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Adsorption of Janus Green B Dye From Industrial Waste Water on The Pistachio Shells

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ABSTRACT

The study of activated pistachio shells carbon as a low cost sorbent for removing dye has drawn attention of various researchers working in this field. In the present work, pistachio shells carbon (PSC) in the form of powder was investigated for removing dyes taking Janus Green B as a model system. The adsorbent was made from pistachio shells procured from north of Iraq and was investigated under variable system parameters such as dose of adsorbent, pH, initial dye concentration, particle size and agitation time. An amount of 1.5 g/l of (PSC) could remove 99.7 % of the dye from an aqueous solution of 50 ppm with the agitation time 120 min. 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 pistachio shells could be employed as a low cost alternative to commercial activated carbon in wastewater treatment for the removal of color and dyes .

Keywords : adsorption capacity, isotherm models, Janus Green B, pistachio shells

امتزاز صبغة (Janus Green B) من مياه الفضلات الصناعية باستخدام قشور الفستق

الخلاصة

تتحرى هذه الدراسة استخدام قشور الفستق المنشطة كمادة مازة لإزالة صبغة (**Janus Green B**) من مياه الفضلات الصناعية. تم اجراء تجارب دفعية (batch) لدراسات الإمتزاز لدراسة تأثير جرعة المادة المازة, زمن التلامس ,pH , التركيز الأولي للصبغة , وحجم الحبيبة للمادة المازة في درجة حرارة المحيط. كانت نسبة الإزالة للصبغة 99.7% عند (1.5 g/L) من السطح المازة,(120 min.) زمن التماس, (50 ppm) تركيز الصبغة تم تطبيق نموذجي لانكماير وفراندلش لوصف علاقات التوازن للإمتزاز. بينت النتائج ان قشور الفستق المنشطة يمكن

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استخدامها كمادة رخيصة وبديلة عن الكاربون المنشط التجاري في معالجة مياه الفضلات لإزالة اللون والأصباغ .

INTRODUCTION

The wastewater treatment for long time has been a main problem of the textile industry. Dyes are widely used in industries such as textiles, rubber, paper, plastics, cosmetics, etc. to colour their products. Due to their good solubility in water, synthetic dyes are frequently found in industrial wastewater as common water pollutants. Pollution of water due to the discharge of effluents from dyeing industries affects the environment due to its toxicity these effluents contain many harmful chemical that pose serious problems to human beings and aquatic life[1,2] .

Due to their molecular structure, dyes are resistant to light, heat, biological degradation. The common method have been used for dye removal from wastewater include biological methods (anaerobic treatment) and physicochemical methods such as coagulation, electro coagulation, floating, filtration, ion exchange, membrane filtration and advanced oxidation[3-7]. However, many of these technologies are expensive, especially when they are used for treatment of large wastewater streams. Consequently, adsorption methods using low cost adsorbents have the most potential for application in industrial wastewater treatment, because of their efficiency is proven in the removal of organic and mineral pollutants and economic considerations[8,9] .

Natural materials that are available in abundance, or certain waste products from industrial or agricultural operations, may have great potential as an inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. The abundance and availability of agricultural by products make them good sources of raw materials for activated carbons. Some of the materials which are used for the preparation of activated carbon in the recent past are, oil palm shell[10], almond shell[11], yam peels[12], coconut shell[13,14],coconut coir[15], pistachio shells[16], hazelnut shell[17], walnut shell[18], palm shell[19], apple pulp[20], chickpea husks[21], rice husk[22], Banana shells[23].

This study aimed at evaluating the adsorbent potential of pistachio shells as a sorbent for the removal of dyes, using Janus Green B (JGB) as a dye model.

Experimental:-

Materials and Methods :-

Preparation of Sorbent:-

pistachio shells (PS) was obtained from local pistachio mills and was washed several times with tap water followed by filtration. The cleaned pistachio shells was oven burning completely at 300 C^0, then cooled, The Activated carbon (PSC) used in this study was washed with distilled water to remove water soluble materials present in the carbon prior to the adsorption study and then sieved to (0.075-0.85) mm size which was used without further treatment. Figure(1(a1-2, b)) shows the pistachio shell carbon before and after burn it.

Figure.(1): Iraqi pistachio shells used in this study, (a-1) The raw pistachio shells before burn (a-2) The raw pistachio shells after burn, (b)-Granular pistachio shells carbon

Preparation of Adsorbate:

Preparation of dye solution :-

Janus Green B (JGB) dye is[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(2).

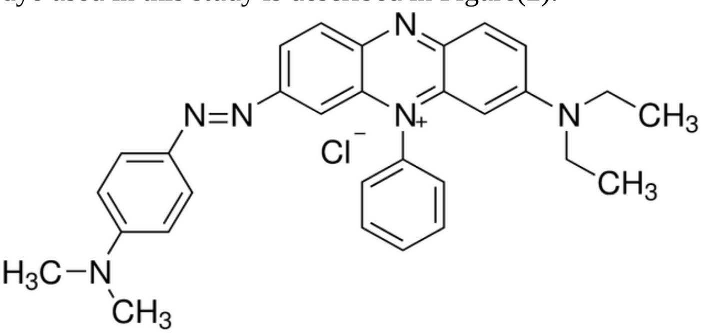


Figure.(2): The chemical structure of Janus Green B dye studied in this work

The physiochemical properties of the JGB dye can be shown by Table (1)[24]

Table (1): Physiochemical properties of Janus Green B dye

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

A stock solution of JGB ($500 mg.l^{-1}$) was prepared by dissolving (0.05g) of dye in distilled water and complete the solution to 500 ml . The experimental solution was prepared by diluting definite volume of the stock solution to get the desired concentration .
All measurements were carried out on a UV - VIS spectrophotometer (model – 1650 PC SHIMATZU).
JGB concentration was determined using the visible absorption at 611 nm after Concentration of calibration curve .
The pH of each solution was adjusted with 0.1 M HCL or NaOH using pH –meter to its effective adsorption pH value.

Batch adsorption studies

Adsorption experiments were carried out by agitating 0.5 to 3 g of adsorbent with a dsorbate solution of 50 ppm concentration at pH from 2.0,7.0 to 12, at temperature room in a shaker for 20,30 and 180 min. .The pH was measured using pH meter. The pH of the solutions was adjusted by means of 0.1M HCl and 0.1M NaOH solutions. The samples were withdrawn from the shaker at predetermined time intervals.

The concentration of final sample is measured by spectrophotometric determination. The amount of Janus Green B dye JGB adsorbed was calculated from the following equation:

$$q_e = \frac{V}{W}(C_o - Ce) \qquad \ldots(1)$$

Where q_e is the amount of dye adsorbed per unit weight of activated pistachio shells (mg/g); C_0 the initial concentration of (JGB) (ppm); C_e the concentration of (JGB) in solution at equilibrium time (ppm); V the solution volume (l); W is the activated carbon dosage (g).

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

$$\text{Removal efficiency (\%)} = \frac{C_o - Ce}{C_o} * 100\% \qquad \text{….(2)}$$

Where C_e 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

A desorption isotherm models:-

Langmuir and Freundlich model:-

The analysis of isotherm data is useful for design purpose. In present study the equilibrium data were treated by Langmuir and Freundlich isotherms. The Langmuir isotherm can be represented by the following equation[25].

$$qe = \frac{q_m K_a C_e}{1 + K_a C_e} \qquad \text{…… (3)}$$

Where, q_e is the amount adsorbed per unit mass of sorbent at equilibrium (mg/g), q_m is the maximum adsorption capacity (mg/g), C_e is the equilibrium dye concentration (mg/L) and K_a is the adsorption equilibrium constant. The plot of C_e/q_e versus C_e (eq .4) is linear which show that the adsorption of dye onto pistachio shells carbon follows Langmuir isotherm model .

$$\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{C_e}{q_m} \qquad \text{….. (4)}$$

The essential characteristics of Langmuir isotherm can be express by a dimensional constant called equilibrium parameter, R_L[26] that is defined by:

$$R_L = \frac{1}{1 + bC_o} \qquad \text{….. (5)}$$

where, b is the Langmuir constant and C_o is the initial concentration. The value of R_L indicates the shape of the isotherm to be either un favorable (R_L >1), linear (R_L=1), favorable (0< R_L<1) or irreversible (R_L=0).

The Freundlich isotherm was also applied for the adsorption of dye by pistachio shells carbon[27].

$$\log q_e = (1 / n) \log C_e + \log k_f \qquad \text{..(6)}$$

where, qe is the amount adsorbed per unit mass of adsorbent at equilibrium (mg/g), C_e is the equilibrium dye concentration of the solution (mg/L). k_f and n are the

Freundlich constants, n gives an indication of the favorability and k_f [mg/g(L/mg)1/n], 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 plate respectively. The value of n lies between 2 and 10, which implies good adsorption .

Result and Discussion:

Adsorption of dye:-

The adsorption of dye were investigated in the study using different parameters such as adsorbent dosage, contact time, pH, intitial dye concentration and particles size of adsorbent.

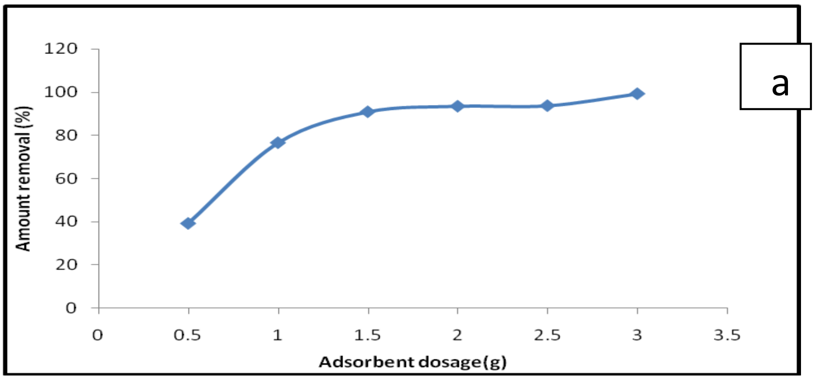
Effect of adsorbent dosage:

The effect of adsorbent dose was also investigated for the removal of dyes from aqueous solution. The experiments were carried out with adsorbent dose varied from (0.5 - 3) gm with keeping other parameters are constant (initial concentration of 50 mg/l and 0.3mm particle size). The percentage removal of dye was found (39.2 – 99.15)% Figure (3a).

The increase in removal of dyes with adsorbent dose due to the introduction of more binding sites for adsorption.Similar results have been reported by the other investigators[28-29] .

However, the adsorption capacity showed a decreasing trend with increasing adsorbent dosage. The amount of JGB adsorbed per unit weight of adsorbent decreased with increase in adsorbent dosage (Figure 3b). The reduction in the value of adsorption capacity (q_e) attributed to make a large number of sites available for a fixed dye concentration[30], These sites remaining unsaturated during the adsorption process.

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, pistachio shells carbon (PSC) and that is 90.82 % .



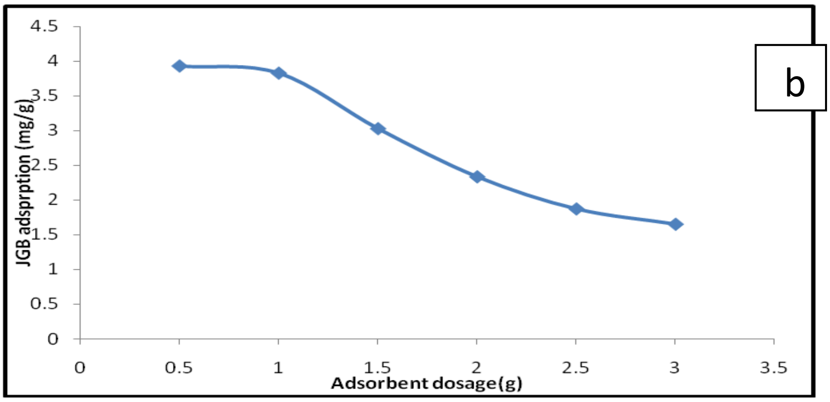


Figure (3) Effect of adsorbent dosage in the removal of JGB by (PSC)

(a)Adsorption percentage. (b) Amount of dye adsorbed(mg/g).

Effect of contact time :-

The experiments were carried out by taking 100 ml sample of dye(concentration 50 mg/L) in conical flasks and treated with 1.5 gm dosage of adsorbent with several time (20, 30, 45, 60, 80, 120,150, 180). The variation in percent removal of dye with the elapsed time has been shown in Figure (4). It is evident from the figure that PSC treatment resulted in 91.08%removal of Janus Green B dye in first 20 min., which increased up to 99.7 % in 120-180 min. . It is due to saturation of active sites which do not allow further adsorption to take place[31,32].

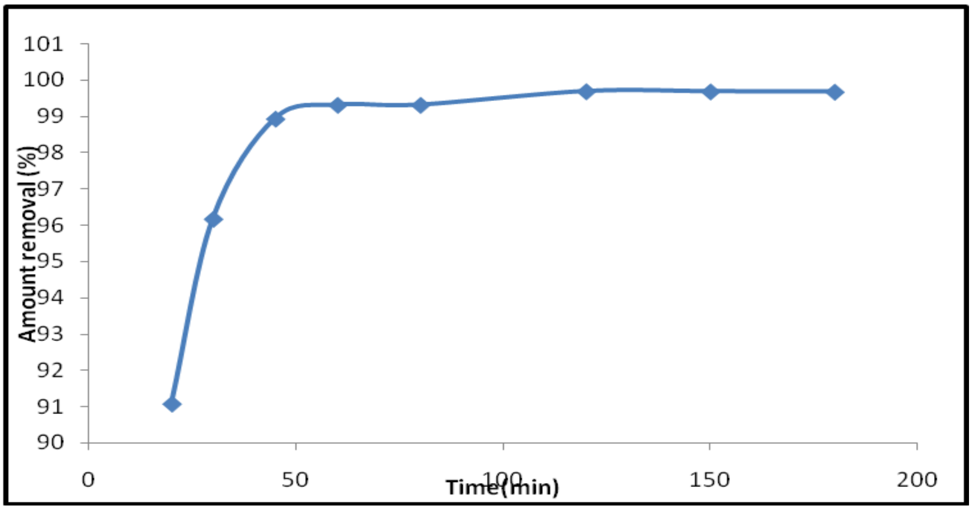
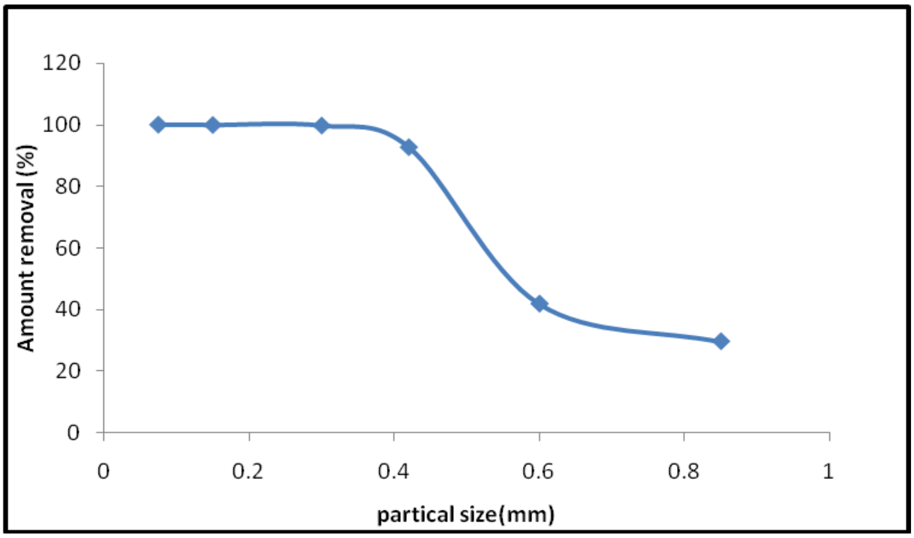


Figure (4) : Effect of contact time for adsorption of (JGB) onto (PSC) at initial dye concentration of 50 mg/l, adsorbent dose of 1.5 g, and particle size of 0.3mm

Effect of Particle size of adsorbent :-

The effect of Particle size of adsorbent (PSC) on adsorption of Janus Green B dye has been studied on pistachio shells particle of varying size (0.075, 0.15 , 0.3 ,0.42, 0.6 ,0.85) mm. The experimental data show that amount of Janus Green B adsorbed decreases with increase in Particle size of the adsorbent. This indicate that the smaller the (PSC) particle size for a given mass of (PSC), the more surface area is available and as a consequence the greater the number of binding sites available[33,34,28]. The results of this study are shown in Figure (5).

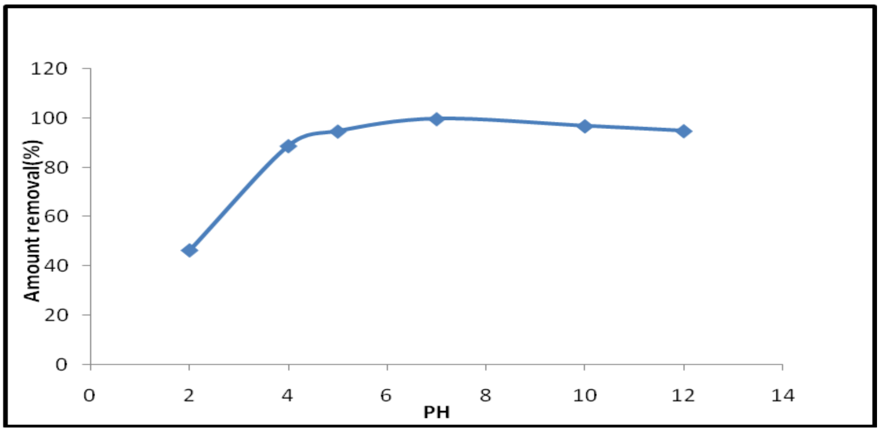


Figure(5) : Effect of particle size on adsorption capacity of (JGB) onto (PSC) at initial dye concentration of 50 mg/l and adsorbent dose of 1.5gm

Effect of pH :-

The aqueous solution of dye (JGB) having concentration of 50 mg/L was treated by 1.5 gm dosage of adsorbent with pH 2 to 12 . The pH was maintained with help of 0.1 N (HCL) and 0.1 N (NaOH) solution. Figure (6) it is evident

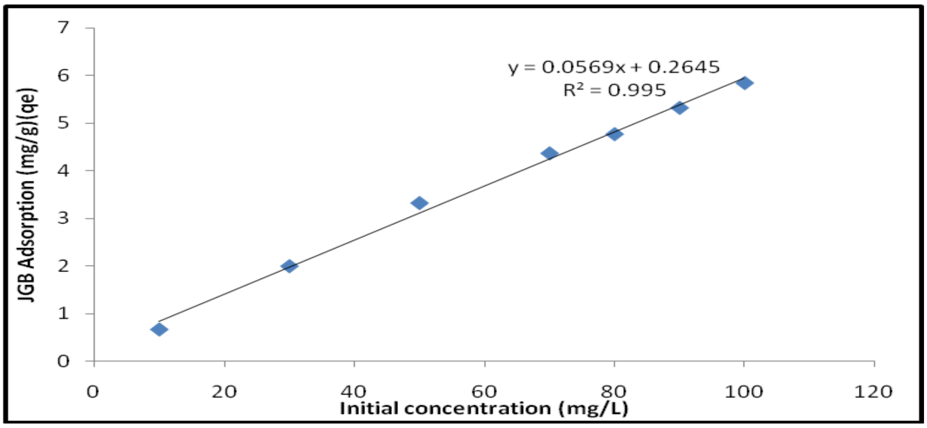
The results obtained are presented in this Figure which describes that it was no significant change in the percentage removal of dye uptake over the entire pH range of (4-12)[35].



Figure(6) : Adsorption of (JGB) by (PSC) as a function of solution pH at initial concentration of 50 mg/l and adsorbent dosage of 1.5 g with 0.3mm particle size

Effect of initial dye concentration:-

The effect of concentration of dye **(JGB)** (10 -100 mg / L) have been also tested with constant dosage of adsorbent for 100 min. . The removal of dye decreased from 100% to 87.7% . The results indicated that the adsorption of dye are much dependent on concentration of solution .Figure (7) illustrated the effect of initial dye concentration on adsorption of JGB onto the adsorbent and can be seen the adsorption capacity increased from (0.66 -5.84) mg/g when **(JGB)** concentration increase from 10 -100 mg/ L for the adsorbent of (PSC). Sites for adsorption becomes fewer for adsorption. 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[28,30].



Figure(7) : Effect of initial concentration on adsorption capacity of (JGB) onto (PSC) (0.3mm particle size and 1.5gm adsorbent dose)

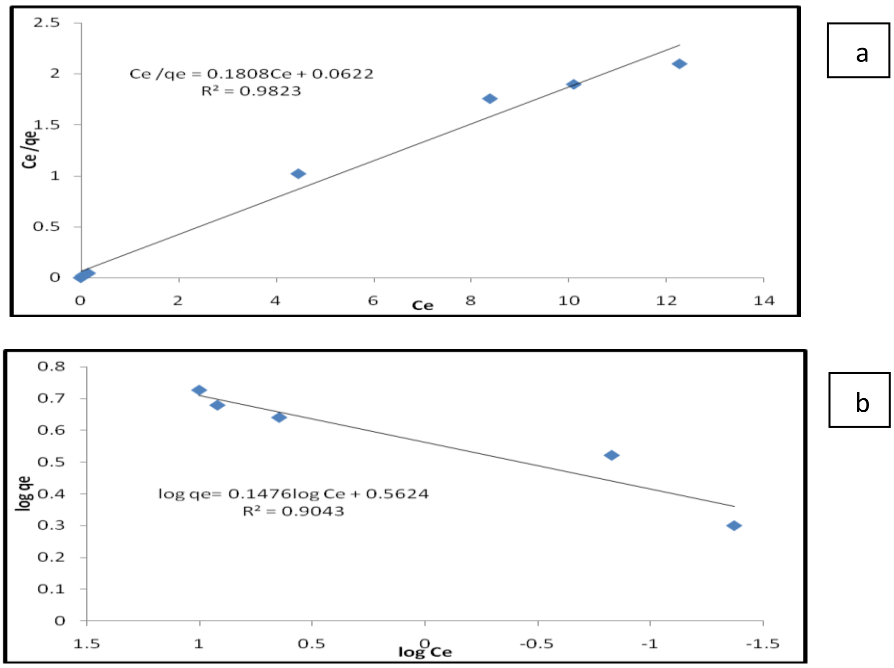
Isothermal analysis :-

The adsorption isotherm were developed from the data collected . Equilibrium adsorption data were fitted to the linear from of Langmuir's and freundlish equation (4,6). Table (2) shows that the adsorption of **(JGB)** dye using (PSC) carbon both satisfies of Langmuir's and freundlish isotherm .

Table (2) : Adsorption isotherm parameters for (JGB) dye removal

Langmuir		Freundlich	
q_m (mg/g)	5.5309	K_F(mg/g)(l/mg)$^{1/n}$	3.6509
K_a (l/mg)	2.**9068**	1/n	0.1476
R^2	0.0.9823	R^2	0.9043
R_L	(0.0332-0.0033)		

The plats of liberalized from of Langmuir and Freundlich are shown in figure (8a-b). The Langmuir equilibrium adsorption curves relating solid and liquid phase concentration of (JGB). and the Freundlich equilibrium adsorption curves relating solid and liquid phase concentration of (JGB).

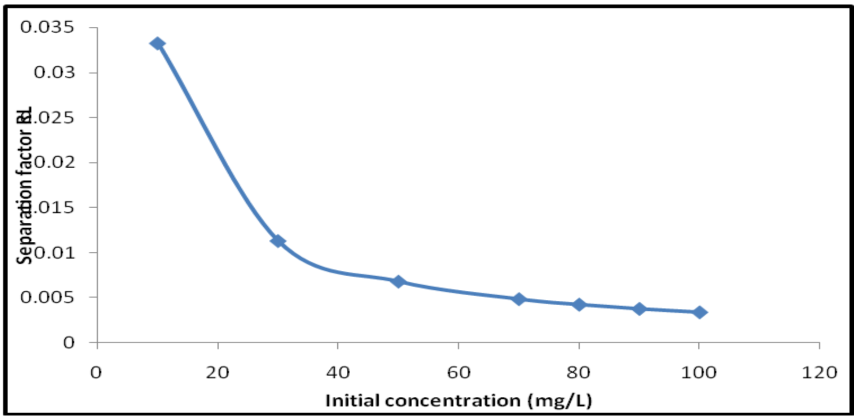


Figure(8): Linearized adsorption isotherm model of (JGB) onto (PSC)

(a) Langmuir model **(b) Freundlich model**

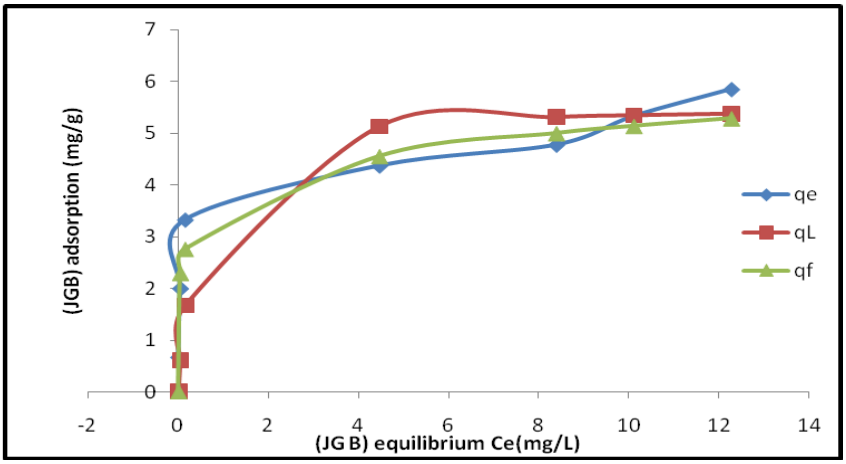
The Langmuir isotherm model assumes monolayer coverage of adsorbate on a homogeneous adsorbent surface. The well fitting of data with Langmuir isotherm indicates to the homogenous distribution of active sites on the adsorbent surface.

The variation of separation factor (R_L) with initial (JGB) concentration is shown in Figure (9). The (R_L) values for the adsorption of (JGB) onto (PSC) are observed to be in the range of (0 – 1), indicating that the adsorption was favorable process.



Figure(9) : Separation factor versus initial (JGB) concentration on to (PSC)

Figure (10) shows the deviation of these models from the experimental data. It appears that the adsorption of (JGB) dye on activated (PSC) could be well fitted by the two isotherms .clearly, the Langmuir equation provided better fitting in terms of R_L .



Figure(10): Comparison of experimental and calculated data by Langmuir and Freundlich equilibrium isotherms for the system (JGB) – (PSC)

This results indicate homogenous nature of (PSC) surface, which means each (JGB) molecule PSC has equal adsorption activation energy. The results also demonstrate the formation of monolayer coverage of (JGB) molecule at the outer surface of (PSC).

CONCLUSION :

The findings of the present work reveal that the PSC which is easily and abundantly available agro waste in our country can be easily converted into good adsorbent by using simple methods of activation. A suitable amount(1.5 g/l) of the PSC adsorbent could decolorize as much as 99.7% of the dye from an aqueous solution (50 ppm) if agitated for 120 min. demonstrated sufficient potential of PSC as an adsorbent for the removal of the dye **(JGB)**, from water solutions. The adsorption of the dye was maximum around the natural pH of the aqueous solution of **(JGB)**. This shows that adsorption of the dye could be carried out on PSC without adjusting the pH of the medium. On applying both Langmuir and Freundlich isotherm .

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