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SYNTHESIS OF POLY-AMIDOXIME RESIN FROM GRAFTED MILLET HUSK CELLULOSE FOR ADSORPTION OF CONGO RED

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ABSTRACT
Poly-amidoxime ligand was synthesized from grafted millet husk for adsorption of Congo red dye from aqueous solution; the grafting process was carried out using Acrylonitrile and Ceric ammonium nitrate as an initiator. The functional group, thermal degradation and morphology of the adsorbent was investigated by Fourier transform infrared (FT-IR), thermal gravimetric analysis (TGA) and scanning electron microscope (SEM) respectively. 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 FT-IR results showed that grafting was successful due to the presences of 2244 cm^{-1} for cyno group (CN) and also band at 1640 cm^{-1} and 1380 cm^{-1} that replaced 2244 cm^{-1} which successful confirmed the synthesis of poly(amidoxime) functional group. The TGA showed two stages of thermal degradation. About 12 % weight loss observed in amidoxime at 240 ^0C which is due degradation of amidoxime functional group then it reduces to 2 % in second stage at 530 ^0C which revealed the improved thermal stability of the material. 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 60mg/L, adsorbent dosage of 0.3g and contact time of 45 min with percentage removal of 95.9 % predictably and 94.89 % experimentally. Finally, it can be concluded that, poly-amidoxime ligand can be efficiently used in treatment of waste water contaminated with dyes
Keywords: Millet husk, Poly-Amidoxime ligand, Acrylonirile, Response surface methodology, Optimization

INTRODUCTION

The subsistence of dyes in aquatic environment can scathel various living species. Discharging aqueous effluents containing dyes are coming from many industrial processes, such industries are textiles, printing, plastics and food coloring those are the common industries that pollutes wastewater with pollution and these dyes are non-biodegradable and tend to accumulate in living organisms, causing many diseases and disorders (Al-Degs *et al.,* 2006). It was estimated that more than 7×10^5 tons of synthetic dyes are produced annually worldwide and 50 % of dyes are Azo dyes (Al-Ghouti *et al.,* 2003; Greluk & Hubicki, 2011).

Congo red is a benzidine based anionic diazo dye, which are commonly used in textile and paper industries (Mane & Babu, 2013). It's a synthetic dye with highly water-soluble and not easily biodegraded or photodegraded due to its structural stability with stable structure that make it hard to biodegrade. It is also known to metabolize to carcinogenic products and causes irritation to the skin, eyes and gastrointestinal tract (Roy & Mondal, 2017).

Dye is a major pollutant that assist in wastewater pollution these dye effluent is toxic and their elimination is highly needed due to its potential toxicity and visibility problems. Diverse method of dye removal has been applied such as biological method, chemical method, precipitation, adsorption, coagulation/flocculation, photo-catalytic decolonization, ozonation, microbial decomposition, electrochemical methods. Among many methods of dye removal researches reported adsorption as the most effective method that provide promising result (Crini,

2006; Gupta, 2009). Various adsorbents have been tried by many researches that can be used economically and effectively, but in this recent years, many agricultural waste by-products could be considered as adsorbent for removal of dyes from aqueous solution or wastewater.

Many scientific workers investigated adsorbent with amidoxime functional group for the removal of dyes from waste water (Seko *et al.,* 2004). 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 (Anirudhan *et al.,* 2010).

Eldin *et al.,* 2016 reported that, an amidoxime-grafted cotton fabric ion exchanger was developed for methylene blue (MB) removal from wastewater. The ability of the amidoxime-grafted cotton fabrics to remove MB ions from an aqueous solution was investigated in equilibrium, kinetics and thermodynamics studies. Also, Saliba *et al.,* 2002 reported the adsorption of metal ions such as Cu (II), Cr (III), Cd (II) and Ni (II) and dyes such as Acid Blue 25, Calmagite and Eriochrome Blue Black B is performed onto amidoximated cellulose (Am-Cell). Abdel-Aziz (2011) also, reported the (acrylic acid–amidoxime) [P(AA–AO)] and poly (maleic acid–amidoxime) [P(MA–AO)] resins prepared by the γ-radiation-induced copolymerization of acrylonitrile with acrylic acid and maleic acid, respectively. The obtained resins were amidoximated by reaction with hydroxylamine. The prepared resins were used for the removal of methyl violet (MV) dye from aqueous solutions.

This study is aimed at the development of new adsorbent from millet husk cellulose for the removal of dyes by adsorption process. A new adsorbent, millet husk cellulose polymerized amidoxime was synthesized through graft polymerization reaction of acrylonitrile (AN) monomer onto millet husk cellulose using ceric ammonium nitrate (CAN) as an initiator, followed by treatment with hydroxylamine hydrochloride then been utilized as an adsorbent for the removal of Congo red (CR-Dye) and optimize using RSM.

MATERIALS AND METHODS

All the reagent used throughout the research were of analytical grade and used as received. Congo red dye, Sodium Hydroxide (97.5 %) and sodium hypochloride (99 %) are from Kem light laboratories LTD Glacial acetic acid (99.5 %) BH15, 1TD England Sulphuric 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

Purification and Cellulose Preparation

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 hrs and 1 hr respectively at 75 ℃ 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 ℃. The mixture was than filtered and washed with deionized water, the process was done twice until white cellulose was obtained. Then the cellulose was oven dried at 50 ℃.

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 mins at 80 ℃ with continues stirring. After 30 mins, the flask was cool to 50 ℃, then 4 mls of diluted sulphuric acid was added to the reaction (H_2SO_4: H_2O, 1:1), after 5 mins 10 mL of diluted CAN was added (2 g in 10 mls of distilled water) the reaction was stirred continuously for 10 mins. Exactly after 10 mins 24 ml of (AN) was added to the mixture with continuous stirring for 90 mins. All the reaction was done throughout under N_2 gas atm (Rahman *et al.,* 2000), with little modification.

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 ℃ to the constant weight.

The percentage of grafting was calculated via the following equation;

$$\mathbf{GP\%} = \frac{W1-W0}{W0} \times 100 \qquad (1)$$

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

Synthesis of Poly (Amidoxime) ligand

About 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 (Rahman *et al.,* 2016).

Then the above-prepared hydroxylamine solution was added to the flask, and the reaction was carried out at 70 °C and 2 h. After 2hrs 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 mins. Finally, the resin was filtered and washed multiple times with methanolic solution (methanol±water/4:1), and then oven dried at 50 °C to a constant weight (Rahman *et al.,* 2016).

Characterization

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

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, twenty 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 (8.00–130 mg/L), contact time (6.00–95.45 mins) and adsorbent dosage (0.05–0.6 g) for CR-dye 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 CR-dye removal.

$$\gamma = \beta_0 + \sum_{i=1}^{3} \beta_i \chi_i \chi_i + \sum_{i=1}^{3} \beta_{ii} \chi_i^2 + \sum_{j=i+1}^{3} \beta_{ij} \chi_i \chi_j \quad \textbf{(2)}$$

Where β0 is the offset term, βi is the linear effect, βii is the squared effect, βij is the interaction effect, xi-dimensionless coded value of the variable Xi. The analysis of variance (ANOVA) with p-value (<0.05), f-value, lack of fit, and R^2 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 of dye was conducted at room temperature by shaking required amount of adsorbents into 50mL of (CR-Dye) aqueous working solution in 250 mL Erlenmeyer flasks and agitated at 200rpm for a chosen contact time. The solution was filtered using filter paper and their initial and final concentration was analyzed using UV-Visible spectrophotometer at the wavelengths of 498 nm.

The experimental data with different mathematical models were evaluated and their ANOVA results showed that the reaction of removals was most properly demonstrated with a "quadratic" polynomial model. The percentage removal of Congo red dye was taken as response (Y) in experimental design and calculated as:

$$Y = \frac{(C0 - Ct)}{C0} \times 100 \quad \textbf{(3)}$$

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

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

$$qe\left(\frac{mg}{g}\right) = \frac{(C0 - Ct)}{M} V \quad (4)$$

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).

RESULTS AND DISCUSSION

Graft Polymerization

The cellulose was successful isolated from millet husk, then converted to graft co-polymer by the used of acrylonitrile (AN) as monomer and ceric ammonium nitrite (CAN) as an initiator, where the reaction occurs under free radical initiation method, with the reaction temperature. and time 50 ^{0}C and 90 mins respectively.

Poly (Amidoxime) Ligand

The poly(amidoxime) ligand was prepared from grafted cellulose by conversion of nitrile group to amidoxime group. The conversion of hydroxylamine was carried out in alkaline medium where $NH_2OH.HCl$ was neutralized with NaOH to pH 10 and the reaction conducted 70 ^0C for 2 hrs. the polymer was treated with methanol/water (5;1) and the reaction medium were determined.

Reaction Mechanism of Grafted Cellulose (PAN) and Poly(Amidoxime) Ligand

Various researchers have been reported the reaction mechanism of grafting which was occur 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 nitrite as an initiator. By this process, ceric (iv) ion attack the OH group of cellulose to form complex ion which was reduced to ceric (iii) ion where the hydrogen atom oxidized. To form Ce^{3+} from Ce^{4+} by forming free radicals of cellulose unit which was 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 the scheme (1) (Rahman *et al., 2016*).

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 dye. The bidentate poly(amidoxime) chelating ligand contributed five membered ring complexes with dye. (Scheme 1).

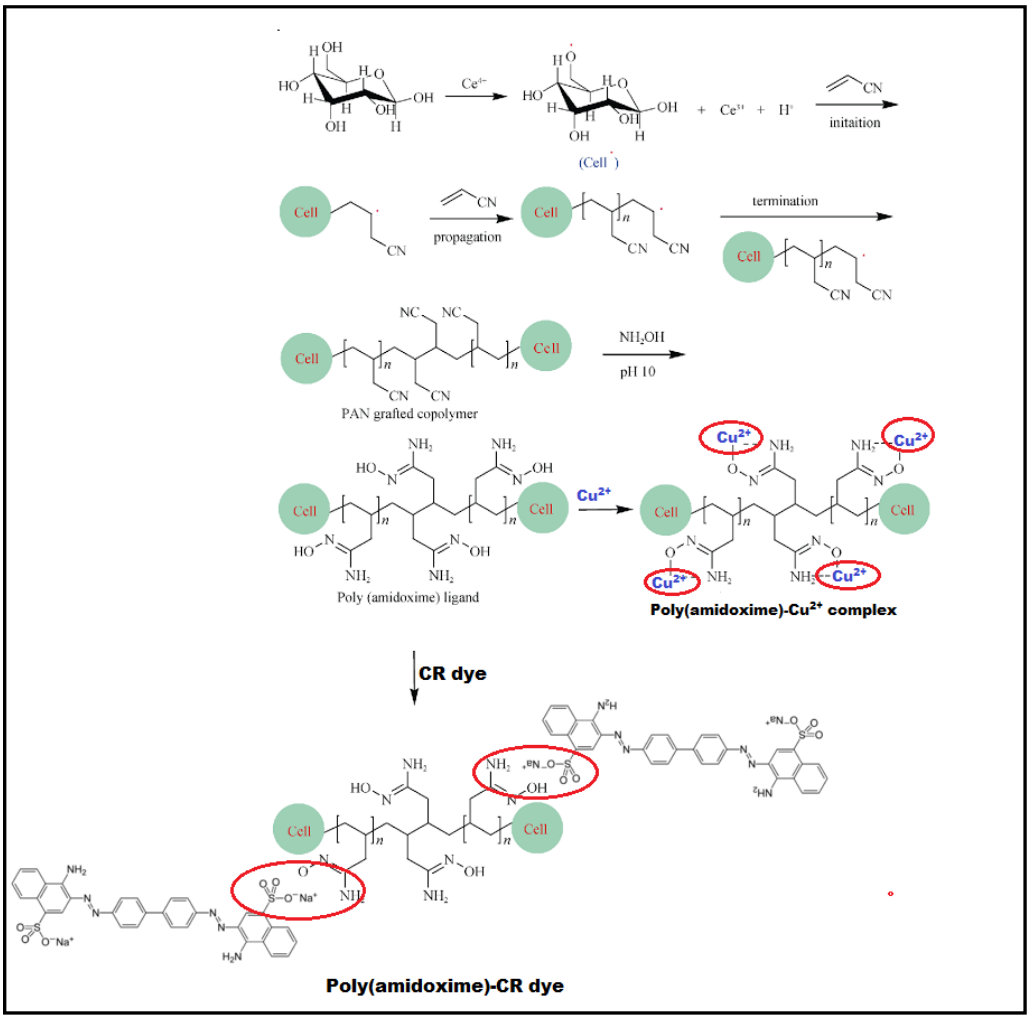

Fig. 1: Scheme of Graft Copolymerization of Acrylonitrile onto Cellulose to Produce PAN-Graft-Cellulose, Poly(Amidoxime), Poly-Amidoxime-Dye …

CHARACTERIZATION

FT-IR Analysis

The FT-IR spectral used to study the functional group in the millet husk. 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.

The spectrum of pure MH-cellulose showed the absorption band at 3327 cm^{-1} and 2895 cm^{-1} which represented the stretching of hydroxyl group and carbon- hydrogen stretching respectively. And also, the peaks at 1372 cm^{-1} and 1033 cm^{-1} belong to bending of hydroxyl and extending carbon-oxygen group. The α-glycosidic linkage between the cellulose unit carbon-hydrogen deformation weak which was present at 899 cm^{-1} which confirmed the structure of cellulose (Rahman *et al.,* 2016). The IR spectrum of Millet Husk- cellulose (PAN) showed new adsorption band at 2244 cm^{-1} due to cyano group (CN) and the remaining peaks are retained from the Millet Husk-cellulose. The presence of band at 2244 cm^{-1} confirmed the grafting of acrylonitrile onto cellulose. The cyano group are observed from the range 2500-2000 cm^{-1} for the backbone of cellulose (Pan *et al.,* 2016). In IR-spectrum of poly(amidoxime) ligand the peak at 2244 cm^{-1} disappeared and formed new absorption band at 1640 cm^{-1} and 1380 cm^{-1} due to C=N stretch and N-H bending mode respectively. Also, the peak at 1380 cm^{-1} were both due to hydroxyl and amide group (Rahman *et al.,* 2020). The band at 2244 cm^{-1} which was replaced with band at 1640 cm^{-1} and 1380 cm^{-1} was successful confirmed the synthesis of poly(amidoxime) functional group from MH-cellulose grafted (PAN).

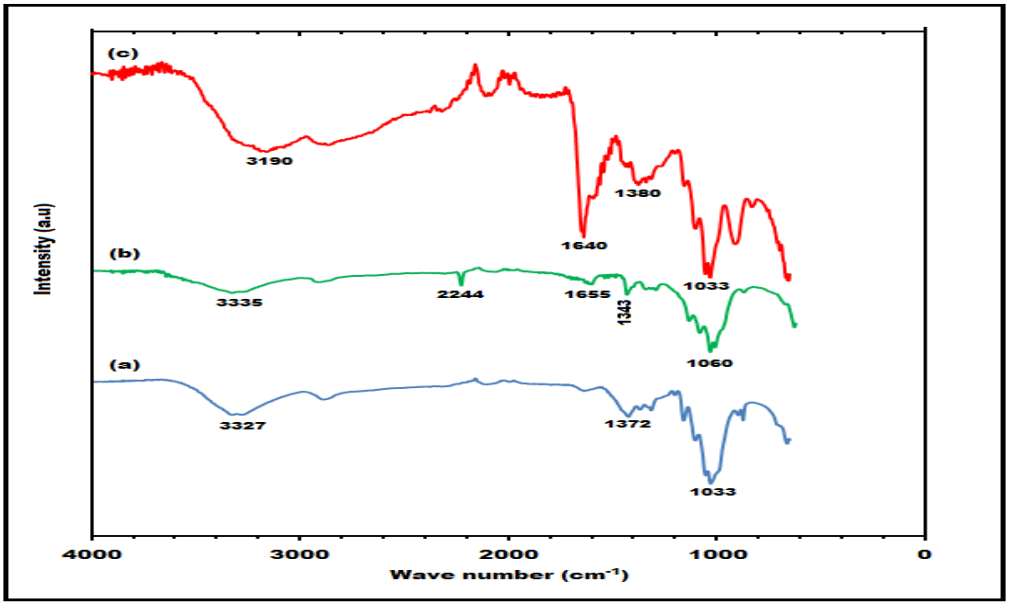

Fig. 2 spectra of (a) cellulose (b) PAN-Grafted cellulose and (c) poly amidoxime ligand

TGA Analysis

The adsorption the thermal degradation of cellulose, (PAN) grafted cellulose and amidoxime ligand was measured by TGA with heating rate 10 $^0Cmin^{-1}$ under N_2 atmosphere and the result obtained are shown in the Figure below.

The weight loss occurs 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 ^0C which is about (10 %) and second stage is at 524 ^0C (70 %) due to degradation of hydroxyl OH and CH_2OH (Rahman *et al.,* 2020) . In term of PAN-Grafted cellulose its loss almost 79.9 % at 224 ^0C-595 ^0C, were the first stage lost about 10.5 % at 250 ^0C and in second stage 8.99 % weight has been loss at 550 ^0C which is due to degradation of poly (acrylonitrile) and the volatile gases (Rahman *et al.,* 2020). 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 ^0C which is due degradation of amidoxime functional group then it reduces to 2 % in second stage at 530 ^0C.

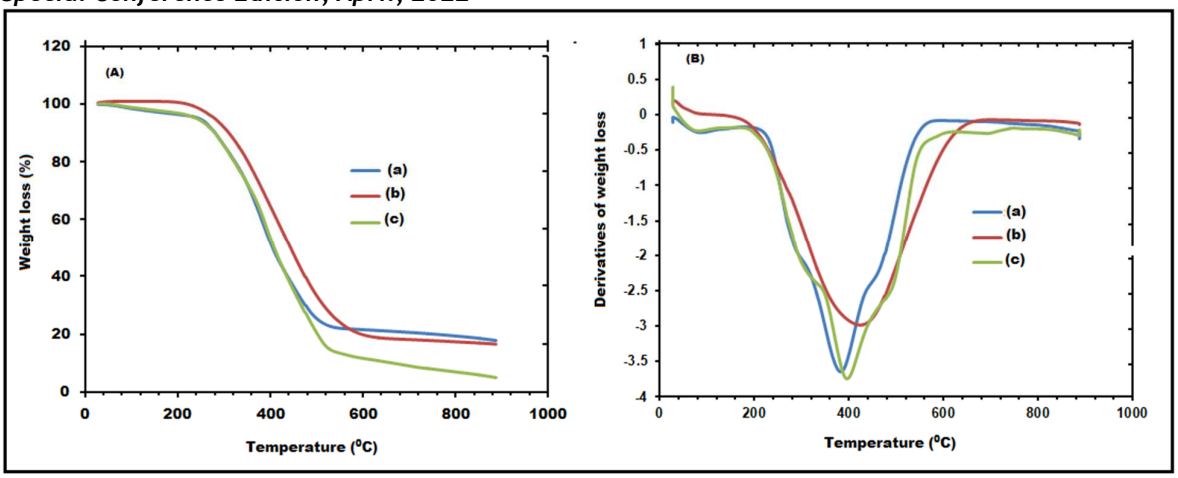

Fig. 3 TGA-DTA of (a) cellulose (b) PAN-Graft-cellulose and (c) poly(amidoxime) ligand

SEM Analysis

The SEM micrographs of the amidoxime ligand, before and after adsorption are shown in Fig. 4. The morphology of amidoxime ligand before adsorption (Fig. 3a) shows many pores on the surface which may be important for dyes adsorption. After adsorption, the ligand surface showed potential compaction resulting from the shrinkage of pore site that were available for adsorption. Subsequently, the observed changes can be linked to liquid bridging resulting from the uptake of pores by dye.

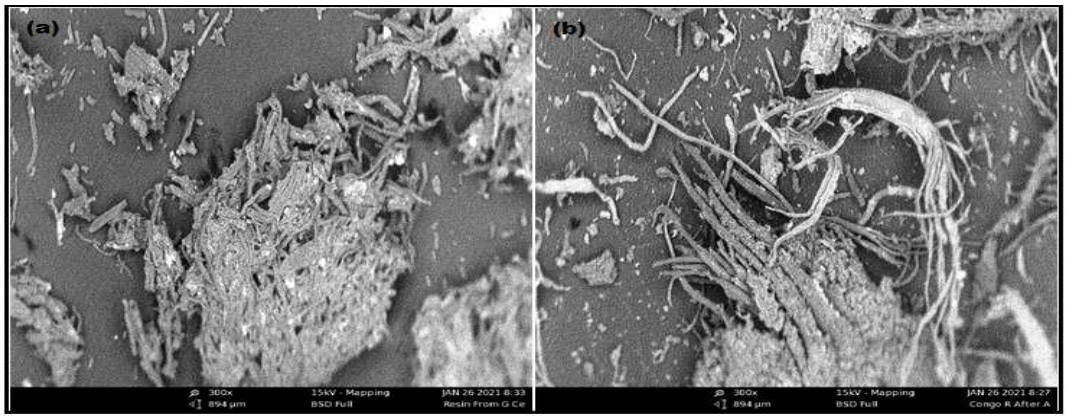

Fig. 4 SEM image of (a) poly(amidoxime) ligand, (b) poly(amidoxime) ligand after Congo red dye adsorption

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 Congo red (CR) dye is summarized in Table 1. 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 CR-dye = 0.9376). The final equation in terms of coded factor relating the removal efficiency and process parameters that are developed for CR-dye shown in equation 5 which indicate the model as quadratic model.

$$\% \text{ Removal (CR-dye)} = 94.89+1.12A+2.9B+1.1C+0.96AB+1.79AC-1.42BC-0.82A^2-3.24B^2-0.064C^2 \quad (5)$$

Table 1 the result obtained from CR-dye by amidoxime ligand

Std	Run	Factor 1	Factor 2	Factor 3	Response	
		A: Initial Concentration (mg/L)	B: Contact Time (Minutes)	C: Adsorbent Dosage (g)	Removal of CR-dye (%)	
					Exp. Value	Pred. value
1	13	20	15	0.1	86.7	86.98
2	6	100	15	0.1	84.7	83.71
3	14	20	15	0.5	93.34	93.7
4	3	100	15	0.5	94.64	94.29
5	4	20	75	0.1	88.6	88.45
6	5	100	75	0.1	93.2	92.34
7	10	20	75	0.5	89	89.48
8	16	100	75	0.5	98	97.22
9	9	8	45	0.3	93.3	92.06
10	20	130	45	0.3	93	94.34
11	17	60	45	0.05	85	86.21
12	8	60	45	0.6	91.91	91.96
13	2	60	6	0.3	93.1	93.35
14	18	60	95.45	0.3	96	96.56
15	1	60	45	0.3	92.7	94.89
16	15	60	45	0.3	96	94.89
17	11	60	45	0.3	95.9	94.89
18	12	60	45	0.3	95.9	94.89
19	19	60	45	0.3	94	94.89
20	7	60	45	0.3	95	94.89

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.

The ANOVA result of CR-dye is quadratic models which indicated that the models could be used to navigate the design space, according to the ANOVA the F-value of CR-dye is 16.69 which suggest the fitness of model. So, the significance of each model was evaluated using probability of error value P-value (prob>F). in Table 2 the value of (prob>F) is less than 0.0500 these indicated that the models are significant. (Garba *et al., 2016;* Bayuo *et al., 2020*). Also, it found that A, B, C, AB, AC, BC A^2 B^2 and C^2 are significant model terms for adsorption capacity of CR-dye using Amidoxime ligand.

According to the model F-value has significant effect on adsorption capacity, were the adsorbent dosage has the highest F-value of 57.57 which implies that they have the most significant influence on the adsorption capacity compared to initial concentration and contact time, (Bayuo *et al., 2020;* Ramakrishna, & Susmita, 2012). Also, in Table 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 (Basaleh *et al., 2019*). The high 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 adequate model the difference should not exceed 0.2. according to Table 2 the R^2 obtained is 0.9376 and the adj.-R^2 and pred.-R^2 has the difference of 0.1925 which confirm the 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 these study is high which is 14.659. These high adequacy precisions confirmed that the models are significant that can be used to navigate the design space.

Table 2 The ANOVA result for quadratic model, data analyzing and modeling of CR-dye

	Removal of CR-dye (%)				
Source	Mean Square	DF	F Value	p-value Prob > F	
Model	28.33	9	16.69	< 0.0001	significant
A-Initial Concentration	15.02	1	8.85	0.0139	
B-Contact Time	97.72	1	57.57	< 0.0001	
C-Adsorbent Dosage	14.54	1	8.57	0.0151	
AB	7.41	1	4.37	0.0632	
AC	25.56	1	15.06	0.0031	
BC	16.19	1	9.54	0.0115	
A^2	7.63	1	4.5	0.06	
B^2	87.04	1	51.28	< 0.0001	
C^2	0.044	1	0.026	0.8758	
Residual	1.7	10			
Lack of Fit	1.62	5	0.91	0.5382	Not significant
Pure Error	1.77	5			
Cor total	271.97	19			
		R^2(Adj)=0.8814	R^2(Pred.)= 0.6889		
Adeq.Precision=14.659	R^2= 0.9376				

Interpretation of 3-Dimentional Response Surface Plot (3D-Plot) and Contour Plot of CR-Dye

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 show the interaction between the variables which are significant as shown in Fig 4

Fig.4 shows the 3D and contour plot of CR-dye with the interaction between initial concentration and adsorbent dosage while contact time is constant at 45min at Fig. 4.5(a). Fig. 4.5(b) show interaction between initial concentration and contact time while adsorbent dosage is constant at 0.3 g and Fig. 4.5(c) show interaction between adsorbent dosage and contact time while initial concentration is constant at 60 mg/L. These show the evident from the Figures that removal of CR-dye increases when the adsorbent dosage increases and decreases when initial concentration increases. Also, removal attains its maximum value when the adsorbent dosage and contact time are at high value.

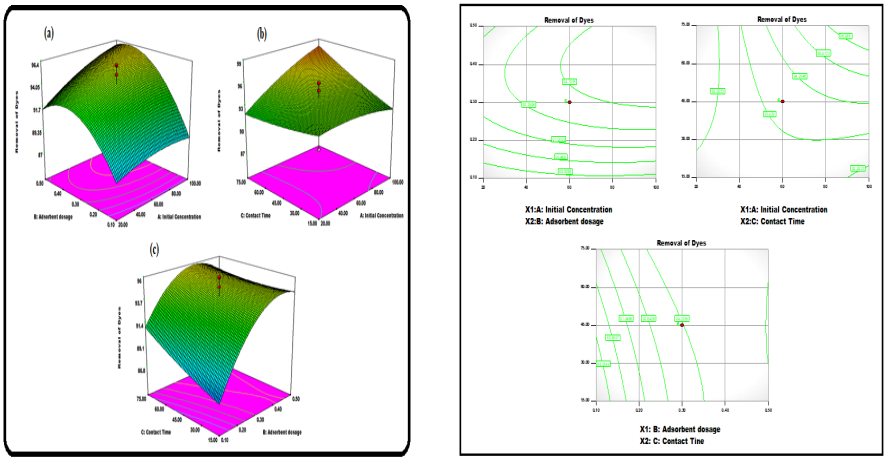

Fig. 5 3D-Plot and contour Plot of CR-Dye Removal

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 CR-dye 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 94.89 % removal for CR-dye as shown in exp. No. 17 of Table 1, which also confirm the 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 60 mg/L, Adsorbent dosage of 0.3 g and contact time of 45 min with the predicted response of 94.89 %. Therefore, percentage removal achieved in this study indicated that the quadratic model was valid in predicting the response.

Table 3: Constraints and optimum condition for removal of CR-dye

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight
A: Initial conc.	is in range	20	100	1	1
B: Contact time	is in range	15	75	1	1
C: Adsorbent dosage.	is in range	0.1	0.5	1	1
% Removal of CR-dye	Target= 100	93.75	96.03	1	1

CONCLUSION

In this study poly-amidoxime ligand have been synthesed from millet husk and used as adsorbent to investigate the removal of CR-dye from aqueous solution. The adsorbent characterized by FTIR, TGA and SEM. The FT-IR results showed that grafting was successful due to the presences of 2244cm^{-1} for cyno group (CN) and also band at 1640cm^{-1} and 1380cm^{-1} that replace 2244cm^{-1} which successful confirmed the synthesis of poly(amidoxime) functional group. The TGA shows the thermal degradation of all the peaks which occur in two stages where the weight loss observed. The SEM successfully showed a clear morphology of the absorbent before adsorption and after adsorption. The effect of initial concentration, adsorbent dosage and contact time have been studied from RSM. The optimum condition was found to be at initial concentration of 60 mg/L, adsorbent dosage of 0.3 g and contact time of 45 min with percentage removal of 95.9 % predictably and 94.89 % experimentally respectively. Thus, the adsorbent was best for removal of dyes. Finally, it can be concluded that, poly-amidoxime ligand can be efficiently used in treatment of waste water contaminated with dyes.

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