MODIFIED IRON-BASED SLUDGE FOR ARSENIC REMOVAL FROM GROUNDWATER

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INTRODUCTION

Arsenic is a naturally occurring element with abundance of 0.5-2.5 ppm in Earth’s crust (Mohan & Pittman, 2007). In natural environment it is found mostly in its inorganic or mineral form. Stability and solubility of arsenic species is controlled by Eo-pH changes (Bowell, 1994). Whereas As(V) species predominate in oxygen-rich conditions, As(III) species are more likely to form in groundwater due to the reduction conditions in soils. In presence of microorganisms, organic forms of arsenic, such as monomethylarsenic (MMAA) and dimethylarsenic (DMAA) acids, may be formed as well. Generally, all arsenic compounds represent severe risk for human health. Long-term exposure to arsenic leads to skin, lung, bladder, and kidney cancer (Ansone et al., 2014) - whilst exposure to high levels (70-200 mg) may be lethal.

Thus, it is desirable to maintain low levels of arsenic in drinking water. The maximum contamination limit (MCL) in drinking water was set to 10 μg/L by the World Health Organization (WHO). However, most of developing countries located in Asia have retained the old value of 50 μg/L due to the alarming concentrations ranging from 100 up to 7000 μg/L (Sazakli et al., 2015). The pollution of water by arsenic may originate either from natural weathering of arsenic minerals (arsenopyrite FeAsS, realgar AsS3S2, native arsenic As) or human activities including both, mining and industry.

Numerous methods regarding the removal of arsenic from water have been developed, out of which, adsorption using suitable sorbent materials seems to be the most effective and easily implemented. Not only that high arsenic removal efficiency is achieved, but also the sorbent materials are becoming economically more accessible for low-income countries since the attention has turned to sorbents base on natural minerals (Yao et al., 2014).

In this paper, we present simple one-step synthesis and characterization of a composite sorbent material from an iron-containing sludge formed as a side-product during the wastewater treatment. Its application for arsenic removal from real groundwater (Pezinok Co., Bratislava region, Slovakia) containing high levels of dissolved As species is demonstrated.

METHODS

The iron-containing sludge was obtained by adjusting the pH value of water containing acidified iron(III) sulfate solution up to 6-7 with Ca(OH)2 suspension. For better settlement of the sludge, a flocculant (SOKOFLOK brand) was added as a 0.1% solution. The sludge was then filter pressed to obtain the solid product in a form of dark brown pellets (Fig. 1). These were crushed in a mortar and further annealed at 1173 K for 60 mins in a furnace leaving 35-40% of original mass.

The annealed material was characterized by X-ray diffractometry, scanning electron microscopy and infrared spectroscopy to determine the phase composition. Atomic absorption spectroscopy was used to determine possible presence of arsenic in the annealed material.

Adsorption tests were carried out in 150 mL reagent bottles. To optimize arsenic adsorption, two series of tests were carried out varying the sorbent loading and pH value.

**Tab. 1** The concentration levels of selected metals in the tested groundwater.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>606</td>
</tr>
<tr>
<td>Sb</td>
<td>455</td>
</tr>
<tr>
<td>Cd</td>
<td>7.2</td>
</tr>
<tr>
<td>Ni</td>
<td>26</td>
</tr>
<tr>
<td>Zn</td>
<td>8.5</td>
</tr>
<tr>
<td>Cu</td>
<td>4.3</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Mn</td>
<td>302</td>
</tr>
</tbody>
</table>
In the first series, 0.4 grams of sorbent were added to 100 mL of polluted water and the pH was adjusted to required value. The suspension was stirred at 500 RPMs for 240 mins at ambient temperature.

In the second series, consequently, different loadings of sorbent (100-800 mg) were added to 100 mL of polluted water at the original pH value of the water. Other parameters of the reaction were left unchanged.

Kinetics of the adsorption was studied varying the reaction time. The sorbent loading 4 g/L and pH 8 were used. Other parameters of the reaction were not adjusted.

The sample for AAS analysis was prepared by filtrating the suspension through 0.45 μm syringe filter.

RESULTS AND DISCUSSION

Material characterization

Both the unprocessed and annealed sludge were characterized by X-ray diffractometry, SEM microscopy, and EDX analysis. In contrast to the amorphous sludge, the diffraction pattern of the annealed material revealed well defined Bragg peaks (Fig. 1). Three phases have been clearly identified from the pattern – hematite Fe₂O₃, magnetite Fe₃O₄, and anhydrite CaSO₄. According to the quantitative Rietveld analysis, hematite represents the major phase in the mixture with approximately 75% content (magnetite 20%, anhydrite 5%).

![Fig. 1 The XRD pattern of annealed sludge compared to the patterns of hematite, magnetite, and anhydrite.](image)

The SEM micrographs of both the sludge before and after annealing step are shown in Fig. 2. Whereas the micrographs of unprocessed sludge reveal formation of polydisperse system composed of agglomerated amorphous iron hydroxo complexes, in the micrographs of annealed sample particles (Fig. 2b) with better defined morphology of particles can be found. The sharp edges of iron oxide nanocrystals are clearly distinguishable in Fig. 2b. According to the results of EDX measurements, besides iron, calcium, and sulfur, aluminum, and silicon are also present in considerable amounts. The presence of these elements is not surprising such that commercially available limestones contain both silica and gibbsite. All calcium atoms are located in the areas with higher sulfur content considering the elemental maps. This is in good agreement with formation of anhydrite phase detected by XRD. Upon annealing at 900 °C silicates of iron may have hypothetically formed as well. The iron content varies in both samples approximately in the range 40-50 % which is lower than expected for the composition calculated from the quantitative Rietveld analysis for annealed sample. However, not all phases were considered during the refinement and inhomogeneity of the material must be also taken in account.

![Fig. 2 (a) as-prepared iron containing sludge, (b) the sludge after annealing at 900 °C for one hour with iron oxide nanoparticles marked by white arrows.](image)
Sorption tests

1. adsorbent loading change

Different loadings of adsorbent were used to find the optimum value for the highest efficiency of arsenic removal. The results are plotted in the Fig. 3. The efficiency follows linear trend up to 400 mg loading of the adsorbent. However, further increase in the adsorbent mass did not lead to 100% removal of arsenic as expected. This may be caused by insufficient homogenization of the adsorbent in the water during the adsorption process. It is proposed that two step adsorption process with lower adsorbent loadings would provide economically more feasible solution. Therefore, further experiments were carried out at the adsorbent loading fixed to 4 g/L.

![Fig. 3 Dependence of arsenic removal efficiency on adsorbent loading at pH = 8.](image)

2. pH value change

The pH values in the range of 2-10 were tested for arsenic removal efficiency at fixed adsorbent loading 4 g/L. The results are plotted in the Fig. 4. In the whole range, the adsorption is linearly dependent on the pH value with the maximum adsorption of 89% at pH 10. This trend can be only partially explained by Eh-pH diagram for arsenic in water environment. Whereas at higher pH values >3, anionic species H₂AsO₄⁻ and HAsO₄²⁻ are present in the water which are electrostatically attracted to the surface of the adsorbent, with decreasing pH values, electroneutral H₃AsO₃ or H₂AsO₄ species are formed. This significantly disfavors adsorption process. On the other hand, pH values >8 lead to the negatively charged surface which causes electrostatic repulsion and lowers adsorption as well. In our case, surprisingly, by adjusting the pH up to 10 the removal efficiency was even higher. As we would have expected parabolic dependence of the efficiency on the pH values it is suggested that at higher values other mechanism must be involved in arsenic removal. This is supported also by formation of white precipitate during pH adjustment to values above 9. At the original pH value of the wastewater, the adsorption reaches maximum value of 66.8% which is 27.4% less than in the case of 8 g/L adsorbent loading at the same pH value. Nevertheless, the material consumption is reduced to a half.

![Fig. 4 Dependence of arsenic removal efficiency on pH values at fixed adsorbent loading of 4 g/L.](image)

3. Kinetic studies

The kinetics of the adsorption was studied at the original pH value of the water and adsorbent loading 4 g/L. Several models are commonly use to estimate sorption rates, namely pseudo-first-order, pseudo-second-order, and intraparticle diffusion model. All three models were applied to experimental data. The best statistics was obtained for the pseudo-first-order model originally proposed by Lagergren. Lagergren’s kinetics equation has been previously used for the adsorption of metal ions from solutions. The linear form of the equation for the pseudo-first order kinetics is given as

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]

where \( q_t \) is the number of ions removed at time t (mg/g), \( q_e \) is the maximum sorption capacity, and \( k_1 \) (min⁻¹) represents the pseudo-first order rate constant. In our case the value 0.023 min⁻¹ was calculated for \( k_1 \) (\( q_e = 0.106 \)). The \( q_t \) values were calculated according to the formula

\[ q_t = \frac{V x (C_0 - C_t)}{m} \]

Upscaling experiment

To investigate potential application in large scale, an experiment using 5 L of contaminated water and the sorbent loading 4 g/L was carried out at original pH value of water. The mixture was stirred with mechanical stirrer at 500 RPMs for 480 min. The
sampling interval was set to 120 mins. The results (Fig. 6) show arsenic removal efficiency to be significantly reduced (only 39%) compared to small scale tests. This may have most probably resulted from insufficient stirring of the mixture with most of the particles settled at the bottom of the reagent bottle during the adsorption process. Agglomeration of particles leading to low surface area may also play the role. Thus, it is questionable whether large-scale deployment of the prepared material is suitable for wastewater with arsenic concentration levels above 500 μg/L.

CONCLUSION

In conclusion, thermally treated iron-based sludge obtained as a side product from wastewater treatment application was successfully applied for arsenic removal from aqueous environment. The prepared material was analyzed by X-ray diffractometry and scanning electron microscopy. The Rietveld analysis revealed formation of a composite mixture composed of hematite, magnetite, and anhydrite phases in a mass ratio of approximately 75:20:5. Other minor phases could not be identified from XRD pattern. The SEM micrographs suggest formation of polydisperse system with nanocrystalline nature. The results of adsorption experiments showed maximum arsenic removal efficiency of 94%. The concentration of sorbent material 4 g/L was found to be the most feasible for industrial application. At this value of sorbent loading and the original pH value of the wastewater, the arsenic removal efficiency reached 67%. To investigate possible large-scale deployment, an upscaling experiment was performed. In this case, comparably smaller removal efficiency was achieved (39%). This makes sorbent suitable for large-scale application only in case of low arsenic concentration in wastewater.

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REFERENCES


