



International Journal of ChemTech Research CODEN (USA): IJCRGG ISSN : 0974-4290 Vol.6, No.10, pp 4525-4532, September 2014

RACE 2014 [12th – 13th July 2014] Recent Advances in Chemical Engineering

Optimization studies on the Sorption of Cu (II) from aqueous solution using marine brown algae: *Sargassum myriocystum*

R.Jayakumar, M.Rajasimman and C.Karthikeyan

Environmental Engineering Laboratory, Department of Chemical Engineering, Annamalai University, Annamalai nagar – 608002, Tamilnadu, India.

*Corres.author: harrishjk@rediffmail.com

Abstract : The ability of marine brown algae *Sargassum myriocystum* for sorption of Cu(II) ions from aqueous solution was studied in batch experiments. The effect of relevant parameters such as function of pH, sorbent dosage, agitation speed and contact time was evaluated by using Response surface methodology (RSM). A maximum percentage removal of Cu (II) by *Sargassum myriocystum* occurs at pH - 4.94, sorbent dosage – 1.99 g/L, agitation speed – 119.59 rpm and contact time – 59.55 min. **Keywords:** Adsorption, Cu (II), RSM, brown algae.

1. Introduction

Heavy metal is applied to a group of elements having atomic density value of more than 6 g/cm^{3} , ¹ Heavy metals like arsenic (As), copper (Cu), cadmium (Cd), chromium (Cr), nickel(Ni), zinc (Zn), lead (Pb), mercury (Hg) and manganese (Mn) are key pollutants of freshwater reserves² because of their toxic, non-biodegradable and persistent nature. Most of the metals are carcinogenic, teratogenic and create severe health problems like organ damage, reduced growth and development, nervous system impairments and oxidative stress³. The increasing industrial growth is the major source of heavy metals introduction into different segments of the environment including air⁴, water, soil and biosphere. These industrial sources include mining, smelting, surface finishing, electroplating, electrolysis, electric appliances and electric boards/circuits manufacturing industries as well as agriculture sector as well as fertilizers, pesticides⁵. Copper is an important trace element essential by humans for its role in enzyme synthesis, tissues and bones development⁶. However, the divalent copper (Cu²⁺) is toxic and carcinogenic when consumed in overload through ingestion. The excessive Cu^{2+} consumption leads to its deposition in liver and subsequent vomiting, headache, nausea, respiratory problems, abdominal pain, liver and kidney failure and finally gastrointestinal bleeding⁶. It has known harmful injurious effects on the soil biota and damages to many plant species including some of the endemic Australian native plant species (Acacia holosericea and Eucalyptus crebra)⁷. The excessive amounts of Cu²⁺in fresh water resources and aquatic ecosystem damage the osmo-regulatory mechanism of the freshwater animals⁸ and cause mutagenesis in humans⁹. Large quantities of Cu^{2+} are released by the disposal of untreated industrial waste⁷. United State Environmental Protection Agency has set its Cu^{2+} permissible limits as 1.3 mg/L in industrial effluents⁹. World Health Organization (WHO) defines the Cu²⁺ permissible limit of 1.5 mg/L in drinking water¹⁰. Conventional methods used to remove metal ions from industrial wastewater include chemical precipitation, electrochemical treatment, ion exchange process, membrane separation and evaporation¹¹. However some of the conventional technologies are ineffective and unfavorable as they cause sludge disposal

problem, expensive and incomplete removal¹². The utilization of sorption technology for the treatment of heavy metal contaminated wastewaters has become an alternative method to conventional treatments^{13,14}. The main advantages of this technique are the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time, and no production of secondary compounds which might be toxic¹⁵⁻¹⁷. Among the biological materials, algae have been found to be potentially suitable sorbents because of their cheap availability both in fresh and saltwater, relatively high surface area and high binding affinity¹⁸. Research in the field of sorption has mostly concerned itself with brown algae¹⁹⁻²¹. The cell walls of brown algae generally contain three components: cellulose, the structural support; alginic acid, a polymer of mannuronic and guluronic acids and the corresponding salts of sodium, potassium, magnesium and calcium and sulphated polysaccharides. As a consequence, carboxyl and sulphate are the predominant active groups in this kind of algae.

The present work aims to investigate the sorption potential of marine macro brown algae *Sargassum myriocystum* as an alternative sorbent material for the removal of Cu(II) ions from aqueous solution. The effect of some operating variables – temperature, pH and initial concentration of Cu(II) – on the sorption process onto the marine macro-algae studied by using a Central composite design method, which gives a mathematical model that shows the influence of each variable and their interactions.

2. Materials And Methods

2.1 Chemicals and equipment

All chemicals used were of analytical reagent grade. Deionized double distilled water was used throughout the experimental studies. Analytical grade HCl, NaOH and buffer solutions (E. Merk) were used to adjust the solution pH. Elico (L1-129) make pH meter was used for pH measurements. The metal concentrations in the samples were determined using Atomic Absorption Spectrophotometer (AAS) (Elico SL - 176).

2.2 Biomass preparation

The sorbentt marine brown algae *Sargassum myriocystum* were collected from the Mandapam coast, Ramanadhapuram district, Tamilnadu, India. They were washed several times using deionized water to remove extraneous materials and salts. The washing process was continued till the wash water contained no dirt. The washed algae were completely dried in sunlight for 10 days. The dried samples were cut into small pieces and powdered using domestic mixer. In this work, the powdered raw algae of 60 mesh particle size were used as sorbents for sorption process.

2.3 Preparation of metal ion solution

A stock solution of Cu(II) supplied by (Merck Ltd.) India (1000 mg/L) was prepared by dissolving 3.801 g of Cu(So₄) in 1000 mL slightly acidified distilled water. Working standards were prepared by progressive dilution of the stock copper solution.

2.4 Batch Sorption experiment

According to CCD all the batch experiments were carried out. The sorbent - sorbate mixtures were taken in a 250ml conical flask and agitated in an incubator shaker (LARK). The samples were centrifuged in the research centrifuge (REMI) at 10000 rpm and the supernatant was used for analysis of metal concentrations by using AAS. Experimental analysis was repeated three times and the results were statistically analyzed. The amount of adsorbed copper per unit mass of adsorbent (q_e , mg/g) was obtained using the following expression:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

The amount of adsorbed copper per unit mass of adsorbent at time t $(q_t mg/g)$ was obtained by using following expression:

$$q_t = \frac{(C_o - C_t)V}{m} \tag{2}$$

where V is the volume of solution treated in liter, C_o is the initial concentration of Copper metal ion in mg/L, C_e is the equilibrium Copper metal ion concentration in mg/L, C_t (mg/L) is the concentration of adsorbents at time t, and m is the biomass in gram.

2.5 RSM experimental design

RSM is an optimizing tool designed to find the optimal response within specific ranges of preestablished factors, through a second-order equation. In industrial applications, RSM designs involve a small number of factors, because the required number of experimental runs increases dramatically with the number of factors [22]. CCD was chosen to study the effects of pH, sorbent dosage (g/L), agitation speed (rpm) and contact time (min) on Cu (II) sorption. In order to describe the effects of these variables on percentage removal of copper, batch experiments were conducted. The coded values of the process parameters were determined by the following equation.

$$X_i = \frac{(X_i - X_0)}{\Lambda X} \tag{3}$$

Where x_i coded value of the ith variable, X_i uncoded value of the ith test variable and X_o uncoded value of the ith test variable at center point. The range and levels of individual variables were given in Table 1. The experimental design was given in Table 2. The regression analysis was performed to estimate the response function as a second order polynomial.

A second-order polynomial equation is

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1, i < j}^{k=1} \sum_{j=2}^k \beta_{ij} X_i X_j,$$
(4)

Where Y is the predicted response b_i , b_j , b_{ij} are coefficients estimated from regression, they represent the linear, quadratic and cross products of x_1 , x_2 , x_3 on response.

	Coded levels						
Independent variable	Code	-2	-1	0	+1	+2	
pН	А	3	4	5	6	7	
Sorbent dosage(g/L)	В	1	1.5	2	2.5	3	
Agitation speed(rpm)	С	40	80	120	160	200	
Contact time(min)	D	20	40	60	80	100	

 Table 1. Experimental range and levels of independent process variables

A statistical program package Design expert 7.1.5 was used for regression analysis of the data obtained and to estimate the coefficient of the regression equation. The equation was validated by the statistical test called ANOVA analysis. After sorption, the contents of the beakers were centrifuged at 10000 rpm for 3 min and the sorbent was successfully separated from aqueous solution. The supernatants were analyzed for residual Cu (II) concentration using AAS. All the experiments were performed in triplicate and average value was reported.

3. Results and Discussion

3.1 Fitting models

According to the CCD, Sorption of Cu (II) was carried out and the results obtained were given in Table 2. The results of theoretically predicted response were given in Table 2. The mathematical expression of relationship to the response with variables is:

 $Y = 94.8000 - 5.57167A - 2.29833B - 1.10250C - 0.160833D - 4.49917A^{2} - 4.03917B^{2} - 4.30917C^{2} - 2.43417D^{2} - 1.89250AB - 1.59375AC - 1.42875AD + 0.941250BC - 1.15125BD - 2.22750CD$ (5)

where Y is the percentage removal of Cu (II) and A, B, C and D are the coded values of pH, sorbent dosage(g/L), agitation speed (rpm) and contact time (min) respectively.

Run		(B) Sorbent	(C) Agitation speed (rpm)	(D) Contact	Percentage Cu (II) removal		
Order	(A) pH	Dosage (g/L)		Time (Min)	Experimen	Predicte	
					tal	d	
1	1 (6)	-1 (1.5)	-1 (80)	-1(40)	77.46	79.98	
2	-1 (4)	1 (2.5)	1 (160)	-1(40)	88.60	88.22	
3	0 (5)	0 (2)	0 (120)	0 (60)	94.80	94.80	
4	0 (5)	-2 (1)	0 (120)	0 (60)	83.16	83.24	
5	0 (5)	0 (2)	0 (120)	0 (60)	94.80	94.80	
6	0 (5)	0 (2)	2 (200)	0 (60)	72.00	75.35	
7	1(6)	-1(1.5)	1 (160)	1(80)	72.30	71.83	
8	2 (7)	0 (2)	0 (120)	0 (60)	65.00	65.66	
9	0 (5)	0 (2)	0 (120)	0 (60)	94.80	94.80	
10	0 (5)	0 (2)	0 (120)	0 (60)	94.80	94.80	
11	0 (5)	0 (2)	0 (120)	-2 (20)	83.11	85.38	
12	0 (5)	0 (2)	0 (120)	0 (60)	94.80	94.80	
13	-1 (4)	-1(1.5)	-1 (80)	1(80)	88.50	90.59	
14	-1 (4)	1 (2.5)	1 (160)	1(80)	87.12	84.00	
15	0 (5)	0 (2)	-2 (40)	0 (60)	81.67	79.76	
16	1(6)	-1 (1.5)	-1 (80)	1(80)	84.06	83.56	
17	0 (5)	0 (2)	0 (120)	2 (100)	85.56	84.74	
18	-1 (4)	1 (2.5)	-1 (80)	-1(40)	81.03	80.90	
19	0 (5)	0 (2)	0 (120)	0 (60)	94.80	94.80	
20	-1 (4)	1 (2.5)	-1 (80)	1(80)	84.16	85.59	
21	-1 (4)	-1 (1.5)	-1 (80)	-1(40)	83.60	81.29	
22	1(6)	1 (2.5)	-1 (80)	1(80)	71.31	70.99	
23	1(6)	1 (2.5)	1 (160)	1(80)	61.60	63.03	
24	0 (5)	2 (3)	0 (120)	0 (60)	72.67	74.04	
25	-1 (4)	-1 (1.5)	1 (160)	1(80)	85.63	85.23	
26	-1 (4)	-1 (1.5)	1 (160)	-1(40)	85.13	84.85	
27	1 (6)	1 (2.5)	-1 (80)	-1(40)	72.50	72.02	
28	1 (6)	-1 (1.5)	1 (160)	-1(40)	79.47	77.16	
29	-2 (3)	0 (2)	0 (120)	0 (60)	87.15	87.94	
30	0 (5)	0 (2)	0 (120)	0 (60)	94.80	94.80	
31	1 (6)	1 (2.5)	1 (160)	-1(40)	75.65	72.96	

Table 2. CCD based experimental design and its response for Copper (II) removal

The ANOVA results for Cu (II) sorption onto brown algae were given in Table 3. F value of 52.72 implies that the model was significant. The fisher F- test with a very low probability value (P_{model} > 0.0001) reveals a very high significance for the regression model. The goodness of fit of the model was checked by coefficient of determination (R²). For a good statistical model, R² value should be close to 1.0. The R² was found to be 0.9801, which implies that more than 98.01% of experimental data was compatible with the data predicted by the model. A low CV value (2.19), indicate that the deviations between experimental and predicted values were low. Adeq precision measures the signal to noise ratio. A ratio greater than 4 is desirable. In this work, the ratio is found to be 25.231, which indicates an adequate signal. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, CD, A², B², C², D² are significant model

terms for the sorption of Cu (II). This implies that the linear effect of pH, sorbent dosage, agitation speed and square effects of pH, sorbent dosage, agitation speed and contact time were more significant factors. The interactive effect of pH , sorbent dosage, pH, agitation speed and agitation speed, contact time was also significant. Values greater than 0.1000 indicate the model terms are not significant.

Source	Sum of	Df	Mean Square	F - Value	P –value
	squares		_		Prob > F
Model	2459.87	14	175.71	52.72	< 0.0001
A – pH	744.06	1	744.06	223.24	< 0.0001
B – Sorbent Dosage, g/L	143.71	1	143.71	43.12	< 0.0001
C – Agitation speed, rpm	40.99	1	40.99	12.30	0.0032
D – contact time, min	0.25	1	0.25	0.075	0.7875
AB	73.26	1	73.26	21.98	0.0003
AC	55.42	1	55.42	16.63	0.0010
AD	14.66	1	14.66	4.40	0.0533
BC	4.04	1	4.04	1.21	0.2880
BD	7.81	1	7.81	2.34	0.1467
CD	46.36	1	46.36	13.91	0.0020
A^2	591.82	1	591.82	177.57	< 0.0001
B^2	478.58	1	478.58	143.59	< 0.0001
\mathbf{C}^2	543.59	1	543.59	163.10	< 0.0001
D^2	177.57	1	177.57	53.28	< 0.0001
Residual	49.99	15	3.33		
Lack of fit	49.99	9	5.55		
Pure error	0.000	6	0.000		
Cor total	2509.87	29			

Table	3. ANOVA	for Copper	(II) removal	using	Sargassum	myriocystum
-------	----------	------------	--------------	-------	-----------	-------------

Std. Dev - 1.83 ; R-Squared - 0.9801 ; Mean - 83.21 ; Adj R-Squared - 0.9615 ; C.V. % - 2.19

Pred R-Squared - 0.8702 ; PRESS - 325.67 ; Adeq Precision - 25.231

3.2 Effect of variables on Cu (II) removal

The sorption efficiency depends on several parameters, like pH, structural properties of both sorbate and sorbent, sorbent dosage, contact time, agitation speed, initial concentration of metal ions etc²³.

3.2.1Effect of pH on sorption

The effects of pH on the sorption of copper onto raw *Sargassum myriocystum* algae biomass were studied by changing the pH from 3.0 to 7.0. The pH of solution significantly influences metal sorption. Further, pH influences surface properties of the sorbent by way of functional group dissociation and also surface charges. At pH 3 sorption of Cu(II) onto *Sargassum myriocystum* biomass was found to be very low. It has been suggested that at low pH, H_3O^+ ions are close to the binding sites of the biomass and this restricts the approach of Cu(II) ions due to repulsion²⁴. With increase in pH, more ligands with negative charges are expected to be exposed and this will attract more positively charged Cu(II) ions for binding. sorption of Cu(II) by *Sargassum myriocystum* biomass had been found to increase with increase in pH and reach maximum at 4.94 and then decrease with further increase in pH up to 7.0 and it was shown in Fig.1. The effect of pH was not studied beyond pH 7.0 because of the precipitation of Cu(II) as hydroxide. Above the pH 7 the decrease in sorption may be attributed to reduced solubility and precipitation of Cu(II)²⁵. Therefore, further experiments were carried out with an initial pH value of 4.94. Similar results also reported that the maximum sorption efficiency for Cu(II) metal ion an biomass was observed at pH 5.0²⁶⁻²⁸.

3.2.2 Effect of sorbent dose

The effect of sorbent dosage on the removal efficiency of Cu(II) was studied using varying amounts of sorbent dosages (1-3 g/ L) and the results are shown in Fig.1. The maximum removal efficiency was attained as the dosage was 1.99 g/L. The sorption percentage increases with increase in sorbent dosage and almost constant at dose higher than 1.99 g/L. This trend could be explained as a consequence of partial aggregation of biomass

at higher biomass concentration, which results in the decrease in effective surface area for the sorption²⁹. Therefore, the optimum algae sorbent dose selected was 1.99 g/L for further experimental studies.



Fig.1 Interactive effect of pH and sorbent dosage on Cu (II) removal by Sargassum myriocystum

3.2.3 Effect of agitation speed

The effect of agitation speeds on sorption of Cu(II) was studied in the range of 40 -200 rpm. The results were presented in Fig.2. From the results, the maximum sorption of Cu (II) occurred at 119.59 rpm for *Sargassum myriocystum* sorbent. At low agitation speed, the sorbent do not spread in the sample but accumulated. This may cover the active sites of the lower layer adsorbent and only the upper layer adsorbent active sites adsorb the metal ion. Therefore agitation rate should be adequate to assure that all the surface binding sites were readily available for metal uptake. But at higher agitation speed, the percentage removal decrease. This may be attributed to an increase desorption affinity of adsorbate molecules³⁰.



Fig.2 Interactive effect of agitation speed and contact time on Cu (II) removal by *Sargassum* myriocystum

3.2.4 Effect of contact time

The rate of sorption is important for designing batch sorption experiments. Therefore, the effect of contact time on the sorption of Cu(II) was investigated. Fig.2 shows the interactive effect of agitation speed and contact time on the sorption of Cu (II) on to the brown algae. The sorption yield of Cu(II) increased considerably until the contact time reached 59.55 min. Further increase in contact time did not improve the sorption, so, the optimum contact time was selected as 59.55 min for further experimental studies. The initial phase may involve physical adsorption or ion exchange at cell surface and the subsequent slower phase may involve other mechanisms such as complexation, micro-precipitation or saturation of binding sites³¹.

Second order polynomial models obtained in this study was utilized to determine the optimum conditions. The optimum conditions were: initial pH - 4.94, sorbent dosage -1.99 g/L, agitation speed -119.59 rpm and contact time -59.55 min.

4. Conclusion

In the present investigation, feasibility of sorption of Copper (II) onto a marine macro brown algae, *Sargassum myriocystum*, which is abundant and cheaply available, was studied. RSM is utilized to optimize the operating conditions and maximize the Copper (II) removal. Analysis of variance showed a high coefficient of determination value ($R^2 = 0.9801$), thus ensuring a satisfactory adjustment of the second order regression model with the experimental data. The findings of the present investigagion indicates that *Sargassum myriocystum* can be successfully used for separation of Cu(II) from aqueous and industrial waste water solutions.

References

- 1. O'Connell. D.W., Birkinshaw. C., O'Dwyer. T.F., Heavy metal adsorbents prepared from the modification of cellulose: a review., Biores Technol, 2008, 99, 6709–6724.
- 2. Babarinde. N.A.A., Babalola. J.O., Sanni. R.A., Biosorption of lead ions from aqueous solution by maize leaf., Int. J. Phys. Sci, 2006, 1, 23–26.
- 3. Lee. J.C., Son. Y.O., Pratheeshkumar.P., Shi. X.L., Oxidative stress and metal carcinogenesis., Free Radical Biol. Med, 2012, 53, 742–757.
- 4. Lee. S.M., Laldawngliana. C., Tiwari. D., Iron oxide nano-particles-immobilized-sand material in the treatment of Cu (II), Cd (II) and Pb (II) contaminated wastewaters., Chem. Eng. J, 2012.
- 5. Wang. J., Chen. C., Biosorbents for heavy metals removal and their future., Biotech. Adv, 2009, 27, 195–226.
- 6. Akar. S.T., Akar. T., Kaynak. Z., Anilan. B., Cabuk. A., Tabak. A.Z., Demir. T.A., Gedikbey. T., Removal of copper(II) ions from synthetic solution and real wastewater by the combined action of dried *Trametes versicolor* cells and montmorillonite, Hydrometallurgy, 2009, 97, 98–104.
- 7. Lamb. D.T., Naidu. R., Ming. H., Megharaj. M., Copper phytotoxicity in native and agronomical plant species., Ecotoxicol. Environ. Saf, 2012, 85, 23–29.
- 8. Lee. J.A., Marsden. I.D., Glover. C.N., The influence of salinity on copper accumu-lation and its toxic effects in estuarine animals with differing osmoregulatory strategies., Aquat. Toxicol, 2010, 99, 65–72.
- 9. Shawabkeh. R., Al-Harahsheh. A., Al-Otoom. A., Copper and zinc sorption by treated oil shale ash., Sep. Purif. Technol, 2004, 40, 251–257.
- 10. Kalavathy. M.H., Karthikeyan. T., Rajgopal. S., Miranda. L.R., Kinetic and isotherm studies of Cu (II) adsorption onto H₃PO₄-activated rubber wood sawdust., J.Colloid Interface Sci, 2005, 292, 354–362.
- 11. Liu.H.L, Chen.B.Y, Lan.Y.W, Cheng.Y.C., Biosorption of Zn(II) and Cu(II) by the bindigenous *Thiobacillus thiooxidans.*, Chem. Eng. J, 2004, 97, 195–201.
- 12. Tuzun.G, Bayramoglu.E, Yalcin.G, Basaran.G, Celik.M.Y, Arica., Equilibrium and kinetic studies on biosorption of Hg(II), Cd(II) and Pb(II) ions onto microalgae *Chlamydomonas reinhardtii*., J. Environ. Manage, 2005,77 (2), 85–92.
- 13. Uslu.G, Dursun.A.Y, Ekiz.H.I, Aksu.Z., The effect of Cd(II), Pb(II) and Cu(II) ions on the growth and bioaccumulation properties of *Rhizopus arrhizus.*, Process Biochem, 2003, 39, 105–110.
- 14. Zouboulis.A.I, Loukidou.M.X, Matis.K.A., Biosorption of toxic metals from aqueous solutions by bacteria stains isolated from metal-polluted soils., Process Biochem, 2004, 39, 909–916.
- 15. Sheng.P.X, Wee.K.H, Ting.Y.P, Chen.J.P., Biosorption of copper by immobilized marine algal biomass., Chem. Eng. J, 2008, 136, 156–163.
- 16. Salehi.P, Asghari.B, Mohammadi.F., Biosorption of Ni(II), Cu(II) and Pb(II) by *Punica geranatum* from aqueous solutions., J. Water Resour. Prot, 2010, 2, 701–705.
- 17. Gupta.V.K, Rastogi.A, Biosorption of nickel onto treated alga (*Oedogonium hatei*): application of isotherm and kinetic models., J. Colloid Interface Sci, 2010, 342, 533–539.
- 18. Sarı.M, Tuzen.M., Biosorption of total chromium from aqueous solution by red algae (*Ceramium virgatum*): equilibrium, kinetic and thermodynamic studies., J. Hazard. Mater, 2008, 160, 349–355.
- 19. Holan. Z.R., Volesky. B., Prasetyo. I., Biosorption of cadmium by biomass of marine algae., Biotechnol.Bioeng, 1993, 41, 819–825.
- 20. Chong. K.H., Volesky. B., Description of two-metal biosorption equilibria by Langmuir-type models., Biotechnol.Bioeng, 1995, 47, 451–460.

- 21. Matheickal. J.T., Yu. Q., Biosorption of lead (II) and copper (II) from aqueous solutions by pretreated biomass of Australian marine algae., Bioresour. Technol, 1999, 69, 223 – 229.
- 22. Rajasimman.M and Murugaiyan.K., Optimisation of process parameters for the removal of zinc using red algae *Hypnea valentiae*., seaweed res.utin, 2011,33(1&2), 99 110.
- 23. Srinivasa popuri.R, kalyani.S, suresh kachireddy.R and krishnaiah., Biosorption of hexavalent chromium from aqueous solution by using prawn pond algae (*sphaeroplea*)., Ind. J. chemis, 2007, 46A, 284 289.
- 24. Deng.S, Ting.Y.P., Characterization of PEI-modified biomass and biosorption of Cu(II), Pb(II) and Ni(II)., Water Res, 2005, 39, 2167–2177.
- 25. Harris.P.O, Ramelow.G.J., Binding of metal ions by particulate biomass derived from *Chlorella vulgaris* and *Scenedesmus quadricauda.*, Environ. Sci. Technol, 1990, 24, 220–228.
- 26. Ertugay.N, Bayhan.Y.K., The removal of copper(II) ion by using mushroom biomass (*Agaricus bisporus*) and kinetic modeling., Desalination, 2010, 255, 137–142.
- 27. Khormaei.M, Nasernejad.B, Edrisi.M, Eslamzadeh.T., Copper biosorption from aqueous solutions by sour orange residue., J. Hazard. Mater, 2007, 149, 269–274.
- 28. Hasan.S.H, Srivastava.P., Batch and continuous biosorption of Cu²⁺ by immobilized biomass of *Arthrobacter sp.*, J. Environ. Manage, 2009, 90, 3313–3321.
- 29. Mata.Y.N, Blazquez.M.L, Ballester.A, Gonzalez.F, Munoz.J.A., Characterization of the biosorption of cadmium, lead and copper with the brown alga *Fucus vesiculosus.*, J. Hazard. Mater, 2008, 158, 316–323.
- 30. Beyene Hagos Aregawi and Alemayehu Abebaw Mengistie., Removal of Ni(II) from aqueous solution using leaf, bark and seed of *Moringa Stenopetala* adsorbents., Bull. Chem. Soc. Ethiop, 2013, 27(1), 35-47.
- 31. Gupta.V.K, Rastogi.A., Biosorption of hexavalent chromium by raw and acidtreated green alga *Oedogonium hatei* from aqueous solutions., J. Hazard. Mater, 2009, 163, 396–402.
