ZORICA LOPIČIĆ[1], MIRJANA STOJANOVIĆ[1], ČASLAV LAČNJEVAC[2] JELENA MILOJKOVIĆ[1], MARIJA MIHAJLOVIĆ[1], TATJANA ŠOŠTARIĆ[1]

Scientific paper
UDC:631.95:546.561/.562

The copper biosorption using unmodified agricultural waste materials

The rapid increase in global industrial activities has lead to the serious environmental pollution that requires systematic and sustainable approach in order to protect environment and biodiversity. Special concern is accented on heavy metal pollution because of their high toxicity, persistence and bioaccumulation tendency. The conventional methods for their removing are often either too expensive or create a large quantities of toxic sludge, so the other technologies, cheaper and more effective should be employed. Biosorption is one of the recently employed promising technologies that use biomaterials as sorbents for different type of pollution. Thanks to their active surface groups, biosorbents pose wider operational spectrum than mono functional ion exchangers. Agricultural waste materials have proved to be highly efficient, low cost and renewable source of biomass that can be exploited for heavy metal remediation, which leads to increase of their life cycle and also solve their disposal problem. The purpose of this paper is investigation of possible application of wasted untreated biomass from "Vino Župa" Company as potential biosorbent that can be used for copper removal from water solutions. For this purpose, several type of biomass have been examined and the preliminary results presented in this paper have showed that this wasted untreated materials can bee used as promising and cheap adsorbents for copper removal from water solutions, but also that further physical and chemical modifications should be done in order to increase their biosorption capacity.

***Key words**: copper biosorption, biosorption capacity, agricultural waste materials, peach stone, sour cherry stone*

1. INTRODUCTION

For the last few decades, an increasing concern world wide has been the remediation of polluted water resources by heavy metals, which may have poisonous or otherwise harmful effects on many forms of life. The most common used methods for heavy metal removing from contaminated water include chemical precipitation, coagulation, adsorption, electrolytic removal, ion exchange, solvent extraction, reverse osmosis… Most of these methods are either too expensive to deal with low concentrations of metals or generate toxic sludge that present problem for further handling.

For these reasons, there is a need to develop low-cost processes for heavy metal removal [1, 2]. Biosorption presents alternative, potentially cost effective technology that removes toxic metals and organic compounds from water solutions using dead or live biomass as adsorbent (for example, fermentation or agricultural waste materials, various kinds of micro organisms or algae…). It can be said that it is an eco-friendly technology because it is selective, effective, and cheap and doesn't generate toxic sludge which makes it suitable for later metal recovery and biosorbent regeneration [2]. Biosorption works very well at low concentrations - it could be employed most effectively in a concentration range below 100 mg/l, where other techniques are ineffective or costly. During the biosorption process, metal ion binding has been found to involve complex mechanisms, such as ion-exchange, process of complexation, electrostatic attraction and micro precipitation [3].

Copper and its compounds are ubiquitous in the nature that is spread out to the environment by different natural phenomena. It is most frequently found in surface water. Also, over the last decades, the production of copper has lifted up and the copper quantities in the environment have notably increased [4]. Copper does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. Soluble copper compounds form the largest threat to human health; the acute intake of copper leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney [5]. The World Health Organization (WHO) has recommended the maximum acceptable concentration of Cu (II) in drinking water of 1.5mg/L.

Author's address: [1]Institute for Technology of Nuclear and Other Mineral raw materials, 86 F. d'Esperey St. Belgrade, Serbia. [2]University of Belgrade, Faculty of Agriculture, 6 Nemanjina St., Belgrade, Serbia.

Paper received: 03. 06. 2011.

For all the reasons previously described, the authors have tried to investigate the possibilities for use of cheap, wasted material from agricultural and food industry as potential adsorbents for copper removal. The purpose of this research was aimed to gain a fundamental understanding of the chemical and physical phenomena associated with the binding of copper to untreated agricultural by products.

2. MATERIAL AND METHODS

All the reagents used in this experiment were of analytical grade. The adsorbents (peach and cherry stones) were obtained from "Vino Župa" Company from Aleksandrovac, where they have been disposed as by-product waste from their Juice Factory.

2.1 Adsorbent preparation

After sampling, the fruit stones were separated from soft fruit residues, washed, dried at room temperature, and kept in polypropylene bottles for further treatment. Prior to experiment, all the samples were crushed and separated from kernels, which were discharged, so for further analyses only hard stone part was taken. The peach stones were used as whole stone, as crushed shell fractions and also as milled fraction of -1.0 + 0.5 mm. The sour cherry stone was taken as whole stone as well as crushed particles, but also as grinded particles, ranging from 0.5mm to 2mm. For all the experiments, 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. Table 1 contain type, size and shape of the biosorbents used in this work.

Table 1 - Different agricultural residues used as biosorbents

Biosorbent	Characteristics
Peach Stone (B1)	Whole stone, ellipsoidal shape, length: 3-5cm, width: 1-1.5cm
Peach Stone (B2)	Crushed stone, irregular shape, size from 0.2-1cm
Peach Stone (B3)	Grinded spherical size, -1+0.5mm
Cherry Stone (V1)	Whole spherical stone, d ~ 6mm
Cherry Stone (V2)	Crushed stone, sickle shaped ~5mm length, ~ 3mm width
Cherry Stone (V3)	Grinded irregular flattened particles, from 0.5mm to 2mm

Cupper solution was prepared by dissolving $CuSO_4 \cdot 5H_2O$ (analytical grade) in distilled water using standard flasks. The initial metal concentration varied from 50 to 100 mg/l, and the initial pH value of solution was adjusted to 5. During the experiment with the biosorption capacity the pH value of solutions was not kept constant, while in the part of experiment done with biosorption kinetics and variations in M/V (mass of adsorbent over the volume of the solution) ratio, the pH value was kept constant and adjusted by adding few drops of either 0.1 M NaOH or 0.1M HCl. All the changes in pH were monitored and recorded.

2.2 Experimental conditions

Adsorption experiments were carried out using two different types of biosorbents: peach and cherry stones, which haven't been modified by any chemical agents for the purpose of their biosorption capacity increase. All the biosorbents have been prepared according to procedure described in chapter 2.1. The experiments were done with shaking for different time periods, at an ambient temperature of $24\text{-}27^{o}C$.

The three sets of experiments were done:

- First experiment was done in order to determine the biosorption capacities of the peach and sour cherry stones. Experiment was conducted under the following operational conditions: M of adsorbent = 1g, V of solution = 100mL, pHi = 5, sorption time with shaking = 24h, Ci = 100 mg/l Cu (II). During this part of experiment, the pH value of the solutions was not kept constant, since the time conditions of investigations (24h) did not allow it;
- The second set of experiments were performed with the grinded peach shell particles (ranging from 0.5 to 1 mm) in order to determinate the biosorption kinetics of copper. The experiment was carried out under the following operational conditions: adsorbent dose M = 0.5g, V of solution = 50mL, pHi = 5, sorption time with shaking = 0-360 minutes (check was done after 24h and there was no significant changes in concentration of Cu remained in the solution), with the initial Cu (II) concentration of 50 mg/l. During the experiment, pH was kept constant all the time.
- The third experiment was the investigation of the influence of different M/V ratio in order to increase the percent removal of copper ions. The initial concentration of Cu (II) ions was 100 mg/l, time of adsorption was 150 minutes, pH = 5, and the M/V ratio varied from 0.001 to 0.5 g/ml.

The amount of adsorption at equilibrium q_{eq} (mg/g) was calculated by the equation 1:

$$q_{eq} = [(C_i - C_{eq})V] / M \qquad (1)$$

The percent removal (%), also called as sorption efficiency [1] was computed according to equation 2:

$$Sorption\ Efficiency = [(C_i - C_{eq}) / C_i] * 100 \qquad (2)$$

The marks in the previous equations represents: C_i and C_{eq}- the initial and equilibrium concentrations, given in mg/L, V - the volume of the adsorbate solution, expressed in litre (L), and M - weight of biosorbents used, given in gram (g).

2.3 Analyses

The total metal concentration in solution was determined with atomic absorption spectrophotometer (Perkin Elmer AAS Analyst 300) while the pH was determined by Consort pH meter type C 830P.

3. RESULTS AND DISCUSSION

3.1 Biosorption capacity

In this stage, a preliminary screening of two different types of biosorbents was carried out to make a comparison of their biosorption capacity. As it can be seen from the data presented in Figure 1, the good results are gained by all biosorbents that are size reduced, and the best are found to be with the peach stone marked as B3. The other adsorbent has also showed a good capacity, similar to those found in literature, but the whole peach stones marked as B1 have had much lower biosorption capacity compared with the one found in literature [6].

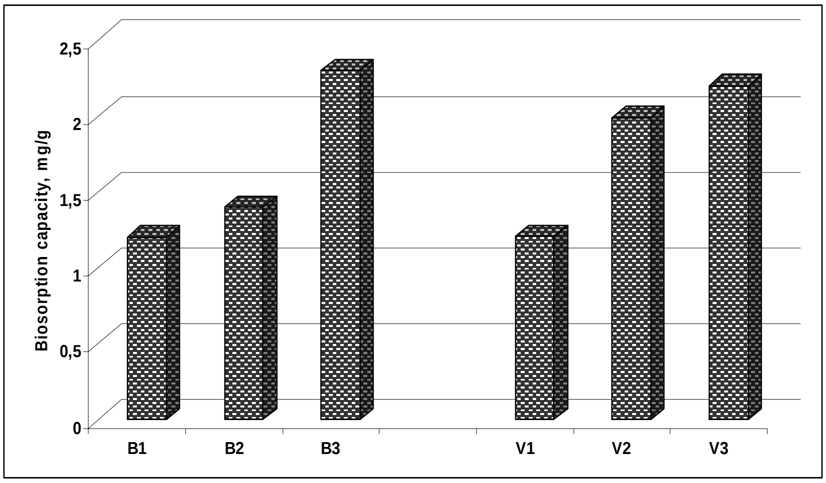

Figure 1 – Biosorption capacities of peach and sour cherry stones

As it can be seen from the Figure 1, the biosorption capacities for the peach stone varied from 1.21 to 2.30 mg/g, and from 1.19 to 2.20 mg/g for the sour cherry stone. The best results are achieved with grinded fractions. The significant difference in biosorption capacity between the different size fractions of the same biosorbent type, like in both cases, has showed that the size of the sorbent plays important role in the sorption efficiency.

3.2 Biosorption kinetics

The experiment with biosorption kinetics was done with the peach shell grinded to -1.0 + 0.5 mm particles fraction, since the investigations of biosorption capacity have showed that this material had the highest metal binding capacity of all examinees. The results of biosorption kinetics are presented Figure 2.

The results have showed that the equilibrium was achieved after 100 minutes, where more that 95% of total Cu removed by this amount of adsorbent, is achieved. As it can be seen from figure 2, the adsorption kinetics includes two phases: a rapid removal stage followed by a much slower stage before the equilibrium is established.

First of all, the plot reveals that the rate of copper removal is higher at the beginning. That is probably due to larger surface area of the peach particles being available at beginning for the adsorption of metals. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. The high initial graph slope has shoved that the initial velocity is relatively high, which means that most of the active places on the surface of the material are occupied in the first 30 minutes.

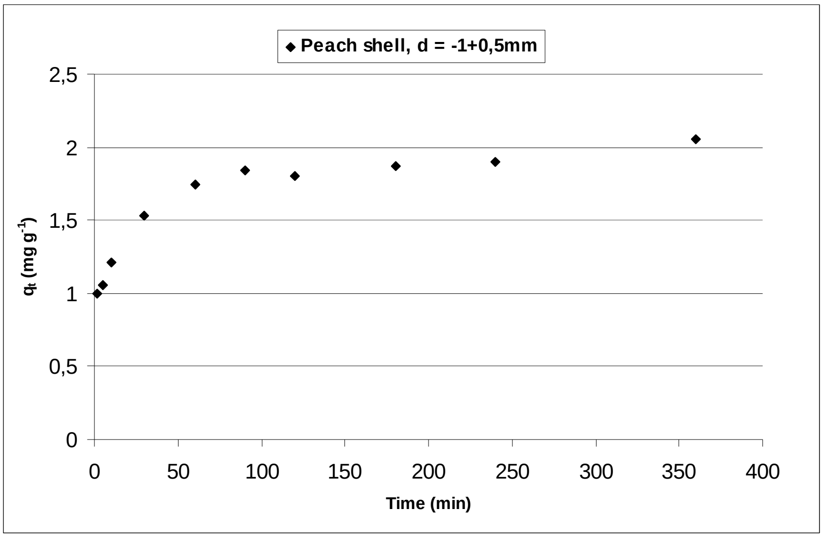

Figure 2 – Biosorption kinetics of grinded peach shell particles: q_t versus time

3.3 Influence of adsorbent dose - variation of the M/V ratio

The material chosen for M/V effect analysis was again grinded peach stone, for the reasons briefly described above. As it can be seen from the Figure 3, the bigger the amount of solid biomass will lead to the higher sorption efficiency or percent removal after equilibrium time.

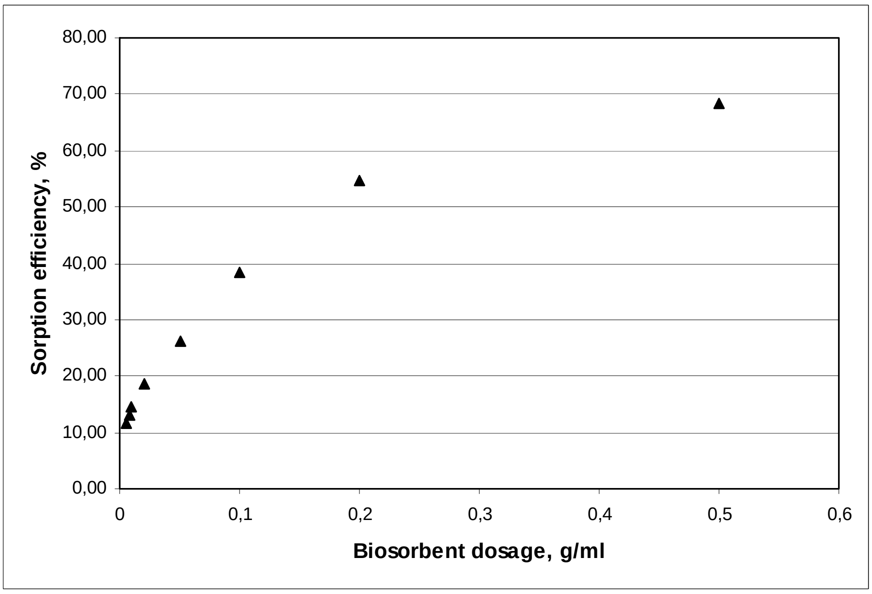

Figure 3 – Cu removal by peach stone - M/V ratio variations

Figure 3 shows that with an increase of solid adsorbent amount, the removal of Cu (II) ions significantly increase, from the beginning 11.70 % (for 0.001 ratios) until the final 68.35 %, for the final ratio investigated. In opposite, the biosorption capacity drastically decreases, from the beginning 2.30 mg/g until final 0.13 mg/g for the M/V ratio of 0.5 g/ml. It is apparent that, with the increase of adsorbent dose the adsorption efficiency increase, but adsorption density, which could be expressed as amount adsorbed per unit mass, decrease. The reason for that could be as following: when we are using large amounts of biomass we can obtain efficient metal removal from the solution (which leads to higher percent removal), but all the active sites on the biosorbent surface are not occupied fully (which leads to lower biosorption capacity) mainly due to unsaturation of adsorption sites through the adsorption reaction [7]

4. CONCLUSION

Due to its relative abundance and satisfactory adsorption capacity, the abundant waste from agricultural and food industry can be considered as a good low-cost adsorbent for removing copper ions from aqueous solutions. This paper has showed that the biosorption capacity for copper of peach stone is 2.30 mg/g which is satisfactory comparing to other natural sorbents: the adsorption capacity of sawdust for copper, for instance, is 1.79 mg/g [8]. But the different authors have also showed that different kind of physical or chemical modifications can lead to significant increase in biosorption capacity. For instance, soybean hulls modified with citric acid had adsorption capacities for Cu from 0.68 to 2.44 mmoles/g, which was much higher than for unmodified hulls (0.39 mmol/g) [9].

The process of biosorption is strongly pH dependent since the process of deprotonation of each functional group depends on pH. In that sense, the authors will do another set of experiments with variations in pH.

The further investigations should be done in order to define the best conditions for Cu (II) removing, such as operational pH, influence of initial concentration as well as different type of modifications (both chemical and thermal) that will enhance the cupper intake.

ACknowledgements

The authors are grateful to Serbian Ministry of Education and Science which has supported this research through the Project N^o TR 31003.

REFERENCES

[1] Vinodhini, V., Anabarasu, V. and Nilanjana, D., Screening of natural waste products for the removal of Cr (VI) ions from industrial effluents, *Indian J. of Nat. Prod. Resour.,* 1 (2) 174-180, 2010.

[2] Ochie, A., V., Trilestari, K., Sunarso, J., Indraswati, N., Ismadji, S., Recent progress on biosorption of heavy metals using low cost biosorbents: characterization, biosorption parameters and mechanism studies, *Clean,* 36 (12) 937-962, 2008.

[3] Volesky, B., Holan, Z.R., Biosorption of heavy metals. *Biotechnol. Prog.* 11, 235–250, 1995.

[4] Li, Y., Helmreich, B., Horn, H., Biosorption of Cu(II) Ions from Aqueous Solution by Red Alga (Palmaria Palmata) and Beer Draff, *Mater. Sci. and Applications*, 2, 70-80, 2011.

[5] Gotoh, T., Matsushima, K., Kikuchi, K., Adsorption of Cu and Mn on covalently cross-linked alginate gel beads, *Chemosphere,* 55, 55-57, 2004.

[6] Hansen, H., Arancibia, F., Gutierez, C., Adsorption of copper onto agriculture waste materials*, J. Hazard. Mater.,* 180, 442–448, 2010.

[7] Raji, C., Anirudhan T.C., Cr (VI) adsorption by sawdust: Kinetics and equilibrium, Ind. *J.Chem Technol.,* 4, 228-236, 1997.

[8] Bin Yu, Y. Zhang, Alka Shukla, Shyam S. Shukla, Kenneth L. Dorris, The removal of heavy metal from aqueous solutions by sawdust adsorption—removal of copper*, J. Hazard. Mater.,* 80, 33-42, 2000.

[9] Marshall, W.E., Wartelle, L.H., Boler, D.E., Johns, M.M., Toles, C.A., Enhanced metal adsorption by soybean hulls modifed with citric acid, *Bioresource Technol.,* 69, 263-268, 1999.

IZVOD

BIOORPCIJA BAKRA PRIMENOM NEMODIFIKOVANE OTPADNE BIOMASE

Problem zagađenja životne sredine usled tehno-ekonomskog i urbanog razvoja zahteva integralan pristup održivog upravljanja i zaštite biodiverziteta. Poseban akcenat usmeren je na teške metale, zbog njihove visoke toksičnosti, postojanosti i tendenciji ka bioakumulaciji. Savremeni trend u rešavanju ovog problema je primena otpadne biomase agroindustrije kao efikasnih biosorbenta polutanata čime se ujedno produžava njihov životni ciklus i rešava problem deponovanja. Biosorpcijaja je ekološki i ekonomski prihvatljivija tehnologija u odnosu na konvencionalne metode, a biosorbenti, zahvaljujući svojim funkcionalnim grupama, poseduju širi spektar dejstva u odnosu monofunkcionalne jonoizmenjivače. Predmet rada je istraživanje mogućnosti primene otpadne biomase (koštice breskve i višnje) iz fabrike "Vino Župa" Aleksandrovac, kao potencijalnog biosorbenta za uklanjanje bakra iz vodenih rastvora. Cilj urađenih istraživanja je bio sticanje fundamentalnih osnova fizičkih i hemijskih fenomena adsorpcije bakra na netretiranoj biomasi. Preliminarni rezultati prikazani u ovom radu i pionirska istraživanja te vrste u Srbiji, pokazali su da se ovaj tip netretiranog otpadnog materijala može koristiti za uklanjanje jona bakra, ali takođe, i da je neophodno ispitati mogućnost njihove hemijske ili fizičke modifikacije kako bi im se povećao biosorpcioni kapacitet.

Ključne reči: *biosorpcija bakra, biosorpcioni kapacitet, otpadna biomasa, koštice breskve, koštice višnje*