



## Research paper

# The potential of clinoptilolite-rich tuffs from Croatia and Serbia for the reduction of toxic concentrations of cations and anions in aqueous solutions



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## ABSTRACT

Natural zeolites have a great potential as low-cost, non-toxic and highly selective sorbents in pollution control, especially in waste-water management. The potential of Croatian and Serbian clinoptilolite-rich (HEU-type zeolite) tuffs from four different deposits have been evaluated for their use in metal removal from aqueous solutions by the application of adsorption equilibrium studies, structural studies of metal-loaded zeolite tuffs and their regeneration or further treatment, which were performed in our laboratories or were reported by other authors. The results showed that metals like copper could be completely removed from aqueous solutions at low metal concentrations using Serbian and/or Croatian zeolites (up to 120 mg Cu/L). At higher concentrations the efficiency of zeolites slowly decreased, also in accordance with the theoretical adsorption capacities. The studies confirmed that a higher content of zeolite in tuffs from Serbia (70–80% vs. 50% for Croatian tuff) resulted in their better adsorption performance for selected metals. Additionally, the pretreatment of zeolites with  $\text{Na}^+$  significantly enhanced the uptake of all metal cations, while the pretreatment with  $\text{Fe}^{3+}$ , which resulted in stable iron-oxo-species on the zeolite surface and positive charge of the framework, enabled the adsorption of anions, like arsenites, arsenates and chromates. The reversibility of the metal uptake depended on the type of metal; for example, post-treatment of the samples with HCl, NaCl or  $\text{NH}_4\text{Cl}$  solutions revealed irreversible adsorption of chromium and arsenic and mostly reversible adsorption of zinc and copper. The possible strategies for the regeneration or immobilization of the used metal-loaded zeolites, like immobilization in cements or the use as catalysts, were also considered.

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## 1. Introduction

A great interest in the use of natural zeolitic tuffs for the removal of toxic metals from waste-water and drinking water in the last two decades is governed by the availability and non-toxicity of zeolites, as well as their robustness, high selectivity and easy removal, which are crucial factors for a successful water management. Several review papers on the potential of natural zeolites for water decontamination were published from the 1990s (Pansini, 1996; Ahmadun et al., 2009; Gikas and Tsihrintzis, 2010; Wang and Peng, 2010). Most of them were concentrated on theoretical and practical aspects of the immobilization of metal cations in natural zeolites, which include ion-exchange or chemisorption (when functional groups on the zeolite framework, mainly  $\text{OH}^-$ , form strong chemical bonds with metal ions) (Bhatnagar and Sillanpaa, 2010; Caputo and Pepe, 2007; Inglezakis, 2005, 2007; Langella et al., 2000; and references therein). The majority of the papers

focused on the adsorption of cations  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{NH}_4^+$  on natural HEU-type zeolite clinoptilolite (Erdem et al., 2004; Stylianou et al., 2007; Minceva et al., 2008; Doula, 2009; Siljeg et al., 2010). The studies showed that cations adsorption mechanisms and capacities crucially depend on the type and charge of the zeolite framework, which mostly relates to (1) the quantity of aluminum present in the zeolite framework, (2) the size and shape of the pores, (3) the phase composition of the zeolite tuff, (4) the nature and concentration of the extra-framework cationic species and (5) the pH of the solvent. Other less relevant factors are (6) the size and distribution of zeolite tuff particles, (7) the temperature of adsorption, etc. The high potential of other zeolites, like heulandite (HEU-type zeolite), chabazite (CHA-type zeolite), stilbite (STI-type zeolite) and some others has also been determined (Ruggieri et al., 2008; Calvo et al., 2009; Guerra et al., 2009; Inglezakis et al., 2010; Zeng et al., 2010a). Recently, the utilization of chemically modified natural zeolites for the removal of toxic anions, like arsenates (Chutia et al., 2009; Jiménez-Cedillo et al., 2009), chromates (Misaelides et al., 2008; Zeng et al., 2010b) and nitrates (Guan et al., 2010; Schick et al., 2010) from water was also initiated. Since negatively charged

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surface of the zeolite and the anionic field strength only allows cations to accommodate in the pores, cationic surfactants or iron salts were used to modify the surface of the zeolites for the anions uptake (Li et al., 1998; Vujakovic et al., 2003; Radosavljevic-Mihajlovic et al., 2004; Coruh, 2008; Davila-Jimenez et al., 2008; Oztas et al., 2008; Tarasevich et al., 2008; Han et al., 2009; Rozic et al., 2009; Elaiopoulos et al., 2010). In most cases, toxic anions were chemically bonded to the zeolite surface by following the chemisorption mechanisms. The capacity of adsorption for a particular anion was mostly defined by the type of zeolite surface modification.

In this paper we comment on the potential of natural clinoptilolites from Croatia and Serbia as cationic and anionic sorbents in water metal-pollution control. The conclusions are based on the adsorption studies and structural determination of zeolitic tuffs, which were performed to help to the development of new cost-effective zeolite-based systems with optimized adsorption performance for pollutant species. The details on our structural studies of zinc- (Cerjan Stefanovic et al., 2007), copper- (Logar et al., 2014), chromium- (Logar et al., 2006; Rozman, 2009) and arsenic-loaded (Siljeg et al., 2009) zeolitic tuffs are described elsewhere. The results of equilibrium studies on Croatian and Serbian zeolites made by us or other authors are also taken into account (Trgo and Perić, 2003; Peric et al., 2004; Trgo et al., 2005, 2006a, 2006b, 2008; Vukojević Medvidovic et al., 2006, 2007; Habuda-Stanic et al., 2007; Smiciklas et al., 2007; Rajic et al., 2009, 2010; Sljivic et al., 2009; Stojakovic et al., 2011a, 2011b). Discussion on future perspectives of these zeolites includes possible routes for immobilization of used zeolites, which only recently become a subject of research interests.

### 1.1. Chemical and phase composition of Serbian and Croatian clinoptilolite-rich tuffs

There are more than 10 deposits of natural zeolites in Croatia and Serbia, mostly with clinoptilolite-rich tuffs. The crystals of clinoptilolite accommodate two different systems of micropores interconnected within the lattice and capable of hosting exchangeable extra-framework cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and  $\text{H}_2\text{O}$  molecules. The two types of

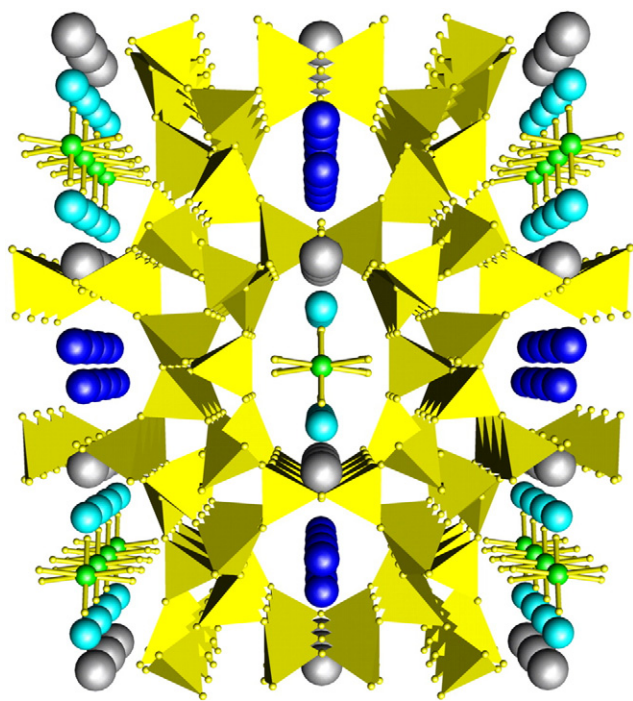


Fig. 1. Schematic presentation of clinoptilolite (HEU-type zeolite) structure ( $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra are yellow, Mg = green, Ca = blue, Na = turquoise; K = gray,  $\text{H}_2\text{O}$  = yellow spheres).

channels ( $7.6 \times 3.0$  and  $4.6 \times 3.3$  Å, respectively) are extended along the *c*-axis and the third type of channels ( $2.6 \times 4.7$  Å) along the *a*-axis (Fig. 1). The pore structure is the same as in the zeolite heulandite, which has a HEU-type topology (Godelitsas and Armbruster, 2003).

The phase composition of four natural zeolitic tuffs from Croatia and Serbia were determined by qualitative and quantitative phase analyses using X-ray powder diffraction (Logar et al., 2006; Cerjan Stefanovic et al., 2007). In all tuffs the presence of clinoptilolite, feldspar and quartz phases was determined (Table 1). The highest content of clinoptilolite was found in the Strezovce deposit. The examination of the diffraction patterns revealed also the presence of mica phases (biotite and muscovite) and mordenite or erionite in trace amounts (not included in Table 1). Some other trace phases, like  $\text{FeS}_2$  and  $\text{BaSO}_4$  were assumed in some samples based on the results of Energy Dispersive X-ray (EDXS) elemental analysis. The results of EDXS analyses, performed on polished clinoptilolite crystals of modified and unmodified zeolite tuffs, which were performed by following the procedure described in Cerjan Stefanovic et al., 2007, are collected in Table 2. Detailed metal-adsorption investigations were so far only performed on the tuffs from Donje Jesenje and Vranjska Banja deposits.

### 1.2. Cation exchangers – pretreatment with $\text{Na}^+$ or $\text{Ca}^{2+}$ solutions

The pretreatment of zeolites with  $\text{Na}^+$  or  $\text{Ca}^{2+}$  cations significantly enhances the uptake of all investigated metal cations in comparison with the unmodified zeolites in majority of the reported studies. This is mostly because the ion-exchange process is more controlled when only one type of extra-framework cations is present in zeolite, instead of four or more (e.g.  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  in clinoptilolite). The literature data about the concentration of  $\text{NaCl}$  or  $\text{CaCl}_2$  solutions used for an efficient zeolite pretreatment vary from 0.4 to 2 mol/L (Filippidis et al., 1996; Li et al., 1998; Langella et al., 2000; Vujakovic et al., 2003; Cerjan Stefanovic et al., 2007; Coruh, 2008; Davila-Jimenez et al., 2008; Oztas et al., 2008; Tarasevich et al., 2008; Han et al., 2009; Rozic et al., 2009; Elaiopoulos et al., 2010).

The Na-pretreatment of zeolite tuff from VB (in  $\text{NaCl}$  solution) revealed that  $\text{Na}^+$  replaced all  $\text{Ca}^{2+}$  ions, up to 80% of  $\text{K}^+$  and up to 60% of  $\text{Mg}^{2+}$  (Cerjan Stefanovic et al., 2007). A comparison of  $\text{Zn}^{2+}$  uptake in clinoptilolite crystals (in at. %) using unmodified or Na-treated forms showed that the uptake of zinc is up to 8-times better in Na-modified samples. The pretreatment of zeolite with  $\text{Ca}^{2+}$  ions ( $\text{CaCl}_2$  solution) revealed that its effect on the adsorption of zinc was less beneficial (up to 2-times better in Ca-treated form than in unmodified one). The  $\text{Ca}^{2+}$ -pretreatment also changes the mechanism of zinc adsorption compared to Na-pretreated or untreated zeolite.

### 1.3. Anion exchangers – pretreatment with $\text{Fe}^{3+}$ solutions

For the adsorption of anions, like chromates and arsenates, the pretreatment is a necessary step in zeolites activation, i.e. the change of zeolite surface charge from negative to positive enables electrostatic interactions with the anions. Several methods are used to achieve acceptable adsorption capacity for anions, such as acid treatment and iron-salt or surfactant functionalization (Li et al., 1998; Vujakovic et al., 2003; Cerjan Stefanovic et al., 2007; Coruh, 2008; Davila-Jimenez et al., 2008; Oztas et al., 2008; Tarasevich et al., 2008; Han et al., 2009; Rozic et al., 2009; Elaiopoulos et al., 2010). Acid treatment is aimed to achieve partial dealumination of the framework, so it is less negative, and also to produce defects on the surface that could act as active sites for anion bonding. These may however result in framework degradation or at least destabilization. In the case of surfactant functionalization, the anion adsorption capacity can be really high, when the concentration of the surfactant is well controlled so that a double layer of surfactant is formed on the zeolite surface. However, the use of surfactants might appear problematic when drinking water treatment is concerned, since the leaching of the surfactant from the zeolite surface is hard to control.

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