COMPOSITES OF PHILLIPSITE-RICH TUFF AND SURFACTANT – THEIR CHARACTERIZATION AND STABILITY

Danijela Smiljanić[1], Aleksandra Daković[1], Milica Spasojević[1], Milena Obradović[1], Marija Marković[1], Alessio Langella[2], Bruno de Gennaro[3]

[1]Institute for Technology of Nuclear and Other Mineral Raw Materials, Franche D' Epere 86, 11000 Belgrade, Serbia

[2]Department of Earth Sciences, Environment and Resources, Federico II University, Via Cinthia, 80126 Napoli, Italy

[3]DICMAPI, Federico II University, Piazzale V. Tecchio 80, 80125 Naples, Italy

E-mail: d.smiljanic@itnms.ac.rs

ABSTRACT

In this work phillipsite-rich tuff (P) was modified by using amounts of cetylpyridinium chloride (C) equivalent to 70% and 140% of the zeolite external cation exchange capacity (ECEC). Accordingly, composites were denoted as PC-70 and PC-140. Prepared composites were characterized by ATR-FTIR spectroscopy. Additionally, to test the stability of surfactant molecules attached to the tuff surface, composites were extensively washed with distilled water, and zeta potential of unwashed and washed samples was measured. FTIR spectra confirmed presence of C in both composites. Zeta potential measurements showed that composite containing surfactant in the amount below the ECEC value (PC-70) has much higher stability and thus is a more appropriate adsorbent for potential practical application for removal of different pollutants.

Keywords: phillipsite-rich tuff, ATR-FTIR, zeta potential, surfactant stability.

INTRODUCTION

Natural zeolites are abundant, low-cost, and eco-friendly minerals, with high cation exchange capacity, physicochemical stability, and good hydraulic characteristics. For these reasons, natural zeolites were extensively investigated for water treatment - especially for the removal of heavy metal cations. Modification of natural zeolites with cationic surfactants provides adsorbent materials with an increased affinity towards low polar molecules and even anionic species depending on the amount of surfactant at the zeolitic surface. When the amount of surfactant is below or equal to the ECEC, the zeolitic surface charge is changed from negative to neutral (monolayer phase made of hydrophobic surfactant tails with an affinity towards hydrophobic molecules) whereas, when the surfactant amount is above ECEC zeolite surface became more positive (bilayer of surfactant, formed through hydrophobic interactions between surfactant tails, capable for adsorption of anions). Therefore, surfactant modified natural zeolites (SMNZs) with different amounts of surfactants were studied for the removal of different pollutants from water - oxyanions, phenolic compounds, dyes, pesticides, emerging contaminants, etc [1–6]. However, since surfactants are also considered as emerging contaminants, before application of SMNZs for water remediation it is necessary to determine the stability of surfactant bounded to the zeolite surface.

The aim of this work was to prepare composites with the amounts of surfactant cetylpyridinium chloride (C) below and above the ECEC value of the phillipsite-rich tuff and to investigate the stability of adsorbed surfactant molecules at phillipsite surface.

EXPERIMENTAL

The starting material used in this study for the preparation of composites with surfactant was a phillipsite-rich tuff from Campanian region (Marano of Naples, Italy) commercialized in Italy from Italiana Zeoliti – CBC Group. Mineralogical and chemical characterizations for the tuff were previously carried out [7]. The phillipsite-rich tuff had 58 wt% of zeolitic

content (44 wt%, 4 wt%, and 10 wt% for phillipsite, chabazite and, analcime, respectively) together with 11 wt% of smectite and 32 wt% of feldspar. The Si/Al ratio and ECEC of the tuff were 2.45 and 0.15 meq/g, respectively.

Phillipsite-rich tuff was treated with two different amounts of cetylpyridinium chloride (CAS: 6004-24-6, M = 358.00 g/mol, Sigma Aldrich, assay: 98.0–102.0%), equivalent to 70% (0.1 meq/g) and 140% (0.2 meq/g) of its ECEC value, and modification was performed according to the procedure given in the literature [6,8]. Furthermore, in order to check the stability of the prepared materials, 1 g of each composite was extensively washed (under vacuum using Büchner funnel and flask) with distilled water (approximately 0.5 L), filtered, and dried at 60 ˚C.

Attenuated Total Reflectance – Fourier Transform Infrared (ATR–FTIR) spectroscopy was used to collect spectra of starting material and composites PC-70 and PC-140, in the spectral range 4000–400 cm^{-1} with resolution 2 cm^{-1} (Bruker Alpha; Opus 7.2 software - Bruker Optik GmbH, Leipzig, Germany). The zeta potentials of P and composites before and after washing were measured using a Zetasizer Nano ZS90, Malvern Instruments. Aqueous suspensions (0.1 mg/mL) for each material were prepared and the average value of 5 measurements was taken. Latex dispersion was used as a calibration standard.

RESULTS AND DISCUSSION

ATR-FTIR spectra of P and composites - PC-70 and PC-140 are presented in Figure 1. Infrared analysis has shown adsorption bands of zeolite-rich tuff associated with internal and external framework vibration of primary and secondary building units [9]. All spectra had a broad peak above 3000 cm^{-1} and a peak at 1635 cm^{-1} from O-H stretching and bending vibration in water molecules, respectively. In the spectra of composites (PC-70 and PC-140) the presence of surfactant was confirmed by: the low-intensity peak at 2956 cm^{-1} that belongs to the CH$_3$ group, and peaks at 2920 cm^{-1}, and 2851 cm^{-1} corresponding to asymmetric and symmetric C-H stretching vibrations of CH$_2$ groups in the alkyl chain of C molecules. Similarly, low-intensity peaks at 1487 cm^{-1} and 1467 cm^{-1} are from C-H bending vibration in surfactant molecules.
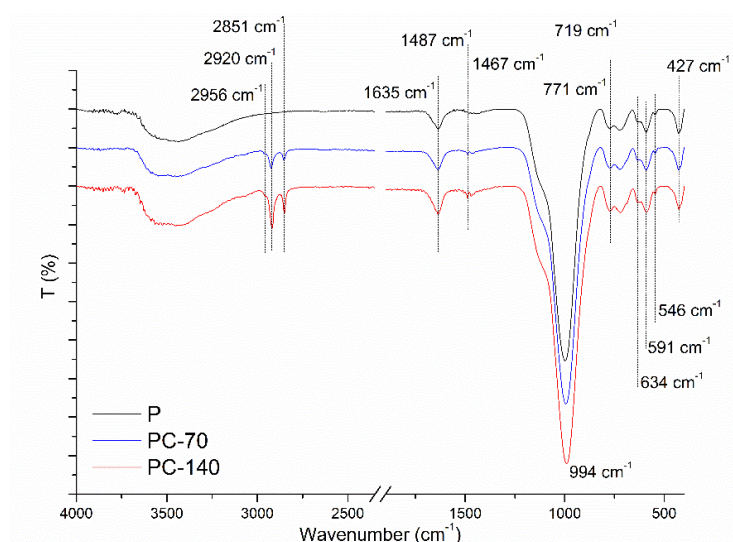

Figure 1. FTIR-ATR spectra of phillipsite-rich tuff before modification and after modification with two different amounts of surfactant.

The vibrations characteristic for silicates were found: at 994 cm^{-1} (with the shoulder on the left side) which belongs to asymmetric stretching of T-O, where T represents Si or Al, and

O is oxygen atom; peaks at 771 cm $^{-1}$ and 719 cm $^{-1}$ are from asymmetric and symmetric stretching of T-O-T, respectively, while peaks at 634 cm $^{-1}$, 591 cm $^{-1}$, 546 cm $^{-1}$, and 427 cm $^{-1}$ are characteristic for T-O-T bending vibrations. These results confirmed presence of C molecules at the zeolitic surface and that modification with surfactant did not change the internal structure of the tuff. Additionally, it is observed that intensities of peaks characteristic for C molecules increased with the increase of the amount of surfactant at the phillipsite surface.

In general, two mechanisms of surfactant adsorption at the zeolitic surface predominate: first, when the amount of surfactant is below or equal to ECEC, a cation exchange of cations at surface with surfactant ions occurs; second, binding of surfactant in excess of the ECEC via hydrophobic interactions between the long tails of the surfactants. It was also reported that desorption of surfactant may occur, especially when the amount of surfactant is above ECEC [10,11].

Zeta potential of P and both composites before and after washing was measured and the change in surface charge was confirmed (Figure 2). According to the literature, when ion exchange of cations with surfactant ions occurs, zeta potential of the SMNZ becomes less negative due to the increased hydrophobicity of the zeolitic surface and approaches zero with amount of surfactant equal to the ECEC value confirming complete hydrophobicity of the zeolitic surface. When amount of surfactant is above ECEC zeta potential becomes positive indicating charge reversal due to the bilayer formation at the zeolite surface.
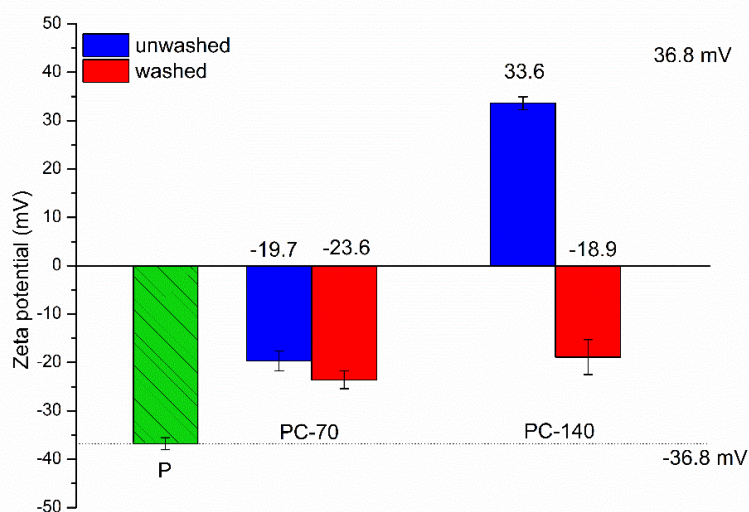

Figure 2. Graphical representation of zeta potential for starting phillipsite-rich tuff, and composites (PC-70 and PC-140) before and after washing.

The zeta potential of P was -36.8 mV, whereas in the case of PC-70, before washing, the zeta potential was less negative (-19.7 mV), confirming that surface is more hydrophobic and that C is tightly bounded at the P surface by ion exchange process. A slightly more negative value of zeta potential (-23.6 mV) was observed after washing, indicating that only a small amount of C was desorbed from the surface of PC-70. At the higher amount of C (sample PC-140), the change in zeta potential value after washing was more visible. Namely, for unwashed composite, the zeta potential was positive (+33.6 mV) confirming charge reversal and presence of C bilayers at P surface. However, after washing, zeta potential became negative (-18.9 mV) indicating desorption of C from bilayers of PC-140. These changes in the zeta potential value of unwashed and washed composite PC-140 suggest that weak

hydrophobic interactions between alkyl chains predominate in bilayer. Additionally, after washing, composites had similar values of zeta potential regardless of the initial amount of C.

CONCLUSION

Phillipsite-rich zeolitic tuff was modified with two different levels of surfactant cetylpyridinium chloride (C) – below (70%) and above (140%) zeolite external cation exchange capacity (ECEC). ATR-FTIR analysis has confirmed a successful modification of phillipsite-rich tuff by C molecules. Zeta potential measurement showed that when amount of C was below ECEC value, the surfactant ions was tightly bound to the zeolitic surface, but when the amount of surfactant was above ECEC value, C molecules were adsorbed creating bilayer and was easily desorbed from P surface. Results showed that zeta potential may be a useful tool in the determination of surfactant stability at surface of SMNZ. The composite containing C in amount below the ECEC value (PC-70) may be a more appropriate adsorbent for potential practical application for removal of different pollutants due to the higher stability. The results also suggest that when using the SMNZs for the removal of emerging contaminants the surfactant stability should be tested prior to the application.

ACKNOWLEDGMENT

REFERENCES

[1] M. Delkash, B. Ebrazi Bakhshayesh and H. Kazemian, *Microporous Mesoporous Mater.*, 2015, **214**, 224–241.

[2] C. Colella, M. de' Gennaro, A. Langella and M. Pansini, *Sep. Sci. Technol.*, 1998, **33**, 467–481.

[3] P. Misaelides, *Microporous Mesoporous Mater.*, 2011, **144**, 15–18.

[4] S. Wang and Y. Peng, *Chem. Eng. J.*, 2010, **156**, 11–24.

[5] J. Lemić, M. Tomašević-Čanović, M. Adamović, D. Kovačević and S. Milićević, *Microporous Mesoporous Mater.*, 2007, **105**, 317–323.

[6] D. Smiljanić, B. de Gennaro, F. Izzo, A. Langella, A. Daković, C. Germinario, G.E. Rottinghaus, M. Spasojević and M. Mercurio, *Microporous Mesoporous Mater.*, 2020, **298**, 110057.

[7] B. de Gennaro, P. Aprea, C. Colella and A. Buondonno, *J. Porous Mater.*, 2007, **16**, 667–673.

[8] B. de Gennaro, M. Mercurio, P. Cappelletti, L. Catalanotti, A. Daković, A. De Bonis, C. Grifa, F. Izzo, M. Kraković, V. Monetti and A. Langella, *Microporous Mesoporous Mater.*, 2016, **235**, 42-49.

[9] M. Mercurio, F. Izzo, A. Langella, C. Grifa, C. Germinario, A. Daković, P. Aprea, R. Pasquino, P. Cappelletti, F.S. Graziano and B. de Gennaro, *Am. Mineral.*, 2018, **103**, 700–710.

[10] Z. Li, S.J. Roy, Y. Zou and R.S. Bowman, *Environ. Sci. Technol.*, 1998, **32**, 2628–2632.

[11] P.J. Reeve and H.J. Fallowfield, *J. Hazard. Mater.*, 2017, **339**, 208–215.