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ORIGINAL ARTICLE

Removal of chromate from aqueous solution using treated natural zeolite

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Abstract This paper present the possible alternative removal options for the development of safe drinking water supply in the chromium-affected areas. The Cr (VI) state is of particular concern because of its toxicity. The mordenite has suitable mineralogical properties that enable them to be used for ion-exchange processes. This includes total cation exchange capacity. However, in the present work, the modified-natural zeolite was used as an adsorbent for the removal of Cr (VI) from aqueous solution. The ability of modified natural zeolite (mordenite) to remove inorganic anion was investigated. Laboratory experiments were conducted examining the effect of the sorption of cationic surfactants. On the basis of the results of this study, the HDTMA-HSO_4 modified zeolite appears suitable as a sorbent for hexavalent chromium whereas EHDDMA-modified zeolite were not removed with the same efficiency. The sorption of chromate on HDTMA-zeolite results from a combination of entropic, coulombic, hydrophobic effects, and HDTMA counterion.

Keywords Natural zeolite · Surfactants · Removal · Chromate · Brazil

Introduction

Rapid growth in industry and population has resulted in environmental degradation. Chromium is a priority metal pollutant introduced into the water bodies from many industrial processes such as tanning, metal processing, electroplating, paint manufacturing, steel fabrication and agricultural runoff. Chromium occurs in the aquatic environment as both trivalent and hexavalent states. Hexavalent chromium, which is primarily present in the form of chromate (CrO_4^-) and dichromate ($Cr_2O_7^-$), possesses significantly higher levels of toxicity than the order valency states (Sharma and Forster 1995; Selvi et al. 2001; Selvaraj et al. 2003).

Natural zeolites have an excellent cation exchange capacity among other naturally occurring products, which enables them to be used as cation exchangers (Ibrahim and Akashah 2004; Pansini 1996; Colella 1996). Mordenite is the most abundant naturally occurring zeolite. Cationic surfactants have been used to modify zeolite surfaces in attempts to enhance the sorptive capabilities of natural zeolites. The use of surfactant-modified zeolite (SMZ) for the sorption of hexavalent chromium was first proposed by Boyd et al. 1988. Laboratory batch and column tests demonstrate that SMZ can simultaneously remove multiple types of contaminants from water, including inorganic anions such as chromate and hydrophobic organics (Zhaohui et al. 1998; Krishna et al. 2001). Recent studies have shown that treatment of clinoptilolite with cationic surfactants, e.g., HDTMA-Br, yields an SMZ that has a strong affinity for selenate and chromate, as well as nonpolar organics, and also has cation-exchange selectivity for cations, such as Pb^{2+} (Bowman et al. 1995). Although data on anion exchange on SMZ are limited compared with the data available on cation exchange on natural zeolites, published studies suggest that surfactant modification offers the potential to further enhance the industrial and environmental

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applications of natural zeolites. The ability of amended natural zeolite to remove inorganic anion from water is investigated. The efficiency of adsorbent towards the removal of chromium was also tested using untreated phase.

Materials and methods

The zeolite used in this study is natural mordenite. The chemical composition and specific surface area are presented in Table 1. The idealized chemical formula of the mordenite may be written as: $Na_3KCa_2(Al_8Si_{40}O_{96})\cdot 28H_2O$. Cation exchange capacity calculated from the idealized unit-cell formula is 2.29 meq g^{-1}, having a Si/Al ratio close to 5. The mineralogical composition of natural zeolite used in experiments is dominated by mordenite (about 96%). The sample was examined using a Siemens D 5,000 X-ray powder diffractometer with Cu Kα radiation, at a step scan of 0.05° and a scan rate of 5° per minute in 2θ. X-ray powder-diffraction analysis indicates that mordenite is the only phase (Fig. 1). The individual mordenite fibres are visible in the scanning electron microscopy (LEO 440i) picture shown in Fig. 2.

Different techniques have been tried to increase the reactivity of natural zeolites to remove the inorganic anion. The addition of chemical activators may result in the possibility of anion sorption. The effect of the cationic surfactants EHDDMA (ethylhexadecyldimethylammonium) and HDTMA (hexadecyltrimethylammonium) on chromate sorption by modified-natural zeolite was examined. The raw zeolite was treated with surfactant to a level of 100 meq kg^{-1} (28.4 g surfactant per kg of zeolite). Samples were equilibrated on a shaker at 650 rpm at 25 ± 0.4°C for 8 h. The amount of surfactants sorbed (meq kg^{-1}) on the zeolites is presented in Fig. 3. After the pretreatment, modified-zeolite was tested for chromate sorption. For comparative purposes, chromate sorption on mordenite was also determined. The natural sample was tested in dynamic experiments (see untreated Mor in Fig. 4). The removal of inorganic anion from water has been tested under dynamic conditions. The simulated drinking water contaminated with Cr (VI) was used in the experiments. A stock solution containing 1,000 mg L^{-1} of Cr (VI) was prepared using potassium dichromate in distilled water. All the chemicals used were of analytical grade. All experiments were conducted in duplicates and the maximum deviation was found to be ± 5%. Batch mode experiments were conducted by agitating 2.5 g of modified-zeolite with 25 mL of hexavalent chromium solution (Fig. 5). The pH values of the equilibrium solution following chromate sorption were on average 5.3 (±0.2) and 4.9 (±0.4) for EHDDMA and HDTMA-HSO_4^- modified samples, respectively. The adsorbent was separated by centrifugation and the supernatant was analyzed spectrophotometrically using 1,5-diphenyl carbazide (APHA 1985). For the effect of Cr (VI) sorption, various initial times such as 30, 60, 90, 120 and 150 min were tested (Fig. 6).

Table 1 Chemical composition (%) and specific surface area (BET) of natural zeolite used in this study

%	Mordenite
SiO_2	67.82
TiO_2	0.07
Al_2O_3	14.96
Fe_2O_3	0.42
MgO	0.18
CaO	1.87
MnO	<0.01
Na_2O	0.32
K_2O	4.47
LOI	9.37
Total	99.55
BET (m^2 g^{-1})	14.6

LOI loss of ignition (50% relative humidity)

Results and discussion

Modified-natural zeolite sample has been tested for hexavalent chromium removal from water in laboratory experiments. Like many clays, most zeolites possess a net negative structural charge resulting from isomorphic substitution of cations in the crystal lattice. Due to this negative charge, natural zeolites have little or no affinity for anionic species. In this study, the efficiency of surfactant-modified natural zeolite on the removal of chromium was examined using ion-exchange batch. Removal of chromate by EHDDMA and HDTMA-HSO_4 (surfactants) on mordenite zeolite was studied separately in the laboratory. Most commonly, zeolites are pretreated with HDTMA, to establish counterions at the surface which are easily displaced by chromium. The cationic surfactant HDTMA on zeolite was tested and the subsequent sorption of hexavalent chromium on the HDTMA-hydrogen sulfate zeolite was also determined. Figure 3 shows the amounts of surfactants (HDTMA and EHDDMA) sorbed on natural zeolite. It can be seen from Fig. 3 that the amounts of HDTMA-HSO_4 and EHDDMA sorbed follow the same trend and increase with respect to the initial surfactant content. However, the strong influence of the surfactant counterion must

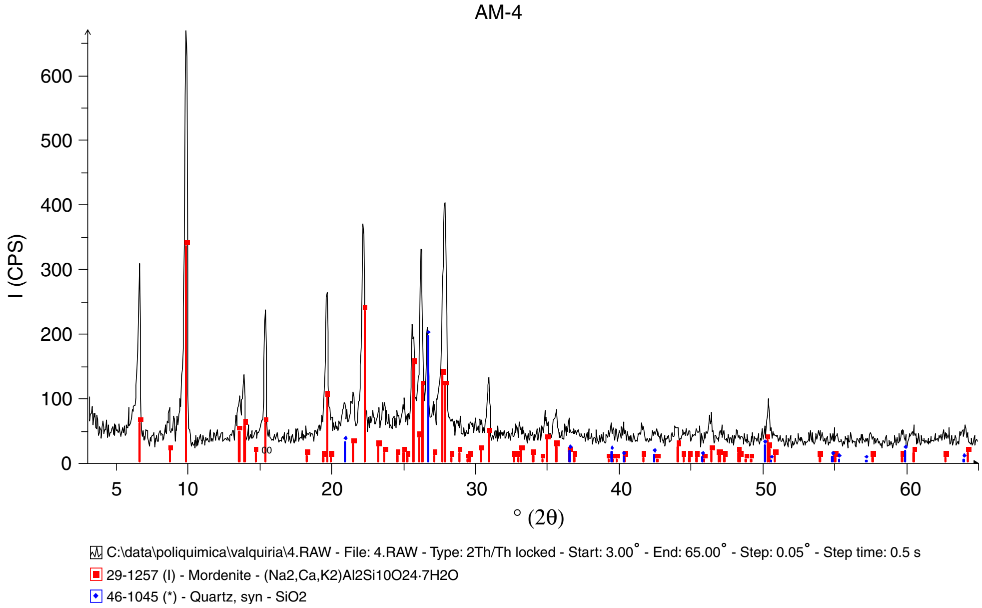

Fig. 1 X-ray powder diffraction pattern of the natural zeolite–mordenite

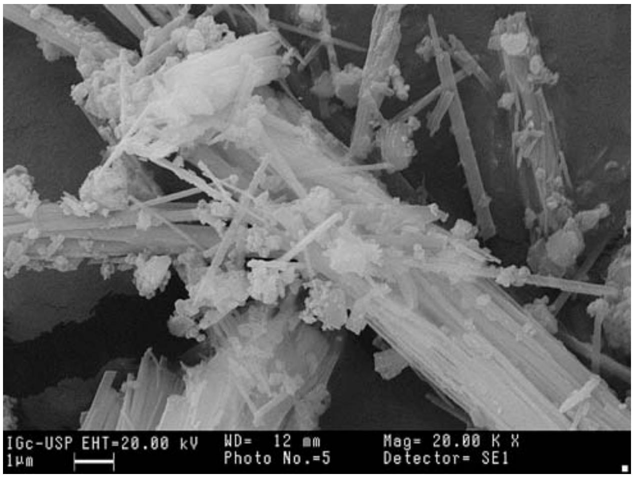

Fig. 2 SEM photograph of the natural zeolite with mordenita fibres (×20,000)

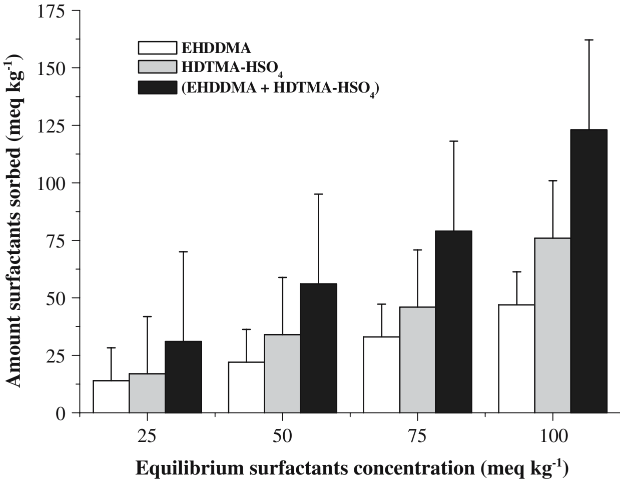

Fig. 3 Treatment of natural zeolite with different surfactants (EHDDMA and HDTMA-HSO$_4$ (meq kg^{-1})

be considered. According to Bowman et al. (1995), sorption of inorganic anions on cationic surfactant-modified zeolite has been attributed to the formation of a surface-anion complex. To sorb anions and form a complex, the modified surface must possess positively charged exchange sites. These sites are formed when positively charged surfactant head groups are presented to the surrounding solution in the form of a bilayer or patchy bilayer. The positively charged head groups are balanced by counterions, and the sorption or exchange of the other anionic constituents involves the replacement of weakly held counterions by more strongly held counterions. The effects of counterions on stabilizing surfactant micelle formation in solution follow the lyotropic series (Kalló 2001). Li et al. (1998) studied counterion effects on the sorption of cationic surfactant on natural zeolite and found that the HDTMA-Br and HDTMA-Cl formed complete bilayers on the zeolite, whereas HDTMA-HSO$_4$ showed less than full bilayer formation.

The efficiency of adsorbent towards the removal of chromium was also tested using untreated phase. Unmodified zeolite had no affinity for chromium (VI) species (Fig. 4). The effect of the counterion (HSO$_4^-$) on chromate sorption by HDTMA treated zeolite was examined (Figs. 5, 6). The charge of the counterion affects the coulombic interaction with the surfactant head group. There is an entropic advantage in binding

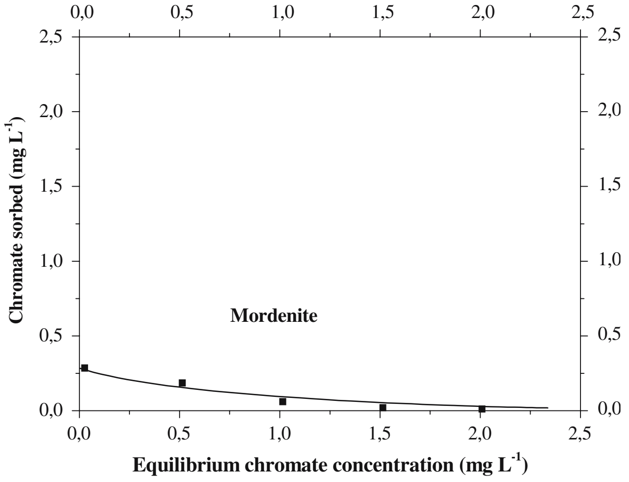

Fig. 4 Chromate sorption on the unmodified material, Mor. Agitation time: 120 min

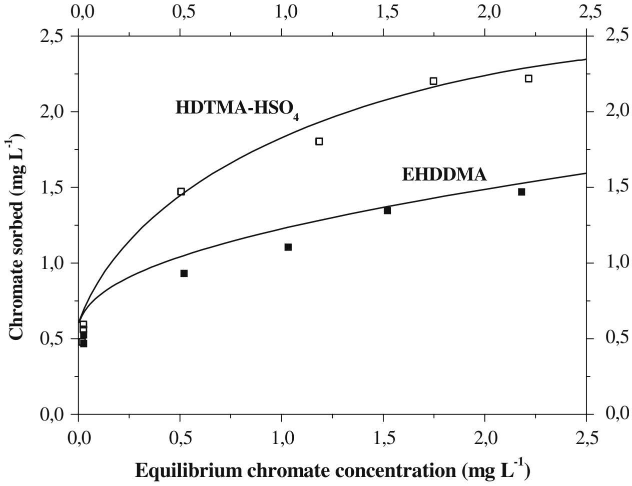

Fig. 5 Hexavalent chromium sorption on the surfactant-modified zeolite. Agitation time: 120 min

a single divalent ion rather than two univalent ions. Divalent anions also have a stronger coulombic interaction with the head group of cationic surfactants and preferentially replace monovalent counterions. This preference for divalent cations is confirmed by the observed strong sorption of chromate in this study as well as by the sorption of chromate, selenate, and sulfate on HDTMA-treated zeolite observed by Haggerty and Bowman (1994).

The percentage sorption of Cr (VI) increased with an increase in agitation time and attained equilibrium after 90 min (Fig. 6). The data indicated that the maximum percentage adsorption was 93% (HDTMA-HSO_4) and 67% (EHDDMA) for the initial chromium concentration of 2.5 mg L^{-1}.

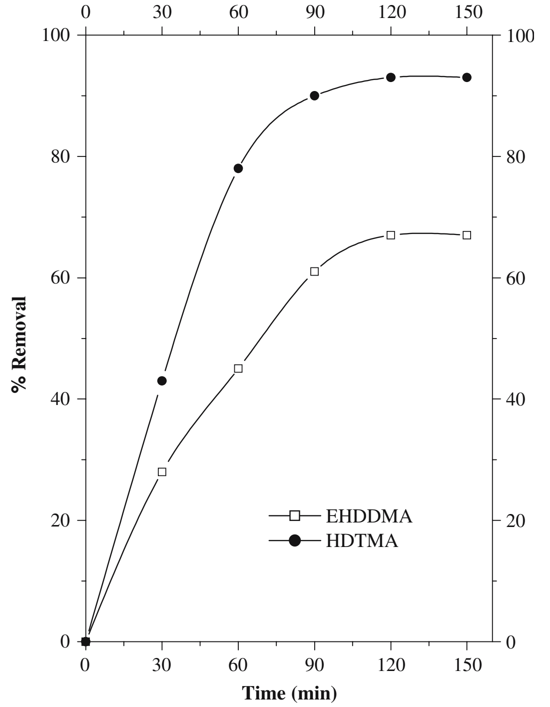

Fig. 6 Effect of agitation time on Cr (VI) removal (2.5 mg L^{-1})

Conclusion

Removal of hexavalent chromium by EHDDMA and HDTMA-HSO_4 cationic surfactants on mordenite zeolite was studied in the laboratory. A comparison with untreated phase indicates that surfactant-modified zeolite is more effective than the natural sample–Mor. While the natural zeolite had no affinity for the oxyanions, the HDTMA-modified zeolite showed significant removal of chromate from aqueous solution. The magnitude and stability of sorption of the surfactant on the mordenite and anion exchange were influenced by the counterion (e.g., HSO_4^-) of the surfactant. The results of the present experimental study showed that the counterion content is an important factor. The cationic surfactant is either exchanged or adsorbed by the zeolite. After the neutralization of the zeolite due to the exchange of the positively charged organic agent with cations in the zeolite, charge reversal of the zeolite may occur. The result is a net positive charge on its surface which results in the possibility of anion adsorption. Chromate sorption was strongly influenced by the HDTMA-zeolite, with chromate sorption maxima decreasing in the order HDTMA-HSO_4 > EHDDMA > Mor. Removal system based on untreated phase and EHDDMA was not found to be suitable due to its lower removal efficiency compared to HDTMA-HSO_4 surfactant. The experimental results, expressed as the percentage removal of hexavalent chromium, showed the chromium adsorption on HDTMA-modified zeolites exceeds the adsorption on EHDDMA-modified zeolites and untreated mordenite. HDTMA-HSO_4 treated zeolite showed the greatest chromate sorption (93%).

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