

Anionic competition on arsenate removal by modified granular ferric hydroxide adsorbent

Hoang Giang Pham¹, Tran Thanh Son Nguyen¹, Thi Thuy Pham^{1*}, Manh Khai Nguyen¹, Bart Vander Bruggen², Thi Thanh Mai Nguyen³

¹Faculty of Environmental Sciences, University of Science, Vietnam National University - Hanoi, 334 Nguyen Trai Street, Thanh Xuan District, Hanoi, Vietnam

²Department of Chemical Engineering, Katholieke University of Leuven, Celestijnenlaan 200F, box 2424, B-3001 Heverlee (Leuven), Belgium

³Long Bien Secondary School, 16/163/3 Tu Dinh Ward, Long Bien District, Hanoi, Vietnam

Received 27 April 2022; accepted 1 July 2022

Abstract:

The presence of inorganic forms of arsenic in water causing a serious threat to human health. Exposure of arsenic can cause serious diseases such as skin discoloration, cancer of skin, kidney and lung, blood vessel diseases, high blood pressure, and reproductive disorders. Removal of arsenic to provide safe drinking water was conducted to investigate the effects of individual and combined anions (sulphate, nitrate, phosphate, and chloride ions) on the arsenate adsorption capacity of modified granular ferric hydroxide adsorbent in batch experiments. The observed adsorption data fit the Langmuir model well. The presence of sulphate (400 mg/l), nitrate (15 mg/l), and chloride (250 mg/l) ions did not significantly affect the arsenate adsorption and the maximum adsorption capacity of arsenic was reduced by less than 5%. In contrary, phosphate ions showed strong competition for the adsorption process as the maximum adsorption capacity of the material was reduced by 59.8 and 73% at concentrations of 0.2 and 0.5 mg/l, respectively. The results also showed that phosphate anions were slightly preferable than arsenate in their competitive adsorption by the adsorbent.

Keywords: arsenate, competing anions, iron hydroxide-based adsorbent.

Classification numbers: 2.2, 5.3

1. Introduction

Nowadays, there has been much research focused on inexpensive adsorbent materials to remove arsenic in water because of the serious effects arsenic has on human health. Among adsorbents, iron-based materials are the most studied because of their low cost, abundance, as well as their arsenic removal efficiency. Iron compounds including FeOOH, Fe₂O₃, Fe(OH)₃ [1-3]... or synthetic materials with the main component of iron such as laterite, hematite, nano-adsorbent particles [4-6]... have been studied with high arsenic treatment efficiency, low cost, and relatively easy operating conditions [2, 5, 6].

Among iron compounds, modified granular ferric hydroxide adsorbents are an iron-rich material combined with low cost and locally-sourced minerals such as bentonite, kaolinite, iron hydroxide or aluminium hydroxide, which are stable in a typical Vietnamese environment [3]. This study evaluated the arsenate removal efficiency of modified granular ferric hydroxide

adsorbents under various parameters affecting the adsorption process such as pH, temperature, and time. In addition, this adsorbent was used in a pilot scale treatment system to demonstrate toxicant removal ability and economic efficiency.

However, the chemical composition of water such as phosphate or nitrate concentrations can significantly affect the removal of arsenic by an iron-based material through mechanisms similar to arsenate adsorption such as anions exchange because phosphate and arsenate can bond to amorphous, crystalline, or coprecipitated forms of iron or iron oxide [7, 8].

Batch studies were carried out using simulated groundwater to assess the effects of phosphate, nitrate, sulphate, and chloride on the removal of arsenic by a modified granular ferric hydroxide adsorbent. The findings presented in this paper will aid in the development of more effective arsenic treatment processes.

*Corresponding author: Email: phamthithuy@hus.edu.vn

2. Materials and methods

2.1. Materials

Adsorbent materials used in this study were developed by P.T. Thuy, et al (2020) consisted of 58.5 percent of iron hydroxide, 10 percent of aluminium hydroxide, 7.5 percent of bentonite, and 24 percent of kaolinite and was formed into tiny balls with practical sizes ranging from 5 to 10 mm [3].

Chemicals including NaCl, NaNO₃, Na₂SO₄, Na₂HPO₄, and Na₂HAsO₄·7H₂O were pure reagent grade materials. Stock solutions of arsenate, chloride, sulphate, nitrate, and phosphate were prepared by dissolving the respective chemicals in deionized water. All these solutions were further diluted to suitable concentrations on the day of use.

2.2. Methods

The experiments were studied at room temperature. First, 50 ml of solution was prepared and placed into 100 ml flasks, then 0.1 g of adsorbent was added.

The initial concentrations of arsenic were 100; 200; 500; 1000 mg/l (in the form of arsenate). To study the effect of anions, the experiments were conducted with solutions that only contain arsenate or contain arsenate and one of the competing anions.

The purpose of this experiment is to evaluate the influence of anions in the real environment, thus, the concentrations of anions were selected based on QCVN 09-2015/BTNMT Vietnamese technical regulation on ground water quality (in the case of phosphate, it is based on QCVN 08-2015/BTNMT Vietnamese technical regulation on surface water quality). Concentrations of competing anions were sulphate (400 mg/l), chloride (250 mg/l), nitrate (15 mg/l), and phosphate (0.2 mg/l and 0.5 mg/l).

The pH was adjusted to 7 by HCl 0.1 M or NaOH 0.1 M. The mixture was shaken at 150 rpm for 120 min at room temperature (25°C). The effluent was filtered

through a 0.45 µm filter paper, and concentrations of As (V) were analysed using (AAS) Shimadzu AA6800, concentrations of other anions were analysed by UV-VIS method.

2.3. Adsorption isotherm models

Adsorption isotherm models have been used to describe the interaction between arsenic in solution and the adsorbents. In addition, isotherm models can be used to explain the distribution of metal ions between the liquid and solid phase when equilibrium is reached. In this work, adsorption isotherm models were generated based on Freundlich and Langmuir models to evaluate the adsorption capacity of the material.

The Langmuir equation is given by:

$$q_e = q_m k_a C_e / (1 + k_a C_e)$$

The linear form is:

$$C_e/q_e = (1/q_m)C_e + 1/(k_a q_m)$$

where q_e is the amount of ion adsorbed (mg/g); C_e is the equilibrium concentration (mg/l); q_m is the max adsorption capacity (mg/g); and k_a is the adsorption equilibrium constant.

The Freundlich equation is given by:

$$q_e = K_f C_e^{1/n}$$

The linear form is:

$$\ln q_e = \ln K_f + (1/n) \ln C_e$$

where the constant K_f is related to the adsorption capacity of materials and $1/n$ is related to the surface heterogeneity.

3. Results and discussion

3.1. The adsorption of arsenate onto modified granular ferric adsorbent

Figure 1A shows that the adsorption of arsenate (without competing anions) onto the adsorbent. Fig. 1B is the linear data fit to the Langmuir isotherm model and

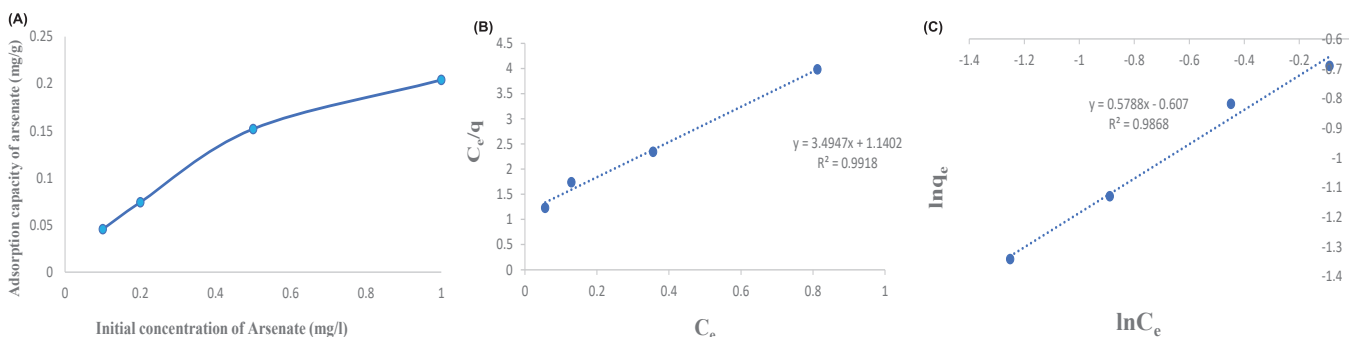


Fig 1. (A) Adsorption capacity of arsenate onto adsorbent; (B) Langmuir isotherm model fit and (C) Freundlich isotherm model.

Fig. 1C to the Freundlich isotherm model. The correlation coefficient of the Langmuir isotherm model is 0.99 and the Freundlich is 0.98, which also indicates that arsenate adsorption characteristics on the material was monolayer adsorption and energetically equivalent, that is, the energy of adsorption is equal to the surface.

Maximum adsorption capacity of adsorbent (q_m) following the Langmuir model is 0.286 mg/g and adsorption equilibrium constant is 3.07. This maximum adsorption capacity is higher than the result of P.T. Thuy, et al. (2020) [3] due to the difference in the particle sizes, for example, in this study it was 5-10 mm compared to about 20 mm in the previous. In case of the Freundlich model, the Freundlich constant (K_f) is 0.247.

3.2. The adsorption of arsenate onto modified granular ferric adsorbent in the presence of competing anions

Figure 2 shows a change in the arsenate adsorption process onto material in the presence of competing anions in solution. Samples containing monovalent anions (chloride and nitrate) showed differences in results ranging from 0 to 3%, which is almost no difference from samples containing arsenate only. In the case of the divalent anion sample (sulphate), arsenate adsorption capacity tends to decrease slightly in the range of 3-5%. The anions having almost no effect on the efficiency of the arsenate adsorption process indicates that the anion exchange mechanism has less contribution in the arsenate adsorption process of this material.

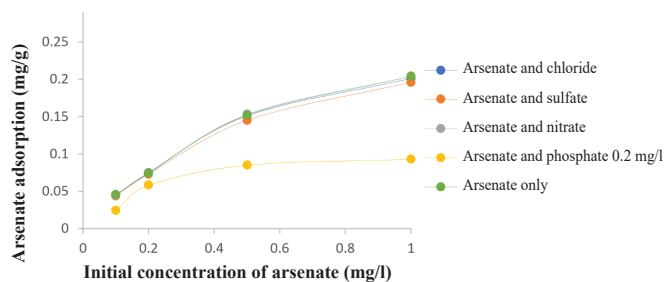
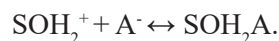
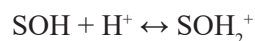


Fig. 2. Adsorption capacity of arsenate onto adsorbent under the influence of competing anions.

On the other hand, phosphate significantly reduced the adsorption capacity of arsenate. These decreases were from 0.456 to 0.246 mg/l (46% decrease) at an initial concentration arsenate = 0.1 and 2.04 to 0.62 mg/l (69.6% decrease) at initial arsenate concentration = 1 mg/l.

There are two main mechanisms for the interaction of anions on the surface of iron hydroxide.

First, the surface of the material is ionized by protons and anions, which will interact with the surface through the affinity adsorption mechanism [8, 9]:

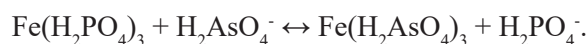


Anions such as phosphate or arsenate form complexes with the surface of the material [10]:



It can be seen that the effect of affinity adsorption mechanism did not play big role. This is explained by the fact that this process depends on the protonation of the surface of the material. At the pH of the reaction (pH=7), the concentration of H^+ ions in the solution is not large enough for the protonation process.

On the other hand, the main mechanism for this competition is the similarity in the chemical properties of phosphate and arsenate (phosphorus and arsenic are both in the group VA). Predictably, phosphates have a complex on the iron surface thereby reducing the potential for iron-arsenate interactions like, for example, the following reaction:



3.3. Effect of phosphate concentration on arsenate adsorption capacity

Figure 3 shows that arsenate adsorption capacity decreased in the range of 22-55% at an initial phosphate concentration of 0.2 mg/l, and 60-70% with an initial phosphate concentration of 0.5 mg/l. It can also be seen that the adsorption capacity of arsenate remains constant when the initial arsenate concentration reaches 0.5 mg/l in solutions with phosphate anions, while this capacity continues to increase in samples without competing anions.

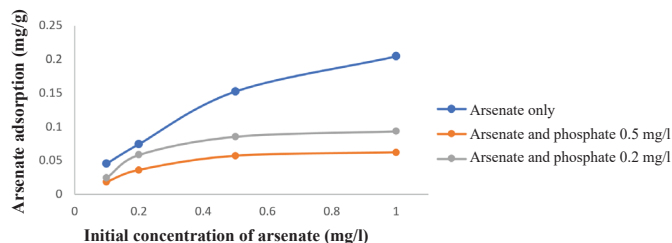


Fig. 3. Adsorption capacity of arsenate onto adsorbent under different concentrations of phosphate.

The Langmuir and Freundlich adsorption isotherm models of arsenate adsorption in the presence of phosphate is shown in Fig. 4. Similar to the case without competing anions, the adsorption processes were fitted to the Langmuir and Freundlich isotherm models with correlation coefficient of 0.97-0.98 and 0.82-0.89, respectively.

The Langmuir isotherm models show that the maximum adsorption capacity of arsenate decreased from 2.86 to 0.115 mg/g at a concentration of phosphate of 0.2 mg/l (59.8%) and from 2.86 to 0.077 mg/g at 0.5 mg/l (73% reduction).

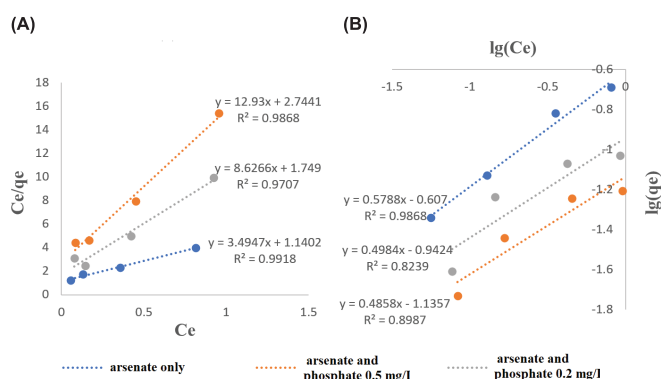


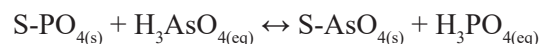
Fig. 4. (A) Langmuir isotherm model and (B) Freundlich isotherm model of arsenate adsorption under different concentrations of phosphate.

3.4. Concentration of competing anions after the adsorption process

The concentration of monovalent and divalent anions after the adsorption process showed no change. This confirms the prediction made in section 3.2 is correct, that is, these anions have absolutely no interaction with the surface of the material.

In the case of phosphate at low concentration (0.2 mg/l), almost all phosphate was adsorbed into the material. When the concentration of phosphate was 0.5 mg/l, 80-98% phosphorus was removed from the solution after the reaction ended (Fig. 5). It is also easy to see the adsorption competition between arsenate and phosphate as the higher the initial arsenate concentration, the lower the phosphate removal efficiency. This proves the above assumptions in section 3.1 about the similarity in chemical properties of these two compounds leading to a competitive reaction on the surface of the iron-rich material. The results also show phosphate anions were slightly preferable than arsenate in their competitive adsorption by the adsorbent.

The general equation describing the reaction between phosphate, arsenate, and the surface of the material can be expressed as follows:



where $S-PO_{4(s)}$ and $S-AsO_{4(s)}$ are complexes of arsenate and phosphate with the surface of the material.

The equilibrium constant of the reaction (K_c) will be:

$$K_c = [H_3PO_4]/[H_3AsO_4]$$

From the calculated data, it is shown that the equilibrium constant for the reaction (K_c) is 5.65 ± 0.33 .

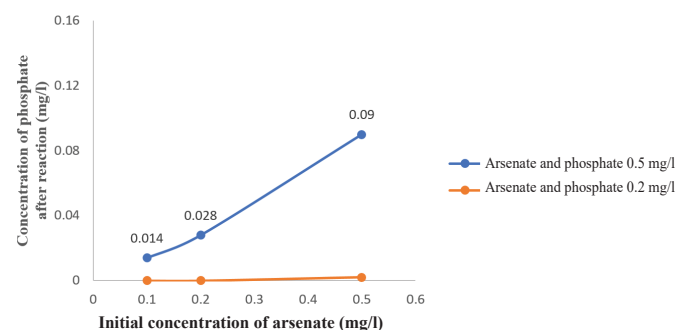


Fig. 5. Concentration of phosphate after the adsorption process.

In comparison to previous studies [8, 11, 12], both monovalent and divalent anions showed significant competition for arsenate adsorption on the material's surface. However, this study's adsorbent indicates that the impacts of these anions are very small, and that any anion competition in the environment is primarily due to phosphates.

4. Conclusions

The presence of sulphate (400 mg/l), nitrate (15 mg/l), and chloride (250 mg/l) ions did not significantly affect the arsenate adsorption, which indicated that the anion exchange mechanism has less contribution in the arsenate adsorption process of an iron-rich adsorbent. In contrary, phosphate ions showed strong competition for the adsorption process with arsenate. The maximum adsorption capacity of the Langmuir isotherm was reduced by 59.8 and 73% at phosphate concentrations of 0.2 and 0.5 mg/l, respectively, due to the similarity in chemical properties of phosphate and arsenate. Therefore, phosphate should be considered in the actual arsenate treatment, and arsenate removal procedures should be calculated based on the actual adsorption capacity in the presence of competing phosphates or phosphate removal prior to passing through arsenate removal materials.

CRediT author statement

Hoang Giang Pham: Conceptualization, Methodology, Formal analysis, Writing, Editing; Tran Thanh Son Nguyen: Data analyst; Thi Thuy Pham: Conceptualization, Methodology, Formal analysis, Writing, Review, Editing; Manh Khai Nguyen: Review, Data analyst; Bart Vander Bruggen: Review, Editing; Thi Thanh Mai Nguyen: Data analyst.

ACKNOWLEDGEMENTS

The research is funded by the Vietnam Ministry of Science and Technology under Independent project DTDL.CN-50/18.

COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES

- [1] R. Ozola, et al. (2019), "FeOOH-modified clay sorbents for arsenic removal from aqueous solutions", *Environmental Technology & Innovation*, **13**, pp.364-372.
- [2] X. Yu, et al. (2019), "Ultrafast and deep removal of arsenic in high-concentration wastewater: A superior bulk adsorbent of porous Fe₂O₃ nanocubes-impregnated graphene aerogel", *Chemosphere*, **222**, pp.258-266.
- [3] P.T. Thuy, et al. (2020), "Removal of As (V) from the aqueous solution by a modified granular ferric hydroxide adsorbent", *Science of The Total Environment*, **706**, DOI:10.1016/j.scitotenv.2019.135947.
- [4] N.T. Hai, et al. (2020), "Laterite as a low-cost adsorbent in a sustainable decentralized filtration system to remove arsenic from groundwater in Vietnam", *Science of The Total Environment*, **699**, DOI:10.1016/j.scitotenv.2019.134267.
- [5] W.Shengsen Wang, et al. (2015), "Removal of arsenic by magnetic biochar prepared from pinewood and natural hematite", *Bioresource Technology*, **175**, pp.391-395.
- [6] L. Adlnasab, N. Shekari, A. Maghsodi (2019), "Optimization of arsenic removal with Fe₃O₄@Al₂O₃@Zn-Fe LDH as a new magnetic nano adsorbent using Box-Behnken design", *Journal of Environmental Chemical Engineering*, **7(2)**, DOI:10.1016/j.jece.2019.102974.
- [7] K.H. Goh, T.T. Lim (2005), "Arsenic fractionation in a fine soil fraction and influence of various anions on its mobility in the subsurface environment", *Applied Geochemistry*, **20(2)**, pp.229-239.
- [8] X. Meng, S. Bang, G.P. Korfiatis, "Effects of silicate, sulfate, and carbonate on arsenic removal by ferric chloride", *Water Research*, **34(4)**, pp.1255-1261.
- [9] Y.M. Pajany, et al. (2011), "Arsenic (V) adsorption from aqueous solution onto goethite, hematite, magnetite and zero-valent iron: Effects of pH, concentration and reversibility", *Desalination*, **281**, pp.93-99.
- [10] F. Zhang, H. Itoh (2005), "Iron oxide-loaded slag for arsenic removal from aqueous system", *Chemosphere*, **60(3)**, pp.319-325.
- [11] X. Meng, et al. (2002), "Combined effects of anions on arsenic removal by iron hydroxides", *Toxicology Letters*, **133(1)**, pp.103-111.
- [12] M. Chen, et al. (2018), "Modeling arsenic (V) removal from water by micellar enhanced ultrafiltration in the presence of competing anions", *Chemosphere*, **213**, pp.285-294.