Preparation and properties of iron oxide composite sorbents for removing arsenic, beryllium and uranium from aqueous solutions

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ABSTRACT
The aim of this study was to prepare composite sorbents based on hydrated iron oxides. Prepared sorbents XAD4-A33 and XAD16-A33 contained iron oxides probably in the form of magnetite, goethite and maghemite. Sorbents showed good chemical stability (at pH 5–9), but not so good mechanical stability. It was found that prepared sorbents can be successfully used for removal of arsenic, beryllium and uranium from aqueous solutions. Removal of beryllium and uranium was less efficient than that of arsenic. Regeneration efficiency of arsenic and beryllium varied between 80 and 90 % and that of uranium was around 50 %.

Keywords: sorption; iron oxide; arsenic; uranium; beryllium

INTRODUCTION

Composite sorbents consist of two or more components, the matrix and the active component. The advantage of using composites can be higher mechanical and chemical stability than in case of separate usage.

Composite sorbents based on hydrated iron oxides can be used for a sorption of toxic substances, such as arsenic or heavy metals from water solutions[1]. These substances are carcinogenic, mutagenic or reproductively toxic[2], and accumulate in organisms, consequently cause serious acute or chronic health problems.

As a matrix for composite sorbents can be used synthetic organic polymeric sorbents, ceramic or some other substances, such as chitosan[3], bentonit[4] or attapulgit[5]. Iron oxides can be impregnated into the matrix in different ways. Iron trichloride can be used followed by precipitation of iron oxides using some base (NaOH or NH_4OH). Iron oxides can also be applied straightly, by molding into tablets, etc[6].

The aim of this study was to prepare composite sorbents for removing toxic substances from water solutions, to check up their characteristics (composition, chemical and mechanical stability, sorption and desorption characteristics) and to determine optimal conditions for preparation of composite sorbents.

EXPERIMENTAL

Nonionogenic sorbents Amberlite XAD 4 and Amberlite XAD 16 were used as a matrix for preparation of composite sorbents. At first nonionogenic sorbents were wetted in ethanol and after that they were rinsed by demineralized water. After drying, the matrix was impregnated by $FeCl_3$ solution and mingled on a shaft stirrer. There was used 10% or 33% solution of $FeCl_3$ in ethanol. After drying, impregnated sorbents were moved into a beaker and ammonia or NaOH solution was poured over them. Then they were shaken. Prepared composite sorbents were rinsed on a sifter (openings 315 μm) with demineralized water and afterwards dried on a Petri dish. If there were still included small pieces of hydrated iron oxides in the composite sorbent, they were disposed on the sifter. Prepared sorbents were stored in dry condition in polyethylene containers.

Iron content in composite sorbents was measured on atomic absorption spectrometer. Sorbents were transferred into a liquid state by the microwave apparatus before that. The type of iron oxides was determined using FTIR and Raman spectroscopy. Before determination it had to be homogenized by a grinder.

Sorbent stability was determined in demineralized water that was adjusted to the pHs of 3, 5, 7, 9 and 11. 1 mL of prepared sorbent

was placed into the sample container with 100 mL of the solution and was shaken. Some amount of iron oxide was dissolved into the solution after 24 h, 48 h and 144 h.

Measurement of particle size distribution was performed with fresh composite sorbents and also with sorbents after use on stirrers, shakers and columns. Macro photography was taken and analyzed by program NIS-Elements AR 3.0.

Batch and column sorption experiments were carried out using model solutions of arsenic, uranium and beryllium in demineralized water with various amounts of coexisting anions or in the tap water. The amount of arsenic, uranium and beryllium in model solutions was determined on ICP-OES.

Sorbents were regenerated in a multistage process: firstly it was rinsed by alkaline brine (2% NaOH and 2% NaCl), then by a demineralized water (firstly slow flow rate, then fast) and in the end it was conditioned by demineralized water saturated by CO_2.

RESULTS AND DISCUSSION

Eight types of composite sorbents were prepared in which the iron content was measured (see Table I).

Table I *Prepared composite sorbents*

Sorbent	Used chemicals	Iron content [wt. %]
XAD4-H10	10% $FeCl_3$ 1 M NaOH	7.1
XAD4-A10	10% $FeCl_3$ 25% NH_3	9.4
XAD4-H33	33% $FeCl_3$ 1 M NaOH	4.2
XAD4-A33	33% $FeCl_3$ 25% NH_3	22.9
XAD16-H10	10% $FeCl_3$ 1 M NaOH	8.2
XAD16-A10	10% $FeCl_3$ 25% NH_3	10.7
XAD16-H33	33% $FeCl_3$ 1 M NaOH	5.4
XAD16-A33	33% $FeCl_3$ 25% NH_3	26.1

Two sorbents with the highest amount of iron were chosen (XAD-A33 and XAD16-A33) and there were determined some of their other properties, e.g. the type of impregnated iron oxide, chemical stability, sorption and desorption properties or distribution of particles.

Prepared sorbents contained iron oxides in form of magnetite, goethite and maghemite and showed magnetic properties (Figure 1). Although iron oxides were measured by FTIR and Raman spectroscopy, reliable data were not obtained due to their high absorbance.
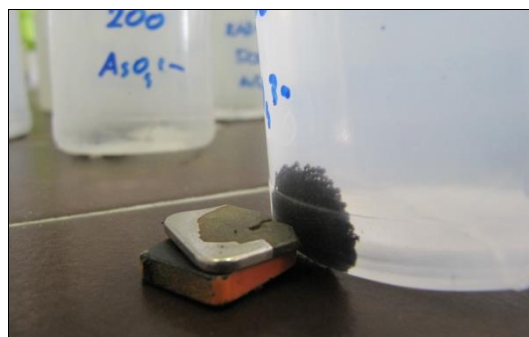

Figure 1 *Magnetic properties of fresh prepared sorbents*

Distribution diagrams of particles are shown in Figures 2 and 3. Diagrams are quite similar, only the sorbent XAD16-A33 has in general larger diameters of particles then XAD4-A33. For this analysis were used following sorbents:

1. Fresh sorbent
2. Sorbent after 72 h of sorption of beryllium at a value of pH 5 on a shaft stirrer
3. Sorbent after 72 h of sorption of beryllium at a value of pH 3 on a shaker machine
4. Sorbent after sorption of arsenic and beryllium in a column

After sorption there is an obvious increase of particles with diameters smaller than 300 μm. Degradation of sorbents is major after using shakers and columns, the least degradation is after using stirrers.
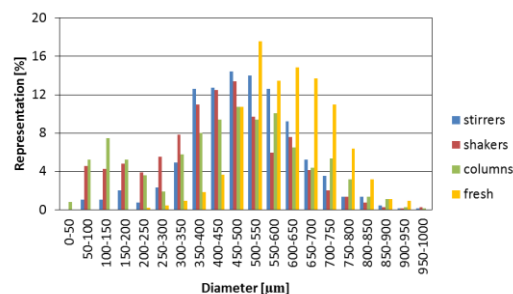

Figure 2 *Distribution of particles of XAD4-A33 before and after sorption*
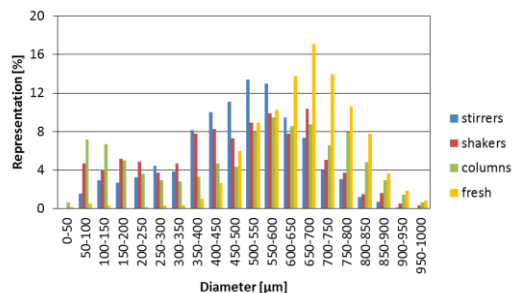
Figure 3 *Distribution of particles of XAD16-A33 before and after sorption*

Since chemical stability of both sorbents was almost identical, only a figure for XAD4-A32 is shown in Figure 4 as a typical result. The sorbents were stable at pH 5–9, while they were dissolved at pH below 3 and over 11.
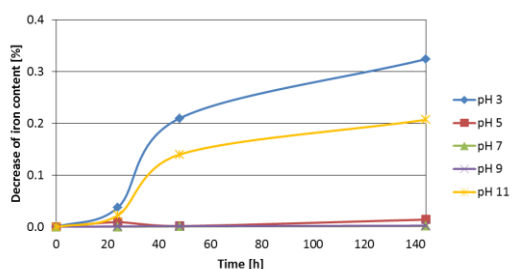

Figure 4 *Chemical stability of XAD4-A33*

Selected results are listed in table II. These experiments were carried out in columns with model solutions of toxic substances in drinking water. Initial concentration of arsenic in model solution was 5 mg·L^{-1}, beryllium 1 mg·L^{-1} and uranium 1 mg·L^{-1}. Sorption capacity was calculated for a limit concentration 0.1 mg·L^{-1} of toxic element. As shown in Table II prepared sorbents had the highest sorption capacity of arsenic, while poor sorption capacities were observed for beryllium and uranium. Although the sorption efficiency of sorbent XAD4-A33 was higher than that of XAD16-A33, the difference is negligible taking account of insecurity of measurement.

Table II *Sorption capacities*

Toxic element	Capacity of XAD4-A33 [mg·mL^{-1}]	Capacity of XAD16-A33 [mg·mL^{-1}]
As	2.73	2.20
Be	0.12	0.07
U	0.24	0.19

It was found that sorbents can be quite well regenerated. The regeneration efficiency after sorption of arsenic or beryllium is around 80–90 % as shown in table III. Regeneration efficiency of XAD16-A33 was round 5 % better than XAD4-A33. In case of sorption of uranium the regeneration efficiency was only about 50 %.

Table III *Regeneration efficiency*

Element	Efficiency of XAD4-A33 [%]	Efficiency of XAD16-A33 [%]
As	77	83
Be	84	91
U	43	55

CONCLUSIONS

1. The best conditions for preparation composite sorbents are (from these that were carried out in this study): using 33% solution of FeCl$_3$ in ethanol for impregnation with afterwards reaction with 25% ammonia solution. To dispose little particles it is necessary to rinse sorbents on a sifter (openings about 300 μm).
2. Sorbents are stable on values of pH between 5 and 9. Using shaft stirrer had the least effect on mechanical stability.
3. Sorbents can be successfully used for sorption of arsenic, with lower sorption efficiency also for beryllium and uranium. Arsenic and beryllium can be desorbed from composite sorbents, the regeneration efficiency is 80–90 %. The bond with uranium is stronger, so the efficiency is only about 50 %.

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