

Equilibrium and Thermodynamic Studies of Pb(II), Cu(II) and Zn(II) Adsorption onto *Dicliptera bupleuroides* Leaves

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Abstract: Biosorption of Cu(II), Zn(II) and Pb(II) ions onto *Dicliptera bupleuroides* leaves (DBL) in a batch system with respect to adsorbent dose, contact time, temperature, pH and initial metal ion concentration was investigated. Langmuir, Freundlich and Temkin isotherm model were applied to describe the equilibrium data. Langmuir isotherm model provided a better fit to the experimental data than the Freundlich and Temkin isotherm. The adsorption capacity is 2.55 mg/g, 1.06 mg/g, and 1.76 mg/g for Cu(II), Zn(II) and Pb(II) respectively. The optimum adsorption conditions obtained were at contact time 75 min, pH 5, initial metal ion concentration 10 mg/L, temperature 45 °C for Cu(II) and 30 °C for Zn(II) and Pb(II) and adsorbent dose 2.5 g. Thermodynamic parameters indicated that the adsorption reactions were spontaneous ($\Delta G^0 < 0$), feasible and exothermic ($\Delta H^0 < 0$).

Keywords: Adsorption, Heavy metals, *Dicliptera bupleuroides* leaves, Isotherms, thermodynamic Parameters

Introduction

Heavy metal contamination of aquatic media is a serious environmental problem, mainly due to the discharge of industrial waste¹. These non degradable metal ions are harmful to living organism and plant species in high concentration. To protect the public health and environment the removal of these metals from wastewater is important². Copper, zinc and lead have been introduced in the environment from a variety of sources like storage battery³, paints and pigments⁴, electronics⁵ fertilisers^{6,7} and electroplating^{8,9}. High concentration of copper leads to severe gastrointestinal irritation and possible necrotic changes in the liver and kidney in human¹⁰. Over accumulation of Zn(II) metal in the human body causes abdominal pain, lack of muscular coordination and acute renal failure though it is essential

element too for several metabolic processes and the development of brain in human. High exposure to Pb(II) in human begins causes learning and behavioural difficulties in children and disturbances to the immune system¹¹. Chemical precipitation¹², membrane filtration¹³, ion exchange¹⁴ and carbon adsorption¹⁵ are few of the methods indicated in literature for the removal of heavy metals from water and wastewater. However, biosorption is economically feasible method and remove trace amount of heavy metal from aqueous solution. In recent years, many plant materials have appeared in the development of low cost adsorbent prepared from cheaper and easily available materials. Some of the recent adsorbents used for removal of copper, zinc and lead are Olive pomace¹⁶, *Phragmites australis* shoot¹⁷, *Azolla filiculoides*¹⁸, Orange peels¹⁹, *Carissa carandas* and *Syzygium aromaticum*²⁰. The objective of the present work is to investigate the possibility of the use of activated *Dicliptera bupleuroides* leaves (Figure 1) (DBL), as an alternative low-cost adsorbent for removal of Cu(II), Zn(II) and Pb(II) ions from synthetic waste water.



Figure 1. *Dicliptera bupleuroides* leaves

Experimental

All the reagents used were of A. R. grade. Stock solutions of 1000 mg/L concentration of lead nitrate $\text{Pb}(\text{NO}_3)_2$, zinc sulphate $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and copper sulphate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were prepared. The working solutions were prepared by diluting the stock solutions using double distilled water. The range in concentration of Pb(II), Cu(II), and Zn(II) ions prepared from stock solution varied between 10 to 50 mg/L. The pH of this solution was adjusted to 4.0 by monitoring it with a Systronic 361 digital pH meter by desired addition of 0.1 N NaOH and 0.1 N HCl solutions.

Collection of DBL and adsorbent preparation

DBL were collected in the month of July from low altitude areas of Almora district (Kumaon hills, Uttarakhand, India). The collected leaves were rinsed with double distilled water to remove dust and soluble materials. The biomass was further dried at room temperature and then kept in hot air oven (Popular Traders S.N.-1680) for 24 h at 70 °C; it was grinded to a fine powder using grinder-mixer then this powdered mass was treated with 0.1 N HNO_3 at room temperature for 24 h, filtered, washed with double distilled water and dried in hot air oven at 70 °C for 2 days and sieved (240 bss) at 63 micron. The treated biomass was kept in air tight bottle. The surface functional groups of the activated biomass were identified by Fourier transform infrared spectroscopy.

Adsorption experiments

The batch sorption experiments were carried out with 250 mL conical flask using 100 mL of working solution with a concentration of 10 mg/L. The experimental conditions applied to examine the effect of adsorbent dose, contact time, pH, temperature and initial metal ion

concentration in adsorption of metal ions on adsorbent. The DBL was separated from the medium with the help of Whatman filter paper number 42. In the filtrate the concentration of Cu(II), Zn(II) and Pb(II) metal ions was measured by Atomic Adsorption Spectrophotometer AAS (Optima 4300 DV ICP, Perkin-Elmer, Boston, MA). The percentage removal of metal ions is calculated using the following formula:

$$\text{Removal \%} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

Where C_i is the initial metal ion concentration (mg/L) and C_e is the equilibrium metal ion concentration (mg/L).

Results and Discussion

Characterisation of adsorbent

A peak at 3357 cm^{-1} represent the stretching of amino (-NH), bonded hydroxyl (-OH) and (-COOH) groups vibration. The band at 2923 cm^{-1} and 2851 cm^{-1} is assigned to aldehyde C-H stretching vibration. The band at 1643 cm^{-1} assigned to carboxyl group. The band observed at 1036 cm^{-1} represents C-O stretching of alcohol and carboxylic acids. The intense band at 1108 cm^{-1} show the presence of -C=S group. These data confirmed that the present functional groups are responsible for metal binding.

Scanning electron microscopic analysis

The irregular, rough and porous structure of the DBL is shown in Figure 2, which is one of the criteria of high adsorption capacity and favourable for adsorption process. Figure 3 is a loaded SEM image of DBL. After adsorption it is clearly seen that the pores are filled with metal solution (Figure 4).

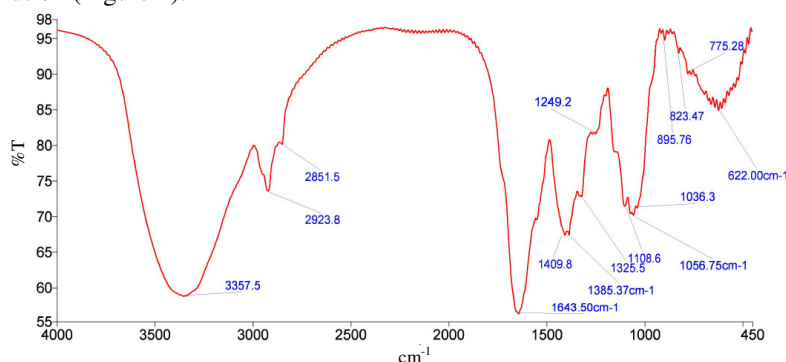


Figure 2. FTIR spectrum of DBL

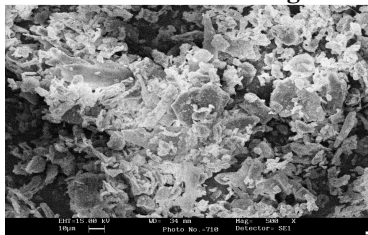


Figure 3. SEM image of DBL before adsorption

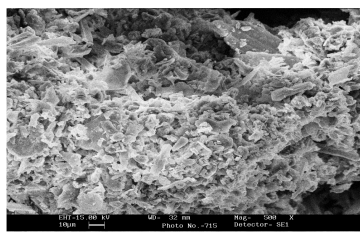


Figure 4. SEM image of DBL after adsorption

Effect of contact time

Figure 5 shows that the percentage removal of Cu(II), Zn(II) and Pb(II), ions increases with increasing reaction time. The percentage of metal removal is rapid initially up to 60 min but after 60 min does not show any remarkable change. This behaviour of removal efficiency has been related to less availability of binding sites with increase in contact time^{21,22}.

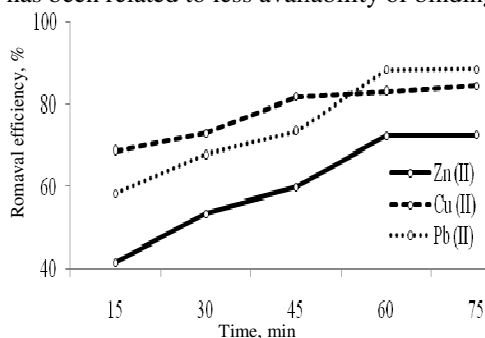


Figure 5. Effect of contact time on Pb(II), Cu(II) and Zn(II) adsorption

(Experimental condition: Initial metal ion concentration 10 mg/L adsorbent dose 1g/100 mL, 22 °C pH 4, agitating speed 170 rpm)

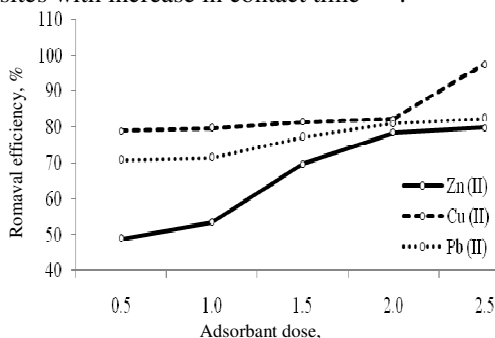


Figure 6. Effect of adsorbent dose on Pb(II), Cu(II) and Zn(II) adsorption

(Experimental condition: Initial metal ion concentration 10 mg/L, contact time 30 min, temp 22 °C, pH 4, agitating speed 170 rpm)

Effect of adsorbent dosage

At a given initial concentration of adsorbent determines the potential of biosorbent to remove metal ions²³. From the Figure 6 and 7 it is revealed that on increasing adsorbent dose from 0.5 g to 2.5 g, the removal efficiency increases and adsorption capacity decreases. This result can be explained by the fact that, with increasing adsorbent dosage, more surface area is available for biosorption due to increase in active sites on the adsorbent²⁴.

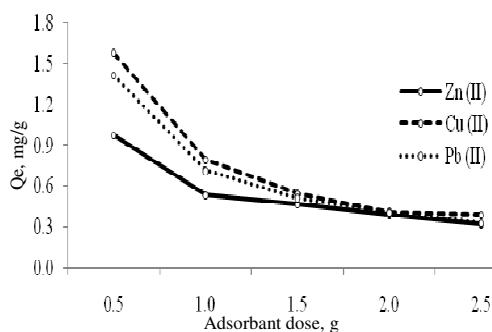


Figure 7. Effect of adsorbent dose on Pb(II), Cu(II) and Zn(II) adsorption capacity

(Experimental condition: Initial metal ion concentration 10 mg/L, contact time 30 min, temperature 22 °C, pH 4, agitating speed 170 rpm)

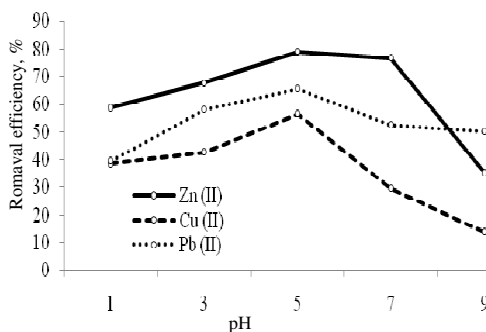


Figure 8. Effect of pH on Pb(II), Cu(II) and Zn(II) adsorption

(Experimental condition: Initial metal ion concentration 10 mg/L, adsorbent dose 1 g/100 mL, contact time 30 min, temperature 22 °C, agitating speed 170 rpm)

Effect of pH

The experimental data show that the percentage removal of the copper(II), zinc(II) and lead(II) ions increases with pH from 1 to 5, after pH 5 the percentage removal decreases (Figure 8)

this is due to the protonation of the active sites on the adsorbent at low pH ($\text{pH} < 5$) and this results in repulsion between metal ions and the adsorbent which decreases biosorption efficiency²⁵⁻²⁷. With pH greater than 3 the adsorbent becomes less protonated and this deprotonation creates more active sites. Removal efficiency decreases again when the pH increases from 5 to 9 this may be attributed to the formation of metal hydroxide at very high pH ($\text{pH} > 5$) the optimum pH value for all metal ions in this case is pH 5.

Effect of initial metal ions concentration

Experimental results show that the percentage removal of Cu(II), Zn(II) and Pb(II) ions decreases with increasing in the metal ion concentrations (Figure 9). This can be associated with the fact that the low initial metal ion concentration in the solution the ions would interact with the binding sites of adsorbent and thus facilitate higher adsorption whereas at higher concentrations, more ions are left unabsorbed in the solution due to the saturation of the binding sites³. However, at the same dose of adsorbent, the metal ions per unit of adsorbent Q_e (Figure 10) have been increased with the increase of initial metal ion concentration.

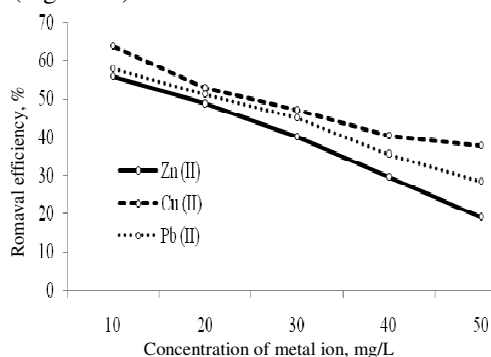


Figure 9. Effect of initial Pb(II), Cu(II) and Zn(II) ions concentration on adsorption (Experimental condition: Adsorbent dose 1 g/100 mL, temperature 22 °C, contact time 30 min, pH 4)

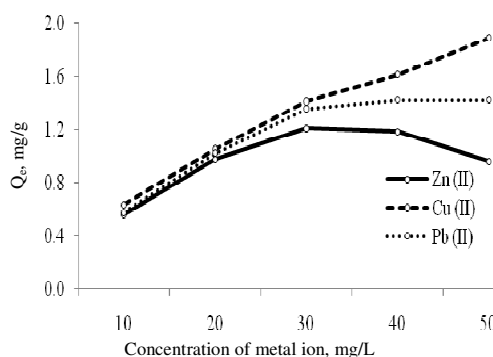


Figure 10. Effect of initial Pb(II), Cu(II) and Zn(II) ions concentration on adsorption capacity (Experimental condition: Adsorbent dose 1 g/100 mL, temperature 22 °C, contact time 30 min, pH 4)

Adsorption isotherm

The equilibrium data of adsorption on the *Dicliptera* leaves were tested with Langmuir, Freundlich and Temkin isotherm models.

Langmuir isotherm

The Langmuir isotherm model is based on the adsorption and involves the attachment of only one layer of molecules to the surface, *i.e.* monolayer adsorption^{28,29}. The equation 2 is the linear form of the Langmuir³⁰ isotherm.

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \quad (2)$$

Where C_e is the equilibrium concentration of Pb(II), Cu(II) and Zn(II) in mg/L. Q_e is the amount of metal adsorbed per specific amount of adsorbent (mg/g), K_L (L/mg) is the Langmuir constant related to the energy of adsorption and Q_{\max} is maximum adsorption capacity (mg/g). Values of Langmuir parameters Q_{\max} and K_L were calculated from the slope

and intercept of linear plot of $\frac{C_e}{Q_e}$ vs. C_e shown in Figure 11. The evaluated constants are given in Table 1.

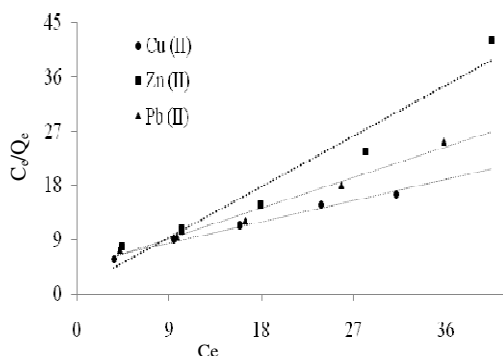


Figure 11. Langmuir Isotherm for biosorption of Pb(II), Cu(II) and Zn(II) ions onto DBL

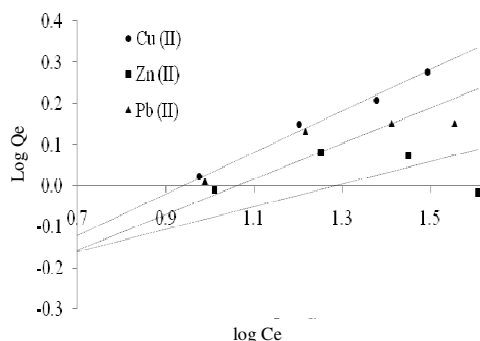


Figure 12. Freundlich Isotherm for biosorption of Pb(II), Cu(II) and Zn(II) ions onto DBL

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor “ R_L ” which is used to predict the adsorption system is favourable or unfavourable and is given as:

$$R_L = \frac{1}{1 + K_L * C_0} \quad (3)$$

Where C_0 is the initial metal ion concentration in mg/L, K_L is the Langmuir equilibrium constant. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). The value of R_L was found less than one and greater than zero in all the cases. This confirms that the Langmuir isotherm model is favourable for adsorption of Pb(II), Cu(II) and Zn(II) onto DBL

Freundlich isotherm

Freundlich isotherm is widely used to describe adsorption on a surface having heterogeneous energy distribution. The linear form of isotherm can be represented as³¹.

$$\text{Log } Q_e = \text{Log } K_F + \frac{1}{n} * \text{Log } C_e \quad (4)$$

Where K_F is a constant related to the adsorption capacity and n is related to the adsorption intensity of the adsorbent. The Constant K_F and $\frac{1}{n}$ can be determined from the linear plot of $\log Q_e$ versus $\log C_e$ (Figure 12). The evaluated constants are given in Table 1.

Temkin isotherm

The Temkin isotherm model suggests that the adsorption energy decreases linearly with the surface coverage due to adsorbate-adsorbent interaction. The equation 5 is the linear form of the Temkin³² isotherm

$$Q_e = B \ln A + B \ln C_e \quad (5)$$

Where C_e concentration of the adsorbate at equilibrium mg/L, Q_e is the amount of metal adsorbed per specific amount of adsorbent (mg/g). $B = RT/b_T$ where R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature in Kelvin, b_T is the Temkin isotherm constant. A is the equilibrium binding constant and B corresponds to the heat of sorption. The value of A and B are given in Table 1.

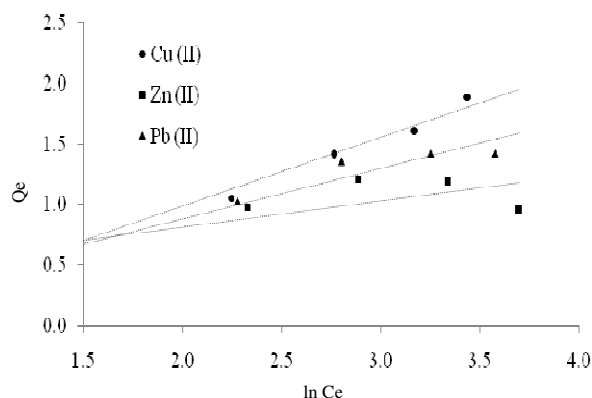


Figure 13. Temkin isotherm for biosorption of Pb(II), Cu(II) and Zn(II) ions onto DBL

Table 1. Adsorption isotherm constants for adsorption of Pb(II), Cu(II) and Zn(II) onto DBL

Metals →	Cu(II)	Zn(II)	Pb(II)
Langmuir parameters			
Q_{\max} , mg/g	2.55	1.06	1.76
K_L , L/mg	0.08	1.15	0.14
R^2	0.98	0.93	0.98
Freundlich parameters			
K_f , mg/g, Lmg^{-1} , $1/n$	0.62	0.704	0.633
N	1.98	3.66	2.32
R^2	0.99	0.44	0.85
Temkin parameters			
B , mg/g	0.57	0.22	0.42
A	0.77	5.62	1.13
R^2	0.98	0.38	0.90

From Table 1 it is observed that the Langmuir isotherm is a good fit to the experimental adsorption data than the Freundlich and Temkin isotherm for Cu(II), Zn(II) and Pb(II) sorption according to the values of R^2 . It is observed from Table 1 that the adsorption capacity Q_{\max} is 2.55, 0.1.06 and 1.76. The Freundlich constant K_F indicates the sorption capacity of the sorbent and the value of K_F is 0.62, 0.70 and 0.63 for Cu(II), Zn(II) and Pb(II). The Temkin isotherm also not followed because of very low regression coefficient.

Biosorption thermodynamics

Thermodynamic parameters such as enthalpy change ΔH° , free energy change ΔG° and entropy change ΔS° used for thermodynamics behaviour of Cu(II), Zn(II) and Pb(II) onto DBL. The free energy change of the sorption reaction is given by the following equation.

$$\Delta G^\circ = -RT \ln K_D \quad (6)$$

Where ΔG° is standard free energy change, R is the universal gas constant (8.314 J/mol K), T is the temperature in Kelvin. $K_D = \frac{C_{Ae}}{C_e}$ is the distribution coefficient³³ where C_e is the equilibrium concentration in solution in mg/L and C_{Ae} is the equilibrium concentration on

the sorbent in mg/L. Free energy change indicates the degree of spontaneity of the adsorption process and the higher (-) ve value a more energetically favourable adsorption^{34,35}.

The value of enthalpy ΔH° and entropy ΔS° were calculated from the slope and intercept of the plot $\ln K_D$ against $1/T$ as given in equation (7). The value of free energy ΔG° , enthalpy ΔH° and entropy ΔS° are listed in Table 2.

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

From Table 2 it is clear that the negative values of ΔG° indicated the spontaneous nature of the adsorption process and indicated low feasibility of biosorption at very high temperature. The negative values of ΔH° suggested the exothermic nature of the adsorption. The negative ΔS° value indicates a decrease in the degree of freedom of the adsorbed species.

Table 2. Thermodynamic parameters for adsorption of Cu(II), Pb(II) and Zn(II) onto DBL

Heavy metals	T, K	ΔG° , kJ/mol	ΔH° , kJ/mol	ΔS° , J/molK
Cu(II)	288	-2.051	-9.49	-22.77
	303	-3.188		
	318	-3.599		
	333	-1.556		
	288	-2.418		
Zn(II)	303	-3.769	-16.25	-45.05
	318	-2.127		
	333	-1.180		
	288	-1.938		
	303	-2.687		
Pb(II)	318	-2.392	-6.06	-12.70
	333	-1.774		

Conclusion

This work attempts to explore the DBL biomass was used for the removal of copper, zinc and lead ions from the synthetic waste water. The adsorption increases with increasing the adsorbent dose and adsorption capacity decreases with increasing adsorbent dose. Adsorption of Pb(II), Cu(II) and Zn(II) ions on DBL decreases with increasing the metal ion concentration and metal uptake capacity increases with increasing metal ion concentration. The maximum removal was found at pH 5.0 for Cu(II), Zn(II) and Pb(II). Langmuir, Freundlich and Temkin adsorption models were used to represent the experimental data. A high correlation was found for Langmuir isotherm model. Thermodynamic analysis suggests that the removal of Pb(II), Cu(II) and Zn(II) from synthetic waste water onto DBL is a spontaneous and exothermic in nature.

References

1. Reddad Z, Gerente C, Andres Y and Cloirec P L, *Environ Sci Technol.*, 2002, **36**(9), 2067-2073; DOI:10.1021/es0102989
2. Uluoğlu O D, Sari A, Tuzen M and Soylak M, *Bioresour Technol.*, 2008, **99**(8), 2972-2980; DOI:10.1016/j.biortech.2007.06.052
3. Naiya T K, Bhattacharya A K, Mandal S and Das S K, *J Hazard Mater.*, 2009, **163**(2-3), 1254-1264; DOI:10.1016/j.jhazmat.2008.07.119

4. Monken A, *Met Finish*, 2000, **98**, 464-470; DOI:10.1016/S0026-0576(00)80355-4
5. Veglio F, Quaresima R, Fornari P and Ubaldini S, *Waste Manage*, 2003, **23**(3), 245-252; DOI:10.1016/S0956-053X(02)00157-5
6. Nicholson F A, Smith S.R, Alloway B J, Carlton-Smith C and Chambers B J, *Sci Total Environ.*, 2003, **311**(1-3), 205-219; DOI:10.1016/S0048-9697(03)00139-6
7. Otero N, Vitoria L, Soler A and Canals A, *Appl Geochem.*, 2005, **20**(8), 1473-1488; DOI:10.1016/j.apgeochem.2005.04.002
8. Castelblanque J and Salimbeni F, *Desalination*, 2004, **167**, 65-73; DOI:10.1016/j.desal.2004.06.114
9. Alvarez-Ayuso E, Garcia-Sanchez A and Querol X, *Water Res.*, 2003, **37**(20), 4855-4862; DOI:10.1016/j.watres.2003.08.009
10. Ajmal M, Khan A H, Ahmad S and Ahmad A, *Water Res.*, 1998 **32**(10), 3085-3091; [http://dx.doi.org/10.1016/S0043-1354\(98\)00067-0](http://dx.doi.org/10.1016/S0043-1354(98)00067-0)
11. Goldstein G W, *Pediatr Ann.*, 1992, **21**(6), 384-388.
12. Matlock M M, Howerton B S and Atwood D A, *Water Res.*, 2002, **36**(19), 4757-4764; DOI:10.1016/S0043-1354(02)00149-5
13. Blocher C, Dorda J, Mavrov V, Chmiel H, Lazaridis N K, and Matis K A, *Water Res*, 2003, **37**(16), 4018-4026; DOI:10.1016/S0043-1354(03)00314-2
14. Rengaraj S, Joo C K, Kim Y and Yi J, *J Hazard Mater.*, 2003, **102**(2-3), 257-275; DOI:10.1016/S0304-3894(03)00209-7
15. Koby M, Demirbas E, Senturk E and Ince M, *Bioresour Technol.*, 2005, **96**(13), 1518-1521; DOI:10.1016/j.biortech.2004.12.005
16. Pagnanelli F, Mainelli S, De Angelis S and Toro L, *Water Res.*, 2005, **39**(8), 1639-1651; DOI:10.1016/j.watres.2005.01.019
17. Southichak B, Nakano K, Nomura M, Chiba N and Nishimura O, *Water Res.*, 2006, **40**(12), 2295-2302; DOI:10.1016/j.watres.2006.04.027
18. Rakhshae R, Khosravi M and Ganji M T, *J Hazard Mater.*, 2006, **134**, 120-129; DOI:10.1016/j.jhazmat.2005.10.042
19. Schiewer S and A. Balaria, *Chem Eng J.*, 2009, **146**, 211-219; DOI:10.1016/j.cej.2008.05.034
20. Mahiya Suresh, Lofrano Giusy and Sharma S K, *Chem Sci Trans.*, 2014, **3**(4), 1228-1241; DOI:10.7598/cst2014.884
21. Ajmal M, Rifaqat A K, Rao, Ahmed J, Anwar S and Ahmed R, *J Environ Sci Engg.*, 2008, **50**(1), 7-10.
22. Abdel-Ghani N T, Hefny H and El-Chaghay G A, *Int J Environ Sci Tech.*, 2007, **4**(1), 67-73; DOI:10.1007/BF03325963
23. Rathinam A, Maharshi B, Janardhanan S K, Jonnalagadda R R and Nair B U, *Bioresour Technol.*, 2010, **101**(5), 1466-1470; DOI:10.1016/j.biortech.2009.08.008
24. Vasudevan P, Padmavathy V and Dhingra S C, *Bioresour Technol*, 2002, **82**(3), 285-289; DOI:10.1016/S0960-8524(01)00181-X
25. KoK K H, Karim M I A, Ariff A and Aziz S A, *Pak J Biolog Sci.*, 2002, **5**(4), 474-478.
26. Apiratikul P R, Sungkhum V, Suthiparinyanont P, Wattan Achira S and MarhabaT M, *Chemosphere*, 2004, **64**, 1122-1127; DOI:10.1016/j.chemosphere.2005.11.076
27. Sag Y, Ozer D and Kustal T, *Process Biochem.*, 1995, **30**, 169-174; DOI:10.1016/0032-9592(95)80008-5
28. Ghaedi M, Najibi A, Hossainian H, Shokrollahi A and Soylak M, *Toxicol Environ Chem.*, 2012, **94**, 40-48; DOI:10.1080/02772248.2011.636043

29. Febrianto J, Kosasih A N, Sunarso J, Y.H. Ju Y H, Indraswati N and Ismadji S, *J Hazard Mater.*, 2009 **162(2-3)**, 616-645; DOI:10.1016/j.jhazmat.2008.06.042
30. Langmuir I, *J Am Chem Soc.*, 1918, **40(9)**, 1361-1403; DOI:10.1021/ja02242a004
31. Freundlich H M F, *J Phys Chem.*, 1906, **57**, 385-470; DOI:10.3390/ijerph9030970
32. Temkin M J and Pyzhev V, *Acta Physiochim.*, 1940, **12**, 217-222; DOI:10.4236/ajac.2015.61007
33. Aravindhan R, Rao J R and Nair B U, *J Hazard Mater.*, 2007, **142(1-2)**, 68-76; DOI:10.1016/j.jhazmat.2006.07.058
34. Dakiky M, Khamis M, Manasra A and Mereb M, *Adv Environ Res.*, 2002, **6(4)**, 533-540; DOI:10.1016/S1093-0191(01)00079-X
35. Aksu Z, *Process Biochem.*, 2002, **38**, 89-99; DOI:10.1016/S0032-9592(02)00051-1