Comparative Removal of Lead, Copper and Cadmium Ions from Wastewater in Single and Ternary Batch Biosorption Systems onto Dry Walnut Shells

FIRAS HASHIM KAMAR[1,2], AURELIA CRISTINA NECHIFOR[1], GHANIM M. ALWAN[3], MIHAELA EMANUELA CRACIUN[1], GHEORGHE NECHIFOR[1]*

[1]University Politehnica of Bucharest, Department of Analytical Chemistry and Environmental Engineering, 1-7 Gheorghe Str., 011061, Bucharest, Romania

[2] Institute of Technology- Baghdad, Middle Technical University, Iraq

[3] Department of Chemical Engineering, University of Technology, Iraq

The present study aims to evaluate the competitive biosorption of Pb(II), Cu(II) and Cd(II) ions by using dry walnut shells. Series of experiments were carried out in batch adsorption via single and triple system to study the effect of process variables on removal efficiency at range of 20 to 50 C°. The selected variables are: inlet metal concentration, pH, contact time and adsorbent dosage. The maximum removal efficiency at optimum condition in single biosorption system were: 86.16, 79.54 and 72.35% for Pb(II), Cu(II) and Cd(II) ions, respectively; these values increased in ternary systems to 58.46, 38.25, and 18.17% in the same sequence. Experimental data showed that the biosorption process obey the pseudo-second-order kinetics model. The thermodynamics parameters as Gibbs free energy change ΔG^o, standard enthalpy change ΔH^o, and standard entropy change ΔS^o indicated that biosorption process was feasible, spontaneous and exothermic. FTIR spectroscopy analysis and Infrared spectrometry confirmed that the carboxyl and hydroxyl on the adsorbent surface were the major active groups responsible for the biosorption process.

Keywords: bosorption; heavy metals; process variables; walnut shells

Toxic heavy metals are considered one of the pollutants that have direct effect on human and life. Industrial wastewater is containing lead, copper, cadmium, chromium etc., which could contaminate groundwater resources and thus lead to a serious groundwater pollution problem [1, 2].

Many industries, like metal plating, mining operations, tanneries, radiator manufacturing, smelting, alloy industries and storage batteries industries, etc. release these severely toxic heavy metal ions in their wastewaters contaminating natural streams were indisposed, which is a major concern due to toxicity to many life forms [3, 4].

Water pollution by heavy metals has received wide spread attention for many decades and has been a major cause of concern due to generation of a high toxicological risk for human health, ecosystem, and agriculture. Most of heavy metals are toxic and due to their non-biodegradability and persistence, they tend to accumulate in living organisms causing various diseases and disorders Therefore, with regard to the numerous disadvantages of heavy metals, their removal from industrial wastewaters is a very important environmental issue [5-7].

A variety of treatment processes for removal of heavy metals from wastewater have been employed including chemical precipitation, chemical oxidation, ion exchange, membrane filtration, floatation, electrochemical treatment, and adsorption. These processes usually require high operation and maintenance costs, hence there is pressing demand for innovative technologies which are low cost, require low maintenance and are energy efficient [8, 9]. The adsorption is defined as the property of certain biomolecules to bind and concentrate selected ions or other molecules from aqueous solution. The major advantage of adsorption technology is its effectiveness in reducing the concentration of heavy metal ions to very low levels in an environment-friendly manner [10, 11].

Biosorption fall under the following categories: bacteria, fungi, algae, yeast, and industrial and agricultural wastes. In the recent years, agricultural by-products have been widely used as adsorbent materials to remove heavy metal ions from industrial waste water such as sawdust, cotton seed hulls, rise husk, peanut shell, banana pith and orange peel [12-14].

The aim of the present work is to study the experimental and theoretical removal of lead, copper, and cadmium ions as single and ternary using simulated wastewater rig based on dry walnut shells as biosorbents. Batch experiments were carried out for isotherm, kinetic and thermodynamic studies on the removal of those ions from aqueous solution. The influence of various important parameters such as initial concentration, *p*H, contact time, and adsorbent dose is investigated.

Experimental part

Materials and methods

Biosorbent and Chemicals

Walnuts were collected from local market, and then were broken to obtain walnut shells. Rinsing the product twice in the distilled water to remove the dust, and dry for 24 h using electrical oven at temperature 100 °C. Milling the dry material and then sieved to 0.5-3 mm and stored in plastic containers ready for use.

* *email: doru.nechifor@yahoo.com*

All the chemicals used in this work were of analytical grade. Stock solution of Pb(II), Cu(II) and Cd(II) ions at concentration of (100 mg/L). Each ions were prepared by dissolving recommended amount of $(CH_3COO)_2$ Pb $3H_2O$, ($CuSO_4.6H_2O$) and $Cd(NO_3)_2$ $4H_2O$ in the standard volume of distilled water. Low concentrations were obtained by further dilution of the stock solution with distilled water. The diluted solutions were kept at room temperature. Before starting of experimental runs, *p*H of solutions was adjusted to the desired-value by adding 0.1 M HCl and 0.1 M NaOH solutions.

Procedure of Biosorption experimental

The experimental rig was designed and constructed in best way to collect the experimental data. Experiments of single and triple system were conducted at different operating conditions (initial concentration of Pb(II), Cu(II) and Cd(II) ions, *p*H,contact time and adsorbent dose). The experimental set-up consisting of 100 mL flasks with volume of 50 mL were kept constant that represents the reaction zone. The flasks were shaken at optimum speed of 200 rpm for recommended time period at 25°C. The kinetics study was carried out by agitating 100 mL flasks containing 0.5 gm of dry walnut shells and 50 mL solutions for each heavy metal ions in shaker at 25°C . The agitation speed is 200 rpm. The contact time was varied from 0 to 180 min. At predetermined time, the flasks were withdrawn from the shaker and the reaction solutions were filtered through Whatman filter paper No. 40.

The isotherm study was achieved by using various concentrations of lead solutions. A 0.5 gm dry walnut shells with 50 mL solution each heavy metal ions of various initial concentrations was shaken at 200 rpm for 150 min at 25°C. The initial *p*H of the solution was adjusted to 6.

For reliability, the experiments were repeated twice. The filtrate samples were analyzed by Atomic Absorption Spectrometer: AAS (GBC 933 plus, Australia). The removal efficiencies (R %) of heavy metal ions from the aqueous solution were calculated according to the following equation:

$$R\% = \frac{C_o - C_e}{C_o} * 100 \quad (1)$$

Results and discussions

Effect of Initial Metal Concentration

The initial concentration of Pb(II), Cu(II) and Cd(II) ions provides an important driving force to outweigh all mass transfer resistance of metal between the aqueous and solid phases. Removal of these heavy metal ions for various initial concentrations (10 to 100 mg/L) by dry walnut shells dosage (0.5 gm/ 50 mL) at optimum operating conditions (contact time of 150 min and at *p*H 6)for single and ternary systems as shown in figure 1. The removal efficiency is increased from 57.78 to 87.05%, 52.47 to 80.95%, and 36.84 to 73.23% for Pb(II), Cu(II) and Cd(II) ions respectively, by decreasing in initial concentration from 100 mg/L to 10 mg/L in single system. At lower metal ions concentration, the efficiency uptake was higher due to larger surface area of sorbent being available for adsorption [15]. When the concentration of metal ions became higher, the removal efficiency decreased since the available sites for biosorption became less due to saturation of adsorption sites. At a higher concentration of metal ions, the ratio of initial number of moles of metal ions to the sorption sites available was higher, resulting in lower biosorption percentage. Best removal efficiency in the single system at 50 mg/L initial concentration were: 86.16, 79.54 and 72.35% for Pb(II), Cu(II) and Cd(II) ions, respectively. The removal of Pb(II) is greater than the Cu(II) and Cd(II) ions onto dry walnut shells in ternary biosorption systems also.

Effect of pH

Effect of solution *p*H on removal efficiency at different initial *p*H values (3, 5, 6, 7, and 8) in single component system is shown in figure 2. The removal efficiency increases with

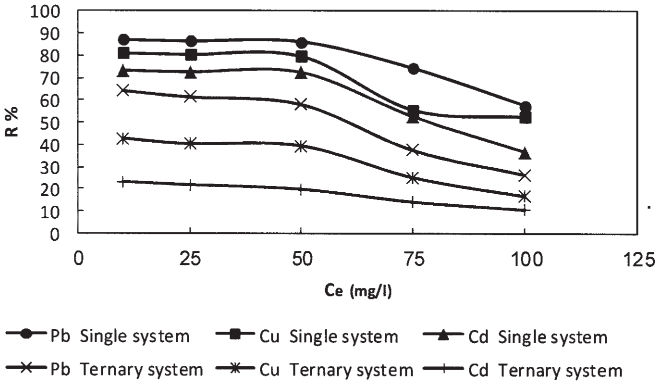

Fig.1. Effect of initial concentration on the batch biosorption single and ternary systems of Pb(II), Cu(II) and Cd(II) ions at optimum values of pH= 6, agitation speed=200 rpm, contact time = 150 min, particles diameter= 1 mm and temperature= 25 °C

increasing the *p*H from 3 to 6. The maximum removal efficiency for single component system for Pb(II), Cu(II) and Cd(II) ions onto dry walnut shells were about 86.16, 79.54%, and 72.35% respectively at *p*H 6. Increase of *p*H more than 6 causes precipitation of metal ions on the surface of the adsorbent by nucleation. This behaviour may be due to the fact that the presence of higher concentration and higher mobility of H^+ ions favoured adsorption compared to M (II) on the other hand in the acidic medium because of high solubility and ionization of metal ions. The surface of the adsorbent becomes more positively charged at high H^+ concentration, and then the attraction between adsorbents and metal cations is reduced. In contrast, with increasing of *p*H the negatively charged surface area becomes more thus facilitating greater metal removal and then at high *p*H the percentage removal decreases [16]. The maximum biosorption was observed within the *p*H range 5 to 6, which might be because of partial hydrolysis of metal ions. On the other hand, in ternary components system, the removal efficiency for each heavy metal ion was increased with increasing *p*H value from 3 to 6 also. The removal efficiency of Pb(II) is greater than Cu(II) and Cd(II) because of the more favorability of Pb(II) to be adsorbed rather than Cu(II) and Cd(II).

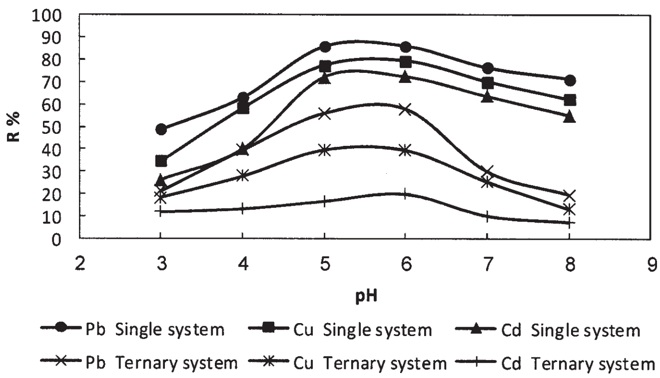

Fig. 2. Effect of pH on the batch biosorption single and ternary systems of Pb(II), Cu(II) and Cd(II) ions onto walnut shells at C_o= 50 mg/L, agitation speed=200 rpm, contact time = 150 min, adsorbent dose=0.5 gm/50 mL, particles diameter= 1 mm and temperature= 25 °C

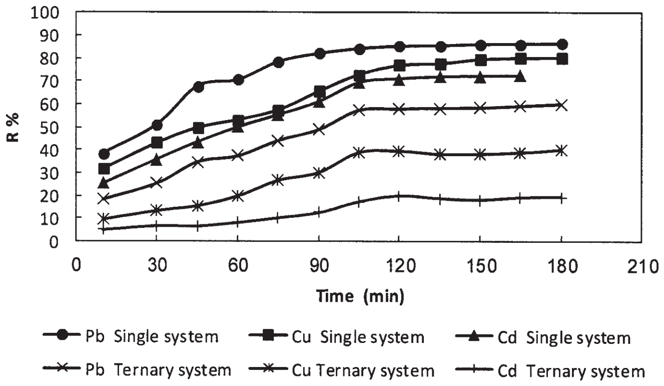

Fig. 3. Effect of contact time on removal efficiency at optimum operating conditions for single and triple systems.

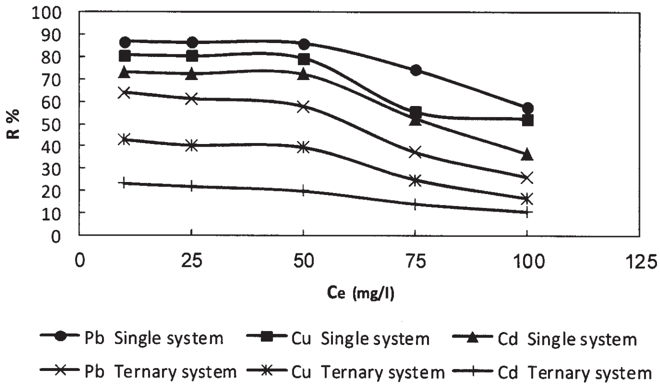

Fig. 4. Effect of adsorbent dosage on removal efficiency at optimum operating conditions for single and triple systems

Effect of Contact Time

The experiments were carried out at range of contact time between 10 and 180 min. The effect of contact time on removal efficiency of metal ions for single and ternary system is shown in figure 3. In single system, it was observed that the rate of metal ions removal was higher at starting during 150 min and after that, the sorption rate becomes practically very slow. The difference in the degree of adsorption may be due to the existence of greater number of adsorbent sites available for the adsorption of metal ions. As the remaining vacant surface sites decreasing, the adsorption rate slowed down due to the formation of repulsive forces between the metals on the solid surface and in the liquid phase [17]. Based on some results, the contact time of 150 min was considered as the optimum value. The same procedure was used for ternary systems. Figure 3 explains that in ternary system the removal efficiency decreased to 58.46, 38.25, and 18.17% for Pb(II), Cu(II) and Cd(II) ions, respectively. This situation is due to the competitive and interaction between metal ions. The results show that the removal of Pb(II) is greater than the Cu(II) and Cd(II) ions as shown in figure 3.

Effect of biosorbent dosage

The effect of biosorbent dosage on the removal of metal ions was studied using dry walnut shells dosage of 0.125-1 gm/ 50 mL at optimum operating conditions for single and ternary systems as shown in figure 4. It was found that the retention of metals increased with increasing amount of sorbent dose up to 0.5 gm / 50 mL of solution, this value was taken as the optimum amount for other trials. The results were expected because for a fixed initial metal concentration, increasing adsorbent amount provides greater surface area or adsorption site [18]. The removal efficiency of Pb(II) is higher than that of Cu(II) and Cd(II) for single and ternary systems. This may be due to the physical and chemical properties of Pb(II) to be more favourable to be adsorbed than Cu(II) and Cd(II).

Biosorption kinetics model

Pseudo- first order and pseudo- second order simplified kinetic models were used to test the experimental data. A linearized two kinetic models were described in linearized equations (2 and3) respectively [19-25].

$$\ln(q_{eq} - q_t) = \ln q_{eq} - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_s q^2_{eq}} + \frac{t}{q_{eq}} \quad (3)$$

The slopes and intercept of $ln(q_{eq}-q_t)$ versus t plot in figure 9 were used to determine the pseudo-first-order rate constants (k_1) and q_{eq}. Plots of t/qt versus t in figure 10 were used to determine the pseudo-second-order rate constant k_2 and q_{eq} values from the slope and intercept.

Table 1 shows that the values of correlation coefficient (R^2) indicate a better fit of pseudo- second- order model with the experimental data compared to pseudo- first- order model. The values of q_e calculated from the second order kinetic model agreed very well with the experimental values, and the correlation coefficient are over 0.97. Therefore, the second-order model can be applied for Pb(II), Cu(II) and Cd(II) biosorption process.

Thermodynamic parameters

The thermodynamic parameters, Gibbs free energy change ΔG°, standard enthalpy change ΔH°, and standard entropy change ΔS° used to understand the effect of temperature on the adsorption [20]. The thermodynamic parameters were calculated for batch adsorption single system by using the following equations [21]:

$$K_c = \frac{C_{ad}}{C_e} \quad (4)$$

$$\Delta G^\circ = -RT \ln K_c \quad (5)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

where C_{ad} is the concentration of heavy metals on the sorbent at the equilibrium and C_e is the equilibrium concentration of the same metals in the liquid phase. The

Table 1
KINETIC MODEL PARAMETERS FOR Pb(II), Cu(II) AND Cd(II) IONS BIOSORPTION WALNUT SHELLS

Model	Parameters	Value		
		Pb(II)	Cu(II)	Cd(II)
Pseudo-first-order model	q_{eq} (mg/g)	5.0505	4.8138	7.2456
	K_1(L/min)	0.0375	0.0266	0.0380
	R^2	0.9775	0.8993	0.8745
Pseudo-second-order model	q_{eq} (mg/g)	4.8614	4.8971	4.5433
	K_2 (g/mg.min)	0.0106	0.0052	0.0054
	R^2	0.9963	0.9769	0.9815

Table 2
THERMODYNAMIC CONSTANTS OF BIOSORPTION OBTAINED FOR Pb(II), Cu(II) AND Cd(II) IONS ONTO DRY WALNUT SHELLS

Metal	Temperature (K)	$-\Delta G^{\circ}$ ($kJ.mol^{-1}$)	$-\Delta H^{\circ}$ ($kJ.mol^{-1}$)	ΔS° ($J.mol^{-1}K^{-1}$)	R^2
Pb(II)	293	5.8465	39.685	0.1276	0.9773
	298	4.5305			
	303	4.5479			
	308	3.7014			
	313	2.6774			
	318	2.0208			
	323	1.2532			
Cu(II)	293	4.3233	35.895	0.1082	0.9717
	298	3.3640			
	303	3.0925			
	308	2.8626			
	313	2.1912			
	318	1.3212			
	323	0.9385			
Cd(II)	293	3.1947	31.368	0.0962	0.9632
	298	2.3831			
	303	2.3967			
	308	2.0333			
	313	1.1149			
	318	0.7851			
	323	0.1966			

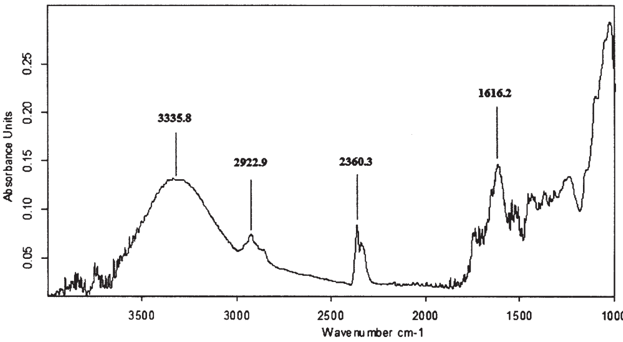

Fig. 5: FTIR analysis of dry walnut shells

value of ΔH° and ΔS° can be calculated from the plot of ΔG° vs. T.

Table 2 shows the values of enthalpy ΔH° was negative for Pb(II), Cu(II) and Cd(II) ions, suggested exothermic nature adsorption. This is also supported by the decreasing in the values of uptake capacity of adsorbents with the rise in temperature. The positive ΔS° reflects the affinity of the adsorbent material for metal ions. The experimental results indicate that the dry walnut shells has affinity for metal ions namely, Pb(II) , Cu(II) and Cd(II).The negative values of ΔG° confirm the feasibility of the process and the spontaneous nature of adsorption [22].

FTIR results

In order to understand the possible adsorbent- metal ion interactions, it is essential to identify the functional groups present on the biomass involved in this process. The main effective binding sites can be identified by FTIR spectral comparison of the dried walnut shells as adsorbent material, Pb(II), Cu (II) and Cd(II) ions- loaded adsorbent. Natural adsorbent material was examined using (SHIMADZO FTIR, 800 series spectra- photometer). Three flasks of 2 L were filled with 1 L of each metal solution 50 mg/L and 10 gm of dried walnut shells. The flasks were placed on the shaker and agitated continuously for 150 min at 200 rpm. Samples of each flask were dried in oven at 50°C for 48 hr. From figures 5-7 and 8, the FTIR spectral indicates to the presence of carboxylic and hydroxyl groups.

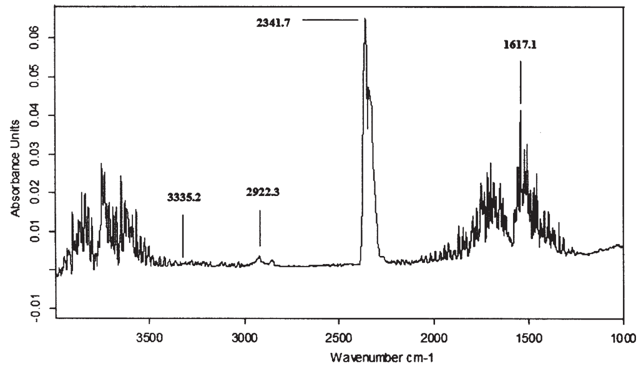

Fig. 6. FTIR analysis of dry walnut shells after loaded by Pb(II) ion

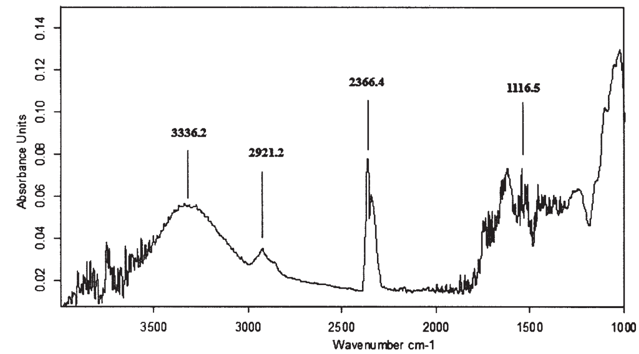

Fig. 7: FTIR analysis of dry walnut shells after loaded by Cu(II) ion.

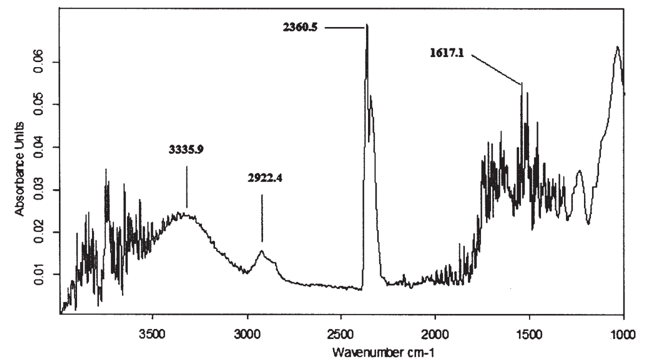

Fig. 8: FTIR analysis of dry walnut shells after loaded by Cd(II) ion.

Conclusions

The present work evaluated the removal of Pb(II), Cu(II) and Cd(II) ions from wastewater using dry walnut shells as adsorbent material in batch adsorption system. Batch experiments showed that dry walnut shells were a good efficient to remove of these metal ions from wastewater at optimum condition; initial concentration 50 mg/L, *p*H 6, contact time 150 min and biosorbent dosage 0.5 gm per 50 mL of solution. The maximum removal efficiency at optimum condition in single biosorption system obtained were 86.16, 79.54 and 72.35% for Pb(II), Cu(II) and Cd(II) ions, respectively; these values reduced in ternary systems in the same sequence. Kinetics study of the equilibrium data showed that the biosorption of Pb(II), Cu(II) and Cd(II) ions onto dry walnut shells obeys the pseudo-second-order kinetic model. The negative values of Gibbs free energy and enthalpy for three metallic ions confirmed the physic-sorption and exothermic nature of adsorption process. FTIR analyses showed that hydroxyl, carboxyl groups could be very effective for capturing these metal ions.

References

1. GHEORGHE, E., BARBU, L., NECHIFOR, G., LUCA, C., Rev. Chim. (Bucharest), **57**, no. 9, 2006, p. 940.
2. ABDEL-GHANI, N. T., ELCHAGHABY, G. A., Int. J. Environ. Sci. Tech., **4**(4), 2007, p. 451.
3. KADIRVELU, K., THAMARAISELVI, K., NAMASIVAYAM, C., Bioresource Technology, **76**, 2001, p. 63.
4.CHAND, R., TAKANORI, W., KASTUTOSHI, I., HIDETAKA, K., LUITEL, H.N., PARAJULI, D., TOSHIO, T., MITSUNORI, Y., Minerals Engineering, vol. **22**, 2009, p. 1277.
5.CHAND, S., AGGARWAL, V.K., KUMAR, P., Indian J. Environ. Health, **36**(3), 1994, p. 151.
6. CHUAH, T.G., JUMASIAH, A., AZMI, I., KATAYON, S., CHOONG, S. Y. T., Desalination, **175**, 2005, p. 305.
7. BAILEY, E., TRUDY, J., OLIN, R., BRICKA, M., ADRIAN, D.D., Water Research, **33**, 1999, p. 2469.
8. MOHAN, D., SINGH, K.P., Water Research, **36**, 2002, p. 2304.
9. RANE, N. M., SAPKAL, R.S., SAPKAL, V.S., PATIL, M.B., SHEWALE, S.P., Int. J. Chem. Sci. Appl., **1**(2), 2010, p. 65.
10. GUPTA, V.K., RASTOGI, A., Journal of Hazardous Materials, **153**, 2008, p. 759.
11. HOSSAIN, M.A., NGO, H.H., GUO, W.S., SETIADI, T., J. Bioresource Technol. **121**, 2012, p. 386.
12. RATHINAM, A., MAHARSHI, B., JANARDHANAN, S.K., JONNALAGADDA, R., NAIR, B.U., J. Bioresource Technol., **101**, 2010, pp. 1466–1470.
13. AJMAL, M., RAO, R.A.K., ANWAR, S., AHMAD, J., AHMAD, R., Bioresource Technology, **86**, 2003, p. 147.
14. WAN NGAH, W.H., HANAFIAH, M. A.K.M., Bioresource Technology, **99**, 2007, p. 3935.
15. KUMAR, P. S., KIRTHIKA, K., Electronic Journal of Environmental, Agriculture and Food Chemistry, **9**(10), 2010, p. 262.
16. ONUNDI, Y. B., MAMUN, A. A., AL KHATIB, M. F., AHMED, Y. M., Int. J. Environ. Sci. Tech., **7**(4), 2010, p. 751.
17. BISHNOI, N. R., PANT, A., GARIMA, B. U J. Sci. Ind. Res., **63**, 2004, p.813.
18. GUPTA S. S., BHATTACHARYYA K. G., Indian Journal of Chemical Technology, **16**, 2009, pp. 457-470.
19. HO, Y. S., Journal of Hazardous Materials, **136**(3), 2006, p 103.
20. CAYLLAHUA, J.E.B., CARVALHO, R.J., TOREM, M.L., Miner. Eng., **22**, 2009, p. 1318.
21. JORDAO, C.P., FEMANDES, R.B.A., RIBEIRO, K.D.L., BARROS, P.M.D., FONTES, M.P.F., SOUZA, F.M.D.P., Water Air Soil Poll., **210**, 2010, p. 51.
22. SULAYMON, A.H., AHMED, K.W., J. Environmental Science and Technology, **42**, 2008, p. 392.
23. SEGARCEANU, M., PASCU, D. E., TRAISTARU, G. A., PASCU (NEAGU), M., TEODORESCU, S., ORBECI, C. Rev. Chim. (Bucharest), **65**, no. 1, 2014, p. 8.
24. NECHIFOR, A.C., PASCU (NEAGU), M., PASCU, D.E. TRAISTARU, G.A., Rev. Chim.(Bucharest), **64**, no. 3, 2013, p. 238.
25. NEAGU, M., PASCU, D.E., TRAISTARU, G.A., CRETU, G., NECHIFOR, A.C., BUNACIU, A.A., ABOUL-ENEIN, H.Y., Analytical Chemistry Letters, **3**(5-6), 2013, p. 314

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