

## Removal of arsenic using synthetic magnetite: Desorption study

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### Abstract

Synthetic magnetite ( $\text{Fe}_3\text{O}_4$ ) was studied as a sorbent for the removal of arsenic from the model aqueous solutions. The sorbent was prepared by the co-precipitation of Fe(II) and Fe(III) under alkaline conditions. The effect of pH, initial arsenic concentration and a the contact time of magnetite and arsenic were investigated in the batch adsorption-equilibrium experiments. Maximum sorption capacity of magnetite obtained at pH 3.5 was 46.7 mg/g. Desorption of arsenic loaded on magnetite was studied under various experimental conditions.

**Key words:** arsenic, iron oxide, magnetite, sorption, desorption

### Introduction

Arsenic is an ubiquitous element. Due to its toxicity it is considered as a high-priority pollutant. Arsenic contamination of the water supplies has become one of the major problems. Even small concentrations of arsenic in the drinking water may have adverse health effects. Known consequences include cancer, pigmentation changes, hyperkeratosis, neurological disorders, cardiovascular diseases and conjunctivitis (Mandal and Suzuki, 2002). Therefore, the World Health Organization (WHO) recommended to reduce the maximum contaminant level (MCL) of arsenic in the drinking water to 10  $\mu\text{g/L}$  from an earlier value of 50  $\mu\text{g/L}$  (WHO, 2004). In natural waters the arsenic can be found in a wide range of concentrations from less than 0.5  $\mu\text{g/L}$  to more than 5 000  $\mu\text{g/L}$  (Smedley and Kinniburgh, 2002).

Arsenic occurs in  $-3$ ,  $0$ ,  $+3$  and  $+5$  oxidation states. In the water environment the most predominant forms are trivalent arsenite As(III) and pentavalent arsenate As(V). Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Generally, As(V) is more prevalent in the surface waters while As(III) occurs in anaerobic ground waters (Václavíková et al., 2008). Arsenic occurs in both organic and inorganic forms in natural waters. Organic arsenic may be produced by biological activity, mostly in the surface waters, but is rarely quantitatively important. The inorganic forms of arsenic are more toxic than its organic forms. Arsenic is more difficult to be removed when it occurs in As(III) form (Smedley and Kinniburgh, 2002).

Arsenic can be removed by various treatment methods, such as coagulation and flocculation, precipitation, ion exchange, reverse osmosis, membrane and adsorption technologies. Among them, coagulation/precipitation followed by filtration is the most commonly used technique.

Ion exchange is effective in As(V) removal but may not be suitable for As(III) removal. The use of reverse osmosis and the membrane technologies is quite expensive compared to other methods (Pokhrel and Viraraghavan, 2007; Václavíková et al., 2008). Adsorption processes are commonly applied and show a good efficiency to cost ratio for arsenic removal. Sorbents based on iron compounds are the most commonly used. Several iron (III) oxides/oxyhydroxides, such as amorphous hydrous ferric oxide (FeOOH), poorly crystalline hydrous oxide – ferrihydrite, goethite ( $\alpha$ -FeOOH) and akaganeite ( $\beta$ -FeOOH) are promising sorbents for the removal of both As(V) and As(III) from aqueous solutions. Other commonly used sorbents based on iron oxides/oxyhydroxides are e.g. iron oxide-coated sand, granular ferric hydroxide, iron-coated cement, iron-coated alumina and the magnetically modified zeolite. Most treatment methods discussed above are more effective in removal of arsenic from the water containing high initial arsenic concentrations (usually  $>100$  mg/L). However, they fail to remove arsenic concentrations below the new decreased limit (10  $\mu\text{g/L}$ ) (Mohan and Pittman, 2007). Therefore, there is a tremendous demand for the developing of inexpensive efficient methods for the removal of arsenic species from the drinking water. Sorption methods are still considered promising, in regard to the cost/efficiency factor and new sorbents are being developed with the aim of obtaining the new target limit (Václavíková et al., 2008).

After the arsenic sorption there is a problem how to deal with used sorbents. Generally, there are two main options for dealing with arsenic waste materials:

- Desorption and regeneration of materials
- Solidification/stabilization followed by the disposal of treated wastes.

Desorption can help to regenerate the adsorbent. A successful desorption process must restore the adsorbent

close to its initial properties for the effective reuse for further arsenic removal. Desorption and regeneration is a critical consideration and contributor to process costs and metal(s) recovery in a concentrated form. Desorption of arsenic from exhausted sorbent is usually achieved using several eluents. Selection of the eluent depends on the arsenic adsorption mechanism and the nature of the adsorbent (Mohan and Pittman, 2007). The most commonly used arsenic eluents are sodium hydroxide (Cumbal et al., 2003; Guo and Chen, 2005; Kundu and Gupta, 2006) and strong acids (Say et al., 2003).

Solidification/stabilization transforms potentially hazardous liquid/solid wastes into the less hazardous or non-hazardous solids before depositing these solids in secure landfills. This solidified/stabilized waste must strictly follow leachability regulatory requirements prior to the disposal. According to USEPA, a waste is deemed as hazardous material if the arsenic concentration in the Toxicity Characteristic Leaching Procedure (TCLP) leachate exceeds 5 mg/L (Leist et al., 2000; Mohan and Pittman, 2007). Several solidification/stabilization processes have been studied to form satisfactory storable solids. These included fixation with Portland cement (Akhter et al., 1990), Portland cement and fly ash (Chu et al., 1991), Portland cement and silicates (Leist et al., 2003), etc.

## Materials and methods

### Reagents

Analytical grade chemicals were used in all experiments. Model solutions were prepared by the dissolving of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (Fluka) in deionized water. The pH of the solutions was adjusted with the suitable concentrations of analytical grade NaOH and  $\text{HNO}_3$ .

### Preparation and characterization of sorbent

Synthetic magnetite was prepared by co-precipitation of Fe(II) and Fe(III) in the presence of  $\text{NH}_4\text{OH}$ . Surface area and pore volume measurements (Gemini 2360, Micrometrics Instruments Corporation, USA), zeta potential measurements (ZetaPlus, Brookhaven Instruments, USA) and magnetic properties measurements (KappaBridge KLY-2, Geofyzika Brno, CZ) were used for materials characterization. The characteristics of sorbent are given in Table 1.

### Sorption experiments

The sorption properties of synthetic magnetite were tested under batch conditions. The effect of pH, initial arsenic concentration and contact time of sorbent and

Tab. 1  
The characteristics of synthetic magnetite

Surface area ( $\text{m}^2/\text{g}$ )	125.7
Total pore volume ( $\text{cm}^3/\text{g}$ )	0.212
$\text{pH}_{\text{PZC}}$	6.5
Magnetic susceptibility ( $10^{-6}$ SI units)	702 778

arsenic solution were studied. The experiments were performed at constant temperature  $23 \pm 1$  °C in a rotary shaker set at 30 rpm and equilibrium time 24 hours. The arsenic quantity in solutions was determined by AAS (Varian 240 RS/240 Z, Australia) before and after the sorption experiments. The amount of the arsenic sorbed (mg) per unit mass of magnetite (g)  $q_{\text{eq}}$ , was calculated using the Eq. (1)

$$q_{\text{eq}} = \frac{C_0 - C_{\text{eq}}}{C_s} \quad (1)$$

where  $C_0$  and  $C_{\text{eq}}$  are initial and equilibrium arsenic concentrations (mg/L), respectively and  $C_s$  is the sorbent concentration in solution (g/L).

### Desorption experiments

Desorption experiments were carried out to study the influence of eluent on to arsenic desorption from the solid adsorption residues. The sorbent used for sorption of 100 mg/L of arsenic solution was separated from the solution by centrifugation, washed gently using deionized water to remove residual arsenic on the surface and dried. After that, it was mixed with desorption agents: deionized water, 0.5 M  $\text{Na}_3\text{PO}_4$ , 1 M  $\text{KNO}_3$ , 1 M NaCl, 1 M  $\text{MgSO}_4$ , 1 M  $\text{HNO}_3$  and 0.1, 0.5 and 1 M NaOH. The mixtures were shaken for 24 hours and the filtrates were analysed to determine the arsenic concentration after desorption.

## Results and discussion

### Effect of pH on As(V) sorption

The pH of adsorption medium is the most important factor influencing the sorption capacity of the sorbent. It is related to the adsorption mechanism onto the adsorbent surface and reflects the nature of physicochemical interaction of the species in solution and the adsorptive site of adsorbent (Aksu and Gönen, 2004). The effect of pH on the removal of As(V) within the range of 2 – 9 is given in Fig. 1. The initial arsenic concentration was 100 mg/L and

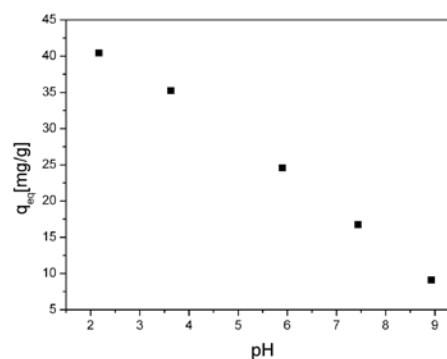


Fig. 1. The effect of pH.

the sorbent concentration was 2 g/L. The removal of As(V) from the aqueous solution decreased with increasing pH and the greatest arsenic uptake was observed at pH 2. The equilibrium As(V) uptake was 40.4 mg/g at this pH value. However, in this case, magnetite was dissolved and iron was detected in filtrates. For this reason, pH 3.5 has been chosen as optimum pH value for all sorption experiments. At pH 3.5 no iron was found in the solution and equilibrium As(V) uptake was 35.2 mg/g.

As mentioned before, pH plays an important role in the solution chemistry. In acidic environment, where the maximum As(V) removal was observed, the As(V) form predominates as the single negatively charged  $\text{H}_2\text{AsO}_4^-$ . In this pH range the magnetite surface is positively charged. So, the attractive electrostatic forces between the negatively charged As(V) species and the positively charged magnetite surface favour the sorption. The point of zero charge of the sorbent was found at pH 6.5 (see Tab. 1). Above this pH of magnetite surface is negatively charged and the double negatively charged form of  $\text{HAsO}_4^{2-}$  predominates. The electrostatic forces are repulsive but sorption still takes place due to the existence of specific forces.

The effect of pH at As(V) sorption by the magnetite has been studied by several authors, as well. Yean et al. (2005) studied As(V) sorption by the magnetite nanoparticles (20 and 300 nm) and they also confirmed the pH dependence of As(V) removal. The maximum sorption capacity of 20 nm magnetite particles was 11.4 and 6.0 mg/g for pH values 4.8 and 8.0, respectively. The maximum sorption capacity of 300 nm magnetite particles was 1.1 and 0.8 mg/g for pH values 4.8 and 6.1, respectively. Chunming and Puls (2008) tested samples of eight commercial available magnetites for arsenic removal and confirmed the pH dependence of As(V) sorption. The sorption of As(V) was more favourable below pH 5.6 – 6.8. Decreasing of As(V) removal by the natural magnetite with increasing pH was observed by Giménez et al. (2007) as well.

#### Effect of initial As(V) concentration

The effect of initial arsenic concentration (20–200 mg/L) was studied with 2 g/L sorbent concentration, ambient temperature and pH values 3.5, 5.0 and 7.0. Sorption isotherms were fitted using the Freundlich model:

$$q_{eq} = K_F C_{eq}^{1/n} \quad (2)$$

where  $q_{eq}$  is amount sorbed per unit mass of sorbent (mg/g) and  $C_{eq}$  is the equilibrium concentration (mg/L).  $K_F$  and  $1/n$  are Freundlich constants related to adsorption capacity (mg/g) and adsorption intensity, respectively; the larger value of  $K_F$  the greater adsorption capacity. The  $n$  value is called heterogeneity factor and its value is in the range from 0 to 1. The more heterogeneous surface, the  $1/n$  value is closer to zero.

The maximum sorption capacity was 46.7, 37.3 and 27.0 mg/g for pH values 3.5, 5.0 and 7.0 respectively. As it is expected, the  $K_F$  value decreases with increasing pH. The  $K_F$  value was 23.5, 13.4 and 8.9 for pH values 3.5,

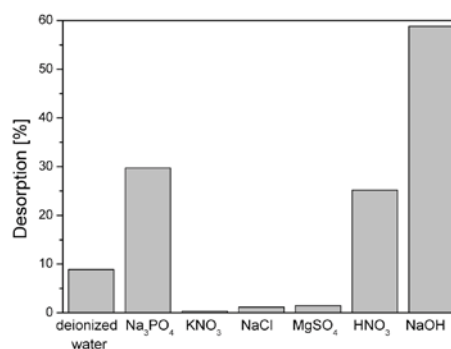


Fig. 2. The effect of various eluent agents on As(V) desorption.

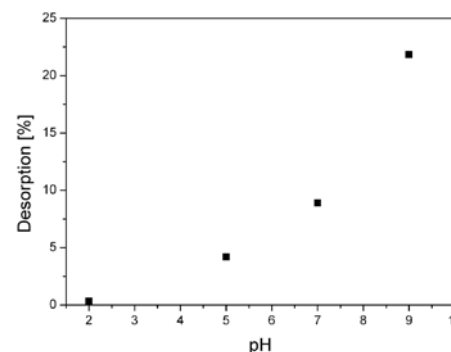


Fig. 3. The effect of pH on As(V) desorption.

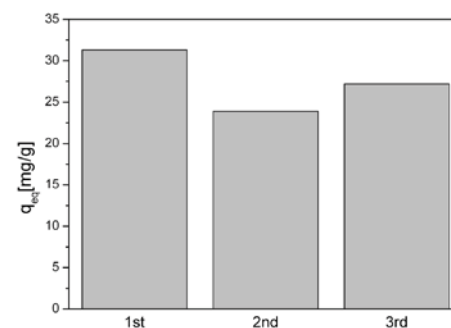


Fig. 4. Sorption capacity of magnetite in three sorption cycles.

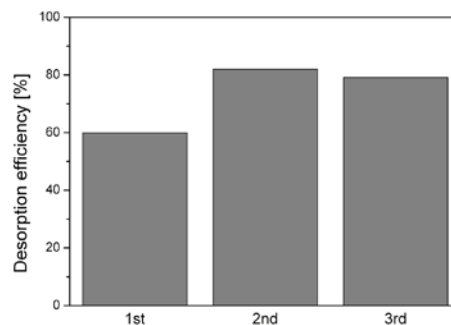


Fig. 5. Desorption efficiency of As(V) in three desorption cycles.

5.0 and 7.0 respectively. The  $1/n$  values indicate favourable adsorption of As(V) onto magnetite. Distribution coefficients  $R^2$  values show a good agreement of the model to the experimental data (Štefušová, 2009).

## Effect of contact time of sorbent and As(V)

The kinetics of As(V) removal from the aqueous solution was studied with an initial arsenic concentration of 100 mg/L, sorbent concentration 2 g/L and pH 3.5. Initially, the uptake of As(V) was very fast within the first 1 h of treatment and the adsorption equilibrium was obtained after 5 h (Štefušová, 2009).

## Desorption studies

Several eluents were used to study As(V) desorption ability from magnetite. Fig. 2 shows that the desorption efficiency varies with desorption agents.

The preliminary study has shown that the desorption of As(V) in deionized water is strongly influenced by pH of solution. The desorption efficiency was enhanced with increasing pH and the maximum desorption was observed at pH 9.0 (21.3 %). The effect of pH on As(V) desorption is given in Fig. 3. Zhang et al. (2007) studied the effect of pH on As(V) desorption from the ferric activated carbon and the pH dependence of As(V) desorption was also confirmed. The maximum desorption (97.3 %) was observed at pH 13 – 14.

Phosphates, sulphates, chlorides and nitrates are the major co-existing anions influencing the arsenic mobility in the waters (Mohan and Pittman, 2007; Henke, 2009). The desorption efficiency of KNO<sub>3</sub>, NaCl and MgSO<sub>4</sub> was not significant (less than 1.5 %), while the desorption with Na<sub>3</sub>PO<sub>4</sub> was more effective (29.7 %). The negligible effect of nitrates, chlorides and sulphates on As(V) desorption from gibbsite and goethite was confirmed by Ladeira and Ciminelli (2004) as well. The desorption of As(V) from goethite in the presence of phosphates and sulphates was studied by O'Reilly et al. (2001). The desorption efficiency of phosphates was around 35 %, while the desorption efficiency of sulphates was less than 2.5 %.

Desorption efficiency using 1 M HNO<sub>3</sub> was 25.2 % but in this case magnetite was dissolved and iron was determined in filtrate (402.7 mg/L). The most effective desorption agent of As(V) from magnetite was NaOH. Preliminary desorption study using NaOH (from 0.1 to 1 M) has shown that the effect of ionic strength of NaOH is negligible and the desorption efficiency of As(V) from magnetite is ranged between 58.4 and 63.1 %.

The reusability of the sorbent was tested in three sorption-desorption cycles. Fig. 4 shows the sorption capacity of the sorbent (initial As(V) concentration 100 mg/L). Fig. 5 shows the desorption efficiency of As(V) from the As-magnetite matrix using 0.1 M NaOH. The 1st sorption cycle was obtained using the fresh sorbent. The results have shown that there were only negligible losses in the sorption capacities of magnetite. The drop of removal efficiency of As(V) with the number of cycles was 11 and 4 % in 2nd and 3rd sorption cycle, respectively. On the other hand, the desorption efficiency increases with the number of cycles by about 20 % after 2nd and 3rd cycle.

## Conclusion

Low cost adsorbent based on synthetic magnetite with good removal capacity of As(V) from the waters has been developed. The maximum capacity of sorbent was 46.7 mg/g with initial As(V) concentration of 200 mg/L and optimum pH 3.5. The adsorption process was fast and equilibrium was obtained after 5 h. The desorption study confirmed that the sodium hydroxide is the most effective eluent of As(V) from the magnetite. The tested sorbent was reused in three sorption-desorption cycles with minimum changes on its sorption properties. Due to its low cost, easy preparation and good removal efficiency, synthetic magnetite seems to be a promising material for the environmental applications.

*Acknowledgements.* This work has been supported by the Science and Technology Assistance Agency, project No. APVT-51-017104 and the Scientific Grant Agency VEGA, project No. 2/0087/08.

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Rukopis doručení 22. 6. 2010

Rukopis akceptovaný red. radou 7. 9. 2010

Revidovaná verzia doručená 19. 10. 2010