Removal of Copper (II) From Aqueous Solution by Khangar

Garima Nagpal[1], A. Bhattacharya[2] and N. B. Singh[1*]
[1]*Research and Technology Development Centre, Sharda University, Greater Noida, India*
[2]*Department of Chemistry, University of Petroleum & Energy Studies, Dehradun-248007 India*

Abstract

Process of removal of Cu(II) from aqueous solution of copper sulphate by adsorption on the surface of Khangar has been studied by orthogonal array L_{16}. The adsorption process parameters viz pH, adsorbent dose, metal ion concentration and contact time have been optimized by using Taguchi's method. The results have been analyzed using signal to noise ratio and ANOVA at 95% confidence level for all considered parameters. By the study it is observed that pH is the most important parameter for removal of Cu(II) from aqueous solution. The optimum results are obtained on pH 7; adsorbent dose 0.7 g/50ml; metal ion concentration 20 mg/L and contact time 120 minutes. To support the analysis, SEM and FTIR examination of Khangar has been done before and after adsorption of Cu(II) from aqueous solution.

Keywords: *Cu(II), FTIR, Khangar, Optimization, Taguchi's method.*

"1. Introduction"

Industrialization has resulted in release of heavy metals in the environment in larger amounts. These contaminants can be accumulated by living organisms throughout the food chain as a non biodegradable pollutant [1]. Among heavy metals, copper poses a significant threat to the environment and public health due to its toxicity. Copper is introduced into natural waters by variety of industrial wastewaters such as electroplating, paper manufacturing, pesticides, herbicides and tannery industries. The continuous intake of Cu by human being leads to necrotic changes in the liver, kidney, mucosal irritation, wide spread capillary damage, depression, weakness, lethargy and lung cancer etc. [2, 3]. To remove heavy metals from aqueous solution many physico-chemical methods such as membrane filtration, coagulation, chemical precipitation, ion exchange and electrodialysis have been used [4-7]. The application of such processes is often limited because of technical/economical constraints. However the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost. The most common adsorbent materials are: alumina silica, metal hydroxides and activated carbon [8]. Many reports have appeared on the development of low-cost activated carbon adsorbents developed from cheaper and readily available materials. Activated carbons with their large surface area, microporous character and chemical nature of their surface have made them potential adsorbents for the removal of heavy metals from industrial waste water. In this paper carbon waste obtained from coal refining industry (known as Khangar) has been used as an adsorbent for removal of Cu(II) from aqueous solution under different conditions. Adsorption studies have been made and optimum conditions for Cu(II) removal have been established. The effect of various operational parameters such as pH, adsorbent dose, metal ion concentration and time were investigated by Taguchi method using MINITAB software [9].

"2. Material and Methods"

2.1 Preparation of adsorbent and adsorbate

In this study the adsorbent used was carbon waste obtained from coal refining industry (Ghaziabad) commonly known as Khangar. The collected material was washed three times with deionized water and then air dried for several days. It was oven dried at 110°C for 2 hrs. The dried carbon waste was crushed in a mechanical grinder and sieved through 350µm mesh sieve to obtain fine powder. Cu(II) solution was prepared by dissolving copper sulphate in deionized water.

2.2 Characterization of adsorbent (Khangar)

The FTIR spectra of Khangar before and after adsorption of Cu(II) were recorded in KBr phase in the wave length range 400 – 4000 cm^{-1}.

SEM pictures of gold coated Khangar before and after Cu(II) adsorption were also recorded. Gold coating was done by sputtering technique.

2.3 Design of Experiment by Taguchi Method

Taguchi's optimization technique is a unique and powerful technique that allows optimization with minimum number of experiments [9]. Taguchi developed a method for designing experiments to investigate how different parameters affect the mean and variance of a process performance characteristic that defines how well the process is functioning [10]. To design the experiment Taguchi used the orthogonal array approach. In our experiment we have used L_{16} Taguchi's orthogonal array. The decision of orthogonal array depends upon the number of process parameters and their levels [11-12]. In this study we used the effect of four parameters *p*H of the solution, adsorbent dose, initial metal ion concentration and contact time and their four levels as shown in Table-1 and Table-2. Taguchi method has been used to assess the interaction of parameters to maximum adsorption of metal ions through the signal to noise (S/N) Ratio by software MINITAB 15. Usually, three types of S/N ratio analysis are applicable: (1) lower is better (LB), (2) nominal is better (NB) and (3) higher is better (HB) [13]. The target of this study is to maximize the metal removal efficiency, so the S/N ratio with HB characteristics are required which is given by following equation:

$$\left(\frac{S}{N}\right)_{HB} = -10\,log\left[{}^{1}\!/_{R}\sum_{j=1}^{R}{}^{1}\!/_{Y_j^2}\right] \qquad (1)$$

Where Y is value of characteristic in an observation j, R is number of repetition in a trial.

"Table 1. Factors and Levels in experimental design"

Factors	Level 1	Level 2	Level 3	Level 4
pH	1	3	5	7
Adsorbent Dose (g/50 ml)	0.1	0.3	0.5	0.7
Metal ion conc. (mg/L)	1	10	20	30
Interaction Time	60	90	120	150

Analysis of Variance (ANOVA) is also a part of Taguchi's analysis to identify the most influential factor in the process. It is a powerful statistical analytical tool that separates the total variability within the data. The Fischer ratio (or F test) of the ANOVA is used to determine significant process factors. The F value for each process factor is simply a ratio of the mean of the squared deviations to the mean of the squared error. In ANOVA F- test is used to calculate expected values of process parameters to identify the variation of results from limits [13-14].

2.4 Experimental procedure

Experiments were performed in batch manner by synthetic solution. A stock solution containing 1000 mg/L of Cu(II) was prepared using copper sulphate in double distilled water. The *p*H of the solution were adjusted using 0.1N NaOH and 0.1N HCl. All reagents used were of analytical grade. The experiment was conducted in batch of three experiment and the process parameters were adjusted as per Table-2.

"Table 2. Experimentation data of OA L_{16}"

S No.	pH of solution	Adsorbent dose (mg/50ml)	Initial metal ion conc. (mg/L)	Contact time (minutes)
1	1	0.1	1	60
2	1	0.3	10	90
3	1	0.5	20	120
4	1	0.7	30	150
5	3	0.1	10	120
6	3	0.3	1	150
7	3	0.5	30	60
8	3	0.7	20	90
9	5	0.1	20	150
10	5	0.3	30	120
11	5	0.5	1	90
12	5	0.7	10	60
13	7	0.1	30	90
14	7	0.3	20	60
15	7	0.5	10	150
16	7	0.7	1	120

The sorption capacity and the percent removal of Cu(II) from aqueous solutions by Khangar were calculated by following equations:

$$q_{eq} = \frac{(C_o - C_e)v}{m} \qquad (2)$$

$$n = \frac{C_o - C_e}{C_o} X100\% \qquad (3)$$

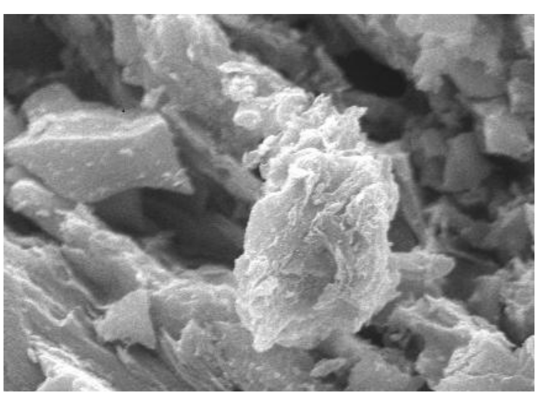
Where q_{eq} is the adsorption capacity (mg/g), n is percent removal (%), C_0 is the initial Cu(II) concentration (mg/L), C_e is the equilibrium Cu(II) concentration (mg/L), m is the sorbent mass (g) and V is the volume of metal solution put in contact with the adsorbent [15-16].

To analyze the obtained data we used regression technique, statistical tool ANOVA and the confidence intervals as suggested by Taguchi, *i.e.*, CI_{POP} (confidence interval for the population), and CI_{CE} (confidence interval for a sample group). They were used at 95% of confidence level. It is the estimated mean of the optimal treatment conditions.

In order to verify the conclusions drawn from the experiments, certain confirmation experiments were carried out at the optimum conditions for the significant parameters. The average of the results of the confirmation experiments are compared with the anticipated average based on the parameters and levels tested.

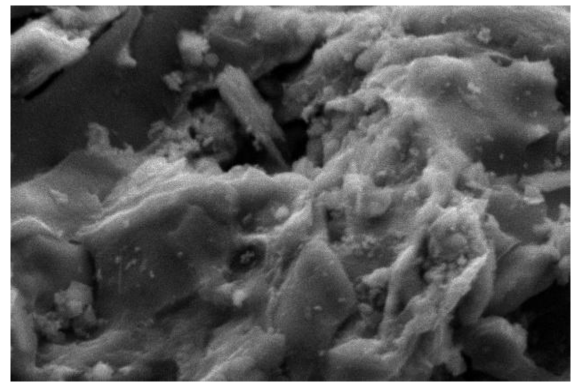
"3. Results and Discussion"

Scanning electron microscopic pictures of Khangar before and after adsorption of Cu(II) are shown in Figures. 1 and 2 respectively.

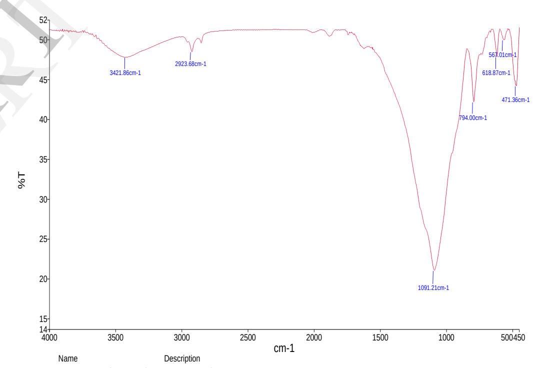


"Figure 1. Khangar before adsorption"

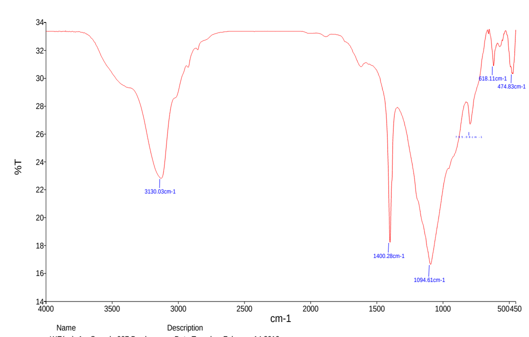
It appears that the surface morphology is slightly changed after Cu(II) adsorption. The FTIR spectrum of Khangar (Figure.3) shows a broad vibrational band at 3420.18 cm^{-1} indicative of the existence of bound OH group due to adsorption of water molecules. Band at about 2900 cm^{-1} is due to CH stretching modes. A strong band at 1091.09 cm^{-1} may be due to =C=O stretching vibrations. In the Cu (II) treated Khangar, two new bands (Figure.4) appearing at around 3180 and 1400 cm^{-1}. First band suggests that Cu is adsorbed on Khangar where hydroxyl groups are present. Appearance of a new band at 1400 cm^{-1} also suggests association of copper with carboxylate group.



"Figure 2. Khangar after adsorption"



"Figure 3. FTIR Image of Khangar Before Adsorption"



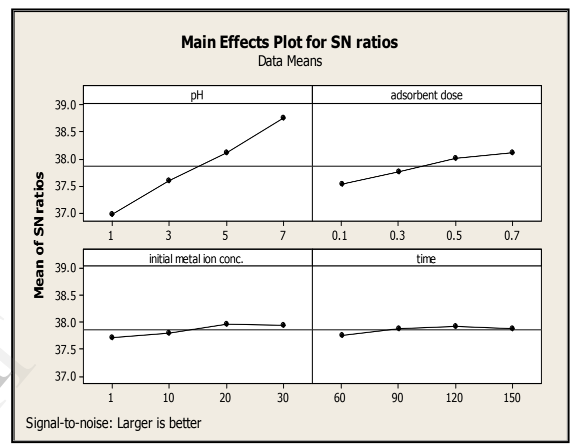
"Figure 4. FTIR image of Khangar after Cu(II) Adsorption"

Analysis of the mean and S/N ratio for each experiment give the optimum level of process parameters for the maximum removal of the metal ions from the aqueous solution. For raw data, mean response and S/N ratio is calculated and shown in Table-3. Response of various parameters on percentage removal of Cu(II) ions clearly shows that the most influential *p*H is 7 at level

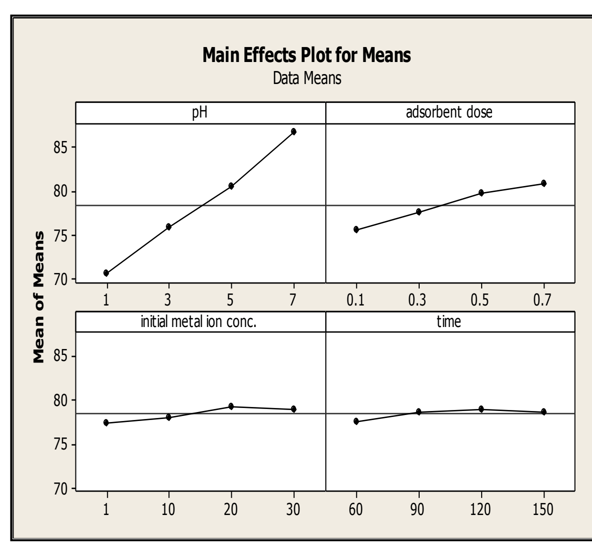
"Table 3. Experimentation results of OA L_{16} of S/N Ratio and Mean"

S No.	pH of solution	Adsorbent dose (mg/50ml)	Initial metal ion conc. (mg/L)	Contact time (minutes)	% Removal	S/N Ratio	Mean % Removal
1	1	0.1	1	60	65.9	36.37	65.9
2	1	0.3	10	90	69.4	36.82	69.4
3	1	0.5	20	120	73.5	37.35	73.5
4	1	0.7	30	150	73.7	37.34	73.7
5	3	0.1	10	120	73.2	37.29	73.2
6	3	0.3	1	150	74.3	37.41	74.3
7	3	0.5	30	60	76.8	37.70	76.8
8	3	0.7	20	90	79.1	37.96	79.1
9	5	0.1	20	150	78.6	37.90	78.6
10	5	0.3	30	120	80.8	38.14	80.8
11	5	0.5	1	90	81.0	38.16	81.0
12	5	0.7	10	60	81.8	38.25	81.8
13	7	0.1	30	90	84.7	38.55	84.7
14	7	0.3	20	60	85.9	38.67	85.9
15	7	0.5	10	150	87.8	38.86	87.8
16	7	0.7	1	120	88.4	38.92	88.4

four, adsorbent dose is most influential *i.e.*, 0.7 gm /50ml at level four, the initial metal ion concentration is most influential at the third level *i.e.* 20 mg/L and contact time for metal removal is most influential at third level *i.e.* 120 min as shown in Table-4. The contribution of individual factors on the adsorption of Cu(II) ions onto Khangar are given in Table-5&6. It shows ANOVA results for S/N ratio data and Mean. The percentage contribution of each parameter is also given in these tables. It is observed that pH parameter is the most significant factor with 87.97 and 86.8% contribution to mean and S/N ratio data, respectively. The value of coefficient of correlation R^2 is near to 1.0 and it shows good agreement with R^2 (adj) 0.996.



"Figure 5. Variation of S/N ratio with pH, Adsorbent dose, Initial Metal ion concentration and Time"



"Figure 6. Variation of Means of means with pH, Adsorbent dose, Initial Metal ion concentration and Time"

"Table 4. Effects of various factors on S/n Ratio and Average Response"

Levels of parameters	For S/N Ratio				For Mean			
	pH of solution	Adsorbent dose (mg/50ml)	Initial metal ion conc. (mg/L)	Contact time (minutes)	pH of solution	Adsorbent dose (mg/50ml)	Initial metal ion conc. (mg/L)	Contact time (minutes)
1	36.97	37.53	37.72	37.75	70.53	75.60	77.40	77.60
2	37.60	37.77	37.81	37.88	75.85	77.60	78.05	78.55
3	38.12	38.02	37.97	37.92	80.55	79.78	79.28	78.97
4	38.76	38.12	37.94	37.89	86.70	80.75	79.00	78.60
Delta	1.79	0.59	0.25	0.17	16.08	5.15	1.38	1.38
Rank	1	2	3	4	1	2	3	4

"Table 5. ANOVA for S/N Ratio (% Removal)"

Source	DF	Seq SS	Adj SS	Adj MS	F	P	% PC
*p*H of The Solution	3	6.95	6.95	2.32	1013.22	0.000	86.8
Adsorbent Dose(mg/50 ml)	3	0.83	0.83	0.28	122.25	0.001	10.3
Intial Metal Ion Conc.(mg/L)	3	0.15	0.15	0.06	22.95	0.014	1.9
Contact time	3	0.06	0.06	0.04	9.41	0.049	0.7
Residual Error	3	0.01	0.01	0.01			0.1
Total	15	8.00					

S/N: Signal to Noise; ANOVA: Analysis of Variance; DF: Degree of freedom
S = 0.04783 R-Sq = 99.9% R-Sq(adj) = 99.6%

Order of significance: 1. *p*H of the solution, 2. Adsorbent Dose, 3. Initial Metal Ion Conc., and 4. Contact time
*Significance at 95% level.

Mean response and S/N ratio (Fig 5, 6) clearly indicate that the removal of Cu(II) from aqueous solution is maximum at near to neutral pH. It can be inferred that at higher H^+ conc., the adsorbent surface becomes more positively charged, thus reducing the attraction between adsorbent and metal ion. As pH increases, negatively charged surface become available, thus promoting greater metal uptake [17, 18]. At higher pH, the Cu(II) ions precipitated as their hydroxides which decrease the rate of adsorption and subsequently the percent removal of metal ions.

Fig 5 & 6 shows an increase in percentage removal of Cu with the increase in dose of adsorbent up to a certain limit and then it remains almost constant. Increase in adsorption with adsorbent dosage can be attributed to the availability of more adsorption sites [19, 20].

From plots of mean and S/N ratio it is found that the percent removal increased with time. However the removal was found to be the maximum at 120 minutes. The time required to attain this value is termed as the equilibrium time [21]. From the figure, it is evident that the percentage removal shows an increasing trend up to 20 ppm and then decreases continuously. It appears that at lower concentrations, all Cu(II) ions present in the sorption could interact with the binding sites of Khangar, hence higher removal. However at higher concentrations, because of the saturation of the sorption

"Table 6. ANOVA for Mean (% Removal)"

Source	DF	Seq SS	Adj SS	Adj MS	F	P	% PC
***p*H of The Solution**	3	561.85	561.85	187.28	3581.49	0.000	87.97
Adsorbent Dose(mg/50 ml)	3	63.55	63.55	21.18	405.14	0.000	9.95
Initial Metal Ion Conc.(mg/L)	3	8.9	8.9	2.99	57.22	0.004	1.39
Contact time	3	4.1	4.1	1.37	26.24	0.012	0.64
Residual Error	3	0.15	0.15	0.052			
Total	15	638.65					

S/N: signal-to-noise; ANOVA: analysis of variance; DF: Degree of freedom

S = 0.2287 R-Sq = 100.0% R-Sq(adj) = 99.9%

Order of significance: 1. *p*H of the solution, 2. Adsorbnet Dose, 3. Initial Metal Ion Conc., and 4. Contact time
*Significance at 95% level.

sites, the percentage uptake of the copper by Khangar shows a decreasing trend. A similar trend was reported by [22].

F- Test was used to predict the results with optimization [10]. The mean at the optimal condition (optimal value at response characteristics) is calculated from following equation:

$$\mu_{\%Removal} = \bar{T} + (\bar{A}-\bar{T}) + (\bar{B}-\bar{T}) + (\bar{C}-\bar{T}) + (\bar{D}-\bar{T}) \quad (4)$$

Where, $\bar{T}$ is the overall mean of the response = 78.43 (Table 3), and $\bar{A}$ is the average removal of metal ion concentration at level four of parameter pH of the solution = 86.70 (Table 4), $\bar{B}$ is the average removal of metal ion concentration at level four of parameter Adsorbent dose = 80.75 (Table 4), $\bar{C}$ is the average removal of metal ion concentration at level three of parameter Initial metal ion concentration = 79.28 (Table 4), and $\bar{D}$ is the average removal of metal ion concentration at level three of parameter contact time = 78.97 (Table 4).

Hence,

$$\mu_{\%removal} = 90.40 \text{ MPa}$$

The confidence interval for the predicted mean for the confirmation experiment can be calculated by following equations

$$CI_{POP} = \sqrt{F_{\alpha}(1,f_e)V_e\left[\frac{1}{\eta_{eff}}\right]} \quad (5)$$

$$CI_{CE} = \sqrt{F_{\alpha}(1,f_e)V_e\left[\frac{1}{\eta_{eff}}+\frac{1}{R}\right]} \quad (6)$$

Where,
F_{α} (1, f_e) = F – ratio at a confidence level of (1 – α) against Degree of freedom (DF) 1& error DF, f_e; V_e = Error variance (from ANOVA); and η_{eff} is calculated from following equation:

$$\eta_{eff} = \frac{N}{1+\text{Total DF involved in estimation of mean}} \quad (7)$$

Where, N = Total number of results
R = Sample size for the confirmation experiment
By substituting values N: total no of results = 16 X 3= 48; f_e =3 and V_e =0.052 (from Table 6); $F_{0.05}(1,3)$ = 10,1 (tabulated F-value) in equations 5 to 7. The 95% confidence intervals (Cl_{pop} and Cl_{CE}) of the predicted ranges for adsorption of Cu(II) ions onto Khangar are given in Table 7.

In Taguchi method confirmation experiment is the last step to verify the results, which we get from Taguchi's experiment approach. The experiment was conducted by setting all the process parameters at optimum level in a batch experiment. The average

"Table 7 Responses at optimum levels of process parameters"

Responses	Predicted Mean value	Experimental value(average)	Confidence Interval
% Removal of metal ions	90.40	90.73	$89.8428 < \mu_{\% \text{ Removal}} < 90.9695$ (CI_{CE})
			$90.0290 < \mu_{\% \text{ Removal}} < 90.7833$ (Ci_{pop})

values obtained are compared with the predicted values (Table 7). The results are in range of predicted values. This shows the successful optimization of experiment.

"4. Conclusion"

From the results it is concluded that 91% Cu(II) can be removed by using Khangar as an adsorbent. This is much better adsorbent as compared to conventionally used carbon powders. The optimized conditions for Cu(II) as found by Taguchi method are – pH - 7; adsorbent dose - 0.7g/50ml; initial metal ion conc. - 20 mg/L and contact time - 120 minutes. It is also found that the experimental values are in the predicted range. To access the commercial feasibility of Khangar as an adsorbent for removal of heavy metal ions particularly Cu(II) ions further experiments are required.

"4. Refrences"

[1] L. Jarup, "Hazards heavy metal contamination", *British Medical Bulletin*, 68, 2003, 167 – 182.

[2] M. Araya, M. Olivares, F. Pizarro, M. Gonzalez, H. Speisky, and R. Uauy, "Gastrointestinal symptoms and blood indicators of copper load in apparently healthy adults undergoing copper exposure", *American Journal of Clinical Nutrition*, 77, 2003, 646 – 650.

[3] Public Health Service, Toxicological profile for copper. Report of the U.S. Department of health and human Services, *United States of America: Agency for Toxic Substances and Disease Registry*, 2004.

[4] Q. Manzoor, R. Nadeem, M. Iqbal, R. Saeed, and T.M. Ansari, "Organic acids pretreatment effect on Rosa bourbonia phyto-biomass for removal of Pb(II) and Cu(II) from aqueous media", *Bioresource Technology*, 132, 2013, 446 – 452.

[5] H.N. Bhatti, R. Khalid, and M.A. Hanif, "Dynamic biosorption of Zn(II) and Cu(II) using pretreated Rosa gruss an teplitz (red rose) distillation sludge", *Chemical Enginnering Journal*, 148, 2009, 434 – 443.

[6] R. Nadeem, M.A. Hanif, M. Riaz, A.A. Azhar, T. Iqbal, and T.M. Ansari, "Kinetics and equilibrium modeling of Cu(II) and Ni(II) sorption onto physically pretreated Rosa centifolia distillation water biomass", *African Journal of Biotechnology*, 9, 2010, 9051 – 9062.

[7] F. Fu, and Q. Wang, "Removal of heavy metal ions from wastewater: A review", *Journal of Environmental Management*, 92(3), 2011, 407 – 418.

[8] K.M. Joseph, and B.T. Christe, "Removal of mercury(II) from aqueous solution using granular activated carbon and Kaolinite clay from mayauom in Cameroon – Kinetic and equilibrium studies", *Research Journal of Chemistry and Environment*, 14, 2010, 60 – 65.

[9] N.M.S. Kaminari, D.R. Schultz, M.J.J.S. Ponte, H.A. Ponte, C.E.B. Marino, and A.C. Neto, "Heavy metals recovery from industrial wastewater using Taguchi method", *Chemical Engineering Journal*, 126, 2007, 139 – 146.

[10] H. Huang, G. Cheng, L. Chen, X. Zhu, and H. Xu, "Lead (II) removal from aqueous solution by spent Agaricus bisporus: Determination of optimum process condition using Taguchi method", *Water Air Soil Pollution*, 203, 2009, 53 – 63.

[11] V.C. Srivastava, I.D. Mall, and I.M. Mishra, "Optimization of parameters for adsorption of metal ions onto rice husk ash using Taguchi's experimental design methodology", *Chemical Engineering Journal*, 140, 2008, 136 – 144.

[12] K. Gholivand, M. Khosravi, S. Kazemi, and S.G. Hosseini, "Investigation of the processing parameters on the chemical removal of fouling lead layer by using an orthogonal array design method", *World Applied Sciences Journal*, 17, 2012, 891 – 899.

[13] P.J. Ross, *Taguchi Techniques for quality Engineering*, McGraw-Hill, New York, 1996.

14. T.B. Barker, *Engineering Quality by Design*, Marcel Dekker, Inc., New York, 1990.

[15] N.G. Turan, and O. Ozgonenel, "Optimizing copper ions removal from industrial leachate by explored vermiculite – A comparative analysis", *Journal of Taiwan Institute of Chemical Engineers*, 44 (6), 2013, 895 – 903.

[16] G. Zolfaghari, A. Esmaili-Sari, M. Anbia, H. Younesi, S. Amirmahmoodi, and A. Ghafari-Nazari, "Taguchi optimization approach for Pb(II) and Hg(II) removal from aqueous solution using modified mesoporous carbon", *Journal of Hazardous Materials*, 192, 2011, 1046 – 1055.

[17] G. Vikal, K. Ruchi, and L. Magan, “Bioremediation of Copper (II) from aqueous solution using Prospis cinevaria leaf powder”, *Research Journal of Chemistry and Environment*, 14, 2010, 51 – 56.
[18] L. Curkovic, M. Trgo, M. Rozic, and N.V. Medvidovic, “Kinetic and thermodynamics study of Copper ions removal by natural clinoptilotite”, *Indian journal of Chemical Technology*, 18, 2011, 137 – 144.
[19] M. Li, Q. Liu, L. Guo, Y. Zhang, Z. Lou, Y. Wang, and G. Qian, “Cu(II) removal from aqueous solution by Spartina alterniflora derived biochar”, *Bioresource Technology*, 141, 2013, 83 – 88.
[20] X. Chen, G. Chen, L. Chen, Y. Chen, J. Lehmann, M.B. McBride, and A.G. Hay, “Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution”, *Bioresource Technology*, 102, 2011, 8877 – 8884.
[21] O. Abdelwahab, “Kinetic and isothermal studies of Copper (II) removal from wastewater using various adsorbents”, *Egyptian Journal of Aquatic Research*, 33, 2007, 125 – 143.
[22] E.S.Z. El-Ashtoukhy, N. Amin, and O. Abdelwahab, “Removal of lead(II) and copper(II) from aqueous solution using pomegranate peel as a new adsorbent”, *Desalination*, 223, 2008, 162 – 173.