Batch adsorption technique for the removal of Reactive Black 5 dye from industrial waste water by using rice husks as adsorbent

Received : 31/12/2013 Accepted : 16/4/2014

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Abstract
The aim of this work is to absorb the Reactive Black 5 of dye with a low cost adsorbent. dye which comes in the effluents of textile industries during dyeing and rinsing processes. Although commercial activated carbon is a preferred sorbent for colour removal, its wide spread use is restricted due to high cost. Currently, the study of activated rice husks carbon as a low cost sorbent for removing dye has drawn attention of various researchers working in this field. In the present work, rice husks carbon (RHC) in the form of powder was investigated for removing dyes taking Reactive Black 5 as a model system. The adsorbent was made from rice husks procured from Central 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 (RHC) could remove 95.48 % of the dye from an aqueous solution of 50 ppm with the agitation time 80 min and pH of the solution was one. 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 husks could be employed as a low cost alternative to commercial activated carbon in wastewater treatment for the removal of color and dyes.

Keywords : rice-husk, adsorption capacity , equilibrium isotherm models.

Chemistry classification : QD450-801

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 lives (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, electrocoagulation, flotation, filtration, ion exchange, membrane filtration and advanced oxidation (3-7). However, many of these technologies are expensive, especially when their 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 rice husks in studies of removal of dyes, using Reactive Black 5 (RB5) as a dye model.

**Experimental:**

**Materials and Methods :**

**Preparation of Sorbent:**

Rice husks (RH) was obtained from local rice mills and was washed several times with tap water followed by filtration. The cleaned rice husks was oven burning completely at 300 °C, then cooled, The Activated carbon (RHC) 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 (75-850) µm size which was used without further treatment. Figure(1(a1-2, b)) shows the rice husks carbon before and after burn it.
Figure(1): Iraqi rice husks used in this study.
(a-1) The rice husks before burn
(a-2) The rice husks after burn
(b)-Granular rice husks carbon

Preparation of Adsorbate:
Preparation of dye solution :-

Reactive Black 5 (RB5) dye [ Synonyms : 2,7- naphthalenedisulfonic acid,4-amino-5-hydroxy-3,6-bis ((4((2(sulfoxy)ethyl)sulfonyl)phenyl) azo) - tetrasodium salt] . The chemical structure of dye used in this study is described in Figure(2).

Figure(2): The chemical structure of Reactive Black 5 dye studied in this work
The physiochemical properties of the RB5 dye can be shown by Table (1)

**Table (1): Physiochemical properties of Reactive Black 5 dye**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C_{20}H_{21}N_{8}Na_{4}O_{19}S_{6}</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>991.82g/mol</td>
</tr>
<tr>
<td>C.I. Name</td>
<td>20505</td>
</tr>
<tr>
<td>Absorption maxima</td>
<td>597 nm</td>
</tr>
<tr>
<td>Nature</td>
<td>anionic dye</td>
</tr>
</tbody>
</table>

An accurately weighed quantity of the dye was dissolved in distilled a stock solution of the dye was prepared by dissolving 0.05 gram of dye in 500 ml distilled water to make a stock solution of 100 (mg / L) . The experimental solution was prepared by diluting definite volume of the stock solution to get the desired concentration.

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

The maximum wavelength \( \lambda \) max. for RB5 was measured at 597 nm . Concentrations during experimental work were determined from a standard 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 1.5 g of adsorbent with 100 ml of adsorbate solution of 50 ppm concentration at pH from (1.0- 8.0) at temperature room in a shaker for 20,30 and 120 minutes. 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 Reactive Black 5 dye (RB5) adsorbed was calculated from the following equation:
\[ q_e = \frac{V}{W} (C_0 - C_e) \] \hspace{1cm} \text{(1)}

Where \( q_e \) is the amount of dye adsorbed per unit weight of activated rice husks (mg/g); \( C_0 \) the initial concentration of (RB5) (ppm); \( C_e \) the concentration of (RB5) 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 (RB5) from the relation

\[ \text{Removal efficiency (\%) } = \frac{C_0 - C_e}{C_0} \times 100\% \quad \text{............(2)} \]

Where \( C_0 \) is the initial concentration of (RB5), \( C_e \) 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\(^{(24)}\).

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

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 rice husks carbon follows Langmuir isotherm model.

\[ \frac{C_e}{q_e} = \frac{1}{q_m K_a} \cdot \frac{C_e}{q_w} \quad \text{................................. (4)} \]

The essential characteristics of Langmuir isotherm can be express by a dimensional constant called equilibrium parameter, \( R_L \)\(^{(25)}\) that is defined by:

\[ R_L = \frac{1}{1 + b C_0} \quad \text{.......................... (5)} \]

where, \( b \) is the Langmuir constant and \( C_0 \) 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 rice husk carbon (26).

\[ \log q_e = \left( \frac{1}{n} \right) \log C_e + \log k_f \]  

where, \( q_e \) 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 \( k_f \) \([\text{mg/g (L/mg)}]^{1/n}\). 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.

**Results 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 0.42 mm particle size). The percentage removal of dye was found (19.06 - 86.38)% 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 (27) (28).

However, the adsorption capacity showed a decreasing trend with increasing adsorbent dosage. The amount of RB5 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 along number of sites available for a fixed dye concentration (29). 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 rice husks carbon (RHC) and that is 52.08 % when concentration of dye 50 mg / L.
Figure (3) Effect of adsorbent dosage in the removal of RB5 by (RHC)

(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) min. The variation in percent removal of dye with the elapsed time has been shown in figure (4). It is evident from the figure that RHC treatment resulted in 52.08% removal of Reactive Black 5 dye in 80 min., which increased up to 52.08 % in 80-120 min. It is due to saturation of active sites which do not allow further adsorption to take place (30)(31).

![Figure (4): Effect of contact time for adsorption of (RB5) onto (RHC) at initial dye concentration of 50 mg/l, adsorbent dose of 1.5 g and particle size of 420µm](image)

Effect of Particle size of adsorbent :-

The effect of Particle size of adsorbent (RHC) on adsorption of Reactive Black 5 dye has been studied on pistachio shells particle of varying size (75, 150, 300, 420, 650, 850) µm. The experimental data show that amount of Reactive Black 5 adsorbed decreases with increase in Particle size of the adsorbent. This indicate that the smaller the (RHC) particle size for a given mass of (RHC), the more surface area is available and as a consequence the greater the number of binding sites available (32)(33)(27). The results of this study are shown in Figure (5).
Effect of pH:

The aqueous solution of dye (RB5) having concentration of 50 mg/L was treated by 1.5 gm dosage of adsorbent with pH 1 to 8. The pH was maintained with help of 0.1 N (HCl) and 0.1 N (NaOH) solution. Figure (6) it is evident it can be seen that the adsorption of RB5 was strongly dependent on the pH of the solution. The highest sorption capacities were obtained in the pH (1). Under these conditions dye removal was almost complete (34)(1). The higher dye removal that was obtained at acidic pH may be explained in terms of electrostatic attraction between dye RB5 and RHC.

Figure (6): Adsorption of (RB5) by (RHC) as a function of solution pH at initial concentration of 50 mg/l and adsorbent dosage of 1.5 g with 300µm particle size
Effect of initial dye concentration :-

The effect of concentration of dye (RB5) (10 -100 mg / L) have been also tested with constant dosage of adsorbent for 80 min. 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 RB5 onto the adsorbent and can be seen the adsorption capacity increased from (0.66 -6.11) mg/g when (RB5) concentration increase from 10 -100 mg/ L for the adsorbent of (RHC). 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\(^{29}(27)\).

![Graph showing the effect of initial concentration on adsorption capacity of RB5 onto RHC](image)

\[ y = 0.0615x + 0.0827 \]
\[ R^2 = 0.9991 \]

**Figure(7) : Effect of initial concentration on adsorption capacity of (RB5) onto (RHC) (300μm 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 Langmuirs and freundlish equation (4,6). Table ( 2 ) shows that the adsorption of (RB5) dye using (RHC) carbon both satisfies of Langmuir,s and freundlish isotherm .
Table (2): Adsorption isotherm parameters for (RB5) dye removal

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td>q_m (mg/g)</td>
<td>7.7041</td>
<td>K_F (mg/g)(l/mg)^{1/n} 2.4076</td>
</tr>
<tr>
<td>K_a (l/mg)</td>
<td>0.4291</td>
<td>1/n</td>
</tr>
<tr>
<td>R^2</td>
<td>0.8554</td>
<td>R^2</td>
</tr>
<tr>
<td>R_l</td>
<td>(0.180 - 0.022)</td>
<td></td>
</tr>
</tbody>
</table>

The plots of linearized from of Langmuir and Freundlich are shown in Figure (8a-b). The Langmuir equilibrium adsorption curves relating solid and liquid phase concentration of RB5, and the Freundlich equilibrium adsorption curves relating solid and liquid phase concentration of RB5.

Figure(8): Linearized adsorption isotherm model of (RB5) onto (RHC)

(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 RB5 concentration is shown in Figure (9). The ($R_L$) values for the adsorption of RB5 onto (RHC) are observed to be in the range of ($0 – 1$), indicating that the adsorption was favorable process.

![Figure (9): Separation factor versus initial (RB5) concentration onto (RHC)](image)

Figure (10) shows the deviation of these models from the experimental data. It appears that the adsorption of RB5 dye on activated (RHC) 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](image)
Freundlich equilibrium isotherms for the system (RB5) – (RHC)

This results indicate homogenous nature of (RHC) surface, which means each RB5 molecule RHC has equal adsorption activation energy. The results also demonstrate the formation of monolayer coverage of RB5 molecule at the outer surface of (RHC).

Conclusion :-

The findings of the present work reveal that the RHC 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 RHC adsorbent could decolourize as much as 95.4% of the dye from an aqueous solution (50 ppm) if agitated for 80 mint demonstrated sufficient potential of RHC as an adsorbent for the removal of the dye RB5, from water solutions. The adsorption of the dye was maximum around the acidity of the aqueous solution of RB5. This shows that adsorption of the dye could be carried out on RHC with adjusting the pH of the medium. On applying both Langmuir and Freundlich isotherm.

References:-


18. Juan F. González ; Silvia Román ; Carmen M. González –lez-García ;


تتحرى هذه الدراسة امتزاز صبغة (Reactive Black 5) من مياه الصرف الصناعية باستخدام قشور الرز كسطح ماز.

لبنى محمد علي
جامعة بابل / كلية العلوم / قسم الكيمياء
تاريخ القبول: 16/1/2014
تاريخ الاستلام: 31/12/2013

الخصائص: 
تتحرى هذه الدراسة امتزاز صبغة (Reactive Black 5) من الصبغات المسرطنة و مصدرها الخلفيات الصناعية خلال عمليات الغسل والصبغة. يعد الكربون المنشط لقشور الرز مادة رخيصة وقلة التكلفة إزالة الإصباغ. لذا توجه أهتمام كثير من الباحثين إلى هذا الحقل. تم اخذ كربون قشور الرز المنشط على شكل مسحوق لإزالة الأصباغ لتكون من قشور الرز العراقية والتي خضعت إلى عدة متغيرات مثل وزن الجرعة، الدالة الحموضية، التركيز الابتدائي للصبغة، حجم الحبيبة. و باخذ 1.5 غرام من بذور الكربون المنشط ممكن إزالة 95.94% من الصبغة من محلول مائي يتركز 50 ملغم/لتر. تم تطبيق نموذج إمكاني película وفرانكلين لوصف علاقات التوازن للإمتزاز. وكانت النتائج إن قشور الرز المنشطة يمكن استخدامها كمادة رخيصة وبديلة عن الكربون المنشط التجاري في معالجة مياه الفضلات لإزالة اللون والأصباغ.

الكلمات المفتاحية: قشور الرز، سعة الامتزاز، المتماثل الحراري.

Chemistry classification: QD450-801