Bayero Journal of Pure and Applied Sciences, 12(2): 49 - 56
Received: July, 2019
Accepted: November, 2019
ISSN 2006 – 6996

CENTRAL COMPOSITE DESIGN OPTIMIZATION OF COPPER (II) IONS REMOVAL IN AQUEOUS SOLUTION USING *Azadirachta indica* (Neem) LEAF POWDER

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ABSTRACT
Biosorption is considered as a potential method for the removal of heavy toxic metals from waste solution and as alternative to other conventional process such as precipitation, ion exchange, electrochemical treatment and evaporative recovery, especially, when the concentration of the heavy metal ion is low. In the present study, (Azadirachta indica) neem leaves Powder (NLP), was investigated for the removal of Cu(II) ions from aqueous solution based on modelling and optimization. Central composite design was successfully applied to develop a response surface to optimize medium conditions. Characterisations of the NLP was conducted, and the effects of contact time (0-180 minutes), Cu(II) ion concentration (10-50 mg/L), temperature (298-318 K) and dosage (0.5-2.5 g/L) were studied in batch process. The optimal adsorption of copper obtained were found to be 308 K, 97.5min and 1.5g respectively resulting in 100% of adsorption of copper The analysis with FTIR indicated that possible hydroxyl and carboxyl functional groups are involved in metal Cu(II) ions biosorption. Adsorption isotherms were modelled by the Langmuir and Freundlich isotherm equations, with the former providing a better fit for the data. Results obtained from this study indicate that NLP is a very promising candidate for the low-cost and high-capacity removal of Cu(II) ions from aqueous solution.
Keywords: Biosorption, Neem, Copper (II), Response surface methodology and Central composite design.

INTRODUCTION

Heavy metals pollution have been a major concern globally, due to their toxicity, bioaccumulation tendency and persistency in nature (Das, 2017) and in order to protect public health, they have to be eliminated from the environment (Chafik, *et. al.,* 2014).

Even though copper has been known to be among the most common toxic heavy metals (Das, 2017), but still plays a vital role in human health as the element is needed in the metabolism of lipids, carbohydrates and even in proper functioning of the heart and blood vessels (Gupta *et. al.,* 2006).

According to international regulation, the concentration limit of copper in water and waste water is 1mg/L (Ayhan and Ozacar, 2008). Excess amount of copper can cause a substantial health hazard as damage to kidney, liver, pancreas and damage human psychology. The major industries discharging copper into the waste stream include fertilizer industries, battery industries, pulp and paper copper polishing and electroplating (Ozturk and Shan, 2015). In view of that, copper concentration in the waste stream has to be reduced to an acceptable environmental regulation.

Various processes, including chemical precipitation, ion exchange, ultra-filtration, reverse osmosis, electroplating and adsorption are applied in the process of heavy metals removal. Of these, adsorption using activated carbon has been the most widely used due to higher efficiency and easy operation (Ozturk and Shan, 2015) However, adsorption onto activated carbon is expensive and may require additional chemicals to improve efficiency This leads to the searching of a cost effective and efficient method for the removal of heavy metals from waste stream (Qi and Aldrich, 2008). Biosorption has recently attracted considerable amount of attention as alternative method used for the removal and recovery of toxic metals present in waste effluents compared to other conventional technologies due to numerous advantages such as low sludge production, low investment and operational cost and above all higher efficiency (Krishnani *et al.*, 2008).

Copper metal removal by biosorption has so far been investigated using different biosorbents Veglio and Beolchini, (1997), such as teak leaves (Rathnakumar *et al*., 2009). *Palmaria palmate and brewery waste* (Yang *et al*., 2011). Green algae (Gupta *et al*, 2006). Fish scales (Huang, 2007), wheat shell (Basci *et al*, 2004). Thiobacillus *ferrooxidans* (Hossain and Anantharaman, 2005). *Penicillium cyclopium (*Ianis *et al,* 2006) and spent tea leaves (Bajpai and Jain, (2010).

The conventional method of optimizing the process variables are expensive, difficult and time consuming as it needs a large number of experimental runs, therefore, response surface methodology technique reduces the number of experiments and provides appropriate model for process optimization (Singh *et. al.,* 2017).

The objective of the present study were to examine the adsorption potential of neem leaves for copper II ions removal from aqueous solution in batch mode, and focus on the application of statistical approach to see interactive effects of combine variables on complex adsorption process using central composite design.

MATERIALS AND METHODS

Biosorbent Collection and Preparation

The neem leaves used in this study was collected fresh from a local tree at the Bayero university kano and identified at the department of plant biology. The leaves were washed severally and rinsed with deionised water to remove all impurities. Crispy dried leaves were obtained after drying at a temperature of about 60°C for 24 hours, and later ground and sieved to a particle size of about 45-62 ɥm. The sieved materials were stored and labelled NLP.

Synthetic Copper Solution

Hydrated Copper(II) chloride was used as a source of copper stock solution. The preparation was done by dissolving appropriate amount of 99% hydrated copper (II) chloride with 1000ml of deionised water to form a standard stock solution of 100mg/L of Copper(II) solutions. Different concentration was later prepared by appropriate dilutions.

Adsorbent characterization

In order to understand the binding mechanism of copper(II) ions, Fourier infrared spectroscopy (FTIR) was used in determining the functional groups available in the neem leaves. The surface morphology was visualized using SEM coupled with EDX.

Batch adsorption Experiment

Batch adsorption of 30 experiments design by central composite design approach using response surface methodology where conducted by the NLP as an adsorbent to study the effect of contact time (0-180 minutes), copper concentration(10-50 mg/L), temperature (298-305K) and adsorbent dosage (0.5-2.5g). The experiment was carried out in a 250ml conical flask placed in a water bath shaker. All the experiments were performed in duplicate and the average values were recorded.

The amount of copper (II) ions adsorbed (mg/g) was determined using the equation (1)

$$q_{e=}\frac{C_o - C_e}{M}\ V \qquad (1)$$

Also the percentage removal of copper was computed as

$$(\%)\ Removal = \frac{C_o - C_e}{C_o}\ x\ 100 \qquad (2)$$

Where Co and Ce are initial and final copper concentration, V is the volume of the biosorbate and M is the weight of the biosorbent.

Design of Experiment and Optimization

A standard response surface methodology design called central composite design, which is the most popular choice to fit second order model, (Ozturk, 2015) was applied in this work to study the variables of adsorption of Cu(II) ions from aqueous solution in a batch process.

Four process variables (Temperature, Concentration, Dosage and Contact time) were studied using the CCD models with the help of design-expert software (Version 6.0). The range of selected independent variables is presented in Table 1.

Table 1: Experimental factor levels used in the design.

Independent Variavble	Factor	Coded Levels	
		-1	+1
Dosage(g)	A	0.50	2.50
Contact Time(Mins)	**B**	15.00	180.00
Concentratio(mg/L	C	10.00	50.00
Temprature (K)	D	298.00	318.00

In order to obtain the interactions between the processed variables and the response, the experimental data were evaluated with the design- expert including analysis of variance (ANOVA). The quality of the fit of the polynomial model was expressed by the coefficient of determination (R^2) and the statistical significance was checked by the F- test.

RESULTS AND DISCUSSION

Surface area of biosorbent (ASAP)

Generally the greater the surface area of a biosorbent, the greater the metal biosorption. Based on the Surface area and pore diameter (ASAP) analysis, the NLP surface area was found to be 2.3102m^2/g. Which is higher than rubber leaves, 0.46m^2/g (Ngah and Hanafiah, 2008), *Spirogyra spp.,* 1.31m^2/g (Gupta *et al.,* 2006), rice bran, 0.46 m^2/g (Montanher *et al.*, 2005) and soya meal shell, 0.76m^2/g (Arami *et al.*, 2006).and also lower than activated carbon, 1100m^2/g (Ozacar and Sengil, 2002), *Moringa oliefera*, 4.01 m^2/g (Kumar *et al.*, 2006) and *Sargasssum sp*, 8.13 m^2/g (Sheng *et al.*, 2008).

Based on the conclusion of many researchers, surface area and pore sizes might be involved in the biosorption mechanism and since NLP does not have a highly porous structure, biosorption might occur through chemical sorption with the presence of functional groups and ion exchange (Sulaiman and Garba, 2014)

Surface functional groups

Different adsorption peaks displayed by the FTIR indicates the presence of various functional groups on the surface of the NLP before and after adsorption. Based on the attribution of peaks, it can be known that NLP contains different types of functional groups and different biosorption processes such as ion exchange, electrostatic attraction and complexation might be involved in the adsorption mechanism.

By comparing the fresh NLP and Cu(II) loaded NLP it can be observed that there are shift in some certain cases in wave number indicating metal binding process on the NLP. The relevance of a shift in the spectra is that there is an effect of metal adsorption on the functional groups (Yazici*et al.*, 2008). For the fresh NLP as shown in Figure 1 the spectra show a band of range 3862.04 to 595.09 cm^{-1}. After Cu(II) ions biosorption the spectra changes from 3905.83 to 582.36 cm^{-1} as in Figure 2.

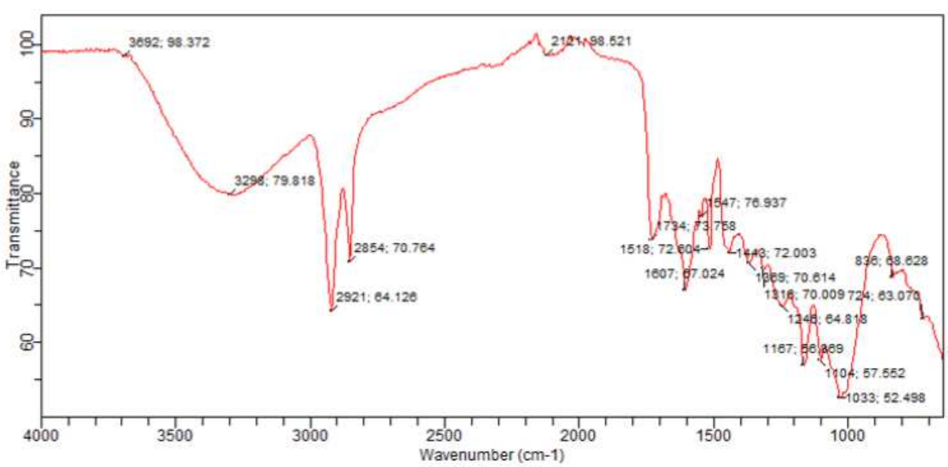

Fig 1: FTIR spectrum for NLP before adsorption

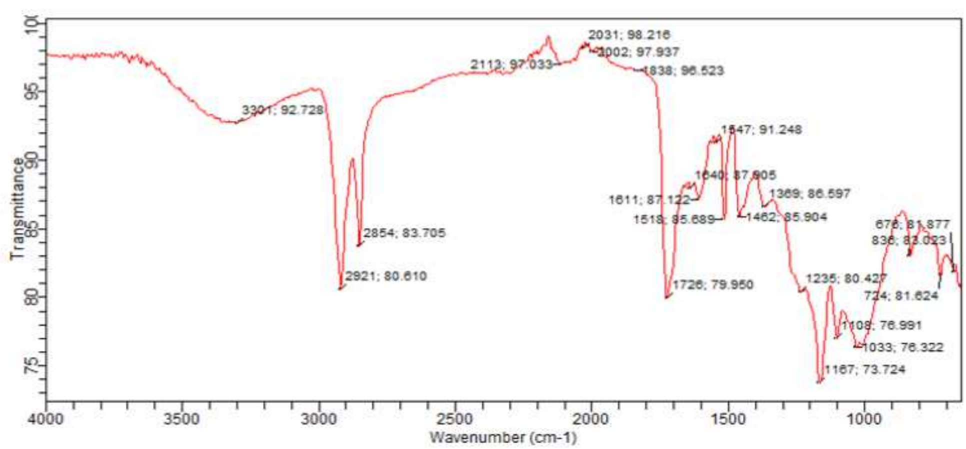

Fig 2: FTIR Spectrum of NLP after Cu(II) ions adsorption.

Surface Topography (SEM/EDX)

SEM (Scanning electron microscope) and EDX (Energy-dispersive X-ray spectroscopy) are useful analytical equipment for evaluating the characteristics of adsorbent elements. Figure 3 showed the SEM-EDX results for NLP before Cu(II) ion adsorption. The SEM images showed that the NLP possess surface morphology with regular pore size which is helpful for Cu(II) ions biosorption, although the SEM results for the NLP before and after bisosorption looks almost the same, however, EDX results clearly indicate that NLP consist of mainly C and O, and small amounts of, Ca, Mg, K, P and S.

While Figure 4 shows SEM and EDX for NLP after the biosorption on which Cu(II) ions was confirmed. From the SEM results, non-uniformed bright spots indicated Cu(II) ions presence, which signifies that not all the functional groups are responsible for Cu(II) ions adsorption from the solution. After the adsorption for the NLP, Mg and K are been replaced by Cu(II) peaks, this clearly indicates that ion-exchange might be one of the mechanisms for Cu(II) removal.

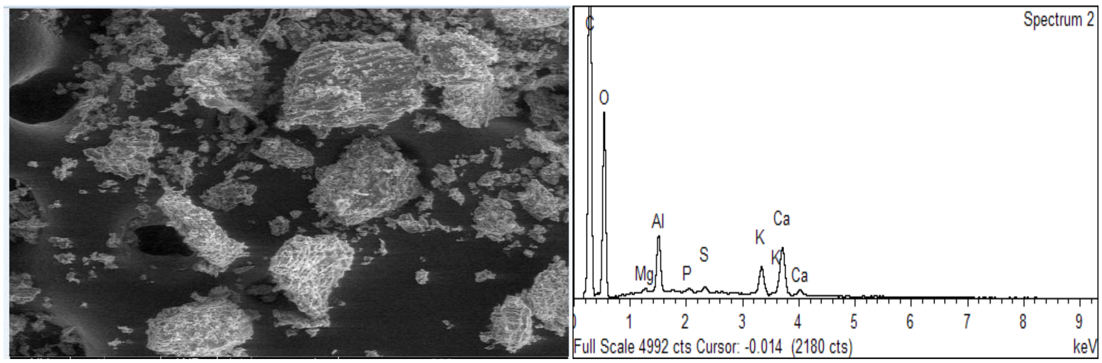

Figure 3: SEM and EDX images of NLP before Cu(II) ions Adsorption

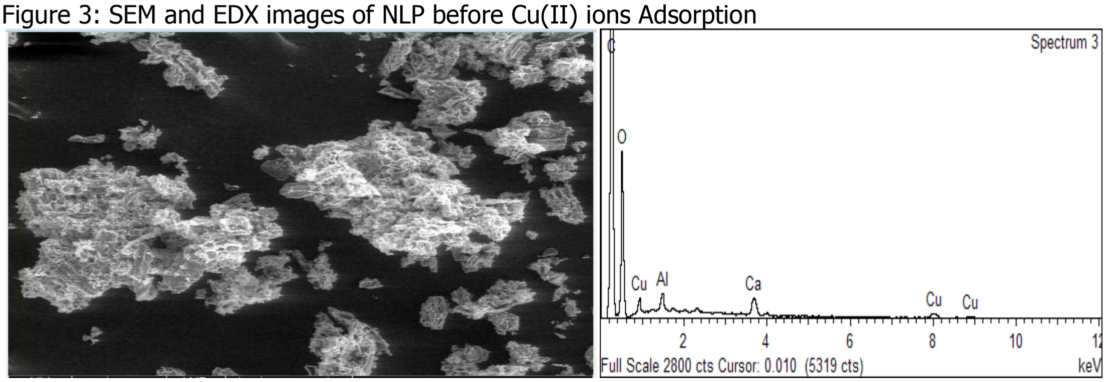

Figure 4: SEM and EDX images of NLP after Cu(II) ions Adsorption

Evaluation of the model

In order to ascertain the different model such as linear, 2FI, quadratic, evaluation was done on the basis of scores from the sequential model sum of squares. The result shows the quadratic model has a higher score. The larger magnitude of F (9.50) and smaller value of P (0.0058) indicates that the quadratic model is highly significant and was found to be good.

Table 2: Sequential Model Sum of Squares

Source	*Sum of squares*	*df*	*Mean square*	*F-value*	*Prob>F*	
Mean	1529.38	1	1529.38			
Block	3.56	1	3.56			
Linear	5.90	4	1.47	0.54	0.7102	
2FI	17.55	6	2.93	1.09	0.4061	
Quadratic	30.12	4	7.53	5.77	0.0058	Suggested
Cubic	1.34	8	2.12	9.50	0.0066	Aliased
Residual	1.34	6	0.22			
Total	1604.77	30	53.49			

Quadratic model for copper (II) adsorption process

To examine the combine effect of four different independent process parameters on percentage removal of copper (II) ion, 30 experiments were performed. The experimental designed is given n the Table 3 along with the experimental data and the predicted responses;

Table 3: CDD Experimental Designed Factors

Run	Dosage (g)	Contact Time (Mins)	Concentration (mg/L)	Temperature (K)	Predicted Value	Actual Value
1	2.5	180	10	298	8.71	8.08
2	2.5	15	50	318	7.64	6.43
3	0.5	180	10	298	8.22	8.27
4	2.5	180	50	298	9.03	8.31
5	1.5	97.5	30	308	6.89	7.53
6	2.5	180	50	318	8.07	8.17
7	1.5	97.5	30	308	7.10	5.87
8	2.5	180	10	318	8.12	8.20
9	2.5	15	10	318	6.67	7.04
10	2.5	15	10	298	2.88	3.90
11	2.5	15	50	298	8.39	8.08
12	1.5	97.5	30	308	6.81	6.62
13	0.5	15	50	298	7.75	8.25
14	0.5	15	10	298	6.99	7.40
15	0.5	180	10	318	5.77	7.44
16	1.5	97.5	30	308	7.85	8.27
17	0.5	15	50	318	5.26	5.02
18	0.5	180	50	318	5.26	5.02
19	0.5	15	10	318	5.26	5.02
20	0.5	180	50	298	5.26	5.02
21	0.5	97.5	30	308	9.35	8.94
22	1.5	67.5	30	308	7.96	8.12
23	1.5	262.5	30	308	8.93	8.45
24	15	97.5	70	308	9.27	9.51
25	1.5	97.5	30	308	6.01	6.95
26	1.5	97.5	30	328	9.22	8.04
27	1.5	97.5	10	308	6.28	7.86
28	1.5	97.5	30	288	8.72	6.90
29	3.5	97.5	30	308	5.26	5.75
30	1.5	97.5	30	308	5.26	5.75

The second order polynomial equation developed represents responses as a function of adsorbent Dosage (A), contact time (B), initial concentration (C) and temperature (D).

An empirical relationship between the response and input test variable in coded units can be express by the following equation.

$$\boldsymbol{Sqrt}(\boldsymbol{Percentage}) = +5.38 - 0.20 * A + 0.27 * B + 0.27 * C - 0.24 * D + 0.70 * A^2 + 0.81 * B^2 + 0.44 * C^2 + 0.41 * D^2 + 0.42 * A * B + 0.57 * A * C - 0.37 * A * D - 0.46 * B * C + 0.21 * B * D + 0.44 * C * D \quad (3)$$

The above equation describe how copper (II) adsorb onto NLP was affected by individual variables. Negative coefficient value indicated that individual or double interaction factor negatively affect copper (II) adsorption, while positive coefficient value represent the factor increases copper (II) percentage.

Among all linear factors studied, adsorbent dosage had a negative effect while contact time, initial concentration and temperature had a positive effect on copper (II) removal.

The adequency and significance of the quadratic model was justified by the analysis of variance (ANOVA) as shown in the Table 4.

Table 4: Analysis of Variance Table

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Block	3.56	1	**3.56**			
Model	53.57	**14**	**3.83**	2.93	0.0266	*Significant*
A	**1.00**	**1**	**1.00**	*0.77*	*0.3953*	
B	**1.69**	**1**	**1.69**	*1.30*	*0.2737*	
C	**1.81**	**1**	**1.81**	*1.38*	*0.2589*	
D	**1.40**	**1**	**1.40**	*1.07*	*0.3186*	
A^2	**13.25**	**1**	**13.25**	*10.16*	*0.0066*	
B^2	*17.90*	**1**	*17.90*	*13.73*	*0.0024*	
C^2	*5.21*	**1**	*5.21*	*3.99*	*0.0654*	
D^2	*4.55*	**1**	*4.55*	*3.49*	*0.0829*	
AB	*2.86*	**1**	*2.86*	*2.19*	*0.1610*	
AC	*5.24*	**1**	*5.24*	*4.02*	*0.0647*	
AD	*2.23*	**1**	*2.23*	*1.71*	*0.2118*	
BC	*3.42*	**1**	*3.42*	*2.62*	*0.1278*	
BD	*0.71*	**1**	*0.71*	*0.55*	*0.4721*	
CD	*3.09*	**1**	*3.09*	*2.37*	*0.1459*	
Residual	18.26	**14**	1.30			
Lack of Fit	18.26	**10**	*1.83*			
Pure Error	**0.000**	**4**	**0.000**			
Cor Total	75.39	**29**				

The analysis was done by means of fisher's "F"-test. The model F-Value was found to be 2.93 enlighten that the model is significant. The parameter are said to be significant if the F-Statistic probabilitty value is less than 0.05. In this case A^2, B^2, C^2, D^2, AC are statistically significant (P<0.05).

Furthermore, the relationship between the actual value and predicted value (Figure 5) show that the actual value are distributed relatively near the straight line, this proves that the predicted response from the empirical model is in agreement with the observed ones, indicating good fitness of the model.

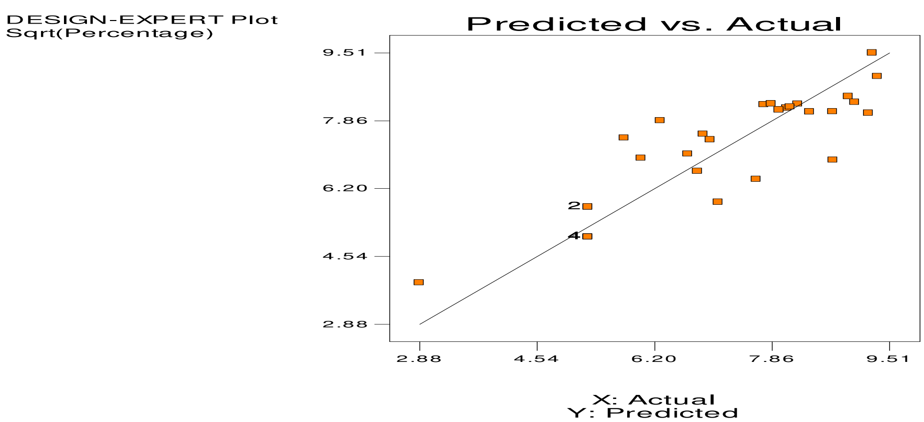

Figure 5: Observed Cu(II) removal versus predicted Cu(II) removal

Adsorption Isotherms

Adsorption isotherms are very important tools used in describing the stability of adsorbate at a fixed temperature and pH. Adsorption units can be design and operated using the isotherm model, which describes the various behaviour of adsorption (Yang *et al.*, 2011). The application of biosorption technique in the commercial scale requires proper quantification of the biosorption equilibrium. Equilibrium of an adsorption is reached whenever there is equal amount of ion adsorbed and desorbed. In this current study, the most frequently used adsorption isotherms, Langmuir and freudlich are been used. Biosorption of Cu(II) ions based on the values of the correlation coefficient (R^2) was found to fit better with the Freudlich isotherm.

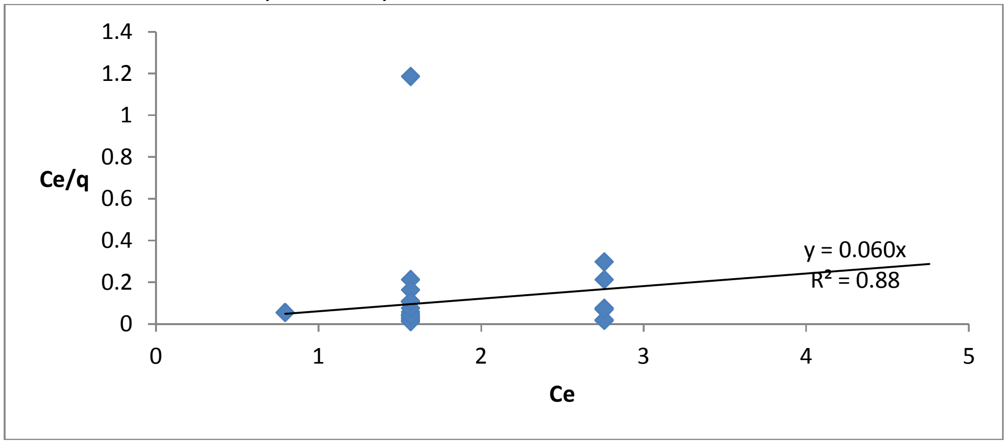

Figure 7: Langmuir plot of Cu (II) ion adsorption on NLP

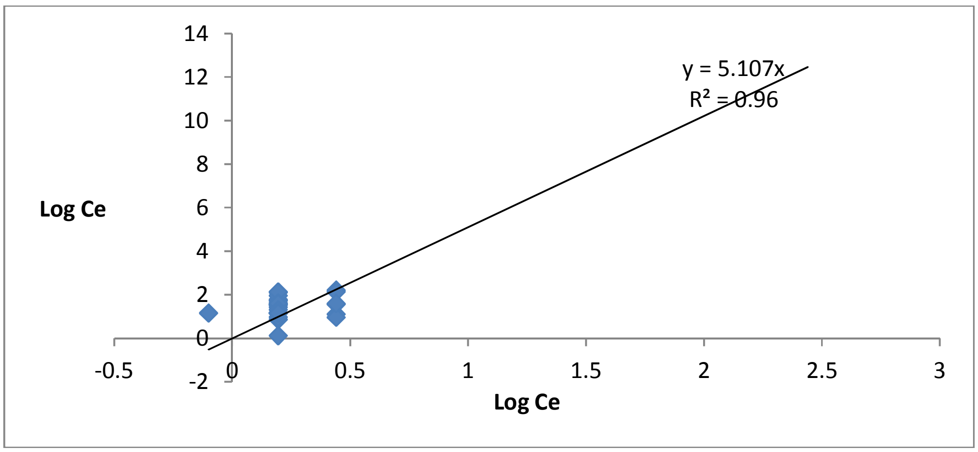

Figure 8: Freudlich plot of Cu (II) ion adsorption on NLP

CONCLUSION

The present investigation was carried to study the removal of Cu(II) from aqueous solution using adsorption over NLP and to conduct process optimisation using RSM for finding the optimum values of parameter affecting the process to achieve maximum removal efficiency. The study showed that NLP dose, contact time, contribute more to adsorption. The parameters were calculated using the experimental data. The experimental values obtained were found to agree satisfactorily with the values predicted by the model. The optimal adsorption of copper was obtained as temperature, contact time and NLP dose and the values of these were found to be 308 K, 97.5min and 1.5g respectively resulting in 100% of adsorption of copper. In this study we found the optimum operating condition for Cu(II) adsorption on NLP, which can be used for adsorption based water treatment process.

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