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## SORPTION OF CHROMATE BY CLINOPTILOLITE MODIFIED WITH ALKYLAMMONIUM SURFACTANTS

*Received December 13, 2006; accepted July 10, 2006*

**Abstract.** Clinoptilolite from Dylągówka (Poland) with an external cation exchange capacity (ECEC) of 16 meq/100 g determined by adsorption of alkylammonium ions was treated with hexadecyltrimethylammonium (C16) and dioctadecyldimethylammonium (2C18) bromides in amounts equivalent to 1.0 and 1.5 ECEC. The products were characterized using IR spectroscopy and C and N determinations. The sorption of chromate on the modified mineral was measured spectrophotometrically as a function of pH, concentration of Cr(VI) or the proportion of the sorbent to solution. The amount of chromate removed from the solution continuously decreased with increasing pH in the range 1.3–10. At pH 2.6–3.1, the maximum adsorption of Cr(VI) by the organo-zeolites (103 and 124 mmol/kg) was observed for the samples modified using a 1.5 ECEC surfactant concentration. Considerably lower adsorption values (37 and 46 mmol/kg) were obtained with sorbents prepared using a 1.0 ECEC concentration of the alkylammonium ions.

*Key-words:* clinoptilolite, alkylammonium surfactants, sorption of chromate

### INTRODUCTION

It is well known that zeolites show a high cation exchange capacity (CEC) reaching values around 450 meq/100 g. In contrast, adsorption of anions on the surface of these silicates is very limited. However, the anion exchange capacity (AEC) of zeolites can be considerably improved by chemical modification of their surface properties using selected organic compounds.

Clay minerals and zeolites modified with quaternary alkylammonium cations are frequently studied because of their potential application as environmental remediation materials (e.g. Boyd et al. 1988; Stockmeyer 1991; Bowman 2003). Some of these sorbents obtained using hexadecyltrimethylammonium bromide have the ability to

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remove Cr(VI) from aqueous solutions (Haggerty, Bowman 1994; Krishna et al. 2001; Bowman 2003; Bajda, Kłapyta 2004). In the case of zeolites, adsorption of these long-chain ions takes place on external exchange sites; these ions are too large to enter the internal pore structure of the silicate. Thus, using alkylammonium ions, the external cation exchange capacity (ECEC) of the zeolite may be determined.

The aim of the work reported here was to compare the chromate sorption capacities of clinoptilolite modified with the hexadecyltrimethylammonium (C16) and dioctadecyldimethylammonium (2C18) surfactants.

## MATERIALS AND METHODS

Clinoptilolite (Cl) from the claystone deposit located in the village of Dylągówka in the Outer Flysch Carpathians of Poland (Wieser 1969; Franus 2002) was selected as the starting material. The claystone consists of about 65% Ca-montmorillonite, 25% clinoptilolite, and 10% quartz, feldspars, illite, illite/montmorillonite, kaolinite and chlorite (Wieser 1969; Franus, Dudek 1999). A zeolite concentrate was separated from the shale by settling. The rock was dispersed in water for 48 hours and, after settling, the <0.025 mm fraction was removed by decantation. The procedure was repeated until the supernatant was clear. Air-dry samples were crushed in a mortar to <0.2 mm. The zeolite concentrate separated in this way consisted of about 95% clinoptilolite and 5% quartz and illite.

Hexadecyltrimethylammonium (C16) and dioctadecyldimethylammonium (2C18) bromides (Sigma Chemicals) were used as received. For ECEC determination, 200 cm<sup>3</sup> aqueous suspensions of 0.5 g of the clinoptilolite and 0.25 mmol of the C16 or 2C18 salt were stirred for 8 hours at 60°C and then washed with hot deionized water and hot ethanol until a negative AgNO<sub>3</sub> test was obtained. The quantity of alkylammonium ions adsorbed on the zeolite was calculated from C and N assays. The ECEC of the clinoptilolite, determined by adsorption of the alkylammonium ions, is 16 meq/100 g.

The clinoptilolite was treated with the C16 and 2C18 bromides in amounts equivalent to 1.0 and 1.5 ECEC. Aqueous suspensions of the silicate and the organic salts were stirred for 2 hours at 60°C and, without washing, left for 24 hours. The procedure was repeated. The samples obtained were dried at 100°C and ground in an agate mortar.

The products were analysed using a Bio-Rad FT165 spectrometer with samples prepared as pressed KBr disks. To determine the amount of alkylammonium surfactant bound by the mineral, C and N contents in the organo-silicates were measured using a Euro EA elemental analyser.

The sorption of chromate on the modified clinoptilolite was measured as a function of pH (1.3–10) and concentration (0.02–6.24 mmol/dm<sup>3</sup>) of Cr(VI) at a sorbent/solution ratio of 20 g/dm<sup>3</sup>. 200 mg of the organo-silicate was placed in a tube and 10 cm<sup>3</sup> of Cr(VI) solution was added. The pH was adjusted with 1 M hydrochloric acid. The mixture was shaken for 24 hours at 25°C and centrifuged. The Cr(VI) concentration in the supernatant was determined spectrophotometrically (APHA 1992).

## RESULTS AND DISCUSSION

In the FTIR spectra of the organo-zeolites (Fig. 1), the intensity of the absorption bands at 2850 and 2920  $\text{cm}^{-1}$  attributed to the stretching vibrations of  $\text{CH}_2$  groups testifies that the surface of the mineral is covered by various amounts of the alkylammonium bromides and/or alkylammonium cations.

The amount of chromate removed by the modified clinoptilolite from the solution with the initial  $\text{Cr(VI)}$  concentration of 2.11  $\text{mmol/dm}^3$  (105.73  $\text{mmol/kg}$  zeolite) gradually decreased with increasing pH in the range 1.3–10 (Fig. 2). In the case of the Cl-C16-1.0 sample involving a C16 surfactant concentration equivalent to 1.0 ECEC, the initial  $\text{Cr(VI)}$  concentration decreased from 67 to 6  $\text{mmol/kg}$ .

A similar relation was found for montmorillonite modified with C16 ions (Krishna et al. 2001). In the paper just quoted, the pH dependence of chromate sorption was attributed to the presence of different  $\text{Cr(VI)}$  anions:

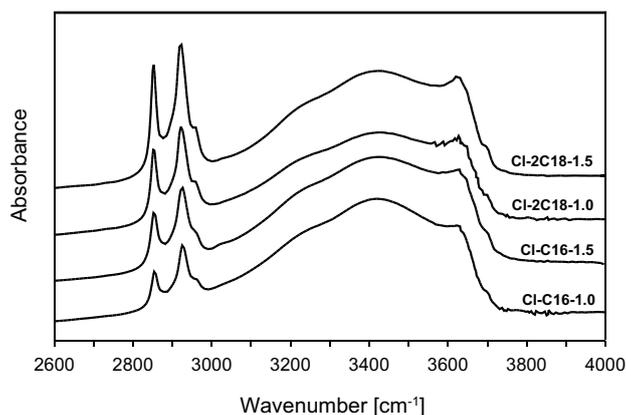


Fig. 1. FTIR spectra of the organo-zeolites obtained using 1.0 and 1.5 ECEC concentrations of C16 and 2C18 surfactants

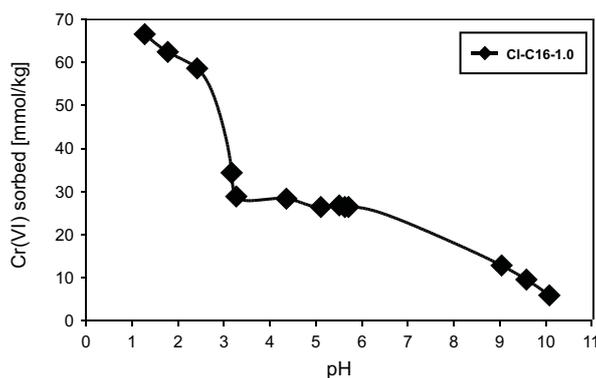
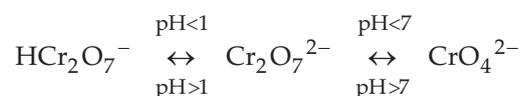


Fig. 2. Sorption of  $\text{Cr(VI)}$  as a function of pH on the organo-zeolite obtained using a 1.0 ECEC concentration of the C16 surfactant. Initial concentration of  $\text{Cr(VI)}$ : 2.11  $\text{mmol/dm}^3$  (105.73  $\text{mmol/kg}$  zeolite)



At pH 2.6–3.1, the maximum sorption of Cr(VI) by the organo-zeolites (124 and 103 mmol/kg) was observed for samples Cl–C16–1.5 and Cl–2C18–1.5 modified using 1.5 ECEC concentrations of the C16 and 2C18 surfactants (Fig. 3). Considerably lower values (46 and 37 mmol/kg) were obtained in the case of the sorbents prepared using 1.0 ECEC concentrations of the alkylammonium ions (samples Cl–C16–1.0 and Cl–2C18–1.0). For these samples, the amount of Cr(VI) removed from the solution does not depend on the size of the alkylammonium ions bound to the mineral surface. In contrast, in the case of the sorbents prepared using 1.5 ECEC concentrations of the surfactants, the sample obtained with the C16 salt shows, as a rule, a higher sorption capacity for chromate than does the sample obtained with the 2C18 salt.

The total quantity of the alkylammonium ions bound by the silicate, as determined from the C and N contents, was used in calculating the chromate/surfactant molar ratio in the chromate-organo-silicate complexes (Table 1). The values of 0.29 and 0.23, respectively obtained for the organo-zeolites Cl–C16–1.0 and Cl–2C18–1.0, increase

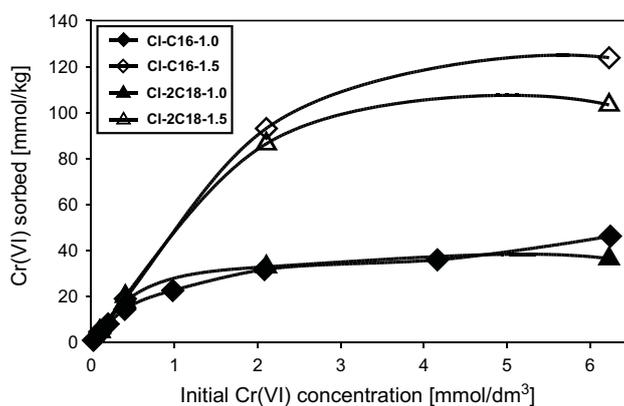


Fig. 3. Sorption of Cr(VI) at pH 2.6–3.1 on the organo-zeolites obtained using 1.0 and 1.5 ECEC concentrations of the C16 and 2C18 surfactants

TABLE 1

Chromate/surfactant molar ratio calculated at maximum Cr(VI) sorption on organo-zeolites

Surfactant	Chromate/surfactant molar ratio	
	1.0 ECEC	1.5 ECEC
C16	0.29	0.52
2C18	0.23	0.43

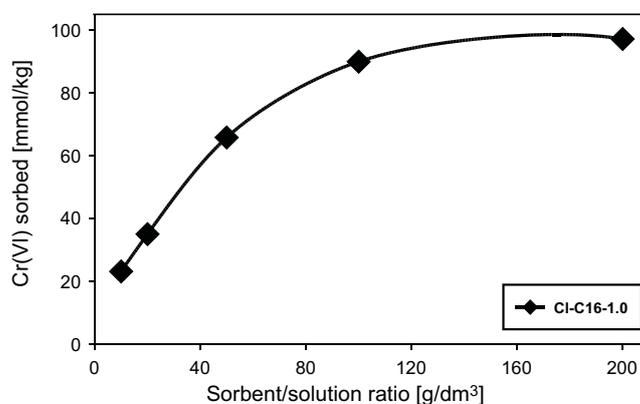


Fig. 4. Sorption of Cr(VI) as a function of the sorbent/solution ratio on the organo-zeolite obtained using a 1.0 ECEC concentration of the C16 surfactant. Initial concentration of Cr(VI): 2.11 mmol/dm<sup>3</sup> (105.73 mmol/kg zeolite)

to 0.52 and 0.43 for the CI-C16-1.5 and CI-2C18-1.5 sorbents. This suggests that surfactant molecules, bound beyond the ECEC to the external surface of the zeolite, show a greater ability to adsorb chromate in comparison with such molecules located on the exchangeable sites.

In order to find the optimum conditions for the uptake of chromate by the organo-silicates, the sorption experiments were performed at various sorbent/solution ratios (10–200 g/dm<sup>3</sup>). Using a sorbent/solution ratio of 10 g/dm<sup>3</sup>, the CI-C16-1.0 sample removed 23 mmol/kg of Cr(VI) from the solution with an initial concentration 2.11 mmol/dm<sup>3</sup> of chromate (Fig. 4). At the highest sorbent/solution ratio (200 g/dm<sup>3</sup>), the organo-silicate shows a chromate sorption capacity 98 mmol/kg.

## CONCLUSIONS

After modification with the C16 and 2C18 surfactants, the clinoptilolite used in this work shows significant ability to remove Cr(VI) from aqueous solutions. The maximum amounts of chromate bound to the organo-silicates strongly depend on pH; the amounts gradually decrease with increasing pH in the range 1.3–10.

At pH 2.6–3.1, the maximum chromate uptake by the organo-zeolites prepared using a surfactant concentration equivalent to 1.5 ECEC is considerably higher than that observed using a concentration equivalent to 1.0 ECEC.

The amount of Cr(VI) removed from solution by the organo-zeolites prepared using surfactant concentration equivalent to 1.0 ECEC does not depend on the size of the alkylammonium ions bound to the mineral surface. In contrast, the sorbent prepared at a 1.5 ECEC concentration of the C16 surfactant shows, as a rule, a higher chromate sorption capacity than that obtained with the 2C18 salt.

The values of the chromate/surfactant molar ratio in the chromate-organosilicate complexes suggest that the surfactant molecules, bound beyond the ECEC to the

external surface of the clinoptilolite, show a greater chromate sorption ability in comparison with alkylammonium ions located on the exchangeable sites of the zeolite.

*Acknowledgements.* This study was supported by the AGH – University of Science and Technology (Kraków, Poland) as the research project 11.11.140.158.

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## **SORPCJA CHROMIANÓW NA KLINOPTILOLICIE MODYFIKOWANYM ALKILOAMONIOWYMI ZWIĄZKAMI POWIERZCHNIOWOZNYMI**

### Streszczenie

Klinoptilolit z Dylągówki o zewnętrznej pojemności wymiany kationów (ECEC) 16 meq/100 g poddano modyfikacji przy użyciu bromków heksadecylotrimetyloamoniowego (C16) i dioktadecylodimetyloamoniowego (2C18) w ilości 1,0 i 1,5 ECEC minerału. Dla produktów reakcji wykonano badania spektroskopowe w podczer-

wieni oraz oznaczenia C i N. Sorpcję chromianów na otrzymanych organo-zeolitach określono spektrofotometrycznie jako funkcję pH, stężenia Cr(VI) lub proporcji sorbent/roztwór.

Ze wzrostem pH w przedziale 1,3–10, ilość chromianów pochłanianych z roztworu systematycznie malała. Dla próbki modyfikowanej przy użyciu soli C16 w ilości 1,0 ECEC, graniczne wartości wynosiły 67 i 6 mmol/kg. Przy pH 2,6–3,1, maksymalną sorpcję Cr(VI) (124 i 103 mmol/kg) stwierdzono dla organo-zeolitów otrzymanych przy zastosowaniu 1.5 ECEC związków C16 i 2C18. Znacznie mniejsze wartości (46 i 37 mmol/kg) obserwowano w przypadku sorbentów zawierających jony alkiloamoniowe w ilości 1.0 ECEC.

Ilość Cr(VI) usuniętego z roztworu przez organo-zeolity otrzymane dla stężenia wymienionych soli 1.0 ECEC nie zależała od wielkości jonów alkiloamoniowych związanych z powierzchnią zeolitu. Natomiast w przypadku stężenia 1.5 ECEC, próbka zawierająca kationy C16 wykazywała z reguły większą chłonność sorpcyjną względem tego pierwiastka w porównaniu z otrzymaną stosując kationy 2C18.