

Operating Conditions for the treatment of groundwater contaminated by arsenic using iron oxides/hydroxides

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In contaminated regions, the range of arsenic concentrations found in natural waters is wide, ranging from less than 0.5 µg/L to more than 5000 µg/L. In Portugal arsenic contaminations can be found in several places; the worse scenario was found in the northeast region in a former mining area, where the total arsenic concentration reaches 850 µg/L.

There are highly efficient methods for arsenic removal like ion-exchange and adsorption using activated alumina, activated carbon and ferric hydroxides either in granular form or as coating material.

The main goal of this research is the study of the operation conditions for the arsenic removal, both as As(III) and As(V), using a granular iron oxide as sorbent; so far we have been using ARM 300 from BASF.

Column experiments were performed in order to study the effect of the specific flow rate and of the oxidation state of arsenic.

The effect of the specific flow rate in arsenic removal is quite evident in the column experiments performed. When it increases it leads to a decrease in the breakthrough time corresponding to a column saturation of 50%.

A loading sorbent capacity around 9500 µg/g was obtained for an inlet concentration around 1050 µg/L; tests also suggest that As(III) is easier adsorbed than As(V).

The results obtained demonstrate the feasibility of applying this material to treat natural underground waters either at surface, in adsorption columns, or in-situ, as a reactive medium for permeable reactive barriers.

Keywords - Arsenic removal, iron oxides/hydroxides, synthetic sorbents, reactive permeable barriers.

I. INTRODUCTION

Arsenic is a constituent of more than 245 minerals. Volcanic eruptions and other natural processes are sources of high arsenic concentrations in the environment. The dissolution of these minerals in surface or underground waters is the main origin for arsenic contaminations. Apart from these natural sources, contamination of water and soil may result from human activities due to the disposal of industrial chemical waste, the smelting of arsenic bearing minerals, the burning of fossil fuels and the application of arsenic compounds in many products (Bissen and Frimmel, 2003a).

Concentrations of As in natural waters are highly dependent on the existence of arsenic sources and on the local geochemical conditions. The mobility of these species is influenced by the pH value, the redox potential, and the presence of adsorbents such as oxides and

hydroxides of Fe(III), Al(III), Mn(III/IV), humic substances, and clay minerals (Bissen and Frimmel, 2003a).

In natural waters inorganic arsenic appears commonly in the oxidation states III and V, respectively as arsenides (As III) or as arsenates (As V). Both forms are toxic and carcinogenic. In contaminated regions, the range of As concentrations found in natural waters is wide, ranging from a few $\mu\text{g/L}$ to more than 5000 $\mu\text{g/L}$. Toxicity depends upon the oxidation state and, in general, As(III) is 60 times more toxic than As(V) (Bissen and Frimmel, 2003a). European Union has recently lowered the permissible maximum concentration for drinking water from 0.05 mg/L to 0.01 mg/L, in accordance with the Council Directive 98/83/CE.

There are natural areas where groundwater has very high arsenic concentrations in Argentina, Chile, Mexico, China, Hungary, India, Bangladesh and Vietnam. In contaminated regions, the range of As concentrations found in natural waters is wide, ranging from less than 0.5 $\mu\text{g/L}$ to more than 5000 $\mu\text{g/L}$. Typical concentrations in freshwater are less than 10 $\mu\text{g/L}$ and frequently less than 1 $\mu\text{g/L}$. (Smedley and Kinniburgh, 2002).

The problem is also relevant in Spain (Catalonian Pyrenees, Valladolid, Madrid, Segovia, etc.). In Portugal slightly anomalous arsenic contaminations can be found in several places. The worse scenario found was in the northeast region, in a former mining exploitation area, where the total arsenic concentrations reached 850 $\mu\text{g/L}$ (Reis *et al.*, 2007).

Research has been focused in the oxidation of As(III) and in the development and optimisation of arsenic removal technologies. Available technologies are co-precipitation, adsorption to solid surfaces, ion exchange, membrane processes and electrocoagulation. Jiang (2001) reported that the commonly used technologies in developing countries are oxidation, coagulation-precipitation, and adsorption by activated carbon, activated alumina, and iron oxide coated materials. Membrane technologies have shown to be effective but the cost is not always affordable.

Removal technologies implemented at community level are well developed but often expensive. In the last decade research has been focused on the development of cheap and easy-to-handle removal technologies especially for decentralized use in rural areas in developing countries (Bissen and Frimmel, 2003b).

In this research an iron based synthetic sorbent was tested for arsenic removal. Continuous experiments were performed in a fixed bed column in order to study the effect of the specific flowrate and the oxidation state of arsenic.

II. EXPERIMENTATION

II.1 Materials

All chemicals were reagent grade and were used without any further purification. All solutions were prepared with deionised water. All glassware was cleaned by soaking in 10% HNO_3 and rinsed with deionised water. Arsenic solutions were prepared by direct dilution of a 1000 mg/L standard solutions from Fluka for As (V) and from Panreac for As(III).

A granular iron oxide, ARM 300 from BASF, was selected for this study.

II.2 Methods for measuring arsenic concentration and pH

Total Arsenic determinations were carried by inductively coupled plasma optical emission spectroscopy with coupled hydride generation. Arsenic III was quantified by cathodic stripping voltammetry using a hanging mercury drop electrode, as described by Ferreira and Barros (2002). Samples that were not immediately preserved by acidification to pH lower than 2 with concentrated HCl and stored in acid washed high-

density polyethylene containers (ISO, 1994). All samples were analysed within 7 days after collection. The pH values were obtained using a pH meter (Crison, GLP22).

III.3 Column experiments

The fix bed column experiments were performed at 20°C. The arsenic solution was pumped (Ismatec, BV-GES) downwards through a column (Omnifit) with an internal diameter of 2.5 cm and a height of 15 cm. The column was filled with 2.50 g of sorbent mixed with an inert material (clean sand with grain sizes between 710 and 1000 μm), after air removal from the sorbent pores (by immersion in distilled water and application of vacuum). An inlet arsenic concentration of 1000 $\mu\text{g/L}$ was used; samples were collected at the column outlet during the experiment allowing for the determination of pH and the As concentration.

Flowrates of 5, 10 and 20 mL/min were tested for each arsenic species. An experiment using both arsenic species was also performed using a flowrate of 10 mL/min.

III. RESULTS AND DISCUSSION

The research aimed at studying the effect of the specific flowrate and the oxidation state of arsenic performing continuous flow experiments in a fixed bed column.

In order to study the influence of the specific flowrate experiments were performed using 5, 10 and 20 mL/min in a column with an internal diameter of 1.25 cm. This corresponds respectively to specific flowrates of 1.019, 2.037 and 3.056 cm/min or, using the I.S. 1.698×10^{-4} , 3.395×10^{-4} and 5.09×10^{-4} m/s. The latest value was the highest that could be safely used, due to the small size of the equipment. The evolution of the arsenic concentrations at the column outlet, normalised by the average inlet concentration for different flowrates and the corresponding fitting to Yan's model, both for As(III) and As(V), are presented respectively in Figures 1 and 2.

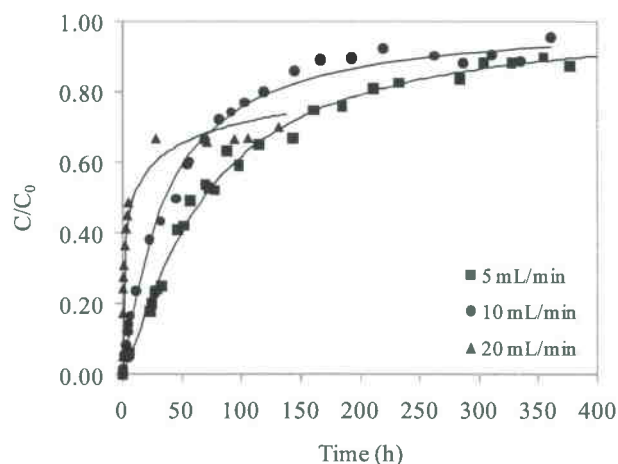


Figure 1 - Evolution of normalised As(III) concentration at the column outlet for different flowrates and corresponding fitting to Yan's model.

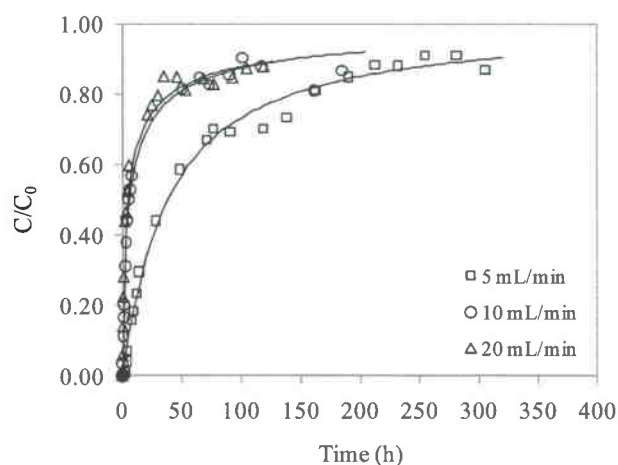


Figure 2 - Time evolution of normalised As(V) concentration at the column outlet for different flowrates and corresponding fitting to Yan's model.

The average inlet concentration (C_0) and the experimental breakthrough time corresponding to a column saturation of 50% ($t_{50\%}$) for each column experiment is presented in Table 1. The influence of the specific flowrate is quite obvious in Table 1. An increase in the flowrate leads to a decrease of the $t_{50\%}$, as expected, due to a reduction in the residence time in the column, although the dependence is not linear. It seems that for a flowrate of 20 mL/min the contact time was not sufficient. When comparing the two arsenic species, it is noticed that $t_{50\%}$ is always higher for As(III) meaning that it is easier adsorbed than As(V), specially for the 5 and 10 mL/min flowrates.

Table 1 - Experimental data from tests in column: inlet concentration (C_0) and breakthrough time corresponding to a column saturation of 50% ($t_{50\%}$).

Arsenic	Flowrate (mL/min)	C_0 ($\mu\text{g/L}$)	$t_{50\%}$ (h)
As(III)	5	1077	58
	10	1024	46
	20	1109	6
As(V)	5	984	35
	10	1046	5
	20	1048	4

Yan's model (Yan and Viraraghavan, 2001) was selected to fit the results from the experiments. This simple model fitted well the results from previous experiments performed with the same systems (data not shown). The software Fig.P, version 2.98, was used for the non-linear adjustment to the model. The statistic treatment of the results allowed the determination of the confidence intervals at 95% for each parameter, the variance (s^2), and the coefficient of determination (r^2) for each fitting. The model parameters are presented in Table 2.

Table 2 - Parameters obtained for Yan's model.

As	Flowrate (mL/min)	Parameters			
		a_Y	q_Y ($\mu\text{g/g}$)	s^2	r^2
As(III)	5	1.25 ± 0.08	9434 ± 410	0.63×10^{-3}	0.993
	10	1.10 ± 0.07	9283 ± 593	0.64×10^{-3}	0.996
	20	0.39 ± 0.06	5412 ± 1780	2.04×10^{-3}	0.970
As(V)	5	1.06 ± 0.08	4748 ± 396	0.91×10^{-3}	0.993
	10	0.71 ± 0.09	1841 ± 350	2.33×10^{-3}	0.982
	20	0.75 ± 0.08	2641 ± 445	1.96×10^{-3}	0.985

The estimated capacity of the sorbent (q_Y) confirms that As(III) is easier adsorbed than As(V). The estimated values are similar for As(III) using either 5 or 10 mL/min flowrates, as it was expected, once capacity should not depend on this factor. However, the value obtained for a flowrate of 20mL/min is rather different and the same occurs when comparing the values for As(V).

Another experiment was performed using a mixture of As(III) and As(V) in order to evaluate the behaviour of the assembled system; a flowrate of 10mL/min was used. Although the experiment was planned for concentrations of 500 $\mu\text{g/L}$ for each arsenic species the final results (Figure 3) show a different reality: the As (V) increased with time as expected, rising above the initial concentration, while As(III) stayed always near to the lower analytical quantification limit. The analysis of the concentration at the inlet revealed that more than 80% of the total arsenic was already in the form of As(V). This suggests that As(III) was oxidised to As(V) prior to its inlet at the top of the column.

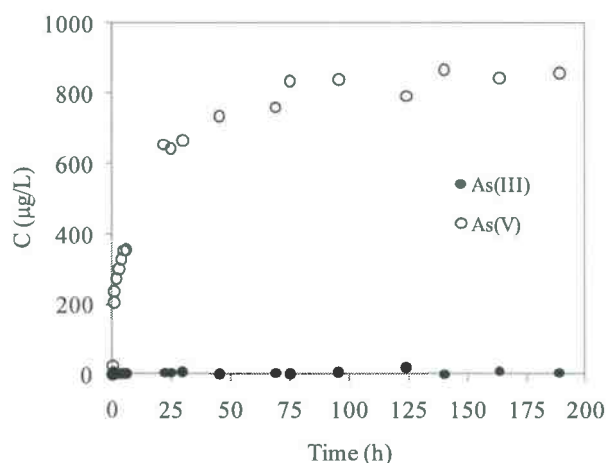


Figure 3 - Evolution of As(III) and As(V) concentrations at the column outlet, using a flowrate of 10 mL/min.

III. CONCLUSIONS

The effect of the flowrate in the arsenic removal becomes evident from the column experiments performed. An increase in the flowrate leads to a decrease of the breakthrough time corresponding to a column saturation of 50%, as expected, due to the decrease of the residence time in the column, although the relationship it is not proportional.

The influence of the arsenic oxidation state was also considered. The estimated capacity of the column confirms that As(III) is easier adsorbed than As(V), for which a loading capacity around 9.500 $\mu\text{g/g}$ was obtained for an inlet concentration around 1050 $\mu\text{g/L}$.

The results obtained demonstrate the feasibility of applying this material to treat natural underground waters either at surface, in adsorption columns or in-situ, as a reactive medium for permeable reactive barriers.

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