



Proceedings of
XVI BALKAN MINERAL PROCESSING CONGRESS
Belgrade, Serbia, June 17-19, 2015



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Nadežda Čalić, Ljubiša Andrić,
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DEVELOPMENT OF HYBRID ORGANIC-INORGANIC (BIO)SORBENTS FOR Pb(II) REMOVAL

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Promising new removal of pollutants and the improvement of existing ones make up development of new sorbents with improved sorbing properties. With this aim, this research include the development of hybrid organic-inorganic and combined (bio)sorbents. The use of biomass originated materials for cleansing of wastewaters is extensively studied. Removal of lead ions from aqueous solutions was examined with different materials: *Myriophyllum spicatum*, peach pits, modified apricot pits, corn cobs, bentonite, zeolite, apatite. Two materials organic and inorganic with best characteristic – capacities of removal Pb(II) were selected for development of combined (bio)sorbents. Selected mixture of 75% *M. spicatum* and 25% bentonite showed lead binding capacity of 45 mg/g. The main effective biding sites were identified by FTIR spectral comparison of the pure and lead (bio)sorbed material: *M. spicatum*, bentonite and their best mixture 75%MS-25%B. Our research is applied to the expansion of ways of updating vegetative waste products and mineral materials with the purpose of improving their ability to selectively remove ions of heavy metals and application of this hybrid organic-inorganic - (bio)sorbents is innovative, simple and low cost.

Key words: hybrid organic-inorganic (bio)sorbents, sorption, lead, FTIR

INTRODUCTION

Lead is dangerous to humans, plants and animals. The lead poisoning can cause different health problems such as: hypertension, nephritis, abdominal pain, constipation, cramps, nausea, vomiting, behavioral changes, brain damage. Main lead pollution has been through in the electroplating, manufacture of storage batteries, painting pigments, ammunition, solder, plumbing fixtures, automobiles, cable coverings, radioactivity shields, caulking and bearings (Ake, et al. 2001, Tunali et al. 2006).

Conventional methods for heavy metals removal from wastewaters, such as: coagulation-precipitation, ion exchange, electrolytic extraction, filtration, complexation, reverse osmosis, evaporation, sorption, flotation, etc., have certain limitations that are described through high operational cost, high energy requirements, sensitive operation conditions and secondary sludge production (Yan et al. 2010). With the aim of decreasing the cost of treatment process, the scientists have been afforded to investigate inexpensive, efficient and easily available sorbents. In this manner, biological-

based materials and natural clay materials such as bentonite have been used to remove lead(II) ions from aqueous solutions by sorption (Ozcan, 2009).

Many materials originate from nature present adsorption and ion exchange properties. The majority of these natural ion-exchange materials consist of crystalline aluminosilicates with cation exchange properties, although certain aluminosilicates may also act as anion exchangers. Some of them are zeolites, apatite, bentonite or diatomite. Many of these have been used to eliminate heavy metals from wastewater (Mellah and Chegrouche, 1997, Ulmanu et al. 1996).

Biosorption can be simply defined as the removal of substances from solution by biological material. Such matters can be organic and inorganic, and in gaseous, soluble or insoluble forms. Biosorption is a physico-chemical process and includes different mechanisms: absorption, ion exchange, surface complexation, precipitation, diffusion, chelation (Gadd, 2009).

A number of analytical techniques that have been used to study the biosorption and

adsorption process. These techniques may harmonize to each other in giving insights into the mechanisms of (bio)sorption (Park et al. 2010). The Fourier Transform Infrared (FTIR) spectroscopy is a significant analytical technique which detects the vibration characteristics of chemical functional groups in a molecule. On interaction of an infrared light with the material, chemical bonds will stretch, contract and bend. As a result, chemical functional group tends to absorb infrared radiation in a specific wavelength range apart from the structure of the rest of the molecule (Nadeem et al. 2008).

MATERIALS AND METHODS

Preparation of the biomass, aluminosilicate minerals and apatite

Samples of freshly harvested *Myriophyllum spicatum* were taken from the artificial Sava Lake, Belgrade, Serbia. The fresh plant has been harvested with a mechanical underwater harvester. With mowing, the amount of unwanted aquatic weed from lake was significantly reduced (approximately 350-400 m³ per harvesting cycle) (Milojković, Mihajlović, et al. 2014). For cleaning impurities from freshly harvested *M. spicatum*, plant was washed with tap water once and then 3 times with distilled water. After cleaning process, plant was dried on room temperature and then on 35 - 40 °C. Dried samples of *M. spicatum* was crushed and sieved to give a particle size of less than 0.2 mm.

Agricultural waste material - peach and apricot stones were obtained from "Vino Župa" Company from Aleksandrovac - Republic of Serbia, where it has been disposed as by-product waste from their Juice Factory. The seeds were removed from stones, so for the experiment described, only hard stone part was taken. Apricot shells were modified with base. Corn cobs were obtained from local farm near the Belgrade, Serbia.

Samples were milled (KHD Humbolt Wedag AG) and then dried at 60° C until constant weight.

Origin of used raw bentonite is Šipovo, Republika Srpska, Bosnia and Herzegovina and zeolite Vranjska Banja, Serbia. Raw bentonite was crushed and sieved to give a particle size of less than 100 μm.

Batch experiments

The batch experiments were carried out in 100 ml Erlenmeyer flasks with 50 ml of lead solution. The flasks were stirred on Heidolph unimax 1010 orbital shaker at room temperature. Initial Pb(II) concentration was 100 mg/l. Amount of used (bio)sorbent was 0.1 g or solid-liquid ratio 2g/l (1:500). Using a precise pH meter (Sension MM340), the pH value was adjusted using 0.1 M HNO₃ or 0.1 M NaOH (analytical grade). The flasks were shaken at 250 rpm for 120 min at pH around 5. The analytical measurements of Pb(II) concentration were performed using atomic absorption spectrometry (Perking Elmer AAnalyst 300).

The amount of Pb(II) adsorbed by the biomass was calculated using Equation 1:

$$q = \frac{V(C_i - C_e)}{m} \quad [1]$$

where q (mg/g) is the amount of Pb(II) adsorbed by *M. spicatum* or bentonite; C_i and C_e are the initial and equilibrium metal concentrations (mg/l), V is the volume of Pb(II) solution (l), and m is the mass of the sorbent (g). Metal removal efficiency (R) is calculated with equation 2:

$$R = \frac{C_i - C_e}{C_i} \cdot 100 \quad [2]$$

Characterization of materials

FTIR-ATR (Fourier transform infrared attenuated total reflection spectroscopy) spectroscopic analyses were carried out at room temperature using a Thermo Fisher Scientific Nicolet IS-50 spectrophotometer in the spectral range of 4000 to 400 cm⁻¹, with a resolution of 4 cm⁻¹. The datasets were averaged over 32 scans. FTIR-ATR spectroscopy was used to identify vibration frequency changes in *M. spicatum*, bentonite and their best mixture before and after contact with Pb(II) ions. To get the information specific to the group, and also on the interaction of the group with other parts of the molecule and on the spatial properties of the group by FTIR, the (bio)sorption study for the Pb(II) ions were carried out holding temperature 25°C, (bio)sorbent loading 2 g/l and initial lead ions concentration 100 mg/l. The adsorption equilibrium experiments for FTIR study were carried out for 2 h at 250 rpm at optimum pH=5.0. After equilibrium the lead loaded (bio)sorbents was filtered. Samples of materials treated with Pb(II) were dried at 35-40°C in a drier.

RESULTS AND DISCUSSION

Best lead uptake capacity q and degree of lead removal showed *M. spicatum* and bentonite (Fig.1).

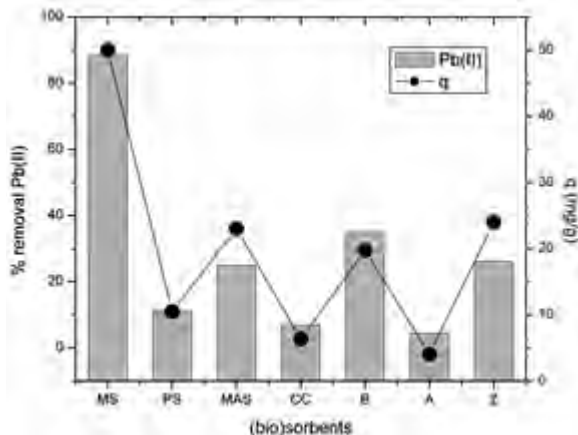


Figure 1, Metal – lead uptake capacity q and degree of lead removal for different (bio)sorbents: MS-*Myriophyllum spicatum*, PS-peach stones, MAS-modified apricot stones, CC-corn cobs, B- bentonite, A-apatite, Z-zeolite (contact time 2 h, Pb(II) initial conc. 100 mg/l, (bio)sorbent dosage 0.1g, agitation rate 250 r/min)

Best lead uptake capacity q and degree of lead removal showed *M. spicatum* and bentonite (Fig.1).

In next step of experiments were investigated different mixtures of *M. spicatum* and bentonite. *M. spicatum*, bentonite and their mixtures for lead uptake capacities q and degree of Pb(II) removal are presented in Figure 2. Gained results of *M. spicatum* capacities q are similar with investigation of Milojković et al., 2014., also they used fresh tissue of *M. spicatum* not dry. For further investigation the mixture of 75% of *M. spicatum* and 25% of bentonite was selected (0.075 g *M. spicatum* and 0.025 g bentonite) This mixture (75%MS-25%B) has capacity q of 45 mg/g of lead ions.

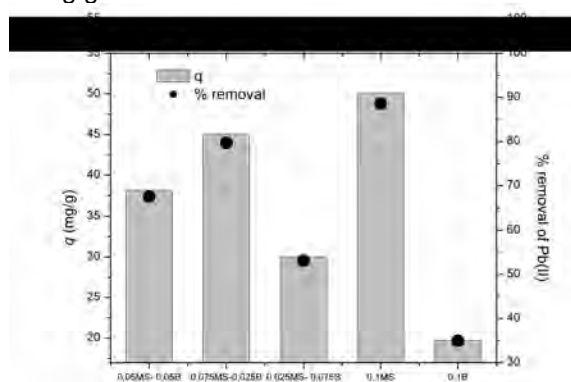


Figure 2, Metal – lead uptake capacity q and degree of lead removal (contact time 2 h, Pb(II) initial conc. 100 mg/l, (bio)sorbent dosage 0.1g, agitation rate 250 r/min)

(Bio)sorbent characterization

FTIR spectroscopy was used to determine the frequency changes in the functional groups in the (bio)sorbent materials after treatment Pb(II). FTIR-ATR spectroscopy was applied on selected mixture (75%MS-25%B) (Figure 3 and 4).

Although bentonite participates with 25% in the selected mixture (75%MS-25%B) there are great differences in FTIR spectra between pure *M. spicatum* and mixture. FTIR spectra of these materials are presented on Figure 4.

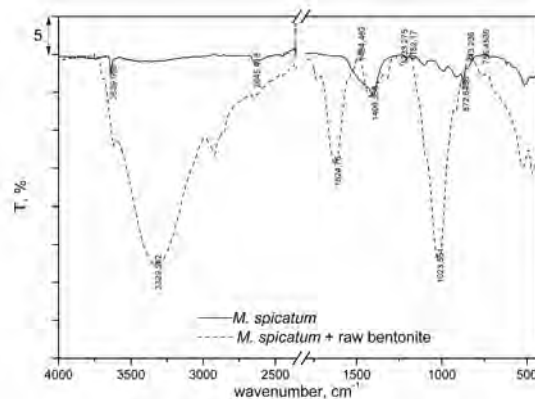


Figure 3, FTIR spectra of *M. spicatum* (washed, dried, particle size less than 0.2 mm) and mixture (75%MS-25%B) of *M. spicatum* and raw bentonite

FTIR spectra in the range of 4000–400 cm^{-1} for selected mixture (75%MS-25%B) and mixture (75%MS-25%B) treated Pb(II) are shown in Figure 5. Shift of broad shape from 3329.5 to 3377.8 cm^{-1} are attributed due to alcohol group and disappearance of peaks at 2990.2 and 2918.8 cm^{-1} on FTIR spectra of treated mixture indicates the presence of carboxylate group. Shift of band of carbonyl bond (C=O stretching band) (Yan et al. 2010) from 1624.8 to 1629.6 cm^{-1} . Comparing FTIR spectra of untreated and treated mixture there are loss of band at 1484.5, 1416.8, 1386.5, 1320.4 carboxylate group and 1285.2 1234.8 and 1182.2 cm^{-1} CH_2 deformation vibration of long aliphatic (Socrates, 2001). Hydroxyl C-OH band at around 1100-1000 cm^{-1} , where can be observed changes in spectra after treatment with Pb(II) ions shifted from 1023.6 to

lower at 992.7cm^{-1} . Transfer of peaks from 843.2 to 810.1 , and 729.3 to 719.8cm^{-1} may be assigned to aromatic systems (Socrates, 2001).

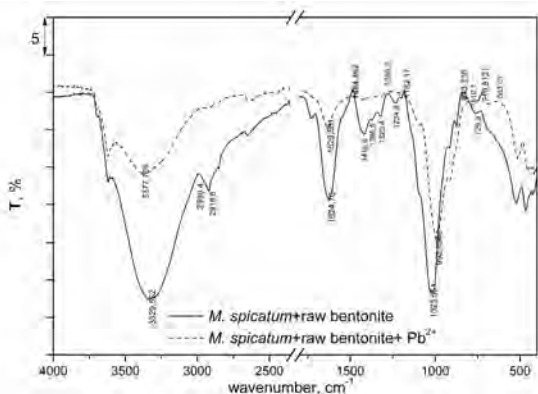


Figure 4, FTIR spectra selected mixture (75%MS-25%B) before and after Pb(II) sorption (contact time 120 min, pH=5, Pb(II) initial conc. 100 mg/l, agitation rate 250 rpm);

CONCLUSION

In this study was investigated the efficacy of removing lead ions from solution with different (bio) sorbents: inorganic - aluminosilicate materials and biomass. Selected (bio)sorbents were combined. Best mixture of mineral clay bentonite and biosorbent aquatic weed *M. spicatum* for lead removal and to identify the presence of functionalities of used (bio)sorbents by FTIR spectroscopy. In previous investigation of Pb(II) removal biosorbent *M. spicatum* was used in different forms: fresh tissue (Yan et al. 2010, Milojković, Mihajlović, et al. 2014), compost (Milojković, Mihajlović, et al. 2014, Milojković, Stojanović, et al. 2014) and dry in this study. Mixture of 75% *M. spicatum* and 25% bentonite - (75%MS-25%B) showed the best lead capacity. In order to identify and compare all functional groups present on the materials involved in this process (*M. spicatum*, bentonite, mixture 75%MS-25%B) were characterized with FTIR. There were several functional groups found in the structure of mixture 75%MS-25%B such as: carboxylate, carbonyl, hydroxyl groups. Selected material mixture 75%MS-25%B can be applied as an efficient, low cost, and environmentally friendly (bio)sorbent for the removal of lead ions from wastewaters.

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