

Ion exchange equilibria of arsenic in the presence of high sulphate and nitrate concentrations

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Abstract The aim of this work was to develop a quantitative description of the ion exchange equilibria of arsenic on a strong anionic resin, in the presence of nitrates and sulphates. First, the ion exchange equilibrium data of As(V) and NO_3^- on a strong anionic resin in chloride form were obtained and described with a model based on the mass action law. Namely, assuming ideal behaviour for both solution and resin phase, the thermodynamic constant of the $\text{As(V)}/\text{Cl}^-$ and $\text{NO}_3^-/\text{Cl}^-$ ion exchange equilibria were estimated by fitting of experimental data. Then, these equilibrium constants were used to predict the ion exchange behaviour of the ternary system $\text{As(V)}/\text{NO}_3^-/\text{Cl}^-$, providing a rather good agreement with experimental results. The ion exchange equilibria involving sulphate ions were also studied, showing a very high affinity to the resin phase. This behaviour did not allow a quantitative robust modelling of the equilibrium pattern. The results discussed in this paper represent a first step toward the development of a comprehensive modelling of the ion exchange process for the removal of As(V) from surface and groundwater in the presence of competitive, naturally occurring anions.

Keywords Arsenic; ion exchange; nitrate; sulphate

Introduction

Arsenic is a naturally occurring inorganic drinking water contaminant, which has been recognized as an acute toxin for a long time. Several recent studies have indicated that prolonged exposure to arsenic contaminated water with concentrations of $50 \mu\text{g/L}$ may yield carcinogenic effects. Thus, recently, the World Health Organization (WHO) has suggested reduction of the maximum allowable arsenic concentration in drinking water to $10 \mu\text{g/L}$, and the United States Environmental Protection Agency has proposed an arsenic maximum contaminant level of $5 \mu\text{g/L}$.

Contamination of both surface and groundwater by arsenic is a widespread problem due to natural processes, such as soil erosion and leaching, and anthropogenic sources, e.g. effluents from metallurgical activities, glassware and ceramic production, dye and pesticide manufacturing, and petroleum refining (Viaraghavan *et al.*, 1999).

In water supplies, arsenic is generally present in the inorganic form. In surface waters, being an oxidizing environment, the pentavalent form As(V), i.e. arsenic acid H_3AsO_4 and the arsenate species, prevail. On the contrary, in groundwater, being an anaerobic reducing environment, the trivalent form As(III), i.e. arsenious acid H_3AsO_3 and the arsenite species, are predominant. As noted by Vagliasindi and Benjamin (2001), occurrence of sequential oxidation and reduction reactions was observed to take place in the same system over a period of days or weeks, whereas in other systems both oxidation and reduction seemed to be proceeding simultaneously. The different oxidation status has also a recognized effect on its toxicity, which is ten times higher for As(III), but also on its mobility in the environment, once again higher for As(III), which is not expected to be absorbed strongly. The distribution of the ionized and un-ionized forms of As(III) and

As(V) depends significantly on the pH level of the solution. At typical pH of natural waters, As(III) is commonly found in the undissociated form, whereas As(V) is in the mono- or di-valent ionic form. Since arsenic may be found in or eventually converted to the ionic form, ion exchange has already been considered in the literature among the feasible treatment processes of arsenic contaminated water. Vagliasindi and Benjamin (1998) reported about the influence of natural organic matter (NOM) on breakthrough experiments in packed bed adsorption reactors, showing that NOM did not affect the system performance; the same authors also investigated the influence of As(III)–As(V) redox cycles on As breakthrough experiments (Vagliasindi and Benjamin, 2001). Packed bed ion exchange experiments were also performed by Baes *et al.* (1997) and Korngold *et al.* (2001), confirming good removal performance of the process.

One of the main drawbacks to the use of ion exchange for arsenic removal from potable water is due to the presence of other ions, such as sulphates or nitrates, that can effectively compete with As(V) for ion exchange sites (Kim *et al.*, 2003). This results in a fast saturation of the ion exchange column, reducing to unacceptable levels the lifetime of the ion exchange column before its regeneration.

Recently, Kim *et al.* (2003) have proposed a novel process based on advanced ion exchange operation (AIXO), where two ion exchange columns are operated in series. The upstream column is regenerated after the As(V) rich zone has been completely eluted from the upstream column, but long before As appears in the effluent from the downstream column. The regenerated column is then returned to the system in the downstream position and the process is then repeated. Using this configuration, arsenic is accumulated in the system, cycle after cycle. The regeneration step is performed on a column saturated by sulphates, whereas the brine is recycled after sulphate removal by precipitation as barium or calcium salt. Kim *et al.* (2003) have demonstrated the feasibility of this process for the treatment of potable water containing 40 µg/l As(V) and 80 mg/l sulphates. Kim and Benjamin (2004) have then applied this process to water containing up to 40 µg/l As(V), together with sulphates from 80 to 125 mg/l and nitrates from 30 to 60 mg/l, and also proposed a short-cut modelling of the process. Accumulation of nitrate in the brine was shown to reduce the brine regeneration efficiency to the point that the brine would have to be disposed of. Despite some information on the breakthrough behaviour of the As/NO₃⁻/SO₄²⁻ system on ion exchange resin having been provided in the above cited papers, it is worth noting that no data on the ion exchange equilibrium of As, alone or in the presence of competing ions, are available in the literature. These data would be of great help in understanding the fundamentals of competitive ion exchange of arsenic and other anions, and could provide a sound reference for a proper process development.

The scope of this work was to describe the ion exchange equilibria of the As/NO₃⁻/SO₄²⁻ system on an anionic resin in chloride form. To this aim, equilibrium data of the binary systems As/Cl⁻, As/NO₃⁻ and As/SO₄²⁻ and of the ternary systems As/NO₃⁻/Cl⁻ and As/SO₄²⁻/Cl⁻ were collected. The ion exchange equilibria of binary systems were fitted with a model based on two mass action laws; such a model was finally applied to predict equilibrium data of the ternary systems.

Methods

Reagents

The resin for arsenic removal was an anionic strong basic resin, Amberlite IRA 400, supplied in chloride form and used as received, without any conditioning step.

Equilibrium experiments

Equilibrium tests were performed in a Jar Tester (Velp Scientifica, Italy), provided with ten 500 mL volume Pyrex beakers. In this apparatus a proper mixing is obtained by means of a blade mixer, connected to a shaft rotating at 2 Hz. Each beaker, properly wrapped in an aluminium foil so as to avoid any photochemical effect, was first filled with 0.5 L of a solution containing sodium arsenate and sodium sulphate, prepared in order to achieve a 5 mg/L initial As(V) concentration and with different sulphate concentrations, up to 200 mg/L and/or nitrate concentrations up to 30 mg/L. Hydrogen peroxide (100 μ L) was added to each beaker, to keep a positive oxidation–reduction (Redox) potential during the whole duration of the experiment, which would keep arsenic in its original pentavalent oxidation state. A given amount of ion exchange resin, in the range between 0.01 and 1.00 g, was then added to each beaker. Based upon preliminary tests, the duration of all experiments was set to 24 hours, which was considered sufficient for achieving equilibrium conditions. Arsenic, sulphate and nitrate concentrations in the liquid phase were measured at the beginning and at the end of each test, by following the methods discussed below. The amount of arsenic, sulphates and nitrates exchanged on the resin was calculated through a simple mass balance.

Ion exchange capacity

The effective ion exchange capacity (q_o) of the tested resin was evaluated using three conditions in terms of solution composition and resin amount:

1. 100 mg/L NO_3^- solution; resin amount: 1 g;
2. 5 mg/L As(V) solution; resin amount: 0.1 g;
3. 240 mg/L SO_4^{2-} solution; resin amount: 1 g.

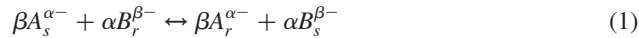
Each of the above solutions was mixed in a 500 mL beaker with the corresponding resin amount and stirred in the jar tester for 24 hours. Then, the resin was allowed to settle and a sample of the supernatant was drawn and analyzed for its residual As(V) concentration. The resin, once separated from the liquid phase, was air dried and then put into contact with a new solution with the same composition as the initial one. The test was repeated several times, until no further uptake by the resin was observed. The effective ion exchange capacity was obtained by adding the uptake values measured in each test.

Analytical methods

The concentration of As(V) was determined using a slightly modified version of the well known Ficklin method (Ficklin, 1983). Namely, Pyrex columns (130 mm length and 15 mm diameter) were packed with 2.3 g of a strong basic resin (Dowex 1X8, 100–200 mesh). A 3 mL volume of 1 M sodium hydroxide was fed to the column, so to convert it into the hydroxide form. After rinsing with 15 mL of ultrapure water, the resin was converted to the acetic form by flowing 5 mL of 1 M acetic acid and rinsed again with 15 mL ultrapure water. Then, a 5 mL sample to be analyzed for arsenic was fed to the column and the resulting 5 mL eluate from the column was collected; then 25 mL of 0.12 M hydrogen chloride is fed to the column and the resulting eluate is separately collected in five consecutive fractions (5 mL each). In this way, a total of six consecutive fractions was obtained: the first three fractions containing only As(III), whereas the last three fractions were made up only of As(V). Each fraction was then analyzed for arsenic concentration by means of a Model 3030B Atomic Absorption Spectrophotometer (Perkin-Elmer, USA) using the hydride method (American Public Health Association/American Water Works Association/Water Environment Federation, 1998). Concentrations of other anions (nitrate, sulphate, chloride) were obtained by a Model 761-IC Ion Chromatography system (Metrohm), using a DualOne column (Metrohm).

Modelling of ion exchange equilibria

The design of ion exchange systems for water treatment requires the accurate simulation of multicomponent ion exchange equilibria, accounting for all competing ions (Melis *et al.*, 1995). The typical approach is to develop thermodynamic models which, based on binary equilibrium data, can predict multicomponent equilibria. This result can be achieved by modelling the ion exchange equilibria by means of a model based on the law of mass action. In this view, the ion exchange process occurring on an anionic resin can be considered as a chemical equilibrium reaction:



where $A^{\alpha-}$ and $B^{\beta-}$ are the two exchanging anions, whereas r and s refer to the resin and solution phase, respectively. Since Equation (1) can be considered as a chemical equilibrium reaction, the corresponding equilibrium constant, assuming ideal behaviour of both solution and resin phase, is given by:

$$K = \frac{(q_{A_r^{\alpha-}})^{\beta} (C_{B_s^{\beta-}})^{\alpha}}{(C_{A_s^{\alpha-}})^{\beta} (q_{B_r^{\beta-}})^{\alpha}} \quad (2)$$

where q_i and C_i are the concentrations in the resin and solution phase, respectively.

The ionic fraction of the generic i th ionic species in solution (x_i) and in the resin phase (y_i) are defined as follows:

$$x_i = \frac{\nu_i C_i}{\sum_{k=1}^N \nu_k C_k} = \frac{\nu_i C_i}{N} \quad y_i = \frac{\nu_i q_i}{\sum_{k=1}^N \nu_k q_k} = \frac{\nu_i q_i}{q_o} \quad (3)$$

where ν_i is the charge of the i th anionic species, N is the solution normality, q_i is the solute concentration in the solid phase and q_o is the total capacity of the resin.

Substituting Equation (3) in Equation (2), the equilibrium constant becomes:

$$K = \frac{(y_{A_r^{\alpha-}})^{\beta} (x_{B_s^{\beta-}})^{\alpha}}{(x_{A_s^{\alpha-}})^{\beta} (y_{B_r^{\beta-}})^{\alpha}} \left(\frac{q_o}{N} \right)^{\beta-\alpha} \quad (4)$$

The equilibrium constant can be evaluated by fitting of experimental ion exchange equilibrium data. As discussed in Melis *et al.* (1995), the ion exchange equilibria of a multicomponent system, made by three components, may be predicted if the equilibrium constants of at least two binary sub-systems are known. This approach was applied to the ternary systems discussed in this paper. Namely, with reference to the $\text{As}/\text{NO}_3^-/\text{Cl}^-$ system, first the two binary equilibrium constants $K_{\text{As}/\text{Cl}}^-$ and $K_{\text{As}/\text{NO}_3}^-$ were estimated by fitting of experimental data. Then, ternary equilibrium predictions were obtained using these constants in the framework of the mass action law model and compared with ternary experimental data.

Results and discussion

Ion exchange capacity

The ion exchange capacities, measured using either nitrates or sulphates as counterions, were both found to be equal to 3.3 meq/g. This value is slightly lower than the theoretical value, as per manufacturer information, which is equal to 4.0 meq/g. The effective capacity of the resin was then used to assess the ionic form of arsenic. Namely, by assuming that the prevailing form of arsenic was monovalent (i.e. as $\text{H}_2\text{As}_2\text{O}_5^-$), the resin capacity was found equal to 1.7 meq/g, whereas by assuming As to be divalent

($\text{HAS}_2\text{O}_5^{2-}$) it was equal to 3.4 meq/g, i.e. very close to the value estimated from the other independent measurements.

Therefore, for the purpose of this work, the ion exchange capacity was set equal to 3.3 meq/g and As(V) was supposed to be always in divalent form.

Ion exchange equilibria of binary systems

The ion exchange equilibrium data of binary systems were collected and fitted with the model based on the mass action law, allowing to estimate the corresponding equilibrium constants. Three binary systems were investigated: Arsenic/Chlorides, Nitrates/Chlorides and Sulphates/Chlorides.

Ion exchange equilibria of arsenic/chlorides. The experimental data for this binary system are reported in Figure 1a, together with the ion exchange isotherm calculated with the equilibrium model based on the mass action law. The equilibrium constant used in the model (see caption of Figure 1a) was estimated by fitting of the experimental data. Since arsenic (As(V)) was supposed to be in divalent form, the model predicts two distinct isotherms at different ionic strengths. The experimental data, collected at two different ionic strengths, follow this behaviour only at very low solution ionic fraction, whereas they overlap at higher ionic fractions. This could indicate that the ionic form of arsenic is not always divalent, as supposed in this work, but dependent upon the operating conditions. In the latter case, a more detailed modelling of this system would be required, combining the ion exchange equilibrium model with an ionization equilibrium model. In this case, accurate pH measurements would also be required, even though difficult to be obtained given the low ionic strength of the solution.

Ion exchange equilibria of nitrates/chlorides. As shown in Figure 1b, the experimental equilibrium data of the nitrates/chlorides system, collected in solutions characterized by different ionic strengths, fall on a single isotherm. This is confirmed by the model based on the mass action law, since the equilibrium constant is independent of the solution normality when the two competing ions have the same charge (see Equation 2). Thus only one isotherm, characterized by the best-fitting equilibrium constant shown in the

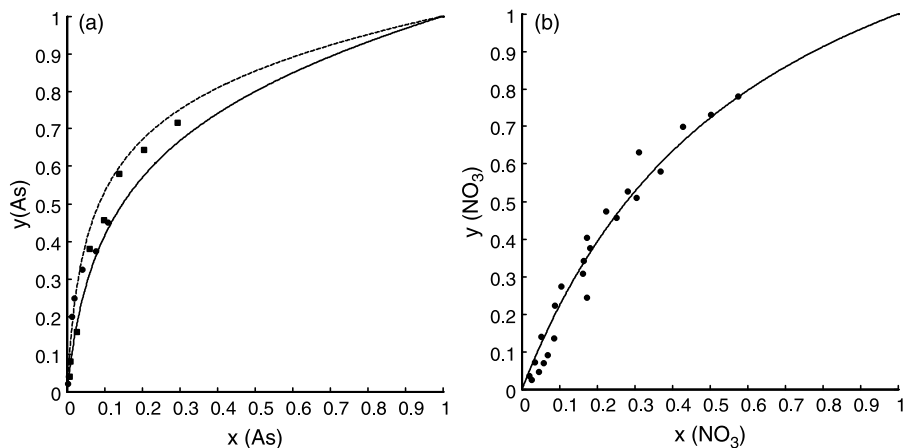


Figure 1 (a) ion exchange isotherm and experimental data of the binary system ($\text{HAS}_2\text{O}_5^{2-}/\text{Cl}^-$). Ionic strength: 0.133 N (circle/dotted line) and 0.266 N (square/solid line); Equilibrium constant $K(\text{HAS}_2\text{O}_5^{2-}/\text{Cl}^-) = 0.8$; (b) ion exchange isotherm and experimental data of the binary system $\text{NO}_3^-/\text{Cl}^-$. Ionic strengths: 0.08–0.48 N. Equilibrium constant $K(\text{NO}_3^-/\text{Cl}^-) = 2.6$

caption of Figure 1b, describes the ion exchange equilibrium of this system for any ionic strength. The shape of this isotherm clearly indicates that nitrates are preferred to chlorides by the resin.

Ion exchange equilibria of sulphates/chlorides. The equilibrium data corresponding to this system have shown that sulphates are dramatically preferred by the resin over chlorides. Whatever initial condition was selected, the resin phase at equilibrium was always enriched in sulphates, whereas sulphate concentration in solution was almost negligible, thus making it difficult to obtain a robust estimate of the equilibrium constant, which was observed to range around 15. For this reason, this estimate was not considered feasible for predicting the behaviour of the ternary system containing sulphate.

Ion exchange equilibria of ternary systems

The model based on the mass action law, with the assumption that both solution and resin phase have an ideal behaviour, can be used to predict the ion exchange equilibrium of ternary systems, provided that at least two binary equilibrium constants were known. In this work this approach was limited to one ternary system, i.e. arsenic/nitrates/chlorides, since the estimate of the sulphate/chloride equilibrium constant was not considered robust enough to model ternary data.

Arsenic/nitrates/chlorides. The experimental results of this ternary system are reported in Tables 1 and 2, with reference to data collected from solutions at 0.3 and 0.6 N, respectively. In the same table, the equilibrium values predicted by the model based on mass action law are also shown. By looking at Table 1, it can be observed that there is a quite good agreement between experimental and predicted values. Namely, both model and experiments agree in indicating an enrichment of the resin phase in both arsenic and nitrates, whereas chlorides are less retained by the resin. Unfortunately, such a good agreement is not observed in Table 2. In this case, the model still predicts reasonably well the chloride concentration in the resin phase, but fails in quantitatively predicting the arsenic/nitrate selectivity. The arsenic concentration is underestimated by the model, specifically at higher nitrate ionic fraction in the liquid phase. This behaviour is most probably due to the poor description of the arsenic behaviour provided in the model. The assumption of considering arsenic in divalent form, although useful for modelling

Table 1 Equilibrium data of ternary system arsenic/nitrates/chlorides. Experimental results and model predictions. Ionic strength: 0.3 N. Binary equilibrium constants: see Figure 1 caption

| Experimental results | | | | | Model results | | | |
|---|-------|-------|--------------------------------|-------|---------------|--|-------|-------|
| NO ₃ ⁻ ionic fraction | | | Cl ⁻ ionic fraction | | | HAs ₂ O ₈ ²⁻ ionic fraction | | |
| Liquid | Resin | | Liquid | Resin | | Liquid | Resin | |
| | Exp. | Model | | Exp. | Model | | Exp. | Model |
| 0.243 | 0.339 | 0.326 | 0.606 | 0.323 | 0.313 | 0.151 | 0.336 | 0.361 |
| 0.168 | 0.338 | 0.264 | 0.744 | 0.335 | 0.449 | 0.087 | 0.326 | 0.287 |
| 0.132 | 0.308 | 0.220 | 0.793 | 0.409 | 0.508 | 0.074 | 0.281 | 0.272 |
| 0.098 | 0.251 | 0.172 | 0.837 | 0.532 | 0.565 | 0.064 | 0.217 | 0.262 |
| 0.088 | 0.205 | 0.164 | 0.865 | 0.614 | 0.619 | 0.047 | 0.181 | 0.216 |
| 0.018 | 0.094 | 0.038 | 0.955 | 0.829 | 0.795 | 0.026 | 0.076 | 0.166 |
| 0.010 | 0.048 | 0.020 | 0.989 | 0.911 | 0.952 | 0.003 | 0.040 | 0.029 |

Table 2 Equilibrium data of ternary system arsenic/nitrates/chlorides. Experimental results and model predictions. Ionic strength: 0.6 N. Binary equilibrium constants: see Figure 1 caption

| Experimental results | | | | | Model results | | | | |
|---|-------|-------|--------------------------------|-------|---------------|--|-------|-------|-------|
| NO ₃ ⁻ ionic fraction | | | Cl ⁻ ionic fraction | | | HAs ₂ O ₅ ²⁻ ionic fraction | | | |
| Liquid | Resin | | Liquid | Resin | | Liquid | Resin | | Model |
| | Exp. | Model | | Exp. | Model | | Exp. | Model | |
| 0.571 | 0.497 | 0.730 | 0.319 | 0.252 | 0.157 | 0.109 | 0.249 | 0.113 | |
| 0.506 | 0.518 | 0.685 | 0.402 | 0.248 | 0.209 | 0.091 | 0.232 | 0.106 | |
| 0.441 | 0.534 | 0.635 | 0.486 | 0.242 | 0.269 | 0.073 | 0.223 | 0.096 | |
| 0.372 | 0.481 | 0.579 | 0.580 | 0.321 | 0.348 | 0.047 | 0.197 | 0.073 | |
| 0.299 | 0.453 | 0.506 | 0.670 | 0.373 | 0.437 | 0.031 | 0.173 | 0.057 | |
| 0.080 | 0.263 | 0.179 | 0.907 | 0.660 | 0.780 | 0.012 | 0.076 | 0.041 | |
| 0.022 | 0.142 | 0.055 | 0.979 | 0.818 | 0.924 | 0.006 | 0.039 | 0.006 | |

purposes and for providing a qualitative description of the system behaviour, is probably too simplistic to provide an accurate description of the system itself.

Conclusions

The ion exchange equilibrium of arsenic in the presence of high sulphate and nitrate concentrations on a commercial anionic resin in chloride form was described by means of a model based on the mass action law, under the assumption of ideality of both liquid and resin phase. Sulphates were shown to be strongly preferred by the resin phase; however, it was not possible to provide a quantitative estimate of the thermodynamic equilibrium constants of the system containing this anion. Ion exchange of arsenic in the presence of high nitrate concentration was quantitatively predicted, using the binary equilibrium constants estimated from simple binary ion exchange experiments. The quantitative agreement was not completely satisfactory, owing to the underlying simplifying assumption of considering arsenic in divalent form. A closer agreement between experimental data and model prediction may probably be obtained if the ion exchange equilibrium is coupled with a model accounting for the ionization equilibria of arsenic in solution. This will require measurement of the equilibrium pH in solution, which cannot always be an easy task, considering the low ionic strength of the tested solutions.

Apart from the limitations arising in this work, which could be overcome as above mentioned, the obtained results represent a first step towards the development of a comprehensive modelling of the ion exchange process for the removal of As(V) from surface and groundwater. Clearly, the real system is a very complex one, being characterized by the presence of several anions and other species that may contribute to a given ion exchange behaviour. Our idea is to start modelling simple systems, obtaining a clear comprehension of these systems and then gradually increasing the level of complexity, by adding one component at a time. In our view, this effort will be of great help in the design of ion exchange systems; it will allow selection of the key components that may alter the process efficiency towards arsenic; it will provide a sound and quantitative theory for the process development activities.

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