

TREATMENT OF ARSENIC-RICH WATERS USING GRANULAR IRON HYDROXIDES

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ABSTRACT

Arsenic is a naturally occurring element in the environment; however, due to certain human activities, high levels of arsenic can be present in aquatic ecosystems leading to serious environmental problems. In some regions, elevated arsenic concentrations in surface and groundwater originate from agricultural and industrial sources, including from the application of pesticides and chemical wood preservatives, glass manufacturing, mining activities such as ore processing and runoff from contaminated sites.

A number of technologies are available for arsenic removal from contaminated water, although in the presented work special attention is given to the adsorption method as a technically feasible, commonly applied and effective technique.

It is known that arsenic has a strong affinity for iron rich materials. Therefore, ion exchange/adsorption on iron-containing surfaces has been explored in the removal of arsenic species from water and wastewater.

Therefore, in this study the granular media - ferric hydroxides (CFH12, Kemira Oyj, Finland) was applied to remove arsenic species from aqueous solutions. The CFH12 was characterized in terms of its composition, moisture content, bulk density, particle size, pH of zero point charge and specific surface area. The kinetics and equilibrium adsorption studies were conducted to determine the efficiency of the tested granular iron-based material in As(III) and As(V) removal. The equilibrium studies showed that the Langmuir isotherm model described the adsorption of arsenic species very well with high correlation coefficients. The maximum adsorption capacity of As(V) onto CFH12 as estimated by the Langmuir model was found to be higher compared to As(III). Results obtained from the kinetics adsorption tests demonstrated a significantly higher removal rate for As(V) than As(III) and indicated the benefits of applying granular ferric hydroxides in the treatment of even highly As-contaminated waters.

Keywords: adsorption, arsenate, arsenite, ferric hydroxide, water treatment

1. Introduction

Arsenic is a naturally occurring element in the environment and its chemical form strongly depends on environmental conditions. In the aquatic ecosystem arsenic is typically present in inorganic forms, mainly in two oxidation states (+5, +3). As(III) is dominant in more reducing conditions whereas As(V) is mostly present in an oxidizing environment.

Due to certain human activities, high levels of arsenic in aquatic ecosystems have become a serious environmental problem. Elevated arsenic concentrations found in surface and groundwater, originate in some regions from agricultural and industrial sources, including from the application of pesticides and chemical wood preservatives, glass manufacturing, mining activities such as ore processing and runoff from contaminated sites (Bissen *et al.*, 2003; Camacho *et al.*, 2011). Therefore, a major concern of industry is to maintain good effluent quality, especially for effluents that are discharged in large volumes. This requires constant monitoring of effluent quality to guarantee the efficient protection of the receiving waters and to quickly react to possible negative impacts of contamination on local communities.

The treatment of arsenic contaminated waters may be challenging especially considering that achieving a high water quality requires the application of more than one physico-chemical process. A number of proven treatment methods are available for arsenic removal from waters and wastewaters including oxidation and precipitation techniques, coagulation, ion exchange and adsorption methods as well as membrane separation. A comprehensive comparison of these technologies with their advantages and disadvantages was presented by (Mohan and Pittman, 2007; Ungureanu *et al.*, 2015).

In this work, special attention is given to the adsorption method as a technically feasible, commonly applied and effective technique for the treatment of arsenic rich waters. It is known that arsenic has a strong affinity towards iron-based materials (Bang *et al.*, 2005; Chen *et al.*, 2007; Szlachta *et al.*, 2012). Therefore, in this research granular ferric hydroxides (CFH12) were applied to remove arsenic anionic species from aqueous solutions. CFH12 can be easily utilized in containers/basins as well as in filter media. In the study, batch adsorption tests (kinetics and equilibrium) were conducted in order to evaluate the potential of the tested material for As(III) and As(V) removal prior to performing additional adsorption experiments under dynamic conditions.

2. Materials and methods

In the study, granular iron hydroxides (CFH12) developed by Kemira Oyj (Finland) were used as the adsorptive material for the removal of As(III) and As(V) from water. A scanning electron microscope was used to analyze the surface morphology whereas the specific surface area (S_{BET}) and pore size distribution were determined on the basis of nitrogen adsorption/desorption analysis.

All chemicals used were of reagent grade and solutions were freshly prepared using Milli-Q water. The stock solutions of As(III) and As(V) were prepared using $NaAsO_2$ and $Na_2HAsO_4 \cdot 7H_2O$, respectively. The pH was adjusted by 0.1 M HCl and NaOH. A solution of 0.01 M NaCl was used in all experiments as a background electrolyte.

To investigate the adsorption equilibrium the isotherm tests were conducted using the bottle point method. 20 mL of synthetic water with an initial concentration of As(III) or As(V) of 1-300 mg/L was added into capped tubes containing 0.1 g of adsorbent. The samples were agitated in a shaker incubator at 22 °C until equilibrium was reached. The pH of 7 was kept constant during the experiment.

In the kinetics tests 5 g/L of adsorbent was added to 500 mL of synthetic water sample spiked with 1 mg/L and 20 mg/L of As(III) or As(V). The initial pH of the solution was adjusted to 7. The test was carried out for 5 h using a magnetic stirrer. Samples were collected at certain time intervals and analyzed for the residual As concentration.

3. Results

3.1. Material characterization

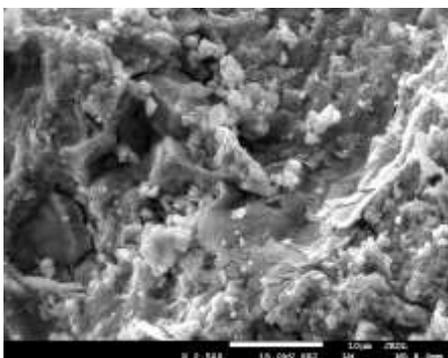


Figure 1: SEM image of the adsorbent CFH12.

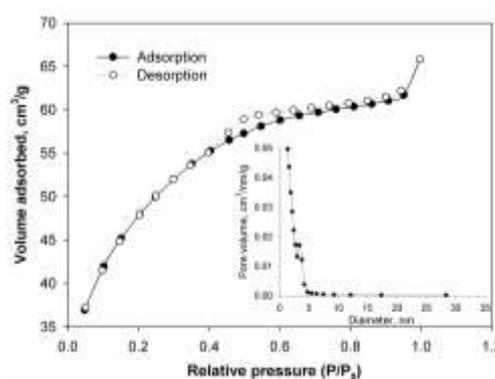


Figure 2: Nitrogen adsorption/desorption isotherms and pore size distribution of CFH12.

The adsorptive material based on ferric hydroxides (CFH12) developed by Kemira Oyj (Finland) was used in the study. Apart from arsenic, the material is able to absorb other inorganic trace contaminants including cadmium, lead, copper, chromium, nickel and manganese (Product information, 2015).

CFH12 is a media of porous morphology (Figure 1) with a specific surface area of 158 m²/g and a pore size ranging from 1.4 nm to 28.3 nm (Figure 2). The granules of CFH12 are of brown and/or reddish brown color with the average equivalent diameter d₅₀ of 1.4 mm. The point of zero charge determined for the tested material was at pH 3 resulting in a negatively charged surface at solution pH values greater than the pH_{PZC}. The properties of the adsorbent used in this work are listed in Table 1.

Table 1: Characterization of the adsorbent CFH12

Parameter	Minimum	Maximum	Typical
Iron, Fe(III), %	39	48	44
Water soluble content, %	0.5	3	2
Moisture, %	13	19	16
Bulk density, kg/L	1.1	1.3	1.2
Particle size – d ₅₀ , mm			1.4
pH _{PZC}			3
S _{BET} , m ² /g			158

3.2. Batch adsorption studies.

The batch adsorption experiments were conducted to evaluate the adsorption of arsenic species onto granular ferric hydroxides CFH12.

The nonlinear form of the Langmuir model was applied to fit the adsorption equilibrium data. The obtained high correlation coefficients indicate that the Langmuir equation was in good agreement with the experimental results (Figure 3). Under the tested conditions (pH 7) arsenate species are negatively charged in water (H₂AsO₄⁻/HAsO₄²⁻ with pK_a 6.97) whereas the dominant form of arsenite is the neutral H₃AsO₃ (pK_a 9.22) (Ungureanu *et al.*, 2015). As a consequence, more unfavorable electrostatic interactions exist between the adsorbent surface (pH_{PZC}=3) and the negatively charged As(V) species than with the fully protonated As(III). Nevertheless, a slightly higher uptake and removal was observed when arsenate was present in the solution indicating that its removal is controlled by the specific adsorption rather than a physical mechanism. The maximum adsorption capacity was calculated to be 44.04 mg/g for As(V) and 43.75 mg/g for As(III). Also, the CFH12 exhibited higher affinity towards arsenate than arsenite. This has been confirmed by the calculated values of the Langmuir *b* parameter which were nearly 4.5 times greater for As(V) compared to As(III) .

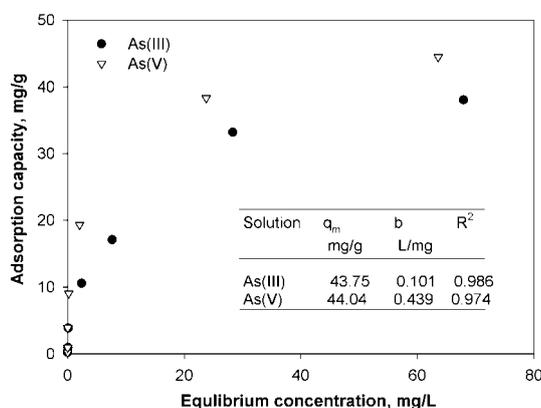


Figure 3: Adsorption isotherms and Langmuir model parameters for As(III) and As(V) by CFH12.

The experimental results obtained in the kinetics study show that the removal of arsenic ions increases with an increasing adsorbent contact time (Figure 4). Furthermore, it was observed that the adsorption kinetics of As(V) was faster in the initial period of the process and after 1 hour the adsorption was found to be almost constant. This contrasts with the results obtained for As(III). Approximately 97.2% of As(V) was removed from the solution with an initial concentration of 1 mg/L after 1 hour of contact time whereas the removal rate for As(III) was just below 45%. After 5 hours the removal of arsenate slightly increased (up to 98.5%), but in the case of arsenite the increment was considerably higher and recorded a maximum removal of 78.2%. Within the 5 hours of contact with CFH12, lower adsorption efficiency was observed when a higher initial concentration of adsorbate was present in the solution. An increase in the initial concentration to 20 mg/L decreased the efficiency of As(III) and As(V) removal to 50% and 85% respectively.

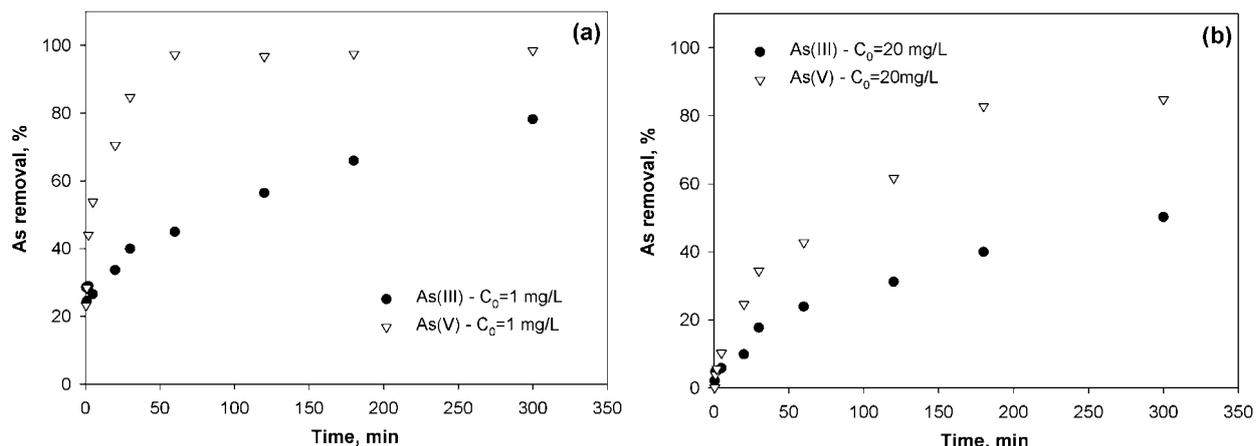


Figure 4: Adsorption kinetics for As(III) and As(V) by CFH12; initial As concentration (a) 1 mg/L and (b) 20 mg/L.

4. Conclusions

In this study, the potential of granular ferric hydroxides (CFH12) for As(III) and As(V) removal from aqueous solutions was recognized. The tested material contains 39-48% of Fe(III) and exhibited high selectivity towards arsenic species. It was demonstrated that the experimental equilibrium data obtained for As(III) and As(V) at pH 7 were well described by the Langmuir model. The calculated maximum adsorption capacity of arsenate (44.04 mg/g) was higher compared to arsenite (43.75 mg/g) as well as the affinity of arsenate towards adsorbent surface. The presented kinetics adsorption results show that the removal of arsenic ions increases with an increasing contact time with the adsorbent and decreases with an increasing initial concentration of arsenic species from 1 mg/L to 20 mg/L. However, under the applied conditions, higher removal efficiency was observed when arsenate was present in the solution. This work confirms that the tested adsorbent CFH12 can be successfully applied in the adsorptive treatment of arsenic contaminated waters and wastewaters and its effectiveness under continuous flow conditions will be evaluated by the authors in a future study.

ACKNOWLEDGEMENTS

This research is part of the study supported by the National Centre for Research and Development grant (2014-2017) "Sustainable and responsible supply of primary resources - SUSMIN" (<http://projects.gtk.fi/susmin>), within the EU ERA-NET ERA-MIN program.

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