Investigation on using rice–husk as low cost adsorbent for dye removal from industrial wastewater

Prof. Dr. Dakhil Nasir Taha
Department of Chemistry
College of Science

Asst. Lec. Luma Ahmed Mohammed
Department of Chemistry
College of Science

Lec. Isra'a Sadi Samaka
Department of Environmental Engineering
College of Engineering

Abstract

This study investigated the use of activated rice- husk as adsorbent for the removal of Janus Green B dye from industrial wastewater.

Adsorption studies were carried out in a batch process with adsorbent dose , contact time , pH , initial dye concentration and adsorbents' particle size at ambient temperature . The well Known Langmuir and Freundlich isotherm models were applied for the equilibrium adsorption data and the various isotherm parameters were evaluated .

The results indicate that activated rice – husk could be employed as a low cost alternative to commercial activated carbon in wastewater treatment for the removal of colour and dyes .

Keywords : adsorption , rice-husk , isotherm model

الخلاصـــــة

تتحرى هذه الدراسة استخدام قشور الرز المنشطة كمادة مازة لإزالة صبغة Janus Green B من مياه الفضلات الصناعية.

تم إجراء تجارب دفعية (batch) لدراسات الإمتزاز لدراسة تأثير جرعة المادة المازة , زمن التلامس , pH , التركيز الأولي للصبغة , وحجم الحبيبية للمادة المازة في درجة حرارة المحيط .

تم تطبيق نموذجي لانكمير وفراندلش لوصف علاقات التوازن للإمتزاز . بينت النتائج إن قشور الرز المنشطة يمكن استخدامها كمادة رخيصة وبديلة عن الكاربون المنشط التجاري في معالجة مياه الفضلات لإزالة اللون والأصباغ .

1. Introduction

The disposal of dyes laden wastewater poses one of the industry's major problems because such effluents contain a number of contaminants including acid or caustic , dissolved and suspended solids , toxic compounds and coloring pigments .

Out of all these contaminants, exposure to the dye has been known to cause an allergic reaction (and possibly anaphylactic shock). The removal of dyes from industrial waste before they are discharged into the water bodies is therefore very important from health and hygiene point of view and for environmental protection[1].

Different treatment methods are described in the literature, including filtration, flocculation, chemical precipitation, ion exchange, membrane separation and adsorption [2].

Among these methods, adsorption has been proven to be more efficient, offering advantages over conventional processes [3] .The most commonly used adsorbent is activated carbon, but it is relatively expressive and difficult to regenerate. This has led to search for cheaper and simplest substituents.

New approaches based on the use of natural, inexpensive adsorbent materials for effluent treatment have been reported [4-9].

The objective of this work has been to evaluate the efficiency of removal of Janus Green B dye from industrial wastewater using rice husk, the waste product.

2.Experimental

2.1 Material and Methods

2.1.1 Adsorbent

The sorbent used in this study was activated carbon produced from rice husk (ARH)

Rice husk (RH) , an undesirable agriculture mass residue in Iraq , is a by – product of local rice milling industry. It is one of the most important agricultural residues in quantity. It represents about 20% of the whole rice product, on weight basis of the whole rice [10] .

Initially, rice husk was washed several times with thoroughly with tap water until al yellow color caused by lignin was completely removed, and then a final wash with distilled water was carried out.

The production of activated carbon consisted of carbonization and activation of the respective rice husk.

The carbonization was selected based on the previous trials of different heating durations. From the various experimental trials performed , it was observed that when the degree of heating and duration was raised the rice husk was completely carbonized to ash .

Then, the produced activated carbon was kept in a desiccators .The main constituents of rice husk are: 64-74% volatile matter and 12-16% fixed carbon and 15-20% ash [10,11]. The rice husk composition are: 32.24% cellulose, 21.34% hemicellulose,21.44% Lignin, 1.82% extractives, 8.11% water and 15.05% mineral ash [12-14] . The mineral ash is 94.5-96.34 % SiO_2 .

2.1.2 Adsorbate

Janus Green B (JGB) dye [Synonyms : 3- diethylamino -7-(4-dimethylaminophenylazo)-5-phenyl-phenazinium chloride , 3- (diethylamino)-7-((p-(dimethylamino)phenyl)azo)-5-phenylphenazinium chloride . The chemical structure of dye used in this study is described in Figure(1).

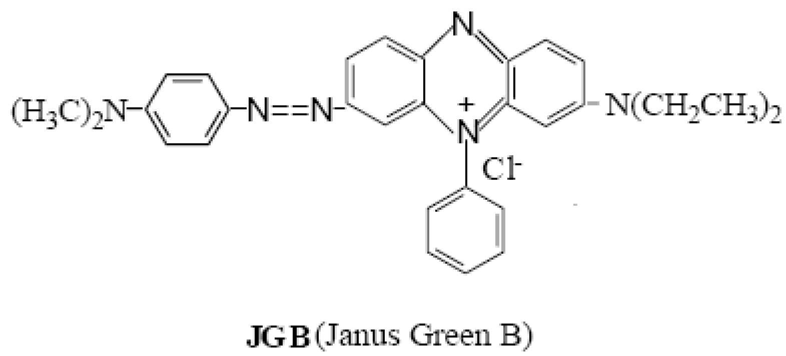

Fig.(1): The chemical structure of Janus Green B dye studied in this work

The physiochemical properties of the JGB dye can be shown by Table (1)

Table (1): Physiochemical properties of Janus Green B

Parameter	Value
Molecular formula	$C_{30}H_{31}N_6Cl$
Molecular weight	511.07g/mol
C.I. Name	11050
Absorption maxima	611nm
Nature	Cationic dye

An accurately weighed quantity of the dye was dissolved in distilled water to prepare a stock solution (1000 mg /L) which was later diluted to required concentrations. Calibration curves were constructed for each dilution and pH separately. The pH of each solution was adjusted with (0.1 M) HNO_3 or NaOH using pH meter to its effective adsorption pH valve .

For absorbance measurements a UV-VIS Spectrophotometer (UV/VIS -1650 PC SHIMATZU) was employed.

The maximum wavelength $\lambda_{max.}$ for JGB was measured at 611 nm.

Concentrations during experimental work were determined from a standard calibration curve.

2.2 Adsorption studies

Adsorption studies were performed using a batch method in which a series of conical flask with capacity of 250 ml filled with 100 ml of JGB solution at room temperature.
Different parameters such as adsorbent dosage, contact time, pH , initial dye concentration ,particle size of adsorbent ,and adsorption isotherm study were investigated under different conditions .

All samples were agitated by a rotary shaker at constant agitation. After shaking the flasks for predetermined time intervals, samples were filtered and analyzed.

All experiments were carried out in triplicate with respect to each condition and mean values were used for further calculations.

The adsorption behaviors of the samples were studied by evaluating the percentage removal efficiency of JGB from the relation

Removal efficiency (%) $=\frac{C_o - Ce}{C_o}$ *100% …………….(1)

Where C_o is the initial concentration of JGB, C_e is the solution concentration after adsorption at any time. Equilibrium studies give the capacity of the adsorbent [15].

The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms , usually the ratio between amount of solute adsorbed per unit amount of adsorbent (solid phase concentration) and concentration of solute in solution at a fixed temperature at equilibrium .

The amount of dye adsorbed onto the activated rice husk (at equilibrium) q_e (mg/g) was calculated according to the following mass balance equation.

$$q_e = \frac{V}{W}(C_o - Ce) \quad \text{……………………………………(2)}$$

Where C_0 and C_e are the initial and equilibrium concentrations mg/L of dye, respectively, V is the volume of the solution (L) , and W is the weight (g) of the activated rice husk used (adsorbent).

2.2.1 Effect of adsorbent dose

To optimize the adsorbent dose of the removal of JGB from its aqueous solutions, adsorption was carried out with different adsorbent dosages. The dose of adsorbent was varied from 0.5 to 2 g/100 ml of dye solution for ARH at fixed pH , temperate , adsorbate concentration, and particle size of adsorbent . Samples were shaking with a fixed time interval, filtered and analyzed for residual dye.

2.2.2 Effect of contact time

This experiment was done to determine the equilibrium time for the adsorption.

To perform this experiment, different mixing time ranging from 20 to 100 minute. The adsorbent dose used was obtained from the best valve received from previous experiment. Other factors were fixed as mentored later.

2.2.3 Effect of pH

To determine the optimum pH conditions for the adsorption of JGB , the effect of pH was observed over the entire pH range (4 -12) with optimum contact time and adsorbent dosage which result from previous experiments with fixed other factors .

2.2.4 Effect of initial dye concentration

These studies were performed by changing the initial dye concentration in the range of (10–100 mg/L) with optimum conditions received from previous experiments with fixed other factors.

2.2.5 Effect of adsorbents particle size

The variation of the rate of adsorption of the substrate with different particle size of adsorbent is another method that is useful for the characterization of the rate – limiting mechanism of a particular system.

In present investigations different particle sizes of adsorbent ranged from 50 to 1000µm were taken at the optimum conditions received from previous experiments.

2.2.6 Adsorption isotherm studies

For adsorption isotherm studies , 100 ml dye solutions of different concentration with increments of 10 mg/L [10 , 20,---------100 mg/L] were equilibrated for specific period of time (equilibrium point) with 1.5 gm and 500 µm particle size of ARH in stoppered conical flasks .

At equilibrium point, the supernatant liquid was removed immediately and the dye concentration evaluated by measuring the absorbance.

2.2.6.1Adesorption isotherm models

Langmuir model

The Langmuir isotherm is valid for monolayer a adsorption onto a surface containing a finite number of identical sites .

The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface.

Based upon these assumptions, Langmuir represented the following equation [16]

$$q_e = \frac{q_m K_a C_e}{1+K_a C_e} \quad \text{……………………...................................(3)}$$

Langmuir adsorption parameters are determined by transforming the Langmuir equation , which is in linear form by the plot between C_e/q_e versus C_e (Eq.4) entire the concentration range .

$\frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{Ka\ qm}$……………………………………(4)

q_e : is the amount of JGB adsorbed in mg/g of the adsorbent
C_e : is the concentration of the dye solution at equilibrium (mg/l) .
q_m and K_a : are Langmuir constants related to the maximum adsorption capacity (mg/g) and the adsorption energy between the adsorbate and adsorbent (L/mg)

The values of q_m and K_a were determined from the slope and intercept of the linear plot.

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L , which is a dimensionless constant referred to as separation factor or equilibrium parameter [17].

$R_L = 1/(1 + bC_o)$ ……………………………………………(5)

Where C_0 is the initial concentration and b is the constant related to the energy of adsorption (Langmuir constant) .
The values of R_L indicate the nature of the isotherm.

Values of RL	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Freundlich model

The Freundlich isotherm model is an empirical equation employed effectively to study the heterogeneity and surface energies [18].

The most common shape of the graph of amount of dye adsorbed per unit weight of adsorbent versus the concentration in the fluid in equilibrium is these data often fit nicely the empirical equation proposed by Freundlich:

$q_e = K_F C_e^{1/n}$…………………………………………………(6)

Where, K_F and n are , Freundlich constants ; q_e = weight adsorbed per unit weight of adsorbent ; C_e = concentration of dye at equilibrium.

Taking logs and rearranging this equation to get the linear form of the Freundlich isotherm as shown below:

$\text{Log } q_e = \log K_F + 1/n \log C_e$ …………………………………..(7)

The constant K_F is an approximate indicator of adsorption capacity ((mg/g) (L/mg)$^{1/n}$) , while 1/n is a function of the strength of adsorption respectively in the adsorption process .

The values of K_F and n can be obtained from the plate of log q_e versus log C_e and they equal to the intercept and slop of the plot respectively.

3. Results and Discussion

3.1 Effect of adsorbent dosage

The effect of adsorbent dosage is illustrated in figure (2 a- b) . It was found that the percentage of dye removal was increased from 68% to 100 % as the adsorbent dosage increased from 0.5 to 2 g 100 ml^{-1} after the equilibrium time. This is due to increased in adsorbent dosage attributed to increase in surface area and availability of more adsorption sites.

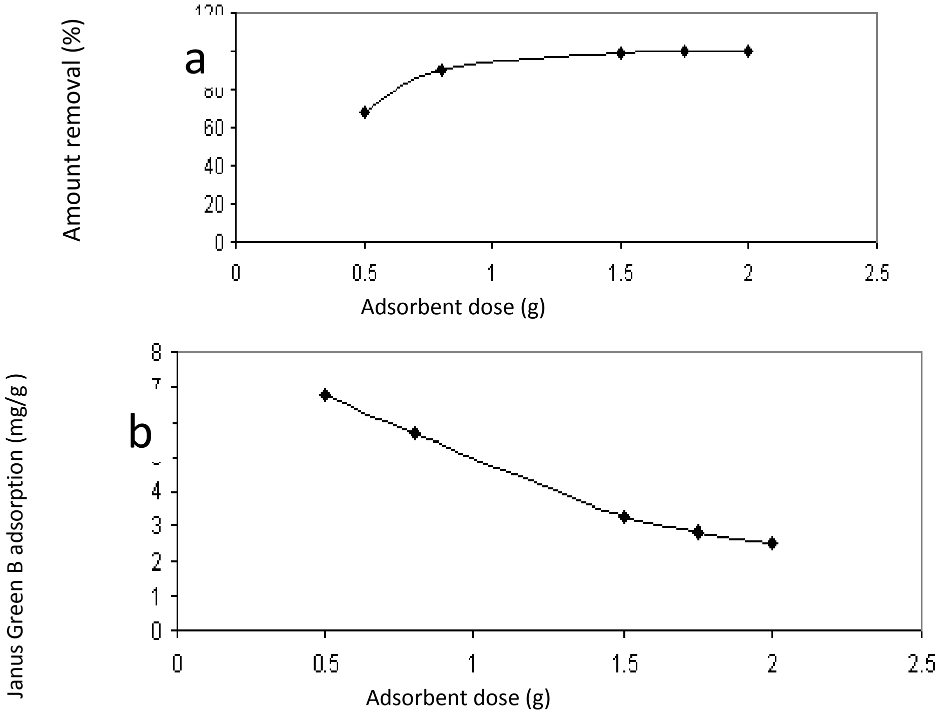

Fig.(2) : Adsorption of Janus Green B by activated rice husk as a function of adsorbent dosage at initial concentration of 50 mg/l and 500µm particle size
(a) Percentage uptake
(b) Amount of dye adsorbed (mg/g).

Similar results have been reported by various authors using low cost adsorbents [19-22] .
However, the amount of JGB adsorbed per unit weight of adsorbent decrease with increase in adsorbent dosage.
Increasing the dosage and keeping the dye concentration constant makes along number of sites available for a fixed concentration of sorbate, hence the reduction in the value of q_e [23] .

The drop in adsorption capacity is basically due to sites remaining unsaturated during the adsorption process [24,25]. Similar observation was departed by [26-28] .
By this study, it was observed that the economical dose with good removal occur at the dose of 1.5 g/100 ml for activated rice husk (ARH) and that is 98.5%.

3.2 Effect of contact time

Figure (3) explains the effect of contact time. It is clear that the extent of adsorption is rapid in the initial stages (20 min.)and the adsorption of the dye increases with increasing contact time and becomes slow till saturation is reached . The final concentration of JGB did not significantly after 30 min. This shows that equilibrium time occur at 30 min. It is due to saturation of active sites which do not allow further adsorption to take place . Similar results for different ionic dyes . were reported by [8,22,27,29].

The curve is single , smooth and continuous leading to saturation , suggesting the possible monolayer coverage of JGB dye on the surface of the adsorbent [30-32].

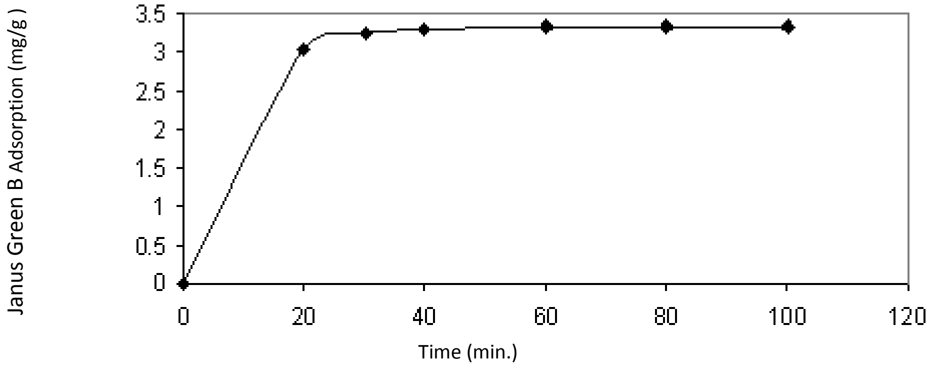

Fig.(3) : Effect of contact time for adsorption of Janus Green B onto activated rice husk at initial dye concentration of 50 mg/l, adsorbent dose of 1.5g, and particle size of 500µm

3.3 Effect of pH

The results obtained are presented in Figure(4 a-b) . which describes that there was no significant change in the percentage removal or dye uptake over the entire pH range of (4-12) .Biosorption of Janus Green B by phosphoric acid carbonized agro- industrial waste was reported to be unaffected by pH in the range of (4 -12) [33] .

Other studies for different ionic dyes were also found to be independent of pH [26,34] . This indicates there is such a strong interaction between the dye and ARH that nighters H^+ nor OH^- ions could influence the adsorption capacity. In other words, the adsorption of Janus Green B dye on ARH does not involve an ion – exchange mechanism.

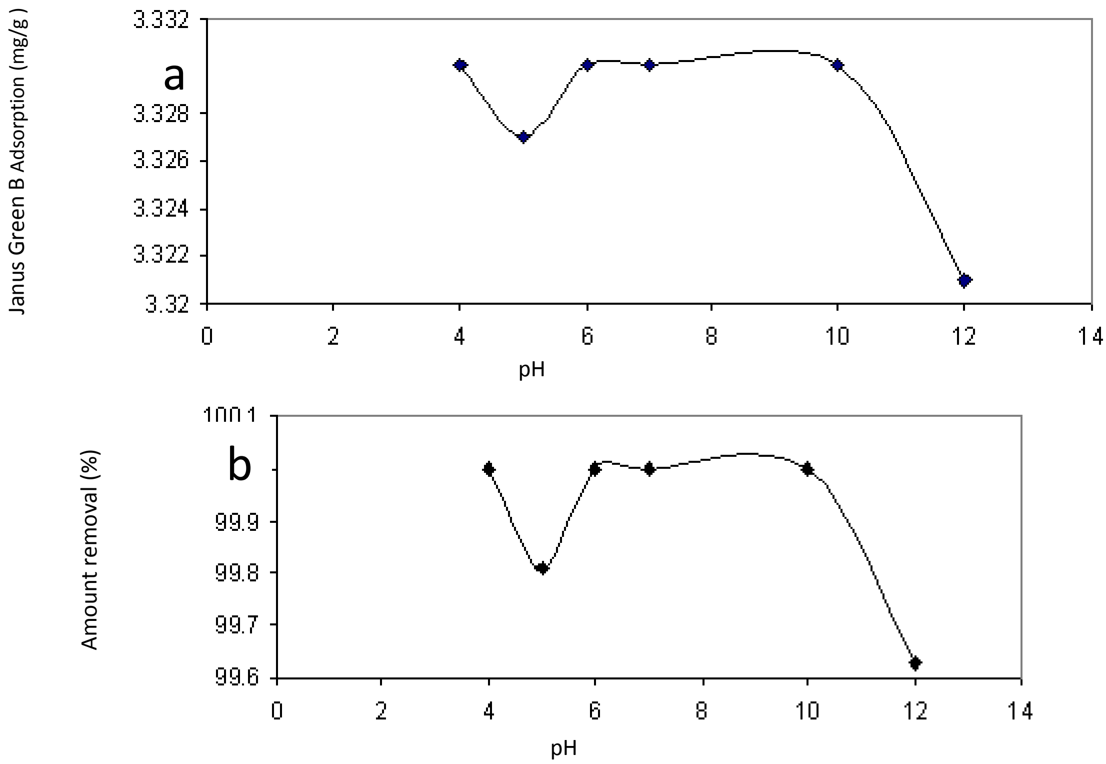

Fig.(4) : Adsorption of Janus Green B by activated rice husk as a function of solution pH at initial concentration of 50 mg/l and adsorbent dosage of 1.5g with 500µm particle size

(a) Amount of dye adsorbed(mg/g)

(b) Percentage uptake

(5) .

It can be seen that the adsorption capacity increased from 0.67 to 5.7 mg/g as the initial concentration varied from 10 to 100 mg/L .

The concentration provides an important driving to overcome all mass transfer resistance of the dye between the aqueous and solid phases[35] .A similar results were observed by [6,7,22,27].

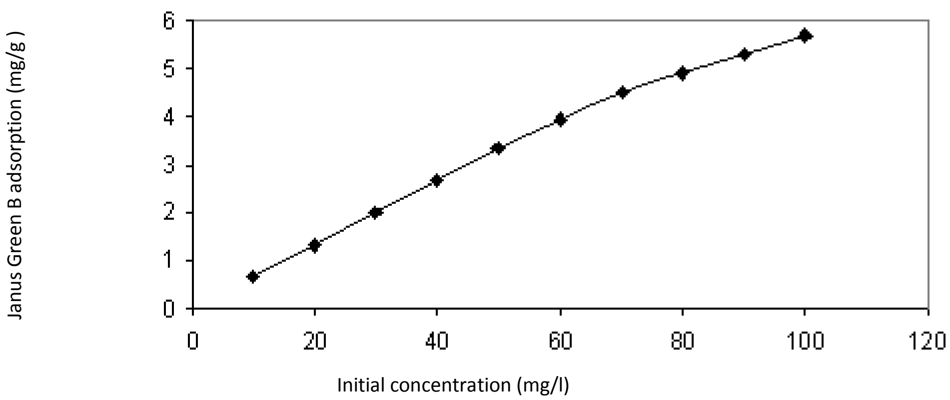

Fig.(5) : Effect of initial concentration on adsorption capacity of Janus Green B onto activated rice husk (500µm particle size and 1.5g adsorbent dose)

On the other hand, at a given constant adsorbent dosage , the percentage of dye removal decrease with increase in initial concentration of dye solution may be due to lack of adsorbent surface are and the available sites for adsorption becomes fewer for adsorption [36]. Also the formation of second layer of the dye molecules is highly hindered at higher initial concentration of the dye , due to the repulsive interaction between adsorbed and unabsorbed dye molecules present on the solid surface and in solution , respectively [37].

5.5 Effect of particle size of adsorbent

The results of this investigation are shown in Figure (6) . It can be seen that the percentage removal of JGB increase with decreasing particle size of the sorbent .

This indicate that the smaller the ARH particle size for a given mass of ARH , the more surface area is available and as a consequence the greater the number of binding sites available [30,38,39]. Adsorption capacity at 1000µm is lower than at other sizes between (50 -500) µm.

Then higher adsorption capacity obtained at any size smaller than 1000 µm.

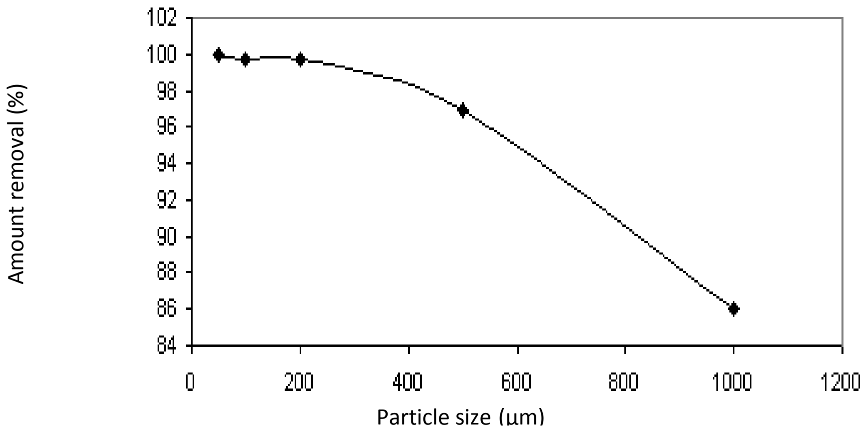

Fig.(6) : Effect of particle size on adsorption capacity of janus Green B onto activated rice husk at initial dye concentration of 50 mg/l and adsorbent dose of 1.5g

5.6 Isothermal analysis

In this study, the equilibrium data for JGB onto ARH were modeled with the Langmuir and Freundlich models.

By using SPSS (V.15) program for statistical analysis of the experimental results , the obtained coefficients and constants , significance , correlation coefficient (R) , determination coefficient (R^2) and standard error of the estimate (S.E.) from linear regression (least squares method) of Langmuir and Freundlich are presented in Table (2) .

Table (2) : Adsorption isotherm parameters for Janus Green B removal

Langmuir (95% Confidence level)		Freundlich (95% Confidence level)	
q_m (mg/g)	5.88	K_F(mg/g)(l/mg)$^{1/n}$	3.54
K_a (l/mg)	4.25	1/n	0.22
R^2	0.9960	R^2	0.9341
Standard error of estimate(S.E.)	0.062	Standard error of estimate(S.E.)	0.081
R_L	(0.0023-0.0229)		

The plots of liberalized form of Langmuir and Freundlich are shown in figure(7a-b) . The Langmuir equilibrium adsorption curves relating solid and liquid phase concentration of JGB at equilibrium are given as:

$q_e = 25C_e /(1+4.25C_e)$ ……………………………….(8)

But, the Freundlich equilibrium adsorption curves relating solid and liquid phase concentration of JGB at equilibrium are given as:-

$q_e = 3.54Ce^{0.22}$ ………………………………………(9)

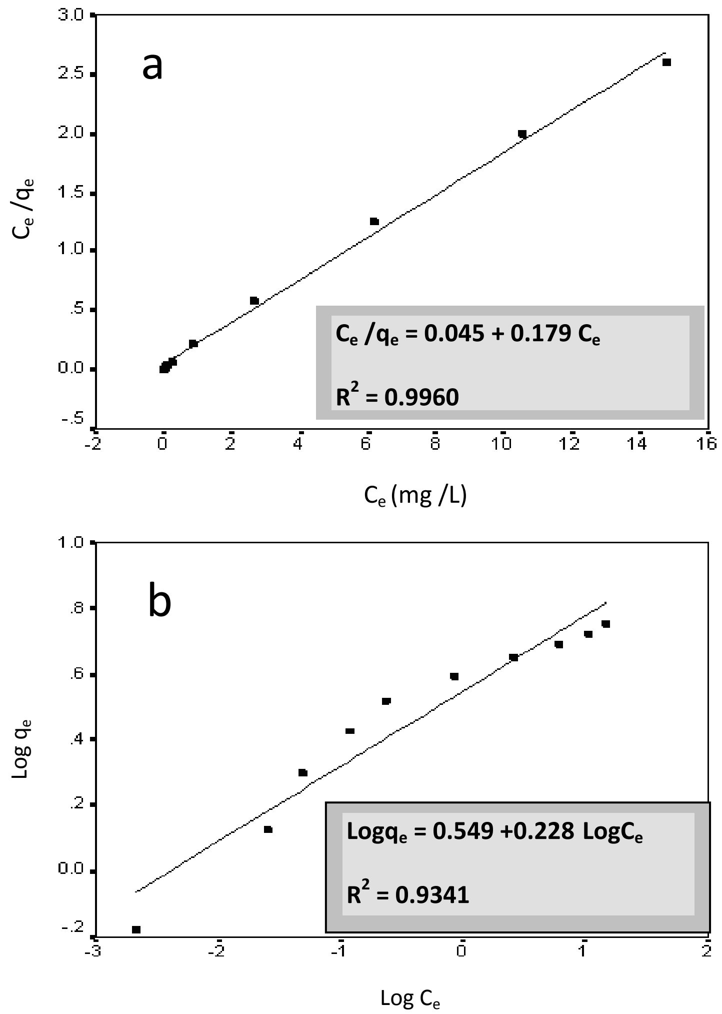

Fig.(7): Linearized adsorption isotherm model of Janus Green B onto activated rice husk
(a) Langmuir model
(b) Freundlich model

By the Langmuir isotherm, the monolayer adsorption capacity of activated rice husk (q_m) was found to be 5.88 mg/g .

The well fitting of data with Langmuir isotherm indicates to the homogenous distribution of active sites on the adsorbent surface [40].

The variation of separation factor (R_L) with initial JGB concentration is shown in Figure 8. The (R_L) values for the adsorption of JGB onto ARH are observed to be in the range of 0 - 1 ,indicating that the adsorption was favorable process [25,41,42].

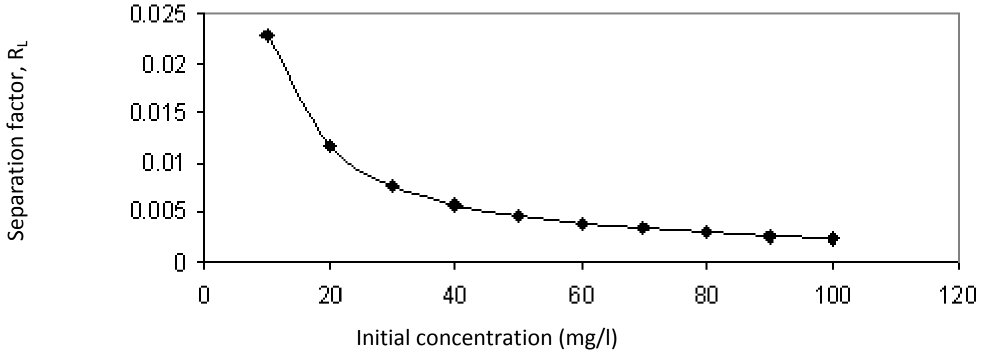

Fig.(8) : Separation factor versus initial Janus Green B concentration onto activated rice husk

From Freurdlich isotherm, the magnitude of Freundlich constant indicates easy uptake of Janus Green B from aqueous solution. The 1/n value, the Freundlich parameter, is a measure of the adsorption intensity or surface heterogeneity, it is becoming more heterogeneous as its value gets closer to zero . A value of 1/n below one indicates a normal Freundlich isotherm while 1/n above one indicative of cooperative adsorption [7].

Figure (9) shows the deviation of these models from the experimental data . It appears that the adsorption of Janus Green B dye on activated rice husk could be well fitted by the two isotherms .clearly , the Langmuir equation provided better fitting in terms of R^2 and S.E. values.

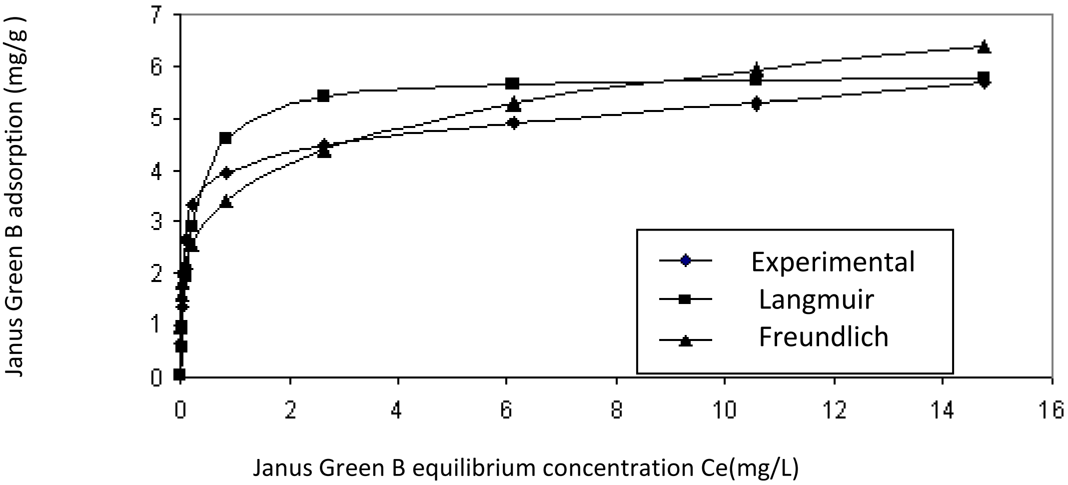

Fig.(9): Comparison of experimental and calculated data by Langmuir and Freundlich equilibrium isotherms for the system Janus Green B-activated rice husk

This results indicate homogenous nature of ARH surface , which means each Janus Green B molecule on ARH has equal adsorption activation energy[7]. The results also demonstrate the formation of monolayer coverage of JGB molecule at the outer surface of ARH.

4. Conclusions

The results obtained from the present investigation reveal that:

■ The rice husk which is easily and abundantly available can be easily converted into good adsorbent by using simple method of activation, thus can act as a better replacement for activated carbon.

■ The ability of activated rice husk to adsorb Janus Green B dye was investigated as a function of adsorbent dosage, contact time, pH, initial dye concentration, and particle size of adsorbent.

The adsorption capacity increased with increased of contact time and achieves equilibrium at 30 minutes. There was no significant change in percentage removal or adsorption capacity of dye over the entire pH range studied.

The removal of Janus Green B increases with increase of adsorbent dosage used. The adsorption capacity decreases with increase of adsorbent dosage, but, increases with increase of initial dye concentration.

■ The equilibrium studies have shown that the Langmuir equilibrium model indicates better correlation between the theoretical and experimental data, for the whole Janus Green B concentration range , than the Freundlich model, indicateving monolayer adsorption on homogenous surface .

■ As the material is a waste product, the use of activated rice-husk as adsorbent would also solve their disposal problem.

■ On the bases of this work , activated rice-husk may Also be effective in removing other harmful species , such as heavy metal ions .

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