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ORIGINAL PAPER

Removal of chromate from wastewater using amine-based-surfactant-modified clinoptilolite

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Abstract This study presents the results of chromate adsorption upon organically modified clinoptilolite obtained by the treatment of Bigadic clinoptilolite with surfactants in primary amine structure, namely 1-dodecylamine, 1-hexadecylamine and oleylamine. Natural and organo-clinoptilolites were characterized by X-ray diffraction, thermal gravimetry and Fourier transform infrared spectrometry which proved the integration of amine groups followed by the order oleylamine > 1-hexadecylamine > 1-dodecylamine. Organo-clinoptilolites were tested for their efficacy in chromate removal under base case conditions which implied 100 ppm initial concentration, pH 4.0, 10 g l^{-1} adsorbent dose and at 298 K. Results showed that amine loading induced chromate removal reaching up to 90 % for oleylamine-modified clinoptilolite. Experimentation was continued to determine the effects of pH, adsorbent dosage and initial concentration on chromate adsorption. Accordingly, maximum removal of 94.0 % was attained with 14 g l^{-1} of oleylamine-modified clinoptilolite, from Cr(VI) solution of 100 ppm initially at pH 3.0. Langmuir isotherm described the adsorption of chromate on oleylamine-modified clinoptilolite with 96.4 % consistency. Maximum theoretical uptake capacity was calculated as 6.72 mg g^{-1}. Kinetic data were consistent with pseudo-second-order model with the controlling steps being film and pore diffusions.

Keywords Clinoptilolite · Primary amine surfactant · Chromate · Adsorption

Introduction

Chromium (Cr) is introduced to environment through effluents of electroplating, leather tanning, corrosion control, dyeing and metal cleaning industries with an average concentration of 50 mg l^{-1} (Warchol et al. 2006). In such aqueous systems, Cr occurs in Cr(III) and Cr(VI) forms of which the latter is highly toxic and mobile (Yang 2003; Aydin and Deveci Aksoy 2009). Cr(VI) pollution is a persistent environmental problem in heavily industrialized regions among the world. Since the maximum allowable total chromium concentration in potable waters is 0.5 mg l^{-1}, intense methods and processes are required for the limitation of Cr(VI) and Cr(III) concentrations in industrial effluents (Guertin et al. 2004).

Precipitation, solvent extraction, ion exchange, membrane separation and adsorption are the mostly involved methods for elimination of toxic metals from wastewater. However, recent literature addresses adsorption as a versatile and effective method over its alternatives due to a number of advantages such as the ease of operation and availability of low-cost adsorbents with high efficiency (Kurniawan et al. 2006; Owlad et al. 2009; Gupta et al. 2010). The metal binding capacities of several natural or synthetic adsorbents, e.g., activated carbons, clays, biomass, agricultural products and industrial wastes, have been investigated previously (Gupta et al. 2015; Kurniawan et al. 2006; Yang 2003). Among these materials, natural zeolites, which can be briefly described as crystalline microporous aluminosilicates, constitute a major group with unique physicochemical properties (Mozgawa and Bajda 2005; Leyva-Ramos et al. 2008).

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The tetrahedral framework of zeolites, composed of SiO_4 and AlO_4, possesses a net negative structural charge that promotes the exchange of cations while hindering the adsorption of anions and organic pollutants (Zeng et al. 2010; Asgari et al. 2013; Xie et al. 2013). However, the negative charge can be tuned by surface modification with either strong acids or with long-chain organic cations such as surfactants. Such surface treatments not only enhance the potential for anion exchange, but also modify the charge, composition, texture and structure, significantly (Vujakovic et al. 2000, 2003; Wang and Peng 2010).

Surfactant-modified zeolites (SMZs) have been suggested for remediation of wastewaters polluted with several organic pollutants, such as phenolic compounds (Lin and Juang 2009), dyes (Xie et al. 2013) and heavy metal ions (Wang and Peng 2010). The interaction between clinoptilolite surface and the surfactant relies on sorption phenomena. Three-dimensional framework of the clinoptilolite holds the high molecular organic matters like surfactants mainly on their outer surface (Bowman et al. 1995). At or below the critical micelle concentration (CMC), the amine head group of the surfactant is strongly bound with hydronium ions on the external surface via Coulombic forces and thus formation of a monolayer or hemimicelle occurs. On the other hand, as surfactant loads beyond CMC are provided, hydrophobic tails of surfactant molecules are oriented to form bilayer or admicelle structure (Vujakovic et al. 2003; Wang and Peng 2010; Yariv and Cross 2002). The excess positive charge accumulated on the clinoptilolite surface improves the affinity for inorganic anionic pollutants, such as chromate ions, through the mechanism of replacement of counter ions (Xie et al. 2013) (Fig. 1).

Surfactant modification has been previously demonstrated as an effective method for enhancing the Cr(VI) uptake capacity of a variety of natural zeolites (Table 1). Multitude of these studies involve quaternary ammonium salts, most frequently, HDTMA-Br, which interact with the exchangeable cations (Na and Ca) on the surface through hydrogen bonding. The advancement in uptake capacity ranged between threefold and 20-fold depending on the compositional and textural properties of the raw material and more importantly, on the extent of surfactant loading (Leyva-Ramos et al. 2008; Zeng et al. 2010; Bajda and Klapyta 2013). An alternative modification route involving primary amine surfactants was proposed by Vujakovic et al. (2000, 2003, 2004) who pretreated zeolites with strong acidic or basic agents to form a stable surface coverage and to obtain strong sites for anion precipitation. Since the surface precipitation is dominant mechanism for Cr(VI) adsorption, modification of strong acid-treated clinoptilolites with primary amine-based surfactants is an appropriate method to prepare high-performance Cr(VI) adsorbent (Vujakovic et al. 2003).

Briefly, the aim of this study was to investigate the Cr(VI) adsorption performance of surfactant-modified Bigadic clinoptilolite. Amine-based surfactants, namely oleylamine, dodecylamine and hexadecylamine, were involved so as to compare the effect of carbon content on adsorption. Optimum conditions were also investigated for batch experiments, namely pH, adsorbent dosage and contact time. Adsorption was also characterized by using Langmuir, Freundlich and Dubinin–Radushkevich isotherm models. The research work was conducted during

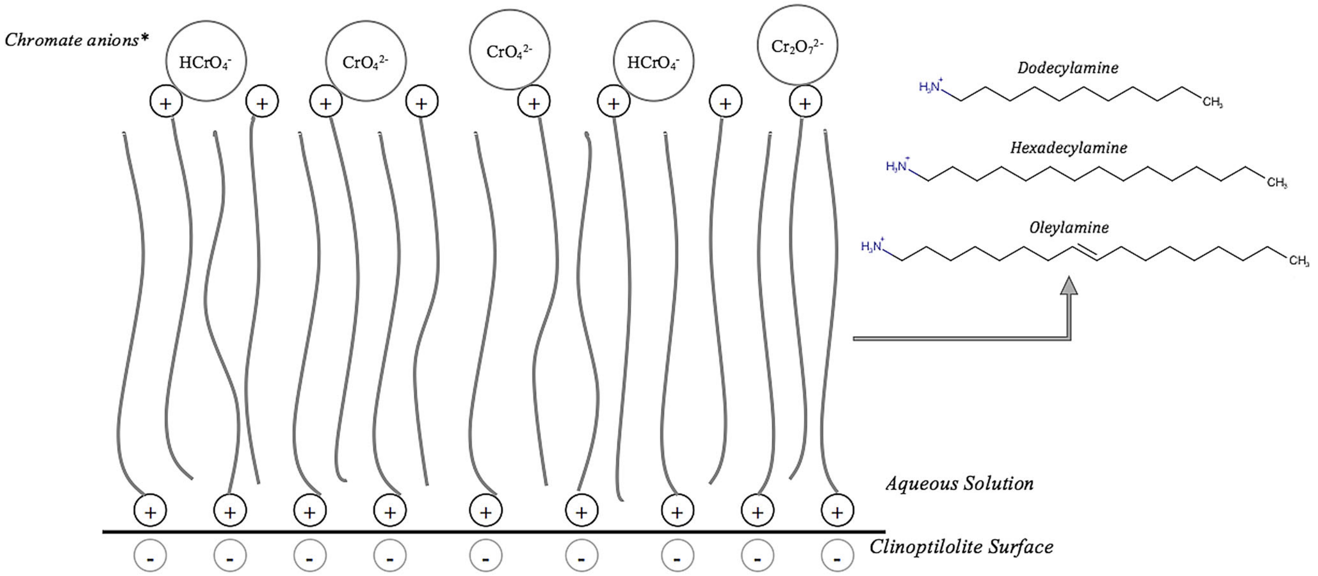

Fig. 1 Schematic diagram of bilayer formation on zeolite surface and adsorption of Cr(VI) anions. *The presence and prevalence of anionic forms depend upon pH

Table 1 Cr(VI) adsorption capacities on different organo-modified zeolite types

Adsorbent	Modification agent[a]	ECEC (mmol kg^{-1})	Maximum Cr(VI) uptake capacity (mg g^{-1})	References
Clinoptilolite	Oleylamine	187	8.32	Vujakovic et al. (2000)
Zeolite	HDTMA-Br	200	0.68	Li and Bowman (2001)
Zeolite	ODA	n.d.	64.93	Chmielewska (2003)
Heu-type zeolite	HDTMA-Br	n.d.	2.18	Warchol et al. (2006)
Heu-type zeolite	ODTMA-Br	n.d.	2.27	Warchol et al. (2006)
Clinoptilolite	HDTMA-Br	n.d.	6.50	Perez Cordoves et al. (2008)
Zeolite	PHMG	n.d.	3.49	Misaelides et al. (2008)
Zeolite	HDTMA-Br	178	5.07	Leyva-Ramos et al. (2008)
Natrolite	HMNA-Br$_2$	n.d.	2.32	Noroozifar et al. (2008)
FAU-type zeolite	CPB	n.d.	1.92	Covarrubias et al. (2008)
Zeolite	HDTMA-Br	190	0.32	Li and Hong (2009)
Clinoptilolite	HDTMA-Br	n.d.	3.55	Zeng et al. (2010)
Zeolite	HDTMA-Br	n.d.	4.40	Asgari et al. (2013)
Clinoptilolite	HDTMA-Br	160	10.4	Bajda and Klapyta (2013)

[a] ODA, octadecylammonium acetate; ODTMA-Br, octadecyltrimethylammonium bromide; PHMG, polyhexamethylene-guanidine; HMNA-Br$_2$, *N*,*N*,*N*,*N*′,*N*′,*N*′-hexamethyl-1,9-nonanediammonium dibromide; CPB, *N*-cetylpyridinium bromide

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Materials and methods

Natural zeolite obtained from Bigadic region of Turkey was ground and wet classified to average particle diameter of 0.425–0.6 mm. Clinoptilolite samples were washed with distilled water for a period of 4 h and dried at 105 °C for 24 h prior to modification.

1-Dodecylamine (Alfa Aesar, $\geq$98 %), 1-hexadecylamine (Alfa Aesar, $\geq$90 %) and oleylamine (ABCR, %40) were used as surface active agents. Extra-pure K_2CrO_4 (Merck) was used in adsorption experiments. All other chemicals were of analytical grade.

Determination of cation exchange capacity

The external exchange capacity (ECEC) and cation exchange capacity (CEC) of clinoptilolite samples were determined by the method described by Ming and Bish (2001). Accordingly, the samples were treated with 1 M NaCl solution (5 % w/w) for 48 h at 60 °C so that exchangeable sites were completely saturated with Na^+. External Na^+ ions were then replaced by large ammonium molecules through treating the samples with 0.05 M HDTMA-Br at 60 °C for 24 h. Samples were filtered and washed twice with fresh HDTMA-Br. Washings were saved for Na^+ analysis to determine ECEC. Na^+ concentration was determined by atomic absorption spectroscopy (Perkin Elmer AAnalyst 800).

Finally, internal Na^+ ions were replaced by ammonium through washing three times with 1 M NH_4OAc. The washings were again saved for Na^+ analysis so as to determine internal exchange capacity, which was then added with the value of ECEC to obtain total CEC. The ECEC value was used as basis for the preparation of surfactant-modified clinoptilolites (SMCs) since the large surfactant molecules are not able to interact with the internal exchange sites of clinoptilolite.

Preparation of surfactant-modified clinoptilolite

Prior to the modification with surfactants, clinoptilolite samples were treated with strong acid solution in order to enhance the degree of H^+-exchange. Accordingly, samples were contacted with 1 M HCl solution with a solid content of 5 % (w/w) in two progressive steps, i.e., stirring for 2 h at 60 °C, continued with 24 h of contact at room temperature. After filtration, the samples were washed with deionized (DI) water to remove Cl^- ions from the surface.

H^+-clinoptilolite was further modified with surfactant by a procedure proposed by Vujakovic et al. (2000). Accordingly, the solid suspension of H^+-clinoptilolite in water (1 % w/v) was supplemented with 0.182 mmol of 1-dodecylamine, 1-hexadecylamine or oleylamine and mixed at 150 rpm and 60 °C for 1 h to obtain DMC, HMC and OMC, respectively. After filtration, modified samples were washed with DI water until being free of amine and dried at 60 °C to constant mass. The filtrates were analyzed for residual amine concentration according to ASTM D-1026 standard protocol.

Cr(VI) adsorption experiments

Stock solution of K_2CrO_4 (1000 ppm) was prepared and diluted as necessary to be used in batch adsorption experiments. All experiments were conducted at 298 K with a shaking rate of 150 rpm. The concentration of Cr(VI) was analyzed spectrophotometrically (Shimadzu UV 1240) at 540 nm using 1,5-diphenyl carbazide as the complexing agent (Mohan and Pittman 2006).

The adsorption capacities of natural zeolite and SMC samples were determined under the conditions of 100 ppm initial Cr(VI) concentration, pH 4.0 and 10 g l^{-1} adsorbent dose. The removal extent and capacity were calculated from Eq. 1 and Eq. 2, respectively. SMC with the highest potential was used in adsorption experiments.

$$\text{Removal}\,\% = \frac{C_0 - C_e}{C_0} * 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e) * V}{m} \tag{2}$$

where C_0 and C_e are the initial and equilibrium Cr(VI) concentration of solution (mg l^{-1}), q_e is the equilibrium uptake capacity (mg g^{-1}), V is the volume of solution (l) and m is the mass of adsorbent (g).

The effect of pH was studied within the range pH 2.0–12.0. Adjustments were made by small additions of 0.1 M HCl or 0.1 M NaOH. Cr(VI) solutions of 50 and 250 ppm were contacted with SMC samples (10 g l^{-1}) for 24 h. Time to reach equilibrium was investigated for initial concentrations of 200 and 600 ppm. Samples were driven out at certain time intervals between 0.5 and 24 h and analyzed for residual Cr(VI) concentration. The effect of adsorbent dose was examined within the range of 2–20 g l^{-1} using Cr(VI) solutions of 100 ppm. All experiments were triplicated, and mean data were accepted as the response.

Optimal conditions of pH, contact time and adsorbent dose were applied in isotherm studies. Cr(VI) solutions of different concentrations (50–300 ppm) were treated with modified clinoptilolite samples, and collected data were fitted to Langmuir (Eq. 3) and Freundlich (Eq. 4) isotherm models.

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{3}$$

$$q_e = K_F C_e^{1/n} \tag{4}$$

where q_e is the equilibrium uptake capacity (mg g^{-1}), C_e is the equilibrium concentration of solution (mg.l^{-1}), q_{max} is the maximum adsorption capacity (mg g^{-1}), K_L is a constant related to the energy of adsorption (mg l^{-1}), K_F is the adsorption capacity (mg g^{-1}) and n is the intensity of the adsorbent.

Kinetic data were fitted to pseudo-first-order, pseudo-second-order (Eqs. 5, 6) and intra-particle diffusion models (Eq. 7).

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

$$q_t = K t^{0.5} \tag{7}$$

where q_t (mg g^{-1}) is the adsorption capacity at any time t (h), k_1 (h^{-1}) and k_2 (g mg^{-1} h^{-1}) are the rate constants of adsorption and K is the intra-particle diffusion constant (mg g^{-1} $h^{-0.5}$) (Aydin and Deveci Aksoy 2009).

Adsorbent characterization

The identification of the crystalline species or impurities in natural zeolite and the change in crystalline structure after modification with surfactant were provided by X-ray diffraction analysis. The XRD patterns were recorded in $2\theta = 10°–40°$ range at 0.58°/min rate with X-ray diffractometer (Philips PANalytical, X'PERT PRO). Thermal gravimetric analysis of natural clinoptilolite and SMCs was carried out by Perkin Elmer, Diamond TG/DTA in air atmosphere, within the temperature range of 25–600 °C, with a heating rate of 5 °C min^{-1}. The FTIR spectra of samples were recorded with Perkin Elmer Spectrum One spectrophotometer within 4000–650 cm^{-1} as an average of four scans.

Results and discussion

Characterization of natural clinoptilolite

The XRD pattern of zeolite tuff (Fig. 2a) confirmed clinoptilolite as the major phase according to the characteristic bands located at 2θ values of 10°, 11.2°, 17.4°, 22.4°, 26°, 28.1°, 30° and 32° corresponding to (2 0 0), (1 1

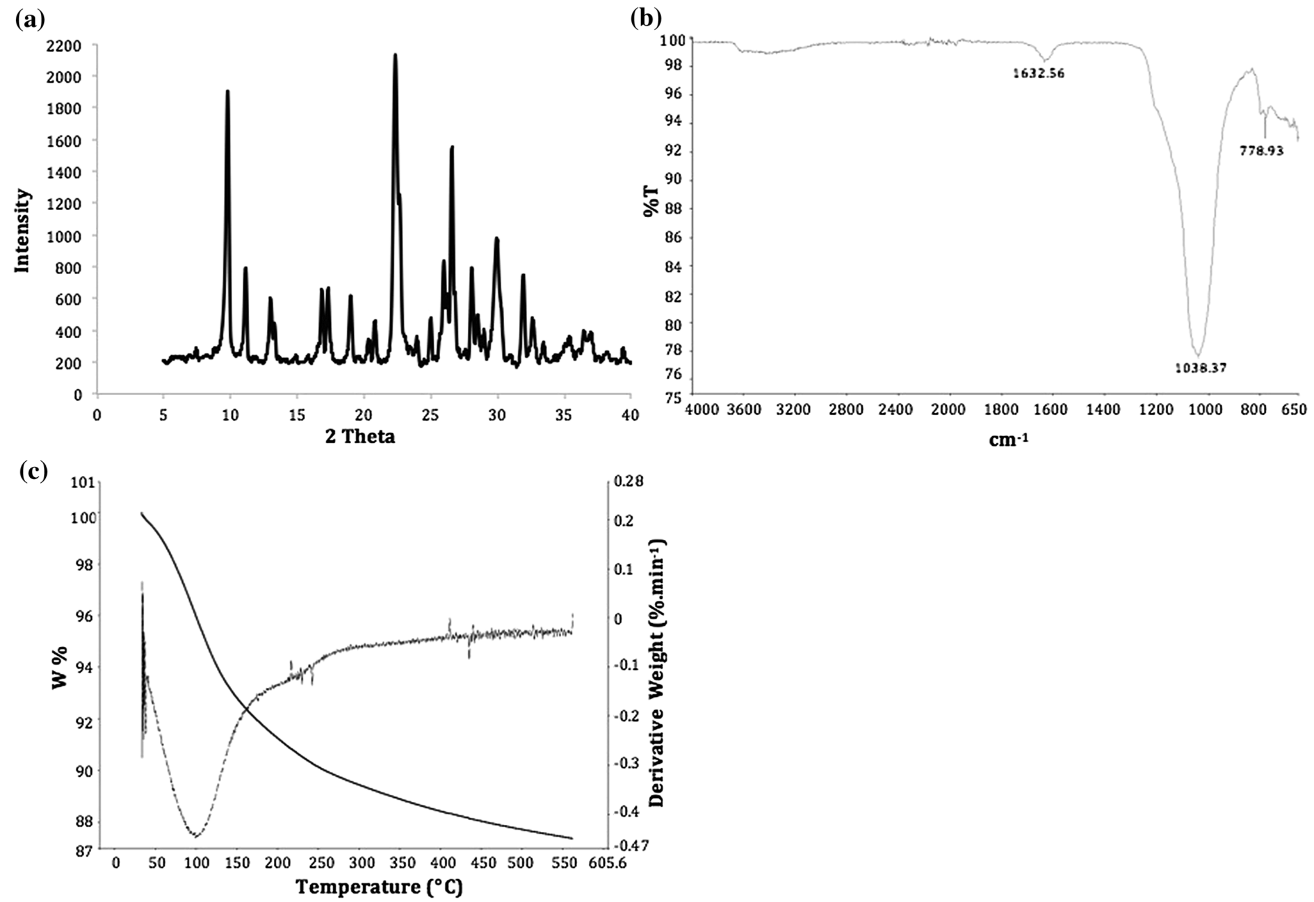


Fig. 2 Characterization of raw Bigadic clinoptilolite. **a** XRD pattern, **b** FTIR spectrum, **c** TGA curve

1), (3 3 0), (2 0 2), (5 1 1), (0 6 2), (3 5 2) and (6 4 1) crystallographic planes, respectively (Chutia et al. 2009). Non-zeolite fraction was identified as quartz and feldspar according to the peaks located at 2θ values of 20°, 26.6° and 27.5°, respectively (Rozic et al. 2009; Chutia et al. 2009). The composition of the zeolite tuff was calculated as 84 % clinoptilolite and 15 % quartz and 1 % feldspar. Conformity to clinoptilolite structure was also verified by FTIR spectrum of NZ (Fig. 2b) which showed typical peaks around 1632, 1038 and 776.4 cm^{-1} (Nezamzadeh-Ejhieh and Shahanshahi 2013). While the former peak was attributed to H–O–H bending vibrations of zeolitic water, the band at 1038 cm^{-1} was assigned to asymmetric Si(Al)–O stretching vibrations (Nezamzadeh-Ejhieh and Shahanshahi 2013; Elaiopoulos et al. 2008). The presence of quartz was shown by the band around 796 cm^{-1} (Yariv and Cross 2002).

The thermal gravimetric analysis curve for H-clinoptilolite (Fig. 2c) provided a single maximum peak at 100 °C, which was attributed to the physically adsorbed water and water between particles. The absence of the peak close to 200 °C indicated that H-clinoptilolite did not contain any zeolitic water (Leyva-Ramos et al. 2008; Nezamzadeh-Ejhieh and Shahanshahi 2013). The physical water content was calculated to be 7 % of the initial mass. This value is slightly higher than reviewed by Gottardi and Galli (1985) as 3 %, approximately. However, higher values up to 10 % have also been reported (Chutia et al. 2009; Nezamzadeh-Ejhieh and Shahanshahi 2013).

The CEC and ECEC of NZ were calculated as 0.432 and 0.182 meq g^{-1}, respectively. While the CEC value of Bigadic clinoptilolite was comparably lower than the values reported by Rozic et al. (2009) and Vujakovic et al. (2000) as 1.35 and 1.42 meq g^{-1}, the ECEC value was quite similar, i.e., 0.12 and 0.19 meq g^{-1}, respectively. The crystal size, aggregate size and aggregate porosity are determinative for the ECEC of a clinoptilolite sample rather than the CEC (Rozic et al. 2009). Thus, the approximate CEC values indicate similar sample properties.

Classification of the surfactants based on adsorptive properties

NC and SMC samples were classified according to their Cr(VI) adsorption ability. The adsorption capacities of

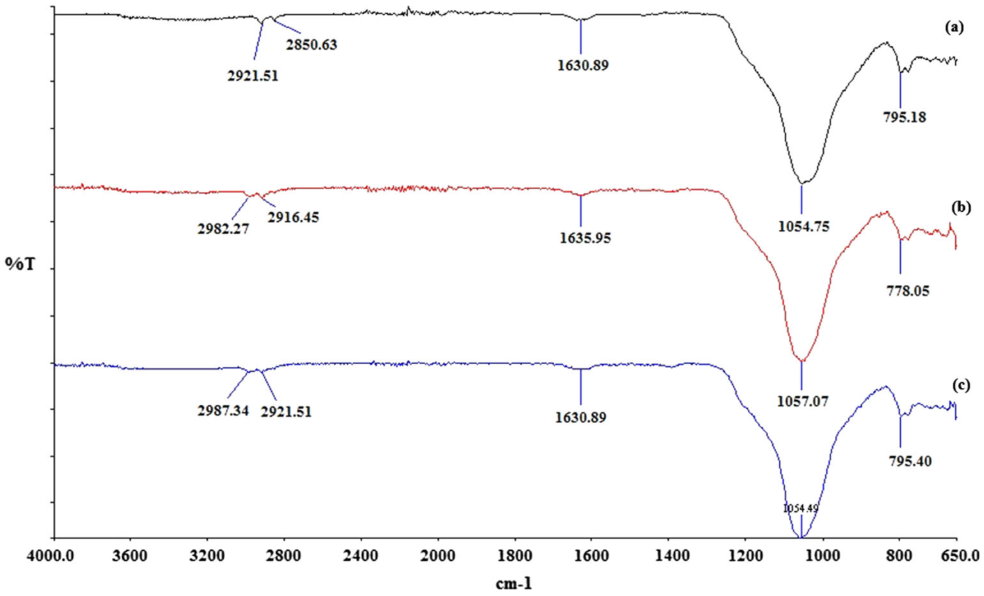


Fig. 3 FTIR spectra of *a* oleylamine-, *b* hexadecylamine-, *c* dodecylamine-modified clinoptilolite

SMCs were determined as 0.72 ± 0.05 mg g^{-1}, 4.43 ± 0.07 mg g^{-1} and 8.92 ± 0.14 mg g^{-1} for DMC, HMC and OMC, respectively. These values were superior over that of NC with 0.45 mg g^{-1} Cr(VI) uptake capacity. Accordingly, the adsorption of chromate was promoted in the order of increasing carbon number of organic modifier. The correlation between surfactant tail's chain length and metal ion adsorption was previously investigated by Li et al. (2002) who concluded that higher chain length elevated the coverage of clinoptilolite surface due to increased hydrophobic interactions. More recently, Xie et al. (2013) have highlighted the effect of ordered chain (*all-trans* zigzag) conformation, which was also shown to increase as the chain length increased. FTIR spectra of SMCs (Fig. 3) confirmed the respective increase in surfactant adsorption with an increased chain length.

The FTIR spectra of SMC and NC showed similarity for the bands related with internal Si–O–Si and Si–O–Al vibrations in tetrahedra or alumino- and silico-oxygen (1200–950 cm^{-1}) (Warchol et al. 2006; Barczyk et al. 2014) due to the fact that surfactant sorption process occurs only on the surface of clinoptilolite (Barczyk et al. 2014). The presence of zeolitic water was also confirmed with the band around 1630 cm^{-1}.

The FTIR spectra of SMCs differed from NC in the bands around 2950, 2921, 2850 and 1395 cm^{-1} which are assigned to asymmetric and symmetric C–H stretching vibration modes of the methylene groups, C–C stretching and C–N stretching modes of hydrocarbon chains and scissoring oscillations of the aliphatic chain, respectively (Warchol et al. 2006; Nezamzadeh-Ejhieh and Shahanshahi 2013; Anari-Anaraki and Nezamzadeh-Ejhieh 2015). The bands around 2950 and 2850 cm^{-1} are known to sharpen with increased surfactant coverage and ordered chain conformation. For the opposite case, the bands shift to higher frequencies and broaden (Xie et al. 2013). While such sharp bands were observed at 2921 and 2845 cm^{-1} in spectrum of OMC (Fig. 3a), gradual shifting to 2987 and 2916 cm^{-1} accompanied with peak broadening was observed in spectra of HMC and DMC (Fig. 3b, c). These verified lower surfactant load and the trend toward a more disordered structure with decreasing surfactant chain length. Thus, further adsorption experiments were conveyed using OMC as the adsorbent.

The oleylamine concentration was further increased by 2.0-fold of ECEC in order to observe the potential effect of double layer deposition and conformation. In addition to the operational instability, a slight decrease of 0.5 % was recorded in the Cr(VI) removal extent.

Excessive use of surfactant is justified for cases when modification is realized by quaternary ammonium surfactants such as HDTMA-Br. Such surfactants reverse the surface charge from negative to positive by forming a bilayer on the surface and thus enhance anion adsorption (Leyva-Ramos et al. 2008; Chutia et al. 2009). More recently, Bajda and Klapyta (2013) have reported a secondary removal mechanism in the presence of excess surfactant. Accordingly, unadsorbed surfactant promoted the formation of a precipitate of alkylammonium chromate at pH < 6. In contrast, monolayer coverage of oleylamine already yields positively charged $–NH_3^+$ ions through protonation of $–NH_2$ heads that interact with acid sites on the H^+-clinoptilolite surface (Vujakovic et al. 2000; 2003). While the use of excess oleylamine leads to partial bilayer coverage, hydrophobicity is concurrently increased leading to a slight decline in anion adsorption. Similarly to Bajda

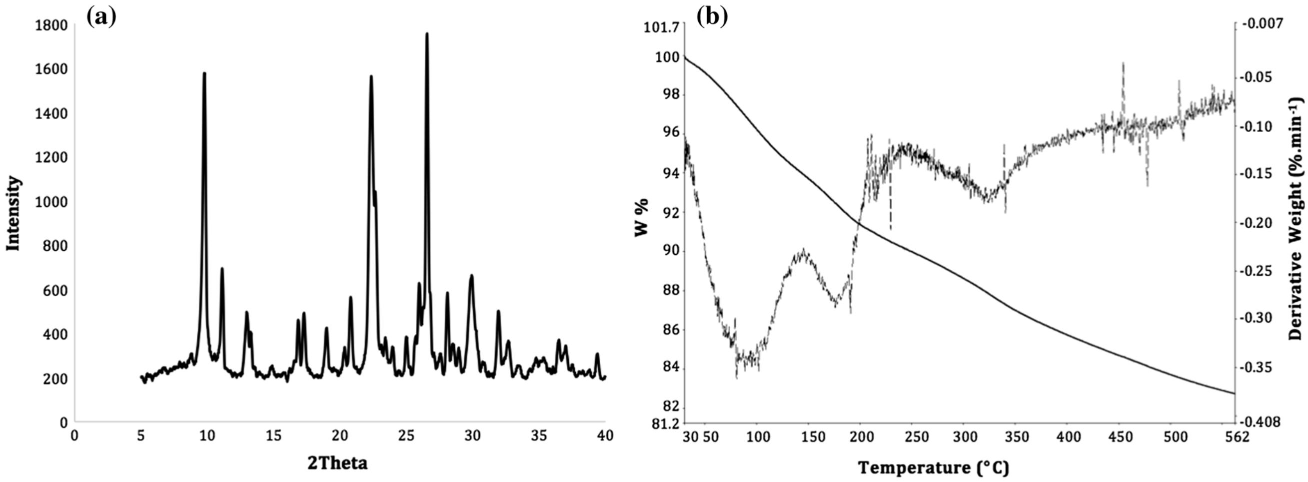


Fig. 4 Characterization of OMC. **a** XRD pattern, **b** TGA curve

and Klapyta (2013), pure oleylamine in equivalent amount to ECEC was able to reduce Cr(VI) concentration of solution by almost 46 % under identical experimental conditions. However, according to the applied procedure for preparation of SMZ, free amines were removed by extensive washing, and thus, this removal mechanism was not valid.

Characterization of OMC

X-ray diffraction analysis

The X-ray diffraction pattern of OMC is shown in Fig. 4a. Characteristic peaks of clinoptilolite structure were visualized similarly at 2θ 10°, 11.2°, 17.4°, 22.4°, 26°, 28.1°, 30° and 32°. However, it was realized that the intensity of these peaks decreased with respect to characteristic peaks of impurities located at 2θ values of 20°, 26.6° and 27.5°. The decline in the intensities of clinoptilolite peaks proved the presence of the surfactant on clinoptilolite surface. Additionally, the relative increase in the intensity of impurity peaks showed that oleylamine interacted only with clinoptilolite fraction, but not with the other species in the tuff (Leyva-Ramos et al. 2008; Chutia et al. 2009).

Thermal analysis

The thermal gravimetric analysis curve of OMC is shown in Fig. 4b. Contrary to the TG curve of H-clinoptilolite (Fig. 2c), two distinguished temperature regions were observed between 20–200 °C and 200–700 °C. While the former region is similarly ascribed to the physical and zeolitic water loss, the latter region is related to organic substance oxidation. The derivative mass-loss curve of OMC provided an additional peak close to 175 °C, which was ascribed to the presence of zeolitic water. While the physical water loss was calculated to be 5.7 % of the initial mass, mass loss from zeolitic water was 2.4 %. The mass loss within the region 20–200 °C declined from 8.9 to 6.67 %, which was assigned to the increase in hydrophobicity. The minor peaks between 220 and 250 °C are attributed to the oxidation of physisorbed oleylamine, and the broad peak observed at about 325 °C represents pyrolysis of the organic substance on clinoptilolite surface (Vujakovic et al. 2004). The mass loss due to the surfactant loading on clinoptilolite was calculated to be 4.4 % totally, which is equivalent to 0.163 mmol oleylamine per g clinoptilolite. This accounts for 90 % of ECEC. The 10 % difference in surfactant load might have been caused either by sample inhomogeneity or by desorption of physically sorbed amines during washing and drying steps.

Chromium removal with OMC

Effect of pH on Cr(VI) removal

pH is one of the most decisive factors in adsorption process due to its influence on the surface properties of adsorbent and metal ionization (Babel and Kurniawan 2004). The results of experiments conveyed at different pH levels are shown in Fig. 5.

The results showed maxima within the pH range of 3.0–4.0, while the extent of removal decreased gradually from 74.0 % to almost zero, as the pH was further increased from 4.0 to 12.0. The significant increase in adsorption capacity of OMC under strong acidic pH (2.0–4.0) is typical of Cr(VI) adsorption and has been verified for multiple adsorbent systems, previously (Kurniawan et al. 2006; Owlad et al. 2009; Aydin and Deveci Aksoy 2009).

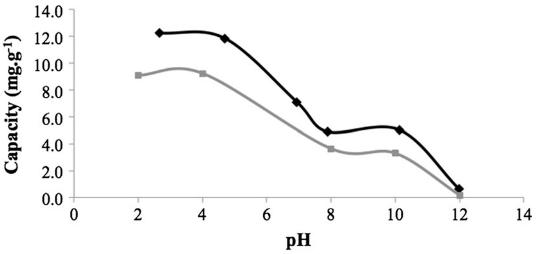


Fig. 5 Effect of solution pH on Cr(VI) adsorption by OMC. (*square*) 50 ppm, (*diamond*) 250 ppm

In aqueous medium, Cr(VI) exists dominantly in anionic forms, i.e., chromate (CrO_4^{2-}) and bi-chromate ($HCrO_4^-$). In the strong acidic pH range, $HCrO_4^-$ is in abundance, while at pH above 6.0, the divalent form takes over gradually (Leyva-Ramos et al. 2008; Bajda and Klapyta 2013). Under acidic conditions, the surface of OMC is protonated by the excess H^+ ions, which enhances the electrostatic attraction and concordantly accelerates the transport and adsorption of $HCrO_4^-$ (Singha et al. 2013). On the other hand, under alkaline conditions, the competition between CrO_4^{2-} and OH^- ions is in favor of OH^- ions that consequently create a negative surface charge and thus a sharp decline is observed in the adsorption of Cr(VI). As the results implied, pH 3.0 was selected as the optimal value and used in further experiments.

Effect of contact time on Cr(VI) removal

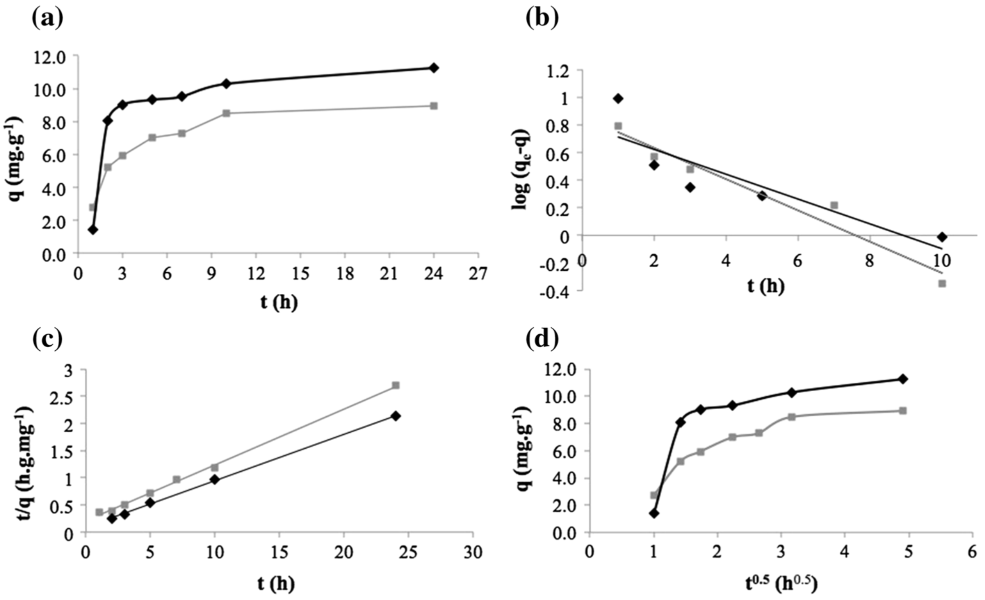
The effect of contact time was investigated in the range of 30 min to 24 h for 200 and 600 ppm initial Cr(VI) concentrations, and the results are shown in Fig. 6a. As seen from Fig. 6a, the uptake of Cr(VI) showed a rapid increase within the first hour of contact and the adsorption nearly reached equilibrium after 2 h. However, it was only after 10 h that the amount of adsorbed Cr(VI) did not significantly change with time.

This result suggested that chromate was adsorbed very fast at the surface within the first hours and in the preceding hours of contact adsorption took place at the inner surface of the clinoptilolite matrix. Due to the pore diffusion of metal ions into the OMC matrix, adsorption rate was significantly slower in the latter period.

It should also be noted that the OMC did not desorb Cr(VI) within 10–24 h of contact time which demonstrated that the interaction between OMC and Cr(VI) involved chemical interactions besides physical adsorption.

The presence of chemical sorption was also verified by further kinetic analyses. Pseudo-second-order kinetic model, which defines chemical sorption as the rate controlling step (Mohan et al. 2005), described data significantly better than pseudo-first-order model due to the regression coefficients of approximately 1.0 for both concentrations (Fig. 6b, c). While the Cr(VI) adsorption capacities were calculated as 9.73 and 11.72 mg g^{-1}, rate constants were determined as 0.05 and 0.08 g mg^{-1} h^{-1}, for 200 and 600 ppm, respectively. There are very few reports on kinetic analysis of Cr(VI) adsorption on surfactant-modified clinoptilolites. An example is the work by Zeng et al. (2010) who studied with HDTMA-Br-modified Pohang clinoptilolite and correlated Cr(VI) adsorption with pseudo-second-order model. Though the calculated rate constants are significantly lower than our values, adsorption capacities and the trend are quite identical.

Fig. 6 Kinetics of Cr(VI) adsorption upon OMC (*square*) 200 ppm and (*diamond*) 600 ppm. **a** Effect of contact time. **b** Description of data by pseudo-first-order kinetic model, **c** pseudo-second-order kinetic model and **d** intra-particle diffusion model



The binary effect of film and pore diffusions was demonstrated by fitting data to intra-particle diffusion model (Fig. 6d). The linear regions in Fig. 6d were attributed to intra-particle diffusion, and corresponding rate constants were calculated as 3.27 and 5.40 mg g^{-1} h^{-1} for 200 and 600 ppm initial Cr(VI) concentrations, respectively.

Effect of adsorbent dose on Cr(VI) removal

The influence of dose on Cr(VI) uptake was studied within the range 2.0–20.0 g l^{-1} of OMC amount, while the other parameters were held constant. Results are summarized in Fig. 7.

According to the figure, the removal efficiency of OMC improved substantially in the order of increasing adsorbent amount and reached as high as 94.0 % for adsorbent doses of $\geq$14 g l^{-1}. This trend is quite straightforward due to the respective increase in the number of available active sites. However, determination of the optimum adsorbent amount is a trade-off between cost and adsorption efficiency and thus the amount of Cr(VI) adsorbed per unit mass of OMC need to be considered as well. The secondary axis in Fig. 7 was included to show the change in uptake capacity with respect to adsorbent dose. The decline in adsorption capacity beyond an OMC dose of 14.0 g l^{-1} was accepted as an indication of the presence of unsaturated adsorption sites. Therefore, 14.0 g l^{-1} OMC was selected as the optimal adsorbent dose and applied in further experiments. Though the optimal dose for zeolites, either raw or modified, often lies in the range of 10.0–30.0 g l^{-1}, in a very recent report by Asgari et al. (2013), it was claimed that 0.7 g l^{-1} of HDTMA-modified zeolite was sufficient to attain $\geq$90.0 % Cr(VI) removal. This dramatic diversity is most probably caused by the difference in the studied concentration ranges. Under similar Cr(VI) concentration, the uptake capacity of surfactant-modified clinoptilolites was reported as 3.1 mg g^{-1} by Leyva-Ramos et al. (2008), 2.5 mg g^{-1} by Zeng et al. (2010) and 10.4 mg g^{-1} by Bajda and Klapyta (2013). At the optimal dose, OMC provided a comparable uptake capacity of 6.72 mg g^{-1}.

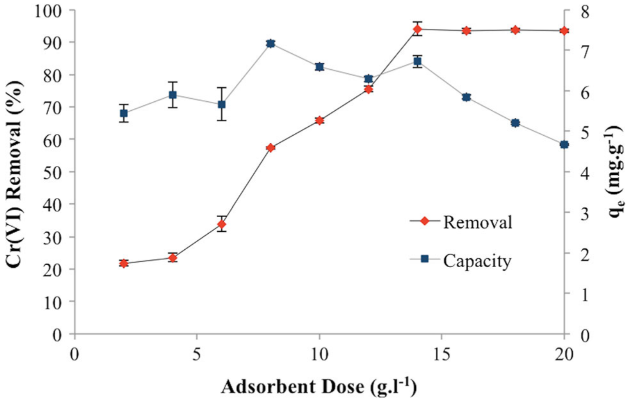


Fig. 7 Effect of adsorbent dose on Cr(VI) removal by OMC

Adsorption isotherm studies

After selection of optimal operating conditions, isotherm studies were conducted to characterize the adsorption of Cr(VI) upon the OMC surface. Langmuir and Freundlich isotherm models were involved to represent the opposing cases in which the uptake of metal ions occur either on a homogenous surface by monolayer adsorption without interaction between adsorbed ions or on a heterogeneous surface by multilayer adsorption with the amount of adsorbed ion increasing proportionally with concentration, respectively (Babel and Kurniawan 2004; Aydin and Deveci Aksoy 2009). Dubinin–Radushkevich model was also applied to determine the dominant sorption

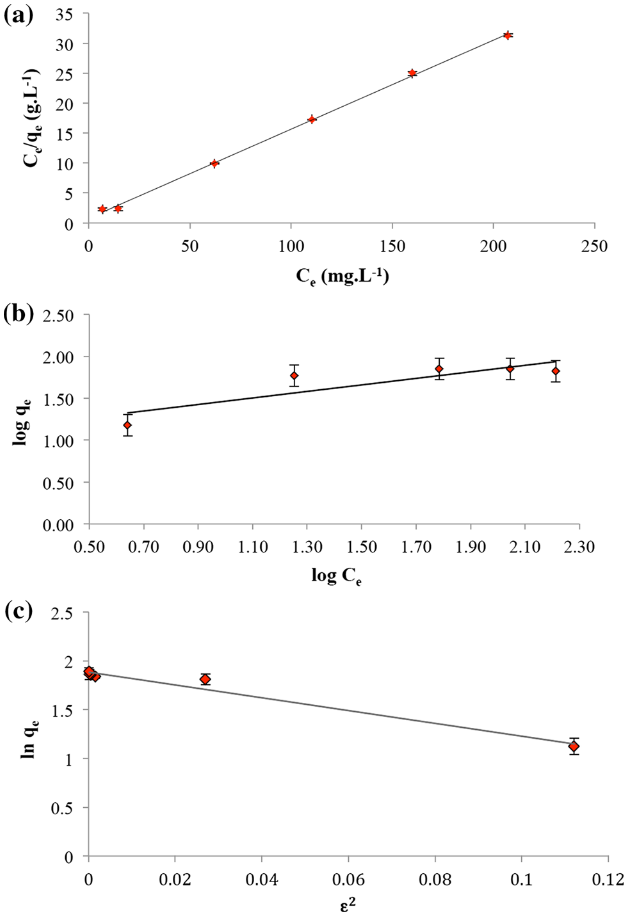


Fig. 8 Experimental data fitted to **a** Langmuir, **b** Freundlich, **c** Dubinin–Radushkevich isotherm models

Table 2 Description of Cr(VI) adsorption upon OMC by isotherm models

Isotherm	q_{max} (mg g^{-1})	K_L (l mg^{-1})	R_L	K_F (mg g^{-1})	n	K_{DR} (mol^2 kJ^{-2})	R^2
Langmuir	6.71	0.19	0.02–0.10	–	–	–	0.99
Freundlich	–	–	–	2.93	5.92	–	0.75
Dubinin–Radushkevich	6.58	–	–	–	–	6.56	0.97

mechanism. Data were fitted to linearized forms of isotherm models (Fig. 8a–c), and results are given in Table 2.

Adsorption data conformed well to the Langmuir isotherm according to a correlation coefficient of 0.99. Similar correlations were reported also by Zeng et al. (2010) and Asgari et al. (2013) for HDTMA-modified clinoptilolite samples and also by Cansever-Erdogan and Ulku (2012) for unmodified clinoptilolite of Turkish origin. Leyva-Ramos et al. (2008) described Langmuir as an eventual model for the adsorption of Cr(VI) on SMZs as the interaction occurred between one $HCrO_4$ anion and a single NH_4 group adsorbed on zeolite, thus confirming monolayer adsorption.

The mean free energy of adsorption was calculated as 0.276 kJ mol^{-1} using the Dubinin–Radushkevich constant, which implied that physical adsorption was the prevailing mechanism for Cr(VI) adsorption on OMC rather than ion exchange (Asgari et al. 2013; Aydin and Deveci Aksoy 2009; Chutia et al. 2009).

Conclusion

The results of this study clearly demonstrated that primary amine surfactants, namely dodecylamine, hexadecylamine and oleylamine, are appropriate organic modifiers to improve Bigadic clinoptilolite's Cr(VI) adsorption capacity. Surface protonation of NZ by strong acids aided in increasing affinity for surfactant loading due to increased electrostatic interaction. The improvement in Cr(VI) adsorption capacity followed the order OMC > HMC > DMC, due to increased surface coverage with increasing carbon chain length. The respective increase in capacity was recorded as high as 19.8-fold for OMC, which was well within the typical range of 3–20-fold from the recent literature. Further adsorption studies conducted with OMC showed that the adsorption of chromate was maximized in the pH range of 3.0–4.0, with 14 g l^{-1} adsorbent after 10 h of contact time. Under optimal conditions, Cr(VI) uptake of OMC was determined as 6.72 mg g^{-1} that corresponded to 94 % removal. Langmuir model was superior over Freundlich in description of isotherm data indicating monolayer coverage of Cr(VI) on OMC. Rate controlling step was defined as chemical sorption due to the almost perfect accordance of data with pseudo-second-order kinetic model. On the contrary, mean free energy of adsorption was significantly lower than 8 kJ mol^{-1}, suggesting the abundance of physical interactions.

Concluding, the availability of natural zeolites at relatively low cost, the simplicity of modification by oleylamine and its relatively high Cr(VI) adsorption capacity make Bigadic clinoptilolite an efficient alternative to conventional adsorbents such as activated carbon, activated alumina and polymeric sorbents. However, a field study involving multiple parameters, such as pollutant concentration, presence of co-ions, temperature, metal speciation, etc., as well as leachability tests of physically adsorbed surfactant molecules must be conducted for verification of results.

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