

## MECHANISM AND KINETICS OF PHOSPHATE REMOVAL FROM WATER MEDIA USING IRON(III)-MODIFIED CLINOPTILOLITE

*Iva Kaplanec*<sup>1</sup>, *Aleksander Rečnik*<sup>2</sup>, *Gregor Mali*<sup>3</sup>, *Nevenka Rajić*<sup>1</sup>

<sup>1</sup>Faculty of Technology and Metallurgy, 11000 Belgrade, Serbia

<sup>2</sup>Jožef Stefan Institute, SI-1001 Ljubljana, Slovenia

<sup>3</sup>Department of Inorganic Chemistry and Technology, National Institute of Chemistry,

SI-1001 Ljubljana, Slovenia

E-mail: ikaplanec@tmf.bg.ac.rs

### ABSTRACT

In this study natural clinoptilolite (Z) modified with Fe(III) was studied as an adsorbent for  $\text{H}_2\text{PO}_4^-$  ions present in water medium at pH=6.5. Iron(III)-modified clinoptilolite (FeZ) was proved to be an effective phosphate adsorbent, the sorption capacity at 298 K for different contact time (30 min-24h) varies from 86 to 42.5 % (for  $C_0 = 50 \text{ mg H}_2\text{PO}_4^- \text{ dm}^{-3}$  and  $C_0 = 400 \text{ mg H}_2\text{PO}_4^- \text{ dm}^{-3}$ ). The adsorption follows the pseudo-second-order kinetics and is in accordance with the Langmuir isotherm model. Langmuir constant ( $R_L$ ) values are in the range 0-1, characteristic of a favourable adsorption. The results of  $^{31}\text{P}$  static spin-echo mapping NMR showed that the phosphate adsorption on FeZ proceeds through electrostatic interactions and covalent bonding.

Keywords: clinoptilolite, modification, phosphate adsorption, kinetics.

### INTRODUCTION

Natural zeolites with their high surface area, porous structure, ion-exchange ability, and availability are good candidates for use in environmental remediation and restoration. Clinoptilolite has versatile application as adsorbent for different types of water pollutants such as ammonium and heavy metal cations<sup>[1]</sup>. In order to be suitable for adsorption of other species (anions or non-polar organics) clinoptilolite surface needs to be modified by inorganic or organic species with affinity towards that specific anions<sup>[2]</sup>. Phosphorus is an essential element for the water ecosystems. However, phosphate ions ( $\text{PO}_4^{3-}$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ ) are pollutants which in high concentration are responsible for lake and river eutrophication. In this study, we investigated mechanism of  $\text{H}_2\text{PO}_4^-$  adsorption onto a clinoptilolite-based adsorbent.

### EXPERIMENTAL

Adsorbent (FeZ) was prepared using clinoptilolite tuff (Z) obtained from Zeodigest (Semnan deposit, Iran). Tuff contains clinoptilolite as a major mineral phase (> 80 wt%), and quartz (< 7.5 wt%) and feldspars (< 13 wt%) as mineral impurities. Z was modified to the Fe(III)-containing form using a slightly modified procedure given by Siljeg *et al*<sup>[3]</sup>.

The crystallinity of FeZ was checked by a powder X-ray diffraction method (PXRD) using APD2000 Ital Structure. The size and morphology of the grains as well as the elemental analyses were studied by a scanning electron microscope JEOL JSM 6610LV. TEM studies were performed using a 200-kV TEM (JEM-2100 UHR, Jeol Inc., Tokyo, Japan) equipped with an ultra-high-resolution. Loss of ignition was determined by thermal analysis using a SDT Q-600 simultaneous DSC-TGA instrument (TA Instruments). The specific surface area was determined by the nitrogen sorption method using an  $\text{N}_2$ -BET automatic sorption analyzer

(Micrometrics ASAP 2020). A  $^{31}\text{P}$  static spin-echo mapping NMR measurement was carried out on a 300 MHz Varian Unity Inova spectrometer equipped with a standard 5 mm Varian MAS NMR probe.

The adsorption mechanism and kinetics were studied at water medium at 298, 308 and 318 K by a batch method using phosphate concentration of 50, 100, 200, 300 and 400 mg  $\text{H}_2\text{PO}_4^-$  for a contact period from 30 min to 24 h. The phosphate concentration was measured in filtrates using PhosVer 3 reagent and an UV–VIS spectrophotometer (Hach DR/2800).

## RESULTS AND DISCUSSION

Chemical composition of the clinoptilolite phase of Z and FeZ obtained by EDS analysis as well as water content of the samples obtained by TG analysis are given in Table 1. The Si/Al molar ratio is similar (about 4.4) for both samples confirming that the clinoptilolite lattice was not influenced by the modification process.

Table 1. Chemical composition (wt%) of the zeolite samples.

	Al	Si	Na	K	Ca	Fe	$\text{H}_2\text{O}^*$
Z	7.09	32.7	2.13	1.40	0.71	0.21	13.0
FeZ	4.87	22.3	2.56	1.45	0.72	18.6	15.8

\*Loss of ignition at 600 °C

PXRD analysis of Z, FeZ and phosphate-containing FeZ confirmed that the tuff contains clinoptilolite as the major mineral phase and that the modification and the phosphate adsorption did not influence the clinoptilolite crystallinity.

A detailed analysis performed by TEM showed that well crystalline clinoptilolite pseudo-hexagonal sheets are covered with flaky Fe(III)-precipitate in FeZ (Fig. 1) The electron diffraction pattern (Fig. 1b) showed that the Fe(III)-precipitate is amorphous. EDS analysis showed that phosphorus is present only at areas with a high amount of Fe(III)-precipitate (EDS-2).

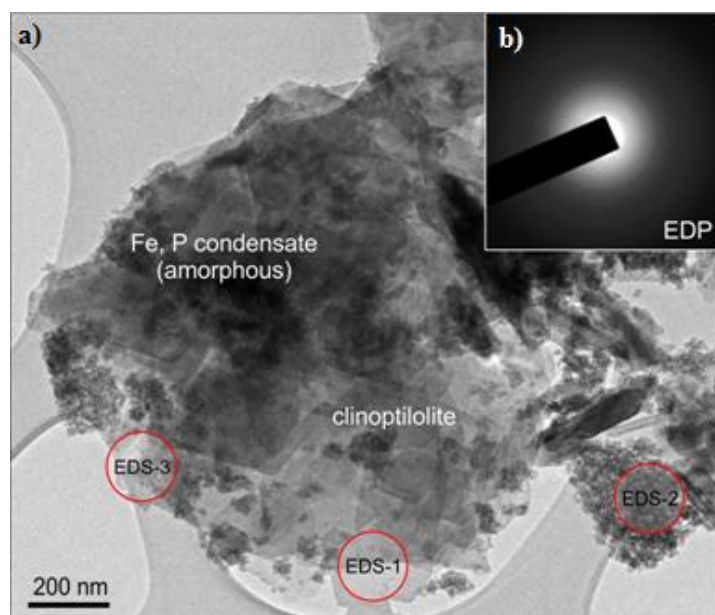


Figure 1. TEM study of FeZ sample: (a) Bright-field TEM image of clinoptilolite sheets covered with flaky Fe-rich precipitate. (b) EDP confirms that the precipitate is amorphous. Red circles show areas with different amount of Fe.

Adsorption isotherms at 298, 308 and 318 K showed that the adsorption capacity of FeZ increases both with temperature and with the initial phosphate concentration in solution. A significant increase of the adsorption capacity was evident at 318 K: from 5.0 mg  $P_{\text{ads}} \text{ g}^{-1}$  (for  $C_0 = 50 \text{ mg H}_2\text{PO}_4^- \text{ dm}^{-3}$ ) to 20.2 mg  $P_{\text{ads}} \text{ g}^{-1}$  (for  $C_0 = 400 \text{ mg H}_2\text{PO}_4^- \text{ dm}^{-3}$ ). Moreover, the equilibrium data were further analyzed using common applied isotherms and for the Langmuir was found to give the most satisfactory fit. The Langmuir dimensionless constants ( $R_L$ ) were in the 0-1 range indicating favourable phosphate adsorption on the FeZ.

Kinetics data for all studied temperatures agreed well with the pseudo-second-order model. The model gave for the equilibrium concentration of the adsorbed phosphate theoretical values in excellent agreement with the experimental data. Finally, in order to get a deeper insight into the phosphate - FeZ interaction,  $^{31}\text{P}$  NMR analysis was performed on the phosphate-containing FeZ. The  $^{31}\text{P}$  spin-echo-mapping NMR spectrum is given in Fig. 2. The sharpest peak with its maximum close to 0 ppm is not shifted by the hyperfine interaction and is ascribed to phosphate units that do not form covalent P–O–Fe bonds. All other signals are severely shifted indicating that the majority (about 85 %) of the phosphate adsorbed onto FeZ is covalently bound to the surface of Fe(III)-precipitate.

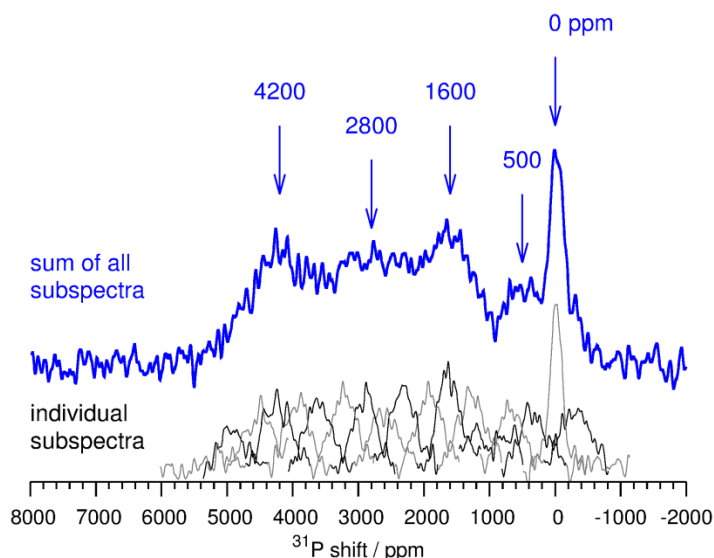


Figure 2. Spin-echo-mapping  $^{31}\text{P}$  NMR spectrum of P-FeZ.

## CONCLUSION

The obtained results show that Fe(III)-containing clinoptilolite is an efficient adsorbent for phosphate removal from water medium at pH~6.5. The adsorbent removes phosphate anions following the pseudo-second-order kinetics and the adsorption isotherm is in accordance with the Langmuir model. TEM and  $^{31}\text{P}$  NMR analyses showed that the adsorbent mainly bound phosphate through formation of covalent bonds between Fe(III) and oxygen atoms from phosphate groups.

## ACKNOWLEDGEMENT

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