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Adsorption Of Direct Red 23 From Aqueous Solution Using Rice Husk Activated By Citric Acid

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ABSTRACT

The goal of this research is to develop a new and efficient adsorbent of direct dyes. Thus, rice husk, a commonly available agriculture waste in Egypt, was investigated as viable materials for treatment of synthetic Direct Red 23 containing industrial wastewater. Activation of rice husk with citric acid was studied in order to increase its capacity to remove the dye. The results obtained from the batch experiments revealed the ability of the rice husk in removing the Direct Red 23 and are dependent on the dye and rice husk concentrations. Kinetics of adsorption was investigated as well as equilibrium isotherm of Direct Red 23 using Langmuir model, which represented a correlation coefficient > 0.96. The maximum adsorption capacity was 13 g of dye per kilogram of dry rice husk. This study showed that the rice husk could be employed as low-cost for the removal of Direct Red 23 from aqueous solution.

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KEYWORDS

Adsorption;
Rice husk;
Direct Red-23;
Isotherms;
Kinetics;
Langmuir model.

INTRODUCTION

Effluent from dyeing and finishing processes is an important source of water pollution. The release of the colored dyes into the ecosystem is a dramatic source of pollution, of eutrophication, and of perturbations in aquatic life. Some azo dyes and their degradation products such as aromatic amines are highly carcinogenic. Proper treatment of the dye plant effluent is thus, a matter of concern before discharge. Different treatment methods are described in the literature, including filtration, flocculation, chemical precipitation, ion exchange, membrane separation, and adsorption[1,2]. New approaches based on the use of natural, inexpensive sorbent materials for effluent treatment have also been reported[3-7].

The adsorption process is one of the efficient methods to remove contaminant from effluent[6,8]. The process of adsorption has an edge over the other methods due to its sludge free clean operation and complete removal of dye even from dilute solutions. Activated carbon is the most widely used adsorbent because of its extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity. However, commercially available activated carbons are expensive and its manufacturing problems such as combustion at high temperature pore blocking, and hydroscopicity.

Rice husk, an agriculture mass residue, is a by-product of the rice milling industry. It represents about 20% of the whole rice produced, on weight basis[9]. Traditionally, rice husks have been used in manufacturing block employed in civil construction as panels and was used by rice industry itself as a source of energy for boilers. It was chosen for an adsorption research because of its granular structure, chemical stability and low production costs. The main constituents of rice husk are: 64.3% volatile matter and 15.9% fixed carbon and 19.8% ash[9]. The rice husk composition is: 32% cellulose, 21% hemicellulose, 21% lignin, 1.8% extractives, 8% water and 15% mineral ash[10]. However, the reported composition of rice husk differs widely, as affected by paddy type and climate[11].

The purpose of this work is to investigate the adsorption capacity of the untreated and activated rice husk on adsorption of direct dyes from aqueous solution. Direct Red 23 (DR-23) dye was selected for the adsorption experiment due to its presence in several industrial effluents such as textile, tannery, paper, soap, cosmetics, polishes, wax etc. DR-23 is toxic and carcinogenic and its biodegradation may lead to primary amines.

MATERIALS AND METHODS

Rice husk was obtained from local rice mills and was washed several times with distilled water followed by filtration. The washed rice husk was oven dried at 105°C for 24 hrs, then cooled and sieved to 250-500 μm size, and used without further treatment. Another part of same size fraction of rice husk was exposed citric acid-activation[12], which 100 g of rice husk were soaked in 0.6M citric acid and allowed to react for 2 h at 20°C. It was dried at 50°C, followed by heating to 120°C, washed repeatedly with distilled water to remove excess of the acid and then oven dried at 100°C for 48 hrs.

Direct Red-23 was obtained from ASMA Company and was used without further purification. Its molecular formula is $C_{35}H_{25}N_7Na_2O_{10}S_2$ and its color index C.I. 29160 (Figure 1). A stock solution of DR-23 was prepared by dissolving 1.0 g of dye in 1000 mL distilled water to make a stock solution of 1000 mg L^{-1} concentration[13]. The experimental solutions were prepared by diluting the stock solution with distilled water to get the desired concentration. UV-VIS spectrophotometer (Milton Roy, Spectronic 21D) was employed for adsorbance measurements using silica cells of path length 1 cm. The maximum wavelength λ_{max} for the DR-23 was determined at 507 nm. Change in pH (1 to 7) of DR-23 solution has no effect on its color concentration. Concentrations during experimental work were determined from calibration curve.

Equilibrium adsorption isotherms for the untreated and activated rice husk were determined by doing the experiments at agitation rate of 150 rpm at room temperature and at different concentrations of dye and rice husk. Adsorbent (0.25-1.0 g) was added in a set of 250-ml Erlenmeyer flasks and 100 ml at various initial dye concentrations (5, 10, 15, 20, 25 mg l^{-1}). The contents were shaken for appropriate time and the supernatant was analyzed for dye contents using UV-VIS spectrophotometer [Concentration = 38.014 × Absorption (SD = ±1.3~3.2) obtained from standard curve]. The adsorption behaviors of the samples were studied by evaluating the removal efficiency of DR-23, in terms of percentage from the relation

$$\text{Removal efficiency} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

Where C_0 is the initial concentration of DR-23

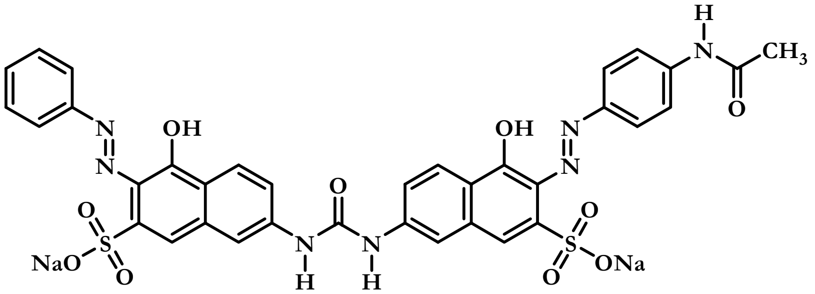

Figure 1: Structure of Direct F.scarlet (Direct Red 23 or Direct F.orange)

and C is the solution concentration after adsorption. Effect of time on the dye removal at various predetermined intervals was monitored by analyzed the solution for the dye content at the end of each contact time. Kinetics of adsorption was determined by analyzing adsorptive uptake of the dye color from aqueous solution at different time intervals. The amount of dye adsorbed onto the rice husk q_e (mg l^{-1}) was calculated according to the following mass balance equation

$$q_e = \frac{(C_0 - C_e)\times V}{w} \tag{2}$$

Where C_o and C_e are the initial and equilibrium concentrations of dye, respectively (mg l^{-1}), V is the solution volume (l), and W is the weight (g) of the rice husk used.

RESULTS AND DISCUSSION

The adsorption of DR-23 on rice husk and citric acid treated rice husk were studied for its possible importance in the remediation of industrial effluents. The effect of agitation time, sorbent and dye concentrations on removal of DR-23 were studied and represented in figures 2 and 3. The percentage of removal was increased with increase of the contact time and biomass concentration and become nearly constant after reading equilibrium. As shown in figures 2 and 3, the rate of removal of colour was rapid at first 30 min and attained nearly constant value beyond which there was no significant increase in color removal. The time required to attain equilibrium was 120 minutes for untreated and 90 minutes for activated rice husk. The curves depicting removal are single, smooth and continuous leading to saturation.

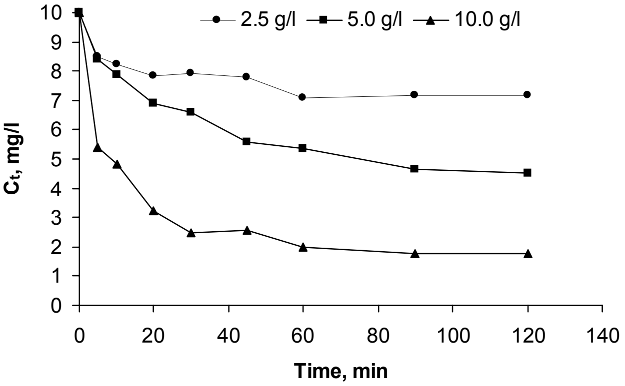

Figure 2: Influence of contact time and weight of untreated rice husk on removal of DR-23 using dye concentration of 10 mg L^{-1}

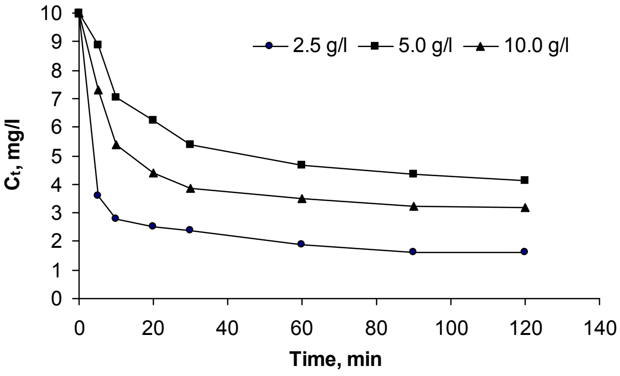

Figure 3: Influence of contact time and weight of activated rice husk on removal of DR-23 using dye concentration of 10 mg L^{-1}

However, the dye color removal pattern showed that increase in the biomass concentration indicated increase dye removal capacity, which may be attributed to the increase of biomass of rice husk gives more surface area for adsorption of the dye molecule

TABLE 1: Langmuir constants for the adsorption of DR-23 using untreated and modified rice husk

Adsorbent	S_m (mg g^{-1})	K_L (L mg^{-1})	R_L	r- value
Untreated rice husk	2.42	0.17	$0 < R_L < 1$	0.99
Activated rice husk	4.35	0.14	$0 < R_L < 1$	0.97

on the surface (Figures 2 and 3) [8]. The incremental increase of 30% was observed for increase of biomass from 2.5 to 5.0 g l^{-1} and another 30% for increase of biomass from 5.0 to 10.0 g L^{-1} for untreated rice husk. While for citric acid treated rice husk, an incremental increase of 10% was observed for every 2.5 g l^{-1} increase of biomass. It can also follow from the above discussion that the rice husk biomass uptake was dependent on the dye concentration and rice husk biomass.

Adsorption data were analyzed according to Langmuir model for both untreated and citric acid treated rice husk. The Langmuir model was originally formulated based on theoretical assumptions: (1) the adsorption reaction can be represented as a coordination reaction with 1:1 stoichiometry (i.e. monolayer adsorption); (2) the activities of the surface sites are proportional to their concentration and (3) the number of adsorption sites is fixed[14-16]. It is based on the physical hypothesis that the maximum adsorption capacity consists of a monolayer adsorption. It is assumed that once a dye molecule occupies a site, no further adsorption can take place at that site[17]. Theoretically, a saturation value is reached beyond which no further adsorption can occur. The Langmuir equation, which has been successfully applied to many adsorption systems[6,18], is given by

$$q_e = \frac{(K_L \times S_m \times C_e)}{(1 + K_L \times C_e)} \qquad (3)$$

Where K_L is the equilibrium adsorption coefficient (l mg^{-1}), S_m is the maximum adsorption capacity (mg g^{-1}), C_e the adsorbate equilibrium concentration. Eq. (3) can be written in the following linear form

$$\frac{C_e}{q_e} = \frac{1}{(K_L \times S_m)} + \frac{C_e}{S_m} \qquad (4)$$

The dye adsorption data were plotted according to linear Langmuir isotherms. A linearized plot of C_e/q_e versus C_e was obtained for the untreated and activated rice husk as shown in figure 4. Regression data and adsorption parameters obtained are indicated in TABLE 1. One advantage of the Langmuir equation in its linear form is that the adsorption maximum can be calculated from the regression. The data for adsorption of DR-23 onto untreated and citric acid treated rice husk were fitted to the Langmuir model (r=0.99 and 0.97, respectively). The fitness of the Langmuir model for this adsorption system indicates the monolayer coverage of dye on the outer surface of biosorbent, in which the adsorption of dye molecule occurs uniformly on the active part of the surface. The fits are quite well for both sorbents, which suggested the applicability of the Langmuir model for the investigated system. S_m and K_L, Langmuir constants, are the measures of maximum adsorption capacity and energy of adsorption, respectively. The values of Langmuir parameters along with the correlation coefficients were computed from the intercept and the slope of the fitted Langmuir equation.

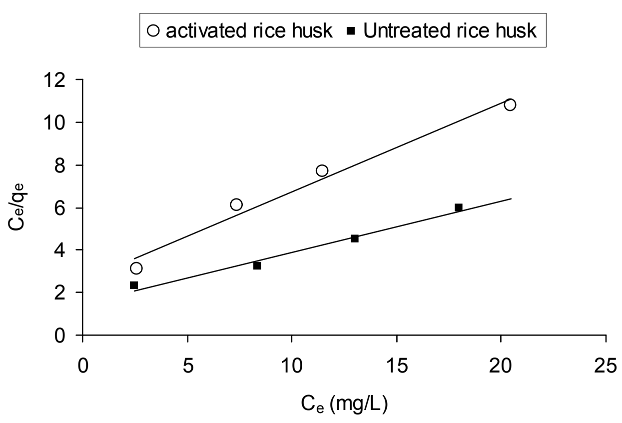

Figure 4: Fitting adsorption data with Langmuir using sorbent concentration of 10g L^{-1}

Activated rice husk is observed to have higher adsorption capacity than the untreated rice husk in the removal of DR-23. The essential characteristic of Langmuir isotherm can be expressed in terms of a dimensionless constant, R_L, which is defined as follows [16,19,20]:

$$R_L = \frac{1}{[1 + (K_L \times C_0)]} \qquad (5)$$

Where C_0 is the initial concentration and R_L indicates the shape of the isotherm. The types of equi-

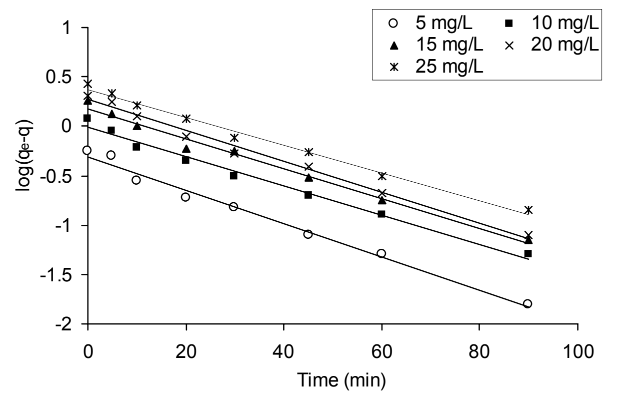

Figure 5: Lagergren plots for the removal of DR-23 by adsorption on untreated rice husk and sorbent concentration of 5g L^{-1}

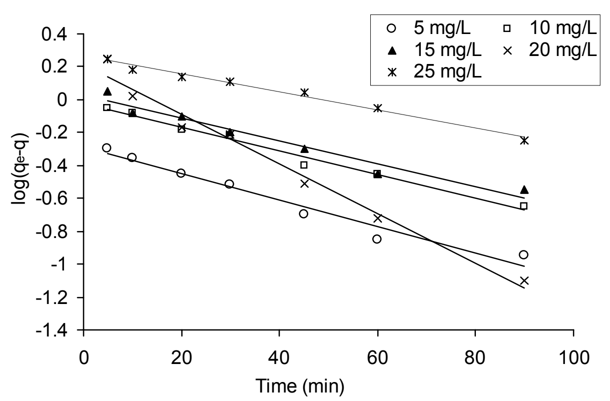

Figure 6: Lagergren plots for the removal of DR-23 by adsorption on activated rice husk and adsorbent concentration of 5g L^{-1}

librium isotherm are related with the R_L values as $R_L > 1$ for unfavorable, $R_L = 1$ for linear, $0< R_L >1$ for favorable and $R_L <0$ for irreversible. In this work, the values of R_L were found to be less than 1 and greater than zero indicating the favorable adsorption of DR-23 on rice husk.

The kinetics of adsorption of DR-23, on both untreated and activated rice husk, was studied by applying the Lagergeren first order rate equation[21-24] as follows:

$$\mathrm{Log}(q_e - q) = \mathrm{Log}q_e - \frac{K}{2.303}t \qquad (6)$$

Where q (mg g^{-1}) is the amount of dye adsorbed at time t, q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium, and K is the equilibrium rate constant of adsorption. The straight line plots of log (q_e – q) versus t for dye at different biomasses under used conditions indicate the validity of Eq. 6 and the process follows first order kinetics (Figures 5 and 6). Rate constants were calculated from the slope of the straight-line curves. In batch stirring reactors, the transport of adsorbate from bulk solution to the interior surface of the pores is often the rate limiting step of the adsorption process[25,26]. The rate parameters controlling intra-particle diffusion for DR-23 with both types of adsorbents are determined using the following equation [18,27]:

$$q_t = K_p \times t^{0.5} \qquad (7)$$

Where q_t (mg g^{-1}) is the amount of dye adsorbed at time t; and K_p is the intra-particle diffusion rate constant (mg g^{-1} $min^{0.5}$). Plotting the amount sorbed per unit weight of sorbent (q_t) versus $t^{0.5}$ as described

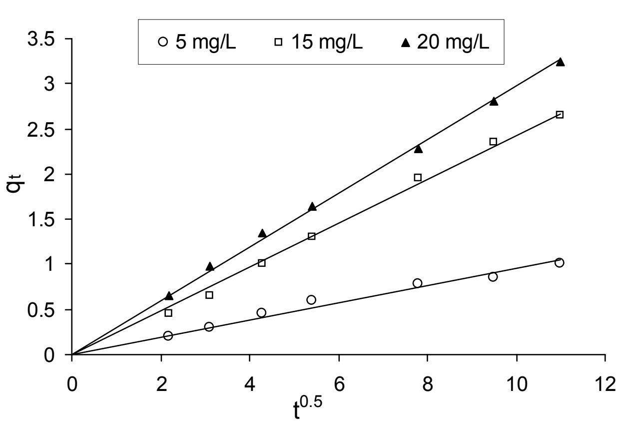

Figure 7: Intra-particle diffusion plots for the removal of DR-23 using untreated rice husk

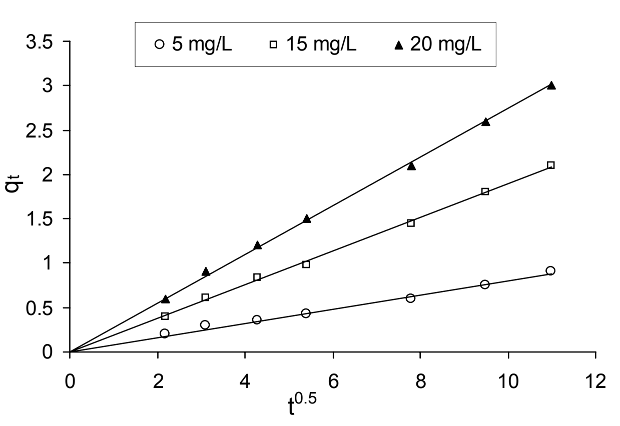

Figure 8: Intra-particle diffusion for the removal of DR-23 on citric acid treated rice husk

by Eq. (7), indicates the intra-particle diffusion rate, K_p, values, which were obtained from the slopes of the linear plots for each initial concentration for both types of adsorbents. Intra-particle diffusion plots are shown in figures 7 and 8. It was found that the plots of different dye concentrations were linear and pass through the origin for both untreated and citric acid treated rice husk, which indicates that the rate determining step may be controlled by intra-particle diffusion.

The results obtained from the present investigation revealed the ability of rice husk in treating azo dye effluents. Adsorption is highly dependent on the contact time, dye concentration and adsorbent dose. The Langmuir isotherm model describes the adsorption isotherm of DR-23 onto rice husk biomass. Kinetics of adsorption follows Lagergren first order kinetic model with film diffusion being the constitutive rate-controlling step. The monolayer adsorption capacity obtained from Langmuir isotherms for DR-23 was found to be relatively higher for the citric acid treated rice husk in comparison to the ones obtained without chemical treatment. The results obtained using rice husk were comparable to that obtained using orange peel adsorbent for removal of DR-23 from aqueous solution[28]. However, it can be said that, rice husk is very cheap biomass, more abundant than orange peel and can be used as potential biosorbent in removal of DR-23 from aqueous solution.

CONCLUSION

The data from batch studies on the adsorption of DR-23 on citric acid activated rice husk provided fundamental information in terms of mass of sorbent and DR-23 initial concentration. This study indicated that the uptake of DR-23 was greatly affected by the initial dye concentration and mass of adsorbent material. Langmuir models fit the isotherm data well for both untreated and treated rice husk. The data obtained may be helpful for designing and establishing a continuous treatment plant for water and waste water enriched in DR-23. The cost of removal is expected to be quit low, as the adsorbent is cheap and easily available in large quantities.

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