MIRJANA STOJANOVIC[1], ZORICA LOPIČIĆ[1], JELENA MILOJKOVIĆ[1], ČASLAV LAČNJEVAC[2] MARIJA MIHAJLOVIĆ[1], MARIJA PETROVIĆ[1] ALEKSANDAR KOSTIĆ[2]

Scientific paper
UDC:504.054:631.872.874

Biomass waste material as potential adsorbent for sequestering pollutants

Conventional treatment technologies for the removal pollutants from the environment usually aren't economically viable or may further generate huge quantity of toxic chemical sludge which requires further treatment. Biosorption is emerging as a potential alternative technique to the existing conventional technologies; its application is economically acceptable because it reuse biological materials with their major advantages: low cost, high efficiency, renewability, minimization of chemical or biological sludge, easy regeneration of biosorbents and possibility of metal recovery. The paper presents the review of the results of the biosorption efficiency of two biosorbents: peach shell, originating from "Vino Župa" Company from Aleksandrovac, as agro-industrial waste and urban waste, aquatic plant, Myriophyllum spicatum, harvested from artificial Sava Lake, Belgrade, as low cost biosorbents for removal of several pollution type: heavy metal ions (Cu, Pb), uranium as radionuclide and mycotoxins. Biosorption treatment method is especially applicable in developing countries where a "low cost tech" approach may be a suitable option.

***Key words:** waste biomass, myriophyllum spicatum, peach shell, biosorption, pollutants.*

INTRODUCTION

The pollution of the environment with heavy metals, radionuclides and organic pollutants as a result of human activities, primarily mining and metallurgy, industrialization, combustion of fuels, agricultural practices and their impact on the ecosystem are of large economic and public-health significance, wherein is the contamination of water with heavy metals is the major problem of global concern. Methods for removing metal ions from aqueous solution mainly consist of physical, chemical and biological technologies. Another type of pollutants of special concern are mycotoxins, small and stable molecules which are extremely difficult to remove, and which are entering the food chain while keeping their toxic properties. The mycotoxins of major concern as feed contaminants are mainly aflatoxins, ochratoxin A, *Fusarium* toxins (trichothecenes like deoxynivalenol, diacetoxyscirpenol, nivalenol, T2-toxin/HT2-toxin, zearalenone and fumonisins) [1] Conventional methods for removing metal ions from wastewaters have been proposed, such as: chemical precipitation, filtration, ion exchange, electrochemical treatment, solvent extraction, reverse osmosis, membrane technologies, precipitation, flocculation, evaporation etc. Major problems some of these methods are high sludge production, handling and disposal problems, high cost, technical constraints...

In recent years, applying biotechnology in controlling and removing metal pollution has been paid much attention, and gradually becomes hot topic in the field of metal pollution control because of its potential application. Biosorption can be defined as the removal of selected ions or other molecules from solution by certain biomolecules (or types of biomass) such as bacteria, fungi, yeast, algae and agricultural, food industrial and urban wastes, etc. These biosorbents possess metal-sequestering property and can be used to decrease the concentration of heavy metal ions in solution from ppm to ppb level [2 - 5].

Processes of metal removal by biosorbents incluside two steps: (1) an initial fast, reversible metal-binding step - biosorption relating to physical-chemical processes such as chelation, Van der Waals' forces, ion exchange, precipitation and adsorption and (2) a slow, irreversible ion-sequestration step – bioaccumulation consisting of biological processes like intracellular uptake, vacuolar deposition and translocation [6] Biosorption is a metabolically passive process, in which metallic ions remain at the cellular surface by different mechanisms while bioaccumulation is an active metabolic process driven by energy from a living organism where contaminants – heavy metals are incorporated inside the living biomass [7].

Selection of adequate target biosorbent characteristics includes complex multidisciplinary procedure: Collected and prepared of biomass -washing, drying, milling of, seeding; Surface modification of biosorbent: nature, chemical (acid, base, impregnation),

Author's address: [1]Institute for Technology of Nuclear and other Mineral Raw Materials, Belgrade, [2]Faculty of Agriculture, University of Belgrade, Serbia

Paper received: 25.06.2012.

physical (heat treatment), biological (microorganism); Characterization of biosorbent: elemental analysis (C,N,H,S), moisture content, loss of ignition, CEC, specific surface area, point of zero change, FTIR (Fourier transformation infra-red analysis – for definition of functional groups), SEM (scanning electron microscope - surface morphology), XRD (x-ray fluorescence spectrometry – concentration of elements), Biosorptive capacity (the maximum sorbent intake refers to maximum amount of sorbate/cation (mg, mmol or meq) which can be removed per weight (g) of adsorbent); Influential factor: pH, temperature – termodynamic control, contact time, initial concentration of pollutants, weight of biomass ; Modeling biosorption: kinetic and equlibrium; model-adsorption isotherms; Desorption and regeneration study.

Based on the above procedure, the paper presents some results of the efficiency of the peach shell as agro-industrial waste and urban waste as aquatic plant *Myriophyllum spicatum (M. spicatum)* as low cost and abundant lignocelluloses biomass for removal of heavy metal ions (Cu and Pb), uranium ions as radionuclide and mycotoxins from aqueous solutions, of the review type.

The major advantages of biosorption over the conventional treatment methods include the use of abundant, renewable biomass, which leads to low cost, high efficiency removing processes, minimization of chemical or biological sludge, regeneration of biosorbents and possibility of later metal recovery.

A review of biosorption research in ITNMS

In this paper are presented investigations in Institute for Technology of Nuclear and other Mineral Row Materials, ITNMS, on removal heavy metals (lead and copper), radionuclide (uranium) and mycotoxins with low cost and eco-friendly biosorbents: aquatic weed and fruit pits as urban and agroindustry west, respectively.

Preparation of the plant biomass

All the experiments were done with two types of biomass: peach stone shell and fresh tissues of aquatic plant *M. spicatum* as well as compost of this plant.

Whole peach stones were obtained from “Vino Župa”, Aleksandrovac, as by-product waste from their Juice Factory. The fruit stones were separated from soft fruit residues, washed, dried at room temperature. All the samples were crushed and separated from kernels, which were discharged, so for further analyses only hard stone part was taken. For all the experiment, different size fractions of hard peach stones were prepared. After milling to wanted fraction, all the samples were first washed several times in tap water, then in 0.001M HCl in order to eliminate surface impurities and then in distilled water until negative reactions with chloride ions. After that, they have been dried at 60^{o}C until the constant mass. This biomass hasn’t been modified by any chemical agents in order to increase their biosorption capacity.

The aquatic plant *M. spicatum* is harvested from artificial Sava Lake, Belgrade, 3 - 4 times / year, with mechanical underwater harvester (Figure 1). With mowing amount of unwonted aquatic weed is significant reducing (around 35 m^3 per day). Harvested plant material is disposing to the open landfill used just for that purpose, where the compost is later formed. After taking, plant biomass was washed with diluted HCl solution (3%) and then with distilled water for three times before being used for experiments. Compost was exposed to air and dried for couple days on room temperature and then dried at 60°C for 6 hours, crushed and sieved to give a particle size less than 0.2 mm.

Chemical composition of plant origin are present in Table 1.Cellulose and lignin as well as ADF and NDF were analysed according to *Van Soests* method [8]. In relation to the peach shell *M. spicatum* had a significantly higher content of protein, crude fat and ash, while the crude fiber content and lignocellulosic fractions (ADF, NDF and lignin) were noticeably smaller.

Table 1 - Chemical composition of adsorbents of plant origin

Parameter (%)	*Myriophyllum spicatum* (MS)	Peach shell (PS)
Dry matter	91.11	92.23
Moisture	8.89	7.77
Crude protein	17.95	1.26
Crude fat	1.28	0.05
Crude cellulose	23.33	58.05
Ash	17.64	0.42
BEM	30.91	32.45
Neutral detergent fiber (NDF)	33.38	71.12
Acid detergent fiber (ADF)	30.96	66.12
Lignin	6.33	16.54

Figure 1 - Mowing of plant material M. spicatum from Sava Lake.

Biosorption of heavy metals

Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders. Investigation of two heavy metals removing, copper and lead was conducted. These two elements were chosen because of their occurrence, toxicity and high regulation norms predicted for their appearance both in drinking and discharging waste waters

Lead biosorption by aquatic plant M. spicatum and its compost

Experiments with sorption of Pb(II) ions by fresh tissues of M. spicatum and its compost was conducted in batch techniques. The efficiency of compost in Pb(II) ion removal was examined depending on the varying pH value and contact time . Fourier transform infrared attenuated total reflection (FTIR-ATR) spectroscopy was used to characterize biomass and its compost. The results revealed that carbonyl, carboxyl, and hydroxyl could be possible binding site for Pb(II) ions on M. spicatum and for compost probably hydroxyl functional group is involved in interaction with metal ions [9].

The effect of pH values on sorption Pb(II) ions onto compost was studied at pH range 2-6, where samples of 0.063 g compost were shaken in 35 ml metal solutions at initial Pb(II) concentration of 100 mg/l for 145 min. Using a pH meter (Consort C 830 P) the initial pH value was regulated to appropriate value with 0.1 $MHNO_3$ or 0.1M NaOH. At pH 5 it was observed slightly better removal of lead, only 1% more than other tested pH values. Thus, all sorption experiments were carried out at pH 5.0 Small differences in the removal of lead by compost at different pH values indicate that pH change has no influence on sorption process.

The effect of contact time *M. spicatum* and compost was studied with initial Pb(II) concentration of 100 mg/l, at pH 5 and contact time ranged from 10 to 145 min (Figure 2). Amount of dry weight of biomass and compost was 0.063 g. Sorption rate was very fast and contact time of 20 min was enough to reach equilibrium. The initial amount of biomass and plant compost were removed 88.2% and 76.01% of lead , respectively.

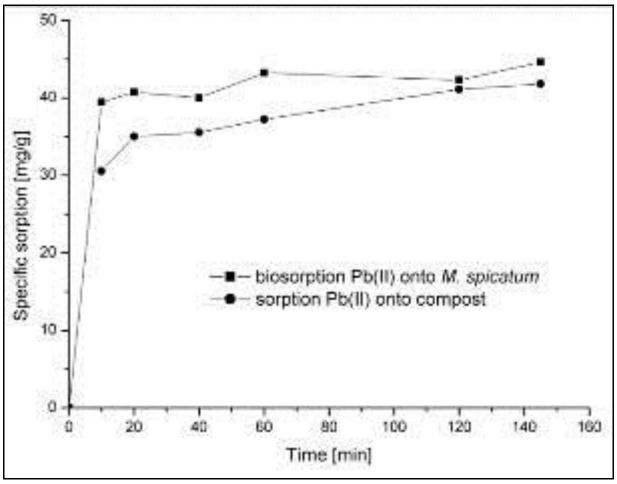

Figure 2 - The effect of contact time Pb sorption onto fresh tissues and compost of M. spicatum (100 mg Pb /l, pH 5.0)

In this work three kinetic models were applied to the experimental data: Lagergren pseudo first order [10], Lagergren pseudo second order [11] and intraparticle diffusion model [12]. It was found that adsorption process was best described by the pseudo second order kinetic where lead binding capacity was proportional to the number of active sites occupied on the sorbent (equation no.1).

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (1)$$

Where, k is the equilibrium rate constant of pseudo second order sorption kinetics [g/mg min], q_e the amount of metal ion adsorbed at equilibrium [mg/g], q_t the amount of sorbate on the surface of sorbent at any time t [mg/g]. Integration of this equation with boundary conditions t=0, q_t=0; t=t and q=q_t results in (linear form), equation no.2 [13].

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_e^2 k} \quad (2)$$

On Figure 3. is shown a plot of t/q_t versus time and in table 2 are listed reaction rate constant and correlation coefficients for pseudo second order reaction model.

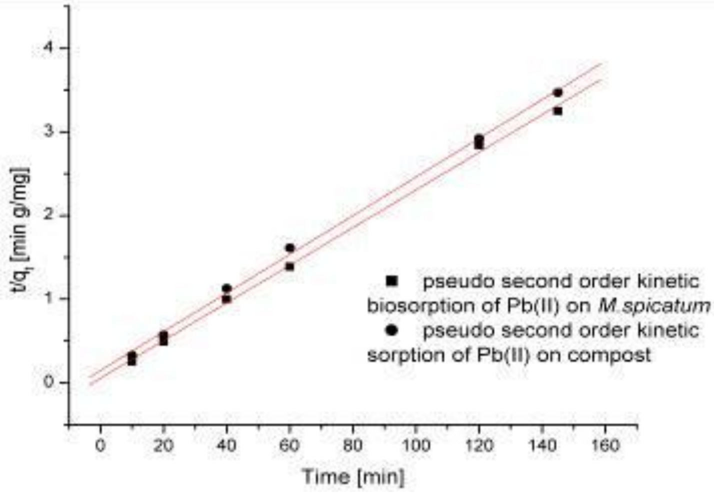

Figure 3 - Pseudo second order kinetic of (bio)sorption Pb(II) onto M. spicatum and compost (initial conc. 100 mg Pb /l, dry weight of M.spicatum and compost 0.063 g, pH 5.0)

Obtained results for pseudo second order kinetic of adsorption Pb(II) onto *M. spicatum* comply with research of Yan *et al*. [14].

Table 2 - Pseudo second order rate constant for lead

(bio)sorbent	Reaction rate constant k [g/mg min]	Correlation coefficient R^2
M. spicatum	0.0090	0.99905
compost	0.0036	0.99914

Copper removal by peach shell

Experiments with sorption of Cu(II) ions by peach stone shell was conducted in batch techniques. The efficiency of in Cu (II) ion removal was examined depending on the varying pH particle size and shape and contact time. In our previous research was found that the best biosorptioni capacity was achieved at initial pHi 5 [15].

The morphology and the nature of the surface of the ground peach shell particles is presented on the SEM image (Figure 4) at 1000 x magnification. The SEM image revealed the nature of the surface of this biosorbent as a multilayer porous surface with irregular laminated structure, with an average pore diameter of about 1µm, which may be beneficial to metal ions diffusion and adsorption [16].

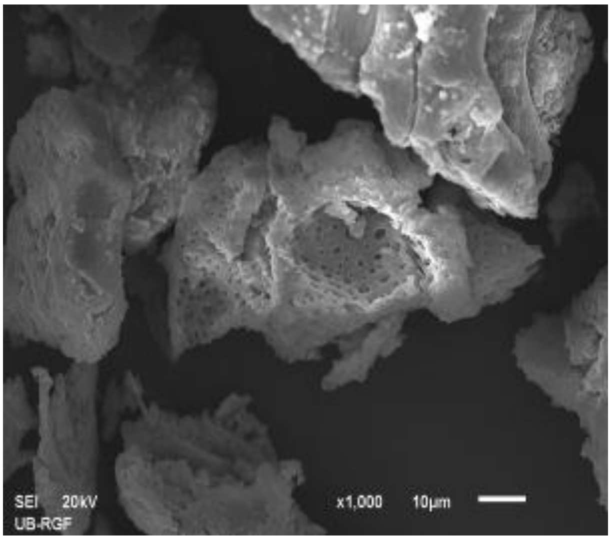

Figure 4 - SEM image of the ground peach shell surface

Effect of contact time on biosorption of Cu (II) ions by two different sizes of peach shell particles was investigated with initial copper concentration, Ci (Cu^{2+}) = 50 mg/l , pHi = 5, biomass concentration as adsorbent mass to sorbate volume ratio, M/V=0.01. Experiments done with shaking, at agitation rate of 150rpm, on T=25±1°C (Figure 5).

The retention of cations from solution as well as biosorption efficiency is the function of the biosorbent shape and size, as it can be seen in Fig.3. Although many authors have proved that for their type of biosorbent, particle size has no influence on biosorption capacity, as well as on equilibrium time, in the case of peach shell particles, the size play important role [17]. This can be well seen from above mentioned picture, where the smaller, approximately spherical particles (d=-1+0,5mm) have significantly higher percentage removing than the crushed particles of irregular shape (d=-1+0,5 cm) under the same operational conditions. This can be attributed to the fact that the smaller biosorbent particles have shorter path for diffusion as well as increased total surface area with higher micro pore volume compared with bigger particles, which enables to cations to penetrate into the all internal pore structure of the biosorbent [18]. Also, the larger particles have much higher diffusion resistance to mass transfer which leads to non-efficient utilization of active sites in the internal surfaces of the particles, giving as result law amount of adsorbed copper cations [19]. The adsorption time under these operational conditions, is less than 5 minutes, and also, that it is enough to lead the process for only 30 minutes, because the obtained concentration is close to equilibrium.

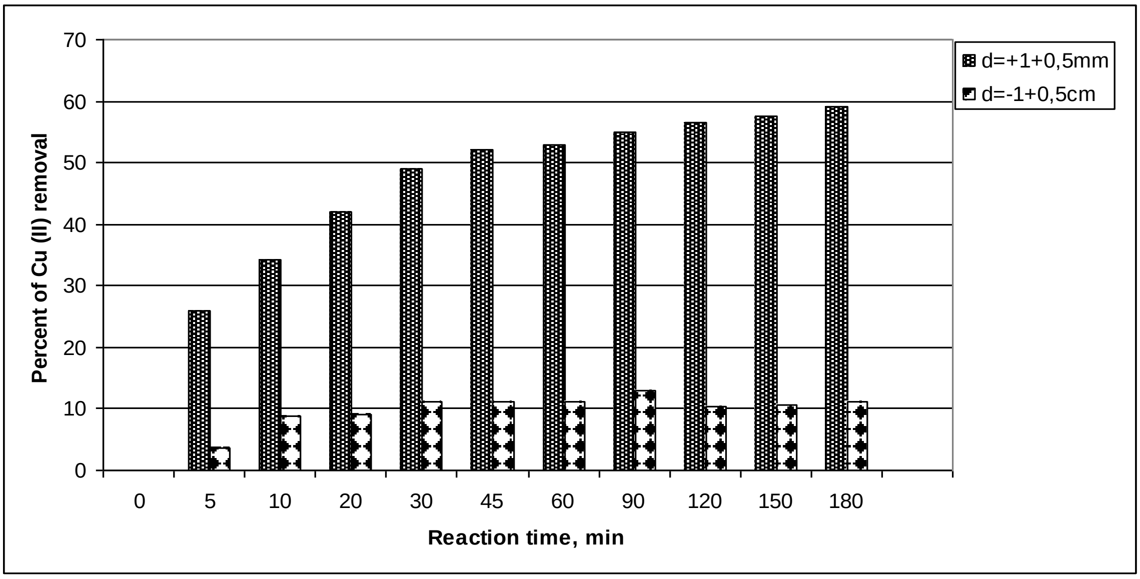

Figure 5 - Effect of contact time on biosorption of Cu (II) ions by two different sizes of peach shell particles

Absorption of mycotoxins by wasted biomass

The aim of the study was to evaluate in vitro the ability of two biosorbents mentioned, to adsorb sixt different mycotoxins: aflatoxin B1 (AFL), ochratoxin A (OTA), deoxynivalenol (DON), zearalenone (ZON), diacetoxyscirpenol (DAS) and T-2 toxin. All the details about the production, quantification and isolation of mycotoxins are briefly described elsewhere [1]. For adsorption experiments stock solution of AFL was diluted to 0.2 µg/ml, of ZON to 0.8 µg/ml, and of all other mycotoxins to 2.0 µg/ml with electrolyte (0.1M K_2HPO_4). pH value of electrolyte was adjusted with 0.1M HCl or 0.1 NaOH to 3.0 and 6.9, respectively.

The in vitro binding ability of M. spicatum and peach stones was tested as follows: aliquots (50 ml) of test solutions were added to Erlenmayer flasks of 250 ml, containing different amounts of single adsorbent for different types of mycotoxins. The pH value of electrolyte was adjusted with 0.1M HCl or 0.1 NaOH to 3.0 and 6.9. The flasks were stoppered, incubated for 1 hour on rotary shaker (185 rpm) at room temperature (22-25 °C) and then filtered. Mycotoxins' concentrations in 25 ml aliquots of electrolyte with adsorbent (C) and without it (C_o) were determined, after extraction with 2 x 15 ml of organic solvents: benzene (ZON), benzene-acetonitrile (AFL), and ethyl acetate (OTA, DON, DAS and T-2) respectively, by TLC methods. The adsorption index of individual mycotoxin was calculated by the equation no.3, and expressed in percentages:

$$\text{Absorption Index} = [(C_0 - C) / C_0] * 100 \quad (3)$$

where, as it is already noted, C represents mycotoxins' concentrations in aliquots of electrolyte with adsorbent and C_o without it. The results obtained are presented in the Figure 7.

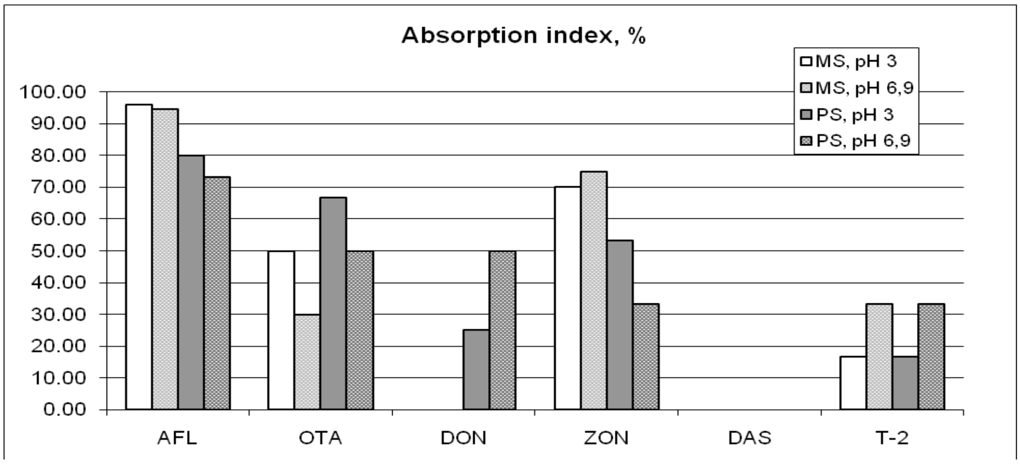

Figure 7 - Absorption index of different mycotoxins for two biosorbents investigated

As it can be seen from Figure 7, both biosorbents have removed certain amounts of mycotoxins, but in tested laboratory conditions, the better adsorbent of plant origin was shown to be peach shell because it bonded in vitro five (AFL, OTA, DON, ZON and T-2) out of six tested mycotoxins. Nonetheless in vivo experiments are indispensable to proof the efficacy of both investigated adsorbents (MS, and PS).

Uranium biosorption

Uranium ions were removed from water solutions using two, already mentioned absorbents: untreated peach shell particles and fresh tissues of M. spicatum, that has been treated as already described. The initial concentration of uranium ions was 100 µg/ml, with initial pH solution of 3,5. The experiments was conducted using batch technique, where 1g of absorbent was placed in 100 ml of uranium solution and leaved in contact for 24h, with shaking. The removing of U by aquatic plant (MS) was significant (79,16 %) comparing to the peach shell particles (KB) (4,11%). This showed that this plant can be successfully used for removal of uranium from water systems. shell particles (KB) (4,11%). This showed that this plant can be successfully used for removal of uranium from water systems.

Acknowledgements

The authors are grateful to Serbian Ministry of Education, Science and Technological Development, which support this research through its Project N^o TR 31003 "Development of technologies and products based on mineral raw materials and waste biomass for protection of natural resources for safe food production".

CONCLUSION

Presented results have showed that wasted investigated biomass of peach shell and aquatic plant/compost can be used for removal of different type of pollutants – heavy metals, radionuclide and mycotoxins. The further investigations should be done in order to define the best operational conditions for pollutants removing, as well as different type of modifications (both chemical and thermal) that will enhance the pollutants intake. Generally, the authors agree that for developing countries such as Serbia, that has large quantities of wasted biomass, biosorption technology creates the possibility of developing efficient and cheap materials for pollutant removal, as well as the possibility of opening new markets.

REFERENCES

[1] Bočarov-Stančić A., Lopičić Z., Milojković J., Adamović J., N Salma N., Pantić V.(2012) The efficiency of in vitro adsorption of mycotoxins by adsorbents of plant origin, CEFood 2012, In press.

[2] Wang J., Chen C. (2009) Biosorbents for heavy metals removal and their future, Biotechnology Advances, 27 , 195–226

[3] Zouboulis A., Lazaridis K., Karapantsios T., Matis K., (2010) Heavy metals removal from industrial wastewaters by biosorption , Int. J. Envir. Eng. Sci., 1(1) 57-78

[4] Volesky B. (2007) Biosorption and me, Water Res., 41, 4017-4029

[5] S. Didanović, G. Sekulić, (2011) Zaštita materijala, 52 (3) 285-293.

[6] Keskinkan O., Goksu M.Z.L., Yuceer A., Basibuyuk M. and Forster C.F. (2003) Heavy metal adsorption characteristics of a submerged aquatic plant (Myriophyllum spicatum). Process Biochem., 39, 179–183.

[7] Chojnacka K.(2010) Biosorption and bioaccumulation – the prospects for practical applications, Environment International, 36 (3) 299–307

[8] Van Soest J., Robertson B., Lewis B. A. (1991) Methods for dietary fiber, neutral detergent fiber and non–starch polysaccharides in relation to annual nutrition. Journal of Dairy Science, 74, 3583 – 3597.

[9] Milojković J., Stojanović M., Grubišić M., Lopičić Z., Mihajlović M., Lead sorption by compost of Myriophyllum spicatum, (2011) 12th International Conference on Environmental Science and Technology – CEST 2011, Rhodes, Greece, 1243-1249.

[10] Lagergren S., (1898) About the theory of so called adsorption of solute substances. Kungliga Sevenska, Vetenskapasakademiens, Handlingar, 24, 1–39.

[11] Ho Y.S. and McKay G. (1999) Pseudo-second order model for sorption processes, Process Biochem. 34, 451–465.

[12] Weber W.J. and Morris J.C. (1963) Kinetics of adsorption on carbon from solution. J. Sanit. Eng. Div. Am. Soc. Civ. Eng., 89, 31–60.

[13] Febrianto J., Kosasih A.N., Sunarso J., Ju J.H., Indraswati N., Ismadji S. (2009) Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies, J. Hazard. Mater., 162, 616–645.

[14] Yan C., Li G., Xue P., Wei Q., and Li Q. (2010) Competitive effect of Cu (II) and Zn(II) on the biosorption of lead(II) by Myriophyllum spicatum, J. Hazard. Mater., 179, 721–728.

[15] Lopičić, Z., Stojanović, M., Lačnjevac, Č., Milojković, J., Mihajlović, M., Šoštarić, T. (2011) The copper biosorption using unmodified agricultural waste materials, Zaštita materijala, 52 (3) 189-193.

[16] Guangqun T., Hongyan Y., Yong L., Dan X. (2010) Removal of lead from aqueous solution with native and chemically modified corncobs, J. Hazard. Mater., 174, 740–745.

[17] Lopičić, Z., Stojanović, M., Milojković, J., Šoštarić, T., Mihajlović, M., Avdalović, J. (2011) Agricultural waste material as potential adsorbent for removing copper from water solutions, 43rd International October Conference on Mining and Metallurgy, 465-469.

[18] Gupta, V.K., Mittal, A., Malviya, A., Mittal, J. (2010) Adsorption of Carmoisine o from Wastewater Using Waste Materials-Bottom Ash and Deoiled Soya, J. Colloid and Interface Sci., 335, 24-33.

[19] Kumar, A., Kumar, S., Gupta, D. V. (2007) Adsorption of phenol and 4- nitro phenol on granular activated carbon in basal salt medium: Equilibrium and kinetics. J. Hazard. Mater., 147, 155-166.

IZVOD

OTPADNA BIOMASA KAO POTENCIJALNI ADSORBENT POLUTANATA

Konvencionalne tehnologije za uklanjanje polutatanata iz životne sredine nisu ekonomski isplative i uglavnom generišu velike količine hemijski toksičnih muljeva. Biosorpcija se promoviše kao potencijalno alternativna tehnologija u odnosu na konvencionalne, zasnovana na primeni ekonomski prihvatljivih bioloških mateirjala koje odlikuje niska cena, visoka efikasnost, obnovljivost, minimiziran hemijski i biološki otpad, regeneracija biosorbenata sa mogučnostošću izdvajanja metala. U radu su prikazani neki rezultati ispitivanja efikasnosti koščica breskve, poreklom iz "Vino Župa" Aleksandrovac, kao agroindustrijskog otpada i urbanog otpada, vodene biljke, Miriophillum spicatum, iz veštačkog Savskog jezera u Beogradu, kao jeftinih biosorbenata za uklanjanje teških metala (Cu, Pb), uranijuma kao radionuklida i mikotoksina iz vodenih rastvora. .Zemlje u razvoju poput Srbije, koje imaju velike količine otpadne biomase, biosorpcione tehnologije otvaraju mogučnost razvijanja efikasnih i jeftinih adsorbenata za uklanjanje različitih tipova polutanata sa perspektivom otvaranja novih tržišta.

Ključne reči: *otpadna biomasa, myriophyllum spicatum, koštice breskve , biosorpcija, polutanti*

Rad primljen: 25.06.2012.

Originalni naučni rad