Regeneration of HDTMA-modified minerals after sorption with chromate anions

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Abstract

Surfactant-modified minerals have been widely used for the sorption of anionic and non-polar organic contaminants. This paper investigates the regeneration of various hexadecyltrimethylammoniun bromide (HDTMA)-modified natural minerals saturated with chromate anions using different solutions for the extraction of chromate that has been sorbed at optimum conditions. The examined minerals include HDTMA-modified zeolite (clinoptilolite), exfoliated vermiculite, bentonite and attapulgite (palygorskite). Deionized water and sodium chloride, potassium chloride and sodium cyanide solutions at different concentrations (0.1 – 3 M) were employed as chromate desorption solutions. The HDTMA-Cr(VI)-mineral type, the desorbing solution type and its concentration and the mineral-solution contact time are key parameters that affect the process. From our results it was deduced that regeneration and reuse of HDTMA- modified minerals saturated with chromate is feasible. Bentonite exhibited greater stability than the other minerals studied in adsorption/desorption processes, maintaining 73% of its initial adsorption capacity after 14 successive regeneration cycles. The regeneration performance of the examined minerals follows the order: Bentonite > Attapulgite > Zeolite > Vermiculite. Kinetic study revealed that desorption was faster than adsorption, while the pseudo-second-order equation was more simulated better the experimental data.

Keywords: chromate desorption; modified minerals; regeneration; desorption

1. Introduction

Natural zeolites and other crystalline aluminosilicate clay minerals are well-known for their cation exchange capacities [1-3]. However, the cationic surfactant-modified forms of these minerals exhibit significant affinity for anionic and organic contaminants due to their negatively charged surfaces [4-19]. Mineral modification with various cationic surfactants when the surfactant concentration is less than the critical micelle concentration (CMC) results in the formation of a monolayer coat. If surfactant concentration exceeds CMC, a second organic layer is retained to the first via hydrophobic interactions and Van Der Waals forces and a bilayer is then formed. A monolayer coat is efficient for neutral non-polar organic compounds sorption [14-15], while a bilayer model is required for the sorption of anionic groups, such as Cr(VI), As (V), Sb (V) [13,20-21].

The concept of materials regeneration after their modification and metal adsorption is of great importance for both environmental and economical reasons and is considered to be a key process in water treatment [21]. It makes metal recovery a feasible process and also allows adsorbent reuse in future applications [22-23]. Z. Li and R. Bowman (2001) attempted first to regenerate a HDTMA-modified zeolitic type saturated with chromates and perchloroethylene, separately, using sodium carbonate/sodium hydroxide and sodium dithionite solutions as desorption mediums [24]. Chutia et al. (2009), investigated the regeneration of HDTMA-modified natural mordenite and HDTMA-modified natural clinoptilolite after arsenate sorption with NaOH and HCl solutions and found that NaOH was more effective with As(V) desorbing up to 70% [21]. Additionally, Zeng et al. (2010), demonstrated that chromate-saturated HDTMA- clinoptilolite and -chabazite regeneration, with Na_2CO_3/NaOH

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solution, it is a quite effective process; obtaining maximum regeneration efficiency 90.6% for HDTMA-clinoptilolite [19].

It may also be noted that while the sorption ability of surfactant-modified minerals for chromates has been widely studied and validated, nevertheless only few research attempts have paid attention to the regeneration of the sorbents. This work attempts to examine the potential of regeneration of four different HDTMA-modified aluminosilicate minerals after their saturation with chromates. Moreover, their stability and reuse possibility is investigated after successive adsorption/desorption cycles using different desorption solutions. The parameters examined include HDTMA-Cr(VI)-mineral type, type and concentration of desorbing solution, desorption time of chromates from each mineral.

2. Materials and Methods

2.1. Materials

The natural zeolite (85% clinoptilolite) and bentonite used in this study were obtained from S&B Industrial Minerals S.A., exfoliated vermiculite from Mathios Refractories S.A. and attapulgite or palygorskite from Geoellas S.A. at Grevena. Samples of these materials were gently washed with deionized water to remove any impurity contents from their surface, ground, sieved (<180 μm), dried at a furnace at $80\ ^0C$ for at least 24h and stored in a desiccator until use. Minerals were then modified by the surfactant HDTMA-Br (99% purity) provided by Acros Organics Co without any extra pre-treatment to reduce the overall cost of the process. $K_2Cr_2O_7$ (>99.9% purity) that was used for the preparation of aqueous chromate solution and also $NaCl$ (>99.5% purity), KCl (>99.5% purity) and $NaCN$ (>95% purity) that were used for the preparation of chromate desorption mediums were all supplied by Merck. HNO_3 46% (>90.0% purity) and NaOH (>99.0% purity) used for pH adjustment were supplied by Sigma‑Aldrich and Carlo Erba, respectively.

2.2. Minerals characterization

Natural and modified minerals were characterized with X-ray diffraction (XRD), X-ray fluorescence (XRF), total organic carbon (TOC), Fourier transform infrared (FTIR), scanning electron microscopy (SEM-EDX) and electrokinetic zeta potential (ζ-potential) methods in order to verify the effectiveness of the modification process. The CEC of unmodified minerals was determined using the NH_4Ac method. Conventional Bragg–Brentano X-ray diffraction (XRD) technique gives important information about determination and evaluation of the crystalline phases of the examined materials. Samples in dust form were scanned and the respective patterns were recorded using a Siemens D5000 powder unit. X-ray fluorescence (XRF) - Wavelength Dispersive analysis was employed on a model ARL ADVANT XP to determine the chemical composition of the natural and modified minerals. TOC analysis was conducted in the solid samples of natural and organically modified minerals using a TOC analyzer (Shimadzu Model TOC-V_{CSH}). Fourier transform infrared (FTIR) spectroscopy with the ATR method and a PRO410-S revealed the characteristic peaks that are attributed to the CH_2 infrared adsorption bands. Scanning electron microscope (SEM) (FEI Quanta 200 model) shows morphology differences between natural and modified minerals. Finally, the integrated energy-dispersive X-ray (EDX) detector (EDX-Genesis 4000) gives a semi-quantitative analysis providing additional information on the elementary composition of examined samples before and after the modification stage. Moreover, electrokinetic ζ-potential measurements on suspensions of the employed samples were conducted with a zetasizer NanoZS of Malvern and the change of their surface charge was recorded. The samples preparation process for all methods is analytically described in a previous paper [25].

2.3. Modification process and Organo-minerals saturation with Cr(VI)

The HDTMA-minerals preparation and the optimization of the process is described in our previous work [25]. The main steps include: zeolite (5 g L^{-1}) was modified in a HDTMA solution at pH 9 and surfactant concentration equal to 1 g L^{-1}. Organo-vermiculite and -bentonite (5 g L^{-1}) were, similarly, prepared at pH 3 and HDTMA concentration equal to 6 and 2 g L^{-1}, respectively, while for attapulgite (5 g L^{-1}) the optimum pH was 8 and the HDTMA concentration 7 g L^{-1}.

The capability of HDTMA-modified minerals to remove chromates from aqueous solutions and the determination of optimal parameters was investigated stepwise in a previous paper [25]. Briefly, all

minerals employed were found to maximize chromate sorption at pH 4. In addition, a mineral concentration of 10 g L^{-1} proved to be the most efficient with respect to Cr(VI) removal.

2.4. Desorption solution and Contact time

Deionized water, sodium chloride, potassium chloride and sodium cyanide were evaluated in terms of their Cr(VI) desorption capability at the following concentrations (except deionised water): 0.1, 0.5, 1 and 3M by performing batch test. The most suitable effective desorption solution was selected for all the subsequent experimental runs. Stock solutions were prepared in 500 mL flasks by dissolving the appropriate quantity of each salt with deionized water. 0.5 g of each HDTMA and Cr(VI) (30 mg L^{-1})-saturated mineral was mixed with 50 mL of stock solution in 100 mL batch reactors and were agitated at 600 rpm for 24 h. Solutions were then filtered and filtrates were analyzed for their chromates content. The contact time affects the efficiency of the process. 5 g of each HDTMA- and Cr(VI)-saturated mineral was mixed with 500 mL of solution and in its appropriate concentration at the optimum concentration which corresponds to maximum Cr(VI) recovery. Then, batch reactors of 1 L were placed in continuous stirring at 600 rpm and at room temperature. Samples of 5 mL were taken at different time intervals during the period of 24 h, and after being centrifuged and diluted their Cr(VI) concentration was measured. The results were compared with existing kinetic models.

2.5. Minerals regeneration

The regeneration of the examined minerals was investigated in successive adsorption/desorption cycles using the optimum solution and concentration. More specifically, mineral-salt and mineral-Cr(VI) (50 mg L^{-1}) solutions of 10 g L^{-1} were placed in batch reactors at 600 rpm and room temperature for 24 h. Then, the samples were filtered, and Cr(VI) in the filtrate was measured. The pH of Cr(VI) adsorption was adjusted with proper dropwise addition of NaOH and HNO$_3$ at pH = 4. For the desorption cycle, the chromate saturated minerals and salt solution were again placed in batch reactors under constant agitation at 600 rpm and at room temperature for a period of 24 h and after filtration of the sample the Cr(VI) content of the filtrate was measured. Between adsorption and desorption, the samples were gently washed and stored in a desiccator for loss of their moisture and then their mass was measured before use in the next cycle.

3. Results and Discussion

3.1. Mineral characterization

CEC (natural phase), TOC and ζ-potential (natural and modified phases) measurements of the four minerals employed in this study was reported previously [25]. Table 1 presents XRF analysis for the natural and organically modified phases of zeolite, vermiculite, bentonite and attapulgite. Bromine detection after modification (Table 1b) which is also accompanied by a lower % w/w of exchangeable ions, is indicative of HDTMA-Br presence and validate the process. The Br content of the modified minerals increases in the following order: % Br zeolite < % Br bentonite < % Br vermiculite < % Br attapulgite and is consistent with the initial required HDTMA quantity for maximizing Cr(VI) adsorption. The latter is also in agreement with TOC analysis [25].

Table 1a XRF analysis for natural minerals (% w/w)

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	Cr_2O_3	BaO	K_2O	SO_3	P_2O_5	NiO	MnO
Zeolite	71.3	12.1	0.14	0.89	0.68	3.38	0.28	-	-	3.66	-	-	-	-
Vermiculite	45.3	15.4	1.22	5.47	27.4	1.31	1.6	0.35	0.2	4.9	-	-	-	-
Bentonite	61.6	19.4	0.86	5.08	3.58	4.42	3.78	-	-	0.71	1.37	0.172	-	-
Attapulgite	58.3	6.27	0.33	12.9	13.3	3.72	-	0.42	-	0.32	-	-	0.372	0.13

Table 1b XRF analysis for HDTMA-modified minerals (% w/w)

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	Cr_2O_3	BaO	K_2O	SO_3	P_2O_5	NiO	MnO	Br
Zeolite	68.5	11.8	0.102	0.767	0.624	3.32	-	-	-	3.51	-	-	-	-	0.858
Vermiculite	21.6	6.15	0.967	5.87	9.53	-	-	0.295	0.218	2.10	-	-	-	-	10.5
Bentonite	59.0	18.0	0.861	5.64	2.99	0.274	-	-	-	0.592	0.448	0.116	-	-	1.0
Attapulgite	33.9	2.54	0.202	9.92	0.792	2.26	-	0.293	-	0.218	-	-	0.314	-	26.8

XRD analysis was conducted for the three phases (natural, HDTMA-modified before and after Cr(VI) sorption) of zeolite and bentonite (Fig. 1 a and b). All the recorded intensities for natural phases are in agreement with the respective ones of another study [28]. As observed in the XRD pattern of HDTMA-zeolite only a lessening but not an expansion of the basal d (001) spacings takes place (Table 2). The first one is attributed to HDTMA sorption on zeolite surface via ion-exchange [9,21] and the second one consists an indication that hydrophilic parts of organic molecules cannot penetrate into the interlayer of zeolite and shows that zeolite is a non-swelling mineral. The crystalline structure of zeolite remains inviolated after both the modification and the Cr(VI) adsorption stage. On the other hand, a gradual expansion of d (001) spacing from 12.41 to 18.91 and finally to 19.38 Å is observed for the three phases of bentonite (Fig. 1b). The latter expansion is indicative of the further intercalation - beyond the existing of organic molecules - of chromates that have adsorbed to the second layer of HDTMA. Similar results are reported by Krishna et al. [26] and Majdan et al. [27] for the case of Cr(VI) sorption into bentonite. In addition, Plachá et al. [14] found similar expansion of basal d-spacings of HDTMA-vermiculite after sorption of naphthalene. It is expected that swelling materials will appear to have greater stability in terms of regeneration and reuse providing that the HDTMA bilayer is maintained stable during adsorption/desorption processes. SEM typical images for zeolite have already been presented [25]. Fig. 2a depicts the typical arrangement of a crystalline silicate mineral and its lamellar microcrystals. Modification and Cr(VI) sorption stages (Fig. 2b and c) do not seem to cause distinct changes in the vermiculite morphology apart from a potential loose of its lamellar structure [29]. The morphology of the natural bentonite surface (Fig. 2d), appears as solid non-uniform granules. However, several morphological changes are noticed after modification (Fig. 2e), wherein small particles form agglomerates and the grains tend to obtain a relatively flat and aggregated morphology [30]. Moreover, chromates sorption makes bentonite surface more compact, rough and porous with a tendency to form sponge- or coral-like agglomerates (Fig. 2f) [31-33]. The SEM microphotographs of attapulgite reveal loosening of its solid and homogeneous structure; potentially due to HDTMA covering (Fig. 2g and 2h) [34-35]. Also, after chromate sorption (Fig. 2i) its fibrous crystals become more distinct.
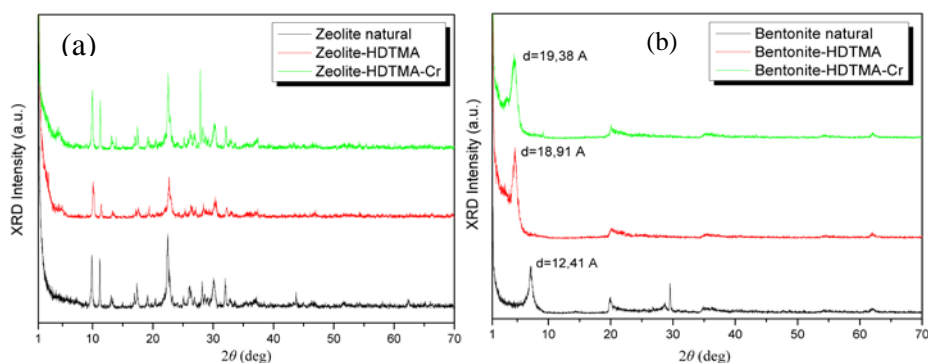

Fig. 1 X-ray diffraction patterns of three phases of (a) zeolite and (b) bentonite

Table 2 Typical XRD peaks for the three different phases of zeolite

h k l	2θ	d (Å)		
		natural zeolite	HDTMA-zeolite	HDTMA-Cr-zeolite
0 2 0	9.887	8.93	8.86	8.96
2 0 0	11.221	7.87	7.84	7.92
2 0-1	13.081	6.76	6.74	6.77
1 1 1	17.358	5.10	5.08	5.10
3 3 0	22.467	3.95	3.94	3.96
2 2-2	26.078	3.41	3.40	3.41
4 0-2	26.310	3.38	3.37	3.38
0 0 2	26.874	3.31	3.30	3.31
4 2-2	28.167	3.16	3.15	3.16
1 5 1	30.075	2.97	2.96	2.96
6 2-1	32.032	2.79	2.78	2.79
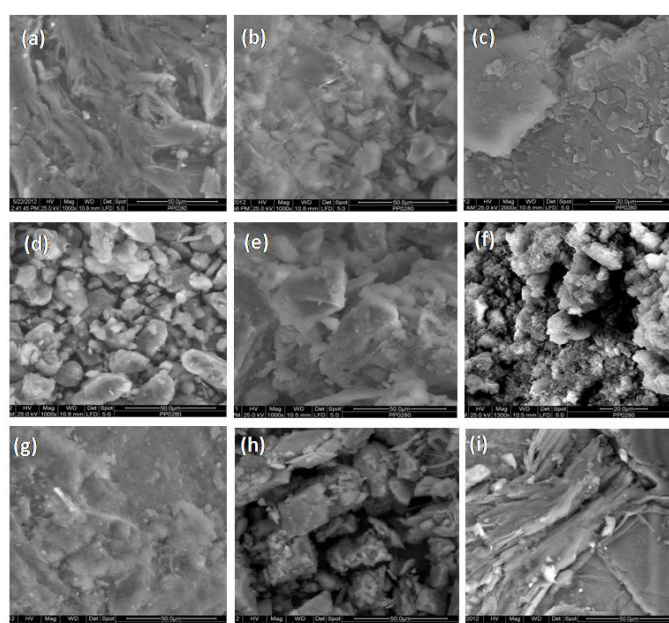
Fig. 2 SEM images of (a) natural vermiculite, (b) HDTMA-vermiculite, (c) HDTMA-Cr(VI)-vermiculite, (d) natural bentonite, (e) HDTMA-bentonite, (f) HDTMA-Cr(VI)-bentonite, (g) natural attapulgite, (h) HDTMA-attapulgite and (i) HDTMA-Cr(VI)-attapulgite

3.2. Desorption media evaluation

Deionized water proved to be not a not efficient Cr(VI) desorption medium, since the chromate desorption was lower to 10%. Similarly results have been reported by Li (1998) for Cr(VI) desorption from HDTMA-modified zeolite [36]. When NaCN is used significant desorption results were pointed out only for the concentration of 0.1M (Fig. 3). An increase of NaCN solution concentration caused a dramatically decrease of Cr(VI) desorption. This can be attributed to a non efficient exchange between cyanides and chromates, possibly due to sodium dichromate precipitation, or complex formation, on the surface, channels or cavities of the minerals, which prevent the completion of the process [37]. In Fig. 4, Cr(VI) desorption from the employed minerals is plotted as a function of NaCl and KCl solution concentration. Significant chromates desorption is achieved for both solutions, which also increases with the increase of salt concentration. This is due to the competition between chromates and chlorides for the available exchange sites. In addition, NaCl is more effective for bentonite (93-96% desorption), while KCl for attapulgite (81-93% desorption). A potential explanation for this is that,

Cr(VI) desorption occurs simultaneously to Cl⁻ adsorption on the second layer of organic molecules and may be a reverse process of chromates sorption process [19,24]. NaCl solution results in higher Cr(VI) desorption than KCl (apart from the case of attapulgite), while similar results were obtained for concentrations of 1 and 3M.
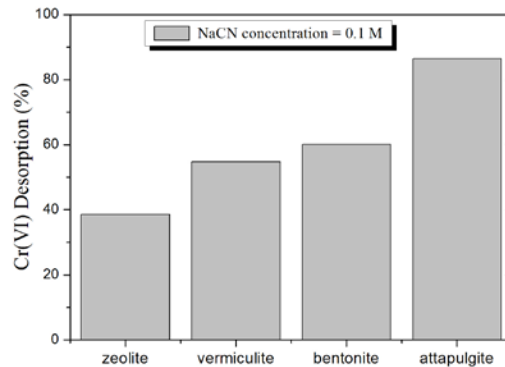

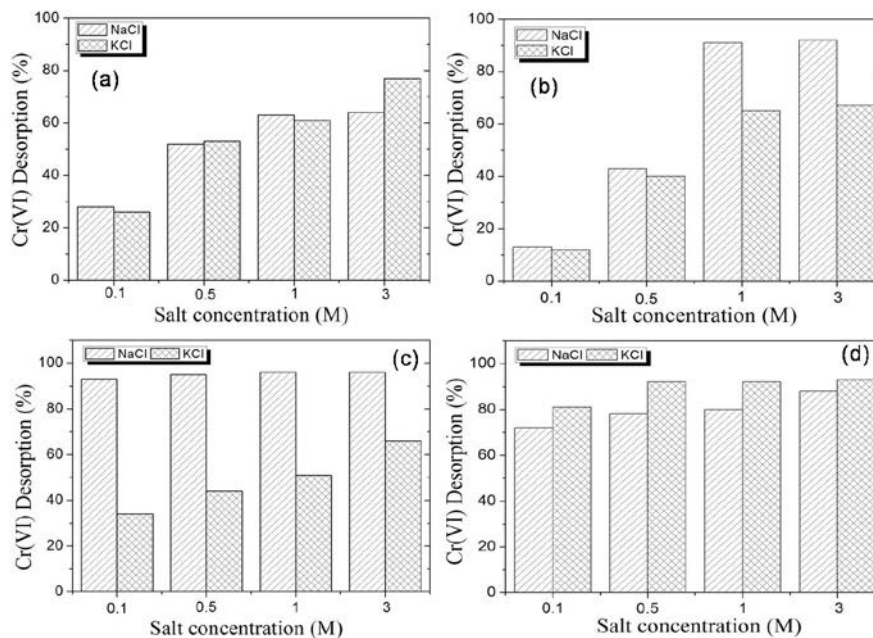**Fig. 3** Cr(VI) desorption at different concentrations of NaCN

Fig. 4 Cr(VI) desorption from (a) zeolite, (b) vermiculite, (c) bentonite and (d) attapulgite for several NaCl and KCl concentrations

3.3. Kinetics of Cr(VI) desorption

Cr(VI) desorption kinetics were studied for zeolite, vermiculite, bentonite and attapulgite. Increase of chromates (Fig. 5) is observed with the increase of contact time with higher rates at the initial stages of the process (i.e. $t = 0-10$ min). Experimental data were simulated by pseudo-first-order, pseudo-second-order and Elovich non-linear equations. Their corresponding equations are described previously [25]. The experimental data and the simulated results are given in Fig. 6, while Table 3 summarizes the predicted kinetic parameters. Pseudo-second-order model describes better the experimental data which is also supported by the comparison of the desorption equilibrium capacities q_{ed} (mg g^{-1}) obtained experimentally with the predicted ones by the model q_{2d} and by comparing the correlation coefficients R^2 for each model. The values of q_{ed}, k_{2d} and t_{eq} follow the order: .

$$q_{ed} \text{ zeolite} > q_{ed} \text{ vermiculite} > q_{ed} \text{ bentonite} > q_{ed} \text{ attapulgite}$$
$$k_{2d} \text{ attapulgite} > k_{2d} \text{ zeolite} > k_{2d} \text{ bentonite} > k_{2d} \text{ vermiculite}$$
$$t_{eq} \text{ vermiculite} > t_{eq} \text{ bentonite} > t_{eq} \text{ zeolite} > t_{eq} \text{ attapulgite}$$

6

The order of desorption rates k_{2d} for the examined minerals indicates that chromates desorption is faster from attapulgite and zeolite (non-swelling minerals) that the respective ones obtained for vermiculite and bentonite. The latter support the hypothesis that chromates adsorption on intercalating organic layers is more stable than the respective one that takes place on the mineral surface.

It is worth noting that the pseudo-second-order kinetic model was found to fits well the experimental data in several other cases, including Cd(II) desorption from attapulgite and sepiolite [38] and Pb(II) desorption from vermicompost and other adsorbents [39].

Table 3 Kinetic parameters for Cr(VI) desorption from modified minerals

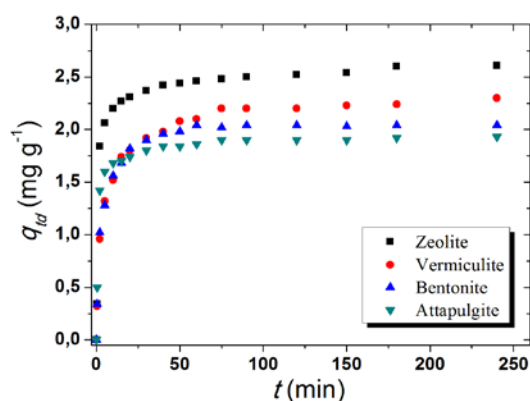| Mineral	Exper.	Pseudo-first-order			Pseudo-second-order			Elovich		
	$q_{ed,\,exp}$(mg g^{-1})	q_{1d}(mg g^{-1})	k_{1d}(min^{-1})	R^2	q_{2d}(mg g^{-1})	k_{2d}(g mg^{-1}min^{-1})	R^2	a_d(mg g^{-1}min^{-1})	β'(g mg^{-1})	R^2
Zeolite	2.66	2.43	0.5311	0.9615	2.54	0.2932	0.9701	31.737	3.611	0.8743
Vermiculite	2.41	2.11	0.1712	0.9386	2.24	0.1206	0.9875	3.247	3.112	0.9729
Bentonite	2.12	1.96	0.2282	0.9569	2.07	0.1806	0.9933	6.430	3.782	0.9385
Attapulgite	2.0	1.83	0.6660	0.9725	1.90	0.5180	0.9859	83.093	5.546	0.9018

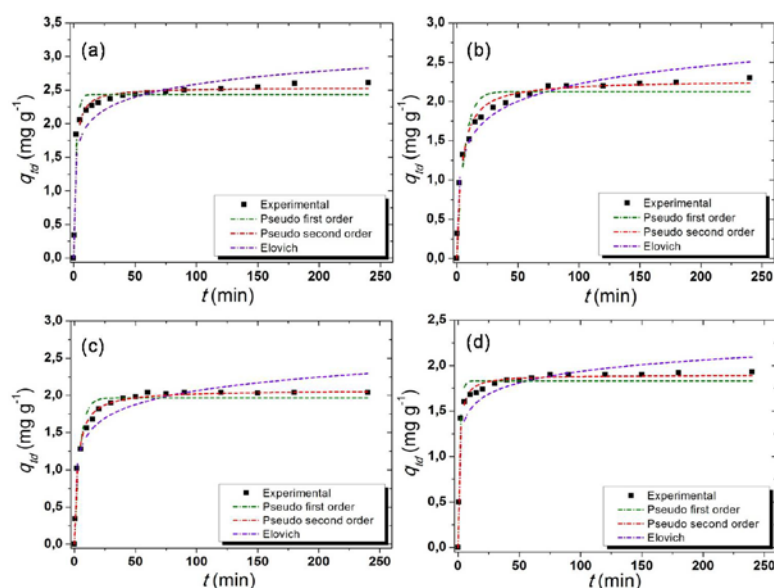**Fig. 5** Effect of contact time on the amount of Cr(VI) desorbed from the minerals

Fig. 6 Kinetic data, pseudo-first-order, pseudo-second-order and Elovich models for (a) zeolite, (b) vermiculite, (c) bentonite and (d) attapulgite.

7

3.4. Regeneration cycles

The adsorption capacity of the regenerated minerals was conducted in order to evaluate their stability and operating performance after successive adsorption/desorption cycles of Cr(VI) (Fig. 7). 1M NaCl was used as the desorption medium. It was observed that the adsorption capacity of vermiculite dramatically decreased within only three cycles. This could be due to the loosening and breakdown of its HDTMA bilayer. Zeolite exhibits better behaviour than vermiculite, but its sorption capacity becomes negligible after 8 cycles. Bentonite and attapulgite demonstrate significant adsorption/desorption capacity and maintain their organic structure intact for more than fourteen and twelve cycles, respectively. After 14 cycles, bentonite maintains 73% of its initial adsorption capacity, while after 12 cycles attapulgite maintains 69% of its initial adsorption capacity. It may also be noted that during the first three adsorption/desorption cycles the use of NaCl enhanced the percentage of Cr(VI) adsorbed on bentonite and attapulgite, which is in agreement with previous studies [44]. Potential explanation include: The removal of specific anionic groups, such as carbonates and sulphates, from the channels and the cavities of the minerals might allow more chromate anions to reach the exchange sites. In addition, some sodium ions of NaCl solution are potentially adsorbed on non-modified sites of the minerals during the initial desorption cycles and remain there even after mineral washing of the minerals. As a consequence, they form inner sphere complexes with chromates during the next adsorption process and thus increase the overall removal of Cr(VI) [23].
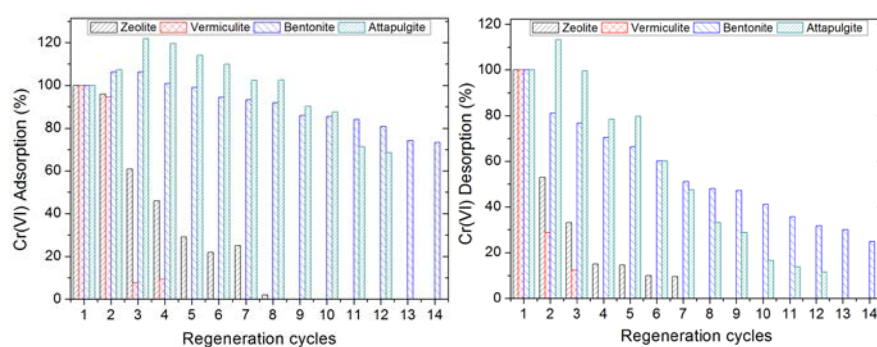

Fig. 7 Percentage (%) of Cr(VI) (a) adsorbed and (b) desorbed at successive regeneration cycles

3. Conclusions

The results of this study showed that regeneration and reuse of HDTMA-modified minerals is a feasible process using suitable desorption solutions. NaCl was the most effective medium resulting in high desorption efficiencies (~96%). Cr(VI) desorption kinetics reveal that the pseudo-second-order model fitted better the experimental data than pseudo-first-order and Elovich equations. Evaluating the whole regeneration process of the HDTMA- chromate saturated minerals employed, it is concluded that bentonite exhibits the highest stability since after fourteen cycles of consecutive use the adsorption capacity is 73% of its initial capacity. The regeneration performance of the examined minerals decreases following the order: Bentonite > Attapulgite > Zeolite > Vermiculite.

References

1. Rida, K., Bouraoui, S., Hadnine, S.: Adsorption of methylene blue from aqueous solution by kaolin and zeolite, Appl. Clay Sci. 83-84, 99-105 (2013)
2. Nezamzadeh-Ejhieh, A., Mirzaeyan, E.: Hexadecylpyridinium surfactant modified zeolite A as an active component of a polymeric membrane sulfite selective electrode, Mat. Sci. Eng. C 33(8), 4751-4758 (2013)
3. Gómez-Hortigüela, L., Pinar, A.B., Pérez-Pariente, J., Sani T., Chebude, Y., Díaz, I.: Ion-exchange in natural zeolite stilbite and significance in defluoridation ability, Microporous Mesoporous Mater. 193, 93-102 (2014)
4. Figueiredo, H., Quintelas, C.: Tailored zeolites for the removal of metal oxyanions: Overcoming intrinsic limitations of zeolites, J. Hazard. Mater. 274, 287-299 (2014)

5. Salgado-Gómez, N., Macedo-Miranda, M.G., Olguín, M.T.: Chromium VI adsorption from sodium chromate and potassium dichromate aqueous systems by hexadecyltrimethylammonium-modified zeolite-rich tuff, Appl. Clay Sci. 95, 197-204 (2014)
6. Vidal, C.B., Raulino, G.S.C., Barros, A.L., Lima, A.C.A., Ribeiro, J.P., Pires, M.J.R., Nascimento, R.F.: BTEX removal from aqueous solutions by HDTMA-modified Yzeolite, J. Environ. Manage. 112, 178–185 (2012)
7. Zhu, X., Han, B.: Adsorption behavior of chromium (VI) on the HDTMA-modified-zeolite, J. Food Agr. Env. 11(3-4), 2488-2492 (2013)
8. Bajda, T., Kłapyta, Z.: Adsorption of chromate from aqueous solutions by HDTMA-modified clinoptilolite, glauconite and montmorillonite, Appl. Clay Sci., In press (2013)
9. Leyva-Ramos, R., Jacobo-Azuara, A., Diaz-Flores, P.E., Guerrero-Coronado, R.M., Mendoza-Barron, J., Berber-Mendoza, M.S.: Adsorption of chromium(VI) from an aqueous solution on a surfactant-modified zeolite, Colloids Surf. A330, 35–41 (2008)
10. Yusof, A.M., Malek, N.A.: Removal of Cr(VI) and As(V) from aqueous solutions by HDTMA-modified zeolite Y, J. Hazard. Mater. 162, 1019–1024 (2009)
11. Noroozifar, M., Khorasani-Motlagh, M., Gorgij, M.N., Naderpour, H.R.: Adsorption behavior of Cr(VI) on modified natural zeolite by a new bolaform N,N,N,N´,N´,N´-hexamethyl-1,9-nonanediammonium dibromide reagent, J. Hazard. Mater. 155(3), 566–571 (2008)
12. Warchoł, J., Misaelides, P.,Petrus, R., Zamboulis, D.: Preparation and application of organo-modified zeolitic material in the removal of chromates and iodides, J. Hazard. Mater. B137, 1410–1416 (2006)
13. Wingenfelder, U., Furrer, G., Schulin, R.: Sorption of antimonate by HDTMAmodified zeolite, Microporous Mesoporous Mater. 95, 265–271 (2006)
14. Plachá, D., Martynkova, G.S., Rummeli, M.H.: Preparation of organovermiculites using HDTMA: structure and sorptive properties using naphthalene, J. Colloid Interface Sci. 327, 341–347 (2008)
15. Huang, Y., Ma, X., Liang, G., Yan, H.: Adsorption of phenol with modified rectorite from aqueous solution, Chem. Eng. J. 141, 1–8 (2008)
16. Chen, H., Zhao, J.: Adsorption study for removal of Congo red anionic dye using organo-attapulgite, Adsorption 15, 381–389 (2009)
17. Erdem, B., Ozcan, A.S., Ozcan, A.: Preparation of HDTMA-bentonite:characterization studies and its adsorption behavior toward dibenzofuran, Surf. Interface Anal. 42, 1351–1356 (2010)
18. Tabak, A., Baltas, N., Afsin, B., Emirik, M., Caglar, B., Eren, E.: Adsorption of reactive red 120 from aqueous solutions by cetylpyridinium–bentonite, J. Chem. Technol. Biotechnol. 85, 1199–1207 (2010)
19. Zeng, Y., Woo, H., Lee, G., Park, J.: Removal of chromate from water using surfactant modified Pohang clinoptilolite and Haruna chabazite, Desalination 257, 102‑109 (2010)
20. Li, Z., Willms, C., Roy, S.,Bowman, R.S.: Desorption of hexadecyltrimethylammonium from charged mineral surfaces, Environ. Geosci. 10 (1), 37-45 (2003)
21. Chutia, P., Kato, S., Kojima, T., Satokawa, S.: Adsorption of As(V) on surfactantmodified natural zeolites, J. Hazard. Mater. 162, 204–211 (2009)
22. Gedik, K., Imamoglu, I.: Removal of cadmium from aqueous solutions using clinoptilolite: Influence of pretreatment and regeneration, J. Hazard. Mater. 155(1-2), 385-392 (2008)
23. Katsou, E., Malamis, S.,Tzanoudaki, M., Haralambous, K.J., Loizidou, M.: Regeneration of natural zeolite polluted by lead and zinc in wastewater treatment systems, J. Hazard. Mater. 189(3), 773-786 (2011)
24. Li, Z., Bowman, R.S.: Regeneration of surfactant‑modified zeolite after saturation with chromate and perchloroethylene, Water Res. 35(1), 322‑326 (2001)
25. Thanos, A.G., Katsou, E., Malamis, S., Psarras, K., Pavlatou, E.A., Haralambous, K.J.: Evaluation of modified mineral performance for chromate sorption from aqueous solutions, Chem. Eng. J. 211, 77‑78 (2012)
26. Krishna, B.S., Murty, D.S.R., Prakash, B.S.J.: Surfactant-modified clay as adsorbent for chromate, Appl. Clay Sci. 20, 65-71 (2011)
27. Majdan, M., Maryuk, O., Pikus, S., Olszewska, E., Kwiatkowski, R., Skrzypek, H.: Equilibrium, FTIR, scanning electron microscopy and small wide angle X-ray scattering studies of chromates adsorption on modified bentonite, J. Mol. Struct. 791, 203-211 (2005)
28. Katsou, E., Malamis, S., Haralambous, K.J., Loizidou, M.: Use of ultrafiltration membranes and aluminosilicate minerals for nickel removal from industrial wastewater, J. Membr. Sci. 360(1‑2), 234‑249 (2010)

29. Yu, X., Wei, C., Ke, L., Hu, Y., Xie, X., Wu, H.: Development of organovermiculite-based adsorbent for removing anionic dye from aqueous solution, J. Hazard. Mater. 180(1-3), 499-507 (2010)

30. He, H., Frost, R.L., Bostrom, T., Yuan, P., Duong, L., Yang, D., Xi, Y., Kloprogge, J.T.: Changes in the morphology of organoclays with $HDTMA^+$ surfactant loading, Appl. Clay Sci. 31 (3-4), 262-271 (2006)

31. Altunlu, M., Yapar, S.: Effect of OH^-/Al^{3+} and Al^{3+}/clay ratios on the adsorption properties of Al-pillared bentonites, Colloids Surf., A 306 (1-3 SPEC. ISS.), 88-94 (2007)

32. Fatimah, I., Huda, T.: Preparation of cetyltrimethylammonium intercalated Indonesian montmorillonite for adsorption of toluene, Appl. Clay Sci. 74, 115-120 (2013)

33. Senturk, H.B., Ozdes, D., Gundogdu, A., Duran, C., Soylak, M.: Removal of phenol from aqueous solutions by adsorption onto organomodified Tirebolu bentonite: Equilibrium, kinetic and thermodynamic study, J. Hazard. Mater. 172(1), 353-362 (2009)

34. Yuan, X., Li, C., Guan, G., Liu, X., Xiao, Y., Zhang, D.: Synthesis and characterization of poly(ethylene terephthalate)/attapulgite nanocomposites, J. Appl. Polymer Sci. 103(2), 1279–1286 (2007)

35. Xi, Y., Mallavarapu, M., Naidu, R.: Adsorption of the herbicide 2,4-D on organo-palygorskite, Appl. Clay Sci. 49(3), 255-261 (2010)

36. Li, Z. : Chromate extraction from surfactant-modified zeolite surfaces, J. Environ. Qual. 27, 240–242 (1998)

37. Katsou, E.: Wastewater treatment with the use of membranes, Ph.D., NTUA, Greece, Athens (2011).

38. Shirvani, M., Shariatmadari, H., Kalbasi, M.: Kinetics of cadmium desorption from fibrous silicate clay minerals: Influence of organic ligands and aging, Appl. Clay Sci. 37(1-2), 175-184 (2007)

39. Duarte Zaragoza, V.M., Carrillo, R., Gutierrez Castorena, C.M.: Lead sorption-desorption from organic residues, Environ. Technol. 32(4), 353-361 (2011)

40. Li, L.Y., Chen, M., Grace, J.R., Tazaki, K., Shiraki, K., Asada, R., Watanabe, H.: Remediation of acid rock drainage by regenerable natural clinoptilolite, Water Air Soil Pollut. 180, 11–27 (2007)