Sorption of toxic oxyanions to modified kaolines

M. Lhotka & B. Dousova

University of Chemistry and Technology Prague, Prague, Czech Republic

ABSTRACT: Natural clay materials are considered effective and perspective sorbents for economical and ecological reasons. In general, aluminosilicates are not selective sorbents for anionic contaminants thanks to a low pH (ZPC). Their simple surface pre-treatment with Fe (II) can significantly change the surface charge and thus strongly improve the affinity to anionic contaminants. This work deals with a sorption of toxic arsenic, antimony and selenium oxyanions on calcinated, Fe-modified, kaolin. The natural kaolin calcinated at 550°C was treated by rehydroxylation in autoclave with 0.6 M solution of FeCl₂. The concentration of initial As/Sb/Se solutions was 2·10⁻⁴ M. The main result of this work is the comparison of sorption efficiency and sorption capacity of modified sorbent from the point of view of the rehydration time and the type of oxyanionic particle.

1 INTRODUCTION

Arsenic, antimony and selenium are among the toxic elements occurring in small quantities in the water and in the earth's crust. The degree of toxicity of these elements depends on the oxidation degree and form of occurrence. The As, Sb, Se and their compounds leads to both acute and chronic poisoning leading to death. The use of kaolinite and rehydroxylated kaolinite as sorbents of these contaminants belongs to very efficient methods. Under the hydrothermal treatment, kaolinite is transformed into semicrystalline and very reactive metakaolinite, and the rehydroxylation of metakaolinite to kaolinite is possible. Rocha *et al.* (1990) studied the rehydration of metakaolinite to kaolinite which was heated at 155–250°C for 1–14 days and concluded that the amorphous metakaolinite can be transformed to crystalline form. The specific surface area was highly increased during the rehydroxylation. Lhotka *et al.* (2012) studied the rehydroxylation of metakaolinite to kaolinite which was heated at 150–250°C for 1–14 days. He found that the rehydroxylation of metakaolinite to kaolinite was strongly dependent on temperature and time of the hydrothermal process. The optimum transformation from the point of view of the surface properties was observed after longer-term autoclaving (4–7 days) at 175°C, when the specific surface S_{BET} of raw kaolinite increased more than three times. Oxyanions showed a higher adsorption affinity for Fe-modified sorbents. During the interaction of raw clay and Fe salt solution, ion-exchangeable Fe³⁺ particles in amorphous and/or poorly crystalline form have been fixed on the clay surface forming active adsorption sites. Substantial variability in growing Fe phases (hydrated Fe₂O₃, non-specific Fe³⁺ species, ferrihydrite) resulted from using different types of aluminosilicate carrier and the treatment conditions (Dousova *et al.*, 2009). The aim of

this work was to prepare kaoline based sorbents using rehydroxylated method and to compare the sorption efficiency and sorption capacity of modified sorbents from the point of view of rehydroxylation time and the type of oxyanionic particle.

2 METHODS/EXPERIMENTAL

2.1 Preparation of modified kaolinites

The crystalline kaolinite from West Bohemia was used for the preparation of modified sorbents. This kaolinite was calcined at 650°C for 3 h and converted to metakaolinite. For the preparation of rehydroxylated kaolinite, 8 g of metakaolinite was mixed with 30 g of water. The suspension was stirred for 2 min at room temperature and then was inserted into autoclave. The autoclave was heated at 175°C for 4, 7, 10 and 14 days. In next experiments, 30 g of 0.6 M FeCl₂ was used instead of water. After removal from autoclave, the suspension was filtered off, washed with distilled water and dried at 100°C for 24 h.

2.2 Analytical methods

The model solutions of oxoanions As(III), As(V), Se(IV), Se(VI), Sb(V) with a concentration of 2·10⁻⁴ M were used. The suspension of model solution and sorbent (6 g L⁻¹) was shaken in sealed polyethylene bottle at room temperature for 24 h. The product was filtered off; the filtrate was analyzed for residual As concentration and pH value. Equilibrium adsorption isotherms of nitrogen were measured at 77 K using static volumetric adsorption systems (TriFlex analyzer, Micromeritics). The adsorption isotherms were fitted in the BET specific surface area and the pore size distribution by the DFT and BJH method. The concentration of As, Sb and Se in aqueous solutions

Table 1. Specific surface area of raw kaolinite, metakaolinite and rehydroxylated sorbents (temperature of rehydroxylation – 175°C).

sample	S _{BET} (m ² g ⁻¹)
Kaolinite (K)	15.84
Metakaolinite (MK)	17.81
S4 (4 days)	98.57
S7 (7 days)	103.10
S4 (4 day-Fe)	70.21
S7 (7 days-Fe)	73.81
S10 (10 days-Fe)	71.05
S14 (14 days-Fe)	69.71

Table 2. As(V)/Sb(V)/Se(IV) adsorption on Fe-modified rehydroxylated kaolinite under the various rehydroxylation time.

sample	As(III)		As(V)		Sb(V)		Se(IV)	
	q*	ε**	q	ε	q	ε	q	ε
K4	0.07	57	0.14	99	0.18	96	0.07	100
K7	0.08	59	0.14	99	0.24	97	0.09	99
K10	0.09	56	0.12	100	0.10	98	0.07	99
K14	0.08	61	0.08	99	0.23	98	0.11	99

*maximum adsorption capacity (mmol g⁻¹)

**maximum sorption efficiency (%).

was determined by HG-AFS using PSA 10.055 Millennium Excalibur.

3 RESULTS AND DISCUSSION

3.1 Textural properties of sorbents

The samples of sorbents were prepared under different reaction conditions. The surface area of newly prepared sorbents was much larger than that of raw kaolinite and metakaolinite (from 15.8 to ~103.1 m² g⁻¹). At the rehydration temperature of 175°C the maximum surface area was achieved. Using the maximum S_{BET} at 175°C (Table 1), this temperature was used for the Fe treatment of samples. The comparison of S_{BET} of sorbents prepared at 175°C with and without Fe ions is shown in Table 1 Fe treated kaolinites reached the maximum S_{BET} after four days reaction time. The decrease of their S_{BET} value compare to Fe-free rehydrated samples corresponded to the binding of Fe³⁺ particles on the surface, forming active adsorption sites (Lhotka *et al.*, 2012).

3.2 Sorption of arsenic, antimony and selenium

The experimental series for the characterization of As/Sb/Se adsorption on Fe-modified kaolinite (175°C, 4–14 days) were performed with 8 samples of varying sorbent dosage for each reaction time. This arrangement enabled to evaluate sorption parameters according to the Langmuir model. The comparison of

Table 3. Theoretical sorption capacities *Q* of Fe-modified kaolinite.

Oxyanion	Theoretical sorption capacity <i>Q</i> (mmol g ⁻¹)			
	4 days	7 days	10 days	14 days
As(III)	–	–	–	–
As(V)	0.09	0.10	0.08	0.08
Se(IV)	0.06	0.08	0.06	0.07
Se(VI)	0.04	0.03		
Sb(V)	0.11	0.16	0.10	0.14

adsorption efficiency ε and maximum sorption capacities q for investigated oxyanions are summarized in Table 2. Sorption parameters evaluated according to the Langmuir model are shown in Table 3.

4 CONCLUSIONS

The aim of this work was the sorption of toxic oxyanions of arsenic, antimony and selenium to FeCl₂ treated rehydroxylated kaolines. Kaolines were divided into 4, 7, 10 and 14 days according to rehydroxylation time. Comparison of sorptive capacities has shown that the sorbent rehydroxylated for 7 days achieved the highest sorption capacities (0.03–0.16 mmol g⁻¹), and thus the best sorption properties. This was also confirmed by the comparison of the Langmuir isotherms for As(V) sorbed on kaolin with different rehydroxylation times. By comparing the sorption capacities for separate oxyanions Sb(V) indicated the best sorption capacity (and the highest affinity to sorbent). The affinity of the oxyanions to the sorbents decreases in the range of Sb(V) > As(V) > Se(IV) > Se(VI) > As(III). The As(III) adsorption did not followed either Langmuir or Freundlich model. In term of adsorption efficiency, the sorbent showed almost 100% removal of all oxyanions except As(III), which reached values of about 60%.

ACKNOWLEDGEMENTS

This work was part of projects 16-13778S (Grant Agency of Czech Republic).

REFERENCES

- Doušová, B., Fuitová, L., Grygar, T., Machovič, V., Koloušek, D., Herzogová, L. & Lhotka, M. 2009. Modified aluminosilicates as low-cost sorbents of As(III) from anoxic groundwater. *J. Hazard. Mater.* 165(1–3): 134–140.
- Lhotka, M., Doušová, B. & Machovič, V. 2012. Preparation of modified sorbents from rehydrated clay minerals. *Clay Miner.* 47(2): 251–258.
- Rocha, J., Adams, J.M. & Klinowski J. 1990. The rehydration of metakaolinite to kaolinite: evidence from solid-state NMR and cognate techniques. *J. Solid State Chem.* 89(2): 260–274.