



The use of an agricultural waste material, Jujuba seeds for the removal of anionic dye (Congo red) from aqueous medium

M.C. Somasekhara Reddy^{a,*}, L. Sivaramakrishna^b, A. Varada Reddy^b

^a Department of Basic Sciences, G.P.R. Engineering College (Autonomous), Kurnool 518007, A.P., India

^b Analytical Division, Department of Chemistry, Sri Venkateswara University, Tirupati 517502, A.P., India

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ABSTRACT

The feasibility of using Indian Jujuba Seeds (IJS) (*Zizyphus maruritiania*), abundantly available in and around the Nallamalla forest in Andhra Pradesh, for the anionic dye (Congo red, CR) adsorption from aqueous solution, has been investigated as low cost and eco-friendly adsorbent. Adsorption studies were conducted on a batch process, to study the effects of contact time, initial concentration of CR, pH and temperature. Maximum colour removal was observed at pH 2. The equilibrium data was analyzed by the Langmuir, the Freundlich and the General isotherms. The data fitted well with the Langmuir model, with a maximum adsorption capacity of 55.56 mg g⁻¹. The pseudo-second-order kinetics was the best for the adsorption of CR, by IJS (*Z. maruritiania*) with good correlation. Thermodynamic parameters, such as standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°), were analyzed. The results suggest that IJS (*Z. maruritiania*) is a potential low-cost adsorbent for the CR dye removal from synthetic dye wastewater.

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1. Introduction

Now-a-days number of dyes are being widely used in textile, paper, rubber, plastic, leather, cosmetic, pharmaceutical, and food industries, which generate huge volumes of wastewater every year [1]. The wastewater contains large amount of dissolved dyestuffs and other products, such as dispersing agents, dye bath carrier, salts, emulsifiers, leveling agents and heavy metals [2]. The disposal of dye wastewater without proper treatment is a big challenge as it causes harm to the aquatic environment, such as reducing light penetration and photosynthesis [3]. Some of the dyes present in wastewater even decompose into carcinogenic aromatic amines under anaerobic conditions and cause serious health problems to human beings as well as other animals [4]. Due to the complex molecular structure, dyes are usually very difficult to be biodegraded, and is too hard to eliminate them under natural aquatic environment [5]. Many dyes and their by-products break down into products which are toxic for living organisms [6].

The dyes have low biodegradability. Conventional biological wastewater treatment processes are not efficient in treating dyes present in wastewater [7]. Therefore, dye-wastewater is usually treated by physical and chemical methods, such as sonochemical

degradation [8], photochemical degradation [9,10], electrochemical removal [11], electrochemical degradation [12], coagulation and flocculation [13], membrane separation [14,15], activated carbon adsorption [16], bio degradation [17], fento-biological treatment scheme [14], photo-fenton processes [11], oxidation or ozonation [18]. However, in developing countries, these methods are still too expensive to be used widely. Developing economical adsorbents to treat dyes wastewater has attracted a great interest in recent years. Recently, the application of low-cost adsorbents for the dyes and metal ions removal has been reviewed [19–22]. Many non-conventional, low-cost adsorbents such as jute stick powder [23], cattail root [1], peanut hull [24], jute processing wastes [25], *Azadirachta indica* leaf powder [26], orange peel [27], coir pith [28], hardwood sawdust [29], bagasse pith [30], soy meal hull [31], rice husk [32], maize stalk [33], hazelnut shells [34], bottom ash and de-oiled Soya [35,36], wheat bran and rice bran [37], *Alternanthera bettzichiana* plant powder [38], jackfruit peel [39], spent brewery grains [40], chitosan based composite hydro gels [41], sunflower seed hull [42], papaya seed [43], Guava (*Psidium guajava*) leaf powder [44], *Posidonia oceanica* (L.) fibers [45], Tamarind Fruit Shell [46], Pumpkin seed hull [47], Broad bean peels [48] etc., have been used to remove dyes from wastewater. But the adsorption capacities of most of the above adsorbents are limited. New, economical, locally available and highly effective adsorbents are still in the process of development.

The objective of this paper is to study and investigate the feasibility of using Indian Jujuba seed to remove CR from synthetic dye wastewater.

* Corresponding author. Tel.: +91 9441034599; fax: +91 8518270957.

E-mail addresses: som16@rediffmail.com, mcsr.gprec@gmail.com (M.C. Somasekhara Reddy), svurams@gmail.com (L. Sivaramakrishna), ammireddy@yahoo.co.in (A. Varada Reddy).

1.1. Theory of adsorption kinetics and isotherms

1.1.1. Kinetic models

The Lagergren's pseudo-first-order model (Eq. (1)) and pseudo-second-order model (Eq. (2)) [1] have been widely used to predict sorption kinetics. The pseudo-first-order equation is generally applicable to the initial stage of the adsorption processes whereas the pseudo-second-order equation predicts the behavior over the whole range of adsorption. These two models were used to fit the experimental data of this study.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \quad (1)$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) t \quad (2)$$

where k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of pseudo-second-order adsorption. q_e , amount of dye adsorbed on adsorbent at equilibrium.

1.1.2. Intra-particle diffusion model

In order to investigate the mechanism of the CR adsorption onto IJS (*Zizyphus maruritiana*), intra-particle diffusion based mechanism is studied. The most commonly used technique for identifying the mechanism involved in the adsorption process is, fitting an intra-particle diffusion plot. It is an empirically found functional relationship, common to the most adsorption processes, where uptake varies almost proportionally with $t^{0.5}$ rather than with the contact time t . According to the theory proposed by Weber and Morris [39].

$$q_t = k_{pi} t^{0.5} + C_i \quad (3)$$

where k_{pi} ($\text{mg g}^{-1} \text{min}^{-0.5}$), the rate parameter of stage i , is obtained from the slope of the straight line of q_t versus $t^{0.5}$ where as C_i is the intercept of the plot that gives an idea about the thickness of the boundary layer.

1.1.3. Thermodynamic parameters

Thermodynamic parameters are calculated using the following equations

$$\Delta G^\circ = -RT \ln K_c \quad (4)$$

$$\text{where } K_c = \frac{C_s}{C_e} \quad (5)$$

$$\ln K_c = \left(\frac{\Delta S^\circ}{R}\right) - \left(\frac{\Delta H^\circ}{RT}\right) \quad (6)$$

where ΔG° , ΔS° and ΔH° are standard free energy change, standard enthalpy change and standard entropy change, respectively, K_c is the equilibrium constant, C_s is the equilibrium concentration of CR on adsorbent (mg L^{-1}), C_e is the equilibrium concentration of CR in solution (mg L^{-1}), R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the adsorption temperature on Kelvin scale.

Langmuir isotherm model was applied to describe the adsorption of CR. The model is represented by the following equation.

$$\left(\frac{C_e}{q_e}\right) = \left(\frac{1}{Q_{\max} K_L}\right) + \left(\frac{C_e}{Q_{\max}}\right) \quad (7)$$

where Q_{\max} is the maximum adsorption capacity of IJS (*Z. maruritiana*) (mg g^{-1}) and K_L is the Langmuir constant related to the adsorption energy (L mg^{-1}).

R_L , a dimensionless constant, is used to determine whether an adsorption is favorable or not and is calculated by

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (8)$$

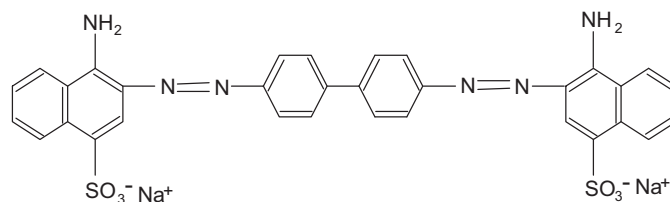


Fig. 1. Chemical structure of CR.

Freundlich isotherm model is also applied to describe the adsorption of CR. Linearized in logarithmic form of Freundlich isotherm model equation is represented by.

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (9)$$

where K_F is the Freundlich constant and ' $1/n$ ' is the heterogeneity factor.

Generalized isotherm model is also applied to describe the adsorption of CR. A linear form of generalized isotherm equation [2] is given by

$$\log \left[\left(\frac{Q_{\max}}{q_e}\right) - 1 \right] = \log K - n_b \log C_e \quad (10)$$

where K is the saturation constant (mg L^{-1}) and n_b the cooperative binding constant.

2. Materials and methods

2.1. Preparation of Indian Jujuba Seeds (IJS) (*Z. maruritiana*) adsorbent

Indian Jujuba Fruits were collected in 2009 summer from Somayajulapally village, located very near to Nandyal town of Kurnool district in Andhra Pradesh State of India. The village is very close to the famous Nallamalla forest. After taking out the pulp of the fruits, the Indian Jujuba Seeds were thoroughly washed with tap water to remove the pulp left, if any and were Sun dried. The dried seed were crushed and sieved to desired mesh sizes varying from $<53 \mu\text{m}$ to $<150 \mu\text{m}$. The prepared sample was abbreviated as IJS (*Z. maruritiana*) and was stored in an airtight container for further use. No other chemical or physical treatments were applied prior to adsorption experiments.

The Indian Jujuba belongs to the family of Rhamnaceae and its botanical name is *Z. maruritiana*.

2.2. Adsorbate

The Congo red used in this study was purchased from Sigma-Aldrich. Its C.I. No. is 22120, FW = 696.7 and $\lambda_{\max} = 497 \text{ nm}$. The chemical structure is shown in Fig. 1. The chemical is used without any further purification.

Stock solution of 1000 mg L^{-1} was prepared by dissolving accurate quantity of the dye in doubly distilled water. The experimental solution was obtained by diluting the stock solution to the designed initial dye concentration.

2.3. Point of zero charge (pH_{PZC})

The zero surface charge characteristics of the IJS (*Z. maruritiana*) were determined, using the solid addition method [43,44]. 40 mL of 0.1 M KNO_3 solution was transferred to a series of 100 mL Stoppered conical flasks. The pH_i values of the solutions were roughly adjusted between 2 and 12 by adding either 0.1 N HCl or NaOH and were measured by using pH meter (Systronics pH system 361 Model, India). The total volume of the solution in each flask was exactly

adjusted to 25 mL by adding KNO_3 solution of the same strength. The pH_i of the solutions were then accurately noted. 50 mg of IJS (*Z. maruritianana*) was added to each flask, and the flask was securely capped immediately. The suspensions were then kept shaking for 24 h and allowed to equilibrate for 0.5 h. The final pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH_f) values (ΔpH) was plotted against the pH_i . The point of intersection of the resulting curve with abscissa, at which pH 0, gave the pH_{PZC} .

2.4. Batch kinetic studies

To study the effect of variables like initial concentration, temperature, adsorbent dosage and pH for the colour removal of CR, batch experiments were carried out, in a 50 mL screw type Erlenmeyer flask and in a thermostatic Julabo water bath shaker at a constant speed of 180 rpm at $30 \pm 1^\circ\text{C}$. Adsorption experiments were carried out by agitating 50 mg of adsorbent, IJS (*Z. maruritianana*) with 25 mL of dye solutions of desired concentration and pH. 25 mL of CR solution of 50 mg L^{-1} , with 50 mg of $<53 \mu\text{m}$ of IJS (*Z. maruritianana*). The original pH of the solution was 6.95 (without any pH adjustment). Similar procedures were followed for another three sets of Erlenmeyer flask containing the same initial CR concentrations and same IJS (*Z. maruritianana*) dosage, but were kept under 40, 50 and 60°C for the thermodynamic studies. The effect of pH on dye removal was studied over a pH range of 2–12. The pH was adjusted by adding a few drops of 1.0 N NaOH or 1.0 N HCl. In this study, 25 mL of a fixed initial concentration of CR at different pH were agitated with 50 mg of IJS (*Z. maruritianana*) adsorbent for 180 min. The effect of IJS (*Z. maruritianana*) dose on the amount of CR adsorbed is obtained by taking different amounts of IJS (*Z. maruritianana*) (10 to 100 mg) and agitated for 180 min with 50 mg L^{-1} solution of CR at original pH of CR. These samples were withdrawn from the shaker at pre-determined time intervals for kinetics and the dye solution was separated from the adsorbent by centrifugation at 10,000 rpm for 20 min. The absorbance of supernatant solution is measured. The concentration of CR is determined spectrophotometrically by monitoring the absorbance at 497 nm using Chemito UV-VIS Spectrophotometer and two 1-cm cells. The wavelength, λ_{max} with maximum absorbance for CR was selected and is found to be 497 nm. The pH of dye solutions was determined using pH meter (Systronics pH system 361 Model, India).

The amount of adsorption at time t , q_t (mg g^{-1}), was calculated by

$$q_t = \frac{[(C_0 - C_t)V]}{W} \quad (11)$$

where C_0 and C_t (mg L^{-1}) are the liquid phase concentrations of dye at initial time and at any time t , respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used (g).

The dye removal percentage is calculated as follows

$$\text{Removal percentage} = \left[\frac{(C_0 - C_e)}{C_0} \right] \times 100 \quad (12)$$

where C_e is the equilibrium concentration in solution (mg L^{-1}).

2.5. Desorption studies

After adsorption experiments, the CR loaded IJS (*Z. maruritianana*) was separated out by filtration using Whatman filter paper No.42 and the filtrate was discarded. The CR loaded IJS (*Z. maruritianana*) was given a gentle wash with double-distilled water to remove the non-adsorbed CR if present. The dye loaded samples were agitated with distilled water by adjusting the initial pH from 2 to 12 for

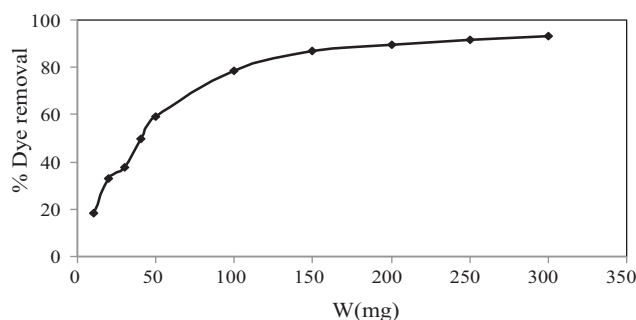


Fig. 2. Effect of adsorbent dose on the adsorption of CR on to IJS (*Zizyphus maruritianana*). Conditions: agitation time = 3 h; $C_0 = 50 \text{ mg L}^{-1}$; $V = 0.025 \text{ L}$; temp. = $30 \pm 1^\circ\text{C}$; speed of agitation = 180 rpm; pH 6.95; size of IJS (*Zizyphus maruritianana*) $\leq 53 \mu\text{m}$.

180 min. The desorbed CR in the solution was separated by centrifugation and analyzed as before. The percentage of desorption was calculated.

2.6. FTIR analysis

FTIR spectra of pristine IJS (*Z. maruritianana*) biomass are obtained by Thermo Nicolet, Nexus 670 Spectrometer with resolution 4 cm^{-1} . Pressed pellets were prepared by grinding the powder specimens with IR grade KBr in an agate mortar.

2.7. Scanning electron microscopy

Scanning electron microscopy of IJS (*Z. maruritianana*) before and after adsorption is visualized by using Hitachi S-3000N Scanning Electron Microscope (SEM).

3. Results and discussion

3.1. Effect of IJS (*Z. maruritianana*) dose

The effect of adsorbent (IJS) (*Z. maruritianana*) dose on the removal of CR from the aqueous solution is shown in Fig. 2. The figure reveals that the removal of CR increases up to a certain limit (150 mg) and then it remains almost constant. An increase in adsorption with adsorbent dose can be attributed to increased surface area and the availability of more adsorption sites [43]. But the amount adsorbed for unit mass of the adsorbent decreases considerably. The decrease in unit adsorption with increasing dose of adsorbent is basically due to the adsorption sites remaining unsaturated during the adsorption process [38]. For the quantitative removal of CR, a maximum dose of 150 mg of adsorbent is required.

3.2. Effect of pH

CR is a diazo dye. It is reported that at and below pH 2, the solution changes its colour from red to dark blue and the original red colour is different above pH 10. Therefore, the effect of pH is studied between 2 and 10. pH values as shown in Fig. 3, the maximum removal efficiency is achieved around pH 2 which is due to the very low solubility of CR at $\text{pH} < 2$. The dye removal is not affected over a pH range of 5–12. It is evident that the maximum removal of dye adsorbed is at pH 2 and below. Low pH leads to an increase in H^+ ion concentration in the system and the surface of the IJS (*Z. maruritianana*) acquires positive charge by adsorbing H^+ ions. As the IJS (*Z. maruritianana*) surface is positively charged at low pH, a significantly strong electrostatic attraction appears between the positively charged sites. A negatively charged surface site on the IJS (*Z. maruritianana*) does not favor the adsorption of anionic CR

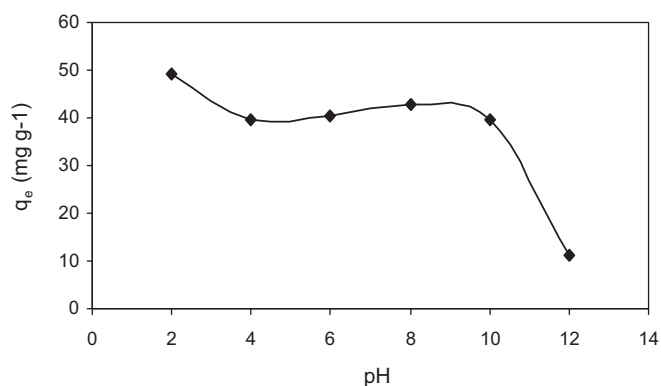


Fig. 3. Effect of pH on equilibrium uptake of CR. Conditions as in Fig. 2 except pH and dose = 50 mg.

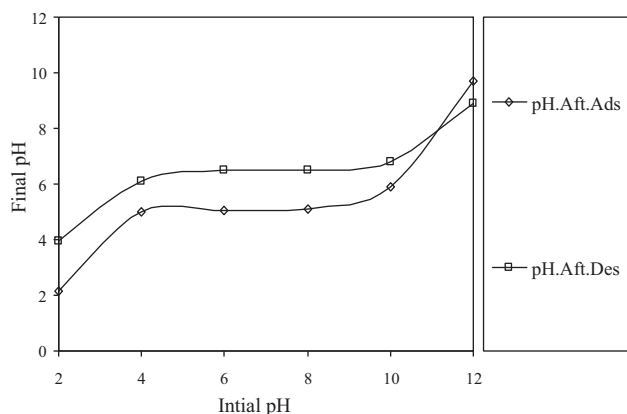


Fig. 4. Initial pH vs final pH of CR. Conditions as in Fig. 2.

molecule due to the electrostatic repulsion. Further, lower adsorption of the CR in alkaline medium is also due to the competition between excess OH^- ions and the anionic CR dye molecule for the adsorption sites. A similar result is observed for the adsorption of CR on cashew nut shell [49], sun flower seed hull [42], soy meal hull [31] and baggese fly ash [50].

The pH of the CR solution was measured after adsorption and for clear understanding purpose it is taken as final pH in presence of CR. In a similar way, pH of the solution was measured after desorption and it is taken as final pH in absence of CR. The initial pH of CR solution was plotted against final pH of solution in presence and absence of CR and this plot is shown in Fig. 4. The final pH was higher than the initial pH the solution with no dye. This may be due to the consumption of H^+ ions during the desorption of alkali metal ions present in the adsorbent and probably, H^+ ions are exchanged with alkali metals as well as with dye molecules. The final pH is lower in the presence of CR compared to the blank. This is due to the release of H^+ ions, during the adsorption of CR. This kind of observation was made for the removal of rhodamine-B by using an agricultural waste, coir pith [51].

3.3. Kinetic study

3.3.1. Effect of initial dye concentration and contact time

The adsorption of CR on IJS (*Z. maruritian*) was studied at different CR concentrations (25–100 mg L^{-1}). Fig. 5 shows the result of effect of initial concentration on adsorption of CR onto IJS (*Z. maruritian*) at $30 \pm 1^\circ\text{C}$. It is observed that dye uptake is rapid for the first 60 min and thereafter proceeds at a slower rate and finally attains saturation. Fig. 5 shows that an increase in initial CR concentration results in increase in the adsorption of CR on IJS (*Z. maruritian*). The

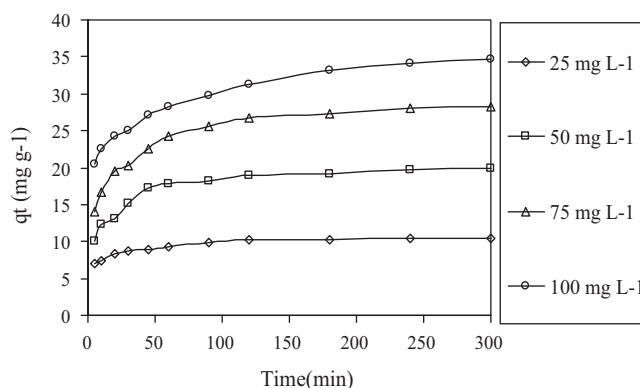


Fig. 5. Effect of initial concentration and contact time on CR adsorption. Conditions: $V = 0.025\text{ L}$; temp. = $30 \pm 1^\circ\text{C}$; speed of agitation = 180 rpm; size of IJS (*Zizyphus maruritian*) $\leq 53\ \mu\text{m}$; dose = 50 mg; pH 6.95.

equilibrium adsorption increases from 10.4677 to 34.6469 mg g^{-1} , with increase in the initial CR concentration from 25 to 100 mg L^{-1} . Thus equilibrium removal of CR gets decreased from 87.95% to 69.87%. The dye attains equilibrium approximately at 1, 1.5, 2 and 2.5 h for dye concentrations 25, 50, 75 and 100 mg L^{-1} , respectively. However, the experimental data is measured at 300 min to make sure that a complete equilibrium is attained. Hu et al. [1] and Somasekhara Reddy [46] studied and reported that the adsorption equilibrium of CR on cattail root [1] and tamarind fruit shell [46] took 3 h and 7 h respectively.

3.3.1.1. Adsorption kinetics. For evaluating the adsorption kinetics of CR, the pseudo-first-order and pseudo-second-order kinetic models are used to fit the experimental data. Using Eqs. (1) and (2), a $\log(q_e - q_t)$ versus t is plotted at different CR concentrations (figure is not shown). The pseudo-first-order model data do not fall on straight lines for most of the initial concentrations indicating that this model is less appropriate. The Lagergren first-order rate constant (k_1) is calculated from the model and is presented in Table 1 beside the corresponding correlation coefficients.

The experimental kinetic data is further analyzed using the pseudo-second-order model. By plotting t/q_t against t for different initial CR concentrations (figure is not shown), a straight line is obtained in all cases and using Eq. (2), the second order rate constant (k_2) and q_e values are determined from the plots. The values of correlation coefficient are very high ($R^2 > 0.9947$) and the theoretical $q_{e\text{ cal}}$ values obtained, from this model are closer to the experimental $q_{e\text{ exp}}$ values at different initial CR concentrations (Table 1). It is important to note that for the pseudo-first-order model, the correlation coefficient obtained in this study, $R^2 < 0.95$ at different initial CR concentrations, is lower compared to the correlation coefficient obtained from the pseudo-second order model. Moreover, from Table 1, it is seen that the experimental values of $q_{e\text{ exp}}$ are not in good agreement with theoretical values calculated ($q_{e\text{ cal}}$) from the pseudo-first-order equation. Therefore, it is concluded that the pseudo-second-order kinetic model provides a better correlation for the adsorption of CR on IJS (*Z. maruritian*) at different initial CR concentrations compared to the pseudo-first-order model. A similar result is reported for the adsorption of methylene blue on jackfruit peel [39] and on Guava leaf powder [44]. The pseudo-first-order and pseudo-second-order kinetic models do not identify the diffusion mechanism. Thus the kinetic results are then analyzed by using the intraparticle diffusion model. Weber and Moris model [47,48] is used with Eq. (3) to investigate intra-particle diffusion mechanism by plotting a graph between, q_t versus $t^{0.5}$ (figure is not shown). If the intra-particle diffusion is the only rate-controlled step, then the plot shall pass through

Table 1
Pseudo-first-order and pseudo-second-order rate constants at 30 °C and different initial CR concentrations. Conditions: size of IJS (*Zizyphus maruritiana*) $\leq 53 \mu\text{m}$; pH of CR solution 6.95; dose of IJS (*Zizyphus maruritiana*) = 50 mg; speed of agitation = 180 rpm.

| C_0 (mg L ⁻¹) | $q_{e \text{ exp}}$ (mg g ⁻¹) | Pseudo-first-order model | | | Pseudo-second-order model | | |
|-----------------------------|---|----------------------------|---|--------|----------------------------|---|--------|
| | | k_1 (min ⁻¹) | $q_{e \text{ cal}}$ (mg g ⁻¹) | R^2 | K_2 (min ⁻¹) | $q_{e \text{ cal}}$ (mg g ⁻¹) | R^2 |
| 25 | 10.4677 | 0.0207 | 10.4887 | 0.9910 | 0.0166 | 10.5177 | 0.9947 |
| 50 | 19.9197 | 0.0138 | 20.2395 | 0.9500 | 0.0059 | 20.0607 | 0.9991 |
| 75 | 28.3407 | 0.0138 | 28.7957 | 0.9820 | 0.0034 | 28.5858 | 0.9982 |
| 100 | 34.6469 | 0.0115 | 35.7775 | 0.9950 | 0.0024 | 34.9472 | 0.9983 |

the origin. Else it is understood that the boundary layer diffusion controls the adsorption to some degree [47]. As seen from the plot t/q_t against t , the plots are not linear over the entire time range, implying that more than one process affected the adsorption and a similar behavior is reported by Hameed et al. [47]. Further, the plot q_t versus $t^{0.5}$ shows at least three regions that represent boundary layer diffusion, are followed by intra-particle diffusion in macro, meso, and micro pores [47]. These three regions are followed by a horizontal line representing the equilibrium of the system.

From q_t versus $t^{0.5}$ plot, there are three linear regions are observed. One at the beginning of adsorption, representing the rapid surface loading, followed by the second representing pore diffusion, and lastly representing the equilibrium. The Microsoft Excel 2003 software package is used to analyze various regions and results of linear regression are obtained from the plot of q_t versus $t^{0.5}$ for various initial concentrations. The intra-particle diffusion parameter, k_{pi} , is determined from the slope of each region, while the intercept of each region is proportional to the boundary-layer thickness. The calculated values of k_{pi} and the intercept, C, for all the linear regions are shown in Table 2. It is obvious from Table 2 that values of k_{pi} for first linear region increases slightly from 0.534 to 2.36 when the initial CR concentration is increased from 25 to 75 mg L⁻¹ and further increase to 100 mg L⁻¹ has little effect. More or less similar trend is observed for all other linear regions. It was also observed that the value of the intercept increases when C_0 is increased from 25 to 100 mg L⁻¹.

3.3.2. Effect of temperature

To understand the effect of temperature on the influence of the removal of CR by IJS (*Z. maruritiana*), experiments were carried out at temperatures 30, 40, 50 and 60 °C at pH 6.95, CR concentration of 50 mg L⁻¹, and adsorbent dosage 2 g L⁻¹ (not shown in figure). The removal efficiency increases with rise in temperature from 30 to 60 °C at the same dye concentration. This process is endothermic thus the increase in the temperature increases the value of Q_{max} .

The adsorption of CR is increased from 79.68% to 99.82 for the initial concentration of 50 mg L⁻¹ with the rise in temperature from 30 to 60 °C. This is mainly due to the increased surface activity suggesting that adsorption between CR and IJS (*Z. maruritiana*) was endothermic. Endothermic adsorption of some dyes on various adsorbents has been reported earlier. The adsorption of methylene blue on chemically treated Psidium Guyava leaves [44], on nanoporous SBA-3 [52] and on neem leaf powder [53] are found to be endothermic (Tables 3 and 4).

Similar to the effect of concentration of CR, the experimental results are analyzed and shown in Table 7.

3.3.2.1. Thermodynamic study. The variation of dye removal efficiency with respect to temperature shall be explained by the thermodynamic parameters, such as ΔG° , ΔH° and ΔS° [1] which are evaluated from Eqs. (4)–(6). The plot of $\ln K_c$ versus T^{-1} of the CR adsorption process is carried out as indicated in Fig. 6, in which the slope and intercept obtained by a curve-fitting program are

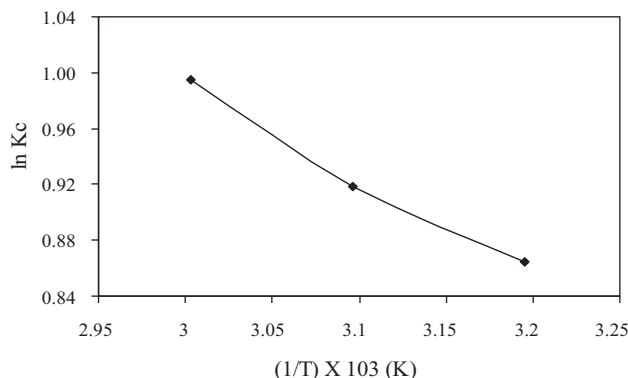


Fig. 6. Plot of $\ln K_c$ against T^{-1} for the removal of CR by IJS (*Zizyphus maruritiana*).

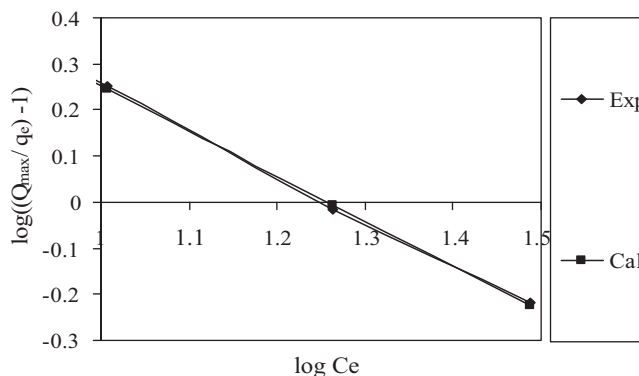


Fig. 7. General isotherm of CR on IJS (*Zizyphus maruritiana*) at 30 ± 1 °C.

used to calculate the ΔH° and ΔS° . The slope of the plot equal to $-\Delta H^\circ/R$ and its intercept is equal to $\Delta S^\circ/R$. The ΔG° , ΔH° and ΔS° are shown in Table 5. The positive value of ΔS° suggests increased randomness at the solid or solution interface during the adsorption of CR on IJS (*Z. maruritiana*) and corresponds to an increase in the degree of freedom of the adsorbed species. Thus, adsorption is favored on CR. This kind of results are observed in case of adsorption of acid violet 17 on sunflower seed hull [42] and adsorption of methylene blue on chemically treated Psidium Guyava leaves [44], nanoporous SBA-3 [52] and neem leaf powder [53].

3.4. Equilibrium modeling

Several mathematical models may be used to describe the experimental data of adsorption isotherms. In this study, the equilibrium data at different concentrations of CR, the adsorption of CR on IJS (*Z. maruritiana*) are modeled with the Langmuir, Freundlich and General isotherm models. The details of the Langmuir, Freundlich and General isotherms are given in Eqs. (7), (9) and (10) and the general isotherm plot is shown in Fig. 7. The values of the Langmuir, Freundlich and general isotherm constants (Langmuir and

Table 2

Intra-particle diffusion constants for different initial CR concentrations at 30 °C. Conditions as in Table 1.

| Linear portion ↓ | Constants ↓ | C ₀ = 25 mg L ⁻¹ | C ₀ = 50 mg L ⁻¹ | C ₀ = 75 mg L ⁻¹ | C ₀ = 100 mg L ⁻¹ |
|------------------|---|--|--|--|---|
| First | K _{p1} (mg g ⁻¹ min ^{-0.5}) | 0.5336 | 1.513 | 2.3614 | 1.6872 |
| | C ₁ (mg g ⁻¹) | 5.7993 | 6.8721 | 8.9803 | 16.887 |
| | R ² | 0.9964 | 0.9747 | 0.993 | 0.9711 |
| Second | K _{p2} (mg g ⁻¹ min ^{-0.5}) | 0.3206 | 0.3802 | 1.5244 | 1.3036 |
| | C ₂ (mg g ⁻¹) | 6.8465 | 14.712 | 12.359 | 18.244 |
| | R ² | 0.9684 | 0.991 | 0.9837 | 0.9543 |
| Third | K _{p3} (mg g ⁻¹ min ^{-0.5}) | 0.042 | 0.1703 | 0.7937 | 0.9664 |
| | C ₃ (mg g ⁻¹) | 9.7207 | 16.984 | 18.057 | 20.666 |
| | R ² | 0.9634 | 0.9858 | 0.9986 | 0.9998 |
| Fourth | K _{p4} (mg g ⁻¹ min ^{-0.5}) | – | – | 0.2542 | 0.5284 |
| | C ₄ (mg g ⁻¹) | – | – | 23.986 | 25.705 |
| | R ² | – | – | 0.9859 | 0.97 |

Table 3

Pseudo-first-order and pseudo-second-order rate constants for different temperatures. Conditions as in Table 1.

| Temperature (°C) | q _{e exp} (mg g ⁻¹) | Pseudo-first-order model | | | Pseudo-second-order model | | |
|------------------|--|-------------------------------------|--|----------------|-------------------------------------|--|----------------|
| | | k ₁ (min ⁻¹) | q _{e cal} (mg g ⁻¹) | R ² | k ₂ (min ⁻¹) | q _{e cal} (mg g ⁻¹) | R ² |
| 30 | 19.9197 | 0.0138 | 20.2395 | 0.9500 | 0.0059 | 20.0607 | 0.9991 |
| 40 | 21.9960 | 0.0069 | 25.1613 | 0.8430 | 0.0311 | 22.0227 | 0.9990 |
| 50 | 22.3090 | 0.0092 | 23.8115 | 0.9070 | 0.0368 | 22.3316 | 1 |
| 60 | 22.7022 | 0.0046 | 30.3141 | 0.8690 | 0.0440 | 22.7212 | 1 |

Table 4

Intra-particle diffusion constants for different temperatures. Conditions as in Table 1.

| Linear Portion ↓ | Constants ↓ | 30 °C | 40 °C | 50 °C | 60 °C |
|------------------|---|--------|-------|--------|--------|
| First | K _{p1} (mg g ⁻¹ min ^{-0.5}) | 1.513 | 0.651 | 0.1241 | 0.208 |
| | C ₁ (mg g ⁻¹) | 6.8721 | 17.49 | 20.293 | 20.841 |
| | R ² | 0.9747 | 0.820 | 0.8758 | 1 |
| Second | K _{p2} (mg g ⁻¹ min ^{-0.5}) | 0.3802 | 0.383 | 0.1763 | 0.1481 |
| | C ₂ (mg g ⁻¹) | 14.712 | 18.67 | 20.296 | 20.982 |
| | R ² | 0.991 | 0.927 | 0.9987 | 0.9666 |
| Third | K _{p3} (mg g ⁻¹ min ^{-0.5}) | 0.1703 | 0.046 | 0.1269 | 0.0139 |
| | C ₃ (mg g ⁻¹) | 16.984 | 20.59 | 20.699 | 22.01 |
| | R ² | 0.9858 | 0.885 | 0.9213 | 0.9168 |
| Fourth | K _{p4} (mg g ⁻¹ min ^{-0.5}) | – | – | – | – |
| | C ₄ (mg g ⁻¹) | – | – | – | – |
| | R ² | – | – | – | – |

Table 5Thermodynamic parameters for the adsorption of CR on IJS (*Zizyphus maruritiana*). Conditions as in Table 1.

| Temperature (°C) | K _c = C _s /C _e | ΔG° (kJ mol ⁻¹) | ΔS° (kJ mol ⁻¹ K ⁻¹) | ΔH° (kJ mol ⁻¹) |
|------------------|---|-----------------------------|---|-----------------------------|
| 30 | 3.9210 | –3.4994 | 0.0579 | 12.9434 |
| 40 | 7.3222 | –5.2646 | | |
| 50 | 8.2902 | –5.7688 | | |
| 60 | 9.8802 | –6.4378 | | |

Freundlich plots are not given) obtained in these studies are presented in Table 6. The Langmuir, Freundlich and General isotherm models are well suited for the experimental data of CR on IJS (*Z. maruritiana*), as per the coefficients of correlation.

The R_L value for the adsorption of CR on IJS (*Z. maruritiana*) is 0.0124 as per Eq. (8), indicating that the adsorption is a favorable process.

The experimental results are in good agreement with the calculated values by using Freundlich, Langmuir and general isotherm parameters.

Similar to above calculations for various concentrations of CR, both Langmuir, Freundlich and general isotherm equilibrium models, are extended to understand the effect of temperature of CR solutions, on the adsorption of CR on IJS (*Z. maruritiana*). The

Table 6Isothermal parameter values for the removal of CR on IJS (*Zizyphus maruritiana*) at different concentrations and temperatures of CR solution.

| Variable | Langmuir constants | | | Freundlich constants | | | General isotherm constants | | |
|-----------------------------------|--|--------------------------------------|----------------|----------------------|---------|----------------|----------------------------|----------------|----------------|
| | Q _{max} (mg g ⁻¹) | K _L (L mg ⁻¹) | R ² | K _F | n | R ² | K | n _b | R ² |
| Conc. of CR (mg L ⁻¹) | 55.5556 | 3.1847 | 0.999 | 4.69 | 1.6639 | 0.987 | 17.02 | 0.979 | 0.999 |
| Temp. (°C) | 18.1818 | 17.5439 | 0.999 | 29.6 | –5.9172 | 0.989 | – | – | – |

Table 7
Adsorption capacities of CR on various adsorbents.

| S. no. | Name of adsorbent | q_e (mg g ⁻¹) | Reference |
|--------|--|-----------------------------|---------------|
| 1 | IJS (<i>Zizyphus maruritianana</i>) | 55.56 | Present study |
| 2 | Jute stick powder | 35.70 | [23] |
| 3 | Sunflower stalks | 31.5–37 | [65] |
| 4 | Cattail root | 38.79 | [1] |
| 5 | Wheat bran | 22.73 | [37] |
| 6 | Rice bran | 14.63 | [37] |
| 7 | Tamarind fruit shell | 10.48 | [46] |
| 8 | Alternanthera bettzichiiana plant powder | 14.67 | [38] |
| 9 | Banana peel | 11.2 | [27] |
| 10 | Orange peel | 7.9 | [27] |
| 11 | Coir pith | 6.72 | [28] |
| 12 | Banana pith | 5.92 | [28] |
| 13 | Cashew nut shell | 5.18 | [49] |

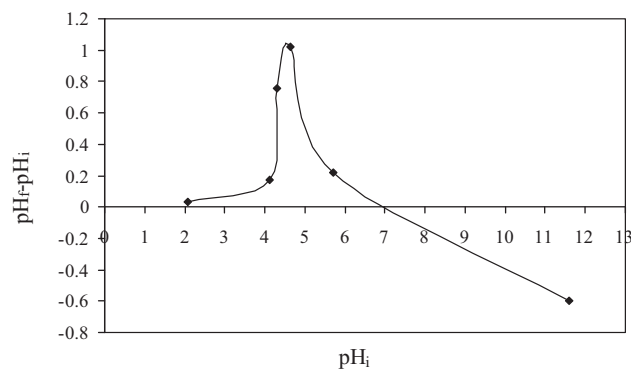


Fig. 9. Determination of the point of zero charge of IJS (*Zizyphus maruritianana*).

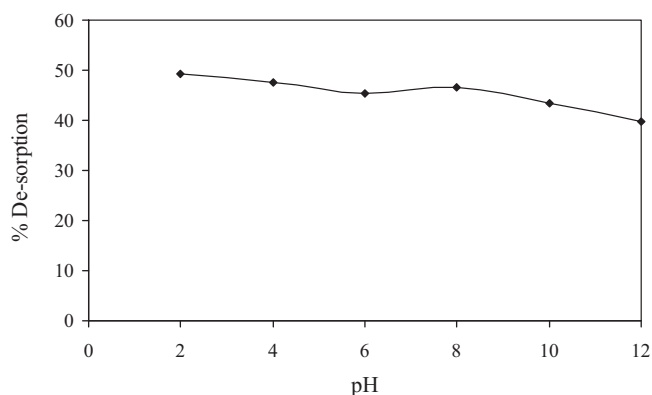


Fig. 8. Desorption studies for the removal of CR.

values of the Langmuir, Freundlich and General isotherm constants calculated from the figures (figures are not shown) are presented in Table 6. Negative values for the Langmuir and Freundlich isotherm constants in Table 6 indicate the inadequacy of the isotherm model to explain the sorption process and are reported in the literature [54–58].

3.4.1. Comparison of various low-cost adsorbents

The adsorption capacity of IJS (*Z. maruritianana*) for the removal of CR is shown in Table 7. The adsorption capacity of various adsorbents for removal of CR is also shown in Table 7 for comparison purpose and the removal capacity of IJS (*Z. maruritianana*) is found to be extremely good. Therefore, IJS (*Z. maruritianana*) is considered to be an excellent adsorbent for the removal of CR from aqueous solution.

3.5. Desorption

Desorption studies help to elucidate the mechanism of adsorption and recovery of the adsorbate and adsorbent. Regeneration of adsorbent makes the treatment process economical. The trend in the desorption process at different pH values is just converse to that of the adsorption process in the pH effect. This is shown in Fig. 8. The percent desorption is decreased from 49.4 to 40 with increase pH from 2 to 12. This indicates that the CR adsorption is mainly due to ion exchange and physical adsorption [29]. Similar type of observation is made in case of desorption of rhodamine-B from the surface of coir pith [51]

3.6. Point zero charge

It is observed from Fig. 9 that the surface charge of the IJS (*Z. maruritianana*) around pH 7 is zero. Hence, the pH_{PZC} at point of zero charge of the IJS (*Z. maruritianana*) is 7.

The effect of pH on the biosorption efficiency of CR is shown in Fig. 3. CR uptake is higher around pH 2, and no significant variations in the pH range from 4 to 7. The high uptake of CR under acidic conditions is probably due to the excessive positive charge on dye anion CR for the adsorption sites. As pH is increased above the PZC value, which is found to be greater than 7, the adsorbent surface becomes predominantly negatively charged, enhancing the electro static repulsion between surface and CR anions. A similar behavior is reported by the adsorption of reactive orange 16 on non-activated Brazilian-pine fruit shell [59] and adsorption of CR on biogas residual slurry [60].

3.7. Cost analysis of IJS (*Z. maruritianana*) waste adsorbent

The maximum adsorption capacity value was used to assess the quantity of adsorbent required to remove 1 kg of CR. This quantity was used as the basis for costing the adsorption process. The relative cost of adsorbents are shown in Table 8, together with adsorption cost to remove 1 kg of CR. Activated carbon was taken as a reference [61] under almost all identical conditions of this study, having a comparative cost of unity.

The results given in Table 8 indicate that the adsorption capacity of IJS (*Z. maruritianana*) is 18.52% of that of activated carbon. The relative cost of the removal of CR onto IJS (*Z. maruritianana*) is only 5.4% of that of activated carbon. In addition, based on the low cost of the IJS (*Z. maruritianana*) compared to activated carbon, there is no need to recover the IJS (*Z. maruritianana*) and the exhausted IJS can also be used as a fuel. Similar type of cost analysis was done by comparing the anionic dye, astrazone blue removal capacity of hardwood with activated carbon [62]. Relative costs of astrazone blue (anionic dye), maxilon red (anionic dye) and telon blue (cationic dye) removal by using number of low-cost materials like bagasse pith, maize cob and natural clay were also reported [63] based on the adsorption capacity of carbon. The cost estimation of another agricultural waste, coconut bunch for the removal of methylene blue was also reported [64].

These results indicate that the removal capacity of CR by activated carbon is higher than that of IJS (*Z. maruritianana*). However, an economic model indicated that IJS (*Z. maruritianana*) may be economically attractive for the removal of CR from aqueous solutions.

Table 8
Relative cost of CR removal.

| Adsorbent | Adsorption capacity | | Mass (kg) of adsorbent required to remove 1 kg of CR | Relative cost kg ⁻¹ adsorbent | Relative cost to remove 1 kg of CR | Reference |
|--------------------------------------|---------------------|-------|--|--|------------------------------------|---------------|
| | mgg ⁻¹ | % | | | | |
| Activated carbon | 300 | 100 | 3.3333 | 1.000 | 1.000 | [61] |
| IJS (<i>Zizyphus maruritiania</i>) | 55.56 | 18.52 | 17.9986 | 0.01 | 0.054 | Present Study |

Table 9
FTIR of IJS (*Zizyphus maruritiania*) adsorbent. Table 1.

| IR peak | Frequency (cm ⁻¹) | | Differences | Assignment |
|---------|-------------------------------|------------------|-------------|--|
| | Before adsorption | After adsorption | | |
| 1 | 3761.36 | 3761.57 | -0.21 | -NH ₂ stretching |
| 2 | 3416.19 | 3419.77 | -3.58 | -OH stretch, H-bonded |
| 3 | 2925.69 | 2925.58 | 0.11 | -CH stretch (strong) |
| 4 | 1741.21 | 1735.60 | 5.61 | -C=O stretch and stretch (strong) aldehyde |
| 5 | 1649.93 | 1625.71 | 24.22 | -C=O stretch (strong) amide |
| 6 | 1519.51 | 1510.16 | 9.35 | -N-O stretch (strong, two bonds) nitro |
| 7 | 1460.03 | 1458.87 | 1.16 | -C-H bending alkane |
| 8 | 1378.50 | 1378.31 | 0.19 | N-O stretch (strong) |
| 9 | 1325.97 | 1322.62 | 3.35 | -C-H bending alkane |
| 10 | 1246.28 | 1254.28 | -8 | -C-F stretch (Strong) alkyl halide |
| 11 | 1048.74 | 1043.16 | 5.58 | C-O stretch (Strong) |
| 12 | 604.66 | 609.08 | -4.42 | C-Cl stretch (strong) |

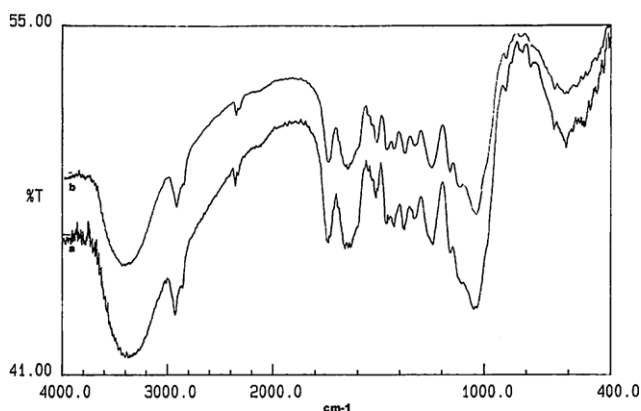
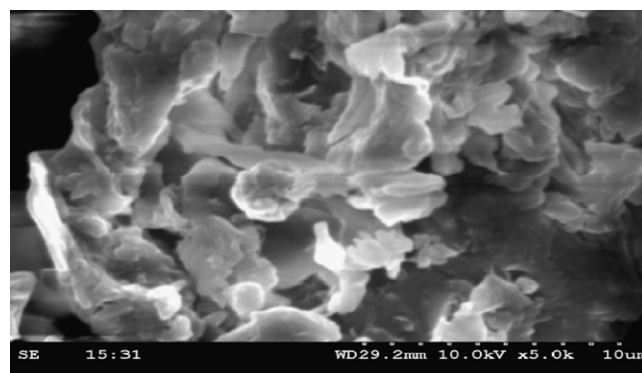
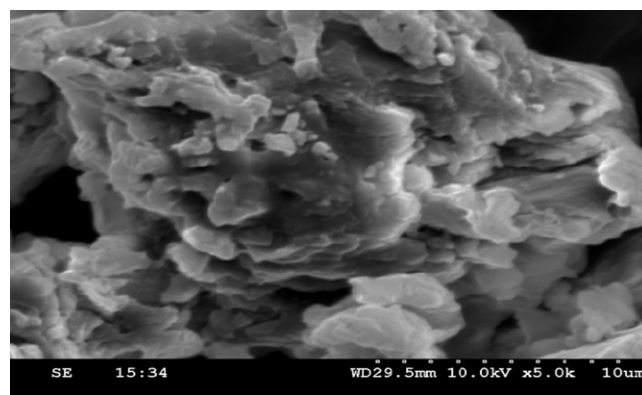
3.8. Characterization of IJS (*Z. maruritiania*)

3.8.1. FTIR analysis

The FTIR spectrum of IJS (*Z. maruritiania*) is shown in Fig. 10 for IJS (*Z. maruritiania*) and CR loaded IJS (*Z. maruritiania*). This figure shows that some peaks are shifted or disappeared and some new peaks are also detected. The change observed in the spectrum indicates the possible involvement of those functional groups on the surface of the IJS (*Z. maruritiania*) in adsorption process. FTIR data of IJS (*Z. maruritiania*) adsorbent is shown in Table 9.

3.8.2. SEM micrographs

Figs. 11 and 12 show the SEM micrographs of IJS (*Z. maruritiania*) sample before and after CR adsorption. It is clear from these figures that IJS (*Z. maruritiania*) has considerable number of heterogeneous layers of pores. Thus, there is a good possibility for CR to be adsorbed. The surface of CR loaded-IJS (*Z. maruritiania*), however, clearly shows that the surface of IJS (*Z. maruritiania*) is covered with CR molecules and the same is observed in Fig. 12.

**Fig. 10.** FTIR spectra of (a) IJS (*Zizyphus maruritiania*) alone and (b) CR loaded IJS (*Zizyphus maruritiania*).**Fig. 11.** Scanning electron microscopic photograph of IJS (*Zizyphus maruritiania*).**Fig. 12.** Scanning electron microscopic photograph of CR loaded IJS (*Zizyphus maruritiania*).

4. Conclusions

The present study establishes the fact that IJS (*Z. maruritiania*) may be used as an adsorbent for the removal of CR from aqueous solutions. The amount of dye adsorbed is found to vary with initial CR concentration and contact time. The Langmuir adsorption

isotherms are found to provide the best fit to the experimental data with a maximum adsorption capacity of 55.56 mg g⁻¹. The adsorption kinetics can be determined by pseudo-second-order kinetics. The results of the present investigation indicate that the IJS (*Z. maritima*) has potential for use in removing CR from aqueous solutions.

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References

- [1] Z. Hu, H. Chen, F. Ji, S. Yuan, Removal of Congo red from aqueous solution by cattail root, *J. Hazard. Mater.* 173 (2010) 292–297.
- [2] B. Noroozi, G.A. Sorial, H. Bahrami, M. Arami, Equilibrium and kinetic adsorption study of cationic dye by a natural adsorbent-Silkworm pupa, *J. Hazard. Mater.* B139 (2007) 167–174.
- [3] J.G. Montano, F. Torrades, L.A. Perez Estrada, I. Oller, S. Malato, M.I. Maldonado, J. Peral, Degradation pathways of the commercial reactive azo dye Procion Red H-E7B under solar-assisted photo-Fenton reaction, *Environ. Sci. Technol.* 42 (2008) 6663–6670.
- [4] K.C. Chen, J.Y. Wu, W.B. Yang, S.C.J. Hwang, Evaluation of effective diffusion coefficient and intrinsic kinetic parameters on azo dye biodegradation using PVA-immobilized cell beads, *Biotechnol. Bioeng.* 83 (2003) 821–832.
- [5] A. Kar, Y.R. Smith, V. Subramanian, Improved photo catalytic degradation of textile dye using titanium dioxide nanotubes formed over titanium wires, *Environ. Sci. Technol.* 43 (2009) 3260–3265.
- [6] M. Sarioglu, U.A. Atay, Removal of methylene blue by using biosolid, *Global NEST J.* 8 (2006) 113–120.
- [7] S. Mondal, Methods of dye removal from dye house effluent—an overview, *Environ. Eng. Sci.* 25 (2008) 383–396.
- [8] M.N. Abbasi, R. Asl, Sonochemical degradation of Basic Blue 41 dye assisted by nanoTiO₂ and H₂O₂, *J. Hazard. Mater.* 153 (2008) 942–947.
- [9] V.K. Gupta, A. Mittal, R. Jain, M. Mathur, S. Sikarwar, Photochemical degradation of hazardous dye—safararin-T using TiO₂ catalyst, *J. Colloid Interface Sci.* 309 (2007) 460–465.
- [10] M.R. Sohrabi, M. Ghavami, Photocatalytic degradation of Direct Red 23 dye using UV/TiO₂: effect of operational parameters, *J. Hazard. Mater.* 153 (2008) 1235–1239.
- [11] V.K. Gupta, R. Jain, S. Varshney, Electrochemical removal of hazardous dye Reactofix Red 3 BFN from industrial effluents, *J. Colloid Interface Sci.* 312 (2007) 292–296.
- [12] L. Fan, Y. Zhou, W. Yang, G. Chen, F. Yang, Electrochemical degradation of aqueous solution of Amaranth azo dye on ACF under potentiostatic model, *Dyes Pigments* 76 (2008) 440–446.
- [13] M.H. Zonoozi, M.R.A. Moghaddam, M. Arami, Coagulation/flocculation of dye containing solutions using polyaluminium chloride and alum, *Water Sci. Technol.* 59 (2009) 1343–1351.
- [14] S. Sachdeva, A. Kumar, Preparation of nonporous composite carbon membrane for separation of Rhodamine B dye, *J. Membr. Sci.* 329 (2009) 2–10.
- [15] G. Ciardelli, L. Corsi, M. Marucci, Membrane separation for wastewater reuse in the textile industry, *Resour. Conserv. Recycl.* 31 (2000) 189–197.
- [16] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption of basic dye on high-surface area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies, *J. Hazard. Mater.* 154 (2008) 337–346.
- [17] N. Daneshvar, A.R. Khataee, M.H. Rasoulifard, M. Pourhassan, Biodegradation of dye solution containing Malachite Green: optimization of effective parameters using Taguchi method, *J. Hazard. Mater.* 143 (2007) 214–219.
- [18] P.K. Malik, S.K. Saha, Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst, *Sep. Purif. Technol.* 31 (2003) 241–250.
- [19] A. Bhatnagar, M. Sillanpaa, Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—a review, *Chem. Eng. J.* 157 (2010) 277–296.
- [20] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, *Bioresour. Technol.* 97 (2006) 1061–1085.
- [21] M.C. Somasekhara Reddy, Utilization of agricultural wastes/by-products in treatment of water and wastewater, in: *Wealth from Waste*, 2nd edition, TERI Press, New Delhi, 2005, pp. 349–409.
- [22] A. Demirbas, Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review, *J. Hazard. Mater.* 167 (2009) 1–9.
- [23] G.C. Panda, S.K. Das, A.K. Guha, Jute stick powder as a potential biomass for the removal of Congo red and rhodamine B from their aqueous solution, *J. Hazard. Mater.* 164 (2009) 374–379.
- [24] R.M. Gong, Y. Ding, M. Li, C. Yang, H.J. Liu, Y.Z. Sun, Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution, *Dyes Pigments* 64 (2005) 187–192.
- [25] S. Banerjee, M.G. Dastidar, Use of jute processing wastes for treatment of wastewater contaminated with dye and other organics, *Bioresour. Technol.* 96 (2005) 1919–1928.
- [26] K.G. Bhattacharyya, A. Sharma, *Azadirachta indica* leaf powder as an effective biosorbent for dyes: a case study with aqueous Congo red solutions, *J. Environ. Manage.* 71 (2004) 217–229.
- [27] C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani, K. Ranganathan, Removal of dyes from aqueous solutions by cellulosic waste orange peel, *Bioresour. Technol.* 57 (1996) 37–43.
- [28] C. Namasivayam, K. Kadirvelu, Coir pith, an agricultural waste by-product, for the treatment of dyeing wastewater, *Bioresour. Technol.* 48 (1994) 79–81.
- [29] H.M. Asfour, M.M. Nassar, D.A. Fadali, M.S. El-Geundi, Colour removal from textile effluents using hardwood saw dust as an adsorbent, *J. Chem. Technol. Biotechnol.* 35 (1985) 28–35.
- [30] G. McKay, E. El-Geundi, M.M. Nassar, Pore diffusion during the adsorption of dyes onto bagasse pith, *Process Saf. Environ. Prot.* 74 (1996) 487–502.
- [31] M. Arami, N.Y. Limaee, N. Mohamoodi, N. Tabrizi, Equilibrium and kinetics studies for the adsorption of direct and acid dyes from aqueous solution by soy meal hull, *J. Hazard. Mater.* B 135 (2006) 171–179.
- [32] G. McKay, G. Ram Prasad, P. Mowli, Desorption and regeneration of dye colours from low-cost materials, *Water Res.* 21 (1987) 375–377.
- [33] V. Meyer, F.H.H. Carlsson, R.A. Oellermann, Decolourization of textile effluent using a low cost natural adsorbent material, *Water Sci. Technol.* 26 (1992) 1205–1211.
- [34] M. Dogan, H. Abak, M. Alkan, Biosorption of methylene blue from aqueous solutions by hazelnut shells: equilibrium, parameters and isotherms, *Water Air Soil Pollut.* 192 (2008) 141–153.
- [35] V.K. Gupta, A. Mittal, A. Malviya, J. Mittal, Adsorption of carmoisine A from waste water using waste materials—bottom ash and de-oiled soya, *J. Colloid Interface Sci.* 355 (2009) 24–33.
- [36] V.K. Gupta, A. Mittal, L. Kurup, J. Mittal, Adsorption of a hazardous dye erythro-sine over hen feathers, *J. Colloid Interface Sci.* 304 (2006) 52–57.
- [37] Xue Song Wang, Jing Ping Chen, Biosorption of Congo red from aqueous solution using wheat bran and rice bran: batch studies, *Sep. Sci. Technol.* 44 (2009) 1452–1466.
- [38] A.K. Patil, V.S. Shrivastava, *Alternanthera bettzichiana* plant powder as low cost adsorbent for removal of Congo red from aqueous solution, *Int. J. ChemTech Res.* 2 (2010) 842–850.
- [39] B.H. Hameed, Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low-cost adsorbent, *J. Hazard. Mater.* 162 (2009) 344–350.
- [40] V. Jaikumar, K. Shathish Kumar, D. Gnana Prakash, Biosorption of acid dyes using spent brewery grains: characterization and modeling, *Int. J. Appl. Sci. Eng.* 7 (2009) 115–125.
- [41] M.M. Perju, E.S. Dragan, Removal of azo dyes from aqueous solutions using chitosan based composite hydrogels, *Ion Exchange Lett.* 3 (2010) 7–11.
- [42] N. Thinakaran, P. Baskaraligam, M. Pulikesi, P. Panneerselvam, S. Sivanesan, Removal of acid violet 17 from aqueous solutions by adsorption onto activated carbon prepared from sunflower seed hull, *J. Hazard. Mater.* 151 (2008) 316–322.
- [43] B.H. Hameed, Evaluation of papaya seed as a novel non-conventional low-cost adsorbent for removal of methylene blue, *J. Hazard. Mater.* 162 (2010) 939–994.
- [44] V. Ponnusami, S. Vikram, S.N. Srivastava, Guava, (*Psidium guajava*) leaf powder: novel adsorbent for removal of methylene blue from aqueous solutions, *J. Hazard. Mater.* 152 (2008) 276–286.
- [45] M.C. Ncibi, B. Mahjoub, M. Seffen, Kinetic and equilibrium studies of methylene blue biosorption by *Posidonia oceanica* (L.) fibers, *J. Hazard. Mater.* B139 (2007) 280–285.
- [46] M.C. Somasekhara Reddy, Removal of direct dye from aqueous solution with a novel adsorbent made from Tamarind Fruit Shell, an agricultural solid waste, *J. Sci. Ind. Res.* 65 (2006) 443–446.
- [47] B.H. Hameed, M.I. El-Khaiary, Removal of basic dye from aqueous medium using a novel agricultural waste material: pumpkin seed hull, *J. Hazard. Mater.* 155 (2008) 601–609.
- [48] B.H. Hameed, M.I. El-Khaiary, Sorption kinetics and isotherm studies of a cationic dye using agricultural waste: broad bean peels, *J. Hazard. Mater.* 154 (2008) 639–648.
- [49] P. Senthil Kumar, S. Ramalingam, C. Senthamarai, M. Niranjana, P. Vijayalakshmi, S. Sivanesan, Adsorption of dye from aqueous solution by Cashew nut shell: studies on equilibrium isotherm, kinetics and thermodynamics of interactions, *Desalination* 261 (2010) 52–60.
- [50] I.D. Mall, V.C. Srivastava, N.K. Agarawal, I.M. Mishra, Removal of Congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analysis, *Chemosphere* 61 (2005) 492–501.
- [51] C. Namasivayam, R. Radhika, S. Suba, Uptake of dyes by a promising locally available agricultural solid waste: coir pith, *Waste Manag.* 21 (2001) 381–387.
- [52] M. Aniba, S. Asl Hariri, Removal of methylene blue from aqueous solution using nanoporous SBA-3, *Desalination* 261 (2010) 61–66.
- [53] K.G. Bhattacharyya, A. Sharma, Utilization of biosorbent based on *Azadirachta indica* (Neem) leaves for removal of water-soluble dyes, *Indian J. Chem. Technol.* 12 (2005) 285–295.

- [54] T. Rabinson, B. Chandran, P. Nigam, Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw, *Water Res.* 36 (2002) 2824–2830.
- [55] T. Rabinson, B. Chandran, P. Nigam, Effect of pretreatments of three waste residues, wheat straw, corn cobs and barley husks on dye adsorption, *Bioresour. Technol.* 85 (2002) 119–124.
- [56] M.A. Abdullah, L. Chiang, M. Nadeem, Comparative evaluation of adsorption kinetics and isotherms of a natural product removal by Amberlite polymeric adsorbents, *Chem. Eng. J.* 146 (2009) 370–376.
- [57] T. Ennil Kose, Agricultural residue anion exchanger for removal of dyestuffs from wastewater using full factorial design, *Desalination* 222 (2008) 323–330.
- [58] A. Hussain, A. Ghafoor, M. Anwar-Ul-Haq, M. Nawaz, Application of the Langmuir and Freundlich equations for P adsorption phenomenon in saline-sodic soils, *Int. J. Agric. Biol.* 5 (2003) 349–356.
- [59] T. Calvete, E.C. Lima, N.F. Cardoso, J.C.P. Vaggetti, S.L.P. Dias, F.A. Pavan, Application of carbon adsorbents prepared from the Brazilian pine-fruit-shell for the removal of reactive orange from aqueous solution: kinetic, equilibrium and thermodynamic studies, *J. Environ. Manage.* 91 (2010) 1695–1706.
- [60] C. Namasivayam, R.T. Yamuna, Adsorption of direct red 12 B by biogas residual slurry: equilibrium and rate processes, *Environ. Pollut.* 89 (1995) 1–7.
- [61] M.K. Purkait, A. Maiti, S. Das Gupta, S. De, Removal of Congo red using activated carbon and its regeneration, *J. Hazard. Mater.* 145 (2007) 287–295.
- [62] H.M. Asfour, O.A. Fadali, M.M. Nassar, M.S. El-Geundi, Equilibrium studies on adsorption of basic dyes on hardwood, *J. Chem. Technol. Biotechnol.* 35A (1985) 21–27.
- [63] M.M. Nassar, M.S. El-Geundi, Comparative cost of colour removal from textile effluents using natural adsorbents, *J. Chem. Technol. Biotechnol.* 50 (1991) 257–264.
- [64] B.H. Hameed, D.K. Mahmoud, A.L. Ahmad, Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: coconut (*Cocos nucifera*) bunch waste, *J. Hazard. Mater.* 158 (2008) 65–72.
- [65] G. Sun, X. Xu, Sunflower stalks as adsorbents for color removal from textile wastewater, *Ind. Eng. Chem. Res.* 36 (1997) 808–812.