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Treatment of arsenic-rich waters using granular iron hydroxides

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ABSTRACT

The granular media, ferric hydroxides (CFH12), 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 demonstrated that both the Langmuir and Freundlich isotherm model described the adsorption of arsenic species notably well with high correlation coefficients. The maximum adsorption capacity of As(V) onto CFH12 estimated by the Langmuir model was comparable to As (III). The results obtained from the kinetics adsorption tests demonstrated a significantly higher removal rate of As(V) than As(III) and indicated the benefits of applying granular ferric hydroxides in the treatment of even highly arsenic-contaminated waters.

Keywords: Adsorption; Arsenate; Arsenite; Batch operation; Granular ferric hydroxide; Water treatment

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1. Introduction

Arsenic is a naturally occurring element in the environment and is widely known for its high toxicity to humans and aquatic organisms. Chronic exposure to arsenic has been linked to health problems, including cancer of the skin, kidney, lung and bladder, as well as skin diseases and diseases of the blood vessels of the legs and feet [1].

In an aquatic ecosystem, arsenic is typically present in inorganic forms, mainly in two oxidation states (+5, +3). As(III) is dominant in the presence of reducing conditions, whereas As(V) is mostly observed in the presence of 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 the surface and groundwater originate in certain regions from agricultural and industrial sources, particularly from the application of pesticides and chemical wood preservatives, glass manufacturing, mining activities, such as ore processing and run-off from contaminated sites [2,3]. Therefore, a major concern in industry is to maintain good effluent quality, discharged in large volumes into a body of

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Presented at CEST2015—14th International Conference on Environmental Science and Technology, Rhodes, Greece, 3–5 September 2015 water. This requires constant monitoring of effluent quality to guarantee the efficient protection of the receiving waters and to react quickly to possible negative impacts of contamination within local communities.

The treatment of arsenic-contaminated waters may be challenging, especially when achieving high water quality requires the application of more than one physiochemical 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 is available in the literature [4–6].

A traditional method for the arsenic removal is coagulation/co-precipitation with Fe/Al salts but for source waters containing high levels of phosphate or silicate, the process can be less effective. Other treatment strategies, such as ion exchange and adsorption processes, exhibit promise for the removal of arsenic, but the viability of these methods are dependent on the material applied. The adsorption of arsenic on iron-based sorbents is an emerging treatment. Many studies have confirmed that arsenic species have a natural affinity for iron compounds under various operating conditions [7–11]. For instance, Hong et al. [9] applied ferric-based, layered double hydroxide with α-alanine intercalation for removing arsenic species from aqueous solutions and observed the strong affinity of arsenite toward the synthesized material. Martínez-Cabanas et al. [10] investigated iron-based biomass-silica gel composites and found that the presence of iron in the composites is a crucial factor determining the arsenic adsorption process. Vitela-Rodriguez and Rangel-Mendez [11] reported that the arsenate adsorption capacity of activated carbons increased after modification with iron hydro(oxide) nanoparticles.

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. In this study, granular ferric hydroxides (CFH12) are 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, are 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 analyse the surface morphology, whereas the specific surface area (S_{BET}) and pore size distribution were determined on the basis of nitrogen adsorption/desorption analysis [12].

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 using 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. Also, 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 was monitored constantly during the experiment.

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

3. Results and discussion

3.1. Material characterization

The granular material, based on ferric hydroxides used in the study, apart from arsenic, is able to absorb other inorganic trace contaminants, such as phosphorus, antimony or nickel [13–15].

CFH12 is a media of porous morphology (Fig. 1) with a specific surface area of 158 m^2/g and a pore size ranging from 1.4 to 28.3 nm (Fig. 2). The CFH12 consists of FeOOH granules with an average equivalent diameter d_{50} of 1.4 mm and iron content up to 48%. The granules are of brown and/or reddish brown colour. The chemical composition of CFH12 is as follows: 3.75% MgO, 0.45% Al_2O_3, 1.18% SiO_2, 8.49% SO_x, 0.27% K_2O, 2.72% CaO, 0.50% TiO_2 and 82.65% Fe_2O_3 [13]. The pH of the point of zero charge (pH_{PZC}) of such an iron-based media is generally in the 7.0–9.0 range [16,17]. Thus, below the pH_{PZC},

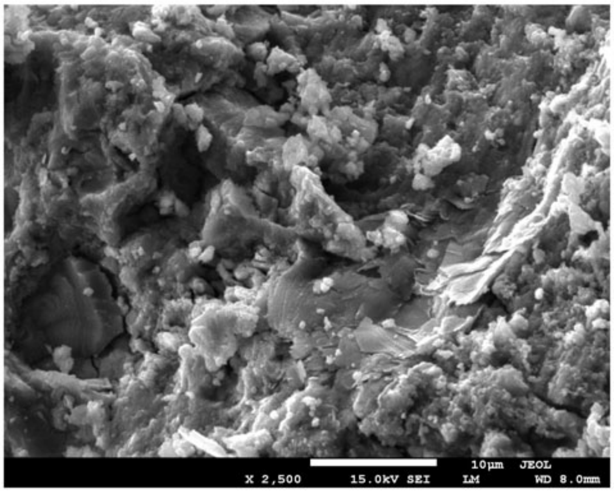

Fig. 1. SEM image of the adsorbent CFH12.

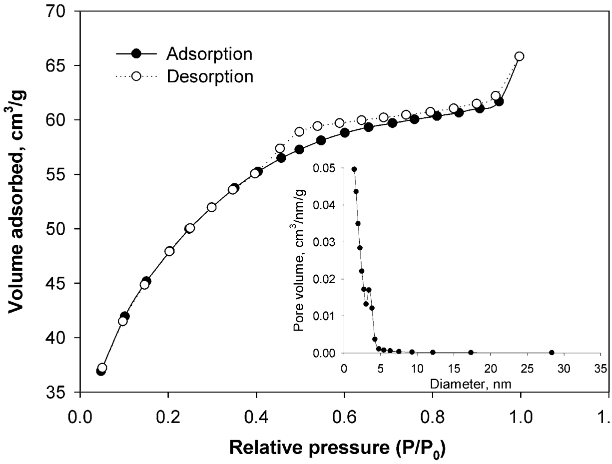

Fig. 2. Nitrogen adsorption/desorption isotherms and pore size distribution of CFH12.

the adsorptive material has a positive surface charge that attaches the negatively charged arsenic anions, while above the pH_{PZC}, the surface is negatively charged and repels the arsenic anion.

The properties of the adsorbent used in this work are listed in Table 1.

3.2. Batch adsorption studies

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

The non-linear form of the Langmuir and Freundlich model is applied to fit the adsorption equilibrium data (Fig. 3). Table 2 shows fitted values of the isotherm parameters along with the correlation coefficients. The obtained high R^2 values indicate that both the Langmuir and Freundlich equations are in good agreement with the experimental results. However, for As(V), the Freundlich model provides slightly better fit, whereas the Langmuir model is more suitable for the description of As(III) adsorption onto CFH12.

The maximum adsorption capacity calculated using the Langmuir equation is 44.04 mg/g for As(V) and 43.75 mg/g for As(III). However, CFH12 exhibits higher affinity towards arsenate than arsenite. This has been confirmed by the calculated values of the Langmuir *b* parameter which are nearly 4.5 times greater for As(V) compared to As(III).

Under the tested conditions, arsenate species are negatively charged in aqueous solution ($H_2AsO_4^-/HAsO_4^{2-}$ with pK_a 6.97), whereas the dominant form of arsenite is the neutral H_3AsO_3 (pK_a 9.22) [19]. As pH decreases during the process (from pH_0 7 to final pH of 3.44–5.45 and 3.50–6.97 for C_0 1–300 mg/L of As(III) and As(V), respectively), the degree of positive surface charge on iron oxide surface increases, enhancing the attractive forces toward anionic species. Therefore, a slightly higher uptake and removal is observed when arsenate is present in the solution, indicating that removal of arsenate may be controlled electrostatically. Because the Coulombic

Table 1
Characterization of the adsorbent CFH12 [18]

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
S_{BET}, m^2/g			158
Colour			Brown-red

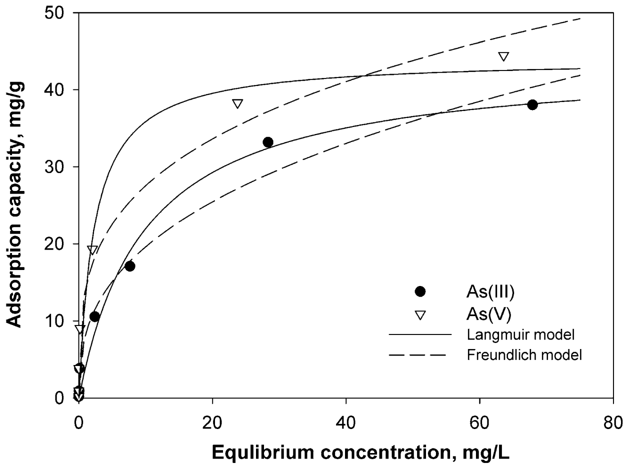

Fig. 3. Langmuir and Freundlich isotherms for the adsorption of As(III) and As(V) onto CFH12.

Table 2
Isotherm parameters for As(III) and As(V) adsorbed onto CFH12

Isotherm	Parameter	As(III)	As(V)
Langmuir model	q_m (mg/g)	43.75	44.04
	b (L/mg)	0.101	0.439
	R^2	0.986	0.974
Freundlich model	K ((mg/g) (L/mg))	8.24	14.17
	n	2.655	3.467
	R^2	0.980	0.981

Notes: q_m—equilibrium adsorption capacity; b—the Langmuir adsorption equilibrium constant; K and n—Freundlich empirical constants.

interaction is practically insignificant for As(III) adsorption, changes in pH during the process have a small impact on the adsorption onto granular ferric oxides compared to As(V). Thus, adsorption of fully protonated As(III) may take place only through ligand exchange reactions [20]. These observations are in agreement with results previously published [16,21].

The experimental results obtained in the kinetics study show that the removal of arsenic ions increases with contact time (Fig. 4). Observations reveal that at the beginning of the process, the adsorption kinetics of As(V) is faster than the absorption kinetics As(III). Moreover, for the lower concentration of arsenate (1 mg/L), the adsorption plateaus within one hour, while for higher concentration (20 mg/L) no significant changes in arsenate adsorption are recorded after three hours of the process. The adsorption of arsenite increases progressively with contact time, regardless of its initial concentration in the solution.

After one hour of contact time, approximately 97.2% of As(V) is removed from the solution containing 1 mg/L, whereas the removal rate for As(III) is close to 45%. After five hours, uptake of arsenate is comparable (98.5%), but in the case of arsenite, the increment is considerably higher, and the recorded maximum removal is 78.2%. Lower adsorption efficiency is observed when a higher initial concentration of adsorbate is present in the solution. After the five hours with an initial concentration of arsenic species of 20 mg/L, the efficiency of As(III) and As(V) removal is approximately 50 and 85%, respectively.

Granular iron-based media have received significant attention recently, possibly because of their application for the treatment arsenic-contaminated water and wastewater, which is being intensively explored.

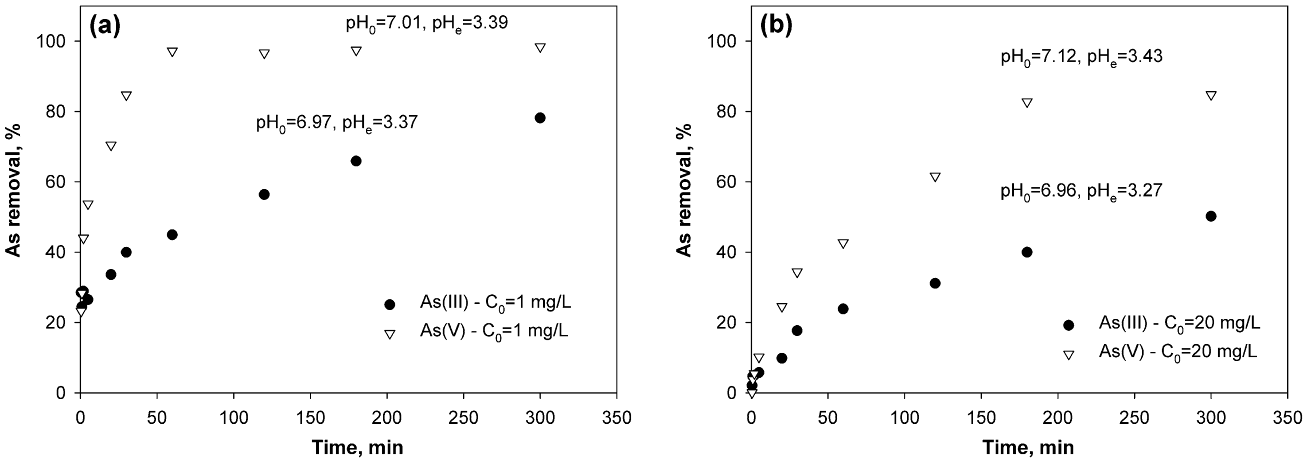

Fig. 4. Adsorption kinetics for As(III) and As(V) by CFH12; initial As concentration (a) 1 mg/L and (b) 20 mg/L.

The experimental observations presented in the literature suggest iron-based adsorbents are very promising materials due to their high arsenic adsorptive capacity and removal efficiency. It is notably difficult to compare the efficiency of other commercially available adsorbents with CFH12. The difference in adsorption capacity is related to the different experimental conditions used in the current and previous studies. For instance, at an equilibrium arsenic(V) concentration of 10 μg/L, the adsorption capacity of granular ferric (hydro)oxide GFH (Wasserchemie, Germany) is estimated to be 1.1 mg/g [20]. For initial concentration of arsenate of 400 μg/L at solution pH 4 the maximum arsenic uptake reported [22] is 170 μmol/g of GHE. In the current study using CFH12, the arsenate uptake is 44.04 mg/g with an arsenate equlibrium concentration of approximately 60 mg/L and initial solution pH 7.0.

4. Conclusions

In this study, the potential of granular ferric hydroxides CFH12 for As(III) and As(V) removal from aqueous solutions was investigated. It was demonstrated that the experimental equilibrium data obtained for As(III) and As(V) at pH 7 were well described by the Langmuir and Freundlich models. The calculated maximum adsorption capacity of arsenate (44.04 mg/g) was comparable to arsenite (43.75 mg/g). The presented kinetics adsorption results showed that the removal of arsenic ions increased with an increasing contact time with the adsorbent and decreased with an increasing initial concentration of arsenic species from 1 to 20 mg/L. However, under the applied experimental conditions, higher removal efficiency was observed when arsenate was present in the solution. This work confirmed that the tested adsorbent CFH12 could be successfully applied for the adsorptive treatment of arsenic-contaminated waters and wastewaters. The effectiveness of using CFH12 as an absorbent under continuous flow conditions will be evaluated by the authors in a future study.

Acknowledgments

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