J. King Saud Univ., Vol. 21, *Science* (Special Issue), pp. 215-220, Riyadh (2009/1430H.)

Chromium(VI) Biosorption From Aqueous Solutions Using Plant Based Biomass Solid Wastes

Taha M. A. Razek [1*], Khaled R. A. Metwally[2]

1-Environmental Basic Sciences Dept., Institute of Environmental Studies and Research, Ain Shams University, Cairo, Egypt.
2- Graduate Student, Agricultural Science Department, Institute of Environmental Studies and Research, Ain Shams University, Cairo, Egypt.
** Corresponding author, e-mail tahaelsabbagh@yahoo.com*

Keywords: Nut shell, Walnut shell, Okra preparation waste, Adsorption isotherms, Wastewater

Abstract. Plant based biomass wastes were tested as adsorbents for the adsorption of Cr(VI) from aqueous solutions. These wastes were okra preparation wastes (OPW), nut shell wastes (NSW), and walnut shell wastes (WSW). Batch scale experiments were carried out to study the main adsorption parameters such as pH, adsorbent concentration, initial adsorbate concentration, and kinetics of biosorption. The process was a pH dependent with an optimal at pH 3. The capacities of the studied biosorbents to bind Cr(VI) were 48.0, 40.0, and 27 mg g-1 for WSW, NSW and OPW, respectively at 5.0 g l-1 adsorbent concentration, and 300 mg l-1 adsorbate initial concentration at pH 3.0. Under optimized test conditions, the equilibrium adsorption data fit the Langmuir adsorption isotherm for WSW, NSW and OPW with correlation coefficients of 0.9819, 0.9783 and 0.9199 for the tested biosorbents, respectively. The effectiveness of the studied biosorbents were demonstrated using wastewater samples emanating from electroplating shops.

Introduction

Industrialization and urbanization have led to an increase in ecological problems. Water is particularly vulnerable to contamination from discharge of wastewaters by various industries. Chromium appears in the waste streams of chemical manufacturing, electroplating, metal refining, textilte, dyes and pigment, leather tanning, minning and wood preserving industries [1-3]. Chromium(VI), even in a small quantities, is toxic to animals and humans, whereas Chromium(III) is an essential nutrient. Potable waters containing more than 0.05 mg l^{-1} are cosidered to be toxic. Chromium(VI) is considered as a powerful carcinogenic agent that modifies DNA transcription process causing important chromosomal aberrations [4]. Removal of Chromium(VI) from wastes is carried out using various techniques including reduction, precipitation with lime or sulfide, ion exchange, reverse osmosis, solvent extraction, membrane filtration, electrochemical treatment and evaporative recovery. These methods suffer from high capital and operational costs [3, 5-7].

In developing countries, there is a pressing need to use available low cost materials for the treatment of wastes with simple working technology. In wastewater treatment, the process of the adsorption has an edge over other methods, due to its sludge free clean operation. Adsorption is classified as Best Available Technology Not Entailing Excessive Costs (BATNEEC) [8]. Adsorption of metals on activated carbon derived from different sources has been studied by some authors [9-10]. Biosorption was demonstrated as a potential alternative to traditional treatment processes of metal ions removal, and it utilizes the ability of biological materials to accumulate heavy metals from waste streams by either metabolically mediated, or purely physico-chemical pathways of uptake [11-12]. Plant based biomass wastes were used as adsorbents for heavy metals. Sekhar et al., 2004 used the bark of *Hemidesmus indicus* for Pb adsorption [13], while Taty-Costodesa et al., 2003 used saw dust of *Pinus sylvestris* to adsorb Cd (II) and Pb (II) [14]. Chromium(VI) adsorption was studied by many authors utilizing different biosorbents [2,15-19].

This work has attempted to utilize the plant based biomass wastes resulted from okra preparation wastes

(*Hibiscus esculentus)* (OPW), nut shell wastes (*Colurna avellana*) (NSW) and walnut shell wastes (*Juglans regia*) (WSW) as abundant inexpensive biosorbents for the removal of hexavalent chromium from aqueous solutions. These economically alternative solid wastes were disposed of as garbage, so it perfectly utilize the interesting option in the environmental management by treating wastes using other wastes. Powdered OPW, NSW, and WSW were used in batch scale experiments for removing chromium(VI) from aqueous solutions.

Materials

The wastes under investigation were thoroughly washed with running tap water then distilled water, dried in the sun in the open air for 2-3 days period, crushed separately into pieces in a brass mortar, blended in a kitchen blender to a mesh size of 0.4 mm., sieved to eliminate undesired fraction size, more dried at 100° C for one hour.

All chemicals used were of analytical grade. A stock chromium(VI) solution (1000 mgl^{-1}) was prepared in distilled water using potassium dichromate $K_2 Cr_2 O_7$. All the working solutions were prepared by diluting the stock solution with distilled water.

The investigated plants (okra, nut and walnut) were purchased from local market.

Experimental Methods

The wastes generated from one kg were collected, dried, and weighed for each of the plants investigated, then the percentage waste per unit mass was calculated. The crushed wastes were ground and the obtained powder was sieved using a set of sieves. The sieves used are those with nominal aperture of 400, 250, 90, 75 and 63 microns. The powder was dried at 100° C for one hour. The obtained powder of OPW, NSW and WSW were then kept in a tightly closed glass container to be used without further modification.

All biosorption studies were carried out at ambient temperature (25± 5°C). 50 ml aliquot of the solution containing the desired quantity of chromium(VI) was treated with 1 g of powdered OPW, NSW, WSW for 24 h. The reaction mixture was filtered and the filtrate was analyzed for the remaining chromium(VI) concentration using the standard diphenylcarbazide spectrophotometric method [20].

Percentage chromium removal (R_e %) was calculated using the formula

$$R_e\ \% = (1 - C/C_o) * 100$$

Where C and C_o are the final and initial concentrations of chromium(VI) in the test solution, respectively.

The effect of pH on the adsorption of chromium(VI) unto OPW, NSW, and WSW was also studied individually using a 50 ml aliquot of a solution containing 300 mg l^{-1} chromium(VI). One gram of OPW, NSW, and WSW was added from each adsorbent separately and the pH was adjusted by adding either dilute H_2SO_4 or NaOH (pH range was 2-11). Chromium solution (300 mg l^{-1}) /sorbent mixture were left for 24 h, and then the amount adsorbed of chromium(VI) was measured as mentioned before.

Adsorbate / adsorbent behavior was studied with Cr(VI) concentration range of 5-1000 mg l^{-1} and adsorbent concentration of 20 g l^{-1}.

Sorbent dose optimization experiment was carried out by adding different weights of OPW, NSW, and WSW with a range of 5.0 – 40.0 g l^{-1} to 50 ml chromium(VI) solution (300 mg l^{-1}) at the optimum pH and left for 24 h. The amount adsorbed of chromium(VI) was calculated as above.

Kinetics of biosorption was also studied for OPW, NSW, and WSW over a time period of 48 hours with initial adsorbate concentration of 200 mg l^{-1} for OPW, NSW and WSW at the optimum pH. The residual quantity of Cr(VI) over the different time intervals was measured as above for the different adsorbents.

Results and Discussion

Annual waste generated from the investigated plants

Okra is cultivated in Egypt with annual production of 99,525 tons/year, while unshelled nut and walnut were imported with an annual tonnage of 719 and 561 ton/year respectively [21]. Okra is prepared for cooking by cutting the lower and upper cones of the fruit. These okra wastes comprised 2.2 % of the fresh weight, while nut and walnut are shelled for consumption, with its shell wastes comprised 61% of the fresh weight. USA produces about 50% of the world production of walnut. Walnut shell is hard deep furrowed shell surrounding

the meat while nut shell is a tough woody shell [22]. Table (1) showed the percentage of waste generated for each plant. It was noticed that the total waste generated annually weighed 2761.2 tons.

Table1. Annual production of okra and imports of walnut and nut with the waste generated.

Plant	Weight, ton	% of waste / unit mass	Annual waste generated, ton/ yr
Okra	90,525	2.2*	1991.6
Nut	719	61.0*	438.6
Walnut	561	59.0*	331.0

* Waste generated from one kg was calculated as %.

Size range of the studied biosorbents

The size range for biosorbents used throughout the study is depicted in Table 2. The data revealed that the dominant fraction that retained on the sieve was with was with 90 microns nominal aperture. The percentage of this fraction for the different adsorbents was 56.4, 55.7, 53.7 for OPW, NSW and WSW respectively.

Effect of pH on Cr(VI) adsorption capacity

It has been reported that the pH of the solution is an important parameter affecting biosorption of heavy metal ions [22]. The effect of pH over the range 3-11 on the adsorption process was studied. The obtained results for the different adsorbents revealed that upon decreasing the pH, the adsorption efficiency and adsorption capacity were increases (Figure 1). A pH of 3 was chosen as optimum to carry out the experiments, at which a maximum adsorption efficiency and adsorption capacity were recorded for OPW, NSW, and WSW. Such pH value also was in the earlier studies by Aoyama and Tsuda, 2001 [1].

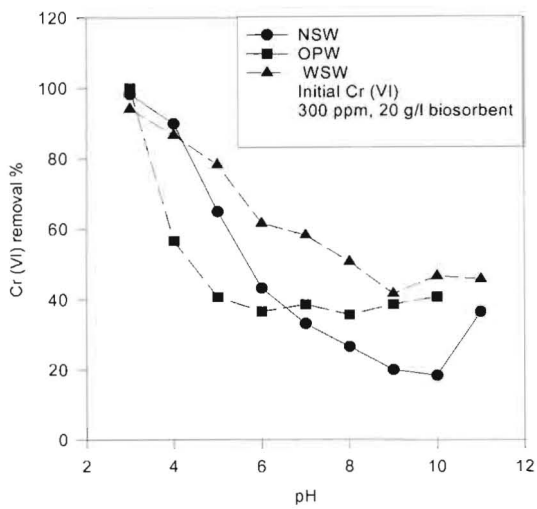

Fig. 1. Effect of pH on Cr (VI) removal.

Effect of contact time on Cr(VI) biosorption

It was shown in the case of WSW that complete adsorption has taken place in the first 15 minutes, with initial Cr(VI) concentration of 300 mg l^{-1} which revealed high affinity for Cr(VI). In regards to the other two adsorbents OPW and NSW results revealed that adsorption increased with time increase until it reached complete adsorption. Chromium removal % was displayed in figure 2.

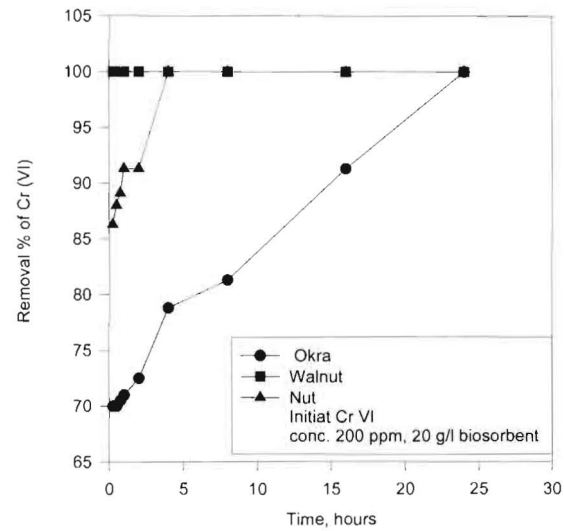

Fig. 2. Percent removal of Cr (VI) vs. time.

Effect of initial Cr(VI) concentration on biosorption

Adsorption capacity and removal percentage against various Cr(VI) concentrations for the OPW, NSW, and WSW were depicted in Figure 3 and 4. The results showed that 100% removal efficiency is achieved for the initial Cr(VI) concentration up to 250 mg l^{-1} of chromium(VI) for OPW, WSW, and NSW respectively, while the values decreased to 57.5, 68.5, and 83.3 % at 1000 mg l^{-1} of chromium(VI) concentration level for OPW, NSW, and WSW respectively (Fig. 3). At the same time, adsorption capacity increases to 28.8, 34.3, and 41.6 mg g^{-1} in the same sequence.

Effect of biosorbent dosages

Effect of OPW, NSW, and WSW dosage on the adsorption removal percentage is depicted in figure 5, which showed that the maximum adsorption capacity achieved was 48.0, 40.0, and 27 mg g-1 for WSW, NSW and OPW respectively, at a dosage of 5.0 g l^{-1} for each biosorbent. The maximum adsorption efficiency (100 %) was obtained at a dose of 15, 20,

and 20 g l^{-1} for WSW, NSW, and OPW respectively, with decreasing in adsorption capacity to 20, 15, and 15 mg g^{-1}in the same sequence. These results could be explained on the basis that some adsorption sites remain unsaturated during adsorption process despite that they are involved in adsorption capacity. Thus in case of high adsorbent dose, the adsorption capacity decreases and 100 % adsorption efficiency is achieved. These results were in agreement with that reported by Ajmal et ai., 1996 [23].

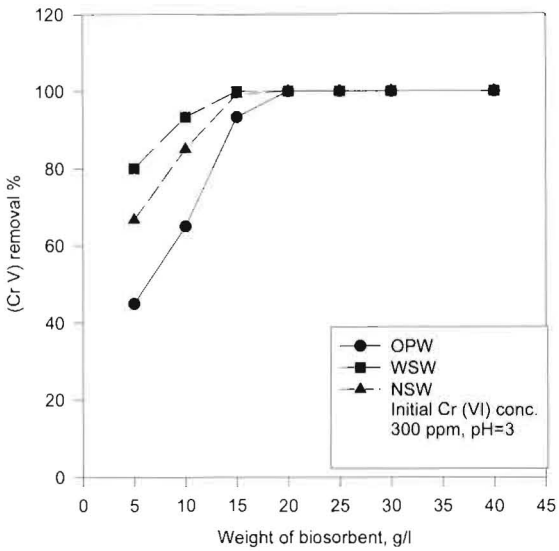

Fig. 3. Effect of Cr (VI) initial concentration on biosorption.

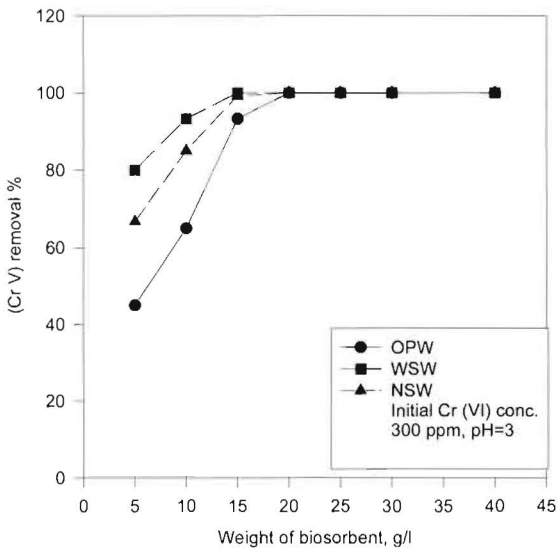

Fig. 4. Effect of bisorbent dose on Cr (VI) removal %.

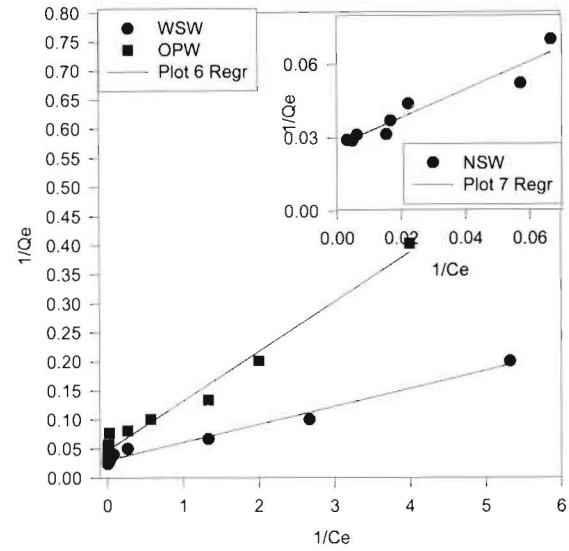

Fig. 5. Langmuir isotherm for the studied biosorbenta.

Sorption isotherms

Adsorption data usually described by adsorption isotherms, such as linear, Langmuir, and Freundlich isotherm. These isotherms relate metal uptake per unit mass of adsorbent q_e to the equilibrium adsorbate concentration in the bulk phase, C_e. The data obtained fit Langmuir isotherm for the different biosorbents. The correlation coefficients for the Langmuir isotherm for WSW, NSW and OPW were 0.9819, 0.9783 and 0.9199 for the three tested biosorbents respectively (Fig. 5). Table 2 summarizes the different isotherm parameters for Langmuir isotherm and correlation coefficient for each adsorbent.

Table 2. Langmuir isotherm parameters for the investigated biosorbents.

Biosorbent	Q^o (mg/g)	b (l/mg)	Correlation Coefficient
OPW	21.32	0.551	0.9783
NSW	37.31	0.047	0.9200
WSW	33.22	0.981	0.9820

It can be noticed from Table 2 that the correlation coefficient is higher than 0.9 which indicates that there a strong positive relationship in the data obtained. In Langmuir isotherm, it was assumed that the number of sorption sites (S), at the interface of the solid is occupied by the asorbate in the solution (M). The validity of this isotherm is regulated by the

Table 3. Summary of adsorptive capacities of various biosorbents

Biosorbent	Maximum adsorptive capacity mg/g	Optimum pH	Maximum initial conc. Used, mg/l	Reference
Saw dust	39.7	2.0	1000	Sharma and Forester, 1994 [26]
Coconut husk fibers	29.0	2.05	-	Tan et al., 1993 [27]
Sugar beet pulp	17.2	2.0	5000	Sharma and Forester, 1994 [26]
Palm pressed fibers	15.0	2.0	-	Tan et al., 1993 [27]
Maize cob	13.8	1.5	300	Sharma and Forester, 1994 [26]
Sugar cane bagasse	13.4	2.0	500	Sharma and Forester, 1994 [26]
Saw dust	3.3	6.0	50	Srivastava, 1986 [28]
NSW	40.0	3.0	1000	Present study
WSW	48	3.0	1000	Peresent study
OPW	27.0	3.0	1000	Present study

Table 3. Summary of adsorptive capacities of various biosorbents

Biosorbent	Maximum adsorptive capacity mg/g	Optimum pH	Maximum initial conc. Used, mg/l	Reference
Saw dust	39.7	2.0	1000	Sharma and Forester, 1994 [26]
Coconut husk fibers	29.0	2.05	-	Tan et al., 1993 [27]
Sugar beet pulp	17.2	2.0	5000	Sharma and Forester, 1994 [26]
Palm pressed fibers	15.0	2.0	-	Tan et al., 1993 [27]
Maize cob	13.8	1.5	300	Sharma and Forester, 1994 [26]
Sugar cane bagasse	13.4	2.0	500	Sharma and Forester, 1994 [26]
Saw dust	3.3	6.0	50	Srivastava, 1986 [28]
NSW	40.0	3.0	1000	Present study
WSW	48	3.0	1000	Peresent study
OPW	27.0	3.0	1000	Present study

following rules 1- equilibrium is obtained when there is a formation of a monolayer on the sorbent, 2- all of the sorption sites are equivalent and the surface is uniform, 3- the capacity of a molecule to be sorbed on a specific site is independent of its occupation of the other near sites [3].

Structure and adsorption mechanism

It is believed that adsorption of chromium(VI) onto the powdered biomass wastes takes place by three mechanisms: either by chelation with the acidic groups, or by exchange process with some anions loaded on the residues [16]. Also, biosorption of Cr(VI) at acidic pH (3) may be attributed to the electrostatic attraction of dominant negatively charged $(HCrO_4)^-$ [23] with positively charged sites on the biosorbents. Positively charged sites are those formed from the protonation of mucilage polysaccharides in okra [24], and tannins present in nut and walnut [17, 25]. The proposed mechanisms may be true because it is noticed that at low pH 3, 100 % adsorption is achieved.

Comparison with other biosorbents

The performance of the studied biosorbents can be justified compared with some other biosorbents tested by many other authors. Table 3 summarized the different adsorption parameters for some biosorbents for the removal of Chromium(VI) from aqueous solutions compared to the studied biosorbents (OPW, NSW, and WSW). It is obvious that WSW is ranked the first among the recorded biosorbents.

Electroplating waste treatment

The studied biosorbents were tested to remove chromium(VI) from chromium plating rinsing tank and the end-of-pipe electroplating shop effluents. The results obtained revealed the potential of the

investigated biosorbents for batch scale removal of chromium(VI) from electroplating effluents. Among the tested biosorbents, WSW was the best for such a task in regards to contact time, concentration of biosorbents and adsorption capacity (Table 4).

Conclusion

The solid wastes investigated in this study were proved to be good adsorbents for Chromium(VI) from wastewater. The adsorption processes which were carried out in a batch scale experiments had the advantages of chemical modification and carbonization-free process. Among the studied adsorbents, WSW showed a high adsorption affinity to Cr(VI) with an adsorption capacity of 48 mg g^{-1}. These adsorbents were elected as promising candidates for adsorption columns to treat industrial wastewater containing chromium(VI).

References

Aoyama, M. and Tsuda, M. 2001. Removal of Cr(VI) from aqueous solutions by larch bark. Wood Sci. Technol. 35: 425.

Ucun, H., Bayhan, Y.K., Kaya, Y., Cakici, A. and Algur, O. F. 2002. Biosorption of Chromium(VI) from aqueous solution by cone biomass of Pinus sylvestris, Bioresour. Technol. 85:155.

Meunier, N., Laroulandie, J., Blais, J.F. and Tyagi, R.D. 2003. Cocoa shells for heavy metal removal from acidic solutions. Bioresour. Technol. 90: 255.

International Agency for Research on Cancer IARC. 1990. International Agency for Research on Cancer Monographs on the Evaluation of the Carcinogenic Risks to Humans, 49, "Chromium, Nickel, and Welding " IARC publications.

Tare, V. and Chaudhari, S. 1987. Evaluation of soluble and insoluble xanthate process for the removal of heavy metals from wastewater. Water Res. 21: 1109.

Changgeng, Z. and Qiaoyun, C. 1995. Preparation of xanthate using alkaline effluent as alkali resource and lead removal from water. Water Treat.10:361.

Sharma, D. C. and Forster, C. F. 1995. Column studies into the adsorption of Chromium(VI) using sphagnum moss peat. Bioresour. Technol. 52:261.

McKay, G. 1995. Use of adsorbents for the removal of pollutants from wastewaters, CRC press.

Babel, S. and Kurniawan, T. A. 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J. Hazard. Mater. B97:219.

Kobya, M. 2004. Removal of Cr(VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies. Bioresour. Technol. 91:317.

Li, Y.- H., Di, Z., Ding, J., Wu, D., Luan, Z. and Zhu, Y. 2005. Adsorption thermodynamic,kinetic and desorption studied of Pb2+ on carbon nanotubes. Water Research. 39: 605-609.

Gupta, V.K., Shrivastava, A.K. and Jain, N. 2001. Biosorption of chromium(VI) from aqueous solutions by green algae Spirogyra species. Water Res. 35: 4079-4085.

Fourest, E. and Roux, J. C. 1992. Heavy metal biosorption by fungal mycelial by-products: mechanisms and influence of pH. Appl. Microbiol. Biotech. 37 :399.

Sekhar, K.C., Kamalaa, C.T., Chary, N.S., Sastry, A.R.K., Raoa, T.N. and Vairamani, M. 2004. Removal of lead from aqueous solution using an immobilized biomaterial derived from a plant biomass. J. Hazard. Mater. 08:111.

|Kumar, U. and Bandyopadhyay, M. 2006. Sorption of cadmium from aqueous solution using pretreated rice husk. Bioresource Technol. 97: 104.

Park, D., Yun, Y.-S., Jo, J.H., Park, J.M. 2005. Mechanism of hexavalent chromium removal by dead fungal biomass of Aspergillus niger. Water Res. 39: 533-540.

Sannasi, P. Kader, J., Ismail, B.S., and Salmijah, S. 2006. Sorption of Cr(VI), Cu (II) and Pb (II) by growing and non-growing cells of bacterial consortium, Bioresource Technol.,97:740-747.

Agarwal, G.S., Buptawat, H. K. and Chaudhari, S. 2006. Biosorption of aqueous chromium(VI) by Tamarindus indica. Bioresource Technol., 97: 949-956.

Sarin, V. and Pant, K.K. 2006. Removal of chromium from industrial waste using eucalyptus bark. Bioresource Technol., 97: 15.

ECAPMS. 2002. Annual book for the "Egyptian Central authority for public mobilization and statistics".

Ronzio, R. A. 1997. The encyclopedia of nutrition and good health, Facts on file Inc.

Matheickal, J. T. and Yu, Q. 1996. Biosorption of lead from aqueous solutions by marine algae. Ecklonia radiata. Water Res. 34:1.

Ajmal, M., Rao, R. A. K. and Siddiqui, B. 1996. Studied on removal and recovery of Cr(VI) from electroplating wastes. Water Res. 30:1478-1482.

Singh, V.K. and Tiwari, P. N. 1997. Removal and recovery of chromium (VI) from industrial wastewater. J. Chem. Technol. Biotechnol., 69:376.

Chevalier, A. 1996. The encyclopedia of medicinal plants, Dorling Kindersely Limited, London.

Thorpe's dictionary of applied chemistry. 1959. 4th ed., Longman, vol. XI.

Tan, W. T., Ooi, S.T. and Lee, K.C. 1993. Removal of chromium (VI) from solution by coconut husk and palm pressed fibers. Environ. Technol., 14:277.

Say, R., Yilmaz, A. and Denizli, A. 2004. Removal of chromium(VI) ions from synthetic solutions by the fungus Penicillium purpurogenum. Eng. Life Sci. 4:276.

Sudha Bai, R. T. and Abraham, E. 2003. Studies on Chromium(VI) adsorption-desorption using immobilized fungal biomass. Bioresour. Technol. 87:17.

Aksu, Z., Ac-ıkel, U., Kabasakal, E., and Tezer, S. 2002. Equilibrium modeling of individual and simultaneous biosorption of chromium (VI) and nickel (II) onto dried activated sludge. Water Res. 36:3063.

Srivastava, H.C.P., Mathur, R.P. and Mehrotra, I. 1986. Removal of chromium from industrial effluents by adsorption on sawdust. Environ. Technol. 7:55.