Optimization of the Production of Ethylene Di-Amine Tetra-Acetic Acid Modified Activated Carbon using Palm Kernel Shell for the Adsorption of Copper ion

Y. Yerima[1*] and I. Eiroboyi[1]

[1]*Department of Chemical/ Petroleum Engineering, Igbinedion University, Okada, Nigeria.*

Authors' contributions

This work was carried out in collaboration among all authors. Author YY designed the study and performed the statistical analysis. Author IE wrote the first draft of the manuscript and managed the literature searches. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Biomass-based activated carbon has received large attention due to its excellent characteristics such as inexpensiveness, good absorption behaviour, and potential to reduce strong dependence towards non-renewable precursors. The potential use of Palm Kernel Shell in modified activated carbon was evaluated by using the Response Surface Methodology. In this study, a 2^3 three-level Central Composite Design (CCD) was used to develop a statistical model for the optimization of process variables, contact time (10-130mins) X_1, pH (5.0 – 8.0) X_2, and adsorbent dose (0.4 -5.0g) X_3. The investigation shows that Ethylene Di-Amine Tetra-Acetic Acid modified activated carbon prepared from Palm Kernel Shell is a promising adsorbent for the removal of copper ions from aqueous solutions over a wide range of concentrations with an optimized efficiency of 99% at the solution pH of 7.2, contact time of 70 minutes and adsorbent dose of 2.1g/L. The adsorption results are in line with the linear and quadratic model representation, which is evident from the models for optimization of copper ions.

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Corresponding author: E-mail: yerima.yakubu@iuokada.edu.ng;

NOMENCLATURE

EDTA   : Ethylene   Di-Amine   Tetra-Acetic Acid;
PKS   : Palm Kernel Shell;
AC   : Activated carbon;
PKS-AC   : Palm kernel shell - Activated carbon;
ANOVA   : Analysis of Variance.

1. INTRODUCTION

Biomass has great potential as a renewable energy source, both for richer and developing countries [1-4]. About 140billion metric tonnes of biomass waste are generated every year from agriculture [5] and nearly approximately 370 million tonnes of available agricultural/biomass waste per year in India [6]. These wastes are one of the serious global environmental problems of the world [7,8], because they accumulate in water sources, resulting in pollution such as unpleasant odour, eutrophication, high levels of biological oxygen demand, and chemical oxygen demand [9]. The wastewater from homes and industries is discharged directly into water bodies or the environment without adequate treatment. Heavy metals (Cd; Cr; Cu; Co; Pb; Ni; Zn; Ag) become more toxic as they build up in our bodies, which may result in nutritional deficiencies, hormonal imbalances, neurological disorders, damage to the brain, cancer, etc [10].

Copper, one of the most widely used heavy mental, is mainly employed in, electrical, electroplating industries, and in larger amounts is extremely toxic to living organisms. The presence of copper (II) ions causes serious toxicological concerns, it is usually known to deposit in the brain, skin, liver, pancreas, and myocardium. Copper usually occurs in nature as oxides and sulphides. Copper is an essential substance to human life. Copper is found in a variety of enzymes and is used for biological electron transport. Like all heavy metals, it is potentially   toxic,   especially   at   high concentrations. Copper has been identified as the second most dangerous toxic metal after mercury; it causes damage to the liver, kidney, and respiratory system [11]. Thirty grams of copper sulfate is potentially lethal in humans. In high doses, it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Wilson"s disease, a disease that causes the body to retain copper can lead to brain and liver damage if untreated. Inhalation of copper produces symptoms similar to those of silicosis and allergic contact dermatitis.

Copper compounds are involved in several industrial and agricultural activities and, thus, can be released into the environment and reach water sources [12]. Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth. The suggested safe level of copper in drinking water for humans varies depending on the source but tends to be pegged at 1.3 mg/L according to the US Environmental Protection Agency. Too much copper in water has also been found to damage marine life. The observed effect of these higher concentrations on fish and other creatures is damage to gills, liver, kidneys, and the nervous system. Common oxidation states of copper include the less stable copper (I) state, Cu^+, and the more stable copper (II) Cu^{2+} [13].

Several agriculture waste materials such as the shells of watermelons, wheat, hazelnuts, cashew nuts,   and   palm   oil   fruit,   the   peels   of pomegranates and oranges, coconut and rice husks, tobacco, sawdust, cassava waste, loquat leaves, garden grass, poplar forest litter, azolla, barley straw, palm fruit fiber, kenaf fiber, peanut hull pellets, capsicum annum seeds, and *uncaria gambir* have been evaluated for Cu adsorption [14,15,16]. The maximum adsorption capacity of copper   varies   depending   on   the   adsorbing materials. Therefore, the need for the sustainable conversion of wastes into useful products arises [17,18]. In recent years, microbial biomass has emerged as an option for developing economic and eco-friendly wastewater treatment process, therefore, applying biotechnology in controlling and removing metal pollution has been paid much attention, and gradually becomes a hot topic in the field of metal pollution control because of its potential application.

An alternative process is biosorption, which utilizes various certain natural materials of biological origin, including bacteria, fungi, yeast, algae, etc [19]. Biosorption can be defined as the ability of biological materials to accumulate heavy   metals   from   wastewater   through metabolically   mediated   or   Physio-chemical pathways of uptake [20]. Biosorption, which is the ability of certain microbial biomaterials to bind and concentrate heavy metals from even the most   dilute   aqueous   solutions,   offers   a technically feasible and economically attractive

alternative [21]. Biosorption is a rapid phenomenon of passive metal sequestration by the non-growing biomass/adsorbents. It has advantages compared with conventional techniques, some of these are listed: (low cost; high efficiency; minimization of chemical and or biological sludge; no additional nutrient requirement; regeneration of biosorbent; and the possibility of metal recovery). The biosorption process involves a solid phase (sorbent or biosorbent; adsorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbet (adsorbate, metal). Due to the higher affinity of the adsorbent for the adsorbate species, the latter is attracted and bound thereby with different mechanisms. The process continues till equilibrium is established between the amount of solid-bound adsorbate species and its portion remaining in the solution. The degree of adsorbent affinity for the adsorbate determines its distribution between the solid and liquid phases.

Activated Carbon (AC) is one of the most effective adsorbents owing to its well, developed porous structure, large active surface area, and good mechanical properties [22]. Researchers are intensifying their search for AC produced from non-fossil sources like lignocellulosic waste from agriculture which are abundant and largely available [23]. Palm kernel shell (PKS) is a useful material to be applied as an adsorbent for the removal of heavy metal ions, as the good quality of organic compounds in it capable of adsorption of metal ions through biosorption mechanisms mentioned. [24,25]. PKS is sustainable agricultural waste produced in millions of tons every year. The disposal of a large quantity of Palm kernel shells causes adverse effects to the environment as it is disposed-off by burning, causing a lot of smoke [26,27]. Research is currently focusing on the use of low cost commercially available materials as viable substitutes for activated carbon. Previous work in this area includes the use of palm kernel shells as an adsorbent for the removal of heavy metals from industrial water [28]. To date, there are no studies reported on the synthesis of activated carbon from PKS using Ethylene Di-Amine Tetra-Acetic Acid (EDTA).Different methods are used in the treatment of waste water which requires the use of chemicals or synthetic resins which are most expensive in the treatment of large volumes. In this study, we utilized the PKS as an adsorbent for the treatment of copper simulated contaminated water. This study emphasizes the

modification of (EDTA) and optimization using response surface methodology (RSM).

2. MATERIALS AND METHODS

The Palm Kernel Shells (PKS) were obtained from Igwuomo, Ovia North- East Local Government Area, Edo State. PKS sample was washed with distilled water to remove dirt and impurities. The chemicals were of analytical grade, produced by BDH Chemicals Ltd, Poole, England, which needed no other form of purification.

2.1 Carbonization Process

Palm kernel shells (PKS) sample was treated with distilled water several times to get rid of any unwanted dirt and impurities [29]. It was sun-dried for 24 hours and then oven-dried at temperature 105°C for 24 hours to remove moisture. The dried PKS was crushed with a mechanical grinder and sieved within a mesh sieve of 250µm. The carbonization process was achieved by weighing 156 g of sample in clean silica crucibles and heating in a muffle furnace at 600°C for 3 hours [30].

2.2 Activation Process

Exactly, 156 g of the carbonized PKS was weighed into a 500ml beaker and mixed with 200cm^3 of 1.0 M(EDTA). The beaker with its content was boiled on a hot plate with stirring at intervals with a stirring rod until the water evaporated and subjected to thermal activation in a muffle furnace at 400°C for 2 hours. After the activation process was completed on the Palm kernel shells activated carbon (PKS-AC), the sample was filtered and rinsed with distilled water several times until the pH value obtained was 6-7, to remove the excess chemical from adsorbent. Lastly, PKS-AC sample was dried in an oven (105°C) for 24 hours and stored in a container.

The amount of metal ions adsorbed by the adsorbent is evaluated using equation 1

$$q_t = \frac{(Co - Ct)V}{W} \qquad (1)$$

The mass balance equation was used to determine the adsorptive capacity (q_e). Equation 2 shows the concentration of heavy metals in waste water when equilibrium is attained.

$$q_e = \frac{(Co - Cg)V}{W} \qquad (2)$$

Where

C$_0$ and C$_t$ are the initial and final concentration of the heavy metals present in the wastewater before and after adsorption for a time t (mg/L)

q$_e$ is the concentration of heavy metals in wastewater when equilibrium is attained (mg/L)

V is the volume of wastewater used in (ml)

W is the mass (g) of the adsorbent used

The percentage of metal ions removed was obtained using equation 3 as reported by [31].

$$\textbf{R (\%)} = \frac{(Co-Ct)}{Co} * 100 \qquad (3)$$

Where **R (%)** is the ratio of differences in metal concentration before and after adsorption.

All experiments were conducted in a batch system using 250 ml Erlenmeyer flasks in a thermostatic shaker (25°C, 200 rpm). Each flask was filled with 100 ml of solution and (adsorbent) as appropriate. The influence of some operational parameters on the adsorption characteristics of the Copper metal such as contact time (10 - 130min) X_1, pH of the aqueous solution (5.0 – 8.0) X_2, and adsorbent dose (0.4 - 5.0g) X_3.and temperature (25−50°C) were assessed. Competitive adsorption of the copper metal ion under mixed conditions was also evaluated.

3. RESULTS AND DISCUSSION

Table 1 shows the physical properties of modified Palm kernel shell - Activated carbon.

Table 1. Characteristics of prepared PKS-AC

Property	Value
Ash Content	0.1wt/wt%
Total surface area	1038m^{2}g
Particle size	250µm
pH	7.1

3.1 Effect of Contact Time and pH

The removal of copper from aqueous solution was studied as a function of contact time in the range of 10 to 130 minutes at about 50mg/L initial metal concentration, 7.16 pH, and 30ºC ambient temperature. The effect of contact time on the removal of copper is shown in Fig. 1. From Fig. 1, it was observed that the rate of copper removal was higher at the beginning until 50min and, thereafter, the adsorption rate became practically very slow and after 110 min, it started decreasing. The difference in the degree of adsorption maybe because in the beginning all sites on the surface of the adsorbent were vacant and the solute concentration gradient was relatively high. As a result, the extent of copper removal decreased with an increase in contact time, which depends on the number of vacant sites on the surface of the adsorbent. pH is done to determine the efficiency of the adsorbent, the pH of wastewater is one of the imperative factors governing the adsorption of metal ions. In this study, a pH of 4 - 10 was used as estimated in DOE. Based on Fig. 1, a time of 70min and pH of 7.20 was considered as the optimum time and pH for copper ions removal. The pH of the solution has a significant impact on the uptake of the metal ions since it determines the surface charge of the adsorbent, the degree of ionization, and the specification of the adsorbate. The variation of pH affects the effectiveness as the hydrogen ion itself is a tough competing adsorbate [32].

The minimum adsorptions were observed at high pH, but lower pH favors the adsorption and this may be because the presence of higher concentration and higher mobility of H$^+$ ions favored adsorption. The optimum result obtained at almost neutral pH was due to the surface of the adsorbent becoming more positively charged at high H$^+$ concentration at slightly more acidic pH such that the attraction between adsorbents and metal cations is reduced. In reverse, with the increase in pH the negatively charged surface area becomes more, thus facilitating greater metal removal, and then at very high pH also the percentage removal decreases. From these results, it was clear that at pH 7, the metals uptake was more, i.e., 96.30%, so pH 7 was taken as the optimum pH.

3.2 Effect of Adsorbent Dose

The doses of adsorbents strongly affect the adsorption phenomenon. This may be due to the availability and accessibility of the surface active sites resulting from the increased dose of adsorbent under specific conditions. The range of the adsorbent used in this work was 0.4 – 5.0 g agitated with the required mass in the solution as estimated using DOE and decanted.

The effect of adsorbent on copper adsorption was studied at variable adsorbent doses

between 0.5 – 4.0 g/L. The result of adsorbent dose on the percentage removal of copper on the activated carbon is depicted in Figs. 2 and 3. Initially, the metal uptake increased very slightly with adsorbent dose 0.5 g/L to 4.0 g/L and then started decreasing continuously. It is due to increased adsorbent surface area and the availability of more adsorption sites. However, at 2.10 g/L the adsorbent dose, the metal ions adsorbed per unit weight of adsorbent decreased which is because at higher adsorbent dose the solution ion concentration drops to a lower value of q (amount adsorbed) indicating the adsorption sites remain unsaturated [33]. The optimum adsorbent dose was 2.1 g/L.
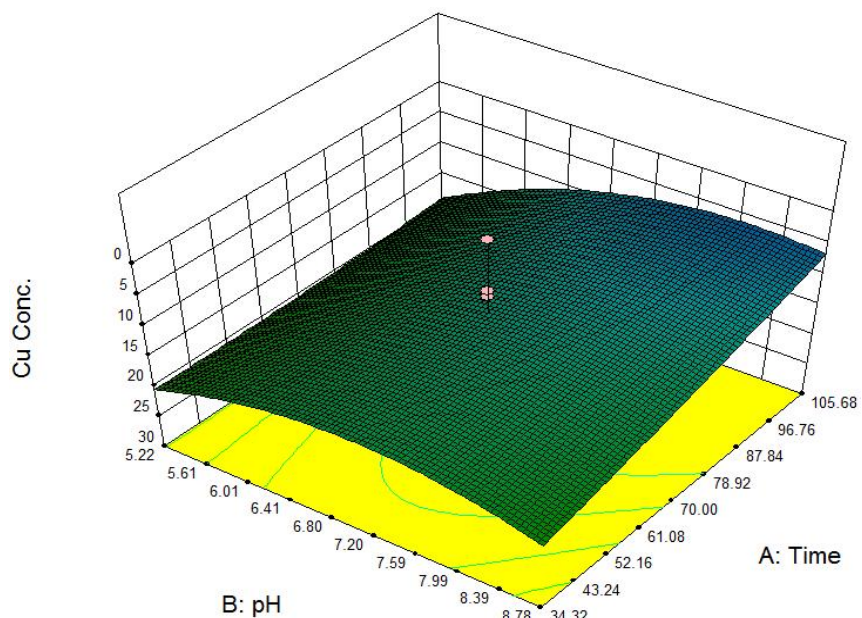
Fig. 1. 3D response surface of the effects of pH and time on metal copper ions concentrations
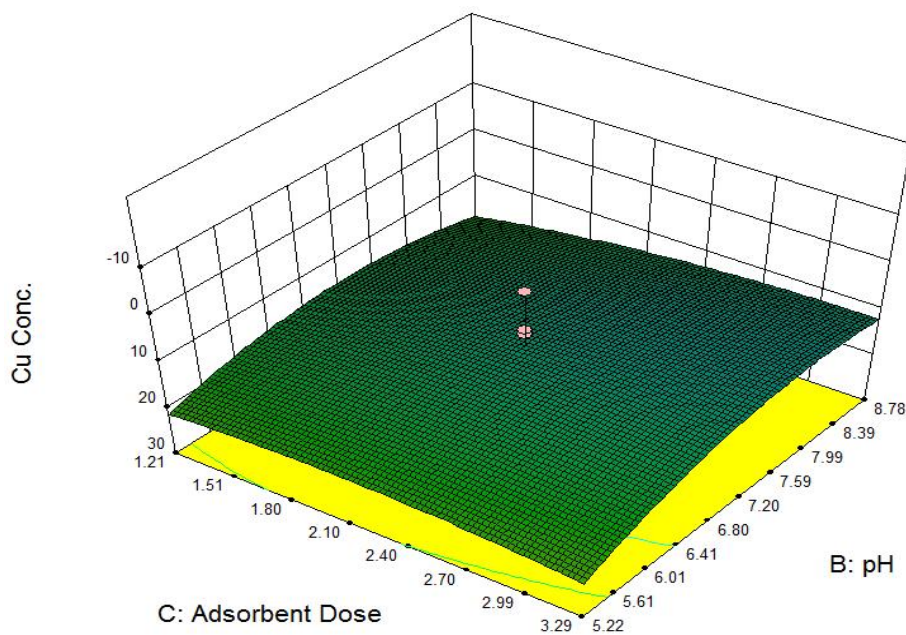
Fig. 2. 3D Response surface of the effects of adsorbent dose on (a) Copper with pH
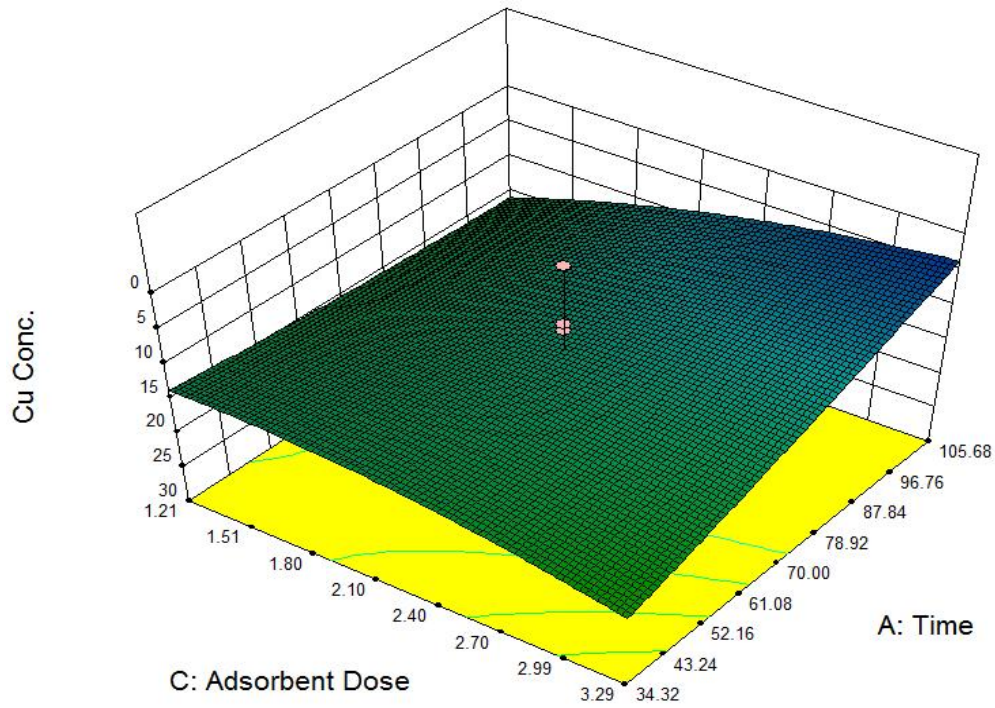
Fig. 3. 3D response surface of the effects of adsorbent dose on copper with time
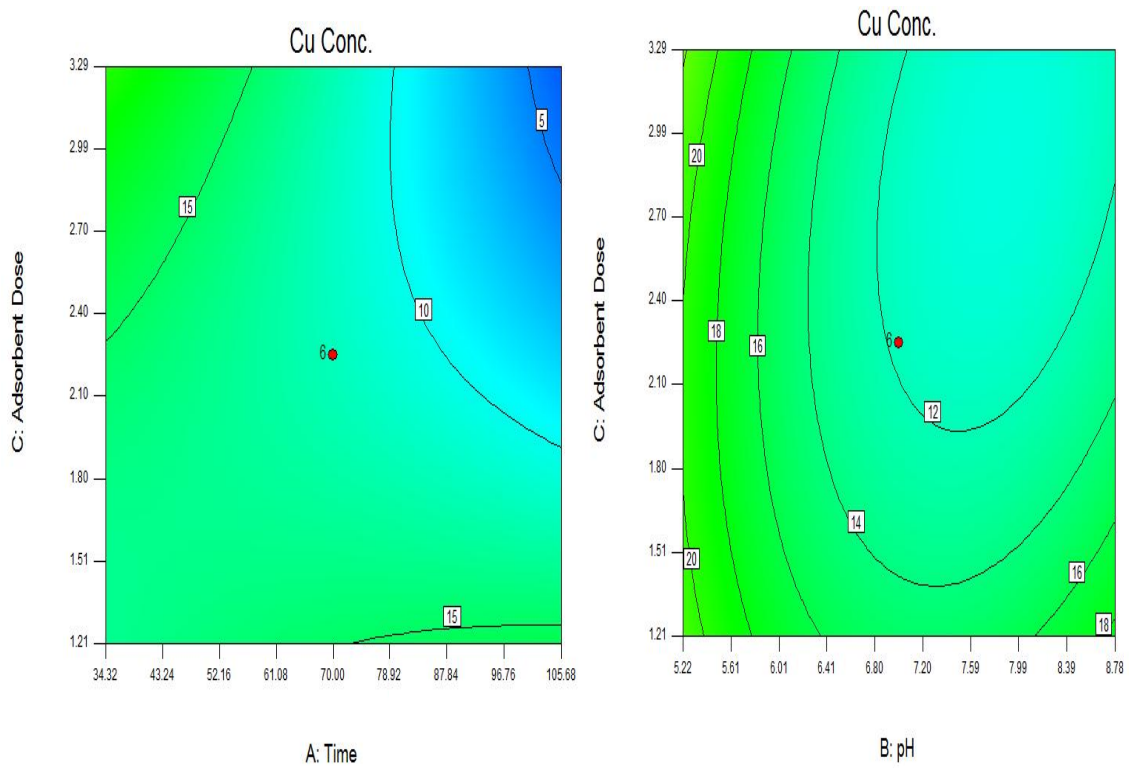
Fig. 4: Contour plot of the interaction between copper ion concentration and adsorption process factors

Analysis of variance (ANOVA) for the response surface quadratic model

The Analysis of Variance is reflected in Tables 2 to 4

Table2 : Cu Conc. Transform: None Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	5104.01	1	5104.01			Suggested
Linear vs Mean	336.26	3	112.09	1.34	0.2977	
2FI vs Linear	262.89	3	87.63	1.06	0.4014	
Quadratic vs 2FI	368.65	3	122.88	1.73	0.2240	Suggested
Cubic vs Quadratic	351.63	4	87.91	1.47	0.3205	Aliased
Residual	359.17	6	59.86			
Total	6782.61	20	339.13			

"Sequential Model Sum of Squares [Type I]": Select the highest order polynomial where the additional terms are significant and the model is not aliased.

Table 3. Lack of fit tests

Source	Sum of Squares,	df	Mean F Square	Value	p-value, Prob > F	
Linear	993.95	11	90.36	1.30	0.4101,	
2FI	731.06	8	91.38	1.31	0.3988	
Quadratic	362.41	5	72.48	1.04	0.4833	Suggested
Cubic	10.78	1	10.78	0.15	0.7103	Aliased
Pure Error	348.38	5	69.68			

"Lack of Fit Tests": Want the selected model to have insignificant lack-of-fit

Table 4. Model summary statistics

Source	Std. Dev.	adjusted Predicted R-Squared	R-Squared	R-Squared	PRESS
Linear	9.16	0.2003	0.0504	-0.2807	2149.82
2FI	9.11	0.3569	0.0601	-0.9963	3350.93
Quadratic	8.43	0.5766	0.1955	-1.0625	3462.09 Suggested
Cubic	7.74	0.7860	0.3224	-0.7144	2877.84 Aliased

"Model Summary Statistics": Focus on the model maximizing the "Adjusted R-Squared"
and "Predicted R-Squared"

3.2.1 Parity plot

The relationship between the predicted and actual metal ions concentrations is shown in Fig. 5, which was plotted by the software. It can be observed from the plot that the data points are distributed near the straight line. This is an indication that there is high correlation (R^2 value close to unity), which means that the data fit well with the model and convincingly is a good estimate of response for the system in the ranges studied. This further indicates that the model could be employed as a significant model for predicting response over the independent input variables.

3.2.2 Normal plot

Fig. 6 shows the normal plots of residuals for the responses. The residual gives the difference between the observed value of a response measurement and the value that is fitted under the theorized model (Prakash Maran *et al.*, 2013). A closer examination of this plot shows that most of the data points are closed to the line, having some points scattered. This was expected with normal data. From the observed distribution, it could thus be concluded that the data was normally distributed.

Response of Cu Conc.

Table 5. Cu Conc. ANOVA for Response Surface Quadratic Model
Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	967.80	9	107.53	1.51	0.2636 not significant
A-Time	164.21	1	164.21	2.31	0.1595
B-pH	146.87	1	146.87	2.07	0.1811
C-Adsorbent Dose	25.18	1	25.18	0.35	0.5649
AB	63.06	1	63.06	0.89	0.3685
AC	167.99	1	167.99	2.36	0.1552
BC	31.84	1	31.84	0.45	0.5185
A^2	2.63	1	2.63	0.037	0.8513
B^2	329.85	1	329.85	4.64	0.0567
C^2	44.08	1	44.08	0.62	0.4493
Residual	710.79	10	71.08		
Lack of Fit	362.41	5	72.48	1.04	0.4833 not significant
Pure Error	348.38	5	69.68		
Cor Total	1678.59	19			

The "Model F-value" of 1.51 implies the model is not significant relative to the noise. There is a 26.36% chance that a "Model F-value" this large could occur due to noise
Values of "Prob > F" less than 0.0500 indicate the model terms are significant
In this case, there are no significant model terms
Values greater than 0.1000 indicate the model terms are not significant
If there are many insignificant model terms (not counting those required to support hierarchy),
model reduction may improve your model
The "Lack of Fit F-value" of 1.04 implies the lack of fit is not significant relative to the pure error. There is a 48.33% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit
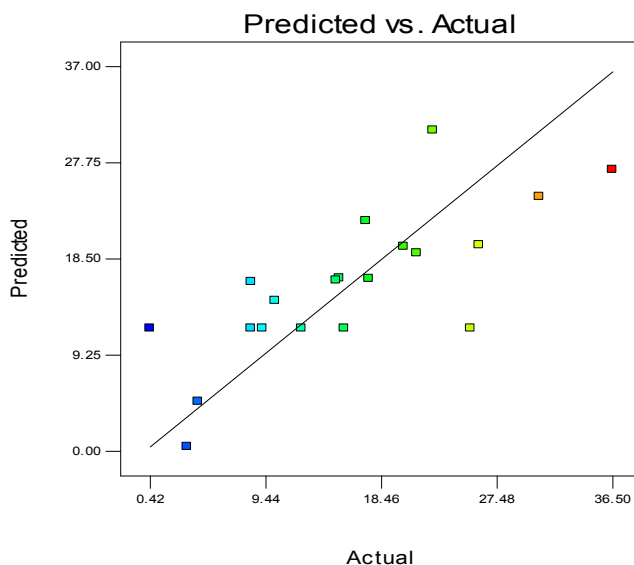
Fig. 5. Parity plot of predicted against actual metals ions (Pb²⁺ and Cu²⁺) concentrations

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Table 6. R squared values

Std. Dev.	8.43	R-Squared	0.5766
Mean	15.98	Adj R-Squared	0.1955
C.V. %	52.78	Pred R-Squared	-1.0625
PRESS	3462.09,	Adeq Precision	5.105,

A negative "Pred R-Squared" implies that the overall mean is a better predictor of your response than the current model;

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 5.105 indicates an adequate signal. This model can be used to navigate the design space

Table 7. Interaction of the process parameters.

Coefficient	Standard	95% CI	95% CI			
Factor	Estimate	df	Error	Low	High	VIF
Intercept	11.81	1	3.44	4.14	19.47	
X_1-Time	-3.47	1	2.28	-8.55	1.62	1.00
X_2-pH	-3.28	1	2.28	-8.36	1.80	1.00
X_3 -Adsorbent Dose	-1.36	1	2.28	-6.44	3.73	1.00
X_1X_2	-2.81	1	2.98	-9.45	3.83	1.00
X_1X_3	-4.58	1	2.98	-11.22	2.06	1.00
X_2X_3	-1.99	1	2.98	-8.64	4.65	1.00
X_1^2-0.43	1	2.22	-5.38	4.52	1.02	
$X_2^2$4.78	1	2.22	-0.16	9.73	1.02	
$X_3^2$1.75	1	2.22	-3.20	6.70	1.02	

Final Equation in Terms of Coded Factors:

$Y_{Cu\ Conc.} = +11.81 - 3.47*X_1 - 3.28*X_2 - 1.36*X_3 - 2.81*X_1*X_2 - 4.58*X_1*X_3 - 1.99*X_2*X_3 - 0.43*X_1^2 + 4.78*X_2^2 + 1.75*X_3^2$

Final Equation in Terms of Actual Factors:

$Y_{Cu\ Conc.} = +56.63211 + 0.53635*Time - 17.38121*pH + 7.59102*Adsorbent\ Dose - 0.044116*Time*pH - 0.12344*\ Time * Adsorbent\ Dose + 07480 * pH * Adsorbent\ Dose - 3.35657E-004*Time^2 + 1.50352*pH^2 + 1.61523* Adsorbent\ Dose^2$
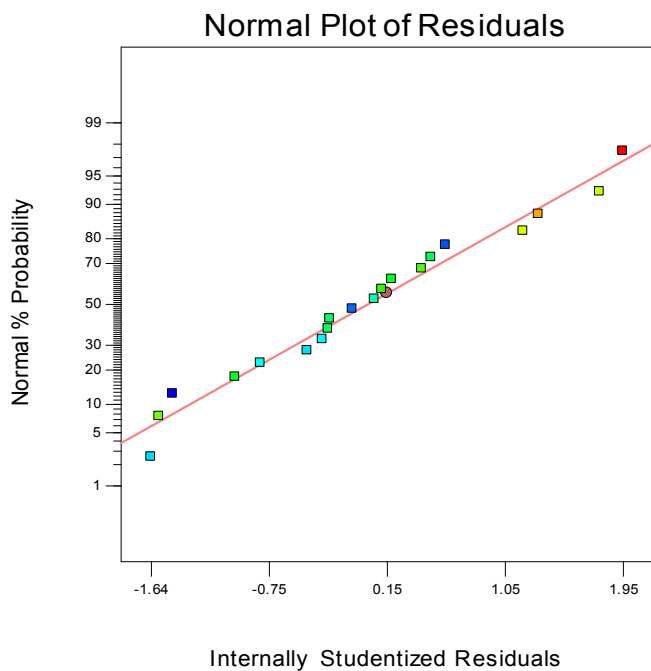
Fig. 6. Normal plot of residuals for the response

4. CONCLUSION

The present investigation shows that EDTA modified activated carbon prepared from palm kernel shell is a promising adsorbent for the removal of copper ions from aqueous solutions over a wide range of concentrations. The copper ions removal efficiency was controlled by solution pH, adsorbent concentration, and contact time. In this study, the interactions and the effects of parameters such as adsorbent dose, adsorbent contact time, and pH on metal ion transfer separation have been investigated.

The copper ions removal from aqueous solution by EDTA modified activated carbon from palm kernel shells had an optimized efficiency of 99% at the solution pH of 7.2, contact time of 70 minutes and adsorbent dose of 2.1g/L.

Based on the values of the coefficient of the correlation R^2 calculated, the Langmuir isotherm model was found to be in good agreement with the experimental data on the adsorptive behavior of copper and lead ions.

The adsorption results are in line with the linear and quadratic model representation, which is evident from the models for optimization of copper ions.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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