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Editors
Tatjana Antonić Jelić
Josip Bronić

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PHOSPHATE ADSORPTION FROM AQUEOUS SOLUTION USING IRON-MODIFIED CLINOPTILOLITE

Jelena Pavlović¹, Iva Kaplanec², Slavica Lazarević², Nevenka Rajić²

¹University of Belgrade, Innovation centre of the Faculty of Technology and Metallurgy, 11000 Belgrade, Serbia

²University of Belgrade, Faculty of Technology and Metallurgy, 11000 Belgrade, Serbia

E-mail: jelena.pavlovic@tmf.bg.ac.rs

ABSTRACT

In this work a clinoptilolite-rich Iranian zeolitic tuff was modified by iron-oxide in order to obtain an adsorbent for removal of phosphate ions from water media. The iron-modified zeolite efficiently adsorbs phosphate at 25 °C increasing the adsorption capacity with initial phosphate concentration. Adsorption follows the pseudo-second-order kinetics and it is in accordance with the Langmuir isotherm model.

Keywords: clinoptilolite, adsorption, phosphate, iron-modified zeolite

INTRODUCTION

Phosphate is one of the major pollutants in water ecosystems. High phosphate concentration in water is responsible for its eutrophication causing that many aquatic systems are severely degraded and need to be restored.

Natural zeolites have versatile application as adsorbents for different types of water pollutants [1]. Since negatively charged aluminosilicate lattice of zeolites does not attract anions, the zeolite surface need to be modified by inorganic or organic species with affinity towards specific anions [2, 3]. In this study, a natural clinoptilolite was modified with iron oxide by a simple procedure and adsorption capacity of the obtained adsorbent was tested for different phosphate concentration at 25 °C.

EXPERIMENTAL

Preparation of the iron-modified zeolite (FeZ): Zeolitic tuff (Z) from Iran (Semnan mine) was used as the starting material. The chemical composition of the clinoptilolite phase determined by an EDS/SEM analysis and expressed by the oxide wt. % is as follows: SiO₂ – 70.08, Al₂O₃ – 11.72, Na₂O – 4.23, K₂O – 5.42, CaO – 0.02; loss of ignition – 8.0 wt. %.

Zeolite was modified by the previously published procedure using Fe₂(SO₄)₃ [2]. The suspension was stirred by a magnetic stirrer over night at 70 °C. The obtained Fe-containing zeolite (FeZ) was separated by centrifugation, washed with deionized water until a negative reaction for sulfate ions and finally, dried at 90 °C to a constant mass. Fe content in FeZ (2.30 wt.%) was determined in solution by AAS (Spectra AA 55B, Varian).

Adsorbent characterization: The crystallinity of the zeolite samples was checked by a powder X-ray diffraction method (PXRD) using APD2000 Ital Structure. Texture of the FeZ surface was studied by a transmission electron microscopy using a 200 kV TEM (JEM-2100). Loss of ignition was determined by thermal analysis using a simultaneous TG/DTG/DTA (SDT Q600, TA Instruments). The samples were heated in synthetic air (100 ml min⁻¹) in the temperature range 20-1000 °C, at a heating rate of 10 °C min⁻¹. The specific surface area and porosity were determined by the N₂-BET adsorption method (ASAP 2020, Micromeritics).

Phosphate adsorption experiments: The adsorption was studied at 25 °C by a batch method using four different initial concentrations: 50, 100, 200 and 300 mg PO₄³⁻ dm⁻³. All solutions were prepared by dissolving an appropriate amount of KH₂PO₄ (Aldrich, p.a.) in deionized

water. 1.0 g of FeZ was suspended in 100 cm³ of the appropriate concentration of phosphate solution and left under shaking in a thermostated water bath at 25 °C (Memmert, WBE 22,) for contact times from 30 min to 1440 min. The phosphate concentration was measured in filtrates by a standard procedure using PhosVer 3 reagent and an UV–VIS spectrophotometer (Hach DR/2800).

RESULTS AND DISCUSSION

A qualitative PXRD analysis showed that the tuff contains about 80 wt.% of clinoptilolite. Quartz and feldspar are major mineral impurities with the strongest diffractions at $2\theta = 26.63^\circ$ and 27.64° , respectively. The PXRD patterns of Z and FeZ given in Fig. 1 indicate that the modification does not influence the clinoptilolite crystallinity. At TEM image (Fig. 2) the modified clinoptilolite appears with well-defined crystal faces which are covered with a flaky precipitate. Electron diffraction pattern (Fig. 2b) shows that the diffraction rings of the precipitate correspond to FeO with wüstite structure.

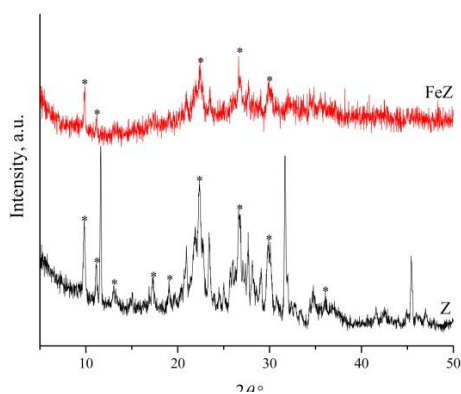


Figure 1. PXRD patterns of the zeolite samples. Diffractions marked by asterisks correspond to clinoptilolite.

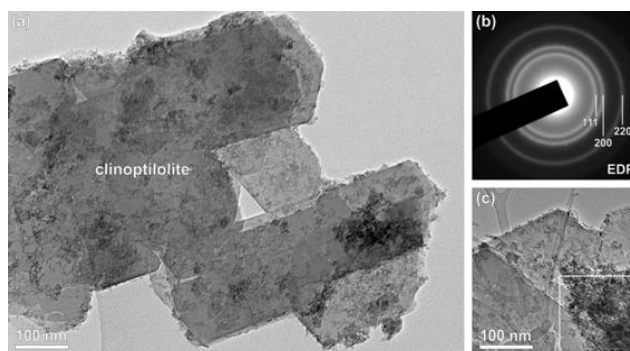


Figure 2. TEM image of the clinoptilolite crystals covered by flakes of iron(II) oxide particles. Electron diffraction pattern (EDP) in Figure (b) was recorded from area marked in Figure (c).

BET measurements show that the modification significantly changes porous characteristics. The specific surface area of NZ and FeZ were 28.6 and 140.3 m² g⁻¹, respectively. Total pore volume of FeZ was also increased in comparison to NZ, which is explained by the formation of a secondary pore structure during the precipitation of the iron(II) oxide at the clinoptilolite phase [2, 4].

The results of adsorption experiments for different initial concentration of phosphates are presented in Fig. 3a. The adsorption capacity of FeZ depends on initial phosphate concentration increasing from 4.95 mg g⁻¹ ($C_0 = 50 \text{ mg dm}^{-3}$) to 24.85 mg g⁻¹ ($C_0 = 300 \text{ mg g}^{-1}$). For initial phosphate concentration of 50 and 100 mg dm⁻³ the equilibrium was achieved for less than 60 min. For higher concentrations (200 and 300 mg dm⁻³) it was accomplished for approx. 240 min.

Two kinetic models (Lagergren's first-order rate and pseudo-second-order rate equations) were applied in order to describe the adsorption kinetics. The obtained results agree well with the pseudo-second-order model (Fig. 3b) which is confirmed by values of R^2 , which is very close to 1 (Table 1). Also, the theoretical values of parameter q_e agree well with the experimental values.

The effect of diffusion on the phosphate adsorption was also examined by Weber-Morris model (not shown). The results indicated that the intraparticle diffusion is not rate-limiting step.

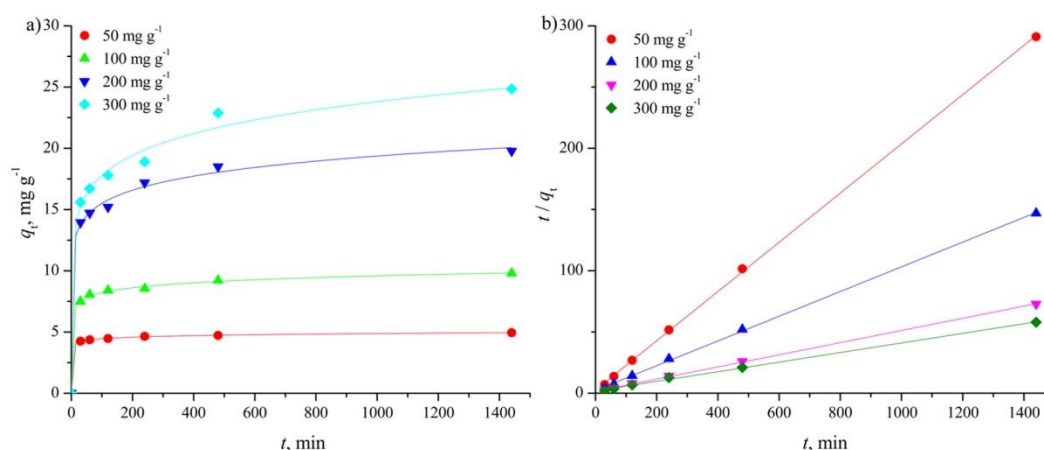


Figure 3. a) Phosphate adsorption kinetics for different initial concentration; b) Pseudo-second order kinetic model applied to the adsorption data; q_t is the amount of the adsorbed PO_4^{3-} (mg per 1 g of FeZ) after time t .

Table 1. Pseudo-second order kinetic parameter for the phosphate adsorption on the FeZ.

| $C_0, \text{mg dm}^{-3}$ | $q_e, \text{mg g}^{-1}$ | $k_2, \text{g mg}^{-1} \text{h}^{-1}$ | R^2 |
|--------------------------|-------------------------|---------------------------------------|--------|
| 50 | 4.98 | 0.9267 | 0.9999 |
| 100 | 9.91 | 0.2685 | 0.9998 |
| 200 | 20.12 | 0.0987 | 0.9998 |
| 300 | 25.52 | 0.0503 | 0.9991 |

The adsorption data at 25 °C were further analyzed by four adsorption isotherms including Langmuir, Freundlich, Temkin and Dubinin-Redushkevich (D-R) models (Table 2).

Table 2. Isotherms parameters of the phosphate adsorption on FeZ at 25°C.

| Isotherm | Equation | Parameters |
|---|---|-----------------------|
| Langmuir | $C_e/q_e = (1/Q_0) \cdot C_e + 1/Q_0 \cdot b$ | |
| $Q_0, \text{mg g}^{-1}$ | | 25.63 |
| $b, \text{dm}^3 \text{mg}$ | | 0.46 |
| R^2 | | 0.9965 |
| Freundlich | $\log q_e = \log K_f + 1/n \log C_e$ | |
| $K_f, \text{mg g}^{-1}(\text{dm}^3 \text{mg}^{-1})^{1/n}$ | | 8.52 |
| n | | 3.64 |
| R^2 | | 0.9834 |
| Temkin | $q_e = B \ln A + B \ln C_e$ | |
| $A, \text{dm}^3 \text{g}^{-1}$ | | 22.44 |
| B | | 3.31 |
| R^2 | | 0.9527 |
| D-R | $\ln q_e = \ln q_m - \beta \varepsilon^2$ | |
| $\beta, \text{mol}^2 \text{J}^{-2}$ | | 4.07×10^{-8} |
| $q_m, \text{mg g}^{-1}$ | | 17.06 |
| $E, \text{kJ mol}^{-1}$ | | 3.50 |
| R^2 | | 0.8484 |

C_e – the equilibrium phosphate concentration in equilibrium solution; q_e – the amount of phosphate adsorbed on the FeZ; Q_0 – maximum amount of adsorbate per unit mass of adsorbent; b – Langmuir constant related to sorption energy; K_f , n – Freundlich constants; A , B – Temkin constants; β – constant of the sorption energy; q_m – maximum sorption capacity; ε – Polanyi potential; E – mean energy of sorption.

The adsorption is best described by the Langmuir equation (Fig. 4a). The dimensionless equilibrium parameter (separation factor) R_L is in the range 0-1 suggesting that the phosphate adsorption on the FeZ is a favorable process. It is evident that R_L values approaches zero with initial concentrations higher than $100 \text{ mg PO}_4^{3-} \text{ dm}^{-3}$ (Fig. 4b) which indicates that the adsorption is less favorable at higher concentration.

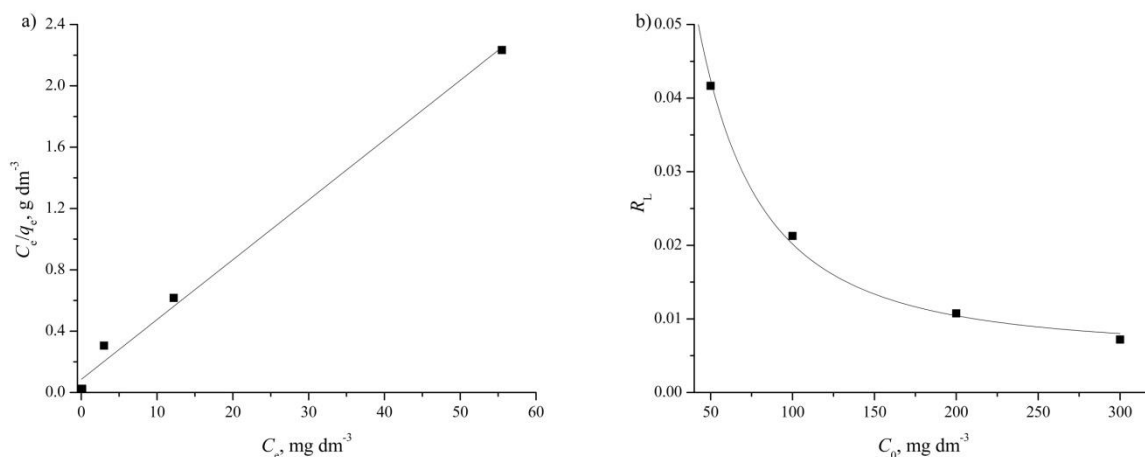


Figure 4. a) Linear plot of Langmuir isotherm; b) variation of separation factor (R_L) with initial phosphate concentrations at 25 °C.

CONCLUSION

The obtained results show that the natural clinoptilolite can be converted into an adsorbent for phosphate ions by a simple modification using an Fe(III) salt. During the modification a new, flake-like assemblies of FeO with wüstite crystal structure were formed and covered the surface of clinoptilolite crystals. The modified zeolite adsorbs phosphate anions at 25 °C following the pseudo-second-order kinetics and the adsorption isotherm is in accordance with the Langmuir model. Taking all into account, it can be concluded that iron-modified clinoptilolite is perspective adsorbent for phosphate removal from water media.

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