# Removal of chromium(VI) from aqueous solutions using zeolites modified with HDTMA and ODTMA surfactants

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ABSTRACT: The removal of Cr(VI) from aqueous solutions under various conditions was investigated using a natural clinoptilolite and a synthetic zeolite derived from fly-ash (Na-P1), modified either with hexadecyltrimethylammonium bromide (HDTMA) or octadecyltrimethylam-monium bromide (ODTMA). The study was focused mainly on the impact of the properties of the zeolite on the sorption capacity, the sorption mechanism, the influence of pH and the durability of the immobilization. The zeolites were modified with HDTMA and ODTMA surfactants up to 100% and 120% of their external cation exchange capacity. Batch and column studies were conducted to evaluate the influence of pH and the initial Cr(VI) concentration on their efficiencies for removing chromates. The organo-zeolites show a significant ability to remove Cr(VI) from aqueous solutions. The amount of Cr(VI) removed by organo-clinoptilolite and organo-zeolite Na-P1 is greater at low pH values, whereas the sorption efficiency decreased with increasing pH. Sorption of Cr(VI) was more efficient with the HDTMA-modified organo-clinoptilolite (150 mmol Cr(VI)/kg) than the ODTMA-modified clinoptilolite (132 mmol Cr(VI)/kg). The maximum sorption capacity was obtained with the $1.2 \times$ ECEC ODTMA-modified clinoptilolite (237 mmol Cr(VI)/kg). The organo-zeolites Na-P1 adsorbed Cr(VI) from aqueous solutions more effectively and were much more durable than the organo-clinoptilolites.

KEYWORDS: clinoptilolite, synthetic zeolite, zeolite Na-P1, Cr(VI) sorption, organo-zeolites, adsorption.

Chromium is a priority metal pollutant that is introduced into water bodies by many industrial processes such as tanning, metal-processing, electroplating, paint manufacture, steel fabrication and agricultural runoff (Campos *et.al*, 2007). Chromium can be characterized as a redox-active metal that exists as either Cr(III) or Cr(VI) in the environment and the oxidation state determines the toxicity and mobility. Cr(VI) is a genotoxic carcinogen which spreads easily and a common environmental pollutant while Cr(III) is less mobile and rather non-toxic in soils (Fendorf, 1995). Hexavalent chromium, which is present primarily as chromate ($CrO_4^{2-}$) and hydrochromate ($HCrO_4^-$) in the environment, was chosen for experiments because it is a major environmental contaminant (Haggerty & Bowman, 1994; Campos *et al.*, 2007). Chromium(VI) is very soluble in aqueous solutions and the occurrence of a particular species depends on the pH. For pH > 6 $CrO_4^{2-}$ ions predominate, whereas in slightly acidic media (pH 2−6) the $Cr_2O_7^{2-}$ and $HCrO_4^-$ species dominate (Tandon *et al.*, 1984; Yusof & Malek, 2009).

Several treatment methods have been developed to remove Cr(VI) from industrial wastewater. They include ion exchange, membrane filtration, reverse osmosis, adsorption and the use of various types of sorbents (Shi *et al.*, 2001; Xing *et al.*, 2007).

Recently, the need for an alternative low-cost, easily available mineral sorbent has necessitated the search for new materials (Jong-Hyok & Dultz, 2008; Bedelean *et al.*, 2009; Swarnkar *et al.*, 2011; Bajda & Kłapyta, 2013). Due to their unusually large specific surface area, stability and their ion exchange, adsorption and molecular sieving properties, zeolites that have been recognized as excellent sorbents for cations (Apreutesei *et al.*, 2008; Chao & Chen, 2012). However, due to the negative charge of their surface, zeolites have little or no affinity for anionic species (Haggerty & Bowman, 1994). Numerous studies have suggested that the application of zeolites as sorbents for anionic forms of Cr(VI) could be expanded by utilizing the outer surface of the zeolite (Faghihian & Bowman, 2005; Campos *et al.*, 2007; Wu *et al.*, 2008; Leyva-Ramos *et al.*, 2008; Swarnkar *et al.*, 2011a; Matusik & Bajda, 2013; Lu *et al.*, 2014).

Cation-exchange properties of traditional aluminosilicate zeolites arise from the isomorphous substitution of Al for Si in tetrahedral sites (Barrer, 1979). Replacement of exchangeable $K^+$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$ ions by organic cations neutralizes the negative charge, but should not reverse it (Bowman, 2003). Surfactant-modification alters the chemistry of the zeolite's surface drastically, allowing the adsorption of non-polar organic solutes and anions for which untreated zeolites have little affinity (Apreutesei *et al*., 2008). Long-chain quaternary ammonium salts are cationic surfactants that possess a permanent positive charge and are well known as efficient surfactants for zeolite modification. The general model of sorption of these surfactants onto zeolite surfaces includes the formation of a monolayer at the solid–aqueous interface via strong ionic bonds (Haggerty & Bowman, 1994). Examples of such salts are hexadecyltrimethylammonium bromide (HDTMA) and octadecyltrimethylammonium bromide (ODTMA), which contain tetra-substituted ammonium cations with permanently charged trivalent nitrogen and a long alkyl chain (C16 for HDTMA and C18 for ODTMA). As the ammonium salt molecules are too large to enter the channels of the zeolite, the modification of the zeolite takes place only on the outer surface of the crystallites (Moon & Lee, 1990). Therefore, the external cation exchange capacity (ECEC) is important in the synthesis of organo-zeolites.

The presence of impurities in natural zeolites often renders them unsuitable for more advanced applications, raising the need for synthetic zeolites. Recently the possibility of using fly ash for the synthesis of zeolite has been examined (Kazemian *et al.*, 2010; Franus 2012; Musyoka *et al.*, 2012; Sommerville *et al.*, 2013). The resulting synthetic zeolites possess very good sorption properties, a large specific surface area and good stability.

The aim of this study was to compare the chromate adsorption capacities of natural and synthetic organo-zeolites modified by hexadecyltrimethylammonium bromide (HDTMA) and octadecyltrimethylammonium bromide (ODTMA) surfactants. Interest was mainly focused on the mechanism of Cr(VI) sorption and the influence of the zeolite type on the sorption capacity, the pH effect and the durability of the immobilization.

# EXPERIMENTAL

## Analytical methods

All zeolite samples were analysed by X-ray diffraction (XRD) with a powder X-ray diffractometer (Philips PW 3020 X Phil-APD Diffractometer with a graphite monochromator) using Cu-*K*α radiation, a step size of 0.05º2θ and a scanning rate of 1 s per step (Moore & Reynolds, 1997). Air-dried uncoated samples were examined by electron microscopy using a variable pressure field-emission scanning electron microscope (FEI Quanta 200) equipped with an energy dispersive spectrometer (EDS) for elemental microanalysis. The chemical composition of the initial clinoptilolite (Table 1) was obtained by wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF) and atomic absorption spectrometry (AAS) (Sprynsky 2009). The external cation exchange capacity (ECEC) and the efficiency of modification of the organo-zeolites

TABLE 1. The chemical composition of clinoptilolite from the Sokyrnytsya deposit, Ukraine (after Sprynsky, 2009).

| Element | Wt.% | Element | Wt.% |
|---|---|---|---|
| $SiO_2$ | 68.6 | MgO | 0.9 |
| $TiO_2$ | 0.3 | $Na_2O$ | 0.3 |
| $Al_2O_3$ | 11.5 | $K_2O$ | 3.1 |
| $Fe_2O_3$ | 1.6 | $H_2O$ | 8.0 |
| CaO | 2.4 | $CO_2$ | 0.1 |

were calculated on the basis of the content of carbon, hydrogen and nitrogen in the samples using an Elementar VarioEL III CHNS automatic analyser. The chromate concentration in the supernatant was determined spectrophotometrically (UV-VIS Hitachi U-1800) using the biphenylocarbazide method (ASTM, 1992). The specific surface area and porosity were determined from $N_2$ gas adsorption/desorption isotherms at 77 K after outgassing for 12 h at 373 K using an ASAP 2020 apparatus (Micromeritics). The BET equation was used for specific surface area calculations ($S_{BET}$) (Brunauer *et al.*, 1938). The total pore volume ($V_{tot}^{0.99}$) was calculated from the amount of $N_2$ adsorbed at a relative vapour pressure ($P/P_0$) of ~0.99. The zeta potential of the samples was measured at room temperature using a Nano-ZS Zetasizer apparatus (Malvern Instruments).

### Clinoptilolite

A clinoptilolite-rich rock from the Sokyrnytsya deposit (Transcarpathian region, Ukraine) was used in the present study. Clinoptilolite was the dominant phase (~75%) associated with minor quartz and K-feldspar (Fig. 1a). The exchangeable cations were $Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$, with $K^+$ being predominant. The clinoptilolite is present in the form of
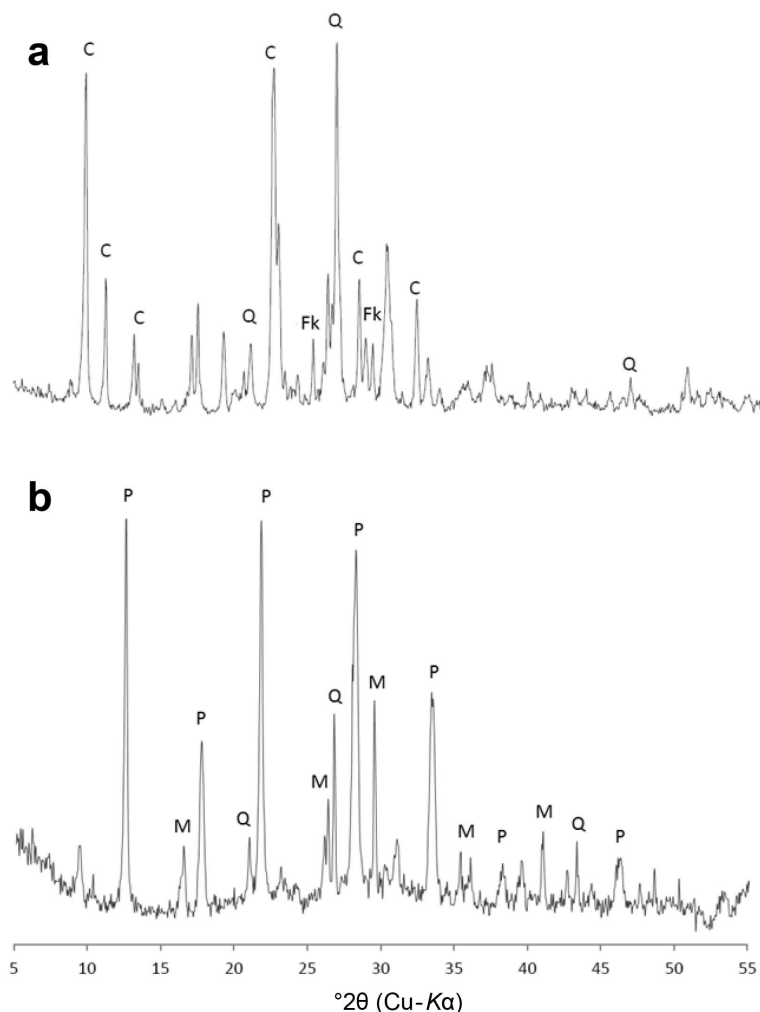


FIG. 1. XRD traces of: (a) the natural zeolite from the Sokyrnytsya deposit, Ukraine; and (b) Na-P1 zeolite. C = clinoptilolite, P = Na-P1, Q = quartz, Fk = K-feldspar and M = mullite.
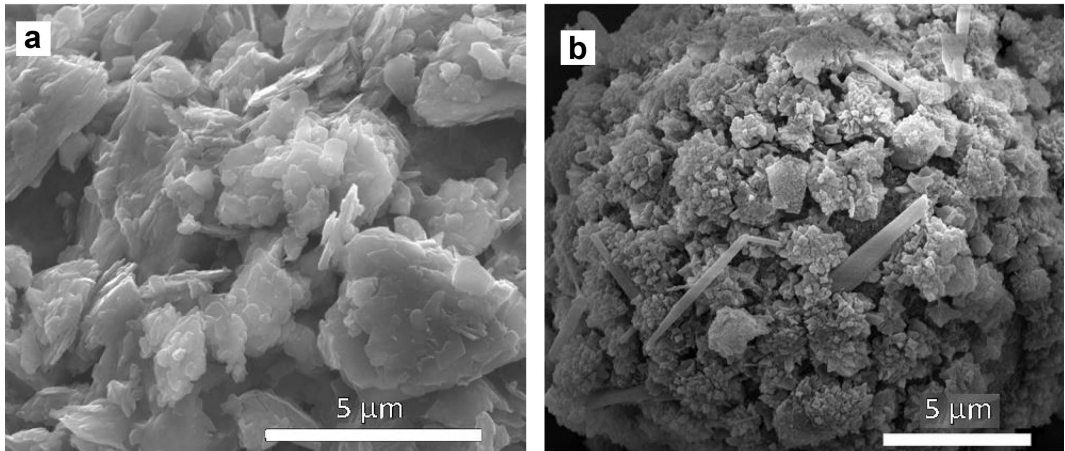
FIG. 2. SEM images of: (a) clinoptilolite from Sokyrnytsya, Ukraine and (b) synthetic Na-P1 zeolite.

aggregates 20−30 μm in size, consisting of platy crystals (Fig. 2a). The cation exchange capacity (CEC) of the clinoptilolite (142 meq/100 g) was determined by exchange with barium chloride (Gillman & Sumpter, 1986). Nitrogen adsorption/ desorption measurements on the raw clinoptilolite yielded a BET type II isotherm with a type H3 hysteresis loop (Fig. 3a), being indicative of a mesoporous material with slit-shaped pores arising from the stacking of platy particles (Sing *et al.*, 1985; Rouquerol *et al.*, 1999). The specific surface area of the natural clinoptilolite was 16.07 $m^2$/g and the total pore volume was 0.049 $cm^3$/g (Table 2).

The organo-zeolite, modified by HDTMA and ODTMA, also yielded a type II isotherm and type H3 hysteresis loop. However, decreases in the specific surface area (4.36 and 4.72 $m^2$/g, respectively) and the total pore volumes (0.032 and 0.033 $cm^3$/g, respectively) were evident.

### Zeolite Na-P1

Zeolite Na-P1 was produced from F-class fly ash obtained from the Rybnik power plant in Poland. The chemical composition of the fly ash was (wt.%): $SiO_2$, 52.1; $Al_2O_3$, 32.2; $Fe_2O_3$, 5.2;
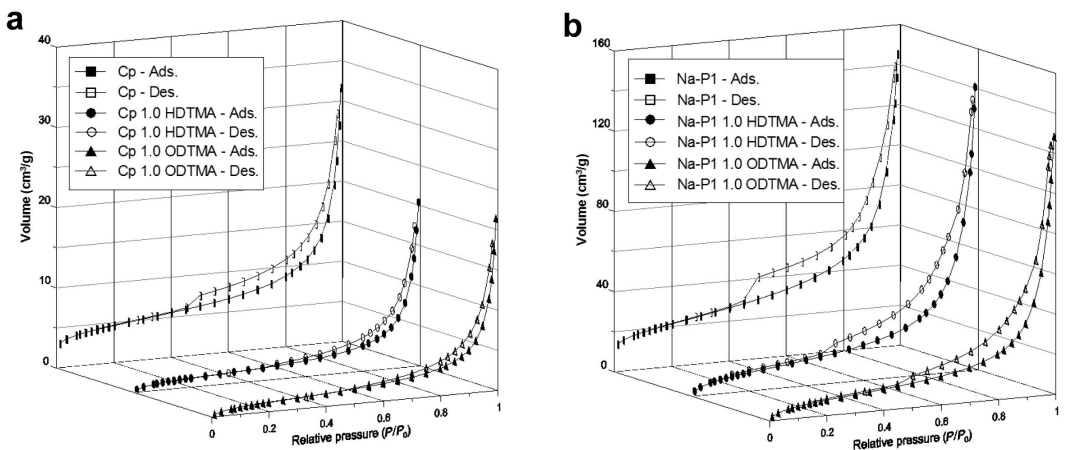


FIG. 3. $N_2$ adsorption/desorption isotherms at 77 K for: (a) clintoptilolite (Cp), HDTMA clinoptilolite (Cp 1.0 HDTMA) and ODTMA-modified (Cp 1.0 ODTMA); (b) Na-P1 zeolite (Na-P1), HDTMA- (Na-P1 1.0 HDTMA) and ODTMA-modified Na-P1 zeolite (Na-P1 1.0 ODTMA).

TABLE 2. Specific surface area and pore volume of the zeolites.

| | Cp | Cp HDTMA | Cp ODTMA | Na-P1 | Na-P1 HDTMA | Na-P1 ODTMA |
|---|---|---|---|---|---|---|
| Specific surface area (BET method), $S_{BET}$ (m$^2$/g) | 16.07 | 4.36 | 4.72 | 74.92 | 36.68 | 30.40 |
| The total pore volume, $V_{tot}^{0.99}$ (cm$^3$/g) | 0.049 | 0.032 | 0.033 | 0.225 | 0.218 | 0.199 |

Cp = clinoptilolite; Na-P1 = fly-ash derived zeolite; HDTMA = HDTMA-modified zeolite at $1.0 \times$ ECEC; ODTMA = ODTMA-modified zeolite at $1.0 \times$ ECEC.

MgO, 1.3; CaO, 1.2; Na$_2$O, 0.5; K$_2$O, 2.9; LOI, 4.6 (Franus, 2012). The hydrothermal synthesis of zeolite Na-P1 was performed according to the following reaction conditions: 20 g of fly ash were mixed with 400 mL of 3 M NaOH at 75ºC for 24 h (Derkowski *et al.*, 2006; Franus 2011). The resulting product was of high purity containing 81 wt.% Na-P1 zeolite and minor mullite and quartz (Fig. 1b). The average ratios of individual cations were: (Na + K + Ca + Mg)/Si = 0.44 and Si/Al = 1.42 (Wdowin *et al.*, 2014). Hence, the resulting Na-P1 zeolite is a low Si-phase with sodium as the main exchangeable cation. The surface morphology of zeolite Na-P1 is shown in Fig. 2b. The Na-P1 forms acicular crystals, but irregular aggregates also occur.

Na-P1 zeolite has a BET specific surface area of 74.92 m$^2$/g, which is five times greater than fly ash (15 m$^2$/g) and total pore volume 0.225 cm$^3$/g (Table 2) The Na-P1 and the HDTMA- and ODTMA-modified Na-P1 zeolite yielded composite BET type II and type IV adsorption/desorption isotherms with a type H2 hysteresis loop (Fig. 3b). The organo-zeolite Na-P1, modified by HDTMA and ODTMA had smaller decreases in the specific surface area (36.68 and 30.40 m$^2$/g, respectively) and total pore volumes (0.218 and 0.199 cm$^3$/g, respectively) compared to the modified clinoptilolites.

### External cation exchange capacity (ECEC)

In order to perform the surface modification of the zeolites with quaternary ammonium salts, the CEC for clinoptilolite and Na-P1 zeolite had to be confirmed. The CEC was determined by adsorption of HDTMA ions. The adsorption of surfactant took place on the external exchange sites only; thus, the measured CEC is related to the ECEC (Haggerty & Bowman, 1994). The procedure was based on the formation of a monolayer of the cationic surfactant (HDTMA) on the surface of the zeolite. The aqueous suspensions (100 mL) of the zeolite (1 g) and the organic salts (1 g) were mixed with a magnetic stirrer for 3 h at 80ºC and were then left for 24 h. The procedure was repeated, and the products were washed 3−6 times with 500 mL of hot (80ºC) deionized water and then with hot (80ºC) ethanol until a negative AgNO$_3$ test was obtained. Subsequently, the zeolite was dried. This procedure ensured that the second layer of the surfactant was washed out and only the monolayer was retained. The differences in the C, H and N content between Na-P1 or natural zeolite and their HDTMA-treated counterparts was used to calculate the ECEC, which was 24.40 meq/100 g for the synthetic Na-P1 zeolite and 11.45 meq/100 g for the natural clinoptilolite.

### Preparation of organo-zeolites

Synthetic Na-P1 zeolite and natural clinoptilolite were modified with the HDTMA and ODTMA surfactants with 100% and 200% of their ECEC ($1.0 \times$ and $2.0 \times$ ECEC, respectively). Zeolite (100 g) was suspended in double-distilled water (1500 mL) in a beaker and the suspension heated at 80ºC, with stirring, for 1 h. HDTMA or ODTMA surfactants were dissolved in double distilled water (500 mL) at 80ºC; the amount of surfactant dissolved depended upon the desired modification ratio (Table 3). The surfactant solution was added to the zeolite suspension, giving a solids concentration of 50 g/L. After heating and stirring at 80ºC for 6 h, the samples were centrifuged and dried at 60ºC. Based on the difference in the C, H and N

TABLE 3. Weight of surfactants (g) used in the preparation of the solutions.

| | Clinoptilolite | | Na-P1 | |
|---|---|---|---|---|
| | $1.0 \times$ ECEC | $1.2 \times$ ECEC | $1.0 \times$ ECEC | $1.2 \times$ ECEC |
| HDTMA | 4.17 | 8.35 | 8.89 | 17.79 |
| ODTMA | 4.49 | 8.99 | 9.58 | 19.15 |

content between samples with and without modifications, the effectiveness of the organophilization was determined. The effectiveness of the modification of the organo-zeolites modified at 1.0 ECEC always exceeded 90%. The natural zeolite was modified at 0.94 and 0.93 ECEC with HDTMA and ODTMA, respectively and the Na-P1 zeolite was modified at 1.01 and 0.98 ECEC with HDTMA and ODTMA, respectively. This indicates that the required single layer of surfactant (1.0 ECEC) was formed. By contrast, using a 2.0 ECEC, a double layer of surfactant was not formed. The surfactants were adsorbed at ~$1.2 \times$ECEC for each of the zeolites by ion exchange and hydrophobic interactions. The instability of the second layer of surfactant is attributed to weak electrostatic interactions between the hydrocarbon chains. In the subsequent experiments, samples with $1.0 \times$ and $1.2 \times$ the ECEC were used.

The surface of clinoptilolite and zeolite Na-P1 modified by HDTMA-Br and ODTMA-Br has permanent positively charged centres, which may attract anions. This confirms the value of the zeta potential, which decreases as the pH increases. However, the surface of organo-zeolites is positively charged, as the point of zero charge did not fall within the pH range 1−13.

*Sorption experiments*

The effectiveness of chromate adsorption onto the organo-zeolite was evaluated with both static and dynamic sorption experiments. The source of Cr(VI) ions was potassium dichromate ($K_2Cr_2O_7$) of analytical grade.

In the static sorption experiments the influence of pH and the initial concentration on the effectiveness of the sorption was examined. The influence of pH was studied at an initial concentration of 5 mmol Cr(VI)/L at pH 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0 and 10.0. The effect of the initial concentration of Cr(VI) was examined at pH = 4 for clinoptilolite and at pH = 1 for Na-P1 zeolite, at concentrations of: 0.05, 0.10, 0.25, 0.50, 2, 5, 10, 25 and 50 mmol/L. In all experiments, 100 mg of organo-zeolite was placed in 8 mL test-tubes and 5 mL of Cr(VI) solution with different pHs, or various initial concentrations, was added. The sorption of Cr(VI) was determined by comparing the initial and equilibrium concentrations after 24 h under stirring, followed by centrifugation for 10 min at 14,000 rpm. All sorption experiments were performed in triplicate.

The dynamic sorption experiments were conducted using a flow technique. An organo-zeolite layer (10 g) was placed in an acrylic glass column (50 cm high and 2.5 cm wide) and secured by glass wool on both sides. The organo-zeolite beds were 1.8 cm tall and 2.5 cm in diameter. Taking into account the specific density of the organo-clinoptilolite and organo-Na-P1 (2.65 and 2.45 g/cm$^3$ respectively) and the bulk density (1.13 g/cm$^3$ for both organo-zeolites), the bed volumes (BV) of the organo-clinoptilolite and the organo-Na-P1 were 5.06 and 4.75 mL, respectively. Then, 500 mL of the Cr(VI) solution with pH 3.5 and an initial concentration of 0.4 mmol/L was added. Portions of the eluent (15 mL) were collected for analysis from each column.

RESULTS AND DISCUSSION
*Static sorption*

*Effect of pH on the sorption of Cr(VI)*. After sorption, the pH of the supernatant solution was greater for both zeolite systems due to the high alkalinity of the suspensions. The most efficient sorption of Cr(VI) by the organo-clinoptilolite was observed within the pH range 2−3, while for the organo-Na-P1 zeolite the optimal range of the pH was 5.7−7.0 (Figs 6 and 7). It can be assumed that at lower pH values, the sorption would probably also have been high for the Na-P1 zeolite; however, due to the alkaline nature of the Na-P1 zeolite it was not possible to attain a lower pH. The organo-zeolites modified with HDTMA are better sorbents
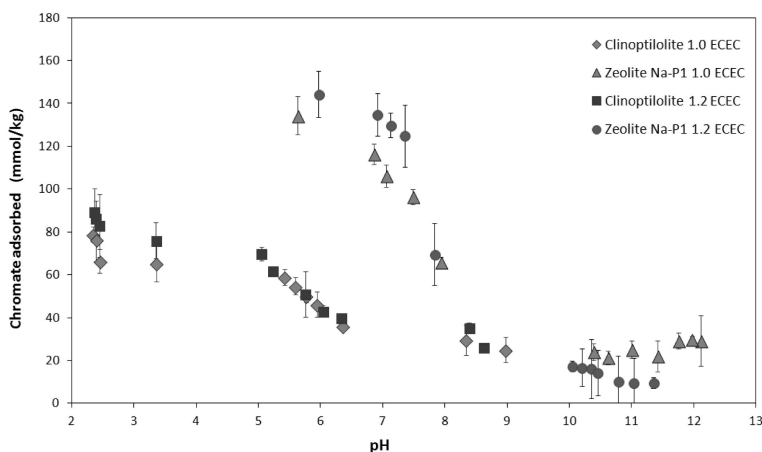
FIG. 4. Comparison of Cr(VI) sorption on HDTMA-modified clinoptilolite with Na-P1 synthetic zeolite as a function of pH.

than the ODTMA-modified zeolites. The maximum sorption of Cr(VI) anions for clinoptilolite (108 mmol/kg) was observed at pH 2.4 for the HDTMA-modified zeolite at $1.2 \times ECEC$ (Fig. 4), while after modification at $1.0 \times ECEC$ the maximum sorption was slightly smaller (96 mmol/kg). Hence, the additional amount of surfactant ($0.2 \times ECEC$) increases the efficiency of Cr(VI) adsorption by little more than 10 mmol/kg, indicating that with an increasing amount of surfactant, the modified surface has only a slightly greater affinity for anions. Therefore, it would be useful to examine whether modification to levels above $1.0 \times ECEC$ is really necessary.

In the case of the Na-P1 zeolite modified by HDTMA to $1.0 \times$ and $1.2 \times ECEC$, the maximum sorption of Cr(VI) was 137 mmol/kg at pH = 5.6 and 144 mmol/kg at pH = 6.0, respectively. Hence, an increased amount of surfactant does not improve the adsorption efficiency for Cr(VI) significantly. The maximum sorption with ODTMA (142 mmol/kg) was observed at pH 5.7 with the $1.2 \times ECEC$ modification (Fig. 5). The slight difference in the sorption efficiency between modification at $1.0 \times$ and $1.2 \times ECEC$ is observed for both surfactants. The reason for such small differences is the incomplete formation of a double layer of surfactant at $2.0 \times ECEC$. The objective of
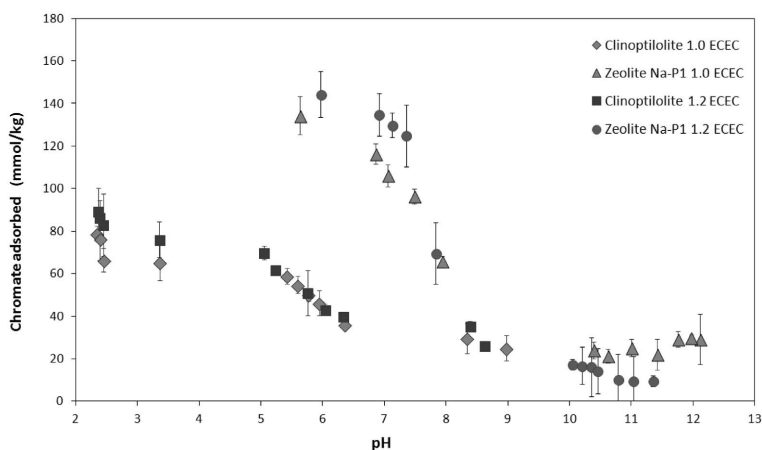


FIG. 5. Comparison of Cr(VI) sorption on ODTMA-modified clinoptilolite and Na-P1 synthetic zeolite as a function of pH.
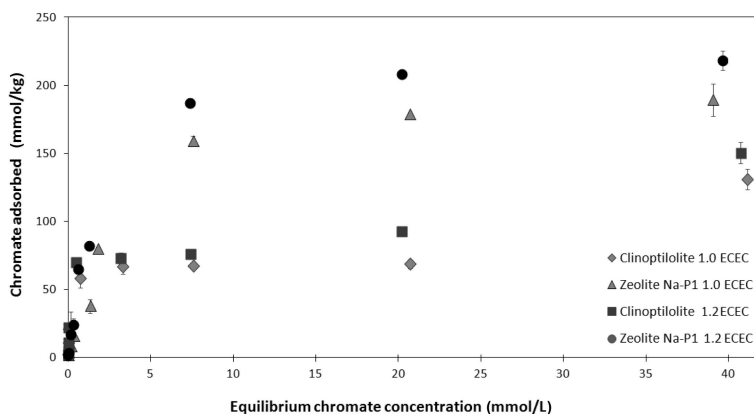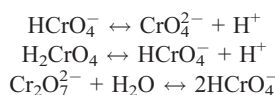
FIG. 6. Comparison of Cr(VI) sorption on HDTMA-modified clinoptilolite and Na-P1 synthetic zeolite as a function of concentration.

this research was to design a low-temperature process that would still modify the zeolite surface effectively. However, it was not possible to obtain a surfactant loading above $1.2 \times ECEC$ even by reducing the amount of water used or by reducing the solid to solution ratio.

A strong relationship holds between the sorption efficiency and the pH of the solution. This is attributed to the influence of pH of the solution on the Cr(VI) ion speciation (Yousof & Malek, 2009); where at pH > 6, $CrO_4^{2-}$ ions dominate, while at pH 2−6, $Cr_2O_7^{2-}$ and $HCrO_4^-$ ions are common:

$$HCrO_4^- \leftrightarrow CrO_4^{2-} + H^+$$
$$H_2CrO_4 \leftrightarrow HCrO_4^- + H^+$$
$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^-$$

The bonding of chromates to zeolites modified by quaternary alkylammonium surfactants has been

attributed by most authors to the formation of a positively charged bilayer, or patchy bilayer of these cations on the surface of the mineral, which attracts counter-ions from the aqueous solution (Haggerty & Bowman, 1994; Li and Bowman, 1998; Bowman *et al.*, 2000; Li, 2004). However, this explanation applies to adsorbents prepared with a surfactant loading greater than the ECEC of the starting minerals. The first layer of surfactants is retained by cation exchange and the second layer by hydrophobic bonding and stabilization by the counter-ions. The $Br^-$ counter-ions from the second layer exchange with chromate anions present in the solution. Precipitation of sparingly soluble salts is the second possible mechanism, where the Cr(VI) anions react with organic cations on the surface of the zeolite. Zeolites with inorganic exchangeable cations partially replaced by HDTMA
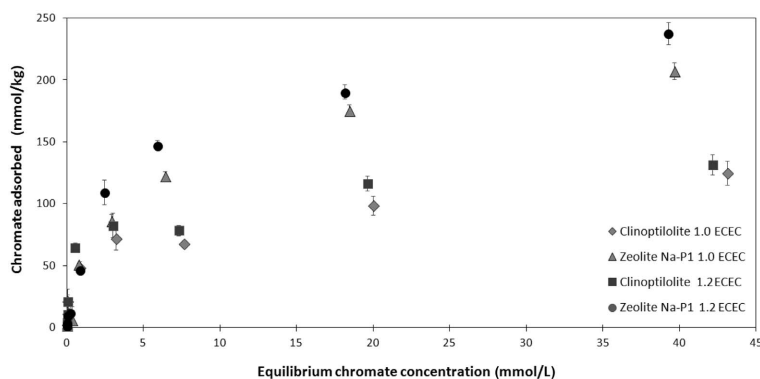


FIG. 7. Comparison of Cr(VI) sorption on ODTMA-modified clinoptilolite and Na-P1 synthetic zeolite as a function of concentration.

TABLE 4. The influence of initial Cr(VI) concentration (in bold) on the final pH after sorption of Cr(VI) on HDTMA-modified clinoptilolite at $1.0 \times$ and $1.2 \times$ ECEC (initial Cr(VI) pH = $4\pm0.01$) and HDTMA-modified Na-P1 zeolite at $1.0 \times$ and $1.2 \times$ ECEC (initial Cr(VI) pH = $1\pm0.01$).

| Concentration of Cr(VI) (mmol/L) | **0.05** | **0.1** | **0.25** | **0.5** | **2** | **5** | **10** | **25** | **50** |
|---|---|---|---|---|---|---|---|---|---|
| Clinoptilolite $1.0 \times$ ECEC | 5.88 | 6.18 | 6.04 | 5.99 | 5.97 | 6.03 | 6.15 | 6.05 | 5.95 |
| Clinoptilolite $1.2 \times$ ECEC | 6.10 | 6.24 | 6.20 | 6.18 | 6.09 | 6.30 | 6.36 | 6.13 | 6.10 |
| Na-P1 Zeolite $1.0 \times$ ECEC | 6.03 | 5.99 | 6.11 | 6.32 | 6.23 | 6.07 | 6.19 | 6.01 | 5.89 |
| Na-P1 Zeolite $1.2 \times$ ECEC | 6.05 | 6.04 | 6.11 | 6.35 | 6.20 | 6.14 | 6.09 | 6.11 | 6.03 |

ions, also showed adsorption of chromates (Li *et al.*, 1998; Bowman *et al.*, 2000). Majdan *et al.* (2006) concluded that the removal of chromate from solution occurs via formation of alkylammonium chromates. Bajda and Kłapyta (2013) have provided evidence that displacement of HDTMA ions from the exchange sites of the silicate and their reaction with chromate ions to form a precipitate of alkylammonium chromate is possible both at low pH and at high pH. Based on their results, it can be concluded that similar processes may be taking place in the present study, depending on the reaction conditions. Adsorption by admicelles is significant at a concentration of HDTMA greater than the ECEC of the silicate, whereas formation of a precipitate with alkylammonium ions bound to the

silicate surface may occur when these ions occupy the exchange sites fully or partially. A very low solubility of the precipitated alkylammonium salts may ensure effective immobilization of Cr(VI) anions. The major differences between the pH of the clinoptilolite and the Na-P1 zeolite suspensions may be attributed to the greater alkalinity of the synthetic Na-P1 zeolite. The low degree of Cr(VI) sorption at high pH levels results from $OH^-$, Cr(VI) and $Br^-$ ions competing for adsorption sites − with an increasing pH as the amount of $OH^-$ increases.

*Effect of initial concentration on the sorption of Cr(VI)*. With all suspensions the pH increased to 5.9−6.1 after the sorption (Tables 4 and 5), indicating that $CrO_4^{2-}$ was the dominant species available.

TABLE 5. Influence of initial Cr(VI) concentration (in bold) on the final pH after sorption of Cr(VI) on ODTMA-modified clinoptilolite at $1.0 \times$ and $1.2 \times$ ECEC (initial Cr(VI) pH = $4\pm0.01$) and ODTMA-modified Na-P1 zeolite at $1.0 \times$ and $1.2 \times$ ECEC (initial Cr(VI) pH = $1\pm0.01$).

| Concentration of Cr(VI) (mmol/L) | **0.05** | **0.1** | **0.25** | **0.5** | **2** | **5** | **10** | **25** | **50** |
|---|---|---|---|---|---|---|---|---|---|
| Clinoptilolite $1.0 \times$ ECEC | 6.01 | 6.17 | 6.06 | 6.03 | 6.02 | 6.08 | 6.11 | 6.21 | 5.96 |
| Clinoptilolite $1.2 \times$ ECEC | 6.09 | 6.21 | 6.08 | 6.02 | 6.04 | 6.13 | 6.25 | 6.29 | 6.10 |
| Zeolite Na-P1 $1.0 \times$ ECEC | 6.06 | 6.04 | 6.15 | 6.22 | 6.21 | 6.12 | 6.21 | 6.09 | 5.98 |
| Zeolite Na-P1 $1.2 \times$ ECEC | 6.07 | 6.09 | 6.19 | 6.20 | 6.24 | 6.14 | 6.19 | 6.11 | 6.05 |

The maximum sorption capacity for an organo-clinoptilolite was obtained through modification with HDTMA at $1.2 \times$ ECEC and amounts up to 150 mmol Cr(VI)/kg. After modification at $1.0 \times$ ECEC with HDTMA the sorption decreased to 131 mmol Cr(VI)/kg (Fig. 6). The additional amount of surfactant increased the sorption efficiency by 20 mmol to Cr(VI)/kg and in addition, the greater the concentration of Cr(VI) in the solution, the greater the sorption efficiency. The sorption efficiency of chromate with ODTMA-modified clinoptilolite, was smaller: 125 and 132 mmol/kg for modifications at $1.0 \times$ ECEC and $1.2 \times$ ECEC, respectively (Fig. 7). The amount of ODTMA used for zeolite modification had little impact on the sorption efficiency for Cr(VI). The HDTMA-modified clinoptilolite showed a greater sorption efficiency than the ODTMA-modified mineral. In the case of the synthetic Na-P1 zeolite, the situation was reversed. The HDTMA-modified Na-P1 zeolite was less effective at adsorbing Cr(VI) than the ODTMA-modified zeolite (Figs 6 and 7). The maximum sorption capacity for the synthetic Na-P1 zeolite was obtained with the ODTMA-modified mineral at $1.2 \times$ ECEC (237 mmol Cr(VI)/kg), while the HDTMA-modified Na-P1 zeolite adsorbed 218 mmol Cr(VI)/kg.

The sorption efficiency increased with increasing concentration of Cr(VI) ions in the solution and the maximum sorption capacity of the organo-zeolites for Cr(VI) ions, the molar ratio Cr(VI)$_{ads.}$/surfactant, was determined (Table 6). The resulting molar ratios for HDTMA and ODTMA are almost identical, suggesting that HDTMA-modified organo-zeolites have an almost equal sorption capacity to ODTMA-modified zeolites. Any minor differences between modification at $1.0 \times$ and $1.2 \times$ ECEC are caused by the lack of a double layer of surfactant on the zeolite surface. The molar ratio, Cr(VI)$_{ads.}$/surfactant, indicates that, under the conditions adopted, the sorption capacity of the natural zeolite is maximized. The adsorption of the surfactants on the surface of the Na-P1 was less effective than on the clinoptilolite surface in the Cr(VI) sorption experiments. The isotherms obtained did not reach a constant adsorption level, suggesting that the optimum sorption capacity of the materials had not been attained. Indeed, the molar ratios of Cr(VI) adsorbed to surfactant were <1, confirming that only 75% of the surfactant was used in the case of the clinoptilolite and 50% in the case of the Na-P1 zeolite.

## Dynamic sorption

Dynamic experiments were used to determine the amount of ions passing through the bed of the sorbent and exchanging with organic cations until breakthrough. For these experiments, three organo-zeolites were selected: HDTMA-modified clinoptilolite at $1.0 \times$ ECEC and Na-P1 organo-zeolites modified at $1.0 \times$ ECEC with HDTMA or ODTMA surfactants (Fig. 8). The selection of the specific organo-zeolites was based on their efficiency in the preparation of the materials with a single surfactant layer. The bed-volume of the ion-exchange column was taken as the unit of volume for these dynamic experiments.

Breakthrough for $1.0 \times$ ECEC HDTMA-modified clinoptilolite occurred after 44.5 bed volumes. For the $1.0 \times$ ECEC HDTMA- or ODTMA-modified synthetic Na-P1 zeolites, breakthrough was observed after 71 or 74 bed-volumes, respectively. After breakthrough, the concentration of Cr(VI) in the eluent increased and the curves shifted towards the initial concentration. Exhaustion of the ion-exchange properties of the HDTMA-clinoptilolite occurred after 311 bed volumes. The Na-P1 organo-zeolites were more durable and the ion-exchange properties were exhausted after 433 and 467 bed volumes for the HDTMA- and ODTMA-modifications, respec-

TABLE 6. Molar ratio of adsorbed Cr(VI) to the HDTMA and ODTMA surfactants for clinoptilolite and Na-P1 zeolite.

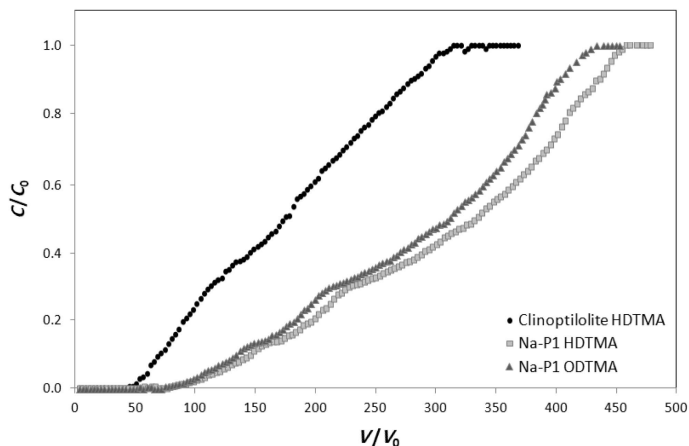| | — Cr(VI)$_{ads.}$/HDTMA — | | — Cr(VI)$_{ads.}$/ODTMA — | |
| | $1.0 \times$ ECEC | $1.2 \times$ ECEC | $1.0 \times$ ECEC | $1.2 \times$ ECEC |
|---|---|---|---|---|
| Clinoptilolite | 0.71 | 0.77 | 0.75 | 0.75 |
| Na-P1 zeolite | 0.49 | 0.58 | 0.47 | 0.51 |

Fig. 8. Breakthrough curves for selected organo-zeolites modified at $1.0 \times ECEC$ over the regenerated reactive adsorbent at 25ºC.

tively. The most efficient sorbent was the HDTMA-modified Na-P1 zeolite, while the least efficient sorbent was the clinoptilolite. These adsorption efficiencies correspond to the relative ECEC of the zeolites (clinoptilolite 11.45 meq/100 g; Na-P1 zeolite 24.40 meq/100 g). The organo-clinoptilolite removed 55% of the Cr(VI) ions from the initial solution, while the HDTMA-Na-P1 zeolite removed 66% and the ODTMA-Na-P1 zeolite removed 64%. These results are also related to the physical and chemical properties of the materials, including hardness and quartz contents. The clinoptilolite formed agglomerates of grains that were detrimental to the flow rate and the whole surface of the zeolite was not available for sorption.

The equilibrium pH of the eluent after Cr(VI) sorption was 4.9−6.8 for experiments with clin-optilolite and 7.5−10.0 for Na-P1 zeolite. Although the sorption capacity of the organo-zeolites under the selected conditions was maximal, the pH was always greater during the experiments than the initial pH value, thus suggesting that the exchange-able cations were not removed completely. Due to the alkaline nature of the Na-P1 zeolite, the final pH was always greater than with the clinoptilolite.

The total amount of the alkylammonium ions adsorbed by the zeolites was used to calculate the chromate/surfactant molar ratio in the chromate-organo-silicate complexes. The calculated ratio provides information on the extent to which the adsorbed surfactant is used for sorption of chromate ions. A ratio of 1.0 would mean that 100% of the adsorbed HDTMA or ODTMA participates in the

process of sorption. The results obtained for [Cr(VI)ads./surfactant] were: 0.31 for the HDTMA-modified clinoptilolite; 0.23 for the HDTMA-modified Na-P1 zeolite and 0.22 for the ODTMA-modified Na-P1. The calculated molar ratios indicate that only ∼20−30% of the surfactant was used during the Cr(VI)-sorption process, suggesting that the conditions for dynamic experiments did not allow maximum utilization of the sorption capacity of the organo-zeolites. It may be possible to improve the sorption efficiency in dynamic conditions by reducing the pH, raising the temperature or using a greater initial concentration.

## CONCLUSIONS

The modification of clinoptilolite and synthetic Na-P1 zeolite by HDTMA and ODTMA surfactants decreased the specific surface areas and total pore volumes of the zeolites as the surfactants covered the surface of the zeolites and blocked the pores. After modification with the HDTMA and ODTMA surfactants, the zeolites exhibited increased capa-cities for removing chromium(VI) contaminants from aqueous solutions. The amount of Cr(VI) removed by both the organically-modified natural and synthetic zeolites is greater at lower pH (2−7) values. The sorption of chromate is more efficient with the organo-zeolites modified by HDTMA than by ODTMA. All experiments have shown that the modified synthetic zeolite is a better sorbent for the anionic Cr(VI) than its natural clinoptilolite counterpart. The results of this research may be

useful in environmental remediation and may shed light onto the properties of surfactant−modified zeolites and their potential applications in environmental protection.

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