Int. J. Environ. Res., 4(3):427-432,Summer 2010
ISSN: 1735-6865

Adsorption of Heavy Metals by *Salvinia* Biomass and Agricultural Residues

Dhir, B.[1*] and Kumar, R.[2]

[1] Department of Environmental Biology, University of Delhi, Delhi-110007, India
[2] Department of Bio & Nanotechnology, Guru Jhambeshwar University of Science and Technology, Hissar- 125001(Haryana), India

Received 10 Feb. 2009; Revised 17 Sep. 2009; Accepted 27 March 2010

ABSTRACT: Batch adsorption experiments were performed to study adsorption potential of agricultural residues viz. rice straw, wheat straw and *Salvinia* plant biomass for removal of heavy metals such as Cr, Ni, and Cd. Plant materials were used in different combinations. Heavy metal removal efficiency was more at low metal concentration (35 mg/L). *Salvini*a biomass possessed higher efficiency for removing heavy metals such as Cr, Ni and Cd followed by a combination where three materials (rice straw, wheat straw, *Salvinia* biomass) were taken together in comparison to other combinations. The adsorption data fitted in Langmuir and Freundlich isotherm models.The present investigations revealed that agricultural residues such as rice straw and wheat straw along with *Salvinia* biomass can serve as low-cost alternative for removal of heavy metals from wastewaters.

Key words: Adsorption, Heavy metals, Rice straw, *Salvinia*, Wheat straw, Biomass

INTRODUCTION

Heavy metal released during different industrial and mining processes pose threat to living organisms, therefore it becomes important to develop technologies that result in effective removal of heavy metals from wastewaters. Various methods for heavy metal removal including chemical precipitation, membrane process, ion exchange, liquid extraction and electrodialysis are non-economical and have many disadvantages such as high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment (Demirbas, 2008). In contrast, adsorption technique can has been proved to be an excellent method to treat industrial waste effluents, offering significant advantages like low-cost, availability, profitability, easy operation and efficiency (Li *et al*., 2007). Biosorption of heavy metals from aqueous solutions is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluents. In recent years, various natural adsorbents such as agricultural wastes including sunflower stalks, *Eucalyptus* bark, maize bran, coconut shell, waste tea, rice straw, tree leaves, peanut and walnut husks have been tried to achieve effective removal of various heavy metals (Sun and Shi, 1998; Karthikeyan *et al*., 2005; Sarin and Pant, 2006; Singh *et al*., 2006; Hashem *et al*., 2007; Demirbas, 2008; Kahraman *et al*. 2008; Nameni *et al*., 2008).

*Corresponding author E-mail: bhupdhir@yahoo.co.in

Biosorption of heavy metal ions by non-living biomass of aquatic plant species *Potamogeton lucens, Salvinia herzogii, Eichhornia crassipes, Ludwigia stolonifera, Ceratophyllum demersum, Hydrilla verticillata* have been reported in literature (Schneider and Rubio, 1999; Elifantz and Tel-Or *et al.*, 2002; Keskinkan *et al.*, 2004, 2007; Bunluesin *et al.*, 2007). In present study, an attempt was made to I) investigate efficiency of *Salvinia* biomass for its metal sorption potential; ii) compare the metal sorption potential of *Salvinia* biomass along with other agricultural residues such as wheat and rice straw; iii) assessment of adsorption potential using Langmuir and Freundlich isotherms; iv) suggest best suitable combination for use as low-cost adsorbent for the removal of toxic heavy metals.

MATERIAL & METHODS

The wheat straw, rice straw and *Salvinia* biomass was ground and passed through standard steel sieves (72 mm mesh size). The fine powder was used without washing or any other physical or chemical treatments. Different combinations namely A, B, C, D, E, F, G were tried. The details are included in Table 1. The amount of adsorbent was kept constant as one gram in all the combinations. Adsorbent was added to 100ml metal solutions with concentrations 35, 50 and 100 mg/L prepared by using $K_2Cr_2O_7$, $Cd(NO_3)_2.4H_2O$ and $Ni(NO_3)_2.6H_2O$ respectively. Samples were agitated at 250 rpm for 2h (pH 5.5). The sorption studies were carried out at 25 ±1°C. A metal and biomass free blank was used as control. The mixtures were filtered through filter paper (pore diameter 11µm) and metal concentrations were determined in the filtrate using Flame Atomic Absorption Spectrophotometer (AA 6300, Shimadzu, Japan). Metal removal (%) at any instant of time was determined by the following equation:

Heavy metal removal (%) = $(C_i – C_f)/ C_i$ X 100
Where, C_i and C_f represent initial and final metal concentration (mg/L) at any instant of time, respectively (Argun *et al*. 2007).

Table 1. Different combination of plant materials used for the study

Combination	Plant materials
A	Wheat straw (35%) + Rice straw (35%) + *Salvinia* biomass (30%)
B	Wheat straw (50%) + *Salvinia* biomass (50%)
C	Rice straw (50%) + *Salvinia* biomass (50%)
D	Wheat straw (50%) + rice straw (50%)
E	Wheat straw (100%)
F	Rice straw (100%)
G	*Salvinia* biomass (100%)

The adsorption data obtained was analyzed using Langmuir and Freundlich isotherm models. Freundlich and Langmuir isotherms are the earliest and simplest known relationships describing the adsorption equation (Jalali *et al*. 2002; Verma *et al*., 2008).The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The linearlized equation allows the calculation of adsorption capacities and the Langmuir constants and is equated by the following equation:

$$C_{eq}/q = 1/q_{max}.b + C_{eq}/q_{max}$$

where q is metal accumulated by biosorbent material (mg/g); C_{eq} is the metal residual concentration in solution (mg/L); q_{max} is the maximum specific uptake corresponding to the site saturation (mg/g) and b is Langmuir equation constant which represents ratio of adsorption and desorption rates (Langmuir, 1918; Igwe and Abia, 2007).

The Freundlich isotherm model was chosen to estimate the adsorption intensity of the sorbent towards the adsorbent. The linearized form of the Freundlich equation was used for analysis and it is given as:

$$\log Q_e = \log K_f + 1/n \log C_e$$

Where, C_e is the equilibrium concentration of the adsorbate (mg/L) and Q_e is the amount adsorbed per unit mass of adsorbent (mg/g), K_f and n are Freundlich equilibrium coefficients (Freundlich, 1907).Standard errors on means and slopes were calculated using the standard Microsoft Excel spreadsheet routines. The data was statistically analyzed using software newMSTAT-C (version 2.1, Michigan State University) (Dhir *et al*., 2009).

RESULTS & DISCUSSION

Batch adsorption studies showed that Cr, Ni and Cd removal (%) was more at lower metal concentration in all the combinations (A-G), irrespective of heavy metal (Fig.1). Nickel removal efficiency followed the order G > A = F > B = C > D = E, Cr removal efficiency followed the order G = F= A > C > E = B > D and Cd removal efficiency followed the order G > A = D > B = E > F = C at 35 mg/L concentration (Table 2). *Salvinia* biomass showed highest metal removal efficiency (G) in all three metal treatments. The adsorption data fitted in both (Langmuir and Freundlich) adsorption isotherms in all treatments. Adsorption was described well by Langmuir model as correlation coefficient (R^2) was greater than 0.9 in all cases (R^2> 0.9), but for Freundlich model correlation coefficient (R^2) the values ranged between 0.84 to 0.99 (Table 3). Langmuir and Freundlich parameters are listed in Table 3. The values of Langmuir and Freundlich constants indicate favorable conditions for adsorption. Out of all combinations tested, maximum Cd, Cr and Ni adsorption capacity (q_{max}) (mg/g) was noted in A (three materials taken together). Maximum adsorption capacity calculated from the Langmuir isotherm was 61 mg/g Cr, 46.9 mg/g Ni and 44 mg/g Cd (pH 5) in combination A. The Freundlich isotherm parameter n and K_f for different metals have been listed in Table 3. The value of n was more than 1 in all combinations irrespective of metal treatment. Higher values of K_f represent greater adsorption intensity.

Salvinia biomass showed higher potential for Cr, Ni and Cd removal in comparison to agricultural residues. Adsorption isotherms give the capacity of the adsorbent based on the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. *Salvinia* biomass possesses good capacity to adsorb Cr, Ni and Cd. Metal adsorption capacity of *Salvinia* is comparable or somewhat higher than those reported for other aquatic plant species (Keskinkan *et al*., 2004, 2007; Bunluesin *et al*.,

Table 2. Heavy metal removal efficiency (%) noted in different plant combinations

Metal Conc. (mg/ L)	Different combinations of plant materials						
	A	B	C	D	E	F	G
				Ni			
35	57.1	51.4	51.4	45.7	45.7	57.1	60
50	54	48	48	46	46	48	50
100	36	33	32	31	30	31	34
				Cr			
35	71.4	64.3	68.8	67	64.8	71.4	71.4
50	60	54	54	52	52.6	52.6	60
100	47	40	41.7	43	38	38	48
				Cd			
35	51.4	48.5	45.7	51.4	48.5	45.7	54.3
50	44	42	44	48	44	44	52
100	32	28	30	28	30	29	32

Table 3. Isotherm constants from Langmuir and Freundlich models

Heavy metal	Langmuir			Freundlich		
	R^2	q_{max}	b	R^2	K_f	n
Ni						
A	0.99	46.94	18.43	0.94	7.59	2.63
B	0.99	45.25	24.67	0.96	5.66	2.36
C	0.99	42.2	21.43	0.95	6.14	2.52
D	0.97	45.25	30.80	0.90	4.32	2.11
E	0.97	41.84	26.75	0.88	4.79	2.27
F	0.99	37.03	13.36	0.99	9.42	3.93
G	0.99	41.32	19.63	0.99	9.24	3.21
Cr						
A	0.98	61.72	17.30	0.98	9.96	2.59
B	0.98	51.54	18.05	0.99	8.68	2.66
C	0.96	53.20	16.94	0.93	10	2.94
D	0.92	58.47	22.5	0.89	8.66	2.61
E	0.98	47.16	15.59	0.98	9.54	3.02
F	0.97	44.05	24.2	0.88	10.3	4.12
G	0.97	39.68	25.53	0.97	9.53	2.48
Cd						
A	0.99	44.05	26.13	0.99	5.53	2.40
B	0.99	35.84	20.15	0.99	6.19	2.82
C	0.99	42.20	29.48	0.94	4.43	2.19
D	0.99	32.78	11.95	0.84	8.79	3.61
E	0.99	40.48	24.20	0.97	5.41	2.46
F	0.98	39.68	25.53	0.92	8.45	2.36
G	0.99	39.06	14.70	0.87	8.19	3.03

2007). The adsorption capacity of *Hydrilla verticillata* was found to be 15.0 mg/g for Cd (Bunluesin *et al.*, 2007), *Myriophyllum spicatum* was found to be 10.37 mg/g for Cu, 15.59 mg/g for Zn, 46.49 mg/g for Pb and *Ceratophyllum demersum* was found to be 6.17 mg/g for Cu, 13.98 mg/g for Zn and 44.8 mg/g for Pb (Keskinkan *et al.*, 2007) and *Vallisneria spiralis* was found to be 53.4 mg/g for Ni, 3.48 mg/g for Cr and 4.38 mg/g for Cd, *Pistia stratiotes* was found to be 5.10 mg/g for Ni, 2.96 mg/g for Cr and 4.49 mg/g for Cd (Verma *et al*. 2008). Agricultural residues showed low heavy metal adsorption capacity in comparison to *Salvinia* biomass. Among agricultural residues, rice straw possessed higher metal adsorption capacity. Earlier, isotherm studies showed adsorption of Pb, Cu, Zn, Cr on rice husk, wheat bran and data fitted well in Langmuir and Freundlich models (Ajmal *et al*., 2003; Mohan *et al*. 2008; Nameni *et al*., 2008).

Both Langmuir and Freundlich isotherm models explained adsorption of heavy metals. The data fitted well in Langmuir adsorption isotherm as compared to Freundlich isotherm. Better fitting of the experimental data to Langmuir isotherm indicate mono-layered

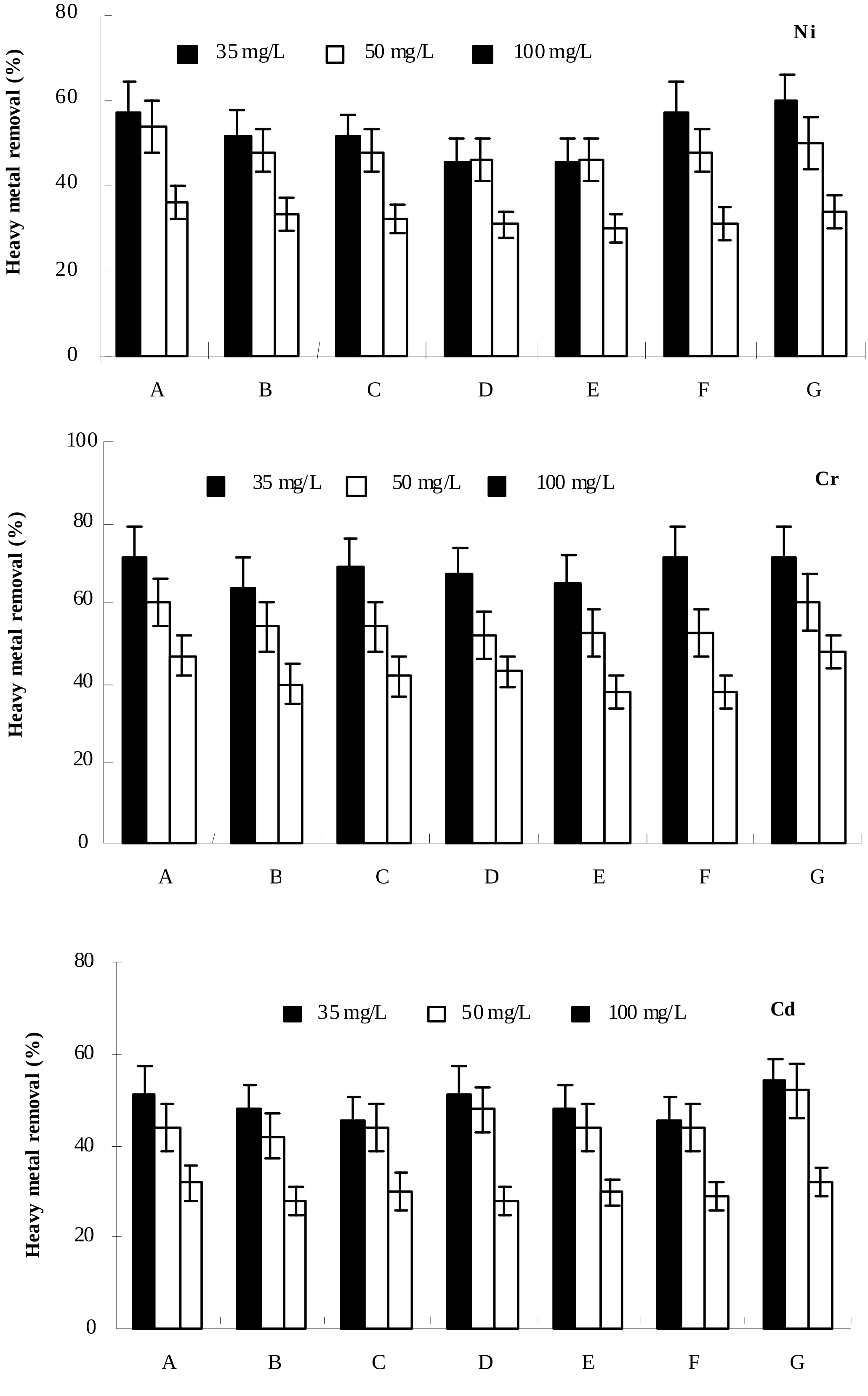

Fig. 1. Heavy metal removal efficiency (%) noted in different plant combinations

tion of Cd, Ni and Cr in all combinations. Langmuir isotherm parameter q_{max} indicates maximum adsorption capacity. Irrespective of metal, maximum adsorption capacity (q_{max}) was noted in combination A where three plant materials were used. The Freundlich equation gives an adequate description of adsorption data over a restricted range of concentration and suggests heterogenity of the adsorption sites on biomass (Juang *et al.* 1996). The Freundlich isotherm parameter K indicates adsorption intensity when concentration of metal ion in equilibrium is unitary. Higher the values of K_f and n, higher is the affinity for adsorption of metals (Jalali *et al.* 2002; Igwe and Abia, 2007). The values of 1/n<1 indicate favorable adsorption of all metals irrespective of treatment and the values of n within the range of 2-10 represent good adsorption (Teng and Hsieh, 1998; Ozer and Pirincci, 2006). Higher values of K_f indicate high adsorption intensity. Previous findings showed that dry biomass of plant species such as *Eichhornia crassipes*, *Vallisneria spiralis*, *Nymphaea* sp and *Pistia stratiotes* possessed good metal sorption capacity and data fitted well into Freundlich is otherm equation (Elangovan *et al.*, 2008; Verma *et al.*, 2008).

CONCLUSION

The present study demonstrated that plant residues can be used effectively in the removal of Cr, Ni and Cd from aqueous solution. *Salvinia* biomass can be utilized as a biological resource with immense potential for heavy metal adsorption. The equilibrium data fitted well with Langmuir isotherm model. Use of agro waste materials and plant biomass can offer as inexpensive and effective metal ion adsorbents as replacements for existing commercial materials.

ACKNOWLEDGEMENTS

The financial assistance from Department of Science and Technology, New Delhi to Bhupinder Dhir is gratefully acknowledged.

REFERENCES

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

Argun, M. E., Dursun, S., Ozdemir, C. and Karatas, M. (2007). Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. J. Hazard. Mat., **141**, 77-85.

Bunluesin, S., Kruatrachue, M., Pokethitiyook, P., Upatham, S. and Lanza, G. R. (2007). Batch and Continuous packed column studies of cadmium biosorption by Hydrilla verticillata biomass. J. Biosci. Bioeng., **103**, 509-513.

sorpDemirbas, A. (2008). Heavy metal adsorption onto agro-based waste materials: A review. J. Hazard. Mater., **157**, 220-229.

Dhir, B., Sharmila, P., Pardha Saradhi, P. and Nasim, S. A. (2009). Physiological and antioxidant responses of Salvinia natans exposed to chromium-rich wastewater. Ecotoxicol. Environ. Safety, **72 (6)**, 1790-1797.

Elangovan, R., Philip, L. and Chandraraj, K. (2008). Biosorption of chromium species by aquatic weeds: Kinetics and mechanism studies. J. Hazard. Mater., **52**, 100-112.

Elifantz, H. and Tel-Or, E. (2002). Heavy metal biosorption by plant biomass of the macrophyte Ludwigia stolonifera. Water Air Soil Pollut., **141**, 207-218.

Freundlich, H. M. F. (1906). Über die adsorption in läsungen. Zeitschrift fur. Physikalische Chemie., **57**, 385-470.

Hashem, A., Akasha, R. A., Ghith, A. and Hussein, D. A. (2007). Adsorbent based on agricultural wastes for heavy metal and dye removal: a review. Energy Edu. Sci. Technol., **19**, 69-86.

Igwe, J. C. and Abia, A. A. (2007). Equilibrium sorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions detoxification from waste water using unmodified and EDTA-modified maize husk. Electron. J. Biotechnol., **10(4)**, DOI: 10.2225.

Jalali, R., Ghafourian, H., Asef, Y., Davarpanah, S. J. and Sepehr, S. (2002). Removal and recovery of lead using nonliving biomass of marine algae. J. Hazard. Mater., **92**, 253-262.

Juang, R., Wu, F. and Tseng, R. (1996). Adsorption isotherms of phenolic compounds from aqueous solutions onto activated carbon fibers. J. Chem. Eng. Data, **41**, 487-492.

Kahraman, S., Dogan, N. and Erdemoglu, S. (2008). Use of various agricultural wastes for the removal of heavy metal ions. Intnl. J. Environ. Pollut., **34**, 275-284.

Karthikeyan, T., Rajgopal, S. and Miranda, L. R. (2005). Chromium (VI) adsorption from aqueous solution by Hevea brasilinesis sawdust activated carbon. J. Hazard. Mater., **124**, 192-199.

Keskinkan, O., Goksu, M. Z. L., Basibuyuk, M. and Forster, C. F. (2004). Heavy metal adsorption properties of a submerged aquatic plant (*Ceratophyllum demersum*). Bioresour. Technol., **92**, 197-200.

Keskinkan, O., Goksu, M. Z. L., Yuceer, A. and Basibuyuk, M. (2007). Comparison of the Adsorption Capabilities of Myriophyllum spicatum and Ceratophyllum demersum for zinc, copper and lead. Eng. Life Sci., **7**, 192-196.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. J. Amer. Chem. Soc., **40**, 1361-1403.

Li, Q., Zhai, J., Zhang, W., Wang, M. and Zhou, J. (2007). Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk. J. Hazard. Mater., **141**, 163-167.

McKay, G., Otterburn, M. S. and Sweeney, A. G. (1980). The removal of color from effluent using various adsorbents-III. Silica rate process. Water Res., **14**, 14-20.

Mohan, S., Gandhimathi, R. and Sreelakshmi, G. (2008). Isotherm Studies for Heavy Metal Adsorption on Rice Husk. Asian J. Water, Environ. Pollut., **5**, 71-78.

Nameni, M., Alavi Moghadam, M. R. and Arami M. (2008). Adsorption of hexavalent chromium from aqueous solutions by wheat bran. Intnl. J. Environ. Sci. Technol., **5,** 161-168.

Ozer, A. and Pirincci, H. B. (2006). The adsorption of Cd(II) ions on sulphuric acid-treated wheat bran. J. Hazard. Mater., **137**, 849-855.

Sarin, V. and Pant, K. K. (2006). Removal of chromium from industrial waste by using eucalyptus bark. Bioresour.Technol., **97**, 15-20.

Schneider, I. A. H. and Rubio, J. (1999). Sorption of heavy metal ions by non-living biomass of freshwater macrophytes. *Environ. Sci. Technol.*, **33**, 2213-2217.

Singh, K. K., Talat, M. and Hasan, S. H. (2006). Removal of lead from aqueous solutions by agricultural waste maize bran. Bioresour.Technol., **97**, 2124-2130.

Sun, G., and Shi, W. (1998). Sunflower stalks as adsorbents for the removal of metal ions from wastewater. Industr. Eng. Chem. Res., **37**, 1324-1328.

Teng, H. and Hsieh, C. T. (1998). Influence of surface characteristics on liquid-phase adsorption of phenol by activated carbons prepared from bituminous coal. Industrial. Eng. Chem. Res., **37**, 3618-3624.

Verma, V. K., Tewari, S. and Rai, J. P. N. (2008). Ion exchange during heavy metal biosorption from aqueous solution by dried biomass of macrophytes. Bioresour. Technol., **99**, 1932-1938.