



## Removal of Cu (II) Ions from Aqueous Solution Using Poly-Amidoxime Resin from Grafted Millet Husk Cellulose

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**Abstract:** Poly-amidoxime ligand was synthesized on the cellulose isolated from millet husk through a graft copolymerization process for adsorption of Cu (II) ion from aqueous solution. The functional group, thermal degradation and morphology of the adsorbent were investigated by Fourier transform infrared (FTIR), thermal gravimetric analysis (TGA) and scanning electron microscope (SEM), respectively. The FTIR results showed that grafting was successful due to the presences of 2244  $\text{cm}^{-1}$  for cyano group (CN) and also band at 1640  $\text{cm}^{-1}$  and 1380  $\text{cm}^{-1}$  that replaced 2244  $\text{cm}^{-1}$  which successfully confirmed the synthesis of poly(amidoxime) functional group. The TGA showed two stages of thermal degradation 12 % weight loss observed in amidoxime at 240 °C which is due degradation of amidoxime functional group then it reduces to 2% in second stage at 530 °C which revealed the improved thermal stability of the material. The SEM image showed a clear morphology of the adsorbent before adsorption and after adsorption. The Initial concentration, adsorbent dosage and contact time were taken as independent variables. The adsorption process was optimized by central composite design (CCD) in Response surface methodology (RSM). The predicted value is in good agreement with experimental value and also the ANOVA result showed that all the independent variables have significant impact with the adsorbent. The optimum condition achieved in the experiment was at initial concentration of 150 mg/L, adsorbent dosage of 0.3 g and contact time of 90 min for  $\text{Cu}^{2+}$  with percentage removal of 55.41 % predictably and 54.92 % experimentally.

**Keywords:** Millet husk, Poly-Amidoxime ligand, Response surface methodology, Optimization.

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### INTRODUCTION

Heavy metals pollution is one of the reasons of industrial revolution that can human life, as well as the environment, in various regions around the world, especially in developing countries. The pollution of environment such as air, water, and land by toxic heavy metal ions such as mercury, cadmium, lead, and chromium, and their accumulation through the food chain has a raised in a number of diseases and disorders (1).

Copper is a component of many plant enzymes (oxidase for example) and is involved in many electron transfer processes. Copper is an essential element for human life, but excessive intake results in its accumulation in the liver and produces

gastrointestinal problems, anemia, liver and kidney damage. Long-term exposure to copper can cause irritation of the nose, mouth and eyes and headaches, stomachaches, dizziness, vomiting, and diarrhea (2).

High abundance of heavy metal ions in environment can harm human health and living organism ecosystem, thus removal of heavy metal ions is highly needed. Various separation techniques have applied for the removal of heavy metals such as chemical precipitation, reverse osmosis, adsorption, ion exchange and coagulation. The frequently techniques that attracted many researchers around the world is adsorption which is due to its highly abundance, easy modification, and high adsorption performance (3, 4). As a result, researchers try

various absorbent that can be used economically and effectively. In recent years, various agricultural waste by-product could be considered as absorbent for removal of heavy metal ions from aqueous solution or contaminated water.

Many researchers encouraging adsorbent that contain amidoxime functional group for the removal of heavy metals from waste water (5-7). This associated with mixing nitrile group into the polymer matrix through graft polymerization reaction of acrylonitrile to a polymer substrate, then converting of the nitrile groups into amidoxime groups using the alkaline solution of hydroxylamine (8).

A fibrous adsorbent that contain amidoxime groups was synthesised through graft copolymerization of acrylonitrile (AN) onto poly (ethylene terephthalate) (PET) fibers using benzoyl peroxide ( $Bz_2O_2$ ) as initiator in aqueous solution, and chemical modification of cyano groups by reaction with hydroxylamine hydrochloride in methanol (9). Also, synthesis of a chelating ion-exchange resin containing amidoxime functional group which was carried out by grafting polyacrylonitrile (PAN) onto starch. Where the PAN grafted copolymer was gained by free-radical initiating process using ceric ammonium nitrate as an initiator. Transformation of nitrile groups of the grafted copolymer into the amidoxime was carried out by treatment with hydroxylamine via alkaline solution (10). Similarly, acrylic acid-amidoxime and poly (maleic acid-amidoxime) resins were synthesised by the  $\gamma$ -radiation-induced copolymerization of acrylonitrile with acrylic acid and maleic acid, respectively. The obtained resins were amidoximated by reaction with hydroxylamine (11).

Various researchers have been reported the reaction mechanism of grafting which occurred by free radical initiation reaction of oxygen atom of hydroxyl group in cellulose unit by polymerization of vinyl or acrylic monomer. In this current study millet husk Cellulose (MHC) was grafted with acrylonitrile monomer by free radical initiation reaction with ceric ammonium nitrate as an initiator. By this process, ceric (IV) ion attack the OH group of cellulose to form complex ion which was reduced to cerium(III) ion where the hydrogen atom oxidized. To form  $Ce^{3+}$  from  $Ce^{4+}$  by forming free radicals of cellulose unit which undergo the addition reaction with acrylonitrile that induced the initiation reaction of grafting. Therefore, the formation of radical resulted in the propagation reaction. The termination of reaction of growing polymer chain on the cellulose monomer are resulted in combination reaction as shown in Scheme 1 (12).

The Millet Husk cellulose grafted cellulose which was merged with nitrile group was transferred to poly (amidoxime) where all the nitrile group reacted with

alkaline solution of hydroxylamine to form polymeric ligand which consisted the poly (amidoxime) functional group. The poly (amidoxime) ligand functional group can participate in rising-up the binding properties with metal ions. The bidentate poly (amidoxime) chelating ligand contributed five membered ring complexes with metal ions as shown in Scheme 1.

## MATERIALS AND METHODS

### Materials

All the reagent used throughout the research were of analytical grade and used as received.  $CuSO_4 \cdot 5H_2O$  were used as source of  $Cu^{2+}$ , Sodium Hydroxide (97.5 %) and sodium hypochlorite (99 %) are from Kem light laboratories LTD Glacial acetic acid (99.5 %) BH15, 1TD England Sulfuric acid (98 %) Loba Chemie pvt. LTD Mumbai Ceric ammonium nitrate (CAN) (99 %) geetraj corporation Acrylonitrile (AN) A.S. Joshi and company Hydroxylamine hydrochloride ACS Chemicals and Methanol (99 %) reagent chemicals.

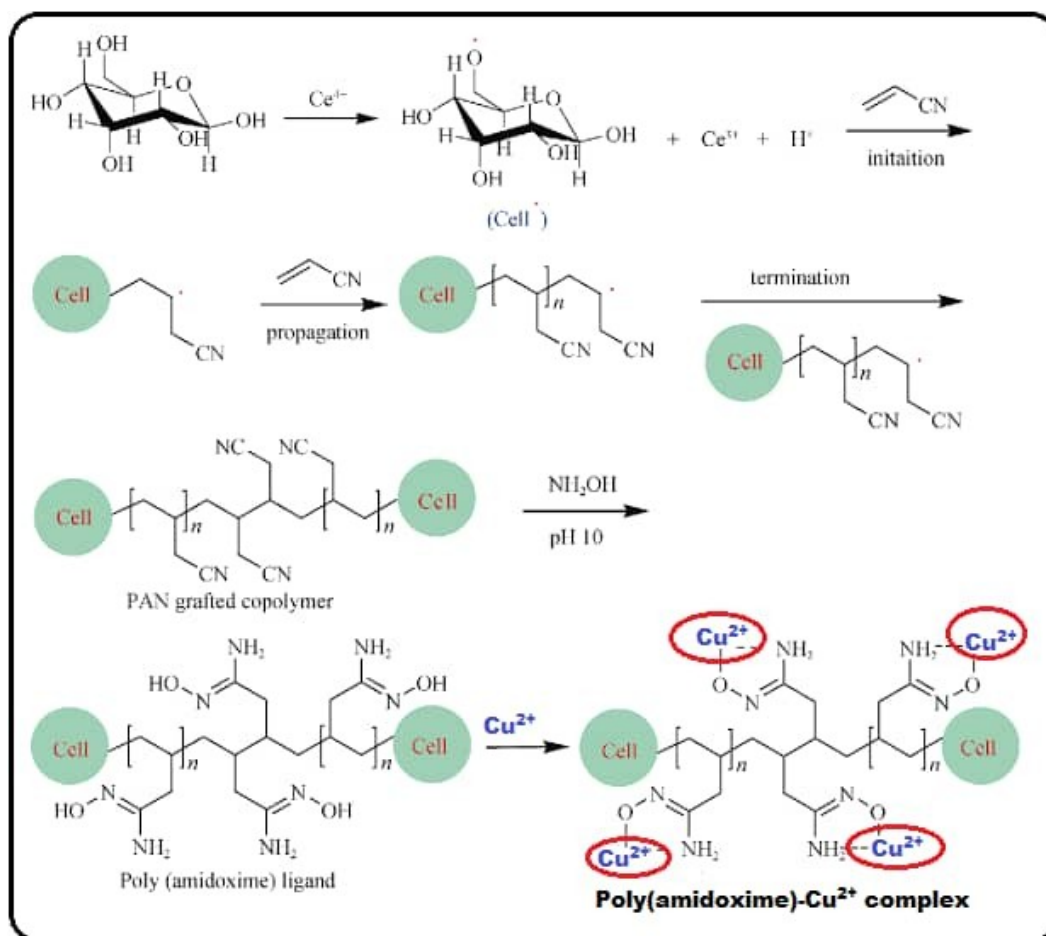
### Methods

#### *Extraction of Cellulose from Millet Husk*

Millet husk was collected from a farm at Farun Bala village, Jibia Local Government Area of Katsina State. It was washed, dried, grinded and sieved into fine powder. Millet husk powder (100 g) was treated with 10 % NaOH (500 mL) and glacial acetic acid (500 mL) for 2 h and 1 h respectively at 75 °C with continuous stirring, and washed with deionized water several times. The alkali method was repeated twice and finally rinsed with deionized water to remove the lignin and hemicellulose. The resultant cellulose was used for bleaching treatment with 2 % NaOCl and 5 % NaOH (400 mL) boil for 3 h at 50 °C. The mixture was then filtered and washed with deionized water, the process was done twice until white cellulose was obtained. Then the cellulose was oven dried at 50 °C.

#### *Graft Copolymerization*

The reaction was carried out in 250 mL three-neck flask which was equipped with a condenser and magnetic stirrer, and then immersed into paraffin oil to maintain a constant temperature. 10 g of cellulose was put into the flask, 50 mL of distilled water was added to the sample and preheated for about 30 min at 80 °C with continuous stirring. After 30 min, the flask was cool to 50 °C, then 4 mL of diluted sulphuric acid was added to the reaction ( $H_2SO_4: H_2O, 1:1$ ), after 5 min 10 mL of diluted CAN was added (2 g in 10 mL of distilled water) the reaction was stirred continuously for 10 min. Exactly after 10 min 24 mL of (AN) was added to the mixture with continuous stirring for 90 min. All the reaction was done throughout under  $N_2$  gas atm [8], with little modification.



**Scheme 1:** Scheme of graft copolymerization of acrylonitrile onto cellulose to produce PAN-graft-cellulose, poly(amidoxime), and poly-amidoxime- $Cu^{2+}$  complex.

When the reaction was completed the reaction flask was cool down under running tap water and the product was poured into 200 mL of methanol to induce the precipitation. The grafted product was washed several times with methanolic solution ( $CH_3OH:H_2O, 4:1$ ) then oven dried the product at  $50^\circ C$  to the constant weight.

The percentage of grafting was calculated via the following equation;

$$GP\% = \frac{W_1 - W_0}{W_0} \times 100 \quad (\text{Eq. 1})$$

Where  $W_0$  is the weight of cellulose backbone  $W_1$  is the weight of grafted cellulose.

#### Synthesis of Poly (Amidoxime) ligand

20 g of hydroxylamine hydrochloride was dissolved in 150 mL methanolic solution ( $CH_3OH; H_2O/5:1$ ). The HCl of  $NH_2OH$  was neutralized by NaOH solution and the precipitate of NaCl was filtrated. The solution was adapted to pH 10 using NaOH solution. 10 g of millet husk grafted cellulose was put into the two-neck flask, which was set with a condenser and magnetic stirrer, and then immersed into paraffin oil to maintain a constant temperature [12].

Then the above-prepared hydroxylamine solution was added to the flask, and the reaction was carried out at  $70^\circ C$  and 2 h. After 2 h of the reaction, the resin was filtered and washed multiple times with methanolic solution (methanol: water /4:1). Then, the resin was treated with 100 mL of methanolic 0.1 M HCl solution for 10 min. Finally, the resin was filtered and washed multiple times with methanolic solution (methanol:water /4:1), and then oven dried at  $50^\circ C$  to a constant weight (10).

#### Experimental Design of ( $Cu^{2+}$ ) Using Design Expert Software

The three parameters i.e. initial concentration of dye, adsorbent dosage and contact time were used as independent variables, nineteen runs of the "Central Composite RotaTable Design "(CCRD) experimental design consisted of eight factorial points, six axial points and also six center points, the three independent variables with (initial concentration (20-320 mg/L), contact time (10-190 min) and adsorbent dosage (0.05-0.6 g) for ( $Cu^{2+}$ ) solution, according to RSM design.

The experimental data belong to second-order polynomial regression analysis and used to predict

the response as the function of independent variables. The equation below is a form of second order polynomial regression model that used to explain the (Cu<sup>2+</sup>) removal.

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{j=i+1}^3 \beta_{ij} X_i X_j \quad (\text{Eq. 2})$$

Where  $\beta_0$  is the offset term,  $\beta_i$  is the linear effect,  $\beta_{ii}$  is the squared effect,  $\beta_{ij}$  is the interaction effect,  $X_i$  dimensionless coded value of the variable  $X_i$ . The analysis of variance (ANOVA) with p-value (<0.05), f-value, lack of fit, and R<sup>2</sup> value were used to determine the fitness of model. The 3-D plot and contour plot was used to show the influence between two variables and the interaction effects of the significant variables respectively.

#### Batch Adsorption Experiment

Batch adsorption experiment for both dye and metal ion were conducted at room temperature by shaking the required amount of adsorbents into 50 mL of (Cu<sup>2+</sup>) aqueous working solution in 250 mL Erlenmeyer flasks and agitated at 200 rpm for a chosen contact time. The solution was filtered using filter paper and their initial and final concentration was analyzed using Atomic Absorption spectroscopy (AAS).

The experimental data with different mathematical models were analyzed and the ANOVA results showed that the reaction of removals was illustrated with a "2FI" polynomial model. The percentage removal of and (Cu<sup>2+</sup>) was taken as response (Y) in experimental design and calculated using:

$$q_t = \frac{(C_0 - C_t)}{M} V \quad (\text{Eq. 3})$$

Where  $C_0$  and  $C_t$  are the initial and final concentration in (mg/L) solutions respectively.

The adsorption capacity  $q_t$  (mg/g) at equilibrium condition per unit mass of adsorbent (m) was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t)}{M} V \quad (\text{Eq. 4})$$

$C_0$  and  $C_t$  are the initial and final concentrations (mg/L).  $V$  is the volume of solution (L), and  $m$  is the mass of adsorbent (g)

#### Characterization

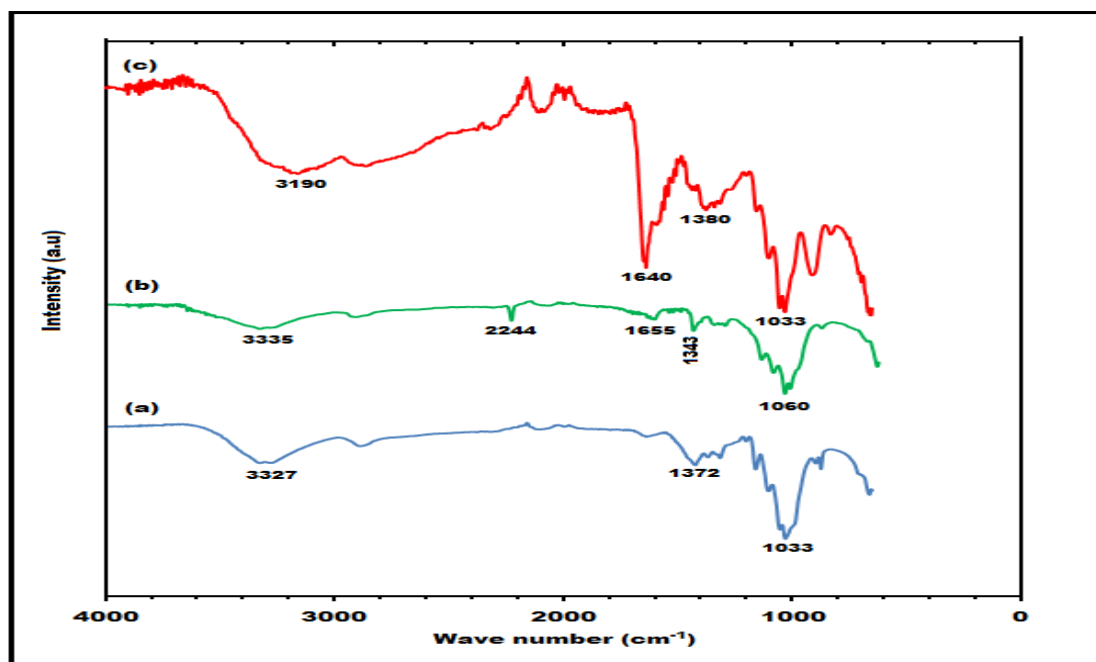
All the changes of functional group in cellulose, grafted cellulose and poly-amidoxime resin were verified using Fourier transform infrared (FTIR) were the spectral been recorded using spectrometer (Model 8400S) Shimadzu Japan from the range of 4000 – 650 cm<sup>-1</sup>. The thermal behavior of cellulose, grafted cellulose and poly-amidoxime resin were analyze in thermogravimetric analyzer (TGA7 Perkin Elmer) at the temperature of 30 °C-950 °C with the constant heating rate 10 °C mn<sup>-1</sup> under Nitrogen gas atmosphere at 20 mL/min. The changes in the morphology of poly- amidoxime ligand and poly-amidoxime ligand after adsorption of Cu<sup>2+</sup> also were observed using scanning electron microscope (SEM- JEOL-JSM-7800F).

## RESULTS AND DISCUSSION

#### FTIR Analysis

The FTIR spectral used to study the functional group in the prepared adsorbent. The main characteristics peaks of this study are assigned to be considered. The spectral for Millet Husk-cellulose, Millet Husk-cellulose grafted (PAN) and cellulose based poly (amidoxime) ligand are overlaid for comparison as shown in the Figure 1.

The spectrum of pure MH-cellulose showed the absorption band at 3327 cm<sup>-1</sup> and 2895 cm<sup>-1</sup> which represented the stretching of hydroxyl group and carbon- hydrogen stretching respectively. And also, the peaks at 1372 cm<sup>-1</sup> and 1033 cm<sup>-1</sup> belong to bending of hydroxyl and extending carbon-oxygen group. The  $\alpha$ -glycosidic linkage between the cellulose unit carbon-hydrogen deformations weak which was present at 899 cm<sup>-1</sup> which confirmed the structure of cellulose [10]. The IR spectrum of Millet Husk- cellulose (PAN) showed new adsorption band at 2244 cm<sup>-1</sup> due to cyano group (CN) and the remaining peaks are retained from the Millet Husk-cellulose. The presence of band at 2244 cm<sup>-1</sup> confirmed the grafting of acrylonitrile onto cellulose. The cyano group are observed from the range 2500-2000 cm<sup>-1</sup> for the backbone of cellulose [13]. In IR-spectrum of poly(amidoxime) ligand the peak at 2244 cm<sup>-1</sup> disappeared and formed new absorption band at 1640 cm<sup>-1</sup> and 1380 cm<sup>-1</sup> due to C=N stretch and N-H bending mode respectively. Also, the peak at 1380 cm<sup>-1</sup> were both due to hydroxyl and amide group [14]. The band at 2244 cm<sup>-1</sup> which was replaced with band at 1640 cm<sup>-1</sup> and 1380 cm<sup>-1</sup> was successful confirmed the synthesis of poly(amidoxime) functional group from MH-cellulose grafted (PAN).

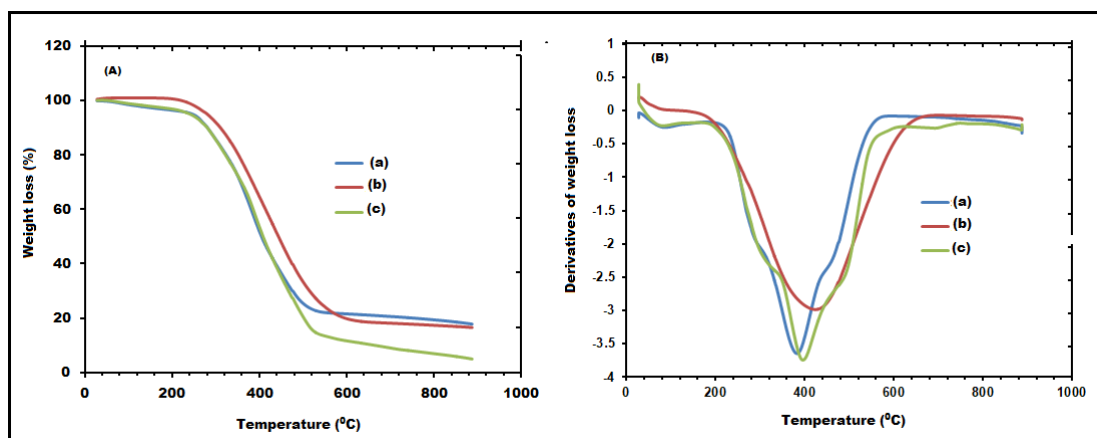


**Figure 1:** FTIR spectra of (a) cellulose (b) PAN-Grafted cellulose and (c) poly(amidoxime) ligand.

### Thermal Gravimetric Analysis (TGA)

Thermal degradation of cellulose, (PAN) grafted cellulose and amidoxime ligand was measured by TGA with heating rate  $10\text{ }^{\circ}\text{Cmin}^{-1}$  under  $\text{N}_2$  atmosphere and the result obtained are shown in the Figure 2 below. The weight loss occur in two stages throughout the experiment and the changes has been observed in the analysis. In cellulose the first stage of weight loss is observed at  $257\text{ }^{\circ}\text{C}$  which is about (10 %) and second stage is at  $524\text{ }^{\circ}\text{C}$  (70 %) due to degradation of hydroxyl OH and  $\text{CH}_2\text{OH}$  (14). In term of PAN-Grafted cellulose its

loss almost 79.9 % at  $224\text{ }^{\circ}\text{C}$ - $595\text{ }^{\circ}\text{C}$ , were the first stage lost about 10.5 % at  $250\text{ }^{\circ}\text{C}$  and in second stage 8.99 % weight has been loss at  $550\text{ }^{\circ}\text{C}$  which is due to degradation of poly (acrylonitrile) and the volatile gases [14]. In amidoxime ligand peak the thermal stability has been observed with high water content which confirm the hydrophilicity of the amidoxime ligand. 12 % weight loss observed in amidoxime at  $240\text{ }^{\circ}\text{C}$  which is due degradation of amidoxime functional group then it reduces to 2 % in second stage at  $530\text{ }^{\circ}\text{C}$ .



**Figure 2:** TGA-DTA of (a) cellulose (b) PAN-Graft-cellulose and (c) poly(amidoxime) ligand.

### Scanning Electron Microscope (SEM)

The SEM micrographs of the amidoxime ligand, before and after adsorption are shown in Figure 3 (a and b). The morphology of amidoxime ligand before adsorption (Figure 3 a) shows many pores and white material on the surface which may be

important for adsorption. After adsorption, the ligand surface became packed and almost all the white material also disappeared, the change in shape and size also been observed after metal adsorption as shown in Figure 3 (b).



**Figure 3:** SEM image of (a) poly (amidoxime) ligand, (b) poly(amidoxime) ligand after  $\text{Cu}^{2+}$  adsorption.

### Design of Experiment

#### Central Composite Design (CCD) and Statistical Analysis from RSM

The chosen three-factors and design from CCD produce by software and the experimental data obtained in batch adsorption of  $\text{Cu}^{2+}$  ion is summarized in Table 1 were the experimental and predicted value has been shown and the designs are properly fitted considering the value of co-efficient determination  $R^2$  ( $R^2$  of  $\text{Cu}^{2+}$  = 0.9976).

The final equation in terms of coded factor relating the removal efficiency and process parameters that are developed for  $\text{Cu}^{2+}$  shown in equation (5) and the equation is 2FI model.

$$\% \text{Removal } (\text{Cu}^{2+}) = 54.92 - 19.04A + 20.1B + 4.1C + 0.098AB + 0.91AC - 1.5BC \quad (5)$$

**Table 1:** Result obtained from the removal of  $\text{Cu}^{2+}$  by amidoxime ligand from RSM.

Std	Run	Factor 1 A: Initial Concentration (mg/L)	Factor 2 B: Contact Time (Minutes)	Factor 3 C: Adsorbent Dosage (g)	Response Removal of $\text{Cu}^{2+}$ (%)	
					Exp. Value	Pred. value
1	12	50	30	0.1	50.21	49.26
2	15	250	30	0.1	9.28	9.17
3	1	50	30	0.5	93.22	92.28
4	11	250	30	0.5	53.09	52.58
5	7	50	150	0.1	58.52	58.66
6	5	250	150	0.1	21.62	22.19
7	10	50	150	0.5	95.92	95.66
8	9	250	150	0.5	59	59.58
9	13	20	90	0.3	78.86	79.68
10	19	320	90	0.3	23.42	22.55
11	8	150	90	0.05	30.69	29.79
12	17	150	90	0.6	85.3	85.07
13	4	150	10	0.3	46.71	49.45
14	16	150	190	0.3	61.69	61.76
15	18	150	90	0.3	55.41	54.92
16	2	150	90	0.3	57.28	54.92
17	3	150	90	0.3	53.29	54.92
18	14	150	90	0.3	55.33	54.92
19	6	150	90	0.3	53.43	54.92

### Statistical Analysis Using (ANOVA)

The analysis of variance (ANOVA) was used to determine the adequacy of the model. The ANOVA statistics for the response % removal is shown in Table 2 for  $\text{Cu}^{2+}$ .

The ANOVA result of  $\text{Cu}^{2+}$  is 2FI model which indicated that the models could be used to navigate the design space, according to the ANOVA (Table 2) the F-value of  $\text{Cu}^{2+}$  is 815.16 which suggest the fitness of model. So, the significance of model was evaluated using probability of error value P-value ( $\text{prob} > F$ ). in (Table 2) the value of ( $\text{prob} > F$ ) is less

than 0.0500 these indicated that the models are significant (15, 16). Also, it found that A, B, C, AB, AC and BC are significant model term for adsorption capacity of  $\text{Cu}^{2+}$  using Amidoxime ligand.

In  $\text{Cu}^{2+}$  models based on F-value has significant effect on adsorption capacity, were the adsorbent dosage has the highest F-value of 2438.66 which implies that they have the most significant influence on the adsorption capacity compared to initial concentration and contact time, (16, 17). Also, in (Table 4.2) the lack of fit F-value is not significant relative to the pure error. The coefficient of determination ( $R^2$ ) was used to investigate the goodness of the model obtained (16). The high the

value of  $R^2$  indicated that the model is more reliable. Furthermore, the difference between the  $R^2$ -adjusted and  $R^2$ -predicted is an indication of model adequacy, for good equate model the difference should not exceeded 0.2, according to (Table 2) the  $R^2$  obtained is 0.9976 and the difference between adj.- $R^2$  and pred.- $R^2$  is 0.0019  $\text{Cu}^{2+}$  which confirm the model adequacy. Moreover, the value of adequate precision that measures the signal to noise and a ratio greater than 4 is desirable. The adequate precision of this study is high which is 101.864 for  $\text{Cu}^{2+}$ . These high adequacy precisions confirmed that the models are significant that can be used to navigate the design space.

**Table 2:** ANOVA result for quadratic model, data analyzing and modeling of  $\text{Cu}^{2+}$ .

Source	Mean Square	DF	Removal of $\text{Cu}^{2+}$ (%)		
			F Value	p-value (Prob > F)	
Model	1595.15	6	815.16	< 0.0001	significant
A-Initial Concentration	4558.57	1	2329.55	< 0.0001	
B-Contact Time	4772.09	1	2438.66	< 0.0001	
C-Adsorbent Dosage	211.06	1	107.86	<0.0001	
AB	0.076	1	0.039	0.847	Not significant
AC	6.55	1	3.35	0.0922	
BC	18.12	1	9.26	0.0102	
Residual	1.96	12	2329.55	< 0.0001	
Lack of Fit	1.58	8	2438.66	< 0.0001	
Pure Error	2.71	4			
Cor total	9594.35	18			
Adeq.Precision=	$R^2(\text{Adj.})=0.9963$	$R^2(\text{Pred.})=0.9944$			
	101.864				
	$R^2= 0.9976$				

### Interpretation of 3-Dimensional Response Surface Plot (3D-Plot) and Contour Plot of $\text{Cu}^{2+}$

The 3D and contour plot are used to estimate the percentage removal efficiency over independent variables. Each plot represents an infinite number of two tested combination variables while the one variable kept constant.

In this study the 3D and contour plot clearly showed the interaction between the variables which are significant as shown in Figure 4. Figure 4 shows the 3D and contour plot of  $\text{Cu}^{2+}$  were Figure 4(a) show interaction between initial concentration and adsorbent dosage while contact time is constant at

90 min, Figure 4(b) show interaction between initial concentration and contact time while adsorbent dosage is constant at 0.3 g and Figure 4(c) show interaction between adsorbent dosage and contact time while initial concentration is constant at 150 mg/L.

These showed the evident from the figure that removal of  $\text{Cu}^{2+}$  increases when the adsorbent dosage increases and decreases when initial concentration increases. Also, removal attained its maximum value when the adsorbent dosage and contact time were at high value.

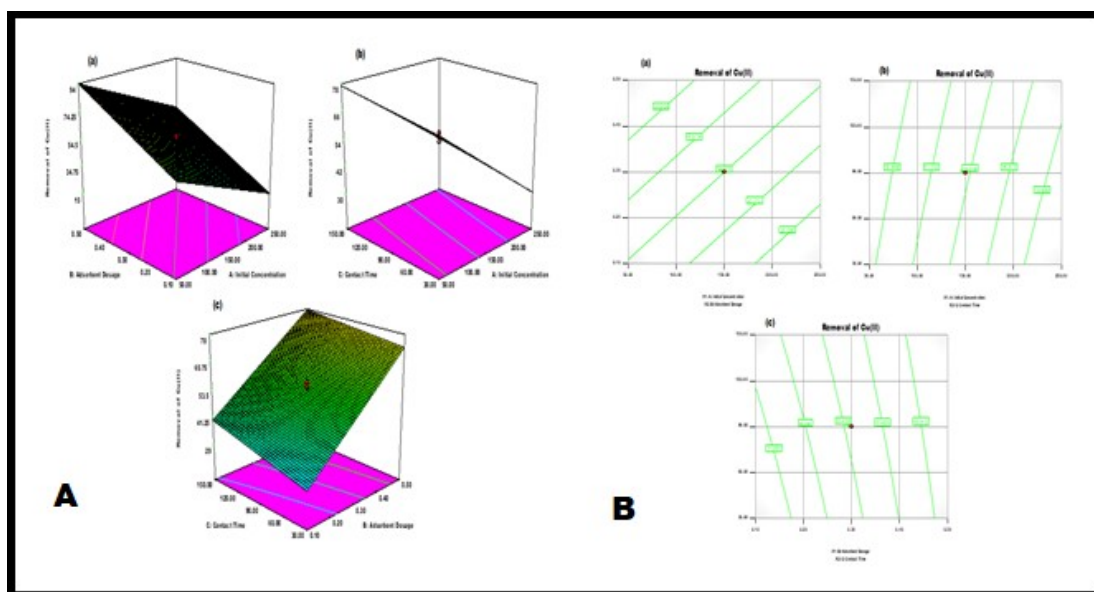


Figure 4: 3D-plot and contour plot of Cu<sup>2+</sup> removal.

**Optimization of the Adsorption Process**

The optimization process was achieved using response surface methodology which is used to identify the maximum value of 3 independent factors and dependent factor (response) which gives the maximum removal for adsorption of Cu<sup>2+</sup> by poly-amidoxime ligand from millet husk.

The target suggested is 100 % with upper and lower weight which was set as 1. The software predicted 54.92 % removal for Cu<sup>2+</sup> and also the confirmation

test for optimum condition carried out with the variables as set by model are shown under Table 3 the combination of factors that are setting in achieving the desired response was found to be at initial concentration of 150 mg/L, Adsorbent dosage of 0.3 g and contact time of 90 min with the predicted response of 54.92 % for Cu<sup>2+</sup>. Therefore, percentage removal achieved in this study indicated that the 2FI model was valid in predicting the response.

Table 3: Constraints and optimum condition for removal of Cu<sup>2+</sup>.

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight
A: Initial conc.	is in range	50	250	1	1
B: Contact time	is in range	30	150	1	1
C: Adsorbent dosage.	is in range	0.1	0.5	1	1
% Removal of Cu <sup>2+</sup>	Target= 100	54.22	55.62	1	1
Initial Conc. (mg/L)	Contact Time (min)	Adsorbent Dosage (g)	Removal of Cu (%)		
150	90	0.3	Exp. Value 55.41	Pred. Value 54.92	

**CONCLUSION**

In this study poly-amidoxime ligand have been synthesized using the millet husk cellulose through graft copolymerization process and used as adsorbent to investigate the removal of Cu<sup>2+</sup> from aqueous solution. The functional group, thermal degradation and morphology of the adsorbent were investigated by Fourier transform infrared (FTIR), thermal gravimetric analysis (TGA) and scanning electron microscope (SEM) respectively. The FTIR results showed that grafting was successful due to the presences of 2244 cm<sup>-1</sup> for cyano group (CN)

and also band at 1640 cm<sup>-1</sup> and 1380 cm<sup>-1</sup> that replaced 2244 cm<sup>-1</sup> which successfully confirmed the synthesis of poly(amidoxime) functional group. The TGA showed two stages of thermal degradation 12 % weight loss observed in amidoxime at 240 °C which is due degradation of amidoxime functional group then it reduces to 2% in second stage at 530 °C which revealed the improved thermal stability of the material. The SEM image showed a clear morphology of the adsorbent before adsorption and after adsorption. The Initial concentration, adsorbent dosage and contact time were taken as independent variables. The adsorption process was



optimized by central composite design (CCD) in Response surface methodology (RSM). The predicted value is in good agreement with experimental value and also the ANOVA result showed that all the independent variables have significant impact with the adsorbent. The optimum condition achieved in the experiment was at initial concentration of 150 mg/L, adsorbent dosage of 0.3 g and contact time of 90 min for Cu<sup>2+</sup> with percentage removal of 55.41 % predictably and 54.92 % experimentally.

Finally, it can be concluded that, poly-amidoxime ligand can be efficiently used in treatment of waste water contaminated with metal ions.

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