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Arsenic(V) sorption on molybdate-impregnated chitosan beads

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Abstract

A new adsorption process for As(V) ion removal from an aqueous solution was studied using molybdate impregnated chitosan beads (MICB). Arsenate ions were strongly adsorbed in the pH range from 2 to 4 with a minimum release of molybdate ions. The sorption mechanism is a complexation between arsenate ions and molybdate ions. Even at low equilibrium concentration, the sorption capacity is high, and allows the process to be used as a finishing treatment. Phosphate ions significantly depressed arsenate collection because of a competing reaction for the active sites. Simultaneously with the arsenate sorption, molybdate is released to a significant extent. This release can be reduced using a treatment of MICB with orthophosphoric acid (to obtain MICB-PO₄). The treatment allows weakly bound molybdenum to be removed from the sorbent during As sorption: molybdate release does not exceed 2%. The Langmuir equation fits best the experimental data for As(V) sorption on MICB-PO₄ at pH 3 up to equilibrium concentration of 80 mg l⁻¹. A selective and total elution can be carried out using a 0.05–1 mol l⁻¹ orthophosphoric acid solution. Three sorption/desorption cycles were performed with no significant decrease in uptake performance.

Keywords: Adsorption; Arsenic; Chitosan; Desorption; Isotherm; Phosphate; Molybdate; Recycling

1. Introduction

Recent epidemiologic studies about arsenic's toxicity and effect on human health involve new guidelines for arsenic in drinking water and in the wastewaters generated in industry [1]. US Environmental Protection Agency was mandated to re-evaluate the maximum contaminant level

(MCL) for arsenic in drinking water for January 2001. In France the environmental standard for industrial wastewaters changed from 0.1 mg l⁻¹ to 50 µg l⁻¹ in February 1998. These elements have raised great interest in the research of effective techniques for arsenic removal. Arsenic is widely distributed in industrial wastewater and natural water in some countries (Chili, India). In industry it is currently used in microelectronics for the manufacturing of GaAs supports [2], as well as in pesticides and wood preservatives. Increased activity in gold mining results in arsenic

contamination of streams and groundwaters. Other mining activities also generate large amounts of contaminated wastewater since arsenic is present as an admixture in molybdenum, lead and copper ores. The wastewater generated during the hydrometallurgical treatment of these minerals usually contains high arsenic levels. Usual treatments for arsenic removal consist of flotation [3], co-precipitation with ferric chloride, sulfide precipitation [4] or lime softening, involving the production of highly toxic sludges, which must be further treated before being environmentally safe for disposal.

As an alternative to these treatments, sorption techniques have been experimented with using activated carbon [5], minerals [6], fly ash [7], industrial wastes [8], coral limestone [9], or biological materials such as living or non-living biomass. However, taking into account the low sorption capacities of these materials and/or the difficulties of using them in column systems, several derived products of biological origin, such as alginate [10], chitin, chitosan [11,12] have been studied as alternatives for metal recovery. While chitosan has been shown to be very efficient for the removal of metals such as uranium, copper, vanadium and molybdenum, with uptake capacities ranging from 2 to 8 mmol g⁻¹ [13–15], for arsenic the uptake levels do not exceed 0.1 mmol g⁻¹ [16], comparable to sorption levels reached using amine modified coconut coir [17].

The modification of sorbent by grafting of ligands has been proposed as a way to improve sorption properties: for example Denizli et al. [18] incorporate a dye-ligand onto synthetic polymers to enhance its metal ion sorption properties. Arsenic sorption on activated carbons can be significantly enhanced by a metal-ion impregnation treatment [19,20]. Such metal-treatment can proceed by adsorption and/or precipitation steps of the corresponding salts into the porous structure of activated carbon. Rajakovic and Mitrovic [20] have shown that the sorption performance for activated carbons is increased by copper impregnation for the removal of As(III), while for As(V) sorption the efficiency is slightly reduced. Recently, Min and Hering [21] have used an impregnation technique for the improvement of arsenate

sorption on alginate beads. The mechanism involved is often an ion exchange/precipitation between the impregnated metal and arsenate ions. However, in most cases, the reuse of the sorbent is difficult to achieve. Thus the development of new processes allowing recycling of the sorbent is needed.

To address this objective in this study we use molybdate ions which have the ability to complex arsenate ions to increase As sorption performance of chitosan. Arsenate can, thus, be eluted from the sorbent selectively by using another complexing agent. Chitosan is a low porous material whose properties are controlled by diffusion so chitosan gel beads have been manufactured [15,22]. In this study arsenic sorption on chitosan gel beads impregnated with molybdate (MICB) was investigated, including a pH optimization, for both the sorption and desorption steps, and the determination of sorption isotherms and kinetics.

2. Materials and methods

2.1. Materials

Chitosan was provided by ABER-Technologies (Brest, France) (Lot No. A17G28). Chitosan characteristics were: pK_a = 6.2, number average molecular mass, MW_n: 125 000, weight average molecular mass, MW_w: 191 000, and deacetylation percentage = 87%. Chitosan gel beads were manufactured using the alkaline coagulation/precipitation procedure of an acetic acid solution of chitosan [15,22]. Bead size was 2.6 mm (± 6%). The water content of the chitosan gel beads was about 95%. Reagents: (NH₄)₆Mo₇O₂₄·4H₂O and Na₂HAsO₄·7H₂O, were purchased from Fluka AG (Switzerland) and Merck (Germany), respectively. Other reagents were purchased from Carlo Erba (Italy).

2.2. Molybdate-impregnation procedure

Previous studies have shown that the optimum pH for molybdenum sorption is around 3, due to a favourable electrostatic balance between the cationic charge of the protonated functions of

chitosan and the high anionic charges of polynuclear hydrolysed molybdate species. Known amounts of wet chitosan beads were put in contact with known amounts (volume–concentration) of ammonium heptamolybdate at pH 3. Dry mass was obtained by weight loss at 105°C. Mo concentration in the sorbent was obtained by mass balance between the liquid and solid phases and was given as a function of the dry mass of chitosan/sorbent. ICP-AES (Jobin-Yvon, France) was used for molybdate analysis in solution. Triplicate experiments showed that the molybdate loading varies by < 5% for different lots of beads, within the accuracy limits of the analytical procedure: the amount of sorbent used in each experiment can be accurately given as a function of the number of beads of sorbent used. MoO₃ content was also obtained by weight loss at 480°C, and deduced from the difference to the dry mass at 105°C. Both methods are consistent with a difference lower than 8%. Total Mo and P (when necessary) concentrations in the gel phase were determined by destroying the gel phase with hydrogen peroxide and nitric acid. Twenty impregnated beads were transferred to a 25 ml volumetric flask, 2 ml of 50% (v/v) hydrogen peroxide and 0.5 ml of 65% (v/v) nitric acid were added and the flask was heated at 90°C in a thermostated bath for 20 min. After cooling the flask was filled with demineralized water. The solution was then filtered through a Whatman filter membrane (pore size 1.2 µm) and the Mo and P concentrations were determined by ICP-AES. Experiments were run in duplicate.

2.3. Arsenate sorption

Preliminary studies had shown that arsenate species are best removed under acidic conditions. For experiments dedicated to the study of the pH effects, the pH was controlled all along the sorption process. For other experiments, unless otherwise specified, the pH was initially adjusted to the optimum pH and was not controlled during metal ion sorption and the final pH was measured. Sorption isotherms were obtained through contact of a varying number of beads (corresponding to known and constant amounts of sorbent) with a

known volume (50 ml) of arsenate solution (concentration: 5, 10 and 20 mg l⁻¹) at room temperature, for at least 120 h. The arsenic concentration was measured by ICP-AES, after filtration through a Whatman filter membrane (pore size 1.2 µm). A control check was carried out to make sure that no unwanted arsenate sorption took place on the experimental apparatus. Concentration in the solid was obtained by a mass balance and hydrolysis procedure using mineralisation of chitosan sorbent with H₂O₂/HNO₃ and further ICP-AES analysis. For the kinetic studies a known amount of sorbent was mixed in 1 l of As(V) solution. At determined times samples were withdrawn and filtered through a 1.2 µm pore size filter before analysis.

The captions of the figures give, where relevant: (a) the Mo-load (mg Mo g⁻¹) with reference to the dry mass of chitosan, (b) the sorbent dosage (SD) with reference to the dry mass of the sorbent and (c) the sorbent dosage (SD_{Mo}) with reference to Mo (mg Mo l⁻¹) (equivalent amount of molybdate per l of solution). The sorbent dosage (SD) has been given to compare As(V) sorption capacity of MICB to that of other sorbents.

2.4. Arsenate desorption

Several elutants were investigated, such as tartaric acid, citric acid and phosphate, by putting a fixed number of chitosan beads (ca. 20 beads) of known arsenate concentration in contact with a fixed volume of elutant (ca. 10 ml) at a controlled pH. Arsenic content was determined by the mineralization procedure and the composition of a single bead was 0.35 mg Mo and 0.03 mg As, respectively.

3. Results and discussion

3.1. pH optimization

Fig. 1 shows the change in As(V) sorption capacity with pH using MICB: the optimum pH appears in a broad pH range (ca. pH 2–4) with a slightly higher As sorption and Mo release at around pH 3. Before molybdate impregnation the

overall charge of the raw biopolymer is positive. This property was used to sorb molybdate and saturate the sorbent: uptake capacity as high as 1000 mg Mo g⁻¹ dry chitosan was obtained. The actual effective mechanism of molybdate sequestration has not been demonstrated: the complexity of molybdate speciation in solution [23] makes difficult the determination of the stoichiometry between Mo and -NH₂ groups [24]. The actual overall charge of the sorbent after molybdate sorption was not clearly established. Arsenate ions at pH ranging between 3 and 4 mainly occur as H₃AsO₄ and H₂AsO₄⁻ [25,26]. According to the speciation diagram for As(V) and P(V) presented

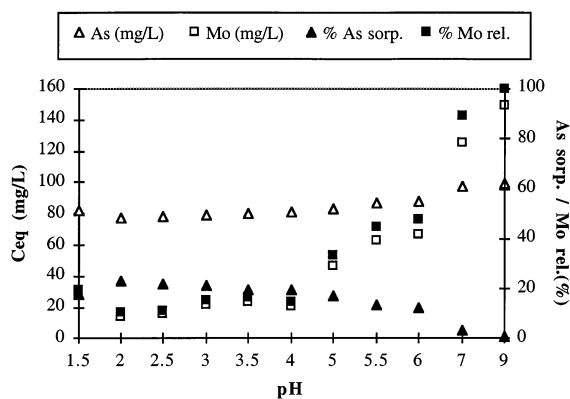


Fig. 1. pH influence on As(V) sorption and Mo(VI) release and Mo(VI) and As(V) equilibrium concentrations (C_o : 100 mg As l⁻¹, Mo-load: 972 mg Mo g⁻¹, SD: 360 mg l⁻¹, SD_{Mo} : 140 mg Mo l⁻¹).

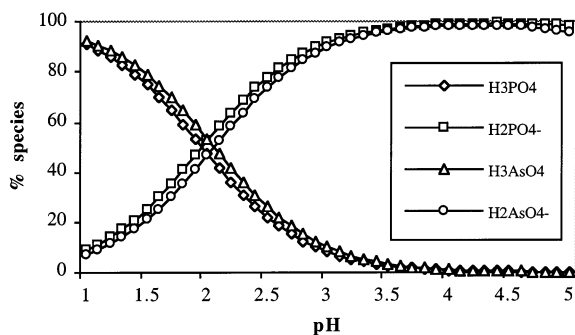


Fig. 2. Speciation diagrams of P(V) and As(V) (computing with Hydraql [27]): pK_a (H₃AsO₄/H₂AsO₄⁻/HAsO₄²⁻/AsO₄³⁻), 2.2/6.7/11.6; pK_a (H₃PO₄/H₂PO₄⁻/HPO₄²⁻/PO₄³⁻), 2.2/7.2/12.4.

in Fig. 2 (calculated using Hydraql software [27] and the stability constants from Charlot [28] and Jekel [29] for phosphate and arsenate, respectively) the predominant arsenate species is H₂AsO₄⁻ between pH 3 and 4. The mechanism involved in arsenate removal by MICB may consist of one or a combination of several reactions including electrostatic attraction, precipitation on molybdate and/or ion exchange. However, Mo(VI) is known to form several complexes in acidic media with As(V), P(V), Si(V) and Ge(IV) [30]. So arsenate sorption is likely to occur through complexation with molybdate ions sorbed on the polymer. Recently Kubota et al. [31] used a molybdate-impregnated activated carbon to sorb As(V) at pH 2 in the first step of an analytical method. The interaction between As(V) and Mo(VI) was explained by the formation of the arsenimolybdate complex on the solid.

In the concentration range investigated in this study, the uptake levels are comparable for IRA-900 [17] and MICB at around 0.7 mmol g⁻¹, while a comparison with Fe(III)-doped alginate beads [21] shows that the latter is significantly higher than the levels exhibited by MICB. Arsenate sorption is followed by molybdate release. The molybdate desorption reaches a minimum in a broad range of pH around 3. At pH 9 molybdate was almost entirely released and arsenate ions were not collected at all. Hence, arsenate sorption can be correlated to the release of molybdate ions from the beads.

Fig. 3 shows the influence of the pH on the sorption isotherms. The influence of the pH is significant in the control of the maximum uptake capacity but also on the steepness of the curve: the initial slope represents the affinity of the sorbent for the adsorbate. At low pH (i.e. pH 1.2), the sorption capacity is two times lower than that obtained at higher pH (ca. pH 2 – 3). For pH 2 and 3 maximum sorption capacity reaches comparable levels, but the sorption is slightly more favourable at pH 2 than at pH 3: the maximum sorption capacity is reached at a lower residual arsenic concentration. Moreover Mo release at pH 3 is twice as high to that observed at pH 2.

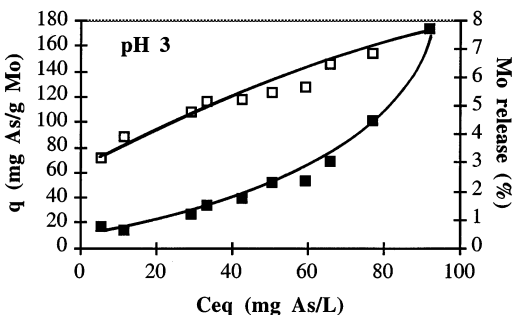
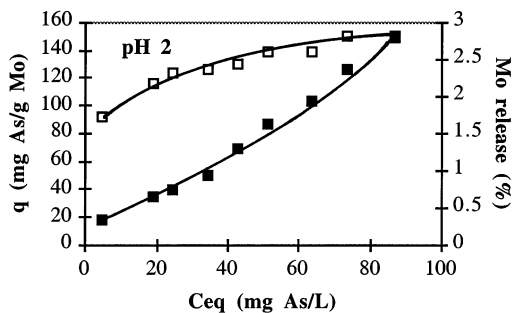
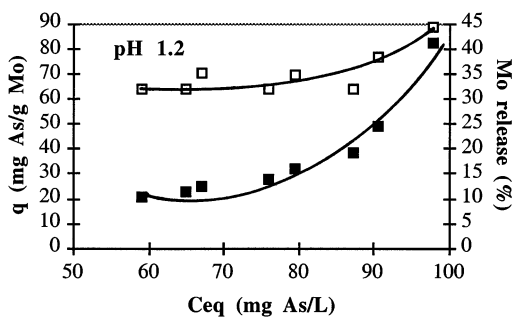


Fig. 3. pH influence on As(V) sorption capacity (opens symbols) and Mo(VI) release (filled symbols) using MICB (Mo-load: 1033 mg Mo g⁻¹).

3.2. Influence of As(V) concentration and sorption isotherms

Fig. 4 shows the effects of the initial arsenic concentration and sorbent concentration on both arsenic removal and molybdate release. Obviously, increasing the sorbent concentration involves a reduction in As(V) removal. The percentage of molybdate released from the sorbent decreases with increasing sorbent dose. Increasing the amount of sorbent involves a

decrease in the residual arsenic concentration. The weakly bound fraction of molybdate is, thus, less attracted by residual arsenic in solution and the release of molybdate is decreased. Molybdate stability on the beads is, thus, improved by high sorbent concentration.

Increasing the initial concentration also increases uptake capacities. This is confirmed by Fig. 5, which shows the sorption isotherms obtained with three different initial arsenate concentrations with varying sorbent mass. The sorption isotherms seem to be independent of the speciation of arsenate in this concentration range (0–20 mg As l⁻¹). This result contrasts with the behaviour of several other metals for which the hydrolysis mechanisms can significantly affect the affinity of the sorbent for the adsorbate [24]: the speciation of metal ions depends on both total metal concentration and pH, which in turn influences the affinity of the sorbent for the metal

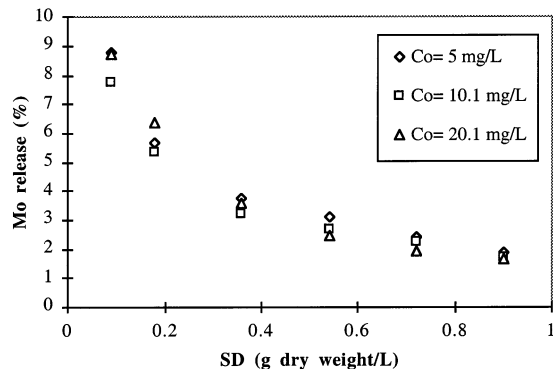
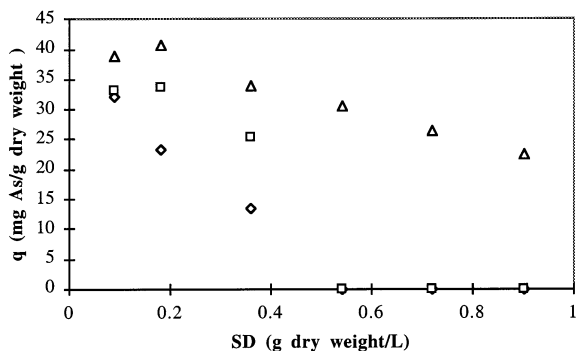


Fig. 4. Effect of initial concentration and SD on As(V) sorption and Mo(VI) release using MICB at pH 3 (Mo-load: 1033 mg Mo g⁻¹).

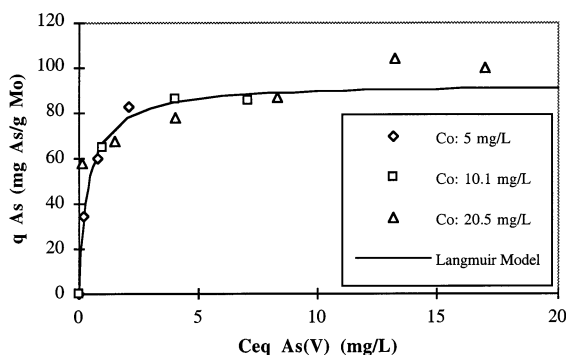


Fig. 5. As(V) sorption isotherms on MICB at pH 3 (experimental points and Langmuir modeling curve) (Mo-load: 972 mg Mo g⁻¹).

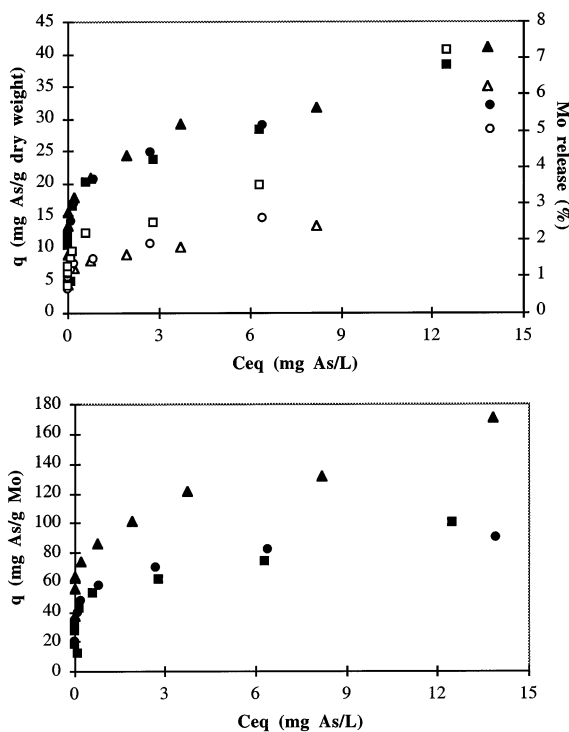


Fig. 6. Effect of Mo content on As(V) sorption (filled symbols) and Mo(VI) release (open symbols) as a function of As(V) concentration by MICB at pH 3 (■/□: 1047, ●/○: 942, ▲/△: 492 mg Mo g⁻¹).

species which predominate. Langmuir equations were used to determine the sorption parameters: the maximum sorption capacity at the monolayer saturation equals 92.95 mg As g⁻¹ Mo, while the

affinity coefficient equals 2.56 l mg⁻¹. The corresponding curve is plotted in Fig. 5:

$$q = \frac{92.95 \times 2.56 C_{eq}}{1 + 2.56 C_{eq}}$$

3.3. Influence of Mo(VI) content on the As(V) sorption isotherm

Fig. 6 shows the influence of Mo(VI) loading on As(V) sorption. The first part of this figure shows that the apparent adsorbed amounts are independent of the molybdate content, if the sorption capacity is expressed as a function of the Mo-impregnated sorbent mass (total mass), while the second part of this figure presents the sorption as a function of the sorption capacity relative to molybdate content. In the latter case increasing the molybdenum content decreases the sorption capacity. This surprising trend may be explained by the co-existence of two kinds of molybdate in the sorbent: a part of the molybdate which has been adsorbed is tightly bound to the polymer network, while another part of the molybdate is weakly bound in the internal volume of the sorbent (similarly to an absorption process), the latter being readily desorbed from the sorbent while the former is more stable. Increasing the amount of molybdate in the sorbent may result in an increase in the proportion of the labile molybdate which is easily released to the solution where it may be complexed with arsenate ions: arseni-molybdate complex is then adsorbed with more difficulty on the sorbent and the sorption capacity decreases.

Molybdate release is almost independent of the Mo content, in percentage, and usually lower than 1.5%, with the exception of the higher As residual concentrations, for which the binding of labile molybdate to arsenate displaces the molybdate sorption equilibrium from the solid to the solution, as suggested above (Fig. 6).

3.4. Effect of competitor ions on As(V) sorption capacity

In order to test the efficiency of the sorbent for the treatment of industrial and/or natural

effluents, the influence of some metal cations (Pb^{2+} , Fe^{2+} , Fe^{3+} , Zn^{2+} , Mn^{2+} , Cu^{2+}) and anions (phosphate, chloride) frequently found in such effluents has been considered. Figs. 7 and 8 show the relative variation of the sorption capacity with several concentrations of co-existing ions: concentration ranges were chosen with reference to the concentrations found in the acid mine drainage effluents of an old polymetallic (Pb/Ag)

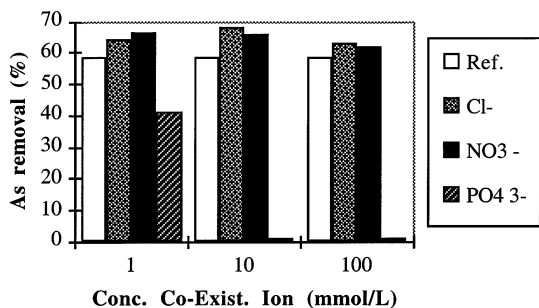


Fig. 7. Effect of co-existing anions on As(V) sorption by MICB at pH 3 (C_0 : 20 mg As l^{-1} , SD: 360 mg l^{-1} , SD_{Mo} : 140 mg Mo l^{-1}).

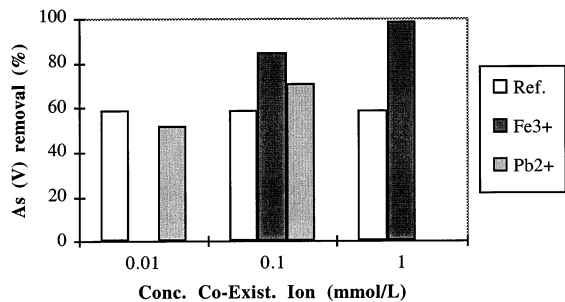
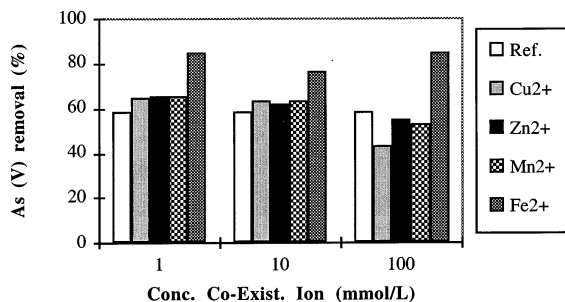


Fig. 8. Effect of co-existing cations on As(V) sorption by MICB at pH 3 (C_0 : 20 mg As l^{-1} , SD: 360 mg l^{-1} , SD_{Mo} : 140 mg Mo l^{-1}).

mining site, containing arsenic. While chloride and nitrate ions have no significant effect on arsenic removal, arsenic sorption is strongly depressed by phosphate ions (Fig. 7). Similar observations are cited by Ohki et al. [9]. This competition is probably explained by the similar chemistry of arsenate and phosphate in aqueous solution: both anions are able to form complexes with molybdate ions in solution. However, the influence of phosphate ions depends on the phosphate excess: for a 3.7 P/As molar ratio, the sorbent efficiency is only reduced by 30%, while for a 37 P/As molar ratio (or higher), arsenic cannot be removed from solution by MICB. The lack of effect of nitrate and chloride proves that the sorption mechanism may be interpreted as a complexation rather than a simple ion-exchange process.

The presence of Cu^{2+} , Mn^{2+} , Zn^{2+} and Pb^{2+} even in large excess, has no significant effect on arsenic removal: the largest reduction in sorption efficiency does not exceed 25% (Fig. 8). Ferrous and ferric ions seem to increase by 30% the efficiency of the treatment. Ferric ions were used to dope sorbents for arsenic removal [21], and the present effect may be due to arsenic bridging with ferric ions: ferric ions were detected on the beads by analysis of the exhausted sorbent.

3.5. Kinetic studies

Kinetic curves of As(V) on MICB for three concentrations are presented in Fig. 9. For each of these initial concentrations, a relatively rapid adsorption takes place during the first 8 h, followed by a slow sorption which lasts from 1 to 4 days. Similar kinetics were observed with mineral sorbents [6], copper-impregnated activated carbon [32] and chrome wastes [8]. For a 20 mg l^{-1} concentration, equilibrium is reached within 25 h. On the other hand, for an initial concentration of 5 mg l^{-1} 70 h are necessary to reach equilibrium. The higher the concentration, the faster the sorption. Similar results for the adsorption of Cr(VI) on chitosan beads were obtained by Bosinco et al. [33], who demonstrated that the adsorption process is kinetically slow and mainly controlled by an ion diffusion step through the polymer.

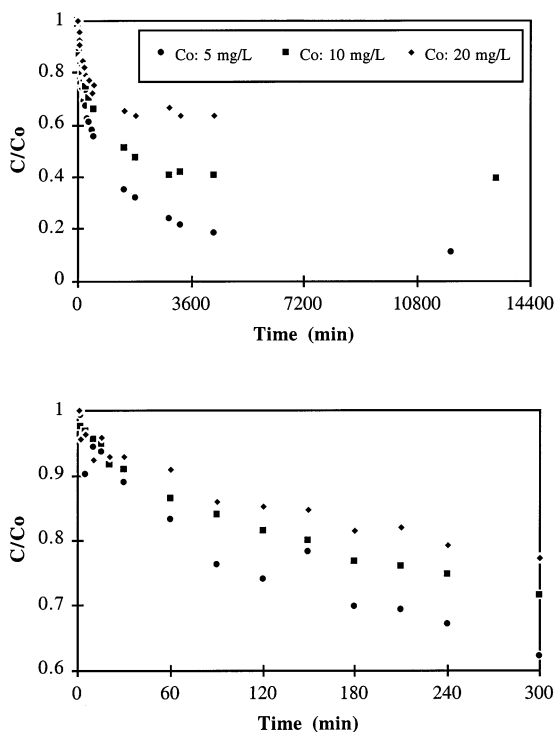


Fig. 9. Kinetic sorption of As(V) by MICB (C_o : 20/10/5 mg l^{-1} , SD: 180 mg l^{-1} , SD_{Mo} : 70 mg Mo l^{-1} , Mo-load: 972 mg Mo g^{-1}).

Sorption kinetics were carried out at a lower pH (i.e. pH 2.5) to verify whether this parameter has a direct influence on the kinetics. It appears (results not shown) that the kinetic curves perfectly overlap: the pH has no significant effect on mass transfer at low pH.

Table 1
Arsenic desorption and molybdenum release from MICB^a

| | Tartaric acid (0.1 M) | Tartaric acid (0.01 M) | Tartaric acid (0.001 M) | Citric acid (0.1 M) | Citric acid (0.01 M) |
|-------------------|-----------------------|------------------------|-------------------------|---------------------|----------------------|
| pH | 2.06 | 2.5 | 3.05 | 2.12 | 2.55 |
| As desorption (%) | 80 | 64 | 8.5 | 100 | 100 |
| Mo release (%) | 60 | 58 | 10 | 86 | 63 |

^a Twenty beads in 10 ml, contact time: 48 h.

3.6. Desorption

To be economically attractive, the treatment of arsenic wastes using MICB, requires the regeneration of the exhausted sorbent. This regeneration was studied by determining the ability of the arsenic to be stripped selectively from the functionalized sorbent, using several elutants such as citric acid, tartaric acid and phosphate. Several elutants are able to desorb arsenate efficiently, however, in many cases molybdate is also released. A simultaneous release of molybdate and arsenate ions does not actually allow the ions to be selectively separated, moreover it also restricts the possibility to re-use the sorbent (Table 1). In the literature arsenic elution is achieved by using strong acidic or alkaline solutions [25], these studies show that As(V) desorption is often coupled with a simultaneous release of the metal which is used for the impregnation, in acid media. With a neutral solution the metal-impregnated sorbent is stable, however, the desorption efficiency is very low. The best results are obtained with alkaline solutions.

The best results with MICB sorbents were obtained with phosphate (Fig. 10). Whatever the fixed pH, desorption efficiency increases with phosphate concentration, while, for a fixed concentration in phosphate, the influence of pH is not significant. Whatever the pH may be, an increase in phosphate concentration involves an increase in molybdate desorption. At a fixed phosphate concentration, increasing the pH involves a large increase in molybdate release.

The optimization of the regeneration of the sorbent has to take into account both pH and phosphate concentration. To address this objec-

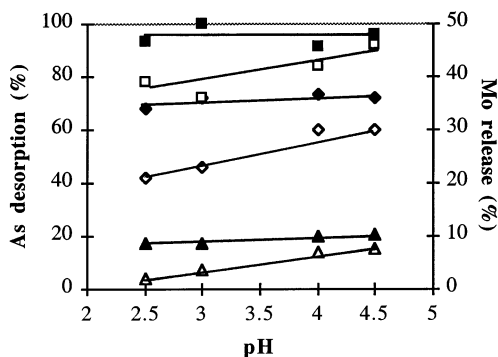


Fig. 10. As(V) desorption (filled symbols) and Mo(VI) release (open symbols) from MICB with phosphates ions at different concentrations (■/□: 0.1 M, ◆/◇: 0.01 M, ▲/△: 0.001 M) (20 beads in 10 ml, Mo-load: 972 mg Mo g⁻¹).

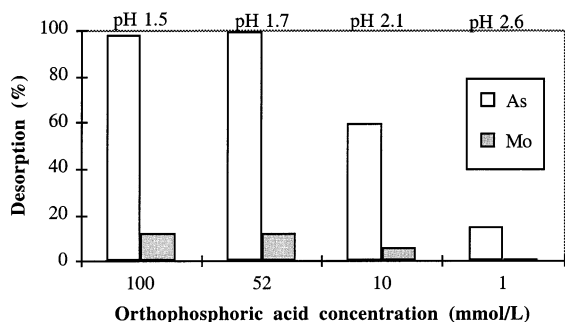


Fig. 11. As(V) desorption and Mo(VI) release from MICB with orthophosphoric acid (20 beads in 10 ml, Mo-load: 972 mg Mo g⁻¹).

tive orthophosphoric acid was carried out at four different concentrations (Fig. 11). Increasing the concentration up to 52 mM increases arsenic desorption, above this concentration desorption is not increased and molybdate release is slightly increased. Total arsenic recovery was obtained with a 52 mM solution which results in a molybdate release which does not exceed 15%. A com-

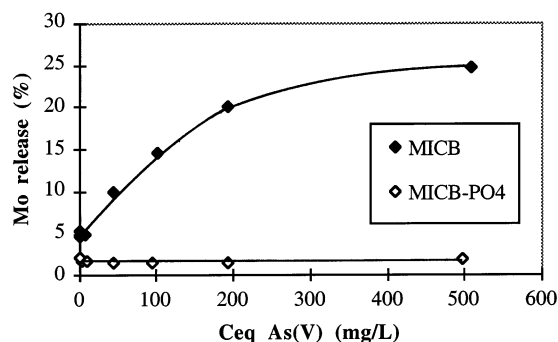


Fig. 12. Mo release as function of As(V) equilibrium concentration: comparison of MICB (Mo-load: 1033 mg Mo g⁻¹) and MICB-PO4 (Mo-load: 972 mg Mo g⁻¹) (20 beads in 50 ml).

plete separation of molybdate and arsenate seems, thus, to be difficult to achieve with this conditioning of the sorbent.

3.7. Modification of the sorbent-reduction of molybdate release

MICB sorbents treated with orthophosphoric acid (MICB-PO4) were prepared by mixing MICB in a 0.1 molar solution of orthophosphoric acid for 24 h followed by extensive rinsing with demineralized water. Total Mo and P concentrations in the gel phase were determined by the analytical procedure described above. The main chemical characteristics of the sorbents (MICB and MICB-PO4) are presented in Table 2.

Fig. 12 shows the difference in the molybdenum release for both MICB and MICB-PO4 sorbents. It clearly demonstrates that the molybdate release does not exceed 2% with MICB-PO4, even at high residual arsenic concentration, while the native sorbent (MICB) releases almost 25% in large excess of arsenic. The chelation of As(V) by Mo(VI)

Table 2
Characteristics of the sorbents

| | Dry weight/bead (mg) ^a | Total Mo/bead (mg) | Total P/bead (μg) |
|----------|-----------------------------------|--------------------|-------------------|
| MICB | 0.900 ± 0.05 | 0.350 ± 0.005 | – |
| MICB-PO4 | 0.900 ± 0.05 | 0.280 ± 0.005 | 38 |

^a Loss on ignition at 105°C.

in solution, which occurs when molybdate is released from the MICB reduces its sorption capacity, is not observed to the same extent with MICB-PO4. The systematic leaching of large amounts of molybdenum observed on the raw material suggests that molybdate ions present in the sorbent may be separated in two fractions: molybdenum strongly bound to the polymer network, and molybdenum simply absorbed in the gel phase of the sorbent. The latter is the weakly bound molybdenum which is readily displaced by arsenic binding in solution. In the case of MICB-PO4 orthophosphoric acid treatment displaces 20% of the initial amount of molybdate: it allows the weakly bound molybdate to be removed and

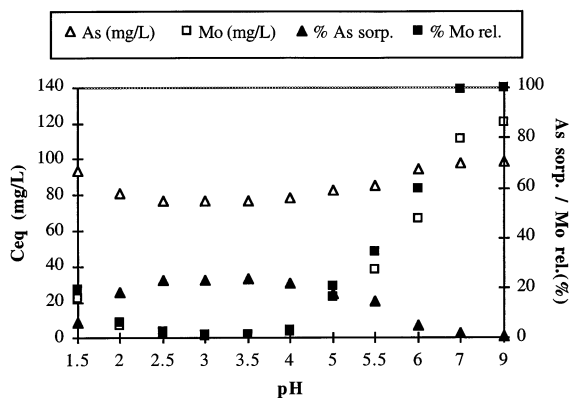


Fig. 13. pH influence on As(V) sorption and Mo(VI) release; and Mo(VI) and As(V) equilibrium concentrations (C_o : 100 mg As l^{-1} , Mo-load: 778 mg Mo g^{-1} ; SD: 360 mg l^{-1} , SD_{Mo} : 112 mg Mo l^{-1}).

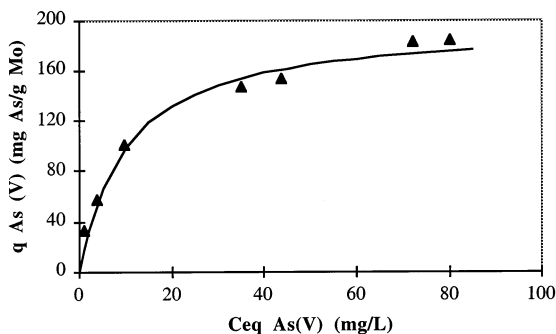


Fig. 14. Sorption isotherm of As(V) on MICB-PO4 at pH 3 (experimental points and Langmuir modeling curve) (Mo-load: 972 mg Mo g^{-1}).

to overcome the problem of molybdate release which occurs when significant amounts of arsenate are present in solution.

Fig. 13 presents the influence of the pH on As(V) removal using MICB-PO4, and can be compared to Fig. 1 obtained with MICB. The optimum pH is obtained around pH 3: As(V) sorption is maximum and Mo(VI) release minimum. This trend is slightly different to that obtained with MICB for which the optimum pH range was broader and for which molybdate release was increased while arsenic sorption was reduced in comparison to the levels observed with MICB-PO4 in similar experimental conditions.

Isotherms were obtained with MICB-PO4 (Fig. 14). This sorbent is characterized by a higher capacity for arsenate ions than MICB, uptake capacity is increased 2-fold by the orthophosphoric acid treatment. This enhancement is directly connected to the removal of weakly bound molybdate. Molybdate release in the solution is decreased and arsenate ions are not complexed by free molybdate species. The change in sorption capacity is thus attributed to an increase in the relative proportion of active molybdenum in the sorbent. It also induces a reduction in the competition of free-molybdate in solution (released from the sorbent) with sorbent-fixed molybdate for arsenic binding.

The Langmuir model best fits the isotherm data. Non-linear least square regression was used for the determination of the isotherm constants and q_m and b were found to be, respectively, $q_m = 198$ mg As g^{-1} Mo and $b = 1.2$ l mg^{-1} .

3.8. Recycling of the sorbent

Preliminary results have shown that arsenate can be removed again on the regenerated sorbent. Further studies will be devoted to the estimation of the maximum number of sorption/desorption cycles to be used, and to the reactivation techniques to be applied for a longer sorbent life. This study was conducted in order to find out whether arsenate ions were able to bind with molybdate when phosphate ions are on the active site. Table 3 shows the results of three cycles of adsorption-desorption using a 0.1 molar solution of H_3PO_4 .

Table 3
As(V) adsorption–desorption and Mo(VI) release over three cycles using packed bed column systems^a

| | Adsorption 1 | Desorption 1 | Adsorption 2 | Desorption 2 | Adsorption 3 | Desorption 3 | Total sorp- tion | Total des- orption |
|-----------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|---------------------|-----------------------|
| As sorption (mg) | 14.7 | 11.1 | 8.5 | 9.0 | 11.1 | 9.6 | 34.3 | 29.7 |
| Molybdate release (%) | 0.9 | 0.3 | 0.5 | 0.3 | 0.6 | 0.3 | – | 3 |

^a Two-hundred beads of MICB-PO4, diameter 1.5 mm, desorption carried out with 20 ml 0.1 M orthophosphoric acid solution.

Experiments were carried with 200 MICB-PO4 beads packed in a 15 mm-diameter glass column. The arsenate acidic solution (pH 3) at a concentration of 153 mg l⁻¹ was injected through the column until saturation. The effluent was analysed for both As and Mo content. The total mass of As sorbed was evaluated by mass balance equilibrium. The desorption step was carried out with 20 ml H₃PO₄ (0.1 mol l⁻¹). The concentration factor in the elutant reached 10 under the experimental conditions. The three cycles were carried out with MICB-PO4, in which weakly bound molybdate had been eliminated. Thus, release of molybdate was very low during both the adsorption and desorption process. Table 3 shows the results obtained for these three cycles and shows that molybdate release does not exceed 3% over the three cycles, while the total arsenic desorption reaches 87%.

An important finding is that arsenate can be sorbed again even if phosphate is present in high concentration, resulting from the presence of residual phosphate after the desorption step. It suggests that As(V) affinity for the sorbent is better than for PO₄³⁻. Computing the binding constant *b* from the isotherm data obtained for arsenate and phosphate sorption on MICB allows this hypothesis to be confirmed: *b* (As(V)) = 203.6 l mmol⁻¹, *b* (P(V)) = 31.0 l mmol⁻¹.

The mechanism of desorption is thought to occur by complexation between PO₄³⁻ and Mo: phosphates ions take the place of arsenate ions on the active sites. Moreover, the phosphomolybdic complex is well known and used for the colorimetric determinations of orthophosphates in solution [34]. Furthermore, phosphate is structurally

and electronically similar to As(V) and exhibits comparable p*K*_a values. At 0.1 mol l⁻¹ (corresponding to pH 1.6) H₃PO₄ is the predominant form among phosphate species, and this neutral form is not able to interact with the sorbent by ion-exchange mechanisms.

4. Summary and conclusions

Molybdate-impregnated chitosan beads were shown to be an effective mean for arsenate removal, reaching high relative sorption capacities even at low residual arsenic concentrations. At pH 2–3 arsenate sorption is maximum and the release of molybdate is minimum. The yield of Mo(VI) release is mainly a function of the arsenic concentration in solution, and is almost independent of the Mo(VI) concentration in the sorbent. Molybdate appears to be bound to chitosan by two different mechanisms and two different strengths: a weakly bound fraction readily released and a tightly bound fraction less desorbable. The fraction of molybdate which is released is able to complex arsenic in solution: this complexation reduced the ability of arsenic to be sorbed on the polymer. An excess of molybdate in the sorbent increases the amount of releasable molybdate. The study of the effect of pH confirms that arsenate sorption efficiency and capacity can be correlated to the release of molybdate ions from the sorbent. At moderate pH molybdate desorption is increased, arsenate may be complexed by molybdate in solution: sorption on immobilized molybdate is thus in competition with free molybdate ions.

Arsenate species are more negatively charged at pH 4 than at pH 2.5 (99 and 75% of H_2AsO_4^- form at pH 4 and 2.5, respectively, Fig. 2). However, the extent of As(V) sorption remained unchanged within this pH range, leading to the conclusion that the adsorption does not occur by ion exchange. The mechanism is likely to occur through complexation between arsenate and molybdate ions, since the molybdoarsenate complex is well-known and currently used for the colorimetric determination of arsenate ions in solution [28]. However, the chemistry of the molybdo-arsenic anions is very complex and only a predominance of several species has been established depending on pH and concentration of both anions. A recent study of the As(V)–Mo(VI) system carried out by Himeno et al. [35] shows that in acidic conditions several complexes can be formed involving the following ratios between As and Mo: 1/10, 2/36 and 2/18.

The change in pH during metal sorption on chitosan can be explained by both metal chemistry in solution and protonation of the amino groups of chitosan. However, during arsenate sorption, pH varies little even with a high concentration of beads. During the sorption process, neither OH^- nor H^+ is released in the solution, which confirms that the mechanism is different to the usual mechanism involved in metal anion accumulation on chitosan-based sorbents. This interpretation is confirmed by the lack of effect of chloride and nitrate ions on As(V) removal since a reduction in sorption performances would be expected for ion-exchange process.

Arsenate desorption can be performed in an acidic medium in the presence of phosphate: desorption efficiency can exceed 95%. A 0.1 molar solution of orthophosphoric acid appears to be the optimum for high arsenic desorption and low molybdenum release.

Current investigations are dedicated to the simplification and optimization of the sorbent fabrication procedure involving a single bead-production and molybdate-impregnation procedure, and the study of sorption/desorption properties of the new sorbent.

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