Application of agricultural fibers in pollution removal from aqueous solution

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ABSTRACT: Discharging different kinds of wastewater and polluted waters such as domestic, industrial and agricultural wastewaters into environment, especially to surface water, can cause heavy pollution of this body sources. With regard to increasing effluent discharge standards to the environment, high considerations should be made when selecting proper treatment processes. Any of chemical, biological and physical treatment processes have its own advantages and disadvantages. It should be kept in mind that economical aspects are important, too. In addition, employing environment-friendly methods for treatment is emphasized much more these days. Application of some waste products that could help in this regard, in addition to reuse of these waste materials, can be an advantage. Agricultural fibers are agricultural wastes and are generated in high amounts. The majority of such materials is generated in developing countries and, since they are very cheap, they can be employed as biosorbents in water and wastewater applications. Polluted surface waters, different wastewaters and partially treated wastewater may be contaminated by heavy metals or some organic matters and these waters should be treated to reduce pollution. The results of investigations show high efficiency of agricultural fibers in heavy metal and phenol removal. In this paper, some studies conducted by the author of this article and other investigators are reviewed.

Keywords: *Biosorption, heavy metals, industrial effluents, aqueous solutions, phenol, adsorption*

INTRODUCTION

In recent years, increasing awareness of water pollution and its far reaching effects has prompted concerted efforts towards pollution abatement (Dönmez *et al.,* 1999). Contamination of aqueous environments by heavy metals is a worldwide environmental problem due to their toxic effects and accumulation through the food chain (Kapoor *et al.,* 1999; Perez-Rama *et al.,* 2002; Sternberg and Dorn, 2002). Heavy metals are major pollutants in marine, ground, industrial and even treated wastewaters (Valdman *et al.,* 2001). The presence of heavy metals in drinking water can be hazardous to consumers; these metals can damage nerves, liver and bones and block functional groups of vital enzymes (Ewan and Pamphlet, 1996). Metal ions in water can occur naturally from leaching of ore deposits and from anthropogenic sources, which mainly include industrial effluents and solid waste disposal. Due to rapid development of industrial activities in recent years, the levels of heavy metals in water system have substantially increased over time

(Apak, 1998; Nouri *et al.,* 2006). Among these metal ions, the ions of Cd, Zn, Hg, Pb, Cr, Cu, etc. gain importance due to their high toxic nature even at very low concentrations. Various methods are available to isolate and remove these heavy metals from the environment. Adsorption is one of the easiest, safest and most cost-effective methods because it is widely used in effluent treatment processes (Balkose and Baltacioglu, 1992). Phenol is one of the most abundant organic pollutants in industrial wastewater (Alnaizy and Akgerman, 2000; Maleki *et al.,* 2005b). It is released to the environment from industries such as petroleum refining, coal tar, steel, tanning, pesticides, pharmaceuticals, etc. (Lesko, 2004; Entezari *et al,* 2003; Lathasreea *et al.,* 2004; Beltran *et al.,* 2005). Phenol has attracted public attention due to its presence in groundwater, rivers and drinking waters (Entezari *et al.,* 2003). Even in small quantities, phenol causes toxicity and foul odor to the water. Most countries specify maximum allowable concentration of phenol in effluent to be less than 1 ppm (Mahamuni and Pandit, 2005; Maleki *et al.,* 2005). This makes it necessary to

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develop methods that allow one to detect, quantify and remove heavy metals and phenol from the effluents (Khalfaour *et al.,* 1995). Techniques for removing heavy metals from industrial effluents include precipitation, ion exchange, adsorption, electrodialysis and filtration. However, these methods have limitations on selective separation and high cost of investment and operation of equipment (Ajmal *et al.,* 2003; Cheung *et al.,* 2001; Dae and Young, 2005; Dezuane, 1990; Peternele *et al.,* 1999). By using natural agricultural waste fibers, the adsorption of pollutants from aqueous solutions can be much more economical with regard to other similar physico-chemical processes. In the last few years, adsorption has been shown to be an economically feasible alternative method for removing trace metals from wastewater and water supplies (Allen and Brown, 1995; Gabaldon, *et al.,* 1996; Mahvi *et al.,* 2004a). Adsorption is an effective purification and separation technique used in industry, especially in water and wastewater treatments (Al-Asheh *et al.,* 2000). Several treatment methods such as chemical oxidation, biological treatment, wet oxidation, ozonolysis and activated carbon adsorption have been proposed for removing phenol from industrial effluents. In recent years, advanced oxidation processes (AOPs) have been developed (Akbal and Nuronar, 2003; Han *et al.,* 2004). One of these technologies is photolysis. This method is based on supplying energy to chemical compounds as radiation which is absorbed by reactant molecules that can pass to excited states and have sufficient time to promote reactions (Esplugas *et al.,* 2002). Direct photolysis has always been considered as one possible alternative because it is possible for the molecules of most organic compounds to transform, cleave bonds and even undergo complete destruction in the presence of UV eradiation (Bolton *et al.,* 1994). Activated carbon is the mostly-used adsorbent; nevertheless, it is relatively expensive among other sorbents and its use depends on the degree of the required treatment process and the local availability of activated carbon (Bailey *et al.,* 1999). Biosorption is the uptake of heavy metal ions and radionuclides from aqueous environments by biological materials, such as algae, bacteria, yeast, fungi, plant leaves and root tissues, which can be used as biosorbents for detoxification and recovery of toxic or valuable metals from industrial discharges (Davis *et al.,* 2003; Figueira *et al.,* 2000; Ma *et al.,* 2003; Veglio and Beolchini, 1997). It has many advantages including low capital and operating costs, selective removal of

metals, biosorbent regeneration and metal recovery potentiality, rapid kinetics of adsorption and desorption and no sludge generation. Biosorption technology has been shown to be a feasible alternative for removing heavy metals from wastewater (Benguella and Benaissa, 2002; Ma *et al.,* 2003; Volesky, 2001). Certain waste materials from industrial or agricultural operations may be potential alternative biosorbents (Baylor *et al.,* 1999; Mahvi *et al.,* 2005). It has been reported that wood wastes such as sawdust, barks and tree leaves effectively adsorb cadmium species from aqueous systems (Kumar and Dara, 1982). The binding mechanisms of heavy metals by biosorption could be explained by the physical and chemical interactions between cell wall ligands and adsorbents by ion exchange, complexation, coordination, chelation, physical adsorption and micro-precipitation (Nouri *et al.,* 2001). The diffusion of the metal from the bulk solution to active sites of biosorbents predominantly occurs by passive transport mechanisms and various functional groups such as carboxyl, hydroxyl, amino and phosphate existing on the cell wall of biosorbents which can bind the heavy metals. Tree leaves from agricultural operations have generally little or no economic value (Veglio and Beolchini, 1997; Volesky, 2001). Cost is an important parameter for comparing the sorbent materials (Bailey *et al.,* 1999). By-products of soybean and cottonseed hulls, rice straw and sugarcane bagasse were evaluated as metal ion adsorbents in aqueous solutions (Marshall and Champagne, 1995; Marshall *et al.,* 1993). Activated carbon prepared from rice husk, ground nut husk, fertilizer waste slurry, peanut hull, jute stick, moringa olefera seed husk, coconut husk and sawdust have been used for wastewater treatment and the potential of their ultimate usage may be determined by their adsorption capacity, regeneration characteristics and physical properties of subsequent products. In recent years, adsorption has emerged as a cost-effective and efficient alternative for removing heavy metals from low strength wastewaters (Manju and Anirudhan, 1997; Raji and Anirudhan, 1997; Warhust *et al.,* 1997). Rice husk are an agricultural waste produced in excess of 100 million tons as a by-product of the rice milling industry of which 96% is generated in developing countries. The utilization of this source of biomass would solve some disposal problem as well as access to cheaper materials for adsorption in water pollutants control system (Williams and Nugranad, 2000). Since

the main components of rice husk are carbon and silica (15-22% SiO_2 in hydrated amorphous form like silica gel), it has the potential to be used as an adsorbent (Khalid *et al.,* 2000; Nakbanpote *et al.,* 2000). When rice husk is burnt, about 20 wt% of the husk remains as ash. The rice husk ash has more than 95 wt% of silica with high porosity and large surface area, because it retains the skeleton of cellular structure. These properties of the rice husk ash could be used to synthesize siliceous raw materials such as clay materials (Aksu and Yener, 2001).

Application of biosorbent in heavy metals removal

Cadmium is introduced into the bodies of water from smelting, metal plating, cadmium-nickel batteries, phosphate fertilizer, mining, pigments, stabilizers, alloy industries and sewage sludge. The harmful effects of cadmium include a number of acute and chronic disorders, such as "itai-itai" disease, renal damage, emphysema, hypertension, and testicular atrophy (Leyva-Ramos *et al.,* 1997). There are two major sources of chromium contamination, wastewater metal finishing industries (hexavalent chromium) and tanneries (trivalent chromium). Chromium occurs most frequently as Cr (VI) or Cr (III) in aqueous solutions. Both valences of chromium are potentially harmful but hexavalent chromium has a grater risk due to its carcinogenic properties (Dakikiy *et al.,* 2002). Hexavalent chromium, which is primarily present in form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), poses significantly higher levels of toxicity in comparision with other valence states (Sharma and Forester, 1995). Toxicity of hexavalent chromium, even in small concentrations, has been well documented (Masakazu, 2003). Since the addition of chromium ions through industrial waste effluents into natural bodies of water causes serious environmental disruption, strict wastewater standards have been setup in many countries. In Japan, the standard on wastewater quality states that the maximum level permitted in wastewater is 2 mg/dm³ for total Cr and 0.05 mg/dm³ for Cr (VI) (Masakazu, 2003). Activated carbon from cheap and readily available sources such as coal, coke, peat wood, rice husk and tree leaves may be successfully employed for the removal of cadmium and other toxic heavy metals from aqueous solution (Elliott and Denneny, 1982; Dadhich *et al.,* 2004; Khalid *et al.,* 2000). Other adsorbents such as a wood charcoal, red mud, sun flower stalks, petioles felt-sheath and rice husk have also been used for the adsorption of cadmium (Lopez *et al.,* 1995; Marzal *et al.,* 1996; Namasivayam and Ranganthan, 1995). The feasibility of *Platanus orientalis* leaf and its ash, as adsorbent for removing cadmium from aqueous solution, was investigated by Mahvi *et al.* (2007b). The results show that adsorption of cadmium increased with increasing contact time and became almost constant after 60 min for POL and 60 min for its ash (Fig. 1). These results also indicate that the sorption process could be considered very fast because of the largest amount of Cd attached to sorbent within the first 60 min of adsorption. Experiments, concerning the effect of pH on the sorption, were carried out with the range of pH that was not influenced by the metal precipitation as metal hydroxide. The suitable pH ranges for cadmium was performed for the pH range variations of 3 to 9. Adsorption of cadmium on POL and its ash increased with increasing initial concentration of Cd. These results may be explained by an increase in the number of metal ions competing for the available binding sites in the adsorbent for complexation of Cd ion at higher concentration levels (Mahvi *et al.*, 2007b). The percentage adsorption of cadmium on rice husk and its ash increased as the pH of the solution increased and reached a maximum value at pH 9 (Mahvi *et al.*, 2005b). Adsorption of metal cation on adsorbent depends upon the nature of adsorbent surface and species distribution of the metal cation. Surface distribution mainly depends on pH of the system (Namasivayam and Ranganthan, 1995). Percent adsorption of metal ion decreased with the decrease in pH, because protons compete with metal ion for sorption sites on the adsorbent surface as well as the concomitant decrease of negative charge of the same surface (Sun and Shi, 1998). It has been reported that precipitation of cadmium starts at pH 8 3 (Ajmal *et al.*, 2003; Sun and Shi, 1998). The results show that adsorption of cadmium increased with increase in contact time and became almost constant after 45 min for rice husk and 30 min for its ash (Mahvi *et al.*, 2005b). These results also indicate that the sorption process can be considered very fast because of the largest amount of cadmium attached to the sorbent within the first 30 min of adsorption. Similar results have been reported by Ajmal *et al.* (2003) and Namasivayam and Panganathan (1995). The percentage adsorption increased from 95 to 97.8% for rice husk and from 96 to 99.4% for rice husk ash when adsorbents doses were increased from 0.5 to 10 g/L for both sorbents, but at the same time, adsorption

density decreased from 38.02 to 1.95 mg/g for rice husk and from 38.4 to 1.99 mg/g for its ash (Mahvi *et al.,* 2005b). Similar results were reported by other researchers (Cheung *et al.,* 2001; Namasivayam and Ranganthan, 1995; Peternele *et al.,* 1999). The efficiency of tea waste has been determined in processing heavy metal removal from both single metal solutions and various mixtures. Metals of interest were cadmium and Lead. They were chosen based on their industrial applications and potential pollution impact on the environment. Cadmium is a inessential and useless element to plants and animals. Lead is a hazardous waste and is highly toxic to humans, plants and animals (Low *et al.,* 2000). In addition, Ni is also one of the important toxic metals to humans, plants and animals (Ajmal *et al.,* 1998a). Biosorption of lead (II) and cadmium (II) from aqueous environments by brown algae *Sargassum spp.* biomass was studied by Nabizadeh *et al.* (2005). Fig. 2 shows the effect of pH on equilibrium uptake capacities of *Sargassum spp.* biomass for Pb^{2+} and Cd^{2+}. The effect of Na^+, K^+, Mg^{2+} and Ca^{2+} on equilibrium capacities of Pb^{2+} and Cd^{2+} biosorption by *Sargassum spp.* biomass is shown in Fig. 3 (Nabizadeh *et al.,* 2005). Biosorption of lead (II) and cadmium (II) from aqueous solutions using various biomasses has been studied. Cadmium (II) biosorption on *Asppergillus oryzae* reached equilibrium in 1 h with 90% biosorption taking place in the initial 10 min (Kiff and Little, 1986). Kinetic data of cadmium (II) biosorption by chitin presented high correlation with the pseudo-second order rate equation (Benguella and Benaissa, 2002). Matheickal and Yu (1999) observed that the maximum uptake capacities of *Durvillaea potatorum* and *Ecklonia radiata* for Pb^{2+} were 1.6 and 1.3 mmol/g, respectively.
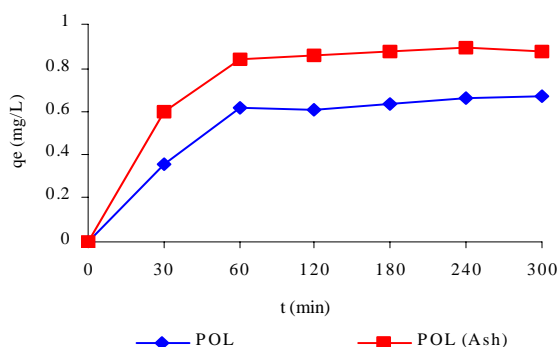

Fig. 1: Effect of contact time on the removal of Cd by POL and its ash (Adsorbent dosage = 2 mg/LCd concentration = 2 mg/L) (Mahvi *et al.,* 2007b)
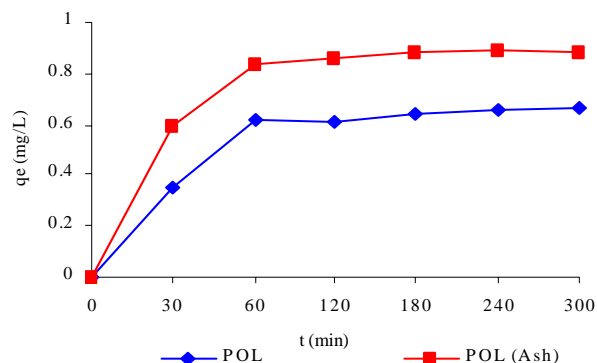

Fig. 2: Effect of pH on equilibrium capacities of Pb^{2+} and Cd^{2+} biosorption by *Sargassum spp.* biomass (Nabizadeh *et al.,* 2005)
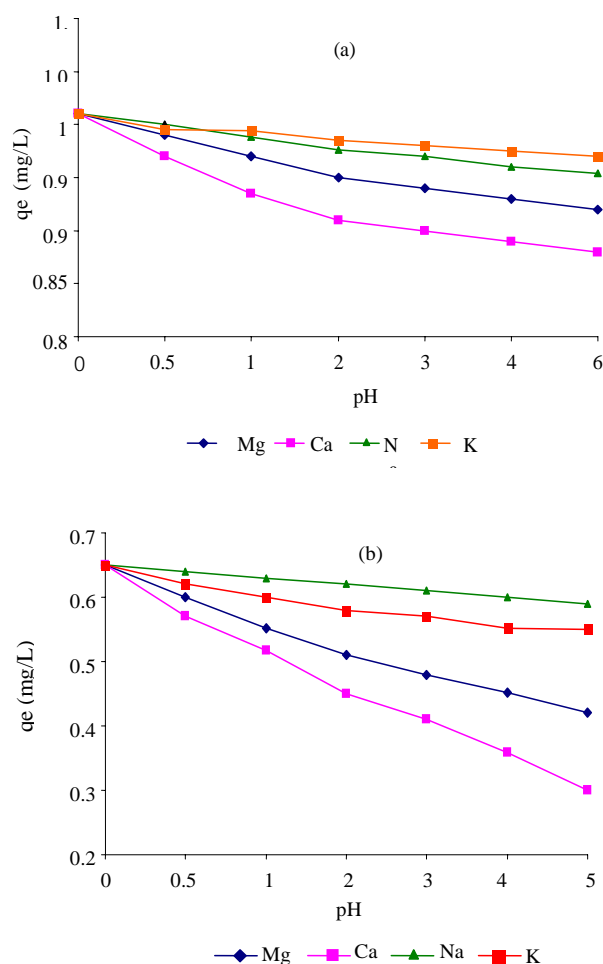

Fig. 3: Effect of Na^+, $K+$, Mg^{2+} and Ca^{2+} on equilibrium capacities of (a) Pb^{2+} and (b) Cd^{2+} biosorption by *Sargassum spp.* biomass (C0 = initial concentration of light metal ions) (Nabizadeh *et al.,* 2005)

Scott and Karanjkar studied cadmium (up to 25 ppm) adsorption on to biofilm covered granular activated carbon (Scott and Karanjkar, 1995; Scott and Karanjkar, 1995). There has been no study on the removal of low concentration (less than 5 ppm) of cadmium by biofilm/GAC. The underlying objective behind using GAC as a support for biofilm was to provide the foundation for remediation processes that could provide metal biosorption concurrently with removing non-metal contaminants such as organic compounds. The objective of this study was to investigate the adsorption characteristics of cadmium (less than 5 mg/L) on to plain (non-biofilm) GAC, biofilm and biofilm/GAC and to determine the effects of temperature and pH on the cadmium uptake isotherms by plain GAC and biofilm/GAC. The results of this study shows that adsorption coefficient (Kad) for BAC is 2 to 3 times greater than those with plain GAC and the bed volumes of water containing 0.5 mg/L Cd^{2+} treated at breakthrough for GAC, biofilm and BAC columns were 45, 85 and 180 BV, respectively. Also it was found that BAC is more efficient than GAC in the removing of Cd from water environment (Danati-Tilaki *et al.*, 2004).

Biosorption of Pb^{2+} and Cd^{2+} by protonated *Sargassum glaucescens* biomass in a continuous packed bed column was investigated by Naddafi *et al.* (2007). Mahvi *et al.* (2007c) performed an investigation on the efficiency of *Platanus orientalis* leaves (POL) and their ashes on removing chromium from diluted aqueous solutions. Adsorption of chromium increased with increase in contact time and became almost constant after 120 min for *Platanus orientalis* leaves and their ashes. These results also indicate that sorption process can be considered very fast because of the largest am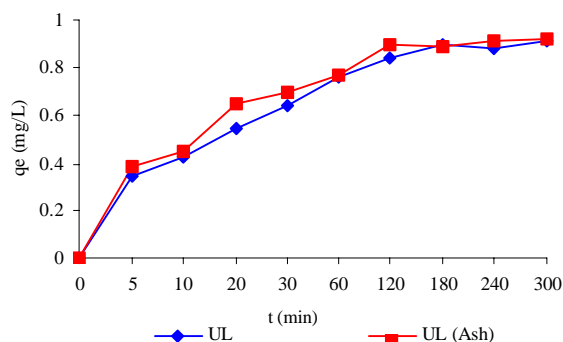ount of chromium attached to sorbent within the first 60 min of adsorption. Adsorption of chromium on POL and its ash increased with increase in initial concentration of Cr(VI) to reach 20 mg/L. Light metals can disturb adsorption of heavy metals on any adsorbent. Ca^{+2} and Mg^{+2} had more effect than Na^+ and K^+ in decreasing qe for Cr(VI) adsorption (Mahvi *et al.*, 2007c). Fig. 4 shows the effect of contact time on the removal of chromium (VI) by plant Ulmus (UL) and its ash. Experiments concerning the effect of pH on the sorption were carried out with the range of pH that was not influenced by the metal precipitation as metal hydroxide. The effect of initial metal ion concentration on the adsorption capacity of UL and its ash was studied under optimum conditions (pH = 6, Temp. = 24-25 °C) (Gholami *et al.*, 2006). It has been reported that precipitation of chromium starts at pH= 6.5 (Ajmal *et al.*, 2003).

Feasibility of rice husk and its ash as an adsorbent for the removal of cadmium from aqueous solution was investigated by Mahvi *et al.* (2005a). The results of this study indicate that the adsorption efficiency is maximum for Pb and minimum for Cd. Fig. 5 represents the adsorption efficiency for various concentrations of lead. As it is obvious, tea waste is a wonderful adsorbent for removing lead from wastewater. Increase in adsorption capacity of the adsorbent seems to be a result of increase in total surface area of the adsorption sites. Thereby, it would increase adsorption by grinding the adsorbent. For example, 94% removal of lead from a 5 mg/L solution was possible by applying 0.5g tea waste whereas the similar amount of adsorbent was not enough to treat a 100 mg/L lead solution to more than about 76%. However, by increasing the amount of tea waste to 1.5 g, it was possible to increase the efficiency of adsorption to about 96.5% for the same

Fig. 4: Effect of contact time on the chromium (VI) removal of (VI) by UL and its ash (adsorbent dosage = 2 g/L. chromium concentration = 2 mg/L) (Gholami *et al.*, 2006)
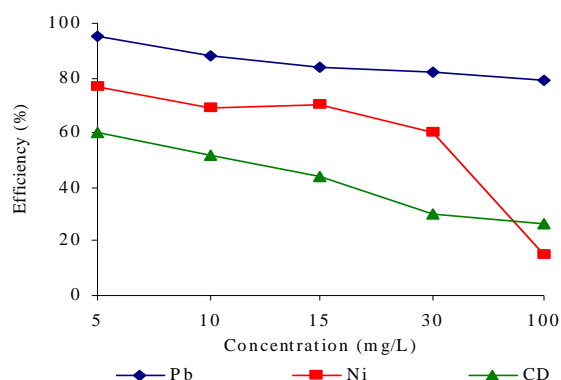

Fig. 5: Adsorption percent of Pb, Cd and Ni by 0.5 g tea waste (Mahvi *et al.*, 2005a)
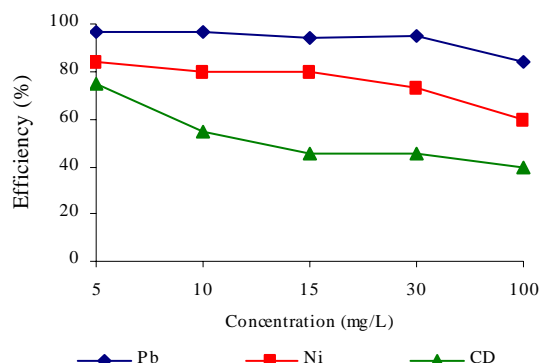
Fig. 6: Adsorption percent of Pb, Cd and Ni by 1.0 g tea waste (Mahvi *et al.,* 2005a)
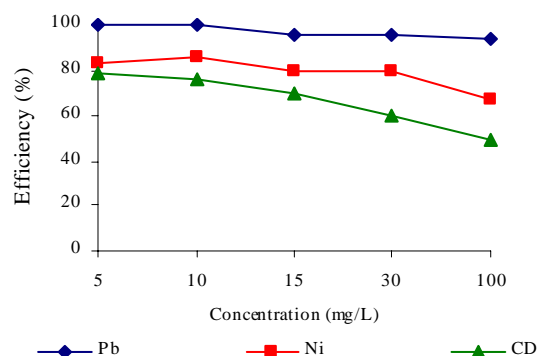

Fig. 7: Adsorption percent of Pb, Cd and Ni by 1.5 g tea waste (Mahvi *et al.,* 2005a)
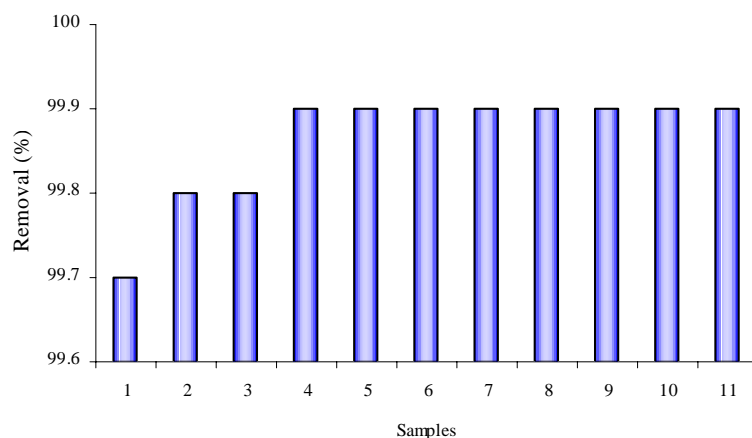

Fig. 8: Removal efficiency of Cd, the side in contact with nutrient (Mahvi *et al.,* 2004c)

solution (100 mg/L Pb). Thus, there would be a better treatment through using excess tea waste (Mahvi *et al.,* 2005a). As this adsorbent is cheap and available, there would be no problem to increase its consumption (Ajmal *et al.,* 1998b).

By comparing the results of the study, it can be concluded that the adsorption efficiency is also dependent upon the type of metal, as for Ni, not more than 76% removal is achieved in the same conditions (0.5 g adsorbent in solutions of 5, 10, 15, 30 and 100 mg/L), but for Pb and Cd the efficiencies are reported to be 94 and 60%, respectively (Figs. 6 and 7). As mentioned before, the maximum and minimum removal efficiencies in the first stage of experiments with 0.5g adsorbent were 94 and 76.3% for Lead, 76 and 14.8% for Ni and 60 and 24.8% for Cd. But for the mixture of these metals, a 3.5% decrease has been observed for lead adsorption whereas Ni adsorption has decreased in most concentrations (12.2%) (Mahvi *et al.,* 2005a). Some bacteria like the heavy metal resistant alcaligenes

eutrophos CH34 strains are able to promote biomineralization, being the biologically induced crystallization of heavy metals. In the presence of heavy metals, this strain may create an alkaline environment in the periplasmic space and outer cell environment appropriate induction of heavy metals resistance mechanisms. In such an environment, metal hydroxides are formed together with metal bicarbonates resulting from the carbonates production by the cell. Also, metals bind to outside cell membrane proteins and the metal hydroxides and bicarbonates precipitate around these nucleation foci inducing further metal crystallization. Mahvi *et al.* (2004c) studied on biological removal of cadmium by alcaligenes eutrophus CH34. The result of this study is presented in Fig. 8. In these studies, it was shown that electrocoagulation process achieves a fast and effective reduction of cadmium (more than 99%) present in industrial effluents (Bazrafshan *et al.,* 2006; Mahvi *et al.,* 2007a).

Phenol removal

Phenols, as a class of organics, are similar in structure to the more common herbicides and insecticides in that they are resistant to biodegration. Phenol is very soluble in water. The odor threshold for phenol is 0.04 ppm (US EPA). Their presence in water supplies are noticed as bad taste and odor problems (Mostafa *et al.,* 1989). In the presence of chlorine in drinking water, phenols form chlorophenol, which has a medicinal taste that is quite pronounced and objectionable (Rengaraj *et al.,* 2002; Street *et al.,* 1995). Phenols are considered as priority pollutants, since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants due to their potential harm to human health. Stringent US Environmental Protection Agency (EPA) regulation call for lowering phenol content in the wastewater to less than 1 mg/L (Banat *et al.,* 2000). There are many methods such as oxidation, precipitation, ion change, solvent extraction and adsorption for removing phenols and its derivatives from aqueous solution (Aksu and Yener, 2001; Rengaraj *et al.,* 2002). Because of the high cost and variable performance of carbon regeneration, single use materials are desirable (Kummar *et al.,* 1987; Rengaraj *et al.,* 2002). This has led many workers to look for more economical, practical and efficient techniques. Bottom ash, brick-kilm ash, fly ash, peat, soil, rice husk, wood, sawdust, bagasse and carbonized bark are some new adsorbent used for organic pollutants (Aksu and Yener, 2001; Edgehill *et*

Table 1: Maximum efficiency removal percentage (Samarghandi *et al.,* 2006)

Pollutant pH	Cd	Pb	Phenol
3.5	26	99.9	51
7	39.9	99.8	44
11	94.5	99.9	76

al., 1998; Kummar *et al.,* 1987; Rengaraj *et al.,* 2002; Srivastava *et al.,* 1997; Street *et al.,* 1995). The possibility of using rice husk and rice husk ash for removing phenol from aqueous solution was investigated by Mahvi *et al.* (2004a). The adsorption of phenol from aqueous solution is dependent on the pH of the solution, which affects the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate species (Mahvi *et al.,* 2004a). The adsorption of phenol by rice husk and its ash were studied at various pH values (Aksu and Yener, 2001; Caturla *et al.,* 1998; Halouli and Drawish, 1995; Kummar *et al.,* 1987; Street *et al.,* 1995). The results are displayed in Fig. 9. As was expected, the adsorbed amount decreases with increasing the pH value. This can be attributed to the dependency of phenol ionization on the pH value (Banat *et al.,* 2000). The results show that equilibrium time required for the adsorption of phenol on rice husk and its ash are almost 6 h and 3 h, respectively. These results also indicate that the sorption process can be considered very fast because of the largest amount of phenol attached to the sorbent within the first 120 min of adsorption. This indicates that rice husk ash would require less residence
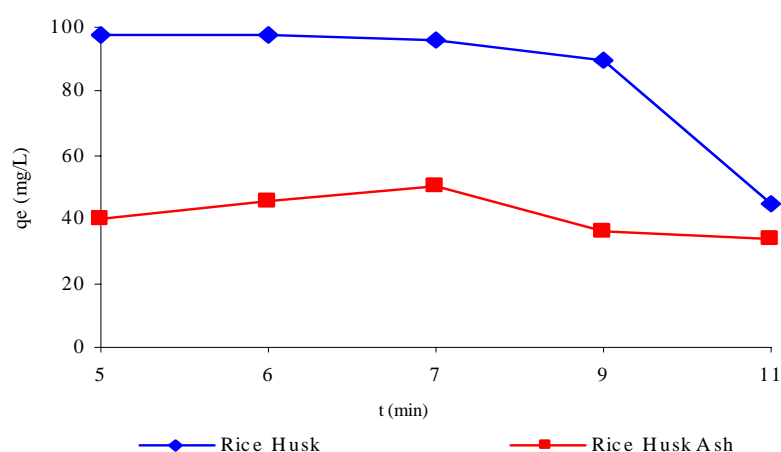

Fig. 9: Effect of pH on the removal of phenol by rice husk and rice husk ash (rice husk dosage = 3 g/100 mL, rice husk ash dosage = 0.5 g/ 100 mL, phenol concentration = 0.2 mg/L) (Mahvi *et al.,* 2004a)

time for the complete removal of phenol compared to rice husk (Mahvi *et al.,* 2004a). Samarghandi *et al.* (2006) investigated on phenol, lead and cadmium by means of UV/TIO$_2$/H$_2$O$_2$ processes. The results of this study are shown in Table 1. These results show that the removal of pollutants such as cadmium and phenol is dependent upon pH. As pH increases from 3.5 to 11, the efficiency removal increases from 26 to 94.5 and from 51 to 76%, respectively. This study indicates that the removal of lead is independent of pH.

CONCLUSION

The analyses of the results indicate that tea waste like most other natural absorbents can be used in the treatment process of heavy metals and the treatment efficiency may be as high as 100% by choosing the adsorbent amount precisely. The concentration of heavy metal has also an important effect on the treatment outcome. Tea waste is a cheep material and thus it would be convenient to use it in industrial wastewater treatment plants. Meanwhile, it is possible to increase the treatment efficiency by pretreatment with some chemicals such as acids, bases and detergents (Ajmal *et al.,* 1998a). In case of *platanus orientalis* leaves, about 99% removal efficiency was observed within 3 hrs of contact time by adsorbent which was carbonized. Also, the removal efficiency of chromium (VI) by Ulmus leaves has been found to be greater than 85%. The kinetic of chromium (III) biosorption by *Sargassum spp.* biomass is fast, reaching 60% of the total uptake capacity within 10 min (Cossich *et al.,* 2002). The biosorption of lead (II) by *Durvillaea potatorum* was rather rapid and 90% of the total uptake occurred within 30 min (Matheickal and Yu, 1999). *Sargassum spp.* can be classified as an efficient biosorbent because of rapid kinetic, remarkable biosorption capacity and selective removal of metals. Thus, the biosorbent has a high potential to be applied in full-scale for removing heavy metals from aqueous environments. Rice husk and rice husk ash adsorption capacity strongly depends on the pH of the solution. The sorption capacity is decreased with increase in pH and initial phenol concentration. Rice husk ash has higher adsorption capacity for phenol. However, the experimental results indicate that rice husk's ability to adsorb phenol and consequently its possible utilization in the treatment of phenol-contaminated solution and its adsorptive capacity is limited.

REFERENCES

Ajmal, M.; Hussain Khan, A.; Ahmad, S.; Ahmad, A., (1998a). Role of sawdust in the removal of copper(II) from industrial wastes, Wat. Res., 32 (10), 3085-3091.

Ajmal, M.; Mohammad, A.; Yousuf, R.; Ahmad, A., (1998b). Adsorption behavior of cadmium, zink, nickel, and lead from aqueous solution by mangifera india seed shell, India J. Environ Hlth, 40 (1), 15-26.

Ajmal, M.; Rao, R. A.; Anwar, S.; Ahmad, J.; Alunad, R., (2003). Adsorption studies on rice husk: removal and recovery of Cd (II) from wastewater, Bioresour. Technol., 86 (2), 147-149.

Akbal, F.; Nuronar, A., (2003). Photocatalytic degradation of phenol. Environ. Monit. Assess., 83 (3), 295-302

Aksu, Z.; Yener, J., (2001). A comparative adsorption/boisorption study of mono-chlorinated phenols onto various sorbent. Waste Manage., 21 (8), 695-702.

Al-Asheh, S.; Banat, F.; Al-Omari, R.; Duvnjak, Z., (2000). Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data, Chemosphere, 41 (5), 659-665.

Allen, S. J.; Brown, P. A., (1995). Isotherm analyses for single component and multicomponent metal sorption onto lignite, J. Chem. Technol. Biotechnol., 62, 7-24.

Alnaizy, R.; Akgerman, A., (2000). Advanced oxidation of phenolic compounds. Adv. Environ. Res., 4 (3), 233-244

Apak, R.; Tutem, E.; Hugul, M.; Hizal, J., (1998). Heavy metal cation retention by unconventional sorbents (red muds and fly ashes), Wat. Res., 32 (2), 430-440.

Bailey, S. E.; Olin, T. J.; Bricka, R. M.; Adrian, D. A., (1999). A review of potentially low-cost sorbents for heavy metals, Wat. Res., 33 (11), 2469-2479.

Balkose, D.; Baltacioglu, H., (1992). Adsorption of heavy metal cations from aqueous solution by wool fiber, J. Chem. Tech. Biotechnol., 54 (4), 393-397.

Banat, F. A.; Al-Bashir, B.; Al-Asheh, S.; Hayajneh, O., (2000). Adsorption of phenol by bentonit, Environ. Pollut., 107 (3), 391-398.

Baylor, S. E.; Olin, T. J.; Bricka, R. M.; Adrian, D. D., (1999). Review of potentially low-cost sorbents for heavy metals, Wat. Res., 33, 2469-2479.

Bazrafshan, E.; Mahvi, A. H.; Nasseri, S.; Mesdaghinia, A. R., Vaezi, F., (2006). Removal of cadmium from industrial effluents by electrocoagulation process using iron electrodes, Iranian J. Environ. Health Sci. Eng., 3 (4), 261-266.

Beltran, F. J.; Rivas, F. J.; Gimeno, O., (2005). Comparison between photocatalytic ozonation and other oxidation processes for the removal of phenols from water, Chem. Technol. Biot, 80 (9), 973-984.

Benguella B.; Benaissa, H., (2002). Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies, Water Res., 36 (10), 2463–2474.

Bolton, J. R.; Carter, S. R., (1994). Homogeneous photodegradation of pollutants in contaminated water: An introduction in aquatic and surface photochemistry. Lewis Publishers, Boca Raton, USA., 467-490.

Caturla, F.; Martin-Martinez, J. M.; Molina-Sabio, M.; Rodrignez-Reinoso, F.; Torregrosa, R., (1998). Adsorption

of substituted phenols on activated carbon, J. Coll. Interface Sci., 124 (3), 528-534.

Cheung, C. W.; Porter, J. F.; McKay, G., (2001). Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char, Water Res., 35 (2), 605-621.

Cossich, E. S.; Tavares, C. R. G.; Ravagnani, T. M. K., (2002). Biosorption of chromium (III) by sargassum spp. Biomass, Electron. J. Biotechnol., 5 (2), 133-140.

Dadhich, A. S.; Beebi, S. K.; Kavitha, G. V., (2004). Adsorption of Ni (II) using agrowaste, rice husk, J. Environ. Sci. Eng., 46 (3), 179-185.

Dae, W. C.; Young, H. K., (2005). Chromium (VI) removal in a semi-continues process of hallow fiber membrane with organic extractants, Korean J. Chem. Eng., 22 (6), 894-898.

Dakikiy, M.; Khami, A.; Manassara, A.; Mereb, M., (2002). Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents, Adv. Environ. Res., 6 (4), 533-540.

Danati-Tilaki, R. A.; Mahvi, A. H.; Shariat, M.; Nasseri, S., (2004). Study of cadmium removal from environmental water by biofilm covered granular activated carbon, Iranian J. Publ. Health, 33 (4), 43-52.

Davis, T. A.; Volesky, B.; Mucci, A., (2003). A review of the biochemistry of heavy metal biosorption by brown algae. Wat. Res., 37 (18), 43 11-4330.

Dezuane, J., (1990). Handbook of drinking water quality standards and controls, Van Nostrand Reinhold, New York, 64-69.

Dönmez, G. Ç., Aksu, Z.; Öztürk, A.; Kutsal, T., (1999). A comparative study on heavy metal biosorption characteristic of some algae, Proc. Biochem., 34 (5), 885-892.

Edgehill, R.; Lu, G. Q., (1998). Adsorption characteristics of carbonized bark for phenol penta phlorophenol, J. Chem. Technol. Biotechnol., 71 (1), 27-34.

Elliott, H.; Denneny, C. M., (1982). Soil adsorption of cadmium from solutions containing organic ligands, J. Environ. Qual., 11 (2), 658-663.

Entezari, M. H.; Petrier, C.; Devidal, P., (2003). Sonochemical degradation of phenol in water: a comparison. a comparison of classical equipment with a new cylindrical reactor, Ultrason. Sonochem., 10 (2) 103-108.

Esplugas, S.; Gimenez, J.; Contreras, S.; Pascual, E.; Rodriguez, M., (2002). Comparison of different advanced oxidation processes for phenol degradation. Water Res., 36 (4), 1034-1042.

Ewan, K. B.; Pamphlet, R., (1996). Increased inorganic mercury in spinal motor neurous following chelating agents, Neur. Tox.

Figueira, M. W.; Volesky, B.; Ciminelli, V. S.; Roddick, F. A., (2000). Biosorption of metals in brown seaweed biomass, Wat. Res., 34 (1), 196-204.

Gabaldon, C.; Marzal, P.; Seco, A., (1996). Cadmium and zinc adsorption on to activated carbon: influence of temperature, pH and mental/carbon ratio, J. Chem. Tech., Biotechnol., 66 (7), 279-285, 1996

Gholami, F.; Mahvi, A. H.; Omrani, Gh. A.; Nazmara, Sh.; Ghasri, A., (2006). Removal of chromium (VI) from aqueous

solution by ulmus leaves, Iranian J. Environ. Health Sci. Eng., 3 (2), 97-102.

Halouli, K. A.; Drawish, N. M., (1995). Effects of pH and inorganic salts on the adsorption of phenol from aqueous systems on activated decolourising charcoal, Sep. Sci. Technol., 30 (17), 3313-3324.

Han, W.; Zhu, W.; Zhang, P.; Zhang, Y.; Li, L., (2004). Photocatalytic degradation of phenols in aqueous solution under irradiation of 254 and 185 rim UV light. Catal. Today, 90 (2), 319-324.

Hayashi, H.; Nakashima, S., (1992). Synthesis of trioctahedral smectite from rice husk ash as agro-waste, Clay Science, 8 (4), 181-193.

Kapoor, A.; Viraraghavan, T.; Cullimore, D. R., (1999). Removal of heavy metals using the fungus Aspergillus niger, Biores. Technol., 70 (1), 95–104.

Khalfaour, B.; Meniai, A. H.; Borja, R., (1995). Removal of copper from industrial wastewater by raw charcoal obtained from Reeds, J. Chem. Tech. Biotechnol., 64 (2), 153-156.

Khalid, N.; Ahmad, S.; Toheed, A., (2000). Potential of rice husks for antimony removal, Appl. Rad. Isotopes, 52 (1), 30-38.

Kiff, R. J.; Little, D. R., (1986). Biosorption of heavy metals by immobilized fungal biomass, in: immobilization of ions by biosorption, Ed., Hunt EH. 1st Ed., Ellis Horwood, Chichster, UK, 219.

Kumar, P.; Dara, S. S., (1982). Utilization of agricultural wastes for decontaminating industrial /domestic wastewaters from toxic metals, Agr. Wastes., 4 (1), 213-223.

Kummar, S., Upadhyay, S. N.; Upadhyay, Y. D., (1987). Removal of phenols by adsorption on fly ash, J. Chem. Tech. Biot., 37 (4), 281-290.

Lathasreea, S.; Nageswara, R. A.; SivaSankarb, B.; Sadasivamb, V.; Rengarajb, K., (2004). Heterogeneous photocatalytic mineralisation of phenols in aqueous solutions. Mol. Catal. A- Chem., 223 (1-2), 101-105.

Lesko, T. M.; (2004). Chemical Effects of Acoustic Cavitation, Ph.D. thesis reported in California Institute of Technology, Pasadena, California, USA.

Leyva-Ramos R.; Rangel-Mendez, J. R.; Men-doza-Barron, J.; Fuentes-Rubio, L.; Guer-rero-Coronado, R. M., (1997). Adsorption of cadmium (II) from aqueous solution on to activated carbon, Water Sci. Tech., 35 (7), 205-211.

Lopez, F. A.; Perez, C.; Sainz, E.; Alonso, M., (1995). Adsorption of Pb (II) on blast furnace sludge, J. Chem. Tech. Biot., 62 (2), 200-206.

Low, K. S.; Lee, C. K.; Liew, S. C., (2000). Sorption of cadmium and lead from aqueous solution by spent grain, Process Biochem., 36 (1), 59-64.

Ma, W.; Tobin, J. M., (2003). Development of multimetal binding model and application to binary metal biosorption onto peat biomass, Water. Res., 37 (16) 3967-3977.

Mahamuni, N. N.; Pandit, A. B., (2005). Effect of additives on ultrasonic degradation of phenol. Ultrason. Sonochem, 13 (2), 165-174.

Mahvi, A. H.; Maleki, A.; Eslami, A., (2004a). Potential of rice husk and rice husk ash for phenol removal in aqueous system, Am. J. Appl. Sci., 1 (4), 321-326.

Mahvi, A. H.; Maleki, A. ; Eslami, A., (2004b). Potential of rice husk and rice husk ash for phenol removal in aqueous systems, Am. J. Appl. Sci., 1 (4), 321-326.

Mahvi, A. H.; Bazrafshan, E., (2007a). Removal of cadmium from industrial effluents by electrocoagulation process using aluminum electrodes, World Appl. Sci. J., 2 (1), 34-39.

Mahvi, A. H.; Diels, L. (2004c). Biological removal of cadmium by alcaligenes eutrophus CH_4, Int. J. Environ. Sci. Tech. 1: 207-212.

Mahvi, A. H.; Naghipour, D.; Vaezi, F.; Nazmara, S., (2005a). Tea waste as an adsorbent for heavy metal removal from industrial wastewaters, Am. J. of Appl. Sci., 2: 372-375.

Mahvi, A. H.; Nouri, J.; Babaei, A. A.; Nabizadeh, R., (2005). Agricultural activities impact on groundwater nitrate pollution, Int. J. Environ. Sci. Tech., 2 (1), 41- 47.

Mahvi, A. H.; Nouri, J.; Omrani, G. A.; Gholami, F., (2007b). Application of platanus orientalis leaves in removal of cadmium from aqueous solution, World Appl. Sci. J., 2 (3), 40-44.

Mahvi, A. H.; Alavi, N.; Maleki, A., (2005b). Application of rice husk and its ash in cadmium removal from aqueous solution, Pakistan J. Biol. Sci., 8 (5), 721-725.

Mahvi, A. H.; Nabizadeh, R.; Gholami, F.; Khairi, A., (2007c). Adsorption of chromium from wastewater by platanus orientalis leaves, Iran. J. Environ. Health Sci. Eng., 4 (3), 191-196.

Maleki, A., Zazoli, M. A.; Eslami, A., (2005). Adsorption of phenol by commercial powdered activated carbon in aqueous solution. Al-Haitham. J. Sci. Tech., 1 (1), 73-78.

Manju, G. N.; Anirudhan, T. S., (1997). Use of coconut fiber Pith-based Pseudo-activated carbon for Chromium (VI) removal, Indian J. Environ. Health, 39 (4), 289-298.

Marshall, W. E.; Champagne, E. T., (1995). Agricultural byproducts as adsorbents for metal ions in laboratory prepared solutions and in manufacturing wastewater, J. Environ. Sci. Health., 30 (2), 241-261.

Marshall, W. E.; Champagne, E. T.; Evans, W. J., (1993). Use of rice milling byproducts (hulls and bran) to remove metal ions as aqueous solution, J. Environ. Sci. Health, 28 (9), 1977-1992.

Marzal, P.; Seco, A.; Gabaldon, C., (1996). Cadmium and zinc adsorption onto activated carbon: influence of temperature, pH and metal/carbon ratio, J. Chem. Tech. Biotech., 66 (3), 279-285.

Masakazu, A., (2003). Removal of Cr (VI) from aqueous solution London plane leaves, J. Chem. Tech. Biotech., 78 (5), 601-604

Matheickal, J. T.; Yu, Q., (1999). Biosorption of lead (II) and copper (II) from aqueous solutions by pre-treated biomass of Australian marine algae, Bioresource Tech., 69 (3), 223 -229.

Mostafa, M. R.; Sarma, S. E.; Yousef, A. M., (1989). Removal of organic pollutants from aqueous solution: part 1, adsorption of phenol by activated carbon, Indian J. Chem., 28 (1), 94-8.

Nabizadeh, R.; Naddafi, K.; Saeedi, R.; Mahvi, A. H.; Vaezi, F.; Yaghmaeian, K.; Nazmara, S., (2005). Kinetic and equilibrium studies of lead and cadmium biosorption from aqueous solutions by sargassum spp. biomass, Iran. J. Environ. Health Sci. Eng., 2 (3), 159-168.

Naddafi, K., Nabizadeh, R.; Saeedi, R.; Mahvi, A. H.; Vaezi, F.; Yaghmaeian, K.; Ghasri, A.; Nazmara, S., (2007). Biosorption of lead(II) and cadmium(II) by protonated sargassum glaucescens biomass in a continuous packed bed column, J. Hazard. Mater. 147 (3), 785-791.

Nakbanpote, W.; Thiravetyan, P.; Kalambaheti, C., (2000). Preconcentration of gold by rice husk ash. Miner. Eng., 13 (4), 391-400.

Namasivayam, C.; Ranganthan, K., (1995). Revoval of Cd (II) from wastewater by adsorption on waste Fe (III)/ Cr (III) hydroxide, Water. Res., 29 (7), 1737-1744.

Nouri, J.: Alloway, B. J.; Peterson, P. J., (2001). Forms of heavy metals in sewage sludge and soil amended with Sludge. Pakistan J Biol. Sci. 4 (12), 1460-1465.

Nouri, J.; Mahvi, A. H.; Babaei, A. A.; Jahed, G. R.; Ahmadpour, E., (2006). Investigation of heavy metals in groundwater Pakistan J. Biol. Sci. 9 (3), 377-384.

Perez-Rama, M.; Alonso, J. A.; Lopez, C. H.; Vaamonde, E. T., (2002). Cadmium removal by living cells of the marine microalga tetraselmis suecica, Bioresource. Tech., 84 (3), 265-270.

Peternele, W. S.; Winkler-Hechenleitner, A. A.; GomezFineda, E. A., (1999). Adsorption of Cd (II) and Pb (II) on to functionalized formic lignin from sugar cane bagasse, Bioresource. Tech., 68 (1), 95-100.

Raji, C.; Anirudhan, T. S., (1997). Chromium (VI) adsorption by saw dust carbon: kinetics and equilibrium, Indian. J. Chem. Tech., 4 (1), 228-239.

Rengaraj, S.; Seuny-Hyeon, M.; Sivabalan, R., (2002). Agricultural solid waste for the removal of organics: adsorption of phenol from water and wastewater by palm seed coat activated carbon, Waste Manage., 22 (5), 543-548.

Samarghandi, M. R.; Nouri, J.; Mesdaghinia, A. R.; Mahvi, A. H.; Naseri, S.; Vaezi, F., (2006). Efficiency removal of phenol, lead and cadmium by means of $UV/TIO_2/H_2O_2$ processes, Int. J. Environ. Sci. Tech., 4 (1), 19-25.

Scott, J. A.; Karanjkar, A. M., (1995). Adsorp-tion isotherms and diffusion coefficients for metals biosorbed by biofilm coated granular activated carbon, Biotech Let-ters, 17 (11), 1267-70.

Scott J. A.; Karanjkar, A. M., (1992). Repeated cadmium biosorption by regenerated Enterobacter aerogenes biofilm at-tached to activated carbon, Biotech Let-ters, 14 (8), 737-40.

Sharma, D. C.; Forester, C. F., (1995). Column studies into the adsorption of Chromium using sphagnum moss peat. Bioresource. Tech., 52 (3), 261-267.

Srivastava, S. K.; Tyagi, R.; Pal, N.; Mohan, D., (1997). Process development for removal of substituted phenol by carbonaceouse adsorbent obtained from fertilizer waste, J. Environ. Eng., 123 (9), 842.

Sternberg, S. P. K.; Dorn, R. W., (2002). Cadmium removal using cladophora in batch, semi-batch and flow reactors, Bioresource. Tech., 81 (3), 249-255.

Street, M., Patrick, J. W.; Camporro-perez, M. J., (1995). Sorption of phenol and p-chlorophenol from water using convention and novel activated carbons, Water. Sci. Res., 29 (2), 467.

Sun, G.; Shi, W., (1998). Sun flowers Stalks as adsorbents for the removal of metal ions from wastewater, Ind. Eng. Chem. Res., 37 (4), 1324-1328.

Valdman, E.; Erijman, L.; Pessoa, F. L. P.; Leite, S. G., (2001). Continuous biosorption of Cu and Zn by immobilized waste biomass Sargassum sp, Process Biochem., 36 (8-9), 869-873.

Veglio, F.; Beolchini, F., (1997). Removal of metals by biosorption: a review, Hydrometalorgy, 44 (3), 301-316.

Volesky, B., (2001). Detoxification of metal-bearing effluents: biosorption for the next century, Hydrometallurgy, 59 (2-3), 203-216.

Warhust, M.; Mcconna, G. L.; Ulmuslardsj, T., (1997). Characterization and applications of activated carbon produced from Moringa oleifera seed husk by single-step steam pyrolysis, Water. Res., 31 (4), 759-766.

Williams, P. T.; Nugranad, N., (2000). Comparison of products from the pyrolysis and catalytic of rice husks. Energy, 25 (6), 493-513.

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