Chemical Engineering Journal 156 (2010) 141–145

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Regeneration and reuse of spent NaOH-treated oil palm frond for copper and zinc removal from wastewater

Babak Salamatinia, Azlina Harun Kamaruddin, Ahmad Zuhairi Abdullah*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

ARTICLE INFO

Article history:
Received 6 November 2008
Received in revised form 5 October 2009
Accepted 6 October 2009

Keywords:
Spent sorbent
NaOH-treated oil palm frond
Heavy metal
Regeneration
Reuse

ABSTRACT

The use of NaOH-treated oil palm frond (OPF) sorbent for Cu and Zn removal and its subsequent regeneration process are reported. The regeneration of the spent sorbent was achieved by desorbing the metals in 0.1 M of sodium hydroxide (NaOH), ethylene diamine tetraacetic acid (EDTA), hydrochloric acid (HCl) and nitric acid (HNO_3) solutions. The reusability study of the sorbent was conducted using 100 mg/l of Cu and Zn at a pH of 4.5 and 5.5, respectively for 1 h. The results were to be correlated with the mechanism of the metal uptake. Freundlich isotherm fitted the data to indicate the presence of heterogeneous metal sorption sites. Zn showed better regeneration efficiency of up to 88% and HCl was the best regeneration agent. The results confirmed that ion exchange was the main mechanism for the metal uptake. The desorption efficiency dropped by merely about 20% while the sorption capacity experienced a drastic drop after reuse for the fourth cycle. The damage occurred on the heavy metal binding sites by the strong acid was responsible for this drop.

1. Introduction

Oil palm biomasses are abundantly produced in Malaysia and NaOH treatment has been demonstrated to turn the oil palm frond (OPF) into an excellent sorbent for heavy metal removal [1–3]. The optimization of the suitable conditions for this modification method and behavior of the sorption process in a batch and continuous modes have been previously investigated [3,4]. Yet, the regenerability and reuse of the spent sorbent are important aspects of the heavy metal sorption that rarely reported and further investigation on these aspects is fully justified.

The higher regeneration cycles without significant destruction to the biomass will make the whole process more economically favorable [4]. It has been reported that the desorption process can usually be carried out in an acidic condition. For instance, Cu and Pb sorbed on sawdust were successfully desorbed using HNO_3 at pH 2.0 [5]. It was also reported that the regenerated sawdust showed better efficiency than the raw sorbent, attributed to the removal of impurities from the biomass during the acid regeneration process. This also led to the creation of more exchange sited for a more favorable metal uptake. Although desorption capacity generally increases with increasing acid concentration (>1.0 M), it may also cause the damage of the binding sites leading to a reduction in the subsequent metal uptake capacity [6]. The immobilized heat-inactivated *Trametes versicolor* and *Pleurotus sajur-caju* were successfully reused in five biosorption and desorption cycles with negligible decrease in their biosorption capacities [7].

Interestingly, Esteve et al. [8] reported the successful use of sodium hydroxide to desorb cadmium and zinc from *Sargassum* sp. In addition, 0.01 M NaOH was the suitable desorbing agent of Cr (VI) from phosphate treated sawdust [9]. Therefore, the most suitable desorbing agent should be greatly influenced by the sorption mechanism involved. However, the exact nature of the sorption mechanism is yet to be fully understood. Our earlier reports on the use of NaOH-treated OPF pointed at ion exchange as the responsible mechanism for the heavy metal uptake [1,3]. However, it could not be confirmed unless the desorption of the metal is studied. Therefore, the results reported here are deemed critical in complementing new information to this research topic.

The mechanisms usually suggested for the sorption of heavy metals are such as mono ion-layer physical sorption, chemisorption, ion exchange and chelation [5]. Therefore, the desorption behavior and the suitable agents to be used are greatly influenced by the nature of sorbate–sorbent interaction. If the sorbed metals on the surface can be desorbed by water, the sorbate and sorbent attachment is suggested to occur through weak bonds [10]. However, if the sorbate can be desorbed by acids, such as H_2SO_4 and HCl, then the main sorption mechanism generally occurs through ion exchange process. Chemisorption generally occurs when the desorption process is made possible by organic acids such as acetic acid [11]. The sorption of Zn and Cu onto rice husk seems to follow an ion exchange mechanism. In this case, the complex formation

---

* Corresponding author. Tel.: +60 4 599 6411; fax: +60 4 594 1013.
E-mail address: chzuhairi@eng.usm.my (A.Z. Abdullah).

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.10.010

Table 1
R^2 and isotherm constants for Langmuir and Freundlich isotherms for sorption of Zn and Cu on untreated and NaOH-treated OPF.

Biomass	Heavy metal	Isotherm	R^2	Langmuir constants		Freundlich constants	
				b	Q_o	n	K_f
NaOH-treated OPF	Zn	Langmuir	0.9591	0.391	23.36	–	–
		Freundlich	0.9948	–	–	3.86	9.10
	Cu	Langmuir	0.9397	0.443	20.28	–	–
		Freundlich	0.9971	–	–	3.73	7.99
Untreated OPF	Zn	Langmuir	0.9402	0.261	37.31	–	–
		Freundlich	0.9929	–	–	4.14	13.82
	Cu	Langmuir	0.9261	0.262	36.10	–	–
		Freundlich	0.9934	–	–	3.96	12.98

on the cell surface lead to the sorption of metal ions onto the biomass [12]. The surface complex formation results from the interaction between the metal ions and negatively charged active groups present in lignin and cellulose structures. The ionic radius and metal valence could also affect the complexation process [13]. In the desorption process of Cu from kyanite, an increase in acidity was found to increase the extent of the desorption to suggest ion exchange as the dominant mechanism for the metal uptake [9].

In this study, the regeneration process was carried out with four different chemical agents i.e. as sodium hydroxide (NaOH), ethylene diamine tetraacetic acid (EDTA), hydrochloric acid (HCl) and nitric acid (HNO_3). The process behavior was to be correlated with the sorption mechanism involved in the removal of copper (Cu) and zinc (Zn). The regenerability and reusability of the spent sorbent after up to three cycle of use was also evaluated.

2. Material and methods

2.1. Sorbent preparation

The OPF obtained from Universiti Sains Malaysia was first thoroughly washed with distilled water and then dried in an oven at 70 °C for 12 h. The biomass was then ground with a blender (Epicson Eb-321) for 1 min. The modification of the OPF sorbent were first carried out using NaOH under optimized treatment conditions i.e. by using 1.0 M NaOH for a treatment time of 45 min. The detail procedure is given in our earlier report [2].

2.2. Sorption experiments

The sorption process was carried out in an incubator shaker using 1.0 g of the sorbent. The solution was shaken at 150 rpm and 30 °C using 100 mg/l of Cu and Zn solutions as reported earlier [1,3]. The mixture was then filtered and the heavy metal concentration in the filtrate was then analyzed using a Hanna copper and zinc meters for the concentration of Cu and Zn, respectively. For the isotherm study, the concentrations of Cu and Zn solutions were varied between 10 and 100 mg/l. The concentration of the heavy metals was then measured once the equilibrium had been reached. For comparison, data for the untreated OPF sorbent were also recorded.

2.3. Regeneration and reusability of sorbent

100 ml of Zn and Cu solutions at a concentration of 100 mg/l were first made into contact with 1.0 g of the NaOH-treated OPF in 250 ml flasks. The mixture was then continuously shaken in an orbital shaker at 150 rpm for 15 min. Next, the solution was filtered and the filtrate was analyzed for the Zn and Cu concentration. Next, the sorbent that had been separated from the solution was oven dried at 70 °C for 12 h. The dry sorbent was then transferred into another conical flasks to be treated with 100 ml of 0.1 M NaOH, 0.1 M HCl, 0.1 M HNO_3 and 0.1 M EDTA as the desorbing agents. The solution was agitated for 60 min and then filtered for the subsequent metal measurement. For the reusability study, the regenerated sorbent was oven dried at 70 °C for 12 h to reach constant weight. It was then reused as the sorbent for a 250 ml solution of Cu and Zn at a concentration of 100 mg/l. The regeneration and reuse cycles were repeated for up to four times.

3. Results and discussion

3.1. Sorption isotherms

Two different isotherms that are commonly used for the heavy sorption process are Langmuir and Freundlich isotherms [4,5,13]. The accuracy of these isotherms to simulate experimental data varies and greatly influenced by the specific interactions between the sorbate and sorbent. The Langmuir isotherm is generally more appropriate to a monolayer adsorption where all metal binding sites are energetically equivalent and there is neither interaction between sorbed molecules nor the transmigration of sorbate in the plane of the surface [4]. Meanwhile, the Freundlich isotherm can be used for non-ideal sorption that involves heterogeneous sorption [4,5]. Thus, it is of great interest to comparatively investigate the accuracy of these isotherms in representing the experimental data for the sorption of Zn and Cu by NaOH-treated OPF. The fitting of the experimental data to certain isotherm would provide some information on the nature of the interaction between the sorbent and the sorbate.

According to Langmuir and Freundlich isotherms, the equilibrium sorption capacity (x/m) can be correlated with the equilibrium sorbate concentration (C_e) by model equations as given in Eqs. (1) and (2), respectively.

$$\frac{x}{m} = \frac{bQ_oC_e}{1+bC_e} \tag{1}$$

$$\frac{x}{m} = K_fC_e^{1/n} \tag{2}$$

The application of Langmuir isotherm to experimental equilibrium isotherm data yields two parameters, the maximum adsorptive capacity, Q_o and a constant related to the energy of sorption, b. Q_o represents a practical limiting sorption capacity when the surface is fully covered with metal ions. This allows the comparison of the performance of the sorbent, particularly in cases where the sorbent does not reach its full saturation [6]. Freundlich isotherm gives the parameter (n) which indicates bond energies between metal ion and the sorbent and K_f, is related to bond strength [9]. Parameter n also gives an indication of the extent of the sorption process and K_f is the sorption capacity of the sorbent. Indirectly, it represents the distribution coefficient for the equilibrium concentration.

The results of the isotherm study show that the Langmuir isotherm unsatisfactory fitted the experimental data for both Zn and Cu sorption processes with R^2 values of less than 0.96 (summarized in Table 1). Clear deviations are observed at medium $1/C_e$ values. Obviously, NaOH-treated OPF showed higher sorptive capacity of both heavy metals. Meanwhile, treatment of OPF with NaOH led to a higher accuracy of the Freundlich isotherm to fit the experimental data. This observation suggested the presence of different types of active sites (or heterogeneous binding sites) that were responsible for the sorption process [4]. As the untreated OPF also had mild metal sorption capability, the NaOH treatment on OPF was deemed to eventually create different types of binding sites in the sorbent. Correspondingly, the metal uptake mechanism would also be different. The metal uptake by natural untreated biomass is generally associated with the complexation or chelation [4,5].

Apart from merely based on degree of fitting, the appropriateness of Freundlich isotherm to represent the sorption data was also made based on the physical translation of the values of model parameter. The parameters for the Langmuir and Freundlich equations at 25 °C along with the correlation coefficients are also summarized in Table 1. Generally, the *n* values obtained are between 1 and 10 and this represent favorable sorption process [13]. Interestingly, the K_f and *n* values for NaOH-treated OPF are relatively lower than those of untreated OPF. It suggests lower bond strength and bond energies. This result indicated that the sorption by the OPF sorbent was not actually favored on the basis of the nature of the interaction. Based on the experimental observation that showed better sorption by this sorbent, one can conclude that the number of metal binding site in the OPF dramatically increased after the NaOH treatment. The K_f value calculated for the NaOH-treated OPF is within the same range with those reported for other types of potential biomasses reported so far such as *Aspergillus niger* biomass [4], rice milling by-product [13], and chitosan [14]. This showed the potential of the OPF-based sorbent which is abundantly available from oil palm industry.

As a main conclusion from the isotherm study of the sorption process, the treatment of OPF with NaOH created higher number of metal binding sites that showed weaker interactions with the heavy metal. On the basis of the nature of interaction involved, the metal complexation or chelation on the binding sites of the untreated OPF was a stronger force leading to the uptake of heavy metals than that occurred on the NaOH-treated OPF. However, the overall effect on the sorption process was mainly governed by the total number of binding sites available in the sorbent. The weaker interactions could be in the combination of ion exchange or simple physical adsorption.

3.2. Regeneration study

If the NaOH-treated OPF can be regenerated and reused as a sorbent material after the first cycle of the sorption process, significant improvement in the economy of the process will be achieved. For this purpose, four different desorbing agents of different chemical natures were investigated for the removal of heavy metals sorbed on the spent sorbent. These agents were hydrochloric acid, nitric acid, ethylene diamine tetraacetic acid and sodium hydroxide. EDTA is a weak acid but a strong chelating agent while HCl and HNO_3 are strong mineral acids while NaOH is a base. Besides the degree of heavy metal recovery from the spent sorbent, particular focus was also given on the elucidation of the interaction between sorbent and sorbate. It should be noted that the use of these desorbing agents could contribute to the overall operation cost, particularly with respect to environmental aspects. Thus, optimized process conditions should be investigated once the most suitable agent has been identified. However, the discussion on the process optimization is beyond the scope of the present work.

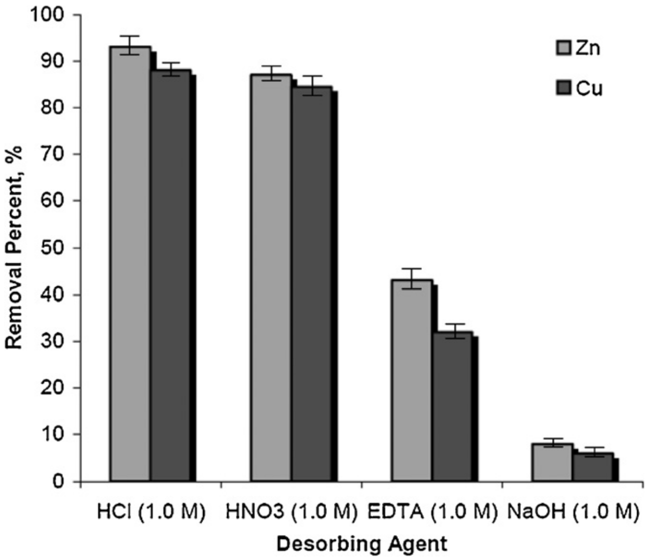

Fig. 1. Zn and Cu desorption efficiency from spent sorbent by different desorbing agents at 1.0 M (data ± standard deviations).

As shown in Fig. 1, HCl gave the best desorption (93%) followed by HNO_3 (87%), EDTA (44%) and NaOH (8%) for Zn. For Cu desorption, 88%, 84%, 32% and 6% of the sorbed metal was successfully desorbed by HCl, HNO_3, EDTA and NaOH, respectively. The results show a higher desorption of Zn compared to Cu with all the desorbing agents. This observation suggests stronger attachment of Cu to the sorbent. The conclusion is in agreement with the theory indicating that ions with smaller radius size can sorb better on the sorbent [4]. The ionic radius for Zn (II) and Cu (II) are 88 and 87 pm, respectively [1,3]. Therefore, Cu with a smaller radius size compared to Zn can sorb more strongly on the NaOH-treated OPF. This observation was in fact lead to the conclusion that ion exchange mechanism is the most dominant metal uptake mechanism in this system. HCl and HNO_3 as strong acids showed significantly better results in desorbing the heavy metal from the biomass. This was because of higher affinity of H^+ to balance the negatively charged functional groups on the biomass than the heavy metal. Furthermore, the high concentration of the acid caused the equilibrium to shift towards the reverse of the meal uptake process. Therefore, it could be concluded that it was ion exchange process that took place between H^+ ions and the heavy metals when the spent sorbents were exposed to the acid solutions. The sorption mechanism of the heavy metals (M = Zn or Cu) from NaOH-treated biomass is described by Eq. (3), while, the desorption mechanism is explained by Eq. (4). In these two equations, *R* represents the sites in the sorbent that are sorbing the heavy metals from the solution through the ion exchange mechanism.

$$2R{\bullet}\mathrm{Na} + \mathrm{M}^{2+} \rightarrow R_2{\bullet}\mathrm{M} + 2\mathrm{Na}^+ \quad (3)$$

$$R_2{\bullet}\mathrm{M} + 2\mathrm{H}^+ \rightarrow 2R{\bullet}\mathrm{H} + \mathrm{M}^{2+} \quad (4)$$

NaOH could not show good removal when used as a desorbing agent. This observation seemed to confirm the ion exchange as the main and dominant mechanism for the metal uptake process. This was due to the higher desirability of metal ions to sit on the binding sites of the biomass compared to Na^+ ions. It was expected that the affinity for the heavy metal ions to sorb on the binding sites of the biomass was greater than that of the Na^+ ions that originally presented in the NaOH-treated OPF sorbent. Thus, in the heavy metal sorption process, an exchange between the heavy metal and the Na^+ ions attached to the biomass occurred. During the desorption process, the heavy metal ions tended to remain interacted with the binding sites of the biomass. However, due to high concentration of NaOH, partial reversal of the sorption process could still occur to consequentially cause the partial removal of heavy metal from the spent sorbent.

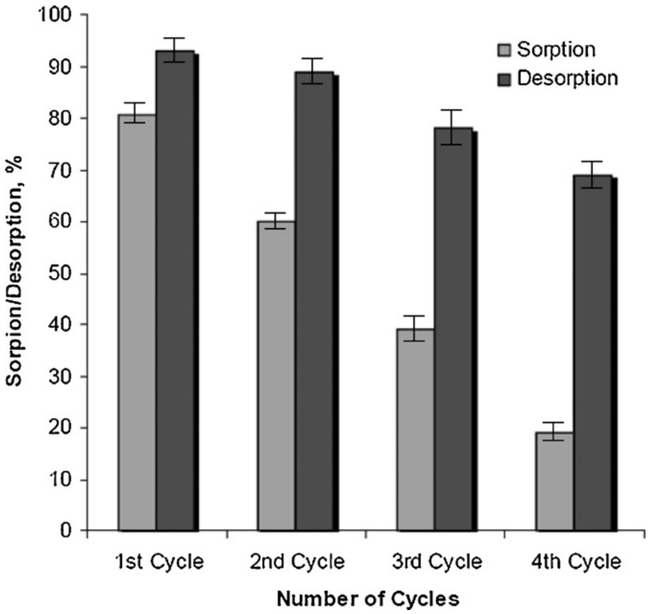

Fig. 2. Efficiency of Zn sorption process and regeneration of spent sorbent with 1.0 M HCl (data ± standard deviations).

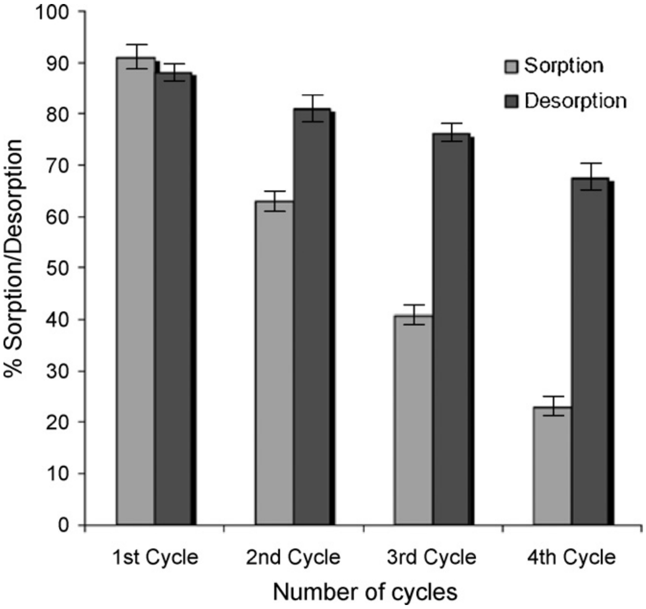

Fig. 3. Efficiency of Cu sorption process and regeneration of spent sorbent with 1.0 M HCl (data ± standard deviations).

The sorption process proceeded through the exchange of Na^+ ions sitting on the biomass surface with the heavy metal ions in the solution. During the desorption process, the metal ions were replaced with H^+ ions from the eluting acid. In the case of regenerated sorbent materials with sodium hydroxide, Na^+ was released into the solution during the sorption process. A loading with Na^+ was required after the desorption step to retain the material's original metal sorption capacity [13]. The desorption mechanism followed proceeded through an ion exchange process between the heavy metal ions attached to the biomass with the H^+ ions in the acid solution. HCl and HNO_3 showed high ability as a desorption agent and the result was associated with the high dissociation of both acids.

3.3. *Reusability of the regenerated spent sorbent*

The ability of the OPF sorbent to sorb heavy metals after the desorption step was investigated for up to three cycles. Figs. 2 and 3 show the performance of the OPF sorbent to sorb 100 mg/l of Zn and Cu, respectively. The desorption efficiency of the sorbed metals from the spent sorbent using 1.0 M HCl are also shown. In these figures, the result of the first cycle is actually obtained using the fresh sorbent. Similar behavior has been demonstrated with Cu and Zn. It is noted in the figures that the amount sorbed after each cycle reduced significantly. The drop was associated with the physical and chemical changes of the sorbent. In the first cycle, Na^+ ion was the counter ion on the metal binding sites and it was used for exchange with Cu or Zn. During the first regeneration step, H^+ was introduced into the sorbent with a relatively stronger interaction with the biomass. Consequently, the affinity towards metal exchange with Cu or Zn in the solution was lower. However, the partial damage to the exchange sites or other sites responsible for metal complexation and chelation due to the exposure to strong acid could not be ruled out [4,5]. The combined effects were observed as a significant drop in the sorption capability.

The drop in the desorption efficiency with the number of cycle was not as severe as that of the sorption process. In general, a drop by about 20% was experienced by the sorbent after the fourth cycle. In all the desorption steps, both metals were exchanged from the sorbent by H^+ from the acid. The observed drop was ascribed to the physical and chemical changes on the metal uptake sites. In this respect, the loss of metal exchange sites could occur with repeated desorption while the irreversible changes to the sites involved in the complexation and chelation could also occur. As the complexation and chelation of the metals were relatively stronger than that of the ion exchange process, the extent of metal desorption was relatively lower.

4. Conclusion

NaOH treatment significantly improved the heavy metal sorption of oil palm frond. The sorption process data satisfactorily fitted Freundlich isotherm to suggest heterogeneity in the sorption sites. Owing to relatively weaker interactions with sorbent, Zn showed better regeneration efficiency of up to 88%. HCl was the best regenerating agent and the same trend was shared by both heavy metals. The isotherm and desorption results suggested that ion exchange was the main mechanism for the uptake of those metals. The desorption efficiency dropped by merely about 20% while the sorption capacity experienced a more drastic drop after the fourth cycle of use. The result was associated with the shifting of the metal exchange sites from sodium cycle to hydrogen cycle. This was further assisted by the physical and chemical damages occurred on the other metal binding sites.

Acknowledgement

The Research University (RU) grant from Universiti Sains Malaysia to support this work is gratefully acknowledged.

References

[1] B. Salamatinia, A.H. Kamaruddin, A.Z. Abdullah, Removal of Zn and Cu from wastewater by sorption on oil palm tree-derived biomasses: a preliminary study, J. Appl. Sci. 7 (15) (2007) 2020–2027.
[2] B. Salamatinia, A.H. Kamaruddin, A.Z. Abdullah, Modeling of heavy metal removal in a fixed-bed up-flow column using NaOH treated oil palm frond: a case study for Cu and Zn, Chem. Eng. J. 145 (2008) 259–266.
[3] B. Salamatinia, A.A. Zinatizadeh, A.H. Kamaruddin, A.Z. Abdullah, Optimization of Cu and Zn removal using pre-treated oil palm frond (OPF) by response surface methodology, Iran. J. Chem. Eng. 3 (2) (2006) 73–83.
[4] A. Kapoor, T. Viraraghavan, Heavy metal biosorption sites in *Aspergillus niger*, Biores. Technol. 63 (1998) 109–113.

[5] B. Yu, Y. Zhang, A. Shukla, S.S. Shukla, K.L. Dorris, The removal of heavy metals from aqueous solutions by sawdust adsorption—removal of lead and comparison with its adsorption with copper, J. Hazard. Mater. 84 (2001) 83–94.

[6] G.M. Gadd, Accumulation of metals by microorganisms and algae, in: H.J. Rehm, G. Reed (Eds.), Biotechnology: Special Microbial Processes, Wiley-VCH, Weinheim, 1988, pp. 422–423.

[7] M.Y. Arica, Ç. Arpa, B. Kaya, S. Bekta, A. Denizli, Ö. Genç, Comparative biosorption of mercuric ions from aquatic systems by immobilized live and heat-inactivated *Trametes versicolor* and *Pleurotus sajur-caju*, Biores. Technol. 89 (2) (2003) 145–154.

[8] W. Esteve, H. Budzinski, E. Villenave, Relative rate constants for the heterogeneous reactions of OH, NO_2 and NO radicals with polycyclic aromatic hydrocarbons adsorbed on carbonaceous particles. Part 1. PAHs adsorbed on 1–2 μm calibrated graphite particles, Atmos. Environ. 38 (35) (2004) 6063–6072.

[9] M. Ajmal, R.A.K. Rao, R. Ahmad, J. Ahmad, Adsorption studies on *Cirus reticulus* (fruit peel of orange): removal and recovery of Ni(II) from electroplating wastewater, J. Hazard. Mater. 79 (2000) 117–131.

[10] B. Acemioğlu, Removal of Fe(II) ions from aqueous solution by Calabrian pine bark wastes, Biores. Technol. 93 (1) (2004) 99–102.

[11] C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani, K. Ranganathan, Removal of dyes from aqueous solutions by cellulosic waste orange peel, Biores. Technol. 57 (1996) 37–43.

[12] N. Khalid, S. Ahmad, A. Toheed, J. Ahmed, Potential of rice husks for antimony removal, Appl. Radiat. Isot. 52 (2000) 31–38.

[13] C.R.T. Tarley, M.A.Z. Arruda, Biosorption of heavy metals using rice milling by-products, Chemosphere 54 (2004) 987–995.

[14] R. Juang, F. Wu, R. Tseng, Adsorption removal of Cu(II) using chitosan from simulated rinse solutions containing chelating agents, Water Res. 33 (1998) 2403–2409.