

Key parameters controlling an adsorption process for the selective removal of arsenic from drinking water

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Abstract Arsenic can be selectively removed from water through adsorption on a natural manganese oxide. This paper presents some of the key parameters controlling such a process. Both production and regeneration steps were studied and the influence of three main controlling parameters was put to light. The water pH greatly influenced the adsorption capacity. Low water pH highly improved the treatment. The adsorption being under mass transfer limitation, flow rate influence was measured and optimization solutions were proposed. Finally, the impact of the regeneration procedure was evaluated on the adsorbent stability. It gave good arsenic elution results but the caustic elution step generated fine particles that could not be avoided. The following neutralization could however be adjusted in order to minimize further adsorbent dissolution.

Keywords Adsorption process; arsenic; drinking water treatment; manganese oxide

Introduction

Arsenic, a well known toxic element, has proved carcinogenic at low ingestion rate (Basu *et al.*, 2001). Hence, its presence in drinking water even at low concentration is a threat for human health. Besides, its occurrence in drinking water in some parts of the world, mainly in Asia, leads to alarming public health problems (Masud, 2000). Many regulatory authorities throughout the world (European Commission, Environment Protection Agency) have therefore followed the World Health Organization recommendations and lowered the critical concentration for total arsenic in drinking water from 50 to 10 $\mu\text{g L}^{-1}$. New highly efficient treatments are then necessary to meet the standards and adsorption processes are particularly attractive. In natural waters, arsenic is mainly found under two oxidation states: As III and As V. Most adsorbents can only deal with As V and a pre-oxidation state is then necessary. Manganese oxides can however readily oxidize As III into As V and adsorb it (Thanabalasingam and Pickering, 1986; Bajpai and Chaudhuri, 1999).

The aim of this paper is to present some key points for the design of such an adsorption process. The main governing parameters of the process are of three kinds. First, the process performances obviously depend on the adsorbent quality. This point won't be discussed. The second point to take into consideration is the water composition. The ionic composition as well as pH may both influence adsorption capacity and/or selectivity. Previous work (Ouvrard *et al.*, 2001) has proved that, although other oxianions (phosphate, sulfate, bicarbonate) could be adsorbed on the material, arsenic remains highly preferred and no competition occurs. We will see here, however, that arsenate adsorption strongly depends on the pH. The process efficiency is then highly linked to the water pH. Third, the process control parameters influence needs to be assessed. The process work on a cycling basis, adsorption is followed by a regeneration step. We will more focus on the flow rate influence on the adsorption and we will evaluate the regeneration impact on the material stability.

Materials and methods

The adsorbent is a natural manganese oxide whose main characteristics are presented in

Table 1. All solutions were prepared with analytical grade salts of sodium arsenate and deionized water. Two main experimental procedures were used: batch and column systems. Batch experiments were performed in 125 ML polyethylene vessels. Column experiments were conducted in glass column Pharmacia type (internal diameter = 10 mm) fed by means of a plug flow pump. Both pH and conductivity were measured on-line at the outlet and fraction collection enabled further ion analysis by AA or ion chromatography.

pH influence on adsorption

Capacity evolution with pH

Batch experiments were conducted to evaluate pH impact on capacity. The results presented in Figure 1 clearly showed that the adsorption capacity for arsenic greatly increased as pH decreased. This behavior followed the electrostatic evolution of the solid/solution system. Indeed, in this pH range arsenate was always under anionic form, whereas the surface charge of the oxide went from positive to negative values as the pH increased with a zero point of charge at 4.7. Below this pH value, electrostatic interactions promoted adsorption and above they were opposed to the solute approach to the surface. Although these phenomena explained the tendency observed on the capacity evolution as a function of pH, they were not the only interactions involved in arsenate adsorption on the manganese oxide since it occurred even in repulsive electrostatic conditions.

Water pH: a key parameter to the treatment efficiency

The major effect of pH on arsenate adsorption capacity made it a key parameter for the treatment capacity estimation. Indeed, depending on the water pH, the adsorption capacity seemed to be highly modified and this parameter should therefore be taken into account for installation dimensioning.

Table 1 Adsorbent main characteristics

Specific surface area (m ² g ⁻¹)	Zero point of charge	Elemental composition (%w)	
		MnO ₂	Al ₂ O ₃
16	4.7	70.9	5.92

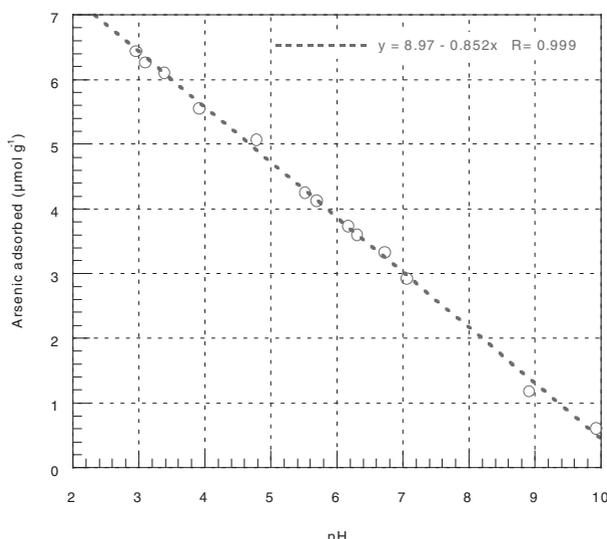


Figure 1 Arsenic adsorption capacity as a function of equilibrium pH for a batch system of 100 ML solution, 2 g adsorbent (As initial concentration 5 mg L⁻¹)

In order to quantify water pH effect more precisely, two column adsorption experiments were run with solutions at the same arsenic concentration but whose pH had been modified with acid addition. The final conditions are reported in Table 2 and the breakthrough curves of these two solutions are plotted in Figure 2. They led to arsenic capacities of 4.69 and 2.66 $\mu\text{mol g}^{-1}$ for the respective pH values of 6.86 and 7.47. These results confirmed batch observations: the pH decrease by less than a unit led to a capacity increase of 76% at this arsenic concentration.

Combining results from batch and column experiments arsenic adsorption isotherms for two different pH were evaluated. They could be roughly well represented by a Langmuir type model whose parameters are presented in Table 3. These results could then be used to evaluate the treatment capacity for an arsenic concentration close to the one found in natural waters: 0.27 $\mu\text{mol L}^{-1}$ (20 $\mu\text{g L}^{-1}$). Results then led to the respective adsorption capacity of 0.3 and 0.6 for 7.47 and 6.86 pH, respectively. This put to light how sensitive the treatment capacity was to the water pH and this parameter clearly appeared as a key one for installation dimensioning.

Mass transfer limitation

Kinetic experiments run in batch reactors have proved the arsenic adsorption rate was controlled by mass transfer through intraparticle diffusion. A Fick law type can easily represent these kinetic limitations. As a consequence, breakthrough curve forms are highly sensitive to both flow rate and adsorbent particle size. The smaller the flow rate and the particle size the more the breakthrough point of the curve is delayed. In real operating conditions, the adsorbent particle size cannot be drastically reduced, to prevent excessive head loss. Therefore, we focus here on the flow rate influence and the way its value could be optimized on an economic basis.

Table 2 Experimental conditions of column adsorption experiments

Experiment	[As] (mM)	pH
1	0.67	6.86
2	0.67	7.47

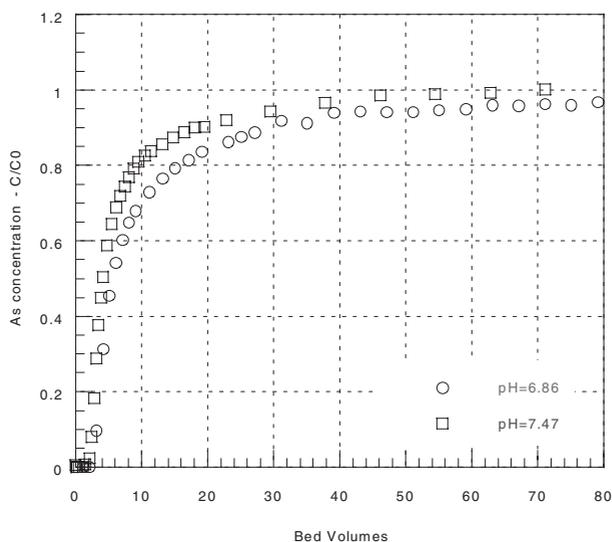


Figure 2 Arsenic breakthrough curves for solutions 1 and 2 (see Table 2; bed volume 5 ML, flow rate 25 ML h^{-1})

Table 3 Experimental conditions of column adsorption experiments

pH	q_{\max} ($\mu\text{mol g}^{-1}$)	K_L ($\text{L } \mu\text{mol}^{-1}$)
6.86	2.3	0.56
7.47	4.7	0.55

Flow rate influence

Breakthrough curves of a 50 mg L^{-1} arsenate solution were measured for three different empty bed residence times (EBRT): 0.60, 12 and 60 minutes. The results presented in Figure 3 showed that the breakthrough point was delayed as the EBRT increased, and the curve was more broadening with longer tailing as the EBRT decreased. These results clearly illustrated the effect of mass transfer limitations.

The experimental breakthrough curves were modeled by means of a computer code developed in our laboratory, combining both the transport equation and mass transfer limitations described with a Fick law equation (Chue, 1991). A very good agreement between experimental and modeled results was found as presented in Figure 3. This code was then further used as an optimization tool.

Optimization tool

For the treatment application, the later the breakthrough point the higher the effective capacity since the treatment is stopped when the limit concentration is reached (e.g. $10 \mu\text{g L}^{-1}$). Small flow rates greatly increased the treatment effective capacity, but to keep the same production rate, the column size needed to be increased. A compromise then had to be found between capacity profit and investment cost.

The breakthrough point of a solution containing $100 \mu\text{g L}^{-1}$ As was calculated with the model and is presented Figure 4b. The obtained curve confirmed that the effective capacity, the number of bed volumes produced at the breakthrough point, increased when the EBRT increased. However, at the same time, for a given column size, the water production rate decreased (Figure 4a). Table 4 presents the performance of an installation for two different

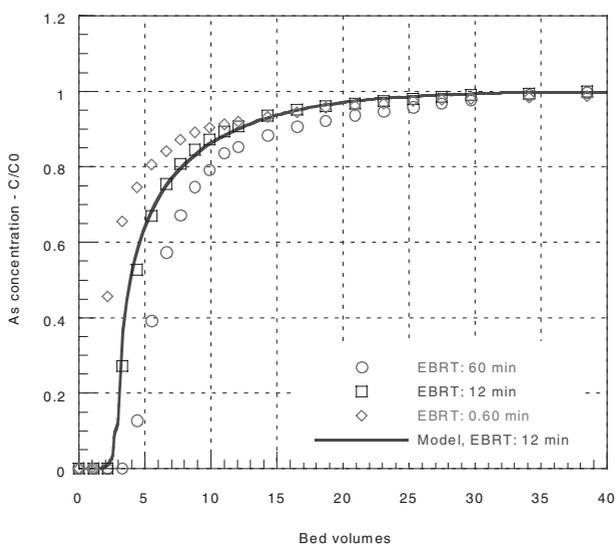


Figure 3 Arsenic breakthrough curves for three empty bed residence times bed volume 5 ML, [As] = 50 mg L^{-1}

EBRT: 10 and 20 minutes. In the second case, to maintain the same production rate, the column size should be twice that of the first one, which means a higher investment cost. However, in the second configuration, regeneration would be less frequent and running costs would therefore be reduced.

Depending on the water production required and the arsenic concentration of the water to be treated, a real global cost optimization could be performed this way using the model developed, in which the EBRT in the column and the installation size should be adjusted.

Regeneration control

The regeneration procedure is in four steps (Jauffret, 1998):

- arsenic elution with concentrated caustic soda;
- washing to remove porous water still highly loaded in arsenic;
- acid neutralization;
- final washing.

The two first stages are efficient enough for total arsenic recovery. However, they are quite chemically aggressive for the adsorbent. The following neutralization step may also lead to some problems. In order to assess the respective effects of each step, two main points regarding the adsorbent stability were investigated:

- fine production
- adsorbent dissolution.

Fine production

The production of fine particles is a drawback in the process and must be avoided. The main mechanisms of fines creation needed to be found in order to prevent it or reduce its effects.

Attrition experiments were conducted with natural manganese oxide. 2 g of adsorbent were stirred in batch reactors with different solution types: caustic soda or water of different ionic strengths (Table 5) and the mass of fine particles generated was determined. The results presented in Figure 5 showed that the production of fine particles was mainly due to the effect of caustic soda. It was not influenced by the washing solution type. In the process,

Table 4 Comparison of two production conditions for a nominal water flow rate of $6 \text{ m}^3 \text{ h}^{-1}$

	EBRT (min.)	Flow rate (BV/min.)	Column size (m^3)	Effective capacity (BV)
Case 1	10	0.1	1	220
Case 2	20	0.05	2	390

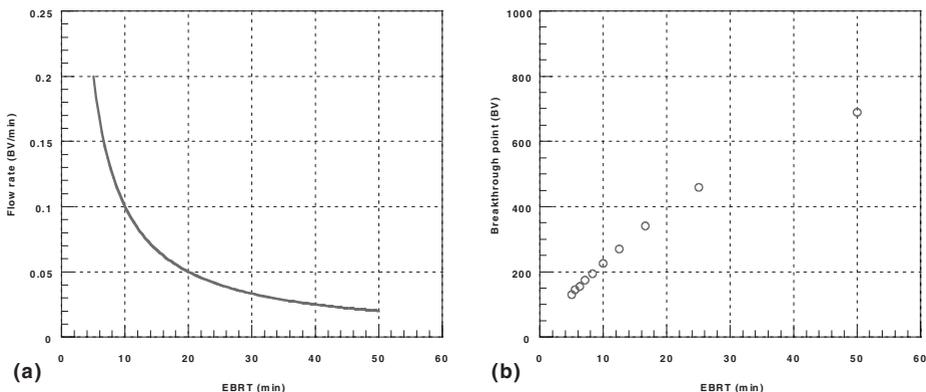
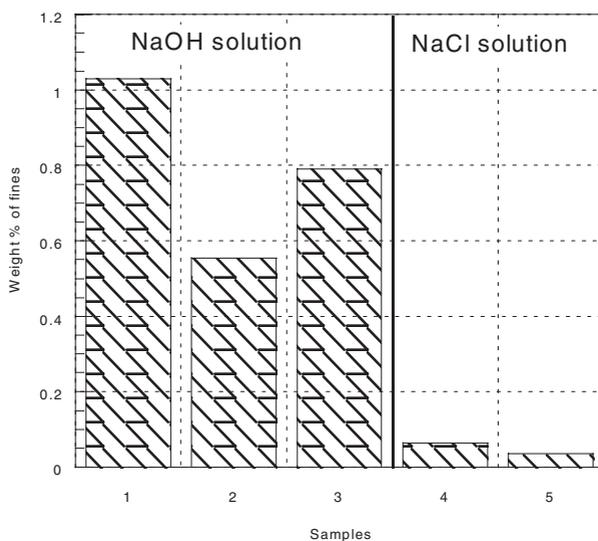
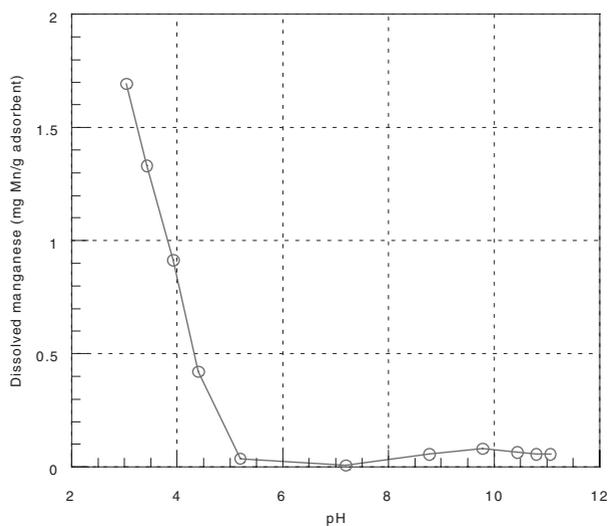


Figure 4 Influence of the EBRT on: (a) water production rate; and (b) effective capacity for a $100 \mu\text{g L}^{-1}$ As solution as given by the model

Table 5 Experimental conditions of the attrition tests on the natural manganese oxide

Sample	1	2	3	4	5
Stirring solution	NaOH 0.5 N	NaOH 0.5 N	NaOH 0.5 N	NaCl 0.5 N	water
Washing solution	water	water	NaOH 0.5 N	water	water

**Figure 5** Fine production quantities for different solutions**Figure 6** Adsorbent dissolution as a function of equilibrium pH

the caustic soda elution was therefore responsible for the production of the fine fraction. This first step is essential for arsenic elution and cannot be avoided. The regeneration procedure should then be adapted in order to remove the created fine fraction, for instance in including a high flow rate counter-current washing.

Adsorbent dissolution

To assess the chemical stability of the adsorbent during regeneration, further experiments

were conducted in batch reactors. We quantified the amount of dissolved manganese produced for a wide range of equilibrium pH: 3–11. The results presented in Figure 6 showed the following tendencies.

- In alkaline conditions, manganese dissolution was low, and the concentration remained steady on the entire pH range. It was probably the consequence of solid/liquid equilibrium, confirmed by the presence of colloids in the suspension.
- In acidic conditions, for pH lower than 5, the dissolved manganese concentration increased dramatically as the pH decreased illustrating the fragility of the adsorbent in acidic solutions.

These observations led to some recommendations for the regeneration control. First, the colloids formed under alkaline conditions were most certainly the premises to fine formations put to light in the previous paragraph. Second, the high fragility of the adsorbent under acidic conditions indicated that the neutralization step should be carefully controlled. Indeed, if the amount of acid used is overestimated, a systematic degradation of the adsorbent could occur.

Conclusion

Adsorption of arsenic on a natural manganese oxide is a promising solution treat water contamination. This work has put to light some essential parameters for installation design. Both production and regeneration steps were considered and the following results were found.

- The water pH highly influenced treatment capacity even in the small range of natural waters. Low pH improved adsorption capacity and its value clearly appeared as a key parameter.
- Adsorption being controlled by mass transfer, breakthrough curves were sensitive to flow rate. This parameter could then modify the effective capacity of the treatment and enters as a major criterion for the installation size choice.
- Life time of the process is governed by the regeneration efficiency. The procedure chosen gave good arsenic elution results but this elution step formed fine particles that had to be removed. The following neutralization step could also lead to adsorbent dissolution.

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