



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis



Sorption phenomena of modification of clinoptilolite tuffs by surfactant cations

M. Rožič^{a,*}, Đ. Ivanec Šipušić^b, L. Sekovanić^c, S. Miljanić^d, L. Čurković^e, J. Hrenović^d^a University of Zagreb, Faculty of Graphic Arts, Getaldiceva 2, 10000 Zagreb, Croatia^b University of Zagreb, Faculty of Food Technology and Biotechnology, Food Control Centre, Jagiceva 31, 10000 Zagreb, Croatia^c University of Zagreb, Geotechnical Faculty, Hallerova aleja 7, 42000 Varazdin, Croatia^d University of Zagreb, Faculty of Science, Horvatovac 102a, 10000 Zagreb, Croatia^e University of Zagreb, Faculty of Mechanical Engineering and Naval Architecture, I. Lucica 1, 10000 Zagreb, Croatia

ARTICLE INFO

Article history:

Received 4 September 2008

Accepted 13 November 2008

Available online 31 December 2008

Keywords:

Benzoate anions

Clinoptilolite tuff

Hexadecyltrimethylammonium bromide

Sorption

Zeolite

ABSTRACT

The sorption of cationic surfactant hexadecyltrimethylammonium (HDTMA) onto the solid/liquid interfaces of different clinoptilolite rich tuffs (CT) is examined. Examined were CT from Serbia with 75% clinoptilolite, CT from Turkey with 70% clinoptilolite, and CT from Croatia with 60% clinoptilolite. The sorption of HDTMA cations increased in the following order: CT from Serbia > CT from Turkey > CT from Croatia. The maximum amounts of sorbed HDTMA cations, normalized with regard to external cation exchange capacities of tuffs, were 1.79, 1.70, and 1.14 for Serbian, Turkish, and Croatian CT. FTIR analysis of samples with the maximum amount of sorbed HDTMA cations showed that HDTMA chains on Serbian CT adopt mainly a stretched all-*trans* conformation, while at the surfaces of CT from Turkey and Croatia the amount of *gauche* conformations increased. The zeta potentials of CT samples with the maximum amount of sorbed HDTMA cations and the sorption of benzoate anions on these samples increased in the following order: CT from Turkey > CT from Serbia > CT from Croatia. It can be assumed that on the surface of CT from Turkey iron (hydr)oxide clusters or nanoparticles with positive surface sites are present, due to which the isoelectric point is sifted toward lower and the zeta potential toward higher values. Therefore, the sorption of benzoate anions on modified CT from Turkey is also higher.

© 2008 Elsevier Inc. All rights reserved.

1. Introduction

Zeolites are crystalline, hydrated aluminosilicates of the group I and group II elements, in particular sodium, potassium, magnesium, calcium, strontium, and barium. Structurally the zeolites are “framework” aluminosilicates that are based on an infinitely extended three-dimensional network of $[\text{AlO}_4]^{5-}$ and $[\text{SiO}_4]^{4-}$ tetrahedra linked to each other by sharing all of the oxygens. In the formation of synthetic or natural zeolites, part of the Si^{4+} atoms by Al^{3+} atoms creates a negative charge at the Al–O tetrahedra that is balanced by an inorganic metal cation (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) [1].

By replacement of inorganic cations with organic cations (usually of quaternary ammonium structure), it is possible to convert a naturally hydrophilic property of zeolite into a hydrophobic and organophilic property.

It was shown for clinoptilolite tuffs (CT) that when the concentration of cationic surfactant hexadecyltrimethylammonium bromide (HDTMA-Br) is changed, the configuration of surfactant changes from monolayer to bilayer. The compensating inorganic cations in the crystal structure of clinoptilolite are not available

for exchange with HDTMA cations. The diameter of carbohydrate chain of HDTMA cation is 0.4 nm, the length is 2.3 nm, and the diameter of the polar head $-\text{N}^+(\text{CH}_3)_3$ is 0.694 nm, which makes it too large to penetrate the largest channels of clinoptilolite, which have dimensions 0.42×0.72 nm. Reactions in the system of CT and HDTMA cations therefore involve only external cation exchange capacity (ECEC, fraction of total CEC), leaving the internal cation exchange capacity unchanged and still accessible for small ions [2].

According to the literature, the HDTMA cation sorption maxima ranged from 58 to 266 mmol/kg CT. The maximum sorption of HDTMA cations and the ECEC appear to be controlled by CT crystal size, aggregate size, and aggregate porosity, rather than by the total CEC [2]. Other factors that can influence the HDTMA sorption maxima should be also taken into account: the geological origin of the zeolites, their cation and framework composition, and their impurities (such as forms of silica, feldspars, clay minerals, metal oxide/hydroxide nanoparticles, clusters, microcrystals, or agglomerates on the external zeolite surface).

Since the sorption of hydrophobic organic species onto a solid is a strong function of the solid's organic carbon content, the CT modified with HDTMA cations can be used as sorbents to remove hydrophobic organic contaminants from water [3]. If sorption of

* Corresponding author.

E-mail address: mirela.rozic@grf.hr (M. Rožič).

HDTMA cations results in the change of a negative surface charge to positive, the sorption of organic and inorganic anions is also possible [4–7].

Understanding the mechanism of surfactant sorption and the subsequent conformation of surfactants on the mineral surface is crucial to understanding the interaction of the sorbed surfactants with organic and inorganic compounds in solution and predicting the stability of the sorbed surfactants [8,9].

The aim of the present work is to examine the sorption phenomena of clinoptilolite tuff modification by HDTMA cations. The isotherms of sorption of HDTMA cations on CT, the zeta potentials of modified CT and the amounts of exchanged cations from CT were examined. FTIR analysis of CT samples with the maximum amount of sorbed HDTMA cations and the sorption of benzoate anions ($C_6H_5COO^-$) onto modified CT were analyzed too.

2. Experimental

2.1. Materials

The quaternary ammonium salt hexadecyltrimethylammonium bromide (HDTMA-Br, Merck), with molar mass 364.46 g/mol and minimum 99% active substance, was used. The critical micelle concentration (CMC) of HDTMA-Br at 30 °C was 0.94 mmol/dm³, as estimated by conductivity measurements of aqueous HDTMA-Br solutions at different concentrations.

The sorption of HDTMA cations was applied to three clinoptilolite-rich tuffs: CT from Turkey (Bigadic), CT from Croatia (Donje Jesenje), and CT from Serbia (Igrös). The samples of CT had particles smaller than 0.125 mm. The mineralogical composition of CT was determined by X-ray powder diffraction (Philips X.pert instrument). The chemical composition of CT was determined by classical chemical analysis. The cation exchange capacity (CEC) of CT was determined by measurement of equilibrium concentrations of exchangeable cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) in the supernatant by atomic absorption spectrometry (AA-6800, Shimadzu) after saturation of the samples with NH_4^+ ions [10].

2.2. Methods

2.2.1. Sorption of HDTMA onto CT samples

Surfactant solutions were prepared with deionized water. Concentrations of HDTMA-Br were 0.045, 0.095, 0.48, 0.70, 0.90, 1.55, 2.6, 3.70, 5.20, 6.60, 8.0, and 9.90 mmol/dm³, i.e., more and less than the CMC. Mixtures of 2.0 g of the CT sample and 0.1 dm³ of surfactant solutions were stirred at 30 °C (above the Kraft point, which is 25 °C) for 48 h on a mechanical shaker (Innova 4080) at 150 rpm. The suspension was centrifuged for 20 min and the supernatant was analyzed. The concentration of residual surfactant was determined as content of total organic carbon (Shimadzu TOC-5050A analyzer) in the obtained supernatant. Concentration of sorbed HDTMA cation in mmol/g was calculated from the mass balance equation (1) as

$$Q_e = (c_0 - c_e) \frac{V}{m}, \quad (1)$$

where c_0 and c_e are the initial and equilibrium liquid-phase concentrations of surfactant solution (mmol/dm³), respectively; V is the volume of surfactant solution (dm³), and m is the mass of clinoptilolite tuff sample used (g).

Supernatant solutions were analyzed by atomic absorption spectrometry for desorbed amounts of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} . The surfactant-modified samples were filtered through a Büchner funnel and filter paper (blue band). The samples were washed with distilled water until reaction with 1% $AgNO_3$ solution was negative. The modified samples were dried at room temperature.

2.2.2. FTIR spectroscopy

FTIR spectra were taken on a Bruker Equinox 55 interferometer using the KBr pressed disk technique. For each KBr pellet, 1 mg of tuff and 100 mg of KBr were weighted, ground in an agate mortar, and pressed. Spectra were recorded over the spectral range between 4000 and 400 cm⁻¹ with a resolution of 4 cm⁻¹.

2.2.3. Electrokinetic (zeta) potential measurements

The zeta potential of surfactant-modified samples was measured by a Zetasizer 3000 instrument. The electrophoretic mobility of the particles was automatically calculated and converted to the zeta potential using the Smoluchowski equation. Each CT sample (0.010 g) was suspended in distilled water (0.050 dm³) by mixing for 15 min. The samples were allowed to stand for 5 min. An aliquot taken from the supernatant was used for measurements of zeta potential. The average value of 10 measurements was taken as a representative potential.

2.2.4. Sorption of benzoate anions onto CT samples modified with HDTMA

An aqueous solution of benzoate anions was prepared by dissolving Na benzoate (Fluka) in deionized water. The sorption of benzoate anions onto CT samples modified with different concentrations of HDTMA was examined. Mixtures of 0.2 g of unmodified or HDTMA-modified CT samples and 0.01 dm³ of 1.0 mmol/dm³ benzoate solution were continuously stirred at 25 °C for 24 h on a mechanical shaker (Innova 4080) at 150 rpm. Then each mixture was centrifuged and the concentration of residual benzoate anions was determined by HPLC method, using an HP 1090 HPLC instrument with a DAD detector.

3. Results and discussion

3.1. Mineralogical and chemical analysis of CT samples

According to X-ray powder diffraction analysis (Fig. 1), the sample of CT from Serbia contained approximately 75% clinoptilolite. Several minor constituents, including calcite, analcime, plagioclase feldspars, biotite, and quartz (approximately 5% of each), were also determined in the sample. The CT from Turkey consisted of approximately 70% clinoptilolite, subordinate opal-CT and quartz (10–15% of each), and traces of K-feldspars and biotite (5% of each). The CT from Croatia consisted of approximately 60% clinoptilolite. Important constituents, present in concentrations of 10–15% each, were plagioclase feldspars and quartz, while K-feldspars and celadonite were present as traces (<5% of each). Results of the quantitative chemical composition of the studied CT are given in Table 1.

3.2. Cation exchange capacities (CEC) of CT samples

Results of the CEC determination (Table 2) show that the main exchangeable cations in samples of CT from Turkey and CT from Serbia were Ca^{2+} ions, whereas Na^+ ions were the main exchangeable cations in the sample of CT from Croatia. The sample of CT from Serbia had the largest CEC of 1.71 meq/g, while CEC of CT from Croatia was 1.60 meq/g and CEC of CT from Turkey 1.35 meq/g. The higher CEC of CT from Croatia than of CT from Turkey could be explained by the mobile extraframework $Na^+(H_2O)_n$ ions as the main exchangeable cation in the Croatian CT and the presence of minerals of secondary importance, such as plagioclase feldspars (tectosilicate group) and celadonite, $KFe^{3+}(Mg,Fe^{2+})Si_4O_{10}(OH)_2$ (mica group), which could increase the CEC numerical values. Also, due to the high content of Fe_2O_3 in CT from Turkey (Table 1), the existence of iron (hydr)oxide clusters or nanoparticles on the external surface cannot be excluded, due

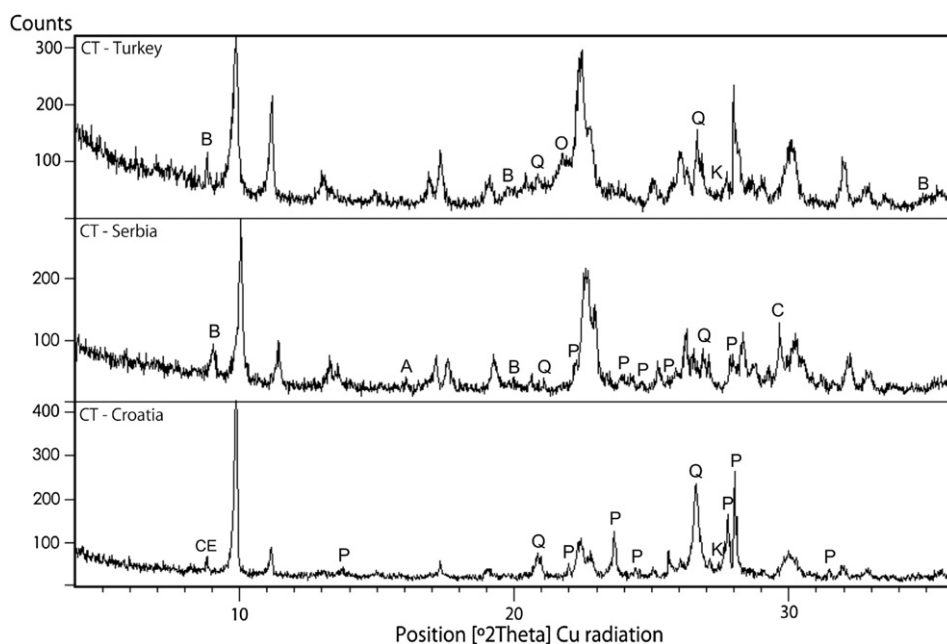


Fig. 1. X-ray powder patterns of CT samples from Turkey, Serbia, and Croatia. Peaks belonging to impurities are marked: (A) analcime, (B) biotite, (C) calcite, (CE) celadonite, (K) potassium feldspars, (O) opal-CT, (P) plagioclase feldspars, and (Q) quartz.

Table 1
Chemical analysis of clinoptilolite rich tuffs.

	SiO ₂ weight (%)	TiO ₂ weight (%)	Al ₂ O ₃ weight (%)	Fe ₂ O ₃ weight (%)	MgO weight (%)	CaO weight (%)	Na ₂ O weight (%)	K ₂ O weight (%)	Loss by glowing at 1000 °C weight (%)
CT Serbia	57.68	n.m.	13.86	2.05	n.m.	6.46	0.66	0.85	14.61
CT Croatia	68.51	0.13	11.17	0.16	0.41	1.04	3.48	2.31	11.27
CT Turkey	56.60	0.65	16.97	4.38	2.05	2.30	1.16	1.63	13.34

Note. n.m.: not measured.

Table 2
Cation exchange capacity of clinoptilolite rich tuffs.

	Ca ²⁺ (meq/g)	Mg ²⁺ (meq/g)	K ⁺ (meq/g)	Na ⁺ (meq/g)	CEC (meq/g)
CT Serbia	1.117	0.268	0.073	0.256	1.71
CT Croatia	0.169	0.047	0.215	1.165	1.60
CT Turkey	0.773	0.215	0.133	0.226	1.35

to which the CEC would decrease. The CT sample from Serbia has the highest mass percentage of clinoptilolite, consisting of zeolite analcime and plagioclase feldspars, and because of this composition has the largest CEC.

3.3. Sorption of HDTMA

The results of sorption of HDTMA cations onto CT samples are presented in Fig. 2. The results indicate that the HDTMA cations can be significantly sorbed by samples of all examined CT. The largest quantity of the surfactant cations sorbed was obtained on CT from Serbia. The maximum value of sorbed HDTMA cations on the CT from Serbia was achieved in solutions with initial HDTMA concentrations higher to some extent than 5.2 mmol/dm³. In the solution of 5.2 mmol/dm³, 0.233 mmol HDTMA/g CT was sorbed, and in the solution of concentration 6.6 mmol/dm³, 0.250 mmol HDTMA/g CT was sorbed. On the CT from Turkey, a smaller number of HDTMA cations were sorbed. The maximum value of HDTMA cations sorbed onto CT from Turkey was achieved in the solution of 5.2 mmol/dm³, where 0.204 mmol HDTMA/g CT was sorbed.

On the Croatian CT, the smallest numbers of HDTMA cations were sorbed. One should assume weakly bonded charge-balancing exchangeable extraframework surface cations from CT. The CT from

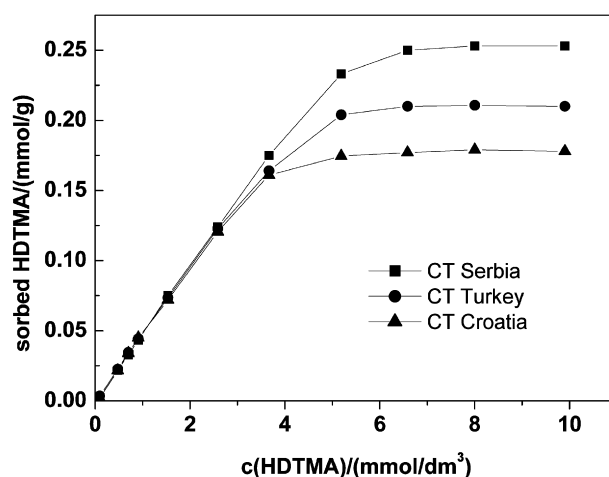


Fig. 2. Sorption of HDTMA cations onto CT samples; $V(\text{solution}) = 0.1 \text{ dm}^3$, $m(\text{tuff}) = 2.0 \text{ g}$. $c(\text{HDTMA})$ is the initial concentration of HDTMA cations in solution.

Turkey was recognized as the Ca-form; hence the CT from Croatia was in the Na-form. Sorption of humic substances onto phillipsite-rich tuff is more effective, when tuff is in the Ca-enriched form instead of the Na-enriched form, whereas pre-exchanges with Na⁺ ions depressed the formation of the organic–mineral aggregate [11]. The type of exchangeable cation in the aluminosilicate structure could influence the surfactant sorption rate [12], and thus the surfactant structure on the zeolite surface. In the surfactant solution of 3.7 mmol/dm³, 0.160 mmol HDTMA/g CT was sorbed;

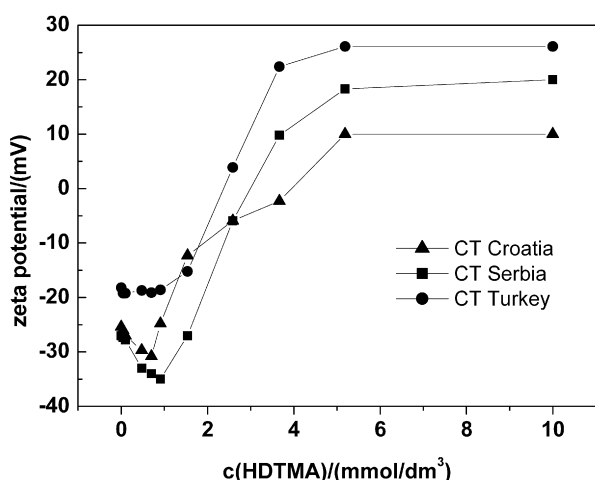


Fig. 3. Zeta potential of the CT samples vs HDTMA concentration.

however, in the solution of 5.2 mmol/dm³, 0.175 mmol HDTMA/g of CT was sorbed.

3.4. Electrokinetic (zeta) potentials

The results of determination of zeta potentials of surfactant-modified CT samples are presented in Fig. 3. The measurements of zeta potential revealed that the examined CT sample surface acquires a negative charge in water at natural pH. It was noticeable that when the surfactant solution concentration increased to the CMC, the negative zeta potentials of Serbian and Croatian CT increased. Measurements of the surface conductivity of different types of aluminosilicates (zeolite and feldspar minerals) have shown that in water and weakly acid medium, hydrolytic damage occurred. Surface dealumination, increased number of siloxane bridges, decreased ionic exchange capability, and creation of a thin surface layer of silica gel also took place because of the recondensation of polysilicic acid with the leached surface [13–15]. When electrophoretic mobility is increased, an increase of negative surface charge takes place as a result.

The isoelectric point (IEP) is characterized by the value zero for electrokinetic potential. Under these conditions, the negative CT surface charges are neutralized. Sorption above this level is expected to be in the form of a bilayer, a patchy bilayer, or admicelles, while sorption below this point is likely to be in the form of monomers or hemimicelles [16].

The HDTMA concentrations at the IEP of surfactant-modified CT samples are approximately 4.0, 3.0, and 2.4 mmol/dm³ for Croatian, Serbian and Turkish CT, respectively. Adequate loads of CT with HDTMA cations in these solutions were 0.160, 0.140, and 0.120 mmol/g for Croatian, Serbian, and Turkish CT, respectively.

In the literature, the number of sorbed HDTMA cations on CT at the IEP is equalized to the ECEC of clinoptilolite tuff [17]. On this basis, it could be assumed that the ECEC values of CT from Croatia, Serbia, and Turkey were 0.160, 0.140, and 0.120 meq/g.

At higher HDTMA concentrations, the surface tuff's sign was reversed from negative to positive. At maximum load with HDTMA cations, the Croatian CT had the lowest zeta potential (+10.0 mV), the Serbian CT had a higher zeta potential (+20.0 mV), and the Turkish CT had the highest zeta potential (+26.1 mV).

3.5. Desorbed exchangeable CT cations

Fig. 4 presents the equivalent amounts of exchanged CT cations depending on the initial concentration of HDTMA in the solution. Fig. 5 presents the total equivalent amounts of exchanged CT cations versus the sorbed amounts of HDTMA cations. The amounts of total exchanged cations and HDTMA cations sorbed were normalized to the ECEC of CT.

The main cations of Turkish CT exchangeable with HDTMA cations are Ca²⁺ ions. In the solution of concentration 2.57 mmol/dm³ (at the IEP) the amount of total exchanged cations from Turkish CT is 0.115 meq/g. The normalized amount of total exchanged cations is 0.97 and the normalized amount of HDTMA cations sorbed from this solution is 1.02. This means that at the IEP of CT from Turkey the sorption of HDTMA cations is a consequence of exchange with exchangeable cations of CT and that the ECEC is exhausted. Above the IEP, at maximum load of Turkish CT with HDTMA cations (concentration of solution 5.2 mmol/dm³), the amount of total exchanged CT cations is 0.107 meq/g. The nor-

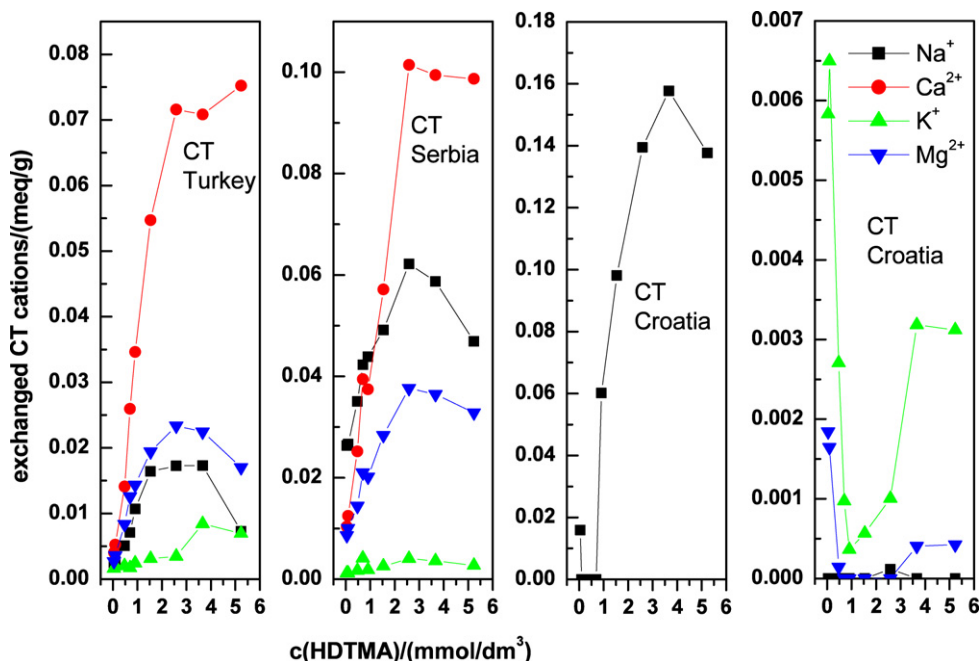


Fig. 4. Equivalent amounts of exchanged cations of CT samples versus the initial concentrations of HDTMA cations in the solution.

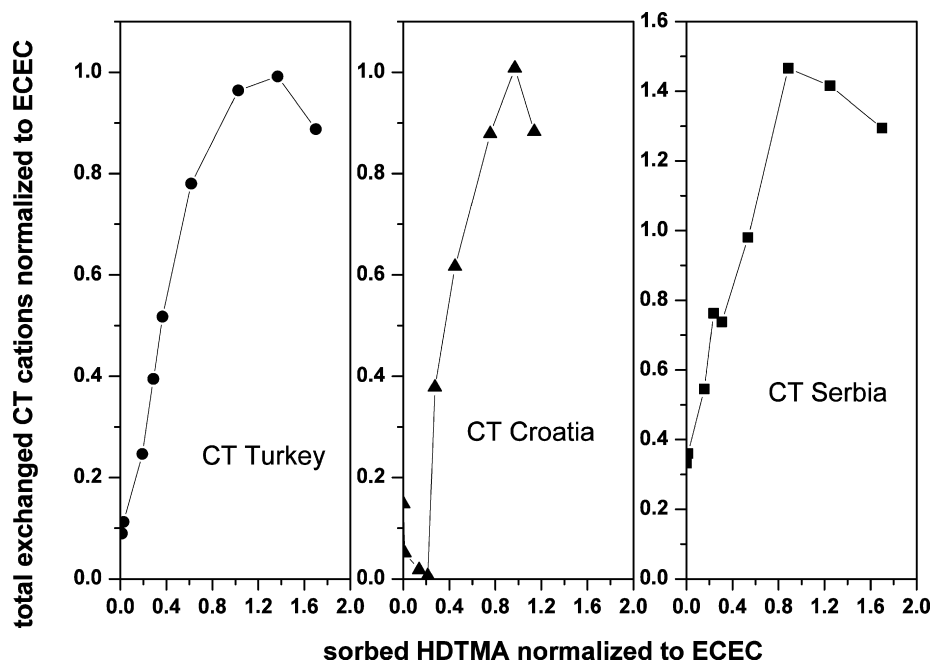


Fig. 5. Total meq of exchanged CT cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) versus sorbed amounts of HDTMA cations.

malized amount of total exchanged CT cations is 0.89 and the normalized amount of sorbed HDTMA cations is 1.70.

The main exchangeable cations in Serbian CT are Ca^{2+} and Na^+ ions. In a solution of concentration 2.57 mmol/dm^3 (approximately at the IEP), the amount of total exchanged cations from Serbian CT is 0.124 meq/g . The normalized amount of total exchanged cations with regard to ECEC is 1.47 and the normalized amount of HDTMA cations sorbed from the solution of the same concentration is 0.89. That suggests that at the IEP of CT from Serbia the sorption of HDTMA cations is a consequence of cation exchange with exchangeable cations of CT. However, due to the normalized total amount of exchanged CT cations being higher than 1, it is possible to assume that CT from Serbia is significantly hydrolyzed, meaning that it exchanges cations with H^+ cations. The equilibrium pH of CT from Serbia in distilled water (2 g/0.1 dm^3) is 8.90, that of CT from Turkey 6.54, and that of CT from Croatia 7.50. At a concentration of 5.2 mmol/dm^3 the amount of total exchanged cations from Serbian CT is 0.180 meq/g . The normalized amount of total exchanged cations from CT is 1.30 and the normalized amount of HDTMA cations sorbed from this solution is 1.70. In a solution concentration 6.6 mmol/dm^3 the normalized amount of sorbed HDTMA cations is 1.79.

The main exchangeable cations in Croatian CT are Na^+ ions. In the solution of concentration 3.7 mmol/dm^3 (approximately at the IEP), the amount of total exchanged cations of CT is 0.160 meq/g . The sorbed amount of HDTMA cations from this solution, normalized with regard to ECEC, is 0.97 and the normalized amount of total exchanged cations of CT is 1.0. This suggests that at the IEP of CT from Croatia the sorption of HDTMA cations is also a consequence of cation exchange with exchangeable cations in CT. At maximum load of HDTMA (concentration of solution 5.2 mmol/dm^3), the amount of total exchanged cations from Croatian CT is 0.140 meq/g . The normalized amount of total exchanged cations from CT is 0.88 and the normalized amount of sorbed HDTMA cations is 1.14. Due to the values of the normalized amount of sorbed HDTMA cations being significantly lower than 2, it can be assumed that at maximum load of Croatian CT with HDTMA cations, a very small share of HDTMA cations were bonded by specific interactions and a significantly larger share by cation exchange.

From Figs. 4 and 5 it can be seen that the exchange of cations from CT with HDTMA cations decreases after the IEP is reached. This may be the result of a more positive zeta potential of the surface of CT and therefore weaker electrostatic interactions of HDTMA micelles with surface of CT. The equilibrium pH of CT from Serbia in distilled water (2 g/100 dm^3) is 8.90, that of CT from Turkey 6.54, and that of CT from Croatia 7.50.

3.6. FTIR spectroscopy

To study the molecular conformation of HDTMA chains on CT, FTIR spectroscopy was used. The most intense absorption bands at 2918 and 2849 cm^{-1} in the FTIR spectrum of the crystalline HDTMA-Br were associated with the antisymmetric ($\nu_{\text{as}} \text{CH}_2$) and symmetric ($\nu_{\text{s}} \text{CH}_2$) C–H stretching vibration modes of the methylene groups, respectively [18,19]. The frequencies and widths of the CH_2 stretching modes depend strongly on the conformation and the packing density of the methylene chains [19–23]. For the all-*trans* alkyl chain, such as in crystalline HDTMA, the positions of the CH_2 asymmetric and symmetric stretching modes are around 2918 and 2850 cm^{-1} , respectively. If conformational disorder is included in the chains, their positions shift to higher wavenumber, depending upon the average content of *gauche* conformers [19].

In the case of high concentration of HDTMA cations, the chains are highly ordered (all-*trans* conformation) and the absorption bands in the FTIR spectra appear at the above-mentioned wavenumbers. On the other hand, if conformational disorder occurs as a consequence of low concentration of HDTMA chains, frequencies of the CH_2 stretching modes shift upward, indicating the presence of *gauche* conformers [20,21].

In the FTIR spectra of HDTMA cations sorbed from the solution of 5.2 mmol/dm^3 on CT from Serbia, Turkey, and Croatia, anti-symmetric CH_2 stretching bands were observed at 2919 , 2920 , and 2921 cm^{-1} , respectively (Fig. 6). Small but observable differences in frequencies implied that HDTMA cations on the Serbian CT have a more ordered structure than HDTMA cations on the Turkish and Croatian CT.

Moreover, the intensity of the absorption bands varied depending on the CT. The most intense band, which is related to the highest concentration of the HDTMA cations, was obtained in the

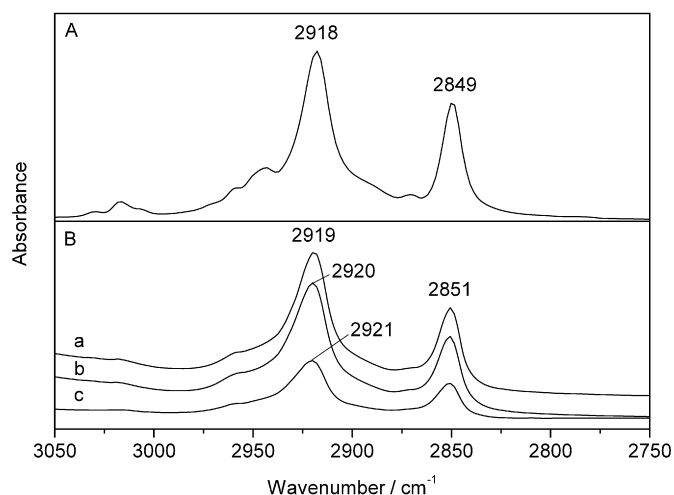


Fig. 6. FTIR spectra of (A) HDTMA and (B) HDTMA sorbed onto CT samples from Serbia (a), Turkey (b), and Croatia (c). Each sample was prepared using surfactant solution, $c = 5.2 \text{ mmol/dm}^3$. Spectra are displaced for visual clarity.

spectrum of the CT from Serbia, whereas the least intense band, which is due to the lowest concentration of HDTMA cations, was observed in the spectrum of the CT from Croatia. These results indicated that HDTMA chains on the Serbian CT adopt a mainly all-*trans* conformation, while increasing the number of *gauche* conformers on the surface of the Turkish and Croatian CT.

In the FTIR spectra of all three CT with sorbed HDTMA cations, the absorption band of the symmetric CH_2 stretching was obtained at the same wavenumber of 2851 cm^{-1} . This is in agreement with the fact that this mode is less sensitive to the chain conformation than the antisymmetric CH_2 stretching mode is [18].

3.7. Sorption of benzoate anions onto CT samples

The results of sorption of benzoate anions from the solution of concentration 1 mmol/dm^3 onto CT modified in solutions of increasing concentrations of HDTMA cations are shown in Fig. 7. The curves of CT from Serbia and Turkey follow the curves of dependence of zeta potential on the concentration of HDTMA. By the changes of zeta potential from negative to positive, the sorption of the benzoate anion increases. The curve of sorption of CT from Turkey appeared above the curve of CT from Serbia, similarly to curves of zeta potential. The unmodified CT from Turkey sorbed more benzoate anions than the unmodified CT from Serbia, which may be the result of the existence of iron (hydr)oxide clusters or nanoparticles adhering to the external surface of CT from Turkey [24,25]. Based on the literature, iron (hydr)oxides have $\text{p}K_{a1}$ and $\text{p}K_{a2}$ values of ~ 7.3 and 8.9 , respectively, resulting in a pH_{ZPC} on the order of 8.1 . At $\text{pH} < \text{pH}_{\text{ZPC}}$, the net surface charge is positive, producing an attractive electrostatic force between $\text{C}_6\text{H}_5\text{COO}^-$ anions and the tuff [26]. As a result, the benzoate anions are most probably sorbed onto the iron (hydr)oxides clusters as well as at the positive ends of the HDTMA bilayer.

The curve of CT from Croatia has a strong minimum. Onto CT from Croatia modified with a surfactant concentration of up to 1 mmol/dm^3 (CMC), the sorption of benzoate anion abruptly decreases (similarly to exchange of cations of CT with HDTMA, Figs. 4 and 5), and after the exchange with solutions at concentrations higher than CMC, the sorption of benzoate anions increases. The mentioned minimum can indicate the sorption of HDTMA cations onto amorphous silicates/aluminosilicates in CT. Amorphous aluminosilicates show relatively low speed of ion exchange [27]. Due to the large number of pores of relatively large diameter or large internal surface, the sorption of larger organic molecules is possible (e.g., the cationic dye molecule methylene blue). The unmodified

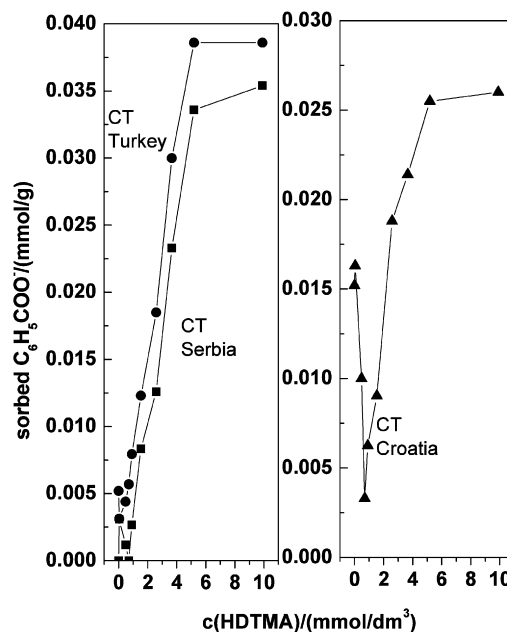


Fig. 7. Sorption of benzoate anions (1 mmol/dm^3 solution of Na-benzoate) onto CT samples modified in solutions of increasing concentrations of HDTMA cations.

CT from Croatia sorbed more benzoate anion than the unmodified CT from Turkey and Serbia. The higher sorption of benzoate anions can be ascribed to the presence of a nonclinoptilolite fraction in CT such as the phyllosilicate fraction (especially celadonite) that sorbs benzoate on edge surfaces, and the amorphous silicates/aluminosilicates fraction.

The largest amount of sorbed benzoate anions was achieved with CT samples with the greatest load of HDTMA cations. The sorption capacity increased in the order CT from Turkey > CT from Serbia > CT from Croatia, which is in agreement with the zeta potential of modified samples.

4. Conclusions

The amounts of HDTMA cations sorbed onto CT are in proportion to the clinoptilolite content in CT used and increased in the order CT from Serbia > CT from Turkey > CT from Croatia. The maximum amounts of sorbed HDTMA cations normalized with regard to ECEC values of CT were 1.14 , 1.70 , and 1.79 for Croatian, Turkish, and Serbian CT, respectively. The results of FTIR analysis showed that at maximum HDTMA loading, HDTMA chains on Serbian CT adopt mainly a stretched all-*trans* conformation, while on the surface of Turkish and Croatian CT increasing partition of *gauche* conformers is observed.

The zeta potentials of CT samples with maximum amounts of sorbed HDTMA cations and sorption of benzoate anions on these samples increased in the following order: CT from Turkey > CT from Serbia > CT from Croatia. It is assumed that on the surface of CT from Turkey the adherent iron (hydr)oxide clusters (nanoparticles) with positive surface sites are present, due to which the IEP is shifted to lower values and the zeta potential toward higher values. Therefore, the sorption of benzoate anions onto CT from Turkey is also higher. The benzoate anions were sorbed onto the positive surface sites of clusters (nanoparticles) and onto the positively charged interface of the HDTMA bilayer.

Acknowledgments

The authors thank Professor Darko Tibljas from the Faculty of Science, Zagreb for the mineralogical analysis of clinoptilolite tuffs.

References

- [1] D.W. Breck, Zeolite Molecular Sieves, Wiley, New York, 1984.
- [2] R.S. Bowman, in: R.S. Bowman, S.E. Delap (Eds.), Zeolite '06 – 7th International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites, Socorro, NM, USA, 2006, p. 56.
- [3] A. Kuleyin, J. Hazard. Mater. 144 (2007) 307.
- [4] U. Wingenfelder, G. Furrer, R. Schulin, Micropor. Mesopor. Mater. 95 (2006) 265.
- [5] Z. Li, R. Beachner, Z. McManama, H. Hanlie, Micropor. Mesopor. Mater. 105 (2007) 291.
- [6] S. Wang, W. Gong, X. Liu, B. Gao, Q. Yue, Sep. Purif. Technol. 51 (2006) 367.
- [7] Z. Li, R.S. Bowman, Water Res. 35 (2001) 322.
- [8] R. Atkin, V.S.J. Craig, E.J. Wanless, S. Biggs, Adv. Colloid Interface Sci. 103 (2003) 219.
- [9] D.W. Fuerstenan, R. Herrera-Urbina, in: D.N. Rubingh, P.M. Holland (Eds.), Cationic Surfactant, Dekker, New York, Basel, 1991, p. 407.
- [10] M. Rožić, Š. Cerjan-Stefanović, S. Kurajica, M. Rožmarić Mačefat, K. Margeta, A. Farkaš, J. Colloid Interface Sci. 284 (2005) 48.
- [11] S. Capass, S. Salvestrini, E. Copola, A. Buondonno, C. Colella, Appl. Clay Sci. 28 (2005) 159.
- [12] A. Patzko, J. Dekany, Colloids Surf. A Physicochem. Eng. Aspects 71 (1993) 299.
- [13] S.D. James, J. Phys. Chem. 70 (1966) 3447.
- [14] K.V. Ragnarsdottir, Geochim. Cosmochim. Acta 57 (1993) 2439.
- [15] E.S. Chardon, D. Bosbach, N.D. Bryan, I.C. Lyon, C. Marquardt, J. Romer, D. Schild, D.J. Vaughan, P.L. Wincott, R.A. Wogelius, F.R. Livens, Geochim. Cosmochim. Acta 72 (2008) 288.
- [16] E.J. Sullivan, J.W. Carey, R.S. Bowman, J. Colloid Interface Sci. 206 (1998) 369.
- [17] R.S. Bowman, E.J. Sullivan, Z. Li, in: C. Colella, F.A. Mumpton (Eds.), Natural Zeolites for the Third Millennium, De Frede Editore, Naples, 2000, p. 287.
- [18] H. Hongping, F.L. Ray, Z. Jianxi, Spectrochim. Acta Part A 60 (2004) 2853.
- [19] X. Yu, L. Zhao, X. Gao, X. Zhang, N. Wu, J. Solid State Chem. 179 (2006) 1525.
- [20] R.A. Vaia, R.K. Teukolsky, E.P. Giannelis, Chem. Mater. 6 (1994) 1017.
- [21] Y. Li, H. Ishida, Langmuir 19 (2003) 2479.
- [22] Z. Li, L. Gallus, Colloids Surf. A Physicochem. Eng. Aspects 264 (2005) 61.
- [23] Z. Li, L. Gallus, Appl. Clay Sci. 35 (2007) 250.
- [24] D.C. Radu, P. Glatzel, W.M. Heijboer, J.H. Bitter, B.M. Weckhuysen, F.M.F. de Groot, Stud. Surf. Sci. Catal. 170 (2007) 796.
- [25] L. Li, Q. Shen, J. Li, Z. Hao, Z.P. Xu, G.Q. Max Lu, Appl. Catal. A Gen. 344 (2008) 131.
- [26] P. Westerhoff, T. Karanfil, J. Crittenden, Aerogel & Iron-Oxide Impregnated Granular Activated Carbon Media for Arsenic Removal, WERC, a Consortium for Environmental Education and Technology Development at New Mexico State University, 2006.
- [27] M.J. Schwuger, H.G. Smolka, Colloid Polym. Sci. 254 (1976) 1062.