

## SELENIUM REMOVAL FROM AQUEOUS MEDIUM BY IRON-MODIFIED NATURAL CLINOPTILOLITE AND A POSSIBLE USE OF THE SELENIUM-LOADED CLINOPTILOLITE

Sanja Jevtic<sup>1\*</sup>, Jelena Pavlovic<sup>1</sup>, Danka Matijasevic<sup>2</sup>, Iztok Arcon<sup>3,4</sup>,  
Miomir Niksic<sup>2</sup>, Nevenka Rajic<sup>1</sup>

<sup>1</sup>Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia

<sup>2</sup>Faculty of Agriculture, Institute of Food Technology, University of Belgrade, Nemanjina 6,  
11080 Belgrade, Serbia

<sup>3</sup>University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia

<sup>4</sup>Institute Jozef Stefan, Jamova 39, 1000 Ljubljana, Slovenia

e-mail: sanja@tmf.bg.ac.rs

### ABSTRACT

In this study, iron(III)-modified natural zeolite tuff (Fe-CLI) from the Serbian deposit Zlatokop has been investigated as an adsorbent for the selenium oxyanions. The results have shown that the adsorption capacity of Fe-CLI for both Se(IV) and Se(VI) depends on pH and decreases with increasing pH-value. The adsorption affinity of Fe-CLI was found to be higher for Se(IV) than for Se(VI). The kinetic data follow the pseudo-second-order model and the obtained parameters  $k$  indicate that the rates of adsorption and desorption are higher for selenate ion. EXAFS and XANES analyses revealed that selenium is bound in the form of oxo-complexes to Fe(III) cations at the zeolite surface. The obtained Se-containing zeolite samples were tested as soil supplements for the cultivation of *Pleurotus ostreatus* mushroom. The mushrooms extracted inorganic Se from the Se-containing zeolite transforming it to a more valuable organically bound form.

Keywords: clinoptilolite, EXAFS, XANES, selenium, mushroom.

### INTRODUCTION

Selenium is an essential element in animal and human nutrition. On the other hand, it is toxic at slightly higher concentrations than nutritional levels [1]. Selenite ( $\text{SeO}_3^{2-}$ ) and selenate ( $\text{SeO}_4^{2-}$ ) are the dominant forms of selenium existing in aqueous systems. Studies of the  $\text{SeO}_3^{2-}$  and  $\text{SeO}_4^{2-}$  adsorption on a variety of mineral surfaces led to a general conclusion that  $\text{SeO}_4^{2-}$  is relatively weakly bonded to mineral surfaces, in contrast to  $\text{SeO}_3^{2-}$  which forms strong complex species on the surfaces [2]. It has also been established that natural iron oxide minerals, such as magnetite, goethite and hematite, exhibit strong adsorption affinity to selenium oxyanions forming stable Se-Fe complexes [3,4].

As a non-toxic, ecological and available material with unique physico-chemical properties, natural clinoptilolite has been considered as a carrier of fertilizer in plant production, due to its possibility to gradually release nutrients [5]. Moreover, the use of selenium fertilizers is strongly encouraged for soils with low Se levels. Consumption of plants grown on this kind of soils has been regarded as safer than a direct ingestion of inorganic Se [6]. Also, Se-enriched mushrooms have been reported to be a good source of selenium [7]. Taking this into account, the aim of this study was to investigate the possibility of selenite and selenate adsorption on a Fe(III)-modified natural clinoptilolite, and the adsorption/desorption mechanism, as well as the possibility of use of the Se-containing zeolitic tuff as a supplement for cultivation of *Pleurotus ostreatus* mushroom.

## EXPERIMENTAL

Zeolitic tuff used in this work was obtained from Zlatokop deposit in Vranjska Banja, Serbia. CLI was previously converted to Na-rich form (Na-CLI) by treating with 2 M NaCl solution. The Fe(III)-modified zeolite (Fe-CLI) was obtained according to the method described by Siljeg *et al.* [8]. The Fe-CLI sample was suspended in aqueous solution of Na<sub>2</sub>SeO<sub>3</sub> and Na<sub>2</sub>SeO<sub>4</sub>. The starting pH values were adjusted using solutions of NaOH or HCl. The suspensions were stirred for different times (5 min–24 h) at room temperature. In both experiments, the solid phase was separated by centrifugation and dried at 90 °C. The samples obtained after the treatment for 24 h in solutions of Na<sub>2</sub>SeO<sub>3</sub> (Se<sub>IV</sub>-CLI) and Na<sub>2</sub>SeO<sub>4</sub> (Se<sub>VI</sub>-CLI) were used for selenium desorption experiments in phosphate buffer (pH 7.0). Additional experiment was performed for testing the adsorption of Se(IV) and Se(VI) on Fe-CLI as a function of pH in the range 3–9. The initial and the equilibrium selenium concentrations in supernatants were determined by atomic absorption spectrometry (AAS).

Pure culture of *P. ostreatus* was grown in Petri dishes with malt agar (HiMedia) and incubated at 25 °C in the dark for 9 days. Mushroom mycelia were then transferred to sterile jars filled with wheat grains and CaCO<sub>3</sub> and incubated at 25 °C in the dark for 2-3 weeks in accord with a standard procedure for the preparation of seeds for bags inoculation [9]. The autoclavable, gas-permeable bags filled with wheat straw (control bags) or with wheat straw and Se<sub>IV</sub>-CLI or Se<sub>VI</sub>-CLI in the concentration of 75 mg/kg were cultivated at 20 °C during four weeks. Dried samples of mushrooms (approx. 0.5 g) were digested by a standard procedure of Milestone and selenium concentrations were determined using AAS.

## RESULTS AND DISCUSSION

For the characterization of all obtained samples different techniques have been used. BET measurements showed that the Fe(III)-modification of the natural zeolite significantly increased its surface area from 42 to 117 m<sup>2</sup>g<sup>-1</sup>. The increase has been explained by the presence of both the surface iron complexes and amorphous iron oxide species [10]. Elemental EDS analysis yielded a high amount of Fe(III) in the Fe(III)-modified zeolite (5.66%) and showed that Se content in the Se-containing zeolite samples depends on the Se oxidation number. Se(IV) is loaded at a higher amount than Se(VI).

The XRPD analysis confirmed that the crystal structure of the clinoptilolite phase is preserved after the Fe(III) modification and the Se-loading. The TG/DTG curves (Fig. 1) showed that the total weight loss increased with the Fe(III) modification and Se adsorption. Differences in the position of DTG maxima on thermograms in the temperature range from 400 to 500 °C indicate that dehydration process proceeds in a different manner after the Se adsorption.

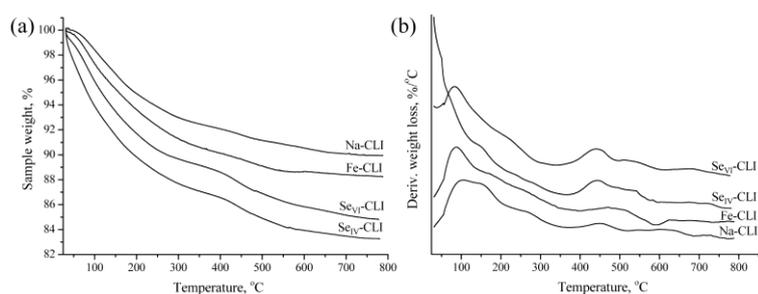


Figure 1. TG (a) and DTG curves (b) of Na-CLI, Fe-CLI, Se<sub>IV</sub>-CLI and Se<sub>VI</sub>-CLI. This is explained by interactions of selenite and selenate ions with the Fe(III)-modified surfaces.

Adsorption of Se(IV) and Se(VI) decreases as pH increases (Fig. 2a). It is also evident that Fe-CLI shows a higher efficiency for adsorption of selenite than for selenate at all investigated pH values. Moreover, Fig. 2b shows that the adsorption equilibrium is established faster for the system with selenate than for selenite. In contrast, the equilibrium amount of Se(IV) is found to be higher (21 mg Se g<sup>-1</sup>) than for Se(VI) (17 mg Se g<sup>-1</sup>).

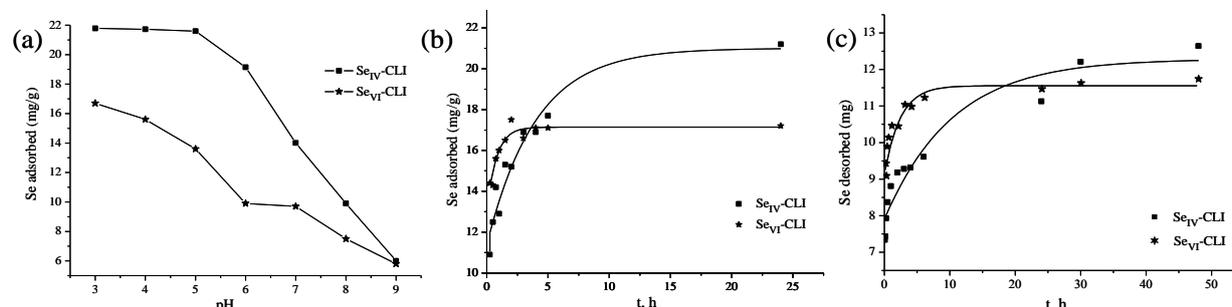


Figure 2. (a) Adsorption of Se(IV) and Se(VI) on Fe-CLI as a function of pH; (b) adsorbed amount of Se(IV) and Se(VI) on the Fe-CLI in time, and (c) desorbed amount of selenium from Se<sub>IV</sub>-CLI and Se<sub>VI</sub>-CLI samples in time.

Kinetic results of the Se desorption from Se-CLI show a similar trend to that observed for the adsorption (Fig. 2c). Whereas about 10 mg of Se is desorbed from the Se(VI)-containing sample during 2 h, desorption of the equivalent amount from the Se(IV)-containing sample requires about 6 h. This could indicate that Se(VI) ions form a more labile complex with the Fe(III)-modified zeolite surface than Se(IV) ions.

Table 1. Pseudo-second-order kinetic parameters obtained for the selenite and selenate ions adsorption on the iron(III)-modified zeolite and the desorption from Se<sub>IV</sub>-CLI and Se<sub>VI</sub>-CLI.

|            | Sample                | $q_e$ [mg g <sup>-1</sup> ] | $k$ [g mg <sup>-1</sup> h <sup>-1</sup> ] | $R^2$  |
|------------|-----------------------|-----------------------------|---|--------|
| Adsorption | Se <sub>IV</sub> -CLI | 21.6                        | 0.0685                                    | 0.9991 |
|            | Se <sub>VI</sub> -CLI | 17.4                        | 0.777                                     | 0.9999 |
| Desorption | Se <sub>IV</sub> -CLI | 12.5                        | 0.105                                     | 0.9982 |
|            | Se <sub>VI</sub> -CLI | 11.7                        | 0.528                                     | 0.9999 |

Adsorption and desorption kinetic data were further analyzed using two reaction-based kinetic models, Lagergren's first-order rate and pseudo-second-order rate equations [11]. It was found that the obtained results were in a good agreement ( $R^2 > 0.99$ ) with the second reaction-based model. Kinetic parameters are listed in Table 1.

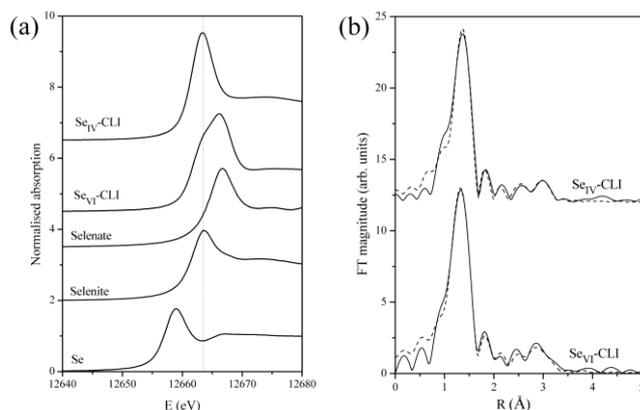


Figure 3. (a) Se K-edge XANES of Se-containing zeolite samples Se<sub>IV</sub>-CLI and Se<sub>VI</sub>-CLI together with reference Se compounds (selenite, selenate and elemental Se); (b) Fourier transforms of k<sup>3</sup>-weighted Se K-edge EXAFS spectra of Se<sub>IV</sub>-CLI and Se<sub>VI</sub>-CLI samples (experiment: solid line; best fit EXAFS model: dashed line).

EXAFS and XANES were used to elucidate Se interactions with the zeolite surface. XANES spectra (Fig. 3a) show that Se<sub>IV</sub>-CLI contains selenium in a four-valent form whereas for Se<sub>VI</sub>-CLI sample 63% of Se(IV) and

37% of Se(VI) have been found. The Se K-edge EXAFS analysis (Fig. 3b) gave an insight into local structure of Se atoms. The results suggest that the Se species in both samples are bound exclusively to Fe(III) cations present on the zeolite surface.

The possibility of use of the Se-containing zeolitic tuff as a supplement for the cultivation of *P. ostreatus* has been finally examined (Fig. 4). It has been known that the mushrooms exhibit an ability to convert the inorganic Se to a more valuable organic form [12]. Chemical analysis of the dried mushrooms showed that the amount of sorbed and organically transformed Se is higher ( $>200 \mu\text{g g}^{-1}$ ) than in a control system ( $0.071 \mu\text{g g}^{-1}$ ). The mushrooms cultivated on the substrate with Se<sub>IV</sub>-CLI contained  $211 \mu\text{g Se g}^{-1}$  whereas that ones growth on the substrate had  $254 \mu\text{g Se g}^{-1}$ . It can be concluded that the transformation of inorganic Se to organically bound one depends on the oxidation number of Se present in the used substrate.



Figure 4. Growth of *P. ostreatus* on the substrate in the presence of the selenium-containing zeolite.

## CONCLUSIONS

This study showed that the iron-modified natural zeolite is a good adsorbent for Se ions present in an aqueous medium. The adsorption efficiency depends on the pH and oxidation number of Se. The adsorption and desorption kinetics are in excellent agreement with the pseudo-second-order model. EXAFS and XANES analyses show that Se is coordinated in a form of oxo-complexes to Fe(III) cations on the zeolite surface. The Se-containing zeolite can be used as a supplement for the cultivation of *P. ostreatus* and production of Se-enriched mushrooms.

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