time to reach equilibrium in their experiments using lignocellulosic substrates loaded with iron, even the sorbent dose used in these works was considerably higher than 1 g L^{-1} (this work). Gu et al.(2005) and Zhang et al. (2005) used much higher sorbent doses (3 g L^{-1} and 5 g L^{-1} respectively) than the dose used in the present work. In general a higher sorbent dose, contributed to a fastest initial concentration decrease.

3.2.3. Adsorption Isotherms

The effect of the initial concentration on the uptake of As by Fe-leonardite was investigated by varying the initial arsenic concentration between 10 to 400 ppb. Results are expressed as amount of As removed per gram of adsorbent against the equilibrium concentration. The data of arsenate adsorption were fitted to Langmuir (Eq.1) and Freundlich (Eq.2) isotherm models. The equations used were:

$$q = \frac{q_{\max}K_L C_e}{1 + K_L C_e} \qquad (Eq.1)$$

$$q = K_F C_e^{1/n} \qquad (Eq.2)$$

Here q is the amount of metal ion adsorbed per unit mass of Fe-leonardite, C_e is the As concentration at equilibrium, q_{max} and K_F indicate the adsorption capacity of the adsorbent and K_L and n are constants

relating to adsorption intensity. Both isotherms with the experimental data are presented in Figure 5. Langmuir and Freundlich isotherm parameters obtained are shown in Table 1. Correlation coefficients suggest that both models are suitable for describing the adsorption equilibrium of arsenate by Fe-leonardite.

The comparison of sorption capacity of Fe-leonardite with other adsorbents reported in the literature (Mohan and Pittman 2007; Yadanaparthi et al. 2009) is complicated, mainly due to the variability of conditions under which sorption experiments were conducted, such as the range of initial concentrations the maximum capacity (q_{max}) obtained from Langmuir model varies over a wide range (Mohan and Pittman 2007). A comparison of q_{max} described in studies with similar arsenic initial concentrations than the used in the present work is summarized in Table 2. Fe-leonardite has less adsorption capacity than the iron–impregnated activated carbon (Chuang et al. 2005), but similar or higher adsorption capacity compared with the cost-effective adsorbents obtained from no-activated materials. Moreover, comparing the affinity constant values (K_L) found for the other sorbents, it can be noted that Fe-leonardite has a high affinity for arsenate than the other adsorbents.

3.3. Column adsorption experiments

The batch adsorption tests described above give fundamental information regarding to the performance of a particular sorbent/sorbate pair. However, in the majority of practical (industrial) applications, batch systems are scarcely found. Continuous operation is the most suitable mode from both economical and process control point of view. In this sense, continuous experiments are needed.

The continuous sorption process is usually characterized by the so called breakthrough curves, i.e. a representation of the effluent concentration-time profile in a fixed bed column. Figure 6 shows the breakthrough curve for a 1 ppm As(V) initial concentration solution passing downflow through the column at a fixed flow rate of 0.4 mL min^{-1}. The curve shows the typical s-shape with a steep slope after 55 h. This pattern allows predicting plug flow behaviour for the column, with the mass transfer zone advancing from the inlet to the outlet without axial dispersion. From the concentration profile it is clear that the column could operate for 27 h until a concentration of 10 ppb was measured at the column outlet (limit value recommended by the World Health Organization for drinking water). After 90 h the column was completely saturated and the experiment finished.

The most important criterion for the design of an adsorption column is the prediction of the bed length, the operating lifespan and the regeneration time of the bed. Several simple mathematical models have been stated for breakthrough curves. Among them, the Bohart-Adams (1920), also known as Bed Depth Service Time model (BDSM), and the Wolborska (1989) model are two of the most widely used. While the BDSM ignores both intraparticle mass transfer resistance and external film resistance, Wolborska considers external mass transfer, which is probably a better approach for the hydraulic conditions in a continuous system. Predictions for both models are shown in Figure 6. Wolborska model is usually used for predicting column behaviour at low-concentration range. In this work, the predictions of this model are indeed suitable for the first stages of the experiment, meaning that the sorption process is mass transfer controlled instead of chemical reaction rate controlled. Once the sorbent is almost exhausted, the BDST model seems to give reasonably good predictions of the column behaviour. Moreover, the sorption capacity of the column can be derived from the BDST model. In this sense, a value of 905 µg g^{-1} was obtained; this value is considerably higher than the value obtained from batch experiments. However, this can be related to the higher initial (inlet) concentration used for the continuous test.

4. Conclusions

In this work an arsenic removal material based on a low-cost modified leonardite with iron loading of aproximately 5 % has been developed.

Results showed that As sorption onto Fe-leonardite was not affected by pH in the studied range of 2.0–10.0.

Batch kinetic studies showed that after 2 h, the majority of the As had been adsorbed and equilibrium time was reached at 24 h of contact time. According to the Langmuir isotherm model, the maximum adsorption capacity for As was 322 µg g^{-1} and this material presents a great affinity for arsenate. In continuous mode, results indicate that industrial application can be reproduced with promising results.

These results indicate that Fe-leonardite could be considered a promising material for removing arsenate at low initial concentrations from contaminated water because it is economical and easy to obtain.

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CAPTIONS

Fig. 1. Amount of iron adsorbed (mg Fe g^{-1} leonardite) versus equilibrium concentration.

Fig. 2 SEM and EDS spectra of leonardite (a) and Fe-leonardite (b).

Fig. 3 Effect of pH on As removal by Fe-leonardite.

Fig. 4 Kinetic evolution of the As removal by Fe-leonardite.

Fig. 5 Experimental and theoretical sorption data obtained by Langmuir and Freundlich models for As removal by Fe-leonardite.

Fig.6 Breakthrough curve from column and data fitting by BDST and Wolborska models.

Table 1. Isotherm model constants and correlation coefficients for sorption of As onto Fe-leonardite.

Table 2. Maximum adsorption capacities for As (q max) and Langmuir constants (K$_L$) reported in the literature using different sorbents and those obtained in this study.