International Journal of Research in Chemistry and Environment
Vol. 2 Issue 3 July 2012(138-143)
ISSN 2248-9649

Research Paper

Cu(II) Removal onto Fungal Derived Biosorbents: Biosorption Performance and the half Saturation Constant Concentration Approach

Chia-Chay Tay[1, 2], Hong-Hooi Liew[1, 3], Soon-Kong Yong[4], Salmijah Surif[5], Ghufran Redzwan[2], Suhaimi Abdul-Talib[1]*
[1]*my*BioREC, IIESM, Faculty of Civil Engineering, University Technology MARA,
40450 Shah Alam, Selangor, MALAYSIA
[2]ISB, Faculty of Science, University Malaya, 50603 Kuala Lumpur, MALAYSIA
[3]Faculty of Civil and Environmental Engineering, University Tun Hussein Onn Malaysia,
86400 Parit Jawa, Johor, MALAYSIA
[4]Faculty of Applied Science, University Technology MARA, 40450 Shah Alam, Selangor, MALAYSIA
[5]Faculty of Science and Technology, University Kebangsaan Malaysia, 43600 Bangi, Selangor, MALAYSIA

Available online at: www.ijrce.org

(Received 11th May 2012, Accepted 06th June 2012)

Abstract: *This study investigates the removing of Cu(II) using Pleurotus ostreatus fungal and Pleurotus ostreatus spent mushroom compost. In these batch biosorption experiments, the half saturation constant of biosorption was determined through Langmuir Linearization 1 plot of biosorbent concentration. This new approach was employed to minimize the use of biosorbent and to obtain results in shorter time. The half saturation constant of Cu(II) biosorption was 0.36 g for fungal Pleurotus ostreatus and 0.7 g for Pleurotus ostreatus spent mushroom substrate. There were three optimum operational parameters undertaken, which were the initial pH of 6, contact time of 10 minutes and 50 mg/L of initial Cu(II) concentration. These parameters were found to have produced results that clearly fitted the Langmuir and Freundlich isotherms, which also matched the pseudo second-order kinetic better than they do pseudo first-order kinetic. These implied that chemisorptions, complexation and ion exchange play a vital role in biosorption mechanism. In the same vein, the results of the FTIR analysis showed that the carboxyl, hydroxyl and amide group of lignocelluloses, chitin and proteins could be hypothesized that they were the functional groups involved in Cu(II) biosorption, in keeping with the findings shown by the said isotherms. Therefore, these biosorbents deem to be highly potential to be developed into a low impact, environment-friendly sustainable technology to remove heavy metals.*

Keywords: biosorption performance, Cu(II) removal, fungal derived biosorbent, mechanisms, the half saturation constant

Introduction

Industrialization has resulted in contamination through production of chemicals, inappropriate use, improper disposal and accidental leakage of these chemicals. The accumulation of heavy metals in food chain has given rise to concern because they are persistent and toxic in the environment as well as mutagenic and carcinogenic to human health. Precipitation of heavy metals in hydroxide is the most common practice for heavy metals removal in Malaysia. However, this conventional method is not environmental friendly due to production of toxic waste and overuse of chemicals. Therefore, recent research on sustainable technology such as biosorption for heavy metals removal has been explored enthusiastically.

Biosorption is developed as an alternative method and sustainable technology for heavy metals removal. It is a physio-chemical passive metabolite independent process by deploying biosorbent from non-living biological materials, especially agricultural or industrial waste. In general, biosorbent is bio-degradable, heavy metals are easily eluted by diluted acid from regeneration process thus converting waste to wealth.

Biosorbent of fungal *Pleurotus ostreatus* [1, 2] and sawdust [3, 4, 5] are promising biosorbents in heavy metals removal. Chen *et al.* [6] also reported that *Lentinus edodes* spent mushroom compost has high heavy metals removal capacity. Fungal *Pleurotus ostreatus* and *Pleurotus ostreatus* spent mushroom compost (PSMC) are selected biosorbents in this study. At present, there is lack of research in selecting the PSMC as biosorbent. In addition, it was found that very few competitive studies of PSMC with other related biosorbent such as *Pleurotus ostreatus*.

Economically, using large amount of easily available waste from mushroom cultivation farm could make a crucial contribution in enhancing the sustainable technology development by offering an effective biosorbent to remove heavy metals. Meanwhile, it also minimizes waste management problems of mushroom cultivation farm thus transforming waste to wealth.

This study investigates the feasibility of fungal *Pleurotus ostreatus* and PSMC as biosorbents. The maximum Cu(II) biosorption performance and mechanism of Cu(II) biosorption were evaluated in order to establish an alternative sustainable technology.

Material and Methods

Preparation of biosorbent and Cu(II) solution: The 15-day old Pleurotus ostreatus mycelium culture in malt extract was harvested and autoclaved for 15 minutes at 121 ^{o}C, 18 psi. After drying in an oven at 60 ^{o}C until constant weight was obtained, it was ground and sieved to particle size of 150 µm and kept in a drying cabinet.

Sample of PSMC was collected from C and C mushroom Cultivation Farm Sdn. Bhd.. After that, it was autoclaved and dried in an oven at 60 ^{o}C until the constant weight was attained. It was then ground and sieved to particle size of 710 µm. This sample was rinsed three times with ultra pure water in ratio of 20g/ L to remove impurities. Finally, prepared biosorbent was kept in a drying cabinet.

Analytical grade $Cu(SO_4)$ (Merck, Germany) was diluted with ultra pure water for Cu(II) solution preparation.

Batch biosorption

In batch biosorption experiments, specific amounts of biosorbents were added into 50 L of 50 mg/L Cu(II) solution respectively. Then, the samples were incubated in an incubator shaker for an hour under 125 rpm and temperature of 25 ± 1 ^{o}C. After filtration, supernatants were analyzed using ICP-OES (7300DV, Perkin Elmer, USA).

All biosorption tests were performed in duplicates with error bars corresponding to ±1 standard deviation value for data analysis. The expressed values represent the average of the acquired results with 1 SD. The effectiveness of biosorbent was calculated from Equation 1.

$$Uptake\ of\ Cu\,(II)\ biosorptio\ n,\ q_e = \frac{(C_o - C_e)\,V}{M} \qquad (1)$$

where q_e = equilibrium Cu(II) biosorption uptake (mg/g), C_o and C_e = initial and final Cu(II) concentration (mg/L), V = volume of Cu(II) solution (L) and M = weight of biosorbent (g)

The experimental results were fitted to the linearized Langmuir and Freundlich isotherm Model as shown in Equation 2 and 3 respectively.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{b\,q_{\max}} \qquad (2)$$

$$\ln q_e = \ln K_F + \frac{1}{n \ln q_e} \qquad (3)$$

where q_e = equilibrium Cu(II) biosorption uptake (mg/g), q_{max} = maximum Cu(II) biosorption uptake (mg/g), C_e = Cu(II) concentration at equilibrium (mg/L), b = Langmuir constant, K_F and n = Freundlich constant.

The Cu(II) biosorption were calculated from the pseudo first-order kinetic model (Equation 4) and second-order kinetic models (Equation 5).

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

where q_e and q_t = Cu(II) biosorption uptake at equilibrium and at time (mg/g), t = time (min), k_1 and k_2 = constant of pseudo first-order and second-order kinetic.

Fourier Transform Infra-Red Analysis

The specific functional groups of biosorbents were identified using Fourier Transform Infra-Red (FTIR) Spectroscopy System (Series 100, Perkin Elmer, USA)

Results and Discussion

Cu (II) removal was investigated in this study using two types of biosorbents, namely, *Pleurotus ostreatus* and PSMC. Optimization parameters of initial pH, contact time and initial Cu(II) concentration were examined in order to evaluate biosorption performance and design of the half saturation constant biosorbent concentration. Functional groups involve in Cu(II) removal were characterized using FTIR.

Biosorbent concentration: Figure 1 shows Cu(II) biosorption uptake for *Pleurotus ostreatus* and PSMC decreased when biosorbent concentration increased. This indicated that the ratio of Cu(II) ions to surface active sites decreased and resulted in partial aggregation.

Therefore, uptake of Cu(II) biosorption had reached limitation and decreased. Jiang *et al.* [7] also reported similar observation in Cu(II) biosorption by modified bagasses.

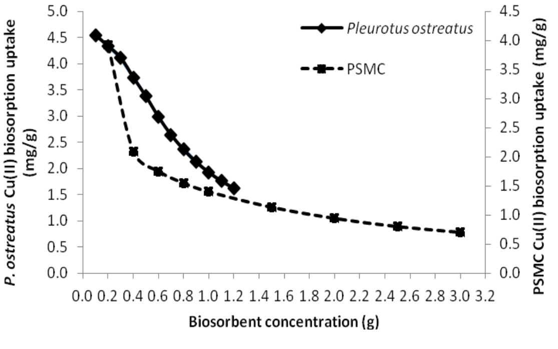

Figure 1: Effect of biosorbent concentration on Cu (II) removal

The half saturation constant of Cu(II) biosorption was determined by Langmuir Linearization 1 plot of biosorbent concentration. From the slope and intercept calculation as shown in Figure 2, the half saturation constant of Cu(II) biosorption was 0.36 g for *Pleurotus ostreatus* and 0.7 g for PSMC. These biosorbent concentration were selected for further experiments in order to obtain results in shorter time and minimize usage of biosorbent.

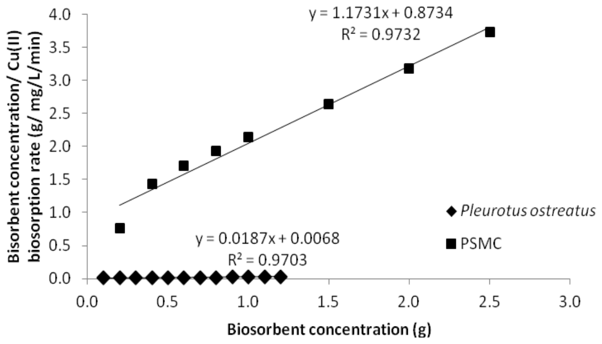

Figure 2: Langmuir Linearization 1 plot of Hanes-Woolf plot for half saturation conatant determination

Initial pH: The Cu(II) biosorption is a pH dependent process as shown in Figure 3. The maximum Cu(II) uptake was found to be at pH 5 for both fungal derived biosorbents of *Pleurotus ostreatus* and PSMC. The poor uptake of Cu(II) biosorption at low pH suggests that protons occupy most of the active sites on biosorbent surface and active sites are being protonated. Consequentially, electric repulsion formed and resulting in reduced of Cu(II) biosorption uptake. As initial pH increase, the active sites are being deprotonated and strengthened the charge attraction, thus leading to significant increase in Cu(II) biosorption uptake. While at highly basic condition, the availability for Cu(II) biosorption is attributed to precipitation of Cu(II) ions as insoluble hydroxides or hydrated oxides. In this regards, Božić *et al.* [8] recorded similar trend and same order of magnitude for maximum Cu(II) biosorption which was based on sawdust of deciduous trees.

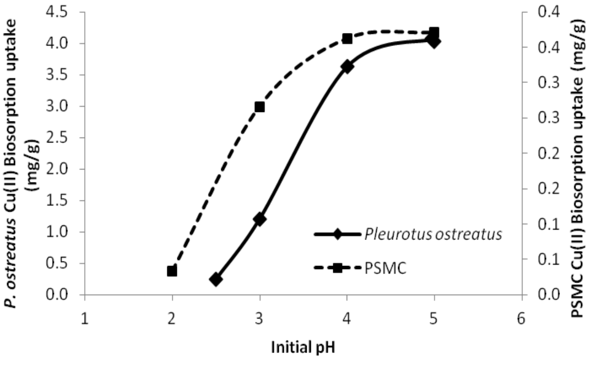

Figure 3: Effect of initial pH on Cu(II) removal

The active sites and Cu(II) species are affected by initial pH, thus influence the biosorption performance. For subsequent experimental design, initial pH was not adjusted since Cu(II) solution has the initial pH of 5 which represent the optimum condition of Cu(II) biosorption uptake.

Contact time: Figure 4 illustrates the Cu(II) biosorption uptake occurring in two phases. A rapid and significant Cu(II) biosorption uptake phase and then follow by an equilibrium phase. Both *Pleurotus ostreatus* and PSMC biosorbents achieved equilibrium phase within 10 minutes. This revealed that microporous surface of biomaterial facilitates the diffusion process and surface active sites are easily occupied by Cu(II) ions. By applying the half saturation constant approach in biosorption, the equilibrium time could be achieved faster as well as minimize biosorbent usage. Table 1 shows this study attained equilibrium phase faster than other researchers who utilized biosorbent concentration at equilibrium stage or random selection. Based on present result, 10 minutes equilibrium time was adopted in designing subsequent experiments.

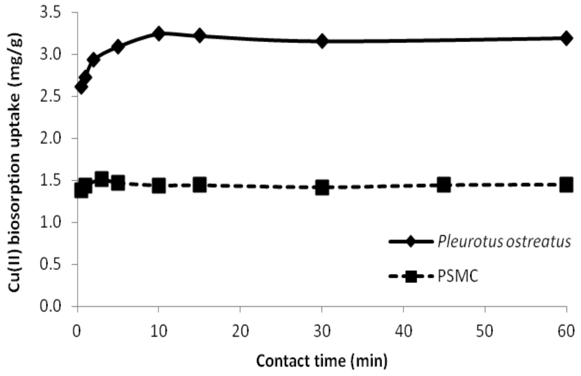

Figure 4: Effect of contact time on Cu (II) removal

Initial Cu(II) concentration : Figure 5 depicts the Cu(II) biosorption uptake increased linearly when initial Cu(II) concentration increased, with co-efficient of 0.9598 for *Pleurotus ostreatus* and 0.9920 for PSMC biosorbent. The initial Cu(II) concentration provides a driving force to overwhelm mass transfer resistances of the Cu(II) ions between the aqueous and solid phase. Findings from the flower distillation sludge [14] and barley straw [15] biosorbents were consistent with this study.

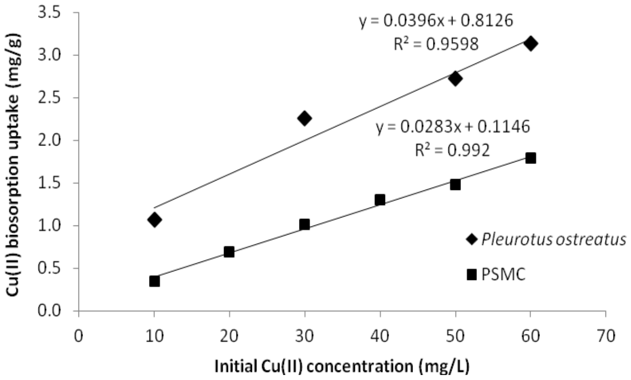

Figure 5: Effect of initial Cu(II) concentration on Cu(II) removal

Langmuir and Freundlich isotherm model: The calculated Langmuir and Freundlich isotherm parameters are summarized in Table 2. The biosorption data fit the Langmuir and Freundlich model, judging by its coefficient value. These fitting deduced that biosorption is governed by the monolayer heterogeneous chemisorptions mechanism. Therefore, there is no further binding process at active sites, once it is being occupied. It seemed that other research also rely on chemisorption for Cu(II) removal as fitted to Langmuir Isotherm.

Furthermore, this study exhibits comparable predicted q_{max} values for Cu(II) biosorption uptake if compared to other.

Table 1
Comparison of contact time for Cu (II) biosorption

Biosorbent	Contact time for equilibrium phase	Reference(s)
Treated leave powder	30 minutes	Kilic *et al.* [9]
Cassia angustifolia tree bark	120 minutes	Mulgund *et al.* [10]
Treated rubber leaves powder	120 minutes	Ngah and Hanafiah [11]
Alga, moss, sawdust	60 minutes	Grimm *et al.* [12]
Tree leave of *U. carpinifolia* and *F. excelsior*	60 minutes	Sangi *et al.* [13]
Fungal *Pleurotus ostreatus*, PSMC	10 minutes	This study

Table 2
Langmuir and Freundlich parameters for Cu (II) biosorption and comparison with other recent studies

Biosorbent	Langmuir Parameters			Freundlich Parameters		
	q_{max} (mg/g)	b	R^2	K_F	n	R^2
Wheat straw [16]	0.18	1.91	0.920	0.11	0.31	0.910
Modified mangrove bark [17]	5.80	0.03	0.936	0.22	1.38	0.999
Fungus on corncob [18]	1.77	0.001	0.882	0.00002	0.59	0.911
Fungal *Pleurotus ostreatus* (This study)	3.59	0.16	0.990	0.08	2.50	0.985
PSMC (This study)	3.87	0.02	0.966	0.12	1.32	0.996

Table 3
Pseudo first-order and second-order kinetic parameters for Cu (II) biosorption and comparison with other related biosorbents

Biosorbent	Pseudo first-order			Pseudo second-order		
	q_e	k_1	R^2	q_e	k_2	R^2
Chestnut shell [19]	1.17	0.014	0.771	4.44	0.08	0.997
Papaya wood [20]	1.72	0.074	0.884	1.99	0.04	0.993
Fungal *Pleurotus ostreatus* (This study)	0.27	0.036	0.430	3.20	3.13	0.999
PSMC (This study)	0.08	0.002	0.023	1.44	31.7	0.999

Pseudo first-order and second-order kinetic model: Table 3 lists the parameters of pseudo first-order and second-order kinetic model. Experimental data excellently fitted the pseudo second-order compared to pseudo first-order. This infers that there are more than one mechanisms occurring simultaneously during the Cu(II) biosorption process. The pseudo second-order kinetic model also corresponded to chemisorption with limit on involving the valency force through sharing or exchange of electrons. Increasing Cu(II) concentration seems to reduce the external diffusion of the biosorbate and enhances intra-particle diffusion. The kinetic parameters obtained are in accordance with those found in the literature [19-20].

FTIR analysis :FTIR spectrum with several intense characteristic bands with functional groups that present in lignocelluloses, chitin and proteins were illustrated in Figure 6. Generally, hydroxyl, carboxyl and amide groups were three identified active sites for Cu(II) biosorption. This result is supported by observation of Cu(II) biosorption occurring at pH below 4 in Figure 3 which indicates the possible presence of hydroxyl and amide groups as active sites besides carboxyl group. This three identified functional groups also supported the Freundlich isotherm model of heterogeneous surface active sites. Javaid et al. [2] and Zakaria et al. [5] noted similar functional groups in their study of Pleurotus ostreatus and rubber tree sawdust, respectively.

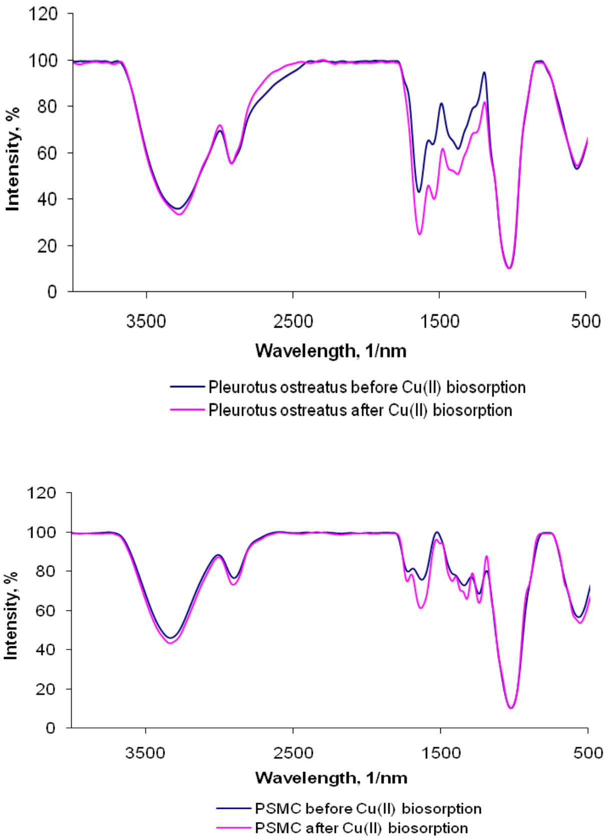

Figure 6: FTIR spectra of *Pleurotus ostreatus* and PSMC before and after Cu (II) removal

It is well established that *Pleurotus ostreatus* contains chitin molecules in its cell wall. The three identified groups of hydroxyl, carboxyl and amide, are some of the main constituent of N-acetylglucosamine, which is a monomer unit of the chitin. The oxygen ring and the hydroxyl groups of N-acetylglucosamine play a pivotal role in binding with Cu(II) via complexation process. Tay *et al.* [21] drew the conclusion that all these functional groups are major contributors in chitin-heavy metals complex.

The Cu(II) biosorption process is mainly accounted for ion exchange with potassium (K) for *Pleurotus ostreatus* and calcium (Ca(II)) for PSMC. A significant release of such light metal ions were observed through ICP-OES and SEM/EDX after Cu(II) biosorption. These collected data inferred that the displacement of K ions of *Pleurotus ostreatus* and Ca(II) ions of PSMC by Cu(II) ions. These further supported that hydroxyl, carboxyl and amide groups from lignocelluloses, chitin and proteins play a vital role in ion exchange mechanism. Similar phenomenon involving olive oil stone biosorbent was stated by Foil *et al.* [22].

Conclusion

Pleurotus ostreatus and PSMC were evaluated as biosorbents through Cu(II) biosorption performance. In batch study, the half saturation constant of biosorption was determined in order to obtain results in shorter time and minimize biosorbent usage. The half saturation constant of Cu(II) biosorption was found at 0.36 g and 0.7 g for *Pleurotus ostreatus* and PSMC respectively. The optimum operation parameters for both biosorbents were similar, which were initial pH of 5, 10 minutes contact time and 50 mg/L initial Cu(II) concentration. These experimental data were well fitted to Langmuir and Freundlich isotherm model. Pseudo second-order kinetic superbly described Cu(II) biosorption if compared to pseudo first-order kinetic model.

Carboxyl, hydroxyl and amide groups of lignocelluloses, chitin and proteins were identified as functional groups in Cu(II) biosorption. Chemisorption, complexation and ion exchange were Cu(II) biosorption mechanisms and were confirmed by the isotherm and kinetic fittings. The PSMC biosorbent has comparable effectiveness and advantages of easily and abundantly available in Malaysia compared to *Pleurotus ostreatus*. Therefore, PSMC biosorbent has higher potential to be developed into an environment-friendly sustainable technology for purification of heavy metals laden effluents as well as reduce solid waste management problems related to mushroom cultivation farm.

Acknowledgement

The authors would like to acknowledge the Ministry of Higher Education and Ministry of Science, Technology and Innovation for the financial support. Appreciation is also extended to C and C Mushroom cultivation farm for supplying samples needed for this study.

References

1. Tay, C. C., Liew, H. H., Yin, C.-Y., Abdul-Talib, S., Surif, S., Suhaimi, A. A. and Yong, S. K., Biosorption of cadmium ions using *Pleurotus ostreatus*: Growth kinetics, isotherm study and biosorption mechanism, *Korean J. Chem. Eng.,* **28(3)**, 825-830 **(2011a)**

2. Javaid, A., Bajwa, R., Shafique, U. and Anwar, J., Removal of heavy metals by adsorption on *Pleurotus ostreatus*, *Biomass Bioenerg.,* **35(5)**, 1675-1682 **(2011)**

3. Ofomaja, A. E., Unuabonah, E. I. and Oladoja, N. A., Competitive modeling for the biosorptive removal of copper and lead ions from aqueous solution by Mansonia wood sawdust, *Biores. Technol.,* **101(11)**, 3844-3852 **(2010)**

4. Rafatullah, M., Sulaiman, O., Hashim, R. and Ahmad, A., Adsorption of copper (II) onto different adsorbents, *J. Disper. Sci. Technol.,* **31(7)**, 918-930 **(2010)**

5. Akmar Zakaria, Z., Suratman, M., Mohammed, N. and Azlina Ahmad, W., Chromium (VI) removal from aqueous solution by untreated rubber wood sawdust, *Desalination,* **244(1)**, 109-121 **(2009)**

6. Chen, G., Zeng, G., Tang, L., Du, C., Jiang, X., Huang, G., Liu, H. and Shen, G., Cadmium removal from simulated wastewater to biomass byproduct of *Lentinus edodes*, *Biores. Technol.,* **99(15)**, 7034-7040 **(2008)**

7. Jiang, Y., Pang, H. and Liao, B., Removal of copper(II) ions from aqueous solution by modified bagasse, *J. Hazard. Mat.,* **164(1)**, 1-9 **(2009)**

8. Božić, D., Stanković, V., Gorgievski, M., Bogdanović, G. and Kovačević, R., Adsorption of heavy metal ions by sawdust of deciduous trees, *J. Hazard. Mat.*, **171(1-3),** 684-692 **(2009)**

9. Kilic, M., Yazici, H. and Solak, M. A., Comprehensive study on removal and recovery of copper(II) from aqueous solutions by NaOH-pretreated *Marrubium globosum* ssp. *globosum* leaves powder: Potential for utilizing the copper(II) condensed desorption solutions in agricultural applications, *Biores. Technol.*, **100(7),** 2130-2137 **(2009)**

10. Mulgund, M. G., Kininge, P. T., Pillai, M. M. and Sanandam, M. R., Biosorptiove removal of heavy metals (Cd, Pb and Cu) from aqueous solutions by *Cassia Angustifolia* bark, *Int. J. Eng. Sci. Technol.*, **3(2),** 1642-1647 **(2011)**

11. Ngah, W. and Hanafiah, M., Biosorption of copper ions from dilute aqueous solutions on base treated rubber (*Hevea brasiliensis*) leaves powder: Kinetics, isotherm, and biosorption mechanisms, *J. Environ. Sci.*, **20(10),** 1168-1176 **(2008)**

12. Grimm, A., Zanzi, R., Björnbom, E. and Cukierman, A. L., Comparison of different types of biomasses for copper biosorption, *Biores. Technol.*, **99(7),** 2559-2565 **(2008)**

13. Sangi, M. R., Shahmoradi, A., Zolgharnein, J., Azimi, G. H. and Ghorbandoost, M., Removal and recovery of heavy metals from aqueous solution using *Ulmus carpinifolia* and *Fraxinus excelsior* tree leaves, *J. Hazard. Mat.*, **155(3),** 513-522 **(2008)**

14. Bhatti, H. N., Khalid, R. and Hanif, M. A., Dynamic biosorption of Zn(II) and Cu(II) using pretreated *Rosa gruss an teplitz* (red rose) distillation sludge, *Chem. Eng. J.*, **148(2-3),** 434-443 **(2009)**

15. Pehlivan, E., Altun, T. and Parlayıcı, S., Utilization of barley straws as biosorbents for Cu^{2+} and Pb^{2+} ions, *J. Hazard. Mat.*, **164(2-3),** 982-986 **(2009)**

16. Dang, V. B. H., Doan, H. D., Dang-Vu, T. and Lohi, A., Equilibrium and kinetics of biosorption of cadmium(II) and copper(II) ions by wheat straw, *Biores. Technol.*, **100(1)**, 211-219 **(2009)**

17. Rozaini, C., Jain, K., Oo, C., Tan, L., Azraa, A. and Tong, K., Optimization of nickel and copper ions removal by modified mangrove barks, *Int. J. Chem. Eng. Appl.*, **1(1),** 84-89 **(2010)**

18. Jonglertjunya, W., Biosorption of lead (II) and copper (II) from aqueous solution, *Chiang Mai J. Sci.*, **35**, 69-81 **(2008)**

19. Yao, Z. Y., Qi, J. H. and Wang, L. H., Equilibrium, kinetic and thermodynamic studies on the biosorption of Cu(II) onto chestnut shell, *J. Hazard. Mat.*, **174(1-3),** 137-143 **(2010)**

20. Saeed, A., Akhter, M. and Iqbal, M., Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent, *Separat. Purif. Technol.*, **45(1),** 25-31 (**2005)**.

21. Tay, C.-C., Liew, H.-H., Redzwan, G., Yong, S.-K., Surif, S. and Abdul-Talib, S., *Pleurotus ostreatus* spent mushroom compost as green biosorbent for nickel (II) biosorption, *Water Sci. Technol.*, **64(12)**, 2425-2432 **(2011b)**

22. Fiol, N., Villaescusa, I., Martínez, M., Miralles, N., Poch, J. and Serarols, J., Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone waste, *Separat. Purif. Technol.*, **50(1),** 132-140 **(2006).**