Implementation of ferric hydroxide-based media for removal of toxic metalloids

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Abstract. Effective removal of inorganic arsenic species is possible by application of the sorption technique with the use of iron-based sorbents. This study investigates the removal of arsenic(III) and arsenic(V) from an aqueous solution by application of a granular ferric hydroxide-based sorbent. The performance of tested media was evaluated based on the batch and fixed-bed adsorption studies. The efficiency of the process was determined with various treatment times, adsorbent doses, initial concentrations of arsenic and various solution temperatures. The obtained adsorption data were fitted with pseudo-first and second-order kinetic models and Langmuir and Freundlich isotherm equations. It was observed that the overall arsenite removal was lower when compared to the arsenate, and all tested operating parameters influenced the process efficiency. The experiments under dynamic conditions showed high treatment capacity and stability of tested adsorbent over a long period of time.

1 Introduction

The pollution of the aquatic ecosystem is a global long-term environmental problem due to the rapid industrial development and urbanisation. Toxic heavy metals or metalloids are widespread and their discharging through air and industrial effluents or leaching from the soil by acid rain into natural waters often is a reason of their severe degradation. Many unwanted contaminants in an excessive concentration in the aquatic environment cause a detrimental effect on human and animals. The accumulation of metal(loid)s species over time in living organisms can be damaging to them and cause serious consequences [1-2].

One of the common metalloid widely known for its high toxicity is arsenic. Cases of severe arsenic poisoning in humans have been reported in many places around the world, including Bangladesh, India, Vietnam, China, Chile, Mexico, Argentina and USA [3-4]. This element occurs as a natural constituent of rock, soil, water and atmosphere as well as may originate from the anthropogenic sources. In natural waters, arsenic is usually present in inorganic forms, as arsenite or arsenate oxyanions. However, trivalent arsenite As(III) is dominant in more reducing conditions, whereas pentavalent arsenate As(V) is mostly present in an oxidizing environment [5-6].

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The removal of various arsenic species from contaminated water and wastewater is possible due to the application of oxidation and precipitation techniques, coagulation, ion exchange and sorption methods or membrane separation [7-11]. Each of these treatment techniques has advantages and may offer a good solution for the treatment of arsenic-rich water/wastewater. However, other factors like objectives of the treatment, capital and operating costs, disposal of generated waste are the key elements in the selection and design of the proper treatment process.

Obviously, effective removal of arsenic is possible by the application of the sorption technique with use of iron-based sorbents (IBS). Many studies have confirmed that arsenic has a natural affinity for iron compounds under various operating conditions [12-15]. Therefore, considering adsorption on iron-containing surfaces for treatment drinking water or industrial wastewater with elevated concentrations of arsenic may be the best choice in many cases.

This study investigated the removal of $\operatorname{arsenic}(\operatorname{III})$ and $\operatorname{arsenic}(V)$ from an aqueous solution by using iron-based sorbent – a granular ferric hydroxide-based material. The performance of the tested media was evaluated based on the batch and fixed-bed adsorption studies carried out on the laboratory scale. The efficiency of the process was determined with various treatment times, adsorbent doses, concentrations of arsenic and various solution temperatures. The obtained adsorption data were fitted with kinetic and equilibrium models.

2 Materials and methods

The ferric hydroxide-based material (CFH12) is a commercial adsorbent (Kemira Oyj, Finland) and was selected for the adsorption laboratory experiments. It is a porous material with a specific surface area of 158 m²/g. A comprehensive characteristic of the tested adsorbent is provided in our previous work [16-17].

To evaluate the performance of CFH12 in arsenic(III) and arsenic(V) removal from model solutions, batch and fix-bed experiments were conducted.

For the batch tests, synthetic solutions were freshly prepared using Milli-Q water and spiked with As(III) and/or As(V). The adsorption equilibrium experiments were performed using various initial concentrations of As(III) or As(V). The samples were agitated in a shaker incubator until equilibrium was reached. The experiments with various material doses (1-10 g/L) and solution temperatures $(5-35^{\circ}\text{C})$ were conducted in a similar way, with an initial adsorbate concentration of 20 mg/L. In the kinetics tests, the pre-weighted material was added to 500 mL of a water sample spiked with As(III) or As(V). The tests were performed for five hours using a magnetic stirrer.

The fixed-bed column set-up consisted of custom-made columns loaded with prewashed granular iron hydroxides. As a feed solution, dechlorinated tap water spiked with arsenic solution was used and passed through the columns downward with a continuous flow rate of 3 mL/min using a peristaltic pump. The samples were collected periodically using an automated samples collector.

The initial pH of the solution was adjusted by the addition of either 0.1M HCl or 0.1 M NaOH. The initial and residual arsenic concentrations were determined using the ICP-OES or ICP-MS technique.

3 Results and discussion

3.1 Kinetics studies

A kinetics study is particularly important in terms of proper assessment of the effect of the treatment time on the performance of the tested material. The mechanism of the process involved as well as the rate of adsorption were analysed based on kinetic parameters determined with the use of the non-linear regression method. Two kinetic models, pseudo-first (Eq. 1) and pseudo-second-order equation (Eq. 2), were used to describe the kinetic data.

$$q = q_e (1 - e^{-k_1 t}) \tag{1}$$

$$q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{2}$$

where q and q_e is the amount of arsenic adsorbed at time t and equilibrium state(mg/g), respectively; t is the contact time (min); k_1 is the rate constant of the pseudo-first-order adsorption (min⁻¹); k_2 is the rate constant of the pseudo-second-order adsorption (g/mg min).

The adsorption of arsenic species onto CFH12 is shown in Fig. 1, while the calculated parameters of kinetic models for 1 mg/L and 20 mg/L of arsenic(III) and (V) are presented in Table 1.



Fig. 1. Adsorption kinetics of As(III) and As(V) on the CFH12; experimental data fitted with pseudo-first and second-order kinetic models

Model	Parameter	$As(III) C_0 = 1 mg/L$	$As(III) C_0 = 20 mg/L$	$As(V) C_0 = 1 mg/L$	$As(V)$ $C_0 = 20 \text{ mg/L}$
	q _{exp} (mg/g)	0.17	1.88	0.24	4.16
Pseudo I order kinetic model	k1 (1/min)	0.313	0.011	0.283	0.014
	q1 (mg/g)	0.11	1.85	0.22	4.15
	R ²	0.480	0.969	0.856	0.986
Pseudo II order kinetic model	k2 (g/mg min)	2.188	0.005	1.605	0.003
	q2 (mg/g)	0.13	2.37	0.23	5.16
	R ²	0.625	0.978	0.938	0.991

Table 1. Parameters of adsorption kinetic models for As(III) and As(V)

The experimental results reveal that the adsorption capacity along with removal efficiency increase with contact time regardless of the initial concentration of arsenic ions. However, at the beginning of the process, the rate of uptake of As(V) was faster comparing to As(III). The percentage removal of 1 mg/L of As(V) after one hour of contact was approximately 97.2%, whereas the removal for As(III) was close to 45%. The extension of the contact time to five hours allows for a slight improvement (1.3%) of As(V) uptake, but in the case of As(III), the increment was considerably higher, and the recorded removal efficiency reached 78.2%. The performance of CFH12 in the treatment solution contained high concentration of arsenic (20 mg/L) resulted in maximum removal of As(III) and As(V) approximately 50% and 85%, respectively, which corresponds to the uptake of 1.88 mg/g and 4.16 mg/g.

The evaluation of the best kinetic models for fitting the experimental data was made based on the correlation coefficient values. Higher values of R^2 were observed for the second-order kinetic equation for both treated solutions (Table 1). Since this model was more representative for simulating the kinetic data than the pseudo first-order kinetic equation, it can be assumed that the adsorption mechanism of As(III) and As(V) follows pseudo-second-order kinetic reaction, and that the chemisorption may be a rate controlling step in the investigated adsorption systems. However, under applied experimental conditions, differences between solutions with lower (1 mg/L) and higher (20 mg/L) concentration of arsenic(III) and (V) were noticeable in the agreement between adsorption capacity predicted by the model and capacity determined experimentally.

3.2 Equilibrium studies

To evaluate the equilibrium adsorption of arsenic(III) and arsenic(V) on the investigated material CFH12, non-linear Langmuir (Eq. 3) and Freundlich (Eq. 4) models were used to fit experimental data.

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{3}$$

$$q_e = KC_e^n \tag{4}$$

where q_e and q_m are the equilibrium and maximum adsorption capacities (mg/g), respectively; C_e is the equilibrium concentration of arsenic in the solution (mg/L), b is the Langmuir adsorption equilibrium constant (L/mg); K is the Freundlich constant ((mg/g)·(L/mg)), and n is the adsorption intensity parameter.

The Langmuir isotherm equation assumes that there is no interaction between the particular molecules of adsorbate, which leads to monolayer formation on the adsorbent surface. Thus, as saturation is reached, no further sorption can take place. The Freundlich model generally suits better for the multilayer adsorption process. The experimental data fitted with both models are shown in Fig. 2.



Fig. 2. Adsorption isotherm of As(III) and As(V) on the CFH12; experimental data fitted with Langmuir and Freundlich models

The applicability of the models was assessed based on the calculated values of correlation coefficients. The experimental results were well correlated to the Langmuir equation ($R^2 = 0.986$ for As(III); $R^2 = 0.974$ for As(V)), however in case of As(V) a slightly better fit of the Freundlich model was observed ($R^2 = 0.980$ for As(III); $R^2 = 0.981$ for As(V)). In the Langmuir isotherm calculated adsorption capacities for arsenite and arsenate are 43.75 mg/g and 44.04 mg/g, respectively. In the Freundlich isotherm, adsorption intensity parameters are found to be 2.655 and 3.467 for As(III) and As(V).

3.3 Effect of material dose and solution temperature studies

The removal of arsenic from an aqueous solution was performed with various adsorbent doses and the obtained results are shown in Fig. 3. As expected, the efficiency of the process increases with the increase of the amount of CFH12 applied. The increase of the removal efficiency could be attributed to the availability of a specific surface area and a higher number of adsorption sites at the solid phase. However, under applied experimental conditions a substantial difference was observed between the removal of arsenic(III) and arsenic(V). As the adsorbent dose was higher than 5 g/L, the As(V) removal extent remained almost constant, indicating the saturation of the adsorption sites. The percentage removal of As(III) gradually increases from 52.9% to 93.8% as the material dose increased from 1 g/L to 10 g/L.

In this study, it was observed that the process temperature has an influence on CFH12 performance in arsenic(III) removal, comparing to arsenic(V) for which no significant change in the percent removal was observed (Fig. 3). Raising the solution temperature from 5° C to 35° C increased As(III) removal from approximately 80% to 92%, suggesting an endothermic nature of the process. The results show that the amount of As(V) removed by the CFH12 remained on the same level (99.0–99.7%) within the range of the tested solution temperatures.



Fig. 3. Effect of the dose of CFH12 (left) and the solution temperature (right) on the removal efficiency of As(III) and As(V)

3.4 Fixed-bed adsorption studies

Granular iron hydroxide CFH12 is a material developed to work under dynamic conditions. Therefore, a series of fixed-bed adsorption tests was run with an empty bed contact time (EBCT) of 23 minutes. This contact time was sufficient enough to maintain a high removal rate of As(III) and As(V) for a very long period of time. The results from the fixed-bed adsorption tests are illustrated in Fig. 4. The curves represent the residual concentration of As in the treated solution (C_{e-As}) as a function of the treated bed volumes (BV) along with the final pH (pH_e). As can be seen, the bed was not exhausted by arsenic during the experiment. The adsorbent CFH12 performed very well and the arsenic concentration in the treated solution remained below 10 μ g/L (the maximal permissible level in drinking water) up to about 15,000 bed volumes. After 15,000 BV, the level of As(III) and (V) gradually increased and reached 15 μ g/L at approximately 20,000 BV.

Initial pH values of the model solutions were between 7.0 and 7.5. It was observed that at the beginning of the process, in case of both As(III) and As(V), pH decreased rapidly to about 2.5. After 700 BV, the pH volume stabilized at 7.3–7.9 and did not change significantly during the experiment.



Fig. 4. Changes of solution pH and breakthrough curves for sorption of arsenic(III) and (V) onto CFH12

4 Conclusions

Tested granular iron hydroxide is a commercial sorbent and its great potential for adsorptive removal of toxic arsenic species from aqueous solutions was confirmed.

The Langmuir and Freundlich isotherm equations were applied for modeling adsorption data and the maximal adsorption capacity calculated by the Langmuir model was comparable for arsenic(III) and arsenic(V). The effect of the contact time, adsorbent dose and solution temperature on the removal of arsenic ions was discussed. It was demonstrated that the percentage removal of arsenic(II) and (V) increased with longer treatment time and significantly higher efficiency of the process was observed for a lower concentration of arsenic present in the solution. The study also reveal that the pseudo-second-order adsorption mechanism is predominant.

The adsorption test results under dynamic conditions demonstrated high adsorbent efficiency and stability over a long period of time. The arsenic concentration in the treated solution remained below $10 \ \mu g/dm^3$ up to about 15,000 bed volumes.

Hence, the application of CFH12 to adsorptive treatment of arsenic-contaminated water and wastewater should be regarded as a robust and effective solution.

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