Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2018.22466

115 (2018) 300–314
May

Use of response surface methodology for the optimization of process parameters for the removal of Congo Red by NaOH treated jute fibre

A.K. Dey[a,*], U. Kumar[b], A. Dey[c]

[a]*Department of Civil Engineering, Central Institute of Technology Kokrajhar, Assam-783370, India, email: ak.dey@cit.ac.in (A.K. Dey)*
[b]*Department of Civil Engineering, National Institute of Technology Silchar, Assam-788010, India*
[c]*Department of Mechanical Engineering, National Institute of Technology Silchar, Assam-788010, India*

Received 18 September 2017; Accepted 5 May 2018

ABSTRACT

Removal of a synthetic azo dye Congo Red has been investigated using a low cost biosorbent i.e. NaOH treated Jute fibre (NTJF). Response surface methodology (RSM) has been employed to optimize the process variables or operating parameters for the removal of the dye (Congo red) from aqueous solution using Design Expert 9.0. To get optimum condition for the dye removal and to obtain maximum adsorption capacity (Q_{max}), four operating parameters were considered as Jute dose (10–18 mg/L), pH (5–9), Dye concentration (50, 100 and 150 mg/L) and temperature (293 K, 303 K and 313 K), which are also taken as input process variables and have been varied accordingly as per experimental design as prescribed by the software, whereas maximum adsorption capacity (Q_{max}) of the jute for the removal of dye is considered as output response. ANOVA analysis was imposed to investigate the influence of process variables and their interactions. For obtaining Q_{max} the optimized conditions are found as (pH = 7.20, temperature 302.130 K, jute dose = 14.524 g/L, dye concentration = 150.00 mg/L). The experimental Q_{max} value was 33.69 mg/g, and the RSM predicted Q_{max} value is found out as 31.20 mg/g, with a desirability of 0.840, showing excellent accuracy of the experimentation processes. Further, a second order quadratic mathematical model has been developed in order to estimate the performance characteristics. The results depicts that Jute dose and temperature have a great influence on the adsorption capacity. Other studies revealed that the adsorption process was entropy driven, following pseudo-second order rate kinetics, endothermic in nature, sorption occurring is mainly physical-adsorption, and the sorption data fits better to Langmuir isotherm model.

Keywords: Adsorption; Congo red; NTJF; Response surface methodology; ANOVA

1. Introduction

Dyes are complex chemical compounds which when come in contact with most of the substance, can get easily attached to them and imparts colour like they do for cloths and fabrics. As per the recent data available, there are about 100,000 different dyes known with an annual production of over 7×10^5 ton/y [1]. Moreover the dye consumption of textile industry alone is 10,000 ton/y worldwide of which 100 ton of dyes are discharged in water bodies on a yearly basis [2]. Due to their complex bonding structure, they are hard to break and thus possesses serious environmental and health hazard issues and apart from other effects some dyes are found to possess carcinogenic characteristics [3]. Based upon the source of material, dyes can be classified as natural dyes and synthetic dyes. Majority of the natural dyes are from vegetable dyes derived from plant sources such as roots, berries, berk, leaves, wood etc., which are readily biodegradable and possess less or no harm to the environment [4]. On the other hand almost any colour we see today is from synthetic dyes, starting from food to wood, clothes to paper, synthetic dye is everywhere and in everything [5]. The main reason for using synthetic dyes are that they are economical to produce, easily applicable in fabrics and other materials.

---

*Corresponding author.

1944-3994 / 1944-3986

Synthetics azo dyes find their use in a wide range of industries but are mainly associated with textile industry [6]. Effluents from textile industries can possess substantial amount of dye concentration. The environmental and simultaneous health hazard issues arising of dye released from textile industries are becoming a subject of scientific investigation [6]. Thereby subsequent Environmental legislations are getting imposed to control the release of dyes, especially azo based dye directly in the free flowing water bodies.

Based upon technique, researchers have employed different method for the removal of dye from wastewater solutions. Some of the techniques include biological treatments [7] oxidation [8], ultrasound irradiation [9], coagulation-flocculation [10], photo catalysis [11], ozonation [12] and membrane separation [13]. Among these, adsorption using activated carbon is found to be one of the most eco-friendly and efficient method and has the capacity to remove almost all the dyes from the aqueous solution. But activated carbon has its own limitation such as initial high cost of production, complexities in regeneration after exhaustion, decrement in removal efficiency after regeneration [14,15]. So that now a days researchers are putting lot of emphasis on use of low cost bio sorbents which are economical, biodegradable, and easily available for the adsorption purpose [16–19]. In this study one such low cost bio-sorbent (jute) is considered for the removal of Congo red dye from aqueous solution using adsorption process. Jute is one of the agricultural product which is abundant in India, and is an important crop in Indian sub-continent. Of the total production of jute in the world, around 85% of the jute is produced in the Ganges Delta (India, Bangladesh) and some parts of China. Principal components of jute fibre are cellulose, hemicellulose, lignin and other low molecular weight hydro-carbons [20]. These components consist of important functional groups such as hydroxyl and carboxyl, which are the responsible agents for adsorption of dye onto the adsorbent in aqueous solution [20]. Previously researchers successfully used surface modified low-cost bio-sorbent for the removal of dye from aqueous solution [16–18]. So recently the focus is also onto surface modification of adsorbent which can be used efficiently as an alternative of activated carbon in removing harmful dyes from waste water [21]. The surface modifications are to enhance the fractions of the influential functional groups such as hydroxyl, carboxyl, sulphate, carboxylate, phosphate groups on the adsorbent surface [21].

Talking of different methods that are in use for the removal of dyes, researchers are not limited to use of experimental models only, there are several mathematical models and software's which are in use to analyse and find out the optimum conditions required for the desired output as necessary. There are several works already being done in the relevant area such as the use of Response surface methodology (RSM) for the optimization of process variables for dye removal using a novel adsorbent [22]. Use of RSM for methylene blue dye removal using low cost adsorbent [23]. Application of statistical designs and surface plots for the optimization and regression analysis for the purpose of decolourization of aqueous dye solution by a novel adsorbent [24]. Application of RSM for optimization of azo dye removal by oxalate catalysed photo electro-Fenton process using carbon nano tube-PTFE cathode [25]. Optimization and modelling for photo catalytic degradation of azo dye (Reactive red) using RSM based on the central composite design [26].

2. Materials and method

2.1. NaOH treated jute as an adsorbent

Jute is a multi-constituent and multicellular fibrous material containing high percentage of cellulose. Apart from large portion of-cellulose (~60%) other two major chemical components available in jute are hemi-cellulose (~23%) and lignin (~14%) and traces of fat and wax. Researchers suggested that there is formation of ester linkage between parts of hemi-cellulose and lignin which are linked chemically by the hydroxyl groups of lignin and those of carboxyl groups of hemi-cellulose [27]. The main reason for the adsorption of dyes from aqueous solution is the presence of functional groups such as hydroxyl and carboxyl groups on the surfaces of the adsorbent.

In the present analysis the adsorbent is pre-treated with NaOH as alkali treatment is view ed as one of the widely employed chemical treatment techniques for surface modification of cellulose based materials for the purpose of improving its adsorption properties [28]. Also the treatment of jute fibre with aqueous sodium hydroxide (NaOH) solutions breaks the covalent association between ligno cellulose components, hydrolysing hemicellulose and de-polymerising lignin [28]. This treatment has a substantial influence on morphological, molecular and supra molecular properties of cellulose, causing changes in crystallinity, pore structure, accessibility, stiffness, unit cell structure and orientation of fibrils in cellulosic fibres [29]. 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 [30]. 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 [31] from aqueous solutions. Since in jute fibres the cellulose and hemicellulose components are also present in huge amount, and Congo red is essentially an azo dye, so an attempt of the feasibility of applying NTJF for the removal of Congo red dye from aqueous solution was explored in the present study.

2.2. Material preparation

Jute which is naturally dried was cut into pieces of size approx to 1 mm and cleaned by washing with distilled water at 60°C. Then the sample was treated with 0.01 M NaOH at 27°C for 4 h. The resulting sample then distilled washed to remove excess chemicals present in fibre, pH for the sample was adjusted to 7.0 using 0.1 M NaOH or 0.1 M HCL, then kept in a container for 24 h after drying at 100°C. The final resulting sample which is NaOH treated jute fibre (NTJF), was considered as the adsorbent.

An azo dye Congo red 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. Congo red is used in the cellulose industries (cotton textile, wood pulp, and paper) is considered as the adsorbate. The dye used is of Analar grade and was obtained from Himedia. Before the start of the experimentation a stock dye solution of (1000 mg/L; pH 7.0; was prepared using double distilled water. The molecular structure of Congo red is shown in Fig.1

3. Theory

3.1. Adsorption capacity and percentage removal

In the present study the main emphasis was to find the maximum sorption capacity (Q_{max}) of CR using NaOH treated jute fibre. The amount of maximum dye adsorbed per unit adsorbent (mg dye per g adsorbent) was calculated according to a mass balance on the dye concentration using Eq. (1):

$$q_{\max} = \frac{\left(c_i - c_f\right)}{m} \tag{1}$$

where Q_{max} = Maximum adsorption capacity (mg/g); C_i = Initial dye concentration in the solution (mg/L); C_f= Final dye concentration in the solution (mg/L); V = Volume of solution (L); = weight of adsorbent (g)

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

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

3.2. Adsorption isotherm

Adsorption isotherm studies are the basic operations which are required to determine the adsorption relation between adsorbent and adsorbate. Isotherms not only check the favour ability of adsorption but also reveals information regarding homogenous or heterogeneous nature interaction between the adsorbent and adsorbate. In the present analysis, the feasibility of adsorption of CR dye onto the NTJF was checked using two basic non-linear form of isotherm equations, namely Langmuir [32] and Freundlich [33] isotherm models.

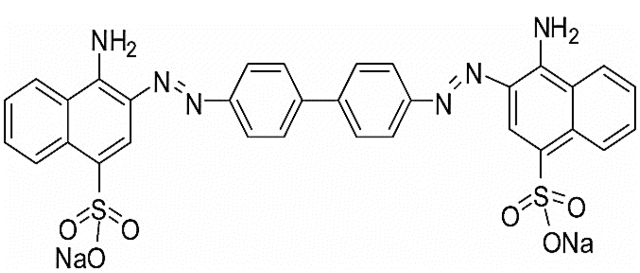


Fig. 1. Molecular structure of Congo Red (CR).

$$\text{Langmuir isotherm model: } q_e = \frac{q_m bCe}{1 + bCe} \tag{3}$$

where q_e = adsorbed value of dye at equilibrium concentration (mg/g); q_m = maximum mono layer adsorption capacity, it is independent of temperature; b = Langmuir adsorption constant, constant related to energy, it is temperature dependant (L/mg); C_e = concentration value of dye in the solution at equilibrium (mg/l).

The nature of Langmuir isotherm can be predicted depending upon whether the adsorption is favourable, linear or unfavourable based on the value of dimensionless constant separation factor R_L [34], given by Eq. (4). Value of R_L reveals the nature of isotherm, whether the adsorption 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 adsorbate/dye concentration in the solution (mg/L)

An empirical equation [35], the Freundlich isotherm equation which describes about the heterogeneity of the adsorbent surface during adsorption is been analysed in the present study.

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

where K_f and $1/n$ are Freundlich constant characteristics of the system; C_e = dye concentration of the solution at equilibrium (mg/L); q_e = adsorption capacity at equilibrium concentration (mg/g).

K_f and n suggests about adsorption capacity and adsorption intensity. If the K_f value increases with increase in temperature then the nature of reaction will be endothermic and if the K_f value decreases with increase in temperature then the process will be exothermic in nature. The other Freundlich constant, $1/n$ suggests the adsorption type. When the case is $0 < 1/n < 1$, then the sorption process is favourable, when it is so that $1/n = 1$, then the adsorption situation will be irreversible, and finally when it is $1/n > 1$, then the sorption is not favourable [35].

3.3. Adsorption 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 [36] and pseudo-second-order [37] 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 (Weber and Morris, 1963) was employed to find the rate controlling steps.

Intra-particle diffusion: $q_t = k_i t^{0.5}$ (8)

3.4. Activation energy and thermodynamic parameters

For the adsorption of CR onto NTJF, activation energy E_a was found out using Arrhenius equation. The equation for the same is listed below

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

After plotting a graph of *ln K vs 1/T,* activation energy E_a can be obtained from the slope of the plot of the same. Where, T = Temperature in kelvin, K = either pseudo first order rate constant or pseudo second order rate constant which again depends on the rate of adsorption favoured in the kinetic reaction. Activation energy reveals about the nature (physical or chemical) of adsorption. Thermodynamic parameters such as $\Delta G°$ = Gibbs free energy change, ΔH° = Enthalpy change, ΔS° = Entropy change were investigated to check the temperature suitability of the adsorption, endothermic or exothermic nature of the sorption process, and also to verify that the adsorption is enthalpy or entropy driven. The investigations were done using the following equations.

$$\Delta G° = -\text{RT} \ln K_{ad} \tag{10}$$

$$K_{ad} = \frac{C_0 - C_e}{C_e^{\,n}} \tag{11}$$

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

The values of ΔH° and ΔS° were obtained from the plot of $\Delta G°$ and T. Where, C_o and C_e are the initial and equilibrium dye concentration of solution. K_{ad} is the rate constant of adsorption process at equilibrium. The value of n is found by rate kinetic analysis by observing which rate model the observed data best fit.

4. Batch wise experimental procedure

At the start of the experiment, a stock dye solution of 1000 mg/L was prepared, from that concentration values of 50 mg/L, 100 mg/L and 150 mg/L solution were prepared, which were used for the analysis in the present study. The aim of the analysis was to find maximum sorption capacity (Q_{max}) as a function of the following input process parameters, which are pH, Jute dose, Temperature and dye concentration. To analyze the removal of CR with the help of variation in the aforementioned process parameters adsorption analysis was done in batch-wise.

The experiment was carried out at pH range 5–9. Let us elaborate the experimentation regarding the influence of a change in pH onto final outcome (Q_{max}). Firstly jute dose 10 g/L was taken in 200 ml of dye solution where the initial pH was adjusted to 5.0, initial temperature 293 K and the dye concentration was adjusted at 50 mg/L. Next, the solution was allowed to agitate and samples were collected to analyze the concentration of sample solution, after each 5 min interval (after 5 min, 10 min, 15 min and so on up to 180 min). After agitation of 180 min adsorption seemed no more time-dependent. UV/VIS spectroscopy (Perkin-Elmer, Lambda 45) was used to calculate the dye concentrations. From that data amount of maximum dye adsorbed, Q_{max} (mg/g) were calculated. Similar kind of experiments was carried out for other pH values by keeping other process parameters constant. Likewise, once the study of pH variation was over then other parameters were studied by varying them similar to the case of first experimentation of process parameters.

To study other parameters, their ranges were considered as jute dose range (10–18 g/L). Temperature range (293, 303 and 323 K) and dye concentration as (50, 100 and 150 mg/L) respectively. For a different set of solutions, separate pH values were adjusted in the range of 5–9 using 0.1 M HCL or 0.1 M NaOH.

It was found that there was no degradation or adsorption of CR by container walls. Experiments were carried out in duplicate and mean values were taken. A similar set of experiments were carried out for all possible combinations of all the process variables. Different process parameter combination sets can be observed from Table 2.

5. Adsorption studies by employing response surface methodology

Response Surface Methodology (RSM) approach is a better tool for optimization and can predict the influence of process variables on performance characteristics [38]. Hence, in this study, the face centred central composite design (CCD) of RSM is employed for the design of experiments. The present work is an emphasis on finding out the Maximum sorption capacity (Q_{max}) of NaOH treated jute fibre for the removal of Congo red from aqueous solution by developing mathematical model and examine the effects of process parameters and their performance characteristics using response surface methodology. Consequently, the quantitative mathematical models have been developed to study the effects of temperature, pH, Jute dose and dye concentration on the adsorption capacity, by using RSM approach [39].

To find the value of maximum adsorption capacity (Q_{max}) at different pH, temperature (K), jute dose (g/L) and dye concentration (mg/L) experiment were done batch wise. Q_{max} was found out once at a time, varying any one of the process parameters and keeping others constant. The value of Q_{max} which were found out in different batches of the experiment were used to find out optimum desirable

Table 1
Process parameters with their levels

Parameters	Labels	Levels		
		–1	0	+1
pH,	A	5	7	9
Temperature, (ºk)	B	293	303	313
Jute dose, (g/l)	C	10	14	18
Dye concentration, (mg/L)	D	50	100	150

condition, using response surface methodology. Response surface methodology (RSM) is a collection of mathematical and statistical techniques utilization for modeling and optimizing the response characteristics, which incorporates quantitative independent variables. The quality characteristic of the system is explained by a second order polynomial quadratic model also called regression model as shown in Eq. (13). The coefficients of regression model can be approximated from the experimental data by 'Design Expert 9.0' software.

$$Y = C_0 + \sum\nolimits_{i=1}^{n} \mathrm{C_i X_n} + \sum\nolimits_{i=1}^{n} \mathrm{d_i X_i^2} \pm \varepsilon \tag{13}$$

The experiments were carried out based on face-centered central composite second order design (CCD) technique in the present work. The CCD full factorial design with all factors combination at two levels (high, +1, and low, – 1) are considered which composed of eight-star points, and six central point's (coded level 0), corresponds to an α value of 1. The "face-centred CCD" includes 30 experimental trials with four distinct process variables. Table 1 shows all the process parameters and their feasible ranges of both actual and coded values. The experimental design layout in the coded form that was espoused in this analysis is shown in Table 2.

Table 2
Design layout and experimental results

Exp. no.	Factor 1 A: pH	Factor 2 B: Temperature (K)	Factor 3 C: Jute Dose (g/L)	Factor 4 D: Dye concentration (mg/L)	Response Q_{max} (mg/g)
1	9	313	18	150	14.24
2	9	313	10	150	11.37
3	7	303	14	100	25.57
4	5	293	10	150	9.89
5	9	293	18	150	17.23
6	5	293	10	50	7.15
7	5	313	10	50	8.56
8	9	293	10	50	10.64
9	5	293	18	150	11.86
10	5	313	18	150	12.47
11	9	293	10	150	14.97
12	5	313	10	150	10.64
13	5	313	18	50	9.75
14	7	303	14	100	25.14
15	7	303	14	100	27.81
16	5	293	18	50	8.46
17	9	313	18	50	10.49
18	9	313	10	50	7.56
19	7	303	14	100	26.86
20	9	293	18	50	12.24
21	9	303	14	100	19.55
22	5	303	14	100	14.42
23	7	303	10	100	20.23
24	7	303	14	150	33.69
25	7	303	14	50	21.46
26	7	313	14	100	23.34
27	7	303	18	100	23.45
28	7	303	14	100	27.15
29	7	303	14	100	26.57
30	7	293	14	100	22.25

6. Results and discussion

6.1. Time decay curve and equilibrium time

Time decay curve is measured by observing the reduction in the concentration of dye by its removal using adsorbent, from the solution over a period of time. It represents the removal of dye from aqueous solution as a function of contact time. For the analysis, an initial concentration of 50 mg/L was considered. Fig. 2. shows the time decay curve for the removal of Congo red dye using NaOH treated jute fibre as the adsorbent. In adsorption, Equilibrium time is said to be achieved when beyond a particular time point there will not be any further significant adsorption of dye onto the adsorbent or in other words, adsorption of dye no more remain a time-dependent phenomenon, which generally can be observed from the time decay curve.

The curve shows that there is a rapid rate of adsorption for the first 30 min of the adsorbate- adsorbent interaction. After that the rate of adsorption drastically reduces. At the initial stages, the rate of adsorption increases due to the availability of a large number of adsorption sites initially available. But as the time passes, the decrease in the amount of adsorption and subsequent decrease in sorption has occurred. It mainly because of the molecule that is available at the adsorption sites gets saturated. For the given study equilibrium time was obtained at 90 min, after which the adsorption process does not remain time dependent. Similar kind of study was undertaken by Ahmed at el. Time decay data were primarily used to find the resulting adsorption of dye which was subsequently used to analyze other parameters.

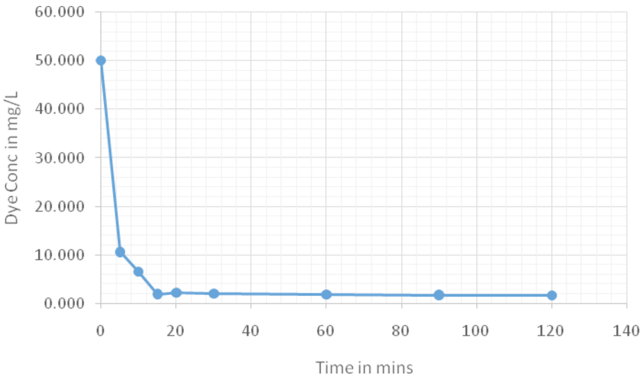


Fig. 2. Time decay curve for the removal of CR onto NTJF.

6.2. SEM analysis of NTJF before and after adsorption

The surface morphology of NaOH treated Jute fibre and also on CR adsorbed NaOH treated jute fibres were done using scanning electron microscope analysis using SEM (MODEL: JSM-6360, JEOL) working conditions were as, resolution: 3 nm in the secondary electron mode at working distance 8 mm and an accelerating voltage 0f 30 KV, accelerating voltage: From 1 KV–30 KV in 1 KV step. From the SEM images shown below in Fig. 3, it can be observed that Fig. 3a shows the image of only NaOH treated jute fibre and in Fig. 3b it can be seen that there are lot of particles of Congo red, which are got attached on the surface of the NaOH treated jute fibre. Both the figures are of 1 μm resolution.

6.3. Characterization using FTIR analysis

FTIR spectra confirms the successful adsorption of CR onto NTJF. FTIR spectra of NTJF before and after is shown in Fig 4. Adsorption was confirmed by the shifting of wavelength bands before and after the adsorption. The broad and strong band at 3444.63 cm^{-1} was due to bounded hydroxyl or a mine groups. The peak observed at 2918.12 cm^{-1} was due to the –CH asymmetric stretching. The peak at 1740.78 cm^{-1} was attributed to stretching vibration of carboxyl group. The bands at 1633.41 cm^{-1}, 1507.43 cm^{-1} and 1461.05 cm^{-1} were attributed to asymmetric and symmetric stretching vibration of C=O groups. The C–N stretching band was observed at 1375.40 cm^{-1}. The band at 1020.51 cm^{-1} were assigned to C–O stretching of alcohols and carboxylic acids. After CR adsorption, the symmetrical stretching vibration bands of hydroxyl or a mine groups were shifted from 3444.63 cm^{-1} to 3443.98 cm^{-1} for CR-loaded NTJF. The stretching band of carboxyl groups was shifted from 1740.78 to 1740.70 cm^{-1}. The stretching bands at 1633.41, 1507.43 and 1461.05 cm^{-1} were also shifted to 1633.68, 1507.55 and 1460.92 cm^{-1} respectively. The C–O peak at 1020.51 cm^{-1} were shifted to 1020.31 cm^{-1}, respectively. The analysis of the FTIR spectral results in terms of frequency shifts indicate that these functional groups above mentioned are responsible for the binding of the CR to the surface of the NTJF.

6.4. Adsorption isotherm

In the present study the results were verified with the help of two nonlinear adsorption isotherms, namely Langmuir and Freundlich isotherm studies. From the plot of q_e vs C_e, from Fig. 5, it has observed that the adsorption process better fits to Langmuir Isotherm, which suggests that there is mono layer adsorption of the CR dyes on the surface of NTJF. Several isotherm parameters are shown in Table 3. Fig. 5 shows the adsorption isotherm studies at the temperature 303 K.

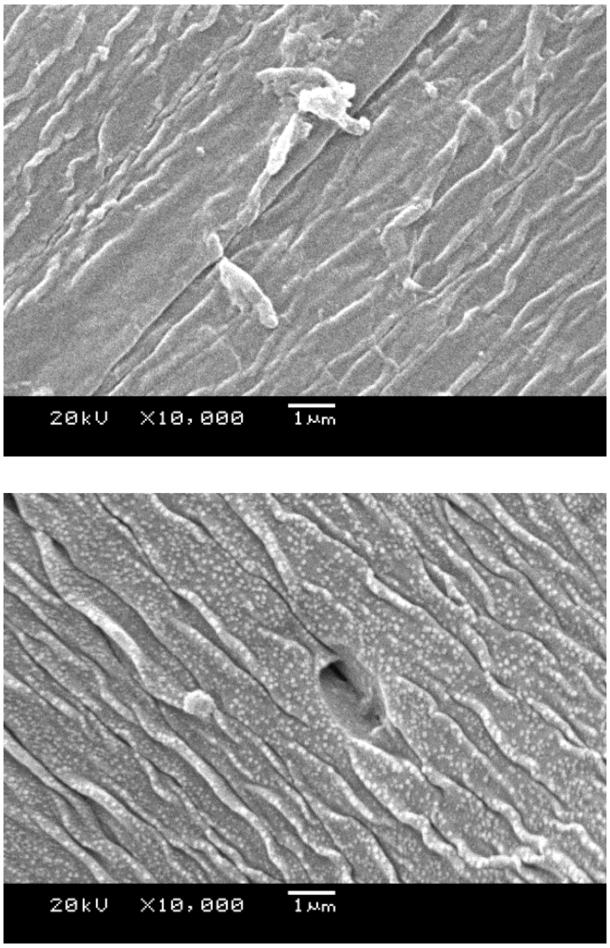


Fig. 3. (a) SEM image of NTJF (b) SEM image of CR adsorbed NTJF.

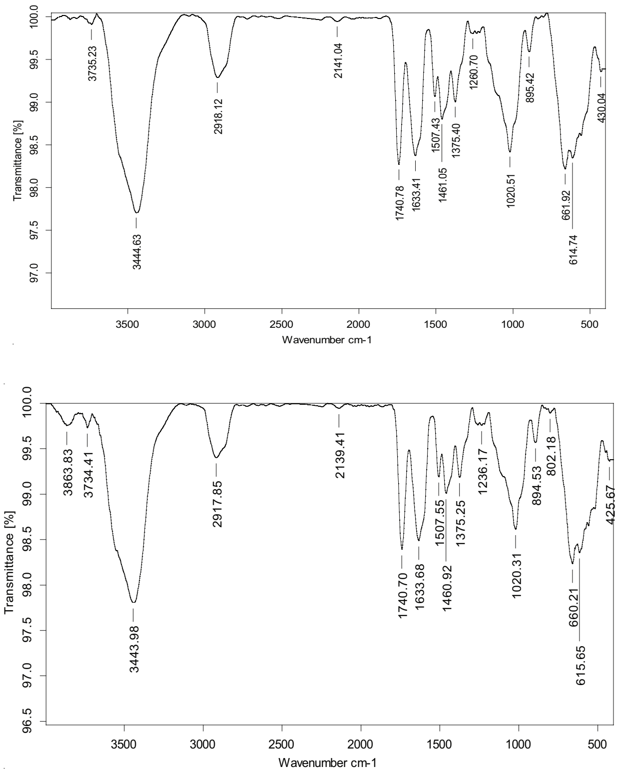


Fig. 4 (a) FTIR spectra of Virgin NTJF, (b) FTIR spectra of CR adsorbed NTJF.

Table 3
Various isotherm parameters for adsorption of CR onto NTJF

Isotherm model	Parameter	Temperature in Kelvin		
		293 K	303 K	313 K
Langmuir model	Q_{max} (mg/g)	28.14	32.21	26.83
	b (L/mg)	7.456	7.877	8.612
	R_L	0.017	0.012	0.022
	R^2	0.913	0.954	0.897
Freundlich model	K_F (mg/g)	11.87	12.23	14.46
	n	5.53	6.12	7.65
	R^2	0.785	0.796	0.768

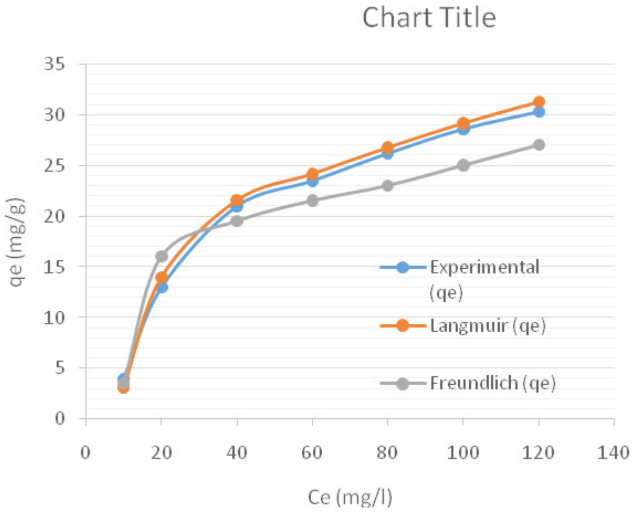


Fig. 5. Adsorption isotherms of CR onto NTJF at temperature 303 K.

6.5. 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 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 sans pseudo-second-order kinetic model, and Fig. 6 shows that pseudo-second-order model fits well with the theoretical data compared to the other kinetic model for the removal of CR onto NTJF.

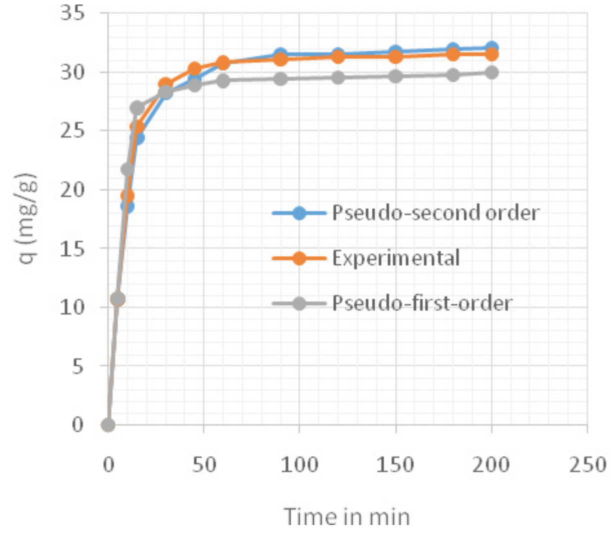


Fig. 6. Adsorption kinetics of CR onto NTJF at a temperature of 303 K.

6.6. Activation energy and thermodynamic parameters

Activation energy E_a, for the process was determined from Arrhenius equation (Eq. (9)) by drawing the Arrhenius plot of CR adsorption onto NTJF. It is found out to determine the nature of adsorption taking place in the process and it thus holds a significant role in determining whether the adsorption taking place is physical or chemical. As low E_a value (< 40 KJ/mol) indicates physical adsorption and higher E_a value (≥ 40 KJ/mol) indicate chemical adsorption. In the present study, the rate of adsorption was better suited as per the kinetics of second order rate constant so the plot was done by taking ln K (K= pseudo second order rate constant) values in Y axis and 1/T (time inverse in Kelvin) in X axis. E_a was determined from the slope of the linear plot, which is found out as 15.12 KJ/mol. From the result we can conclude that the following process is predominantly governed by physical adsorption [40]. Fig. 7 shows the Arrhenius plot for the determination of E_a.

One of the thermodynamics parameters, change in Gibb's free energy (ΔG°) was found out using the values of equilibrium rate constant (K_{ad}) and other two parameters, entropy (ΔS°) and enthalpy (ΔH°) were found out from the intercepts of the plot of ΔG° vs time (T). Along with the plot, the parameters were found out using Eqns. (10)–(12). The values of ΔG° for the temperature values of 293 K, 303 K and 313 K were found out as –6.2, –7.61 and –9.38 KJ/mol respectively. Decrease in the value of change in Gibb's free energy with increase in temperature indicates that the adsorption was favourable at slightly higher temperature. The rise in sorption capacity with rise in temperature also suggests for the rise in kinetic energy of the sorbent particles. Positive value of ΔS° (0.1551 KJ/mol K) indicates there is increase in the randomness at the solid/solution interface during adsorption and entropy driven. Positive value of ΔH° (23.22 KJ/mol) suggests that the reaction involved in the process is endothermic [41]. Also the value of ΔH° suggests whether the adsorption is physical or chemical in nature, in general if the value of ΔH° is in the range of 8–25 KJ/mol, it indicates physical adsorption and if the value is in the range of 80–200 KJ/mol, means the process is governed by chemical adsorption. In the present study, by observing the value of

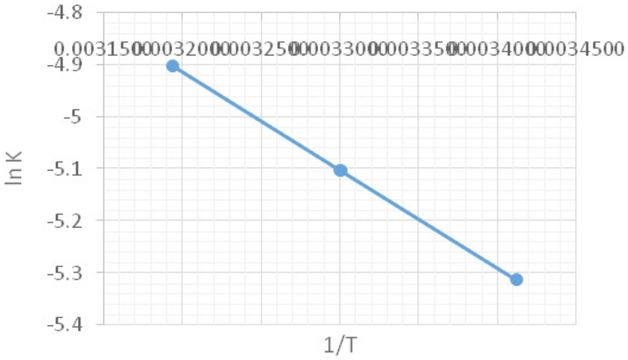


Fig. 7. Arrhenius plot for the adsorption of CR onto NTJF.

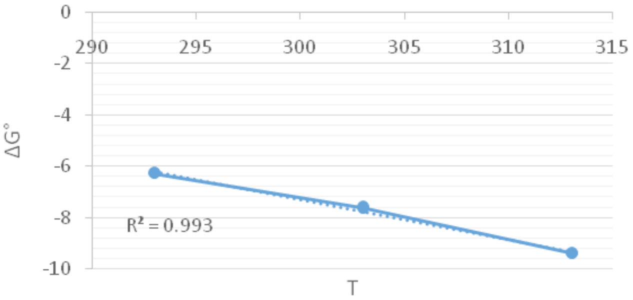


Fig. 8. Plot for change in Gibb's free energy (ΔG°) vs Temperature (T) for adsorption of CR onto NTJF.

Table 4
Thermodynamic parameters for the adsorption of CR onto NTJF

Parameters	Temperature in Kelvin		
	293	303	313
ΔG° (KJ/mol)	–6.285	–7.61	–9.386
ΔS° (KJ/mol K)	0.1551		
ΔH° (KJ/mol)	23.22		

ΔH° it is revealed that the adsorption is governed by physical adsorption which justifies the study of activation energy. The plot for ΔG° vs T is shown in Fig. 8. Table 4 shows the different thermodynamic parameters.

6.7. Modelling of maximum adsorption capacity, Q_{max}

For the analysis of $Q_{max,}$ description of a model fit summary is shown that the second order quadratic model is statically significant. The results for the quadratic model are shown is ANOVA in Table 5. The model F value indicates that the model is significant. The probable value of F is more than the value of F given for the model are less than 0.05 (i.e.,α = 0.05, or –95% confidence) which implies that the developed models are evaluated to be statically significant and it implies that the model term have significant influence at the performance characteristic [42]. The evaluated response model has better fits with actual data when the multiple regressing co efficient R^2 approaches to unity which indicates the less deviation between the actual and predicted value. Fig. 9 shows the actual and predicted value for Q_{max} which indicates the degree of proximity. Maximum values are near to straight line implying the errors are distributed normally. In addition, the value of adequate precision (AP) in this model which compares the span of predicted value at the design point to the mean prediction error. This represents the model is discrimination. The developed model proposes the higher value of the determination coefficient (R^2) and adequate precision (AP) at the same time. The evaluated value is as follows: $R^2 = 0.84$ and AP = 19.78 for Q_{max}; therefore the developed quadratic mathematical model can be influenced significantly and evaluating the result and concurrently the lack of-fit test also found to be important. The process of backward elimination eradicates the significant factor to alert the fitted quadratic response surface models. This model term can be eliminated and the test of lack of fit reveals to be insignificant. The model of response surface equations obtained by using backward elimination technique is shown in Eq. (14) as given below.

The ultimate response surface equations for Q_{max} is-:

$$Q_{max} = 0.10 + 0.065 * A + 0.17 * B - 0.019 * C + 0.026 * AB - 0.020 * BC + 0.15 * B^2 \tag{14}$$

6.8. Effect of process parameters on Q_{max}

6.8.1. Effect of pH

Fig.10 depicts the approximated response surface plot for Q_{max} in relation to the process parameters of solution pH, jute dose, temperature and RPM. pH play as an important influential factor for the removal of dye onto adsorbent in an aqueous solution. pH influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule [43]. Subsequently there is change in adsorption process depending on the change in surface properties of both the parties that are in consideration. It was observed that the Q_{max} increases with the increase in pH. The reason behind that is at lower pH, the functional groups present on the adsorbent surface undergoes protonation, due to this phenomenon, absorbent surface gets positively charged, which is followed by decrease in adsorption of dye ions due to electrostatic repulsion. And on the increment of pH of the dye solution, there is increment in the adsorption process due to eventual deprotonation of the functional groups of the adsorbent, and thereby enhances the electrostatic attraction between the dye cations and negatively charged sites on the adsorbent.

6.8.2. Effect of jute dose

It is very important parameter which acts as a variable in determining the rate of adsorption capacity of adsorbate onto the adsorbent. In the present study, jute (adsorbent) dose was taken in the range of 10–18 g/L, to determine the rate of adsorption at various jute dose concentrations. It has been observed that there is an increase in adsorption and subsequent dye removal rate as the jute dose increases. This

Table 5
The ANOVA results for Q_{max}

ANOVA for response surface quadratic model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Block	573.50	1	573.50			
Model	1085.31	14	77.52	17.17	< 0.0001	*significant*
A-pH	*34.97*	*1*	*34.97*	*7.75*	*0.0147*	
B-temperature	*2.18*	*1*	*2.18*	*0.48*	*0.4981*	
C-jute dose	*20.44*	*1*	*20.44*	*4.53*	*0.0516*	
D-dye concentration	*98.65*	*1*	*98.65*	*21.85*	*0.0004*	*Significant*
AB	*14.98*	*1*	*14.98*	*3.32*	*0.0900*	
AC	*0.71*	*1*	*0.71*	*0.16*	*0.6986*	
AD	*2.21*	*1*	*2.21*	*0.49*	*0.4961*	
BC	*0.18*	*1*	*0.18*	*0.039*	*0.8461*	
BD	*0.60*	*1*	*0.60*	*0.13*	*0.7208*	
CD	*0.23*	*1*	*0.23*	*0.050*	*0.8263*	
A^2	*224.41*	*1*	*224.41*	*49.70*	*< 0.0001*	
B^2	*32.76*	*1*	*32.76*	*7.26*	*0.0175*	
C^2	*52.49*	*1*	*52.49*	*11.63*	*0.0042*	
D^2	*12.65*	*1*	*12.65*	*2.80*	*0.1163*	
Residual	63.21	14	4.51			
Lack of fit	*58.57*	*10*	*5.86*	*5.06*	*0.1661*	*Insignificant*
Pure error	*4.63*	*4*	*1.16*			
Cor total	1722.02	29				

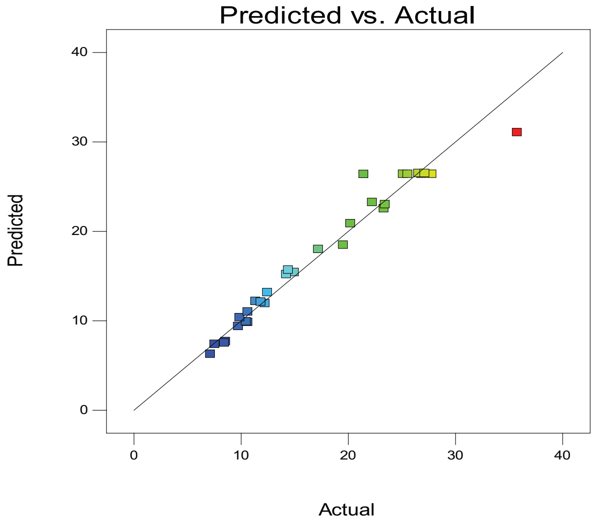


Fig. 9. Predicted vs. actual plot for Q_{max}.

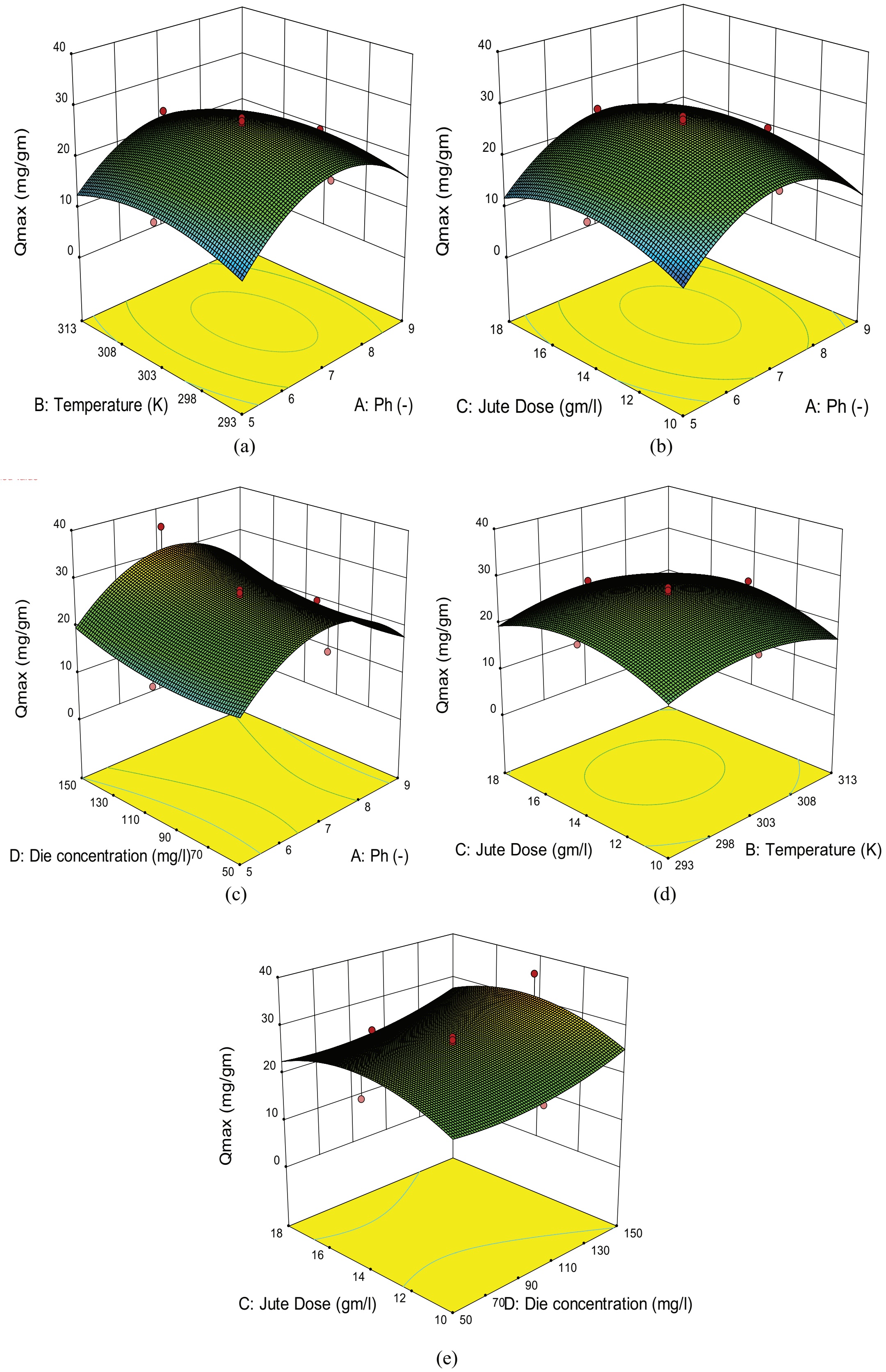
increase in dye removal rate with increase in jute dose could be due to increase in adsorbent surface area, resulting in morenumber of adsorption sites available for adsorption of adsorbates onto adsorbent [43,44]. The same phenomena was observed when the jute dose was increased from 10 to 14.905 g/L. Further increase in jute dose decreases the adsorption rate. The decrease in adsorption rate with increase in jute dose at constant volume of solution and constant dye concentration may be attributed to particulate interaction such as aggregation [45] which results in adsorption site saturation. Particulate interaction will result in decrease in available adsorption sites, due to decrease in total surface area of the adsorbent and increase in diffusional path length [46]. Results are depicted in Fig. 10.

6.8.3. Effect of temperature

As observed in Fig.10, the adsorption rate and percentage removal of CR is higher at lower temperature and V is a versa. At higher temperature, there is weakening of bonds between adsorbent binding sites and adsorbate dye molecules [47]. This is may be reason that adsorption phenomena is better suited at lower temperatures. Moreover, the observed pattern of decreasing dye removal at increasing temperature hints that the adsorption process is kinetically controlled and is exothermic in nature, and the same is justified from the experimental analysis of the same which also suggested the same.

6.8.4. Effect of contact time and dye concentration

Dye concentration of the adsorbate into the solution plays a pivotal role in determining the adsorption rate of that adsorbate onto the adsorbent. If the dye concentration



(a) (b) (c) (d) (e)

Fig. 10. Response surface graph for Q_{max}, (a) temperature vs. pH; (b) jute dose vs. pH; (c) dye concentration vs. pH; (d) jute dose vs. temperature and (e) jute dose vs. dye concentration.

in the solution will be less than the affinity of the adsorbate particles will have a lesser tendency to get deposited on the surfaces of adsorbent. On the other hand if the dye concentration of the solution is more than the solute dye particles will readily available to come out of near saturated solvent and get attached to the surfaces of adsorbent by adsorption. In the experimental study, three different dye concentrations were considered are 50 mg/L, 100 mg/L and 150 mg/L. It was observed that adsorption was maximum for dye solution with a concentration of 150 mg/L. Results are shown in Fig.10.

7. Desirability based multi response optimization

The goals and ranges of process variables viz. pH, temperature, jute dose and dye concentration and the response characteristics viz. Q_{max} is given in Table 6. The goal of RSM approach is to find a set of optimal processing conditions that will encounter all the goals. 1.0 desirability value is not obligatory, as the value is entirely reliant on how intently the upper and lower limits are set relative to the real optimum.

A set 30 optimal solution is acquired for the specific design space constraints for Q_{max} using statistical Design Expert software 9.0.0.2. The set of parametric conditions possessing highest value of desirability is preferred as optimal processing condition for the desired performance characteristics [48,49]. The optimal parametric condition with greater desirability function is given in Table 7. Once the optimal set of the input parameters is chosen, the final measure is to predict and verify the enhancement of the response characteristics using the optimal level of the processing parameters. Confirmation experiment was performed at the above optimal setting of process parameter for pH, Temperature, jute dose and dye concentration to verify and compare with optimal value of response characteristics. The calculated percentage of error for experimental validation of the generated response models with optimal setting of process parameter during experimentation in given in Table 8. The observation reveals that the calculated error is small as depicted in Table 6. Noticeably, this confirms excellent reproducibility of the experimental outcomes.

The desirability function for performance characteristics using ramp function graph and bar graph illustrates in Figs. 11 and12 respectively. Each dot on the ramp indicates the parameter settings or response prediction for that performance characteristic. The elevation of the dot reveals the amount of desirability of that response. A linear ramp function is generated between the high value and the goal or the low value and the target as the weight for each factor was set equal to one. Bar graph depicts the overall desirability function of the quality characteristics. Depending upon the proximity of the response towards goal the value of desirability varies from 0 to 1. The bar graph illustrates how well each process variable satisfies the design criterion, desirability value close to one are appraised good.

3D desirability plots were drawn by considering the process parameters in range and response characteristics

Table 7
Input process parameters and their optimum value

Parameter	Goal	Optimum value
pH,	in range	7.20
Temperature, (^{0}k)	in range	302.130
Jute dose, (g/l)	in range	14.524
Dye concentration (mg/L)	in range	150.00
Desirability		0.840

Table 8
Predicted and observed values of responses of Q_{max}

Responses	Q_{max} (mg/g)
Goal	Maximize
Predicted value	31.20
Observed value	33.69
Error (%)	7.98

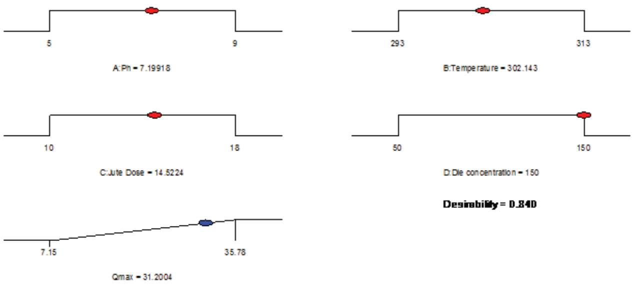


Fig. 11. Ramp function plot of desirability for Q_{max}.

Table 6
Range of input parameters and responses for desirability

Name	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance
A:pH	is in range	5	9	1	1	3
B:Temperature	is in range	293	313	1	1	3
C:Jutedose	is in range	10	18	1	1	3
D:Dyeconcentration	is in range	50	150	1	1	3
Q_{max}	maximize	7.15	33.69	1	1	5

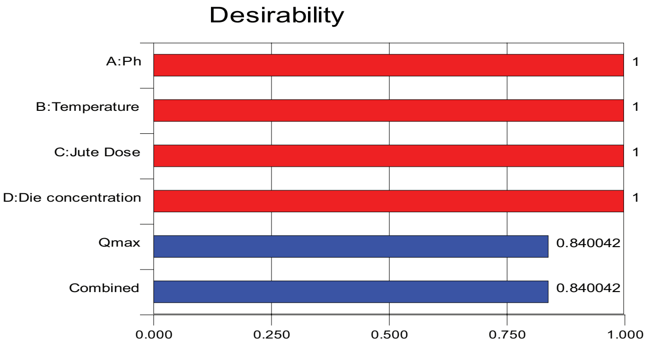


Fig. 12. Bar graph of desirability Q_{max}.

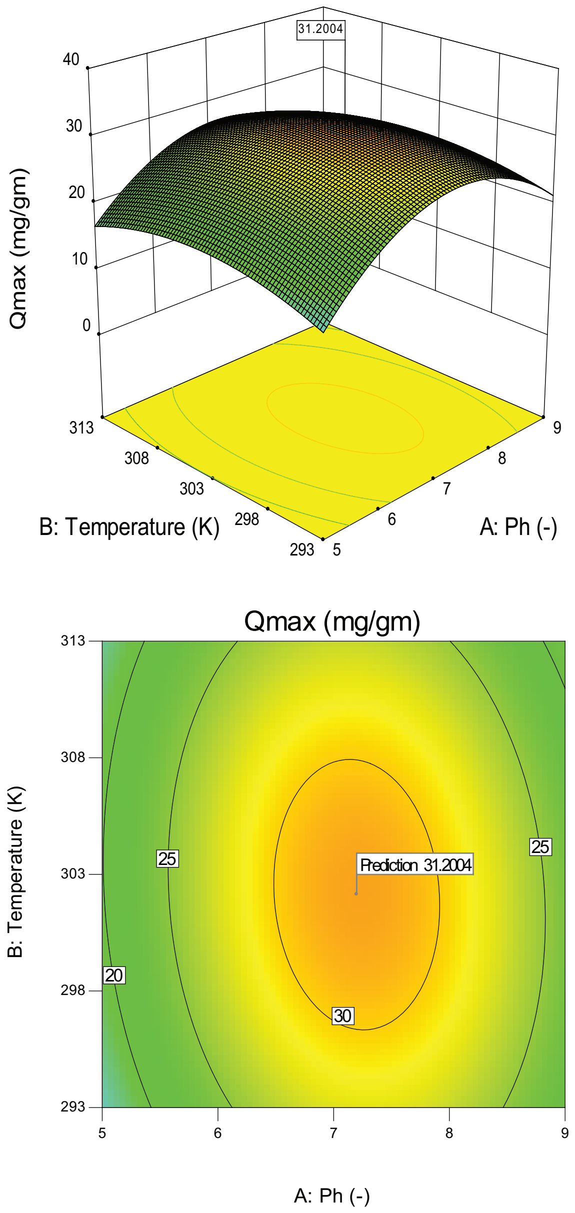


Fig. 13. 3D Surface plot of desirability of Q_{max} (a) and (b).

Q_{max} at maximum. The distribution of desirability function for desired response of Q_{max} inconsonance with temperature and jute dose are shown in Fig. 13. It can be interpreted that the value of overall desirability is less at higher pulse current and pulse on time region. The region for optimal desirability was located near the top region of the plot, which shows the overall desirability value greater than 0.840042 that gradually decreased while moving right and backwards. Hence, the elucidated desirability value of 0.840042 illustrates the proximity of the response towards target.

8. Mechanism of adsorption

One of the interesting challenge in any adsorption study is to understand the adsorption mechanism. To do the same, it is important to consider two key points, (1) The structure of the adsorbate and (2) To know the functional groups present in an adsorbent responsible for adsorption. In the present study of CR it is revealed that the dye contains amino groups which are responsible for formation of hydrogen bond with the exposed hydroxyl groups present in NTJF. The results obtained from SEM and FTIR study suggests and justifies that NaOH treatment of Jute fibre changes the surface morphology, reduce silica content and increase the crystallinity of the cellulose fraction. The same has also been discussed elaborately in section 2.1 of this article. This change in surface characteristics of treated jute fibre will probably favour chemical interaction between the hydroxyl exposed adsorbent and dye ions and favour mechanical bonding due to more affinity of dye ions towards the modified and suitable adsorbent molecular structure.

As discussed in the section 5.1, the adsorption was very rapid for the first 30 min for all the cases, thereafter gradually slowed down and eventually the equilibrium time reached at 120 min suggests that there was mainly intra-particle diffusion supported by film diffusion. The sorption was maximum at around pH of 7.0, Jute dose and RPM played a vital role in determining sorption capacity.

Based on the findings the following adsorption mechanism may be listed as:

- Transfer of CR dye from bulk of the solution to the Jute fibre surface.
- Diffusion of dye particles from aqueous solution through boundary layer to the surface of adsorbent.
- Successful adsorption of dye molecules on the surface jute fibres probably due to formation of hydrogen bond

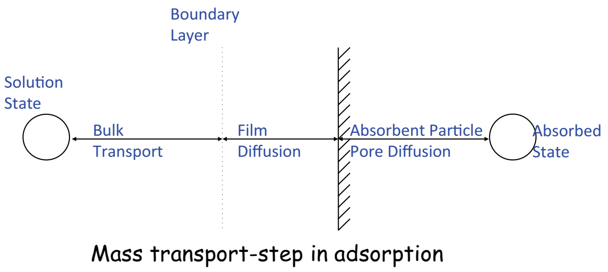


Fig. 14. General mass transport step in adsorption.

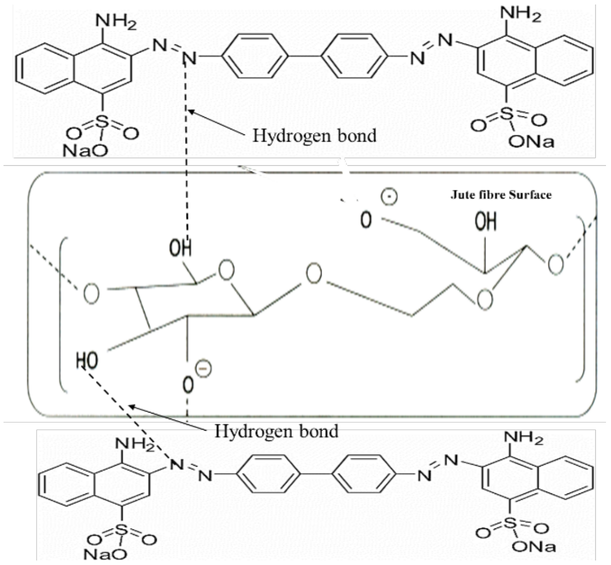


Fig. 15. Adsorption mechanism of CR onto NTJF.

Table 9
Comparison of NTJF with other adsorbents

Adsorbent	q_{max} (mg/g)	References
NaOH treated rice husk	44.87	[50]
Eucalyptus wood saw dust	66.6	[51]
Neem leaf powder	41.2	[52]
Sugar cane bagasse	38.2	[53]
Jute stick powder	35.7	[54]
Orange peel	14.3	[55]
Jujuba seed	55.56	[56]
Coniferous pinus bark powder	32.78	[57]
Activated red mud	7.08	[58]
Neem sawdust	3.8	[59]
Sugar cane dust	3.8	[60]
Jalshakti polymer	12.9	[61]
Rubber seeds	9.82	[62]
Coir pith	2.56	[63]
Sugar cane fibre	10.44	[64]
NTJF	33.69	This study

between amino groups of dye and the exposed hydroxyl group present in jute fibres. The same is depicted in Fig. 15. Fig. 14 shows a general mass transport step in adsorption.

9. Comparison of NTJF with other adsorbents

A comparative observation for the adsorption of CR dye with various types of adsorbents is presented in Table 9. Upon comparison with other adsorbents [50–64] it is revealed that adsorption capacity of NTJF is quite significant among various adsorbents suggesting that NTJF can be successfully employed for the removal of CR dye.

10. Conclusions

In the present study removal of CR dye was successfully carried out using NaOH treated jute fibre as an adsorbent. Use of input process parameters pH, temperature, jute dose and dye concentration were successfully investigated for designing the output of maximum adsorption capacity using face centered central composite design of response surface methodology by attending 30 experimental trials with repetition of three in each of the process parameters at three different levels. Modelling results reveals that neutral pH, low to moderate temperature, moderate to high jute dose and high dye concentration will be crucial for optimum adsorption capacity. The obtained predicted value of R^2 for Q_{max} as 0.840042 justifies the same, which reflects the models adequacy. The jute dose and dye concentration are the two main significant factors that affected the outcome of $Q_{max.}$ Rate of adsorption increased with increase in jute dose, and at moderate dye concentration. The effect of each process parameters and the reasoning's for the same are discussed in the relevant sections of the paper. The combination of optimum parameter setting for Q_{max} obtained are pH 7.20, temperature, 302.130K, jute dose 14.524g/l and dye concentration 150.00 mg/L for maximizing the Q_{max}. The agreeable error percentage of 7.98 between the predicted and observed values for Q_{max} confirm precision of the methodology.

Acknowledgements

The authors would like thank CIT Kokrajhar, NIT Silchar,NEHU Shillong andSAIF IIT Bombay for contributing to the work directly or indirectly.

References

[1] T.K. Sen, S. Afroze, H. Ang, Equilibrium, kinetics and mechanism of removal of methylene blue from aqueous solution by adsorption onto pine cone biomass of Pinus radiata, Water Air Soil Pollut., 218 (2011) 499–515.

[2] M.T. Yagub, T.K. Sen, H. Ang, Equilibrium, kinetics, and thermodynamics of methylene blue adsorption by pine tree leaves, Water Air Soil Pollut., 223 (2012)) 67–82.

[3] G.A. Saygili, Synthesis, characterization and adsorption properties of a novel biomagnetic composite for the removal of congo red from aqueous medium, J. Mol. Liq., 211 (2015) 515–526.

[4] P.S. Vankar, Chemistry of natural dyes, Resonance, (2000) 73–80.

[5] M.T. Yagub, T.K. Sen, S. Afroze, H.M. Ang, Dye and its removal from aqueous solution by adsorption: A review, Adv. Colloid Interface Sci., 209 (2014) 172–184.

[6] V.K. Gupta, D. Pathania, S. Sharma, S. Agarwal, P. Singh, Remediation and recovery of methyl orange from aqueous solution onto acrylic acid grafted Ficus carica fiber: iso-therms, kinetics and thermodynamics, J. Mol. Liq., 177 (2013) 325–334.

[7] I.K. Kapdan, R. Ozturk, Effect of operating parameters on color and COD removal performance of SBR: sludge age and initial dyestuff concentration, J. Hazard. Mater., B123 (2005) 217–222.

[8] 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.

[9] Y.L. Song, J.T. Li, H. Chen, Degradation of C.I. Acid red 88 aqueous solution by combination of Fenton's reagent and ultrasound irradiation, J. Chem. Technol. Biotechnol., 84 (2009) 578–583.

[10] T. Panswad, S. Wongchaisuwan, Mechanisms of dye wastewater colour removal by magnesium carbonate-hydrated basic, Water Sci. Technol., 18 (1986) 139–144.

[11] M.N. Chong, B. Jin, C.W.K. Chow, C.P. Saint, A new approach to optimize an annular slurry photo reactor system for the degradation of congo red: statistical analysis and modelling, Chem. Eng. J., 152 (2009) 158–166.

[12] M. Koch, A. Yediler, D. Lienert, G. Insel, A. Kettrup, Ozonation of hydrolyzed azo dye reactive yellow 84 (CI), Chemosphere, 46 (2002) 109–113.

[13] G. Ciardelli, L. Corsi, M. Marcucci, Membrane separation for wastewater reuse in the textile industry, Resour. Conserv. Recycl., 31 (2000) 189–197.

[14] D.H.K. Reddy, S.M. Lee, Application of magnetic chitosan composites for the removal of toxic and dyes from aqueous solutions, Adv. Colloid Interf. Sci., 201–202 (2013) 68–93.

[15] D.H.K. Reddy, Y.S. Yun, Spinel ferrite magnetic adsorbents: alternative future mate-rials for water purification, Coord. Chem. Rev., 315 (2016) 90–111.

[16] T. Zhou, W. Lu, L. Liu, H. Zhu, Y. Jiao, S. Zhang, R. Han, Effective adsorption of light green anionic dye from solution by CPB modified peanut in column mode, J. Mol. Liq., 211 (2015) 909–914.

[17] C. Namasivayam, M.V. Sureshkumar, Anionic dye adsorption characteristics of sur-factant modified coir pith, a waste lignocellulosic polymer, J. Appl. Polym. Sci., 100 (2006) 1538–1546.

[18] Y. Su, B. Zhao, W. Xiao, R. Han, Adsorption behavior of light green anionic dye using cationic surfactant modified what straw in batch and column mode, Environ. Sci. Pollut. Res., 20 (2013) 5558–5568.

[19] S. Ibrahim, I. Fatimah, H.M. Ang, S. Wang, Adsorption of anionic dyes in aqueous solution using chemically modified barley straw, Water Sci. Technol., 62 (2010) 1177–1182.

[20] S. Liang, X. Guo, N. Feng, Q. Tian, Isotherms, kinetics and thermodynamic studies of adsorption of Cu^{2+} from aqueous solutions by Mg^{2+}/K^{+} type orange peel adsorbents, J. Hazard. Mater., 174 (2010) 756–762.

[21] V.S. Munagapati, D.-S. Kim, Adsorption of anionic azo dye Congo Red from aqueous solution by cationic modified orange peel powder, J. Mol. Liq., 220 (2016) 540–548.

[22] K. Ravikumar S Krishnan, S. Ramalingam, Optimization of process variables by the application of response surface methodology for dye removal using a novel adsorbent, Dyes Pigments 72 (2007) 66–74.

[23] S. Chatterjee, A. Kumar, S. Basu, S. Dutta, Application of Response surface methodology for methylene blue dye removal from aqueous solution using low cost adsorbent, Chem. Eng. J., 181–182 (2012) 289–299.

[24] K. Ravikumar, B. Deebika, K. Balu, Decolourization of aqueous dye solutions by a novel adsorbent: Application of statistical designs and surface plots for the optimization and regression analysis, J. Hazard. Mater., 122 (2005) 75–83.

[25] A.R. Khataee, M. Zarei, L. Moradkhannejhad, Application of response surface methodology for optimization of azo dye removal by oxalate catalyzed photo electro-Fenton process using carbon nano tube-PTFE cathode, Desalination, 258 (2010) 112–119.

[26] I.-H. Cho, K.-D. Zoh, Photo catalytic degradation of azo dye (*Reactive Red 120*) in TiO_2/UV system: Optimization and modeling using a response surface methodology (RSM) based on the central composite design, Dyes Pigments, 75 (2007) 533–543.

[27] A. Agarwal, H. Singh, P. Kumar, M. Singh, Optimisation of power consumption for CNC turned parts using response surface methodology and Taguchi's technique – a comparative study, J. Mater. Process. Technol., 200 (2008) 373–384.

[28] T.L. Taweel, S.A. Gouda, Performance analysis of wire electrochemical turning process – RSM approach, Int. J. Adv. Manuf. Technol., 53 (2010) 181–180.

[29] P.K. Ganguly, S. Chanda, Dyeing of jute: Effect of progressive removal of hemicellulose and lignin, Indian J. Fibre Textile Res., 19 (1994) 38–41.

[30] J. Vadiveloo, B. Nurfariza, J.G. Fadel, Natural improvement of rice husk, Animal Feed Sci. Technol., 151 (2009) 299–305.

[31] V.S Munagapati, D.-S. Kim, Adsorption of anionic azo dye Congo Red from aqueous solution by cationic modified orange peel powder, J. Mol. Liq., 220 (2016)540–548.

[32] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Amer. Chem. Soc., 38 (1916) 2221–2295.

[33] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem., 57 (1906) 385–471.

[34] T.W. Webi, R.K. Chakravort, Pore and solid diffusion models for fixed-bed adsorbents, AIChE J., 20 (1974) 228–238.

[35] Y. Chen, D. Zhang, Adsorption kinetics, isotherm and thermodynamics studies of flavones from Vaccinium bracteatumThunb leaves on NKA-2 resin, Chem. Eng. J., 254 (2014) 579–585.

[36] S. Lagergren, about the theory of so-called adsorption of soluble substances. KungligaSvenskaVetenskapsakademiensHandlingar, 24 (1898) 1–39.

[37] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[38] B.S. Ndazi, C. Nyahumwa, J. Tesha, Chemical and thermal stability of rice husks against alkali treatment, BioResources, 3(4) (2007) 1267–1277.

[39] S. Chowdhury, R. Mishra, P. Saha, P. Kuskwaha, Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk, Desalination, 265 (2011) 159–168.

[40] R. Ahmed, Studies on adsorption of crystal violet dye from aqueous solution onto coniferous Pinus bark powder (CPBP), J. Hazard. Mater., 171 (2009) 767–773.

[41] Y. Liu, Y.-J. Liu, Biosorption isotherms, kinetics and thermodynamics, Separ. Purif. Technol., 61 (2008) 229–242.

[42] H.K. Kansal, S. Singh, P. Kumar, Technology and research developments in powder mixed electric discharge machining (PMEDM), J. Mater. Process. Technol., 184 (2007) 32–41.

[43] A. Saeed, , M. Sharif, , M. Iqbal, Application potential of grapefruit peel as dye sorbent: Kinetics, equilibrium and mechanism of crystal violet adsorption, J. Hazard. Mater., 179 (2010) 564–572.

[44] R. Ahmad, Studies on adsorption of crystal violet dye from aqueous solution onto coniferous pinus bark powder (CPBP), J. Hazard. Mater., 171 (2009) 767–773.

[45] O. Aksakal, H. Ucun, Equilibrium, kinetic and thermodynamic studies of the biosorption of textile dye (Reactive Red 195) onto Pinus sylvestris L, J. Hazard. Mater., 181 (2010) 666–672.

[46] G. Crini, , H.N. Peindy, F. Gimbert, C. Robert, Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies, Separ. Purif. Technol., 53 (2007) 97–110.

[47] S. Chowdhury, P. Saha, Sea shell powder as a new adsorbent to remove Basic Green 4 (Malachite Green) from aqueous solutions: Equilibrium, kinetic and thermodynamic studies, Chem. Eng. J., 164 (2010) 168–177.

[48] T.A. Taweel, Multi-response optimization of EDM with Al–Cu–Si–TiC P/M composite electrode, Int. J. Adv. Manuf. Technol. 44 (2009) 100– 113.

[49] K.T. Chiang, Modeling and analysis of the effects of machining parameters on the performance characteristics in EDM process of Al_2O_3 + TiC mixed ceramic, Int. J. Adv. Manuf. Technol. 37 (2008) 523–533.

[50] S. Chakraborty, P.D. Saha, Adsorption of crystal violet from aqueous solution onto NaOH-modified rice hask, J. Carbohyd. Polym., 86 (2011) 1533–1541.

[51] V.S. Mane, P.V. Vijay Babu, Kinetic and equilibrium studies on the removal of Congo red from aqueous solution using Eucalyptus wood (Eucalyptus globulus) saw dust, J. Taiwan Inst. Chem. Eng., 44 (2013) 81–88.

[52] K.G. Bhattacharyya, A. Sharma, Azadirachtaindica leaf powder as an effective biosorbent for dyes: a case study with

aqueous Congo red solutions, J. Environ. Manag., 71 (2004) 217–229.

[53] Z. Zhang, L. Moghaddam, I.M. O'Hara, W.O.S. Doherty, Congo red adsorption by ball milled sugarcane bagasse, Chem. Eng. J., 178 (2011) 122–128.

[54] 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.

[55] G. Annadurai, R.-S. Juang, D.-J. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, J. Hazard. Mater., 92 (2004) 263–274.

[56] M.C.S. Reddy, L. Sivaramakrishna, A.V. Reddy, The use of an agricultural waste material, Jujuba seeds for the removal of anionic dye (Congo red) from aqueous medium, J. Hazard. Mater., 203–204 (2012) 118–127.

[57] R. Ahmed, Studies on adsorption of crystal violet dye from aqueous solution onto coniferous pinus bark powder (CPBP), J. Hazard. Mater., 171 (2009) 767–773.

[58] A. Tor, Y. Cengeloglu, Removal of congo red from aqueous solution by adsorption onto acid activated red mud, J. Hazard. Mater., 138 (2006) 409–415.

[59] S.D. Khattri, M.K. Singh, Colour removal from synthetic dye wastewater using a bio adsorbent, Water Air Soil Pollution, 120 (2009) 283–294.

[60] S.D. Khattri, M.K. Singh, Colour removal from dye wastewater using sugarcane dust as an adsorbent, Adsorp. Sci. Technol., 17 (1999) 269–282.

[61] R. Dhodapkar, N.N. Rao, S.P. Pande, T. Nandy, S. Devotta, Adsorption of cationic dyes on Jalshakti, super adsorbent polymer and photo catalytic regeneration of the adsorbent, React. Funct. Polym., 67 (2007) 540– 548.

[62] M.A. Zulfikar, H. Setiyanto, L. Rusnadi, Solakhudin, Rubber seeds (Heveabrasiliensis): an adsorbent for adsorption of congo red from aqueous solution, Desal. Water Treat., 56 (2015) 2976–2987.

[63] C. Namasivayam, R. Radhika, S. Suba, Uptake of dyes by a promising locally available agricultural solid waste: Coir pith, Waste Manage., 21 (2001) 381–387.

[64] H. Parab, M. Sudersanan, N. Shenoy, T. Pathare, B. Vaze, Use of agro industrial wastes for removal of basic dyes from aqueous solutions, Clean Soil Air Water, 37 (2009) 963–969.