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Adsorption of Congo Red Dye from Aqueous Solutions by Wheat husk

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ABSTRACT

The Wheat husk is one of the common wastes abundantly available in the Middle East countries especially in Iraq. The present study aimed to evaluate the Wheat husk as low cost material, eco-friendly adsorbents for the removal of the carcinogenic dye (Congo red dye) from wastewater by investigate the effect of, at different conditions such as, pH(3-10), amount of adsorbents (1-2.3gm/L),and particle size (125-1000) µm, initial Congo red dye concentration(10, 25 , 50 and 75mg/l) by batch experiments. The results showed that the removal percentage of dye increased with increasing adsorbent dosage, and decreasing particle size. The maximum removal and uptake reached (91%) , 21.5mg/g, respectively for 25 initial concentration, pH 6.7 and 1.5 g/l Wheat husk dosage. The experimental data fitted well to Langmuir isotherm mode. The kinetic data support the assumptions of chemisorption were indicates a good fitting to the pseudo-second-order model.

Keywords: Congo red dye, Wheat husk , Batch sorption, Kinetic and Isotherm models

امتزاز صبغة الكونكو الحمراء من المحاليل المائية باستخدام قشور الحنطة

الخلاصة

تعد قشور القمح واحدة من النفايات الشائعة المتوفرة في دول الشرق الأوسط وخاصة في العراق وتهدف هذه الدراسة إلى تقييمها كمادة مازة منخفضة التكلفة و صديقة للبيئة لإزالة صبغة الكونغو الحمراء من المحاليل المائية بطريقة الدفعة ولقد تم دراسة تأثير ظروف مختلفة مثل الدالة الحامضية (3و 4و 5و 6و 8 و 10) وكمية المادة المازة (1و1.3و1.5و1.7)غم/لتر و حجم دقائق (125−1000)مايكروميتر وتركيز اولي للصبغة (10و 25 و50و75) ملغم/لتر وأظهرت النتائج أن نسبة إزالة الصبغة تزداد بزيادة كمية المادة المازة وانخفاض حجم الدقائق وبلغت أقصى

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كفاءة إزالة (91٪) وأقصى امتصاص لها (21.5 ملغم/ غم) عند تركيز اولي للصبغة (25 ملغم/ لتر) و دالة حامضية (6.7) و كمية القشور (1.5غم/لتر) كما تم التوصل الى ان الموديل (Langmuir) كان أفضل موديل رياضي يمثل النتائج العملية وكان موديل التفاعل الحركي من الدرجة الثانية افضل موديل يمثل النتائج العملية.

الكلمات الرئيسية : صبغة الكونكو الحمراء ، قشور الحنطة ، طريقة الدفعة ، الموديلات الرياضية والحركية

1. INTODUCTION

Environmental pollution due to speedy development of industries causes harmful effect in human health and ecosystem. The textile dyeing industries had generated a massive pollution problem because it is considered one of the most industries which used a wide range of dyes in their production. Consequently, it is the most polluting water sources, **Kant, 2012** .In general, dyes are classified into three categories: (a) anionic: direct, acid, and reactive dyes; (b) cationic: basic dyes; and (c) nonionic: disperse dyes. The chromophores in anionic and nonionic dyes mostly consist on azo groups or anthraquinone types**, Mishra and Tripathy, 1993**

Among different kinds of anionic dyes, Congo red (CR) (4-aminonaphthalene-1-sulphonic acid) is a benzidine-based anionic diazo dye, which generated by some industries, including textiles, printing and dyeing, paper, rubber and plastic industries. It toxic for many organism and is doubted carcinogen and mutagen dye, **Omidi et al.,2016** and thus its introduction to water stream are potential health, environmental, ecological concern. Therefore, CR containing effluents have to be efficiently treated before they are discharged into the water bodies or the environment.

Over the past few decades, several processes have been used for the removal of dyes from wastewater like biological (aerobic and anaerobic), chemical precipitation, coagulation/ flocculation, solvent extraction, membrane filtration, ion exchange, ozonation, electrochemical destruction and adsorption, **Kumar and Bilal, 2018**

The more efficient and simple method is the adsorption process as well as the availability of a wide range of adsorbents**, Rafatullah et al., 2010.** A number of studies had focused on biomaterials that are capable of removing Congo red dye from wastewater such as untreated sawdust**, Alam et al. ,2015 ;**tea waste**, Foroughi-Dahr et al.,2015** ; thorn apple leaf powder; and aloe vera leaves shell**, Khaniabadi et al., 2017.**.. etc.This work aims to examine the biosorption of CR dye from aqueous solution with Wheat husk biomass (WH) under an influence of various important parameters, such as pH, temperature, and initial concentration. In addition the isotherm of CR dye biosorption was investigated to understand the biosorption behavior of WH. The biosorption kinetics has investigated the develop and an understanding of controlling reaction pathways (e.g., chemisorption vs. physisorption).

2. MATERIALS AND METHODS

2.1Materials

Wheat husk as organic sorbent has been collected from one of the wheat fields in Wasit province. The foreign matter was removed manually and then washed the WH several times with tap water and distilled water to remove impurities and dirt. The washing material were crashed, sieved to obtain different grain sizes then 2hr. dried at 125 ºC in oven , allow to cool to room temperature and stored in stoppered bottle until use, as shown in **Fig.1**. simulated wastewater in this experiment prepared with the required dye concentration. All the chemicals used in this study were of analytical grade. The concentration of the dye was subsequently determined using Spectrophotometer (Advanced Microprocessor UV-VIS Spectrophotometer Single Beam LI-295). Addition of 1 mol/l of NaOH or HCl was used to adjust the initial pH of the working solution using a pH meter (WTW, inoLab 720, Germany).

Figure 1. Wheat husk (WH) before and after grinding.

2.2 Adsorbate

The Congo Red (CR) dye is a sodium salt of 3, 3-([1,1-biphenyl]-4,4-diyl)bis(4-aminonapthalene-1-sulfonic acid) used in the current study (Origin: Merck Company, Germany) ,with chemical formula¼$C_{32}H_{22}N_6Na_2O_6S_2$, and its molecular weight is 696.66 g/mol. Congo red dye is water soluble and reactive dye used in textiles and medicine,**Sharma et al.,2009** .The molecular structure of CR dye is illustrated in **Fig.2**.

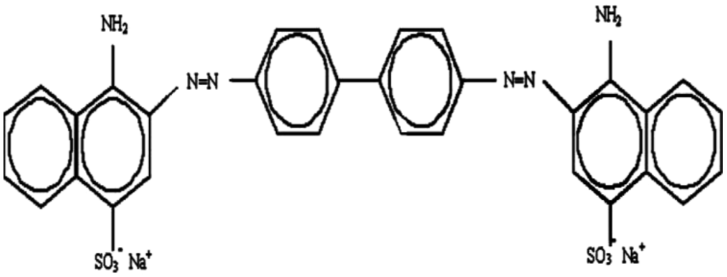

Figure 2. Molecular structure of CR dye, **Foroughi-Dahr et al., 2015.**

2.3 Experimental Work

2.3.1 Adsorption Experiments

Six conical flasks of 250 ml volume were filled with 200 ml of known concentration of dye solutions, pH of aqueous solutions in each flask was adjusted to the desired value. A known weight of WH was added into each flask, and then the flasks were placed on a shaker incubator and agitated continuously for desired time and at room temperature

(~30)ºC. The effect of different parameters pH(3, 4, 5, 6 ,8, and10), agitation speed (100, 200 and 300 rpm), sorbent dosage(1, 1.3 , 1.5, 1.7, 2 and 2.3g/l) ,contact time (10 , 20, 30, 60, 90, 120, 150, and 180 min), initial dye concentration (10, 25, 50 and 75ppm) and particle size of (125,250, 600and 1000µm) were studied , after each experiment, the samples were filtered using filter paper (WHATMAN, diameter 7 cm) and sample analyzed for remain dye content by using by Spectrophotometer (Advanced Microprocessor UV-VIS Spectrophotometer Single Beam LI-295).The dye adsorption percentage was calculated from the following equation:

$$\%\text{Adsorption}=\frac{C_o-C_e}{C_o}\times 100\% \qquad (1)$$

Where: C_o: dye concentration before adsorption ,and C_e: dye concentration after adsorption.

2.3.2 Fourier-Transform Infrared (FTIR)

FTIR spectral analysis an important in identify the characteristic functional groups in the surface of adsorbent, which is responsible for adsorption of dyes. The FTIR spectra of the wheat husks before and after sorption of CR dye from aqueous solution was examined us (SHIMADZU FTIR, 8000 series spectrophotometer) at Chemical Dept./Collage of Science/Baghdad University, Normally, the spectra are measured within the range of 400–4000 cm^{-1}.

2.3.3 Isotherm Model

The experiments for sorption isotherm for CR dye onto WH were investigated. The experiments were conducted in in 250 ml conical flasks have 200 ml of CR dye synthetic solution. The adsorbed amount is calculated by using Eq. (2):

$$q_e=\frac{V(C_O-C_e)}{m} \qquad (2)$$

Where:”q_e the (adsorption) capacity of equilibrium biosorption (mg/g); Co and Ce were the initial and equilibrium adsorbate concentrations in water (mg/l), respectively; V the volume of used solution (l); and(m) is the mass of used adsorbent (g).

The experimental isotherm data were fitted with the two well-known sorption isotherm model, namely, Langmuir and Freundlich models. The Langmuir model is the simplest theoretical model for monolayer sorption onto a surface and assumes that all of the sorption sites have equal adsorbate affinity **,Mohammed and Al-Musawi,2016; Sharker and Acharya, 2006** as can be seen in Eq.(3). The Freundlich isotherm model is used to uniform system in which the heat of sorption decreases in magnitude with an increased extent of sorption **,Kavitha and Namasivayam , 2007** as can be seen in Eq.(4). This model describes the ratio of the amount of solute that adsorbed into given mass of adsorbent in the concentration of solute in the solution.

$$\mathrm{q_e}=\frac{\mathrm{q_m bC_e}}{(1+\mathrm{bC_e})} \qquad (3)$$

Where: q_m : maximum sorption capacity, (mg/g); b the constant with the affinity of the binding site, (L/mg).

$$q_e = KC_e^{1/n} \tag{4}$$

Where: K constant indicative of the relative adsorption capacity of the adsorbent, $(mg/g)(L/mg)^{1/n}$, and 1/n: constant indicative of the intensity of the adsorption.

2.3.4 Kinetic Model

Kinetic model can been helpful to understand the mechanism of sorption and evaluate the performance of adsorbent, **Mohammed and Al-Musawi, 2016** Kinetic adsorption experiments were conducted in 250 ml volumetric flasks filled with 200 ml of 25 mg/L initial concentration CR dye then, 1 gram of WH was added to the flasks and the pH of solution was adjusted to the best value based on the pH study. The mixture was shaken at a constant speed of 200 rpm for 3 hours until equilibrium was achieved. During the adsorption, a sample was withdrawn at the preferred time intervals (10, 20, 30, 60, 90, 120, 150 and180 minute) filtered and analyzed .The biosorption capacity (qt mg/g) for each time interval was calculated using Eq. (2).The pseudo-first-order ,Eq.(5) and pseudo-second-order, Eq.6) kinetic model was used in this study. The parameters for each kinetic model were determined by fitting the equations to the experimental data by using Microsoft Excel.

$$\ln\left(q_{eq} - q_t\right) = \ln q_e - k_1 t \tag{5}$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}\right) \tag{6}$$

Where: q_{eq} :the amount of dye sorbed at equilibrium, (mg/g); k_1 is the equilibrium rate constant, (1/min) and k_2 is the rate constant of sorption, (g/mg.min).

3. RESULTS AND DISCUSSION

3.1 Fourier-Transform Infrared (FTIR) Analysis

The results of the FTIR spectrum showed that different functional groups were detected on the surface of the wheat husk. The broad peak detected in the spectra at 3347.35 cm^{-1} could be assigned to the hydroxyl and amides groups (–OH and –NH) which shows presence of phenols and alcohols. Functional groups were identified in **Table 1**.

3.2 Influence of pH

As the initial pH have direct influence in the dye and adsorbent in aqueous solution, so it plays an important role for adsorption process. **Fig.3** shows the results of pH ranged between 3 and 10 on the removal efficiency , it can be seen from the this figure that the color of CR in aqueous solution transport to deep blue at acid pH and different to red at alkaline pH(10) , but this red color is different from original red at the neutral pH . CR exists as anionic form basic pH (sulfonate groups) and cationic format acid pH. At pH 2 significantly high-electrostatic attraction exists between the positively charged surface of the adsorbent and anionic dye. The pH of system increases, number of negatively charged sites increase and the number of positive charged sites decreased .A negative charge surface site in the adsorbent does not favor the adsorption of dye anions due to the electrostatic repulsion. Also lower adsorption of CR at alkaline pH is due to the presence of excess OH ions competing with the dye anions for the adsorption sites ,**Kaur et al. , 2013)** , pH6.7 was chosen for the next experiments.

Table 1. Summary of functional groups for wheat husk before and after adsorption.

Assignment Functional Groups	Before adsorption	After adsorption of CR cm^{-1}
Hydroxyl group (-OH), amides (N-H stretch)	3458.13	3411.84
Carboxyl (C-H aldehyde stretch)	2925.81	2923.88
Amides (C=O aldehyde stretch)	1726.17	1731.96
Nitro aliphatic group ($-NO_2$)	1369.37	1365.51
Carboxyl (C-C ketone stretch), alcohol(C-O stretch), Phosphine oxide P=O, Alkyl halides (C-F stretch)	1161.07	1155.28
Alkyl halides (C-F stretch), Alcohol (C-O stretch)	1051.13	1041.49
Aromatic (C-H bend), sulfonate (S-O stretch), Phosphines (P-H bend)	900.70	904.55
alkyl halides [(C-Cl) stretch and (C-I) stretch]	570.69	528.46

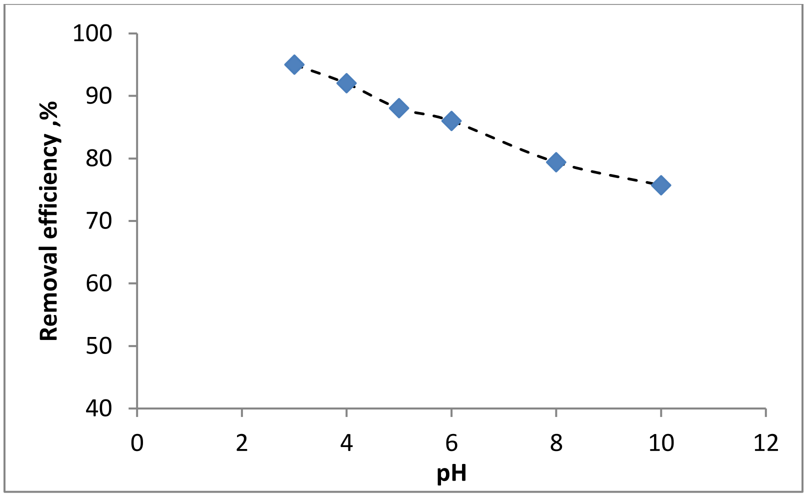

Figure 3. Effect of pH on the removal of CR dye by WH (C_o=25 mg/L; WH dosage=1 g/L; agitation speed =200rpm ; time=180 min).

3.3 The Contact Time and Dye Concentration

Fig.4 presents the effect of the initial dye concentration and contact time in the removal efficiency of CR dye, it can be seen from this figure that the removal efficiency of CR dye decreased from (90,88, 63and34) %, and the adsorption capacity increased (9.63, 21.5, 30.9 and 25.4mg/g)as the initial CR dye concentration increased from (10, 25,50 and75) mg/L, respectively due to reduced surface area and saturated the active sites ,**Omran et al. , 2016.** It is also apparent from that figure that by increasing the contact time, the amount of adsorbed dye increased till it reached equilibrium state .The adsorption process was rapid for the first stage of the adsorption, and subsequently the adsorption rate slowed down for all the initial concentrations, gradually approaching equilibrium, the equilibrium time took 90 min, for the adsorption of CR dye on WH, with increasing in contact time, the vacant sites were filled by CR. Thus, adsorption capacity gradually increased**, Khaniabadi et al.,2017**.

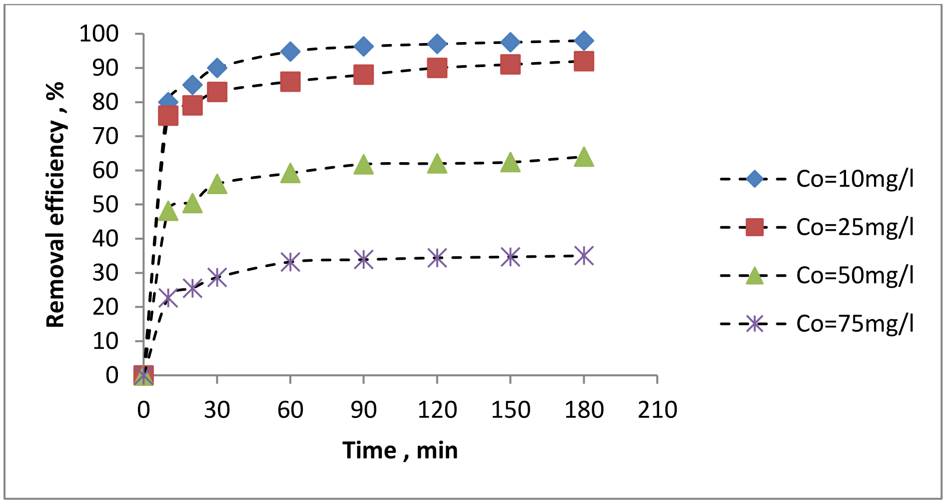

Figure 4. Effect of initial concentration and contact time on the removal of CR dye by WH (pH=6.7; WH dosage=1 g/L; agitation speed =200rpm; time=180 min).

3.4 Influence of Wheat Husk Dosage

The effect of WH dosage on the removal of dye was studied using 1-2.3 g/l wheat husk dosage while keeping other parameters constant, 25 mg/l of CR dye concentration at shaking speed of 200 rpm at pH 6.7 for 90 min. The results plotted in **Fig.5**, this figure indicate that the retention of CR dye increases with increase amount of sorbent up to 150 mg/l. A further increase in sorbent dosage has a small or limited increase in the removal efficiency. The increase in sorption with sorbent dose can be attributed to increased sorbent surface area and hence the number of binding sites available, but the amount adsorbed on unit mass of the adsorbent decreases consider. The decrease of unit adsorption with increase dose of adsorbent due to the adsorption sites remaining unsaturated during the adsorption process**, Han et al., 2007.**

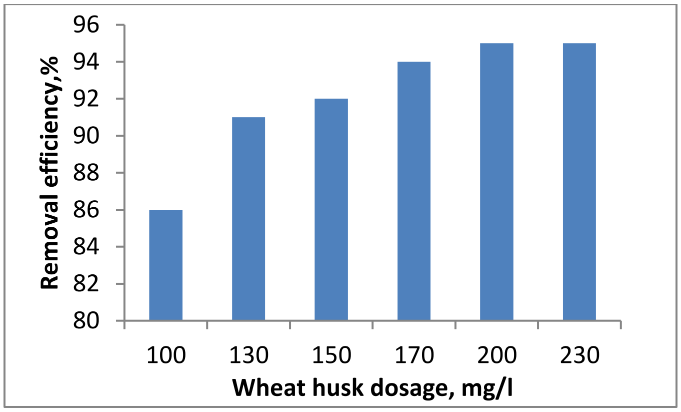

Figure 5. Effect of WH dosage on the removal of CR dye (C_o=25 mg/L; pH=6.7; agitation speed =200 rpm; time=90 min).

3.5 Influence of Agitation Speed

The effect of different agitation speed (100, 200and 300) rpm on the removal efficiency of CR dye was investigated and their results were plotted in Figure 6 while keeping other parameters constant from previous experiments. **Fig.6** shows that the removal efficiency of dye increased with increasing of agitation speed from 100 to 200 rpm and further increases have no significant effect (i.e., above 200 rpm), this may be due to increasing turbulence led to increasing removal efficiency and as a consequence decreased the film resistance to mass transfer surrounding the adsorbent particles**, Shaikh et al., 2011**. Moreover, these results indicate that agitation speed of 200 rpm is sufficient to obtain maximum removal by reducing the boundary layer thickness to a minimum value.

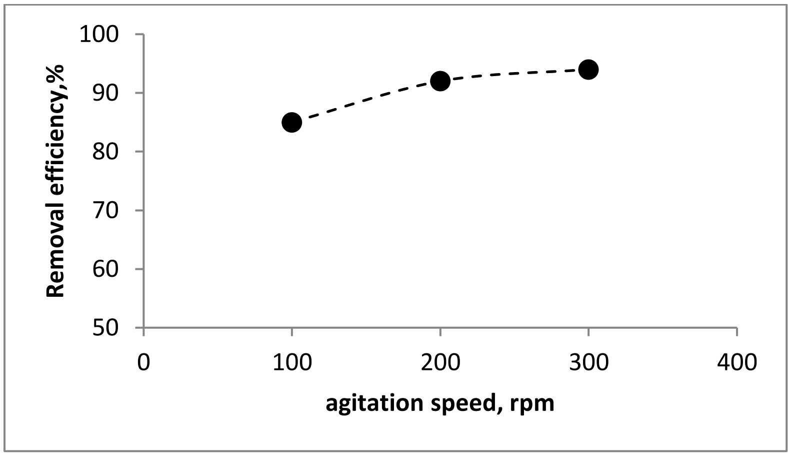

Figure 6. Agitation speed effect on removal of CR by WH (pH=6.7,C_o=25 mg/L, dosage=1.5g/L, time=90 min.)

3.6 Optimization of Particle Size

Effect of different particle size(125,250,600 and1000µm) was investigated while kept other parameters constant for previous experiments as can be seen in **Fig.7**, can see in this figure that the removal efficiency decrease with increasing particle size. This is because of the decrease in specific surface area of the biosorbent with an increase in the particle size of the biosorbent, **Kumar and Bilal, 2018.**

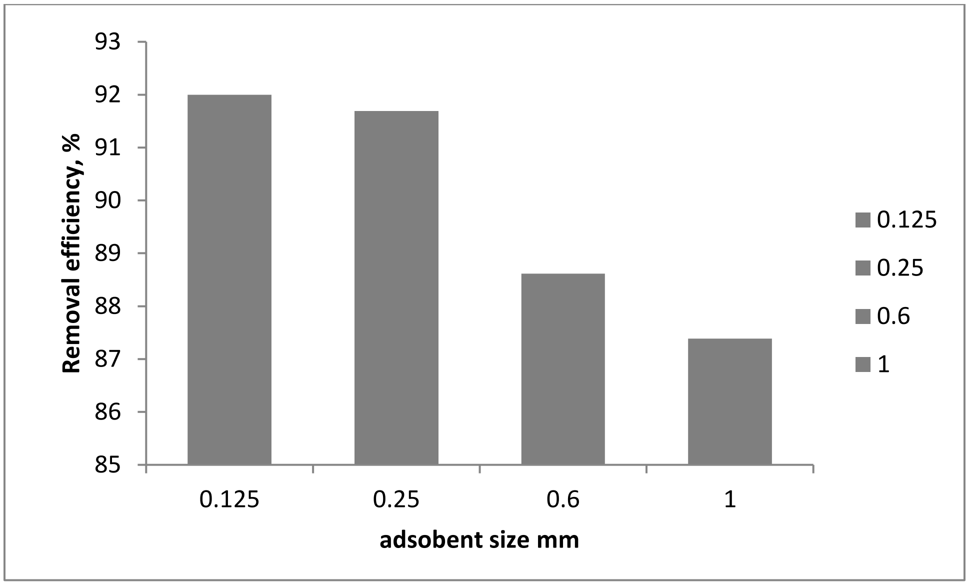

Figure 7. Effect of particle size on removal of CR by WH (C_o=25 mg/L; pH=6.7; dosage=1.5g/L; time=90 min; agitation speed=200 rpm)

3.7 Isotherm Models

The analysis of sorption process by models of isotherm is an important to establish the relationship between the amount of adsorbate adsorbed by the unit mass of adsorbent and equilibrium concentrations at constant temperature. The parameters for Langmuir and Freundlich, model were obtained by fitting the experimental data to the equations using Microsoft Excel are present in **Fig.8** and tabulated with correlation coefficient in **Table 2.** It can be seen from that Table, depending on the value of coefficient of determination (R^2) Langmuir model described the sorption data better than Freundlich model.

Table2. Isotherm constants for CR onto WH

Langmuir		**Freundlich**	
Parameters	**CR**	**Parameters**	**CR**
b (l/mg)	0.3558	K_f,(mg/g)(L/mg)$^{1/n}$	0.8313
q_m (mg/g)	38.61	n	1.5574
R^2	0.976	R^2	0.942

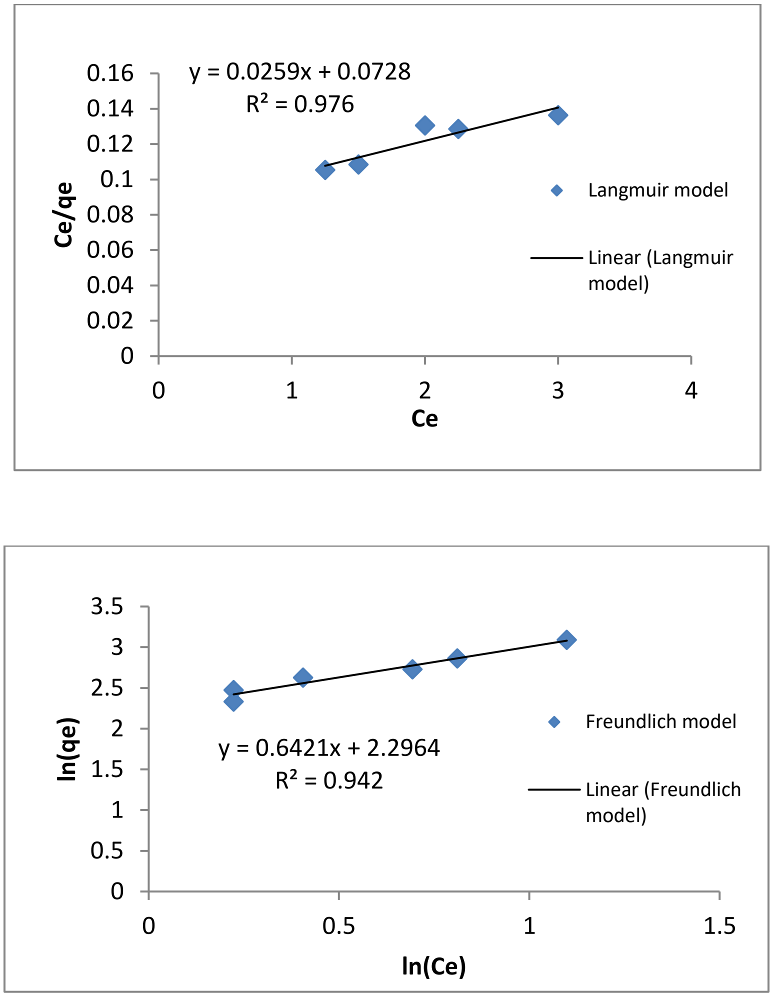

Figure 8.Sorption isotherm models for CR dye onto WH.

3.8 Sorption Kinetic Models

The kinetics of CR dye sorption onto wheat husk was analyzed used pseudo-first-order, pseudo-second-order as shown in **Fig.9** and the constants of these models are listed in **Table 3**. It is clear that the two models are able to explain the relationships between the experimental and predicted values .However, pseudo-second order model for sorption gave a better fit based on the values of R^2. This indicated that the sorption process was chemisorption **,Klimmek et al., 2001.**

Table 3. Comparison of sorption rate constants, experimental and calculated q_e values for the reaction kinetics for CR dye sorbed onto WH

.

Pseudo-first-order			**Pseudo-second-order**		
k_1 1/min	**q_e calculated** mg/g	**R^2**	**k_2**g/mg. min	**q_e calculated** mg/g	**R^2**
0.0558	0.64846	0.9098	0.015515	22.17295	0.9993

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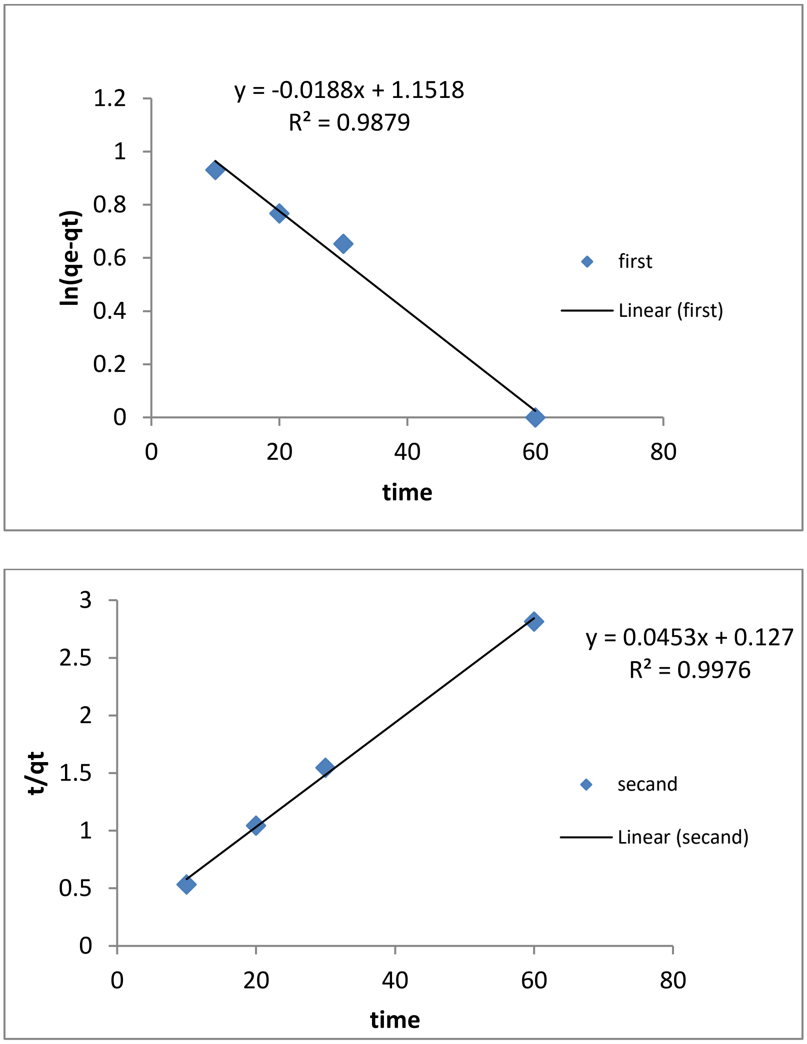

Figure 9. kinetic model for sorption of CR on wheat husk

4. CONCLUSION

This study showed that the Wheat husk is considered as a low cost natural sorbent for the removal of Congo red from aqueous solutions. A contact time of 90 min is quite sufficient for the sorption experiments .It was found that the amount of adsorbed dye increased with the initial CR concentration decreasing and contact time but the removal percentage is decreased. The experimental data best fitted with the langmuir isotherm, with a maximum adsorption capacity of 21.5 mg/g. The kinetics of process for the removal of CR dye was analyzed by pseudo first and second order kinetic model and observed that removal process is governed by pseudo second order kinetic model.

NOMENCLATURE

C_o	Initial dye concentration	Mg/l
C_e	Final dye concentration	Mg/l
FTIR	Fourier Transformation Infrared	
K_1	First-order rate constant of kinetic adsorption	Min^{-1}
K_2	Second-order rate constant of kinetic adsorption	g/mg.min
q_e	Equilibrium dye uptake	mg/g
q_t	Dye uptake at time t	mg/g
T	Temperature	°C

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