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Adsorption of anionic azo dye Congo Red from aqueous solution onto NaOH-modified jute fibre

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ABSTRACT

Adsorption of Congo red onto NaOH-modified jute fibre was studied for different concentrations of dye solutions (50, 100, 150 and 200 mg/L). Experiments were carried out as function of contact time, initial solution pH (3–9), adsorbent dose (10–20 g/L) and temperature (293, 303 and 313 K). Adsorption data fit better to Langmuir model in comparison with the Freundlich model. This indicates the monolayer adsorption on the homogeneous surface of the adsorbent with identical binding sites of the adsorbent. The adsorption process followed the pseudo-second-order kinetic model. The maximum sorption capacity (q_{max}) was found to be 32.24 mg/g. The maximum adsorption occurred at pH 7.0. The effect of adsorption dose was studied and optimum adsorption was obtained at a jute dose of 16 g/L.

Keywords: Adsorption; NaOH-modified jute fibre; Congo Red; Isotherm; Equilibrium studies; Pseudo-first-order; Pseudo-second-order

1. Introduction

In human world, colour is a very essential aspect. In our daily life whatever commodity we use consist of different colours. Eventually various studies are there for the production of colour. More than 10,000 dyes available commercially nowadays and annually 700,000 tons of dyes are produced [1]. There are various kinds of dyes available commercially like some of them are acidic, while some are basic and so on.

The textile industry is the largest consumer of dye stuffs. During the colouration process, a large percentage of the synthetic dye does not bind and is lost to the waste stream [2]. Approximately 10%–15% dyes are released into the environment during dyeing process making the effluent highly coloured and aesthetically unpleasant. The effluent from textile industries thus carries a large number of dyes and other additives which are added during the colouring process [3]. These are difficult to remove by conventional water treatment procedures and can be transported easily through sewers and rivers especially because they are designed to have high water solubility. They may also undergo degradation to form products that are highly toxic and carcinogenic [4]. So dyes possess potential risk to the environment. Hence it is required to protect the nature from these complex components. And to do so, it is important to identify suitable methods to identify and treat/remove such hazardous components from water bodies. Adsorption by activated carbon is a well-known commercial technique to extract/remove dyes from waste water bodies, but due to the high cost involved in the process, researchers are continuously trying to figure out other low-cost bio-sorbents which are effective and economical in the removing process of dyes from aqueous solution.

Congo Red (CR) is the sodium salt of 3,3′-([1,1′-biphenyl]-4,4′-diyl)bis(4-aminonaphthalene-1-sulfonic acid) (formula: $C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight: 696.66 g/mol). It is a secondary diazo dye, which is synthesized by coupling tetrazotised benzidine with two molecules of napthionic acid. It has a strong, though apparently noncovalent, affinity to cellulose fibres. CR is used in the cellulose industries (cotton textile, wood pulp and paper). Due to its complex structure it is difficult to break and has high toxicity and tendency to run and change colour when touched by sweaty fingers.

Jute is one of the valuable agricultural material produced in India. Around 85% of world's jute production

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is concentrated in the Ganges Delta (Bangladesh, India) and parts of China. Jute fibre principally consists of cellulose, hemicellulose, lignin, and other low molecular weight hydro-carbons [5]. These components contain various functional groups, such as carboxyl and hydroxyl, which make jute fibre a potential adsorbent material for removing dyes from aqueous solutions. In recent years, research interest has been focused on increasing the sorption capacity of agricultural products through physical and chemical modifications. These modifications are aimed at increasing the fraction of the effective functional groups such as carboxylate, hydroxyl, sulphate, phosphate, amide and amino groups on the adsorbent surface. In this study, NaOH-modified jute fibre (NMJF) was chosen as an adsorbent for the removal of CR from aqueous solution.

It is well known that use of activated carbon for the treatment of waste water (removal of dyes from waste water) is a very well established technique, but due to the high cost involved in the process, researchers are constantly working on finding other low-cost bio-sorbents which are effective in removal of dyes from waste water.

Thus it is important to remove CR before its transformation. In order to design adsorption treatment systems, knowledge of kinetic and mass transfer process is essential. In this work, we have attempted to use an agricultural product, NMJF, for the removal of a very harmful carcinogenic dye CR from aqueous solution.

2. Materials and methods

2.1. Adsorption scope for CR dye onto NMJF

Jute is a multi-cellular and multi-constituent fibre and apart from α-cellulose (~60%), other two major chemical constituents of jute are hemicellulose (~23%) and lignin (~14%) and traces of fat and wax. It has been reported that portion of lignin and hemicellulose are linked chemically through ester linkage formed by the carboxyl groups of hemicellulose and by the hydroxyl groups of lignin [6]. The availability of functional groups such as carboxyl and hydroxyl groups is the main reason for the adsorption of dyes from aqueous solution.

In this study, the adsorbent is pre-treated with NaOH, as alkali treatment is viewed as one of the widely employed chemical treatment techniques for surface modification of cellulose-based materials for the purpose of improving its adsorption properties. Also the treatment of jute fibre with aqueous sodium hydroxide (NaOH) solutions breaks the covalent association between lignocellulose components, hydrolysing hemicellulose and de-polymerising lignin [7]. This treatment has a substantial influence on morphological, molecular and supramolecular properties of cellulose, causing changes in crystallinity, pore structure, accessibility, stiffness, unit cell structure, and orientation of fibrils in cellulosic fibres [8]. NaOH also improves mechanical and chemical properties of cellulose such as structural durability, reactivity and natural ion-exchange capacity. Treatment with NaOH removes natural fats and waxes from the cellulose fibre surfaces thus revealing chemically reactive functional groups like –OH [9]. Previous findings indicated that NaOH-modified rice husk (rich in cellulose compound) could be employed as an effective adsorbent for the removal of azo dyes [10] from aqueous solutions. Since in jute fibres the cellulose and hemicellulose components are also present in huge amount, so an attempt of the feasibility of applying NMJF for the removal of CR dye from aqueous solution was explored in the present study.

2.2. Materials

Sun-dried jute fibres obtained from market are cut into sizes of 1 mm size and washed with distilled water and dried at 60°C thus raw jute was obtained. The sample was processed with 0.01 M NaOH at 27°C for 4 h, then distilled water washed so as to remove excess chemicals in fibres and pH was adjusted to 7.0 using 0.1 M HCL or 0.1 M NaOH, then dried at 100°C for 1 d and was kept in container. Thus we get the pre-treated NMJF.

An azo dye CR, having a strong, though apparently noncovalent, affinity to cellulose fibres, having molecular formula: $C_{32}H_{22}N_6Na_2O_6S_2$; and molecular weight: 696.66 g/mol with C.I. No. 22120, CAS No. 573-58-0, was chosen as adsorbate (Fig. 1). All the chemicals used were of Analar grade and obtained from Himedia, Mumbai. A stock solution (1,000 mg/L; pH 7; λ_{max} = 498 nm) of dye was prepared using double distilled water.

2.3. SEM analysis of jute fibres

Scanning electron microscope (SEM) analysis was also carried out to characterize the surface structure and morphology of distilled washed jute fibre, NMJF and also CR adsorbed NMJF. SEM study was done using SEM (Model JSM 6360, JEOL/EO) at an electron acceleration voltage of 20 kV. The samples were coated with a thin layer of carbon using a sputter coater to avoid charging under the electron beam.

2.4. Batch adsorption procedure and equilibrium studies

Adsorption analysis was done batchwise to analyse the removal of CR with the help of variation in temperature, pH, initial dye concentration and contact time. First the effect of pH variation onto the removal of CR by NMJF was studied and found that the maximum adsorption occurred at pH 7.0. Next from the stock dye solution of 1,000 mg/L different combinations of dye solutions were prepared for solutions with different initial concentrations viz. 50, 100, 150 and 200 mg/L at pH 7.0. Initial NMJF dose was taken as 10 g/L and the same rate of dose was mixed with each of the prepared solutions, agitated mechanically with the help of rotary shaker at 27°C at 150 rpm until the equilibrium was reached. For time t = 0 min, 5 min, 10 min and so on, until equilibrium, the dye concentrations were measured from absorbance values obtained using UV/Vis spectroscopy (Lambda 45, PerkinElmer, Bengaluru). The data were used to calculate the amount of dye adsorbed, q (mg/g). Effect of NMJF dose was studied upon the absorption of CR dye by varying adsorbent dose at 10, 15, and 20 g/L. Experiments were carried out at different pH values ranging from 3.0 to 9.0. The pH values were adjusted in the range of 3–9 using 0.1 M HCL or 0.1 M NaOH. A fixed amount of NMJF (1 g) was added to the 100 mL of 50 mg/L of CR solution at different pH values (3.0–9.0) and agitated for 3 h at 27°C to assess the influence of initial pH on CR concentration, by taking and measuring the samples after each 5 min of agitation. Experiments were also carried out to check for adsorption of CR by the container walls in the absence of jute. It was found that there was no degradation or adsorption of CR by container walls.

Variation of temperature affect was evaluated for 293, 303, and 313 K. Experiments were carried out in duplicate and mean values were taken. The amount of dye adsorbed per unit adsorbent (mg dye per g adsorbent) was calculated according to a mass balance on the dye concentration using Eq. (1):

$$q_e = \frac{\left(C_i - C_e\right)V}{m} \tag{1}$$

The percent removal (%) of dye was calculated using the following equation:

$$\text{Removal}(\%) = \frac{\left(C_i - C_e\right)}{C_i} \times 100 \tag{2}$$

3. Theory

3.1. Adsorption isotherm

The adsorption isotherm is the basic principle in defining the adsorption behaviour between adsorbate and adsorbent and thus they are essential in designing the adsorption process. In the given study, the isotherm modelling of CR was tested at various temperatures by keeping the initial CR concentration constant at 50 mg/L and varying the dose of NMJF. Widely used isotherm equilibrium modelling such as the Langmuir [11] and Freundlich [12] isotherm models are being used in the present study for analysing the adsorption feasibility of CR onto NMJF.

$$\text{Langmuir}: q_e = \frac{q_m b C_e}{1 + bC_e} \tag{3}$$

where q_e = equilibrium solute concentration of dyes in solution (mg/L); q_m = maximum monolayer adsorption capacity, it is independent of temperature; b = Langmuir constant, constant related to energy, it is temperature dependant; C_e = concentration of solute in solution at equilibrium.

The nature of the Langmuir isotherm can be analysed by checking whether the adsorption was favourable, linear or unfavourable, in terms of dimensionless constant separation factor R_L [13], which is represented in Eq. (4). R_L indicates the nature of isotherm, whether it is favourable ($R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$):

$$R_L = \left(\frac{1}{1 + bC_0}\right) \tag{4}$$

where C_0 = initial concentration of the adsorbate in the solution (mg/L).

$$\text{Freundlich}: q_e = K_f C_e^{\,1/n} \tag{5}$$

where K_f and $1/n$ are constants; C_e = concentration at equilibrium; q_e = equilibrium sorption capacity.

3.2. Kinetic modelling

Time depending experimental results were next used to study the kinetic parameters of the sorption system. Well-known kinetic models viz. pseudo-first-order [14] and pseudo-second-order [15] were used to achieve the rate constant and optimum sorption capacity at various temperature range:

$$\text{Pseudo-first-order}: q_t = q_1\left[1 - \exp\left(-k_1 t\right)\right] \tag{6}$$

$$\text{Pseudo-second-order}: q_t = \frac{q_2^2 k_2 t}{1 + q_2 k_2 t} \tag{7}$$

The above kinetic models has a limit when they are associated with finding the diffusion mechanism of the sorption process, so a diffusion model [16] was employed to find the rate controlling steps.

$$\text{Intra-particle diffusion}: q_t = k_i t^{0.5} \tag{8}$$

3.3. Activation energy and thermodynamic parameters

For CR sorption upon NMJF, Arrhenius equation [17] was used to determine the activation energy E_a, the equations are listed below:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{9}$$

where activation energy E_a can be obtained from the slope of a plot of ln$k$ vs. $1/T$. Thermodynamic characteristics of CR sorption onto NMJF was studied using $\Delta G°$, $\Delta H°$, and $\Delta S°$. The mentioned parameters were calculated using the following equations:

$$\Delta G° = -RT \ln K_C \tag{10}$$

$$K_C = \frac{C_a}{C_e} \tag{11}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{12}$$

A plot of $\Delta G°$ vs. temperature, T, will generally be linear with the slope and intercept giving the values of $\Delta H°$ and $\Delta S°$, where $\Delta G°$ = Gibbs free energy change, $\Delta H°$ = enthalpy change, and $\Delta S°$= entropy change.

4. Results and discussion

4.1. Characterization of NMJF

The SEM micrographs of distilled washed jute fibre and NMJF are shown in Figs. 2(a) and (b). Both the materials have an uneven, rough, and porous surface which provides a large exposed surface area for the dye adsorption. Surface morphology of distilled washed jute fibre changed after treatment with sodium hydroxide and more pores and cavities of various dimensions are clearly visible. Eventually the adsorption of CR onto NMJF can be depicted from Fig. 2(c).

4.2. Effect of contact time and initial dye concentration

The experimental results of adsorption of CR onto NMJF at various concentrations (50, 100, 150, and 200 mg/L) with contact time shows that percent adsorption decreased with increase in initial CR concentration, but the rate of CR adsorbed per unit mass of jute increased with increase in CR concentration. The unit adsorption of CR was increased from 40.27 to 84.63 mg/g (figure not shown) as the CR concentration varied from 50 to 200 mg/L. Equilibrium was established at 90 min for all the concentrations studied. During the adsorption of dyes, initially the dye molecules reach the boundary layer; then they have to diffuse into the adsorbent surface to get adsorbed. So, this phenomenon will not take place too early but will also not consume too much time to complete. The study shows that there is a possible monolayer coverage of CR on the jute surface.

4.3. Effect of pH

pH of an aqueous solution holds a significant role upon the adsorption process of adsorbate onto the adsorbent due to the fact that pH has a great impact with regarding to the affinity of the adsorbate molecules to get adsorbed at the surface of the adsorbent. [20]. Therefore the sorption behaviour of CR onto NMJF was analysed for a pH range of 3–9 for a volume of 100 mL taken from the solution having concentration of 50 mg/L agitated for 3 h at 303 K, with jute dose 10 g/L, rotated at 150 rpm. The analysis shows that percentage removal of CR increases with increase in pH of the dye solution significantly upto 6, after this value of pH further increment of the same does not show same rate of increment of CR adsorption onto NMJF. Because maximum adsorption occurred at pH 7.0, every future analysis was done at pH 7.0. The results are shown in Fig. 3. Same kind of pH effect was studied for the adsorption of Crystal violet (CV) on modified rice husk [18]. This variation of adsorption due to change in pH is due to the fact that at low pH values, the surface of the adsorbent becomes positively charged, and this decreases the adsorption of the positively charged dye ions through electrostatic repulsion. As there is an increment of pH in dye solution, enhancement in sorption occurs due to deprotonation of positively charged sorbent surface converting the sites into negatively charged, thereby increasing the electrostatic attraction between the adsorbent surface and the positively charged adsorbate.

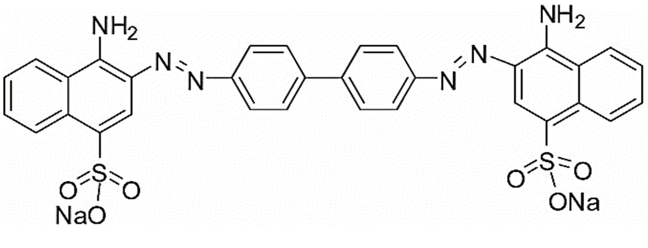

Fig. 1. Molecular structure of Congo Red.

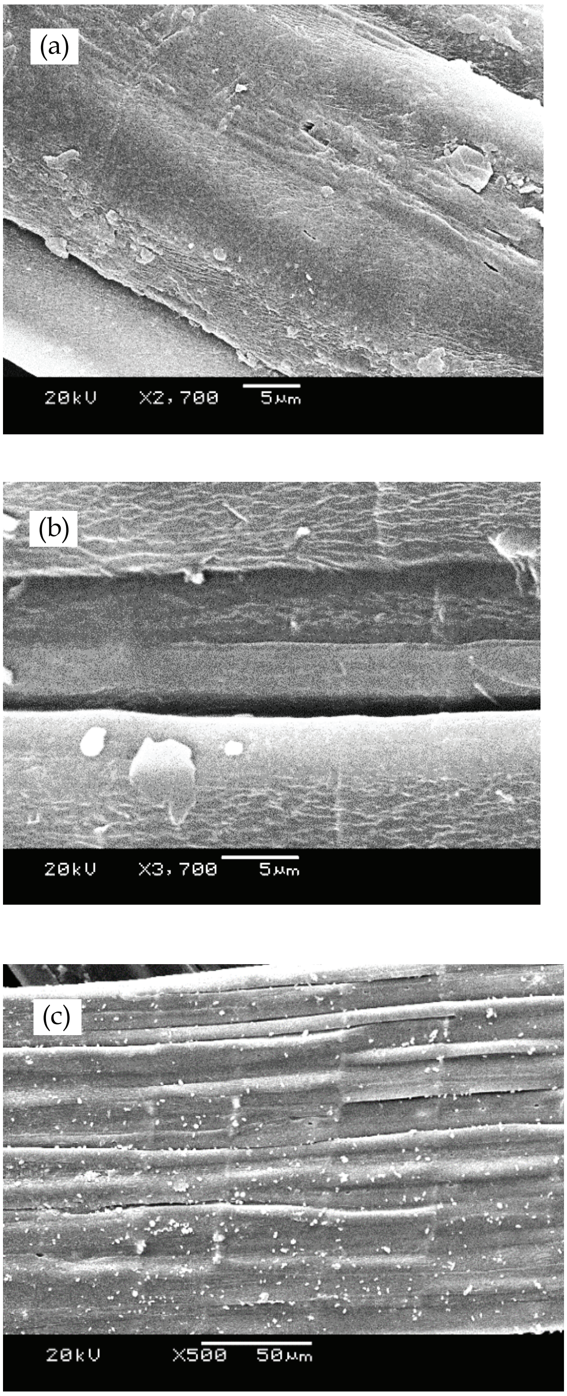

Fig. 2. SEM micrographs: (a) distilled washed jute fibre (b) NaOH-modified jute fibre (c) CR adsorbed NMJF.

4.4. Effect of NMJF dose

The adsorption process of dye also depends upon the adsorbent dose which is an important parameter that strongly affects the process adsorption capacity. Therefore the influence of adsorbent dose on CR removal by NMJF dose was studied in the dose range of 10–20 g/L for different CR dye concentrations (50, 100, 150, and 200 mg/L) at pH 7.0 (Fig. 4). The adsorption efficiency increased from 30% to 98.2% as the adsorbent dose increased from 10 to 16 g/L for 200 mg/L of CR. The result depicts that as the amount of adsorbent increased, the percentage of dye removal also increased, this corresponding increase in dye removal is may be due to the certain increase in the sorbent surface area, since as the surface area increased more number of adsorption sites were available for dyes to get adsorbed, similar kind of results were studied by Ahmed [23]. Much higher adsorbent dose also resulted in reduced level of sorption of CR. This decrease in sorption capacity with further increasing dose of adsorbent at constant dye concentration and volume is because, there may be saturation of the adsorption sites due to particulate interaction such as aggregation [19]. Such aggregation might have led to enhancement of diffusional path length due to decrement in the total surface area of the sorbent. [21]. Therefore, in the following experiments, the adsorbent dose was fixed at 16 g/L. Similar kind of observations are reported earlier by other researchers for the sorption of dyes by different bio-sorbents [18–20].

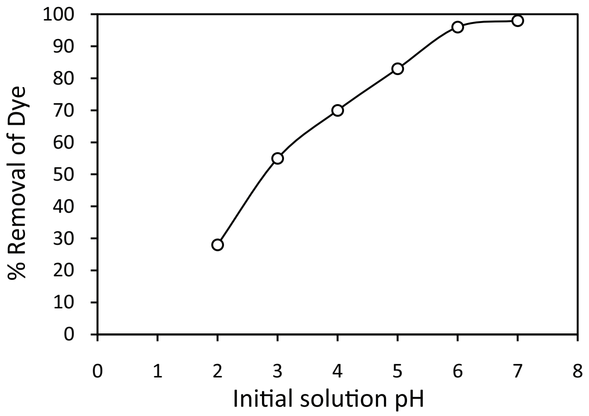

Fig. 3. Effect of pH on adsorption of CR onto NMJF.

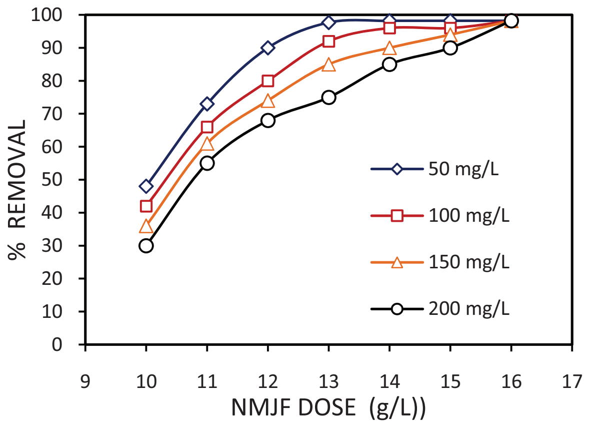

Fig. 4. Effect of NMJF dose on CR removal at initial concentration of 50, 100, 150 and 200 mg/L.

4.5. Effect of temperature and contact time on CR adsorption

Investigation depicts that the percentage removal of dye decreased with increasing temperature. Fig. 5 shows the adsorption of CR which is dependent upon the contact time between the adsorbate and sorbent, the experiment was conducted under different temperature. This is due to the weakening of the bonds between the dye molecules and the binding sites of the adsorbents [21]. The investigation pattern shows that there is decrease in dye removal capacity with increasing temperature which concludes that sorption of CR by NMJF is an exothermic process. Moreover, there is high rate of CR adsorption onto NMJF during the first 60 min of the dye–sorbent contact. This quick rate of adsorption is due to the availability of large amount of active sites/surface area for adsorption of the dye molecules. As the contact time gradually keep on increasing, the rate of adsorption also decreases, and gradually leading to adsorption equilibrium. This reduction in adsorption of CR onto NMJF is due to decrease in total active sites available for adsorption and hence less available binding sites [21]. The equilibrium time for maximum dye uptake is found to be 120 min. After this equilibrium period, the amount of dye adsorbed does not show time-dependent change. Similar analysis has been done for CV removal on modified rice husk [22] CV removal onto coniferous pinus bark powder [23].

4.6. Adsorption kinetics

For the study of sorption kinetics, the pseudo-first-order and pseudo-second-order kinetic models were analysed to study and compare with experimental results, to analyse the rate constants, and to measure the equilibrium adsorption capacity at various temperature. The pseudo-first-order rate constants, k_1 and q_e, were evaluated from slopes and intercepts of the plots of log($q_e - q_t$) vs. t (figure not mentioned). The results of correlation coefficients R^2

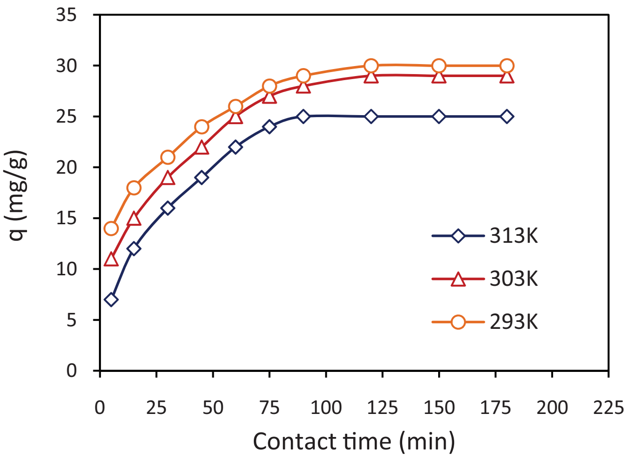

Fig. 5. Adsorption of CR at different temperatures with contact time.

obtained for pseudo-first-order, comparable studies of theoretical and experimental equilibrium sorption capacities of pseudo-first-order kinetic model shows that that is a considerable variation between this kinetic model and theoretical studies. Similar studies were also conducted for theoretical data without pseudo-second-order kinetic model, and Fig. 6 shows that pseudo-second-order model fits well with the theoretical data compared with the other kinetic model for the removal of CR onto NMJF.

4.7. Activation energy and thermodynamic parameters

The values obtained from pseudo-second-order rate constant K_2 was used as rate constant in Arrhenius equation (Eq. (10)) and activation energy (E_a) for the adsorption of CR onto NMJF by plotting a linear plot as shown in Fig. 7, between lnK_2 vs. $1/T$. E_a was determined from the slope of and was found to be 29.63 kJ/mol. The magnitude of activation energy gives an idea regarding the nature of adsorption taking place between the adsorbent and adsorbate. Low activation energy (<40 kJ/mol) obtained for the present study suggests that although both chemical and physical adsorption are taking place, adsorption phenomena is prominently governed by physical adsorption [23].

The change in Gibb's free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were determined using Eqs. (11)–(13). At first the value of equilibrium rate constant (K_c) was determined and used to find the $\Delta G°$ values. $\Delta G°$ values were found to be 80.99, 121.54, and 184.66 J/mol at temperatures of 293, 303, and 313 K, respectively. Increase in value of $\Delta G°$ with respect to increase in temperature suggests that adsorption was suitable at lower temperature. $\Delta H°$ and $\Delta S°$ values were also obtained from the plot of $\Delta G°$ vs. time (T) as shown in Fig. 8. The negative value of $\Delta H°$ (–1.44 kJ/mol) indicates that the reaction was exothermic. The negative value of $\Delta S°$ (–5.18 J/mol) suggests that the adsorption process is enthalpy driven.

4.8. Adsorption isotherm

Adsorption isotherms of CR onto NMJF at different temperatures are shown in Fig. 9. It is clear that data fit better to Langmuir model in comparison with the Freundlich model. This indicates the monolayer adsorption on the homogeneous surface of the adsorbent with identical binding sites of the adsorbent. The various isotherm parameters are shown in Table 1.

5. Comparison with other adsorbents

A comparison between the results obtained in this work with the similar data from literature [22–39] is presented in Table 2. The value of CR uptake found in this work is significantly higher than reported for other adsorbents. Thus, the comparison of adsorption capacities shows that the NMJF is an efficient adsorbent for the uptake of CR.

6. Conclusion

NMJF was successfully used as a novel adsorbent for the quantitative removal of CR from aqueous solution in batch mode. The effect of different operating parameters such as pH of solution, contact time, initial dye concentration, and temperature were evaluated. The optimum removal was achieved at pH 7.0, 16 g/L of adsorbent dose, and temperature of 293 K. The adsorption equilibrium was obtained at 90 min. Isotherm studies were done using Langmuir and Freundlich isotherm models and observations showed

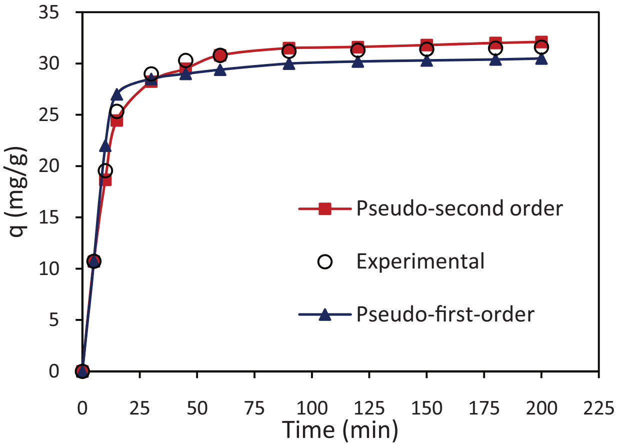

Fig. 6. Adsorption kinetics of CR onto NMJF at a temperature of 293 K.

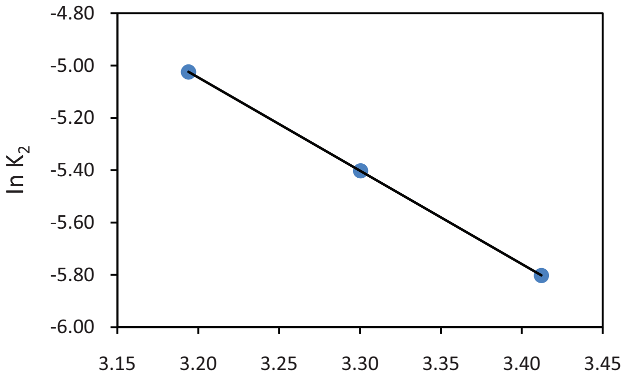

Fig. 7. The Arrhenius plot for the adsorption of CR onto NMJF.

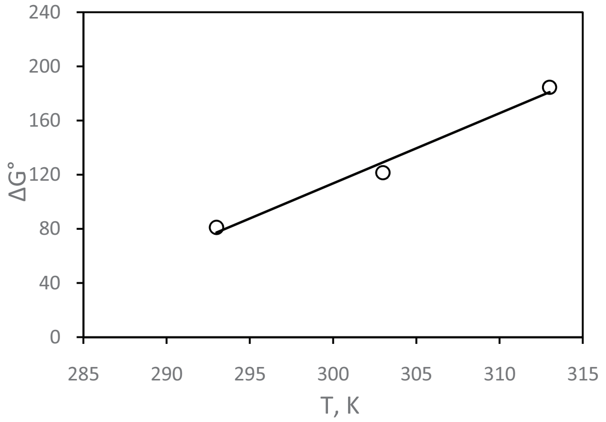

Fig. 8. Plot of change in Gibb's free energy ($\Delta G°$) vs. temperature (T) for adsorption of CR onto NMJF.

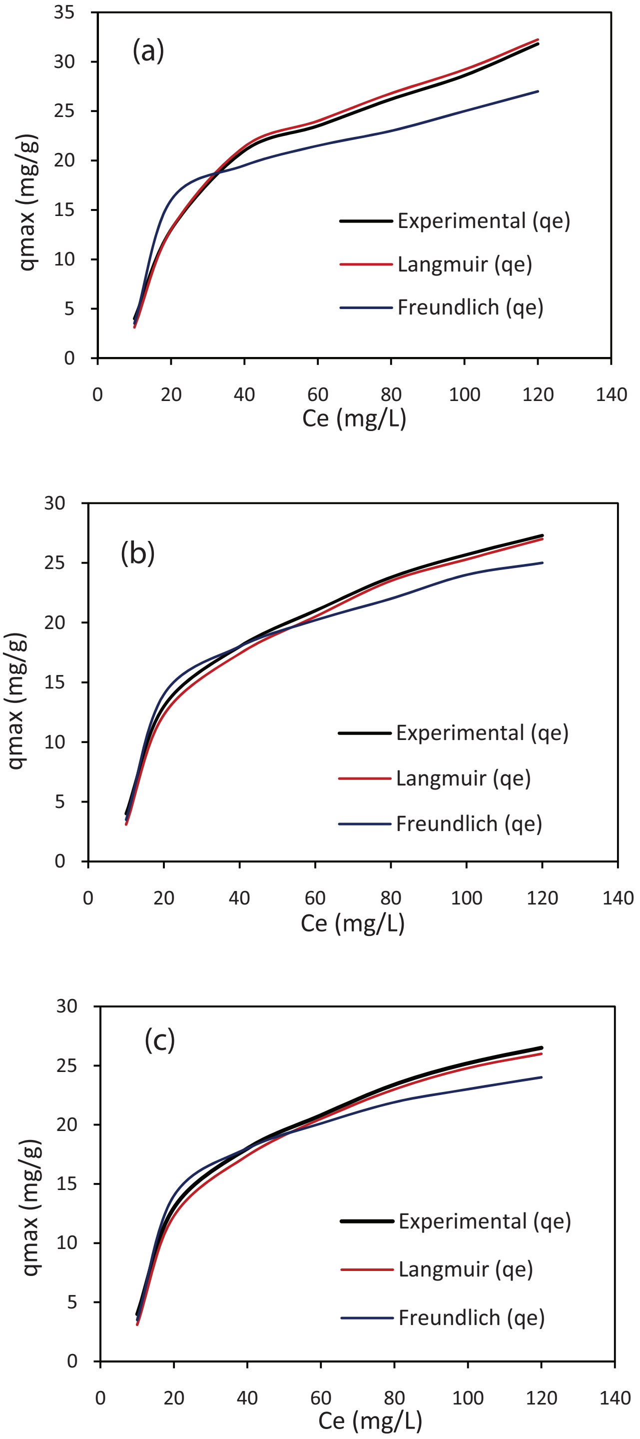

Fig. 9. Adsorption isotherms of CR onto NMJF at different temperatures (A) 293 K, (B) 303 K and (C) 313 K.

that Langmuir isotherm fits well with the experimental data. The adsorption capacity was found to be 32.24 mg/g. The intra-particle diffusion played the significant role in the adsorption process. The kinetic studies revealed that the adsorption process followed well for pseudo-second-order kinetic model as compared with pseudo-first-order kinetic model. The activation energy (E_a = 29.63 kJ/mol) indicated

Table 1
Various isotherm parameters for adsorption of CR onto NMJF

Isotherm model	Parameter	Temperature in kelvin		
		293 K	303 K	313 K
Langmuir model	q_{max} (mg/g)	32.24	27	26
	b (L/mg)	9.500	6.205	3.789
	R_L	0.002	0.003	0.005
	R^2	0.875	0.863	0.847
Freundlich model	K_f (mg/g)	34.39	28.57	23.34
	n	3.26	2.82	1.93
	R^2	0.755	0.787	0.752

Table 2
Comparison of CR sorption capacity of NMJF with that of different adsorbents

Adsorbent	q_{max} (mg/g)	References
NaOH-modified rice husk	44.87	[22]
Neem leaf powder	41.2	[24]
Eucalyptus wood saw dust	66.6	[25]
Jute stick powder	35.7	[26]
Sugarcane bagasse	38.2	[27]
Jujuba seed	55.56	[28]
Coniferous pinus bark powder	32.78	[23]
Orange peel	14.3	[29]
Rice bran	42.25	[30]
Neem sawdust	3.8	[31]
Sugarcane dust	3.8	[32]
Activated red mud	7.08	[33]
Coir pith	2.56	[34]
Crosslinked cellulose dialdehyde	42.03	[35]
Fe-Zn bimetallic nanoparticles	28.56	[36]
Rubber seeds	9.82	[37]
Jalshakti polymer	12.9	[38]
Sugarcane fibre	10.44	[39]
NMJF	34.24	This study

that both physical as well as chemical adsorption. Increase in value of $\Delta G°$ with respect to increase in temperature suggests that adsorption was suitable at lower temperature. The negative value of $\Delta H°$ (–1.44 kJ/mol) indicates the reaction was exothermic. The negative value of $\Delta S°$ (–5.18 J/mol) suggests that the adsorption process is enthalpy driven. Based on the results and comparisons, it can be concluded that NMJF is an effective and efficient adsorbent for the removal of CR from aqueous solutions.

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