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Journal of Chemical and Pharmaceutical Research, 2016, 8(7):452-462

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Adsorption of methylene blue dye by citric acid modified leaves of *Ricinus communis* from aqueous solutions

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ABSTRACT

The study was conducted for the removal of Methylene blue dye from aqueous solutions onto citric acid modified leaves of Ricinus communis (CALRC). The properties of this adsorbent were characterized by Yield, Iodine value, surface acidity and basicity, Boehm's titration, zeta potential and FTIR measurements. Adsorption experiments were carried out systematically by batch mode experiments to investigate the influence of different factors, such as contact time, initial concentration of dye solution and pH of the solutions. The maximum adsorption of MB dye was observed at 5.26 pH for CALRC (81.29 %). The Langmuir, Freundlich, Temkin and Dubin-Radushkevich isotherm models were used to analyze the equilibrium data. The data were also fitted to kinetic models such as pseudo-first order, pseudo-second order, Intra particle and Elovich model. The adsorption equilibrium data were well fitted by the Langmuir model. Kinetic studies showed that the adsorption followed pseudo-second order model and intra particle diffusion also. According to the experimental results, the adsorbent derived from this material is expected to be an economical product for metal ion remediation from water and waste water.

Keywords: Adsorption, Chemisorption, Citric acid, leaves of *Ricinus communis*, Langmuir isotherm and Pseudo - second-order kinetics.

INTRODUCTION

Dyes, pigments and heavy metals represent common and dangerous pollutants, originating in large quantities from dye manufacturing, textile as well as pulp and paper industries. They are emitted into wastewaters and produce difficult to treat water contamination, as the colour tents to persist even after the conventional removal process. Contamination of water resources with dyes is not desirable, as they are aesthetically displeasing. The dyes also prevent reoxygenation in receiving waters by cutting off sunlight penetration. In addition, most of the dyes used as colouring material are toxic to aquatic organism. Methylene blue (MB) is a cationic dye and widely used for printing calico, dyeing, printing cotton, tannin and dyeing leather. Although not strongly hazardous, MB can have various harmful effects. The dye can cause eye burns, which may be responsible for permanent injury to the eyes of human and animals, irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea and also cause methemoglobinemia, cyanosis, convulsions, tachycardia, and dyspnea. Contact of MB with skin causes irritation [1]. So the removal of cationic dye such as methylene blue from waste water is the important one.

Existing technologies for dyes effluent treatment such as advanced oxidation process electrochemical reduction, etc. may be efficient in the removal of dyes but their initial and operational costs are high. Adsorption has proved to be more versatile and efficient compared to conventional physico-chemical methods of dye removal. The recovery of dyes/organics and easy operational procedures made adsorption technique is being widely used for wastewater treatment. Activated carbon was widely used in removal dyes from textile effluent, which had relatively high sorption capacity for a wide variety of dyes. Commercially available activated carbons are usually derived from natural materials such as wood or coal, therefore, are still considered expensive [2]. Due to economical reasons, it was investigated for a long time that agricultural byproducts and waste materials used for the production of activated carbon. Examples of these attempts included rattan sawdust [2], rice husk [3], lemon peel ([4], granular kohlrabi [5], jute fiber [6] and coconut husk [7].

Agricultural by-products are high volume, low value and underutilized lignocellulosic biomaterials, and contain high levels of cellulose, hemicelluloses and lignin[8]. However, adsorption capacity of crude agricultural by-products is low in general. Chemical modification has shown great promise in improving the adsorption and the cation exchange capacity of agricultural by-products [9-12]. Citric acid (CA) is a low cost material used extensively in the food industry. Wing [10] derivatized corn by-products with CA and observed considerable improvement in Cu^{2+} binding. When heated, CA will dehydrate to yield a reactive anhydride which can react with the sugar hydroxyl groups to form an ester linkage. The introduced free carboxyl groups of CA increase the net negative charge on the straw fiber, thereby increasing its binding potential for cationic contaminants [11-14].

In this study, the cheap and abundantly available agricultural waste product leaves of *Ricinus communis* is used as an adsorbent. The low-cost activated carbon was prepared from leaves of *Ricinus communis (*LRC) by modifying the adsorbent surface with citric acid for the adsorption of methylene blue dye from aqueous solution. The adsorption ability of classical activated [15] and microwave assisted zinc chloride chemical activated [16] *Ricinus communis* was previously investigated for the adsorption of MG dye from aqueous solution.

The objective of this study was to modify leaves of *Ricinus communis* with CA after being washed with sodium hydroxide to enhance its ability to adsorb MB dye, then the adsorption process was investigated as a function of initial pH and concentration of MB dye and contact time.

EXPERIMENTAL SECTION

Preparation of Citric acid modified Leaves of *Ricinus communis* (CALRC) adsorbent

Raw *Ricinus communis* leaves were obtained from a agricultural farm in Pollachi, TamilNadu. The collected leaves was air-dried and powdered in a grinder. The dried *Ricinus communis* leaves were base washed by stirring 50 g powder 1 L of 0.1M NaOH. The slurry was stirred at 500 rpm for 1 h at 20 ◦C. Then the slurry was rinsed with deionized water. This procedure was repeated two more times for base washed *Ricinus communis* leaves to ensure removal of base from the *Ricinus communis* leaves. The base washed *Ricinus communis* leaves was then dried overnight at 50 ◦C.

The chemical modification of *Ricinus communis* leaves was made according to the similar method previously described by Vaughan et al. [13]. Base washed (BW) *Ricinus communis* leaves were mixed with 0.6 M CA at a ratio of 1.0 g *Ricinus communis* leaves to 10mL CA. After being stirred at 500 rpm for 30 min at 20 ◦C, acid *Ricinus communis* leaves slurry was placed in a stainless steel tray and dried at 50 ◦C in an air oven. After 24 h, the thermo chemical reaction between acid and leaves was preceded by raising the oven temperature to 120 ◦C for 90 min. After cooling, the reacted products were washed with 200mL deionized water per gram of products to remove any excess of CA. This volume of water was sufficient to remove unreacted CA since no turbidity from lead (II) citrate was observed when the washed leaves was suspended in 10 mL of water to which 10 mL of 0.1M lead (II) nitrate was added. Lastly, citric acid modified *Ricinus communis* leaves (CALRC) were dried at 50 ◦C until constant weight and preserved in a desiccator as adsorbent for further use [17].

Adsorbate used

The hazardous toxic cationic dye such as commercial grade methylene blue was used as adsorbate in this study. The dye stock solution was prepared by dissolving 0.5 g of pure methylene blue dye in one liter of double distilled water. The serial dilutions were made by diluting the dye stock solution in accurate proportions to the desired initial concentrations. The initial pH was adjusted with 0.1 M HCl or 0.1 M NaOH.

Characterization of the Adsorbent

Physico - chemical characteristics of the adsorbent

The characteristics (Yield, Iodine number, moisture content, pH determination surface acidity and basicity) of the adsorbents prepared from Leaves of *Ricinus communis* were determined. The yield of the prepared carbon samples was estimated according to,

$$\mathrm{Y} = \frac{\mathrm{M}}{\mathrm{M_0}} \times 100 \qquad (1)$$

Where M is the weight of CALRC and M_0 is the weight of air dried *Ricinus communis* leaves.

Iodine is considered as probe molecules for assessing the adsorption capacity of adsorbents for solutes of molecular sizes less than 10 Å. Iodine number (mg/g adsorbent), was determined by use of standard 0.1 M iodine solution. The titrant used was 0.1 M sodium thiosulfate.

Surface acidity and basicity was estimated by mixing 0.2 g of adsorbent (CALRC) with 25 mL of 0.5 M NaOH and 0.5 M HCl in a closed flask, the flask was agitated for 48 h at room temperature (28°C). The Suspension was decanted and the remaining NaOH or HCl was titrated with 0.5 M HCl or O.5 M NaOH using phenolphthalein as indicator.

Determination of surface group (Boehm's titration)

The adsorbent material mixed with 0.1 M solution of NaOH, $NaHCO_3$ and Na_2CO_3. The NaOH and Na_2CO_3 were volumetric standards. 0.2 g of dried adsorbent was weighed into 50 mL conical flask and 20 mL of different bases added. The flask is then sealed and agitated in shaker for 48 h. 5 mL of filtrate were titrated with 0.1 M volumetric HCl standard using water - ethanol solution of methyl red as the indicator or 0.1 M NaOH using phenolphthalein as indicator. The number of the basic sites calculated from the amount of HCl that reacted with the adsorbent material. Then the various free acidic groups were derived using the assumption that NaOH neutralize carboxyl lactone and phenolic groups, Na_2CO_3 neutralizes carboxyl and lactones, and $NaHCO_3$ neutralizes only carboxyl groups respectively.

Functional group analysis

Functional groups in CALRC were determined by use of Fourier-transform infrared spectroscopy, at room temperature, by use of spectrum SHIMADZU, IR Affinity-1 with KBr pellet with a scanning range of 4000 - 400 cm^{-1}.

Batch equilibrium studies

To study the effect of parameters such as adsorbent dose, dye concentration and solution pH for the removal of adsorbate on CALRC, batch experiments were performed. Stock solutions of Methylene blue dye was prepared and further diluted to the 25 – 200 mg/ L concentrations for the experiments. pH adjustment was fulfilled by adding 0.1 M HCl or 0.1 M NaOH into the solutions with known initial metal concentrations. Batch adsorption experiments were conducted in asset of 250 mL stoppered flasks containing 0.2 g adsorbent and 50 mL of dye solutions with different concentrations (25- 200 mg / L) at pH 5. The flasks were agitated using a mechanical orbital shaker, and maintained at room temperature for 2 h at a fixed shaking speed of 120 rpm until the equilibrium was reached. The suspensions were filtered and dye concentrations in the supernatant solutions were measured using a Digital photo colorimeter (model number-313). From the initial and final concentrations, percentage removal can be calculated by use of the formula:

$$\%\ \text{of Removal} = \frac{(C_0 - C_f)}{C_0} \times 100 \qquad (2)$$

Where C_o is the initial concentration of MB dye in mg/L and C_f is the final concentration of MB in mg/L. The results obtained in batch mode were used to calculate the equilibrium metal uptake capacity. The amounts of uptake of MB dye by CALRC in the equilibrium (q_e) were calculated by the following mass-balance relationship:

$$q_e = \frac{(C_0 - C_e)}{W} \times V \qquad (3)$$

Where q_e is the equilibrium uptake capacity in mg/g, V is the sample volume in liters, C_o is the initial metal ion concentration in mg/L, C_e the equilibrium metal ion concentration in mg/L, and W is the dry weight of adsorbent in grams.

Adsorption isotherms

Adsorption isotherm is the most important information which indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when adsorption process reaches on Equilibrium state. When the system is at Equilibrium is of importance in determining the maximum sorption capacity of CALRC towards dye solution. Equilibrium data are a basic requirement for the design of adsorption systems and adsorption models, which are used for the mathematical description of the adsorption equilibrium of the MB dye by the adsorbent. The results obtained for adsorption of MB dye were analyzed by use of well-known models given by the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich, isotherms. For the sorption isotherms, initial dye concentration was varied whereas solution pH and amount of adsorbent were held constant. The sorption isotherms for MB dye were obtained for CALRC at solution pH 5.26.

Langmuir isotherm

The Langmuir model is based on the assumption of a structurally homogeneous adsorbent where all adsorption sites are identical and energetically equivalent. The Langmuir model is used for the fitting of a monolayer and/or chemical adsorption. It is represented as follows [18]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \qquad (4)$$

Where q_e (mg/g) is the amount of phosphate adsorbed at equilibrium, C_e (mg/L) is the liquid-phase phosphate concentration at equilibrium, q_{max} (mg/g) is the maximum adsorption capacity of the adsorbent, and b (L/mg) is the Langmuir adsorption constant, respectively.

Freundlich isotherm

The Freundlich model is applied to describe a heterogeneous system characterized by a heterogeneity factor of 1/n. This model describes reversible adsorption and is not restricted to the formation of the monolayer. The Freundlich model is expressed as follows [19]:

$$\log q_e = \frac{1}{n} \log(C_e) + \log K \qquad (5)$$

Where Ce (mg/L) is the liquid-phase concentration at equilibrium, K is the Freundlich isotherm constant, and 1/n (dimensionless) is the heterogeneity factor, respectively.

Temkin isotherm

Temkin adsorption isotherm is expressed as:

$$q_e = B \ln A + B \ln C_e \qquad (6)$$

Where A is Temkin constant representing adsorbent–adsorbat interactions and B is another constant related with adsorption heat [20].

Temkin isotherm takes into account the adsorbing species–adsorbent interactions. Isotherm constants A and B can be determined from plot of qe versus ln Ce.

Dubinin–Radushkevich (D–R) isotherm model

To determine the adsorption occurred is physical or chemical in nature, the equilibrium data were applied to D–R model [21]. The linearized form of the D–R model is given below:

$$\ln C_{ads} = \ln C_m -' Y\varepsilon^2 \qquad (7)$$

Where C_{ads} is the adsorbed metal ions on the surface of adsorbent (mg/L), C_m is the maximum adsorption capacity (mg/g), 'Y is the activity coefficient related to mean adsorption energy (mol^2/J^2) and ε is the Polanyi potential (kJ^2 mol^2).

Polanyi potential [22] can be calculated by using the following equation:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad (8)$$

The mean adsorption energy, E (kJ/mol) is calculated with the help of following equation:

$$E = \frac{1}{\sqrt{-2'Y}} \qquad (9)$$

Batch kinetic studies

The kinetic experiments were performed using a procedure similar to the equilibrium studies. Samples containing Adsorption studies were conducted in 250 mL shaking flasks at a solution pH of 5.26. The adsorbent dose of 0.2 g was thoroughly mixed with 50 mL of copper solution (100 mg/L) and the suspensions were shaken at room temperature at required time intervals, filter the clear solutions and analyzed for residual MB concentration in the solutions. In order to determine the best kinetic model which fits the adsorption experimental data, the pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion model were examined.

Pseudo-first-order kinetic model

The Lagergren pseudo-first-order rate expression is given by the equation [23]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{10}$$

Where q_e (mg/g) is the amount of MB dye adsorbed at the phase of equilibrium, q_t (mg/g) is the amount of nickel ions adsorbed at time t and k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption model.

Pseudo-second-order kinetic model

The pseudo-second-order model is given by equation [24]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{11}$$

Where k_2 ($gmg^{-1}\ min^{-1}$) is the rate constant of the pseudo-second order kinetic model. In the pseudo-second-order model chemical sorption is the rate limiting step [25]. In reactions involving chemisorption of adsorbate onto a solid surface without desorption of products, adsorption rate decreases with time due to an increased surface coverage.

Intra particle diffusion model

The Intra particle diffusion can be described by three consecutive steps:

(i) The transport of adsorbate from the bulk solution to the outer surface of the adsorbent by molecular diffusion.

(ii) The internal diffusion, the transport of adsorbate from the particles surface into interior sites.

(iii) The adsorption of the solute particles from the active sites into the interior surface of the pores.

The effect of intra particle diffusion resistance on adsorption can be determined by the following relationship [26]:

$$q_t = k_{ip} t^{1/2} + C \tag{12}$$

k_{ip} is the intra particle diffusion rate constant ($mg\ g^{-1}\ min^{-1/2}$). To follow the intra particle diffusion model, a plot of q_t against $t^{1/2}$ show yields a linear line where the slope is k_{ip}.

The simplified Elovich equation

$$q_t = \frac{1}{\beta \ln(\alpha\beta)} + \frac{1}{\beta \ln t} \tag{13}$$

Where α ($mg\ g^{-1}\ min^{-1}$) is the initial adsorption rate constant and the parameter β ($g\ mg^{-1}$) is related to the extent of the surface coverage and activation energy for chemisorptions [27]. The values of α and β can be calculated from the plot of q_t against 1/ln t.

RESULTS AND DISCUSSION

Characterization of the Adsorbent

Physico - chemical characteristics of CALRC

Characteristics of the adsorbents such as yield, iodine value, moisture content, pH, surface acidity and basicity of CALRC were determined. The results are summarized in Table 1. This result indicated that yield and iodine number can be correlated with ability to adsorb low-molecular-weight substances and provides a measure of surface area or capacity available to small molecules. The higher the yield and iodine value, the higher will be the adsorption ability of the adsorbents. The measure of moisture content has been reported that if the moisture content of the adsorbent is more, it dilutes the action of carbon and necessitates utilizing some extra load of carbon [28]. CALRC has the surface acidity of 3.803 mmol / g and 4.06 mmol / g surface basicity. Acidity and basicity were confirmed by Boehm titration method. Boehm titrations quantify the basic and oxygenated acidic surface groups on activated carbons [29]. From Boehm titration method we conclude that the activated carbon containing phenyl carboxyl groups. This is confirmed by the FTIR analysis results. This proves the higher adsorption ability of CALRC.

Zero surface charges - the characteristic analysis of CALRC

The zero surface charge of CALRC was determined by using the solid addition method [30]. The experiment was conducted in a series of 250 mL glass stoppered flasks. Each flask was filled with 50 mL of different initial pH $NaN0_3$ solutions and 0.2 g of CALRC. The pH values of the $NaN0_2$ solutions were adjusted between 2 to 9 by adding either 0.1 M HNO_3 or 0.1 M NaOH. The suspensions were then sealed and shaken for 2 h at 150 rpm. The final pH values of the supernatant liquid were noted. The difference between the initial pH (pH_0) and final pH (pH_f)

values (pH = pH_0 - pH_f) was plotted against the values of pH_0. The point of intersection of the resulting curve with abscissa, gave the pH_{zpc}.

Table 1. Physico - chemical characteristics of CALRC

Parameters	CALRC
Yield (%)	54.6
Iodine Value (mg/g)	1062.4
Moisture content (%)	8.33
pH Determination	5.42
Surface acidity (m.mol/g)	3.803
Surface basicity (m.mol/g)	4.06
Boehm'sTitration (m eq/g)	
NaOH	5.48
Na_2CO_3	3.45
$NaHCO_3$	1.98

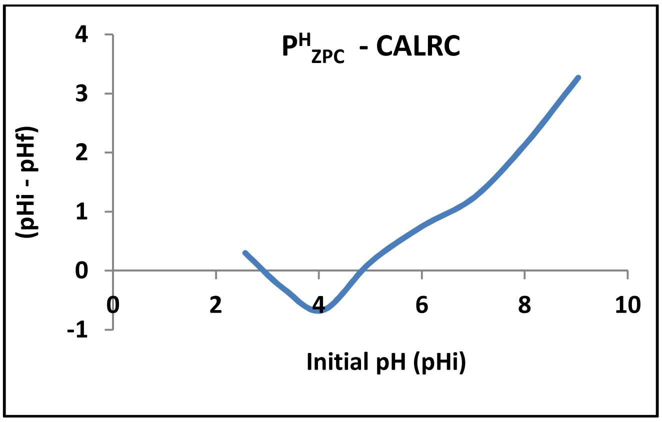
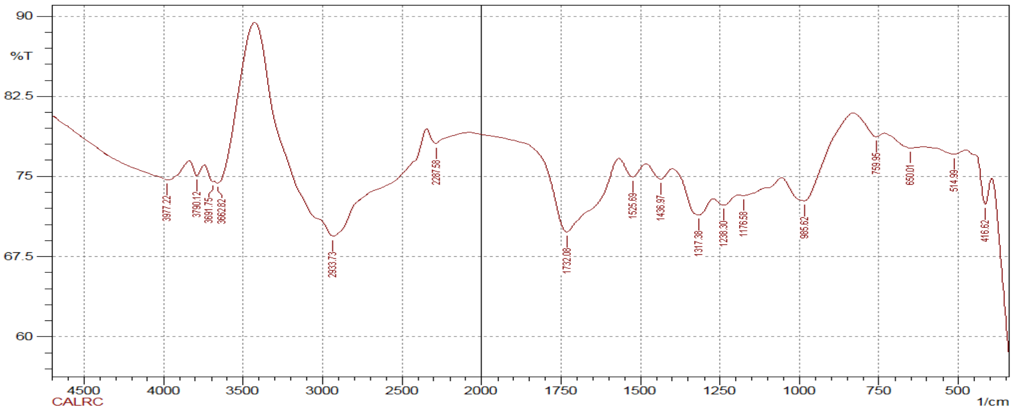


Figure 1. Zero point charges of CALRC

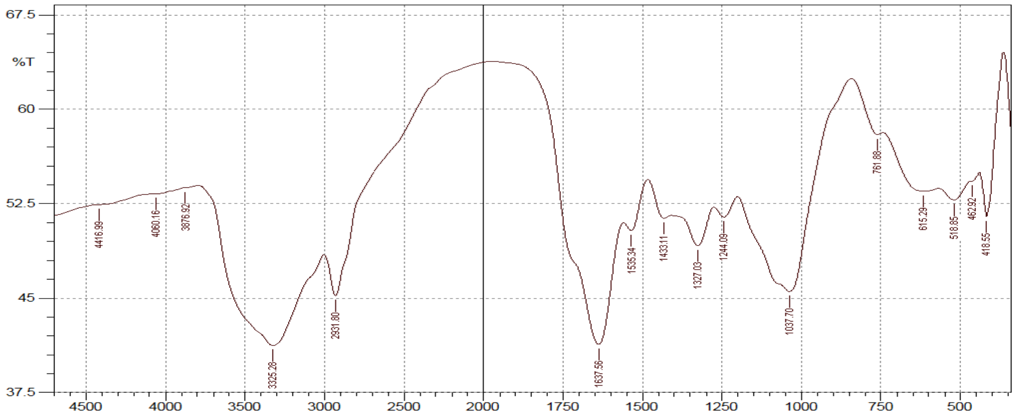
The pH_{ZPC} of an adsorbent is a very important characteristic that determines the pH at which the adsorbent surface has net electrical neutrality. Fig. 1 shows that the plot between ΔpH, i.e. (pH_i – pH_f) and pH_i for pH_{ZPC} measurement. The point of zero charge for CALRC is found to be 4.08. This result indicated that the pH_{ZPC} of CALRC was depended on the raw material and the activated agency. The zero point charge (pH_{ZPC} = 4.08 for CALRC) is below the solution pH (pH = 5.26) and hence the negative charge density on the surface of CALRC increased which favours the adsorption of MB dye [31].

Infrared (IR) spectroscopic studies

The aim of using FTIR analysis is to determine the existence of functional groups and the identification of the characteristic peaks is based on studies. The adsorbent (CALRC) was subjected to Fourier Transform Infrared (FTIR) spectroscopy in the form of KBr pellet and the percentage transmissions for various wave numbers are determined. The FTIR spectrum of CALRC is presented in Fig. 2. The absorption bands identify in the spectra and it revealed corresponding functional groups.



(a)



(b)

Figure 2. FTIR spectra for (a) CALRC and (b) CALRC-MB

The band at 3325 cm^{-1} represents the presence of –OH and –NH groups. The band observed at 2931-2933 cm^{-1} is associated to asymmetric stretches of –CH group. Atmospheric CO_2 bands are present at 2287 cm^{-1} (anti symmetric C=O stretch). The bands at 1637, and 1433-1436 cm^{-1} indicates the presence of –COO, -C=O and –NH groups. The peak at 1535 cm^{-1} is attributed to the formation of oxygen functional groups such as a highly conjugated C-O stretching in carboxylic groups [19] and due to the presence of quinone structure [32]. The broad band between 1325 and 1037 cm^{-1} has been assigned to C-O stretching in alcohols and phenols [19]. Another absorption band appearing around 1244 and 615 cm^{-1} can be attributed to the Si-C stretch and C-O-H twist. The peak present at 1176 cm^{-1} indicates the presence of aromatic heterocyclic molecules, but this peak is absent in CALRC-MB. This indicates that there is a possibility of ring cleavage after the acid treatment [33]. The FTIR data shows that the functional groups present in the adsorbent (CALRC) does not eliminated after the adsorption of MB.

Batch Mode Adsorption Studies

Effect of pH on dye adsorption

The zeta-potentials of the CALRC particles in water were measured at different pH. It was found that the CALRC particles are positively charged at low pH and negatively charged at high pH, having a point of zero charge (pH_{zpc}) at pH 4.08. Therefore, it can be expected that positively charged MB are likely to be absorbed by the negatively charged CALRC particles at a pH > ZPC for CALRC.

The pH of the aqueous solution is an important factor affecting the adsorption process. To study the influence of pH on the adsorbent capacity of leaves of *Ricinus communis* on cationic dyes, the experiments were carried out using different initial solution pH values, varying from 2 to 10. The effect of solution pH is very important when the adsorbing molecules are capable of ionizing in response to the current pH [34]. The pH of an aqueous phase has greater influence on the surface of the adsorbents molecules. The magnitude of electrostatic charges imparted by ionized dye molecules is primarily controlled by the pH of medium. The maximum adsorption capacity of the adsorbents with respect to the initial pH of the adsorbent is depicted in Fig. 3. The percentage removal of dyes increases with increase in the solution pH and reaches the maximum up to 81.52 % (MB onto CALRC) at 5.26 pH.

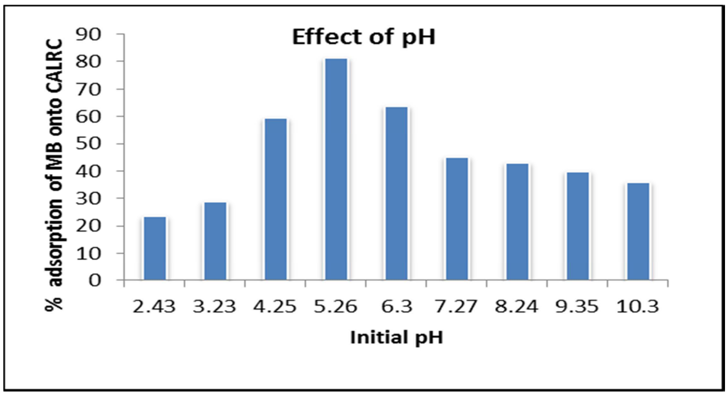


Figure 3. Effect of pH on the adsorption of MB onto CALRC

The adsorption capacity increased with increase in solution pH and attains the maximum adsorption at pH 5.26. The optimum pH value for the adsorption of MB onto CALRC was observed. That may be attributed to the hydrophobic nature of the developed carbon which led to absorb hydrogen ions (H^+) onto the surface of the carbon when immersed in water and make it positively charged. Low pH value (1.0 to 4.0) leads to an increase in H^+ ion concentration in the system and the surface of the activated carbon acquires positive charge by absorbing H^+ ions. On the other hand, increase of the pH value led to increase of the number of negatively charged sites. As the adsorbent surface is negatively charged at high pH, a significantly strong electrostatic attraction appears between the negatively charged carbon surface and cationic dye molecule leading to maximum adsorption of MB from waste water [35]. The lowest adsorption occurred at pH 2.0 and the greatest adsorption occurred at pH $\sim$ 5.0. Adsorbents surface would be positively charged up to pH < 4, and heterogeneous in the pH range 4 – 5, thereafter it should be negatively charged. Moreover, the increasing in the adsorption of dye with increasing of pH value is also due to the attraction between cationic dye and excess OH^- ions in the solution [36].

When solution pH increases, high OH^- ions accumulate on the adsorbent surface. Therefore, electrostatic interaction between negatively charged adsorbent surface and cationic dye molecule caused the increase in adsorption. Furthermore, the solution pH is above the zero point of charge (pH_{zpc} – 4.17 for CALRC) and hence the negative charge density of the surface of the adsorbents were increased which favors the adsorption of cationic dye [31]. The optimal pH value of MB dye onto CALRC was used for the subsequent experiments. Similar trends was reported for the Removal of malachite green from aqueous solution by activated carbon prepared from the epicarp of *Ricinus communis* by adsorption [15] and removal of crystal violet onto *Ricinus communis* pericarp [28].

Effect of Contact Time on the adsorption of MB Dye

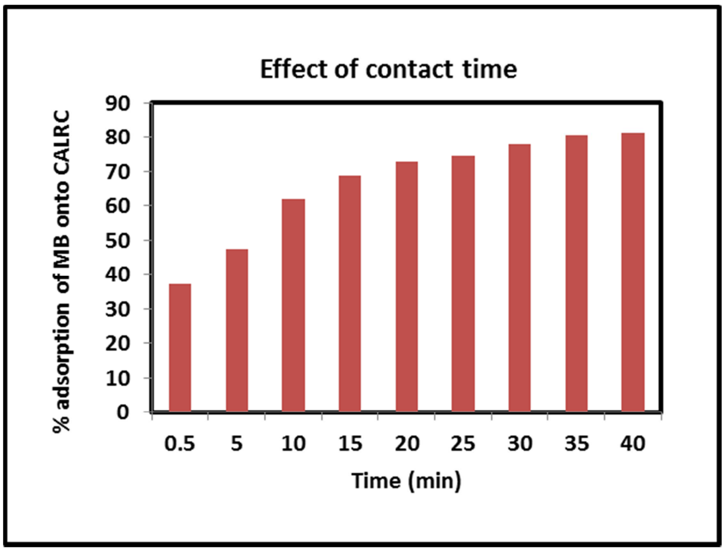


Figure 4. Effect of Contact time on the adsorption of MB onto CALRC

The effect of time on the sorption of MB by CALRC was studied. Fig. 4 indicates that the removal efficiency increased with an increase in contact time before equilibrium is reached. This may be due to the attainment of equilibrium condition at 40 min of contact time for CALRC, which is fixed as the optimum contact time. At the initial stage, the rate of removal of MB ions was higher, due to the availability of more than required number of active sites on the surface of carbons and became slower at the later stages of contact time, due to the decreased or lesser number of active sites. Further, the attainment of maximum adsorption within 40 min suggests that a very minimum contact time is sufficient enough for the removal of MB from water by these adsorbent.

Effect of initial dye concentration on MB dye adsorption

The data for the uptake of MB onto CALRC as a function of dye concentration is presented in Fig. 5. It can be seen that the percentage of adsorption of MB decreased with the increase in initial concentration. The percentage removal shows that, with an increase in the initial concentration of dyes, the percent removal was decreased from 89.74 % - 56.82 % at 665nm for the dye concentration of 50 to 200 mg/L.

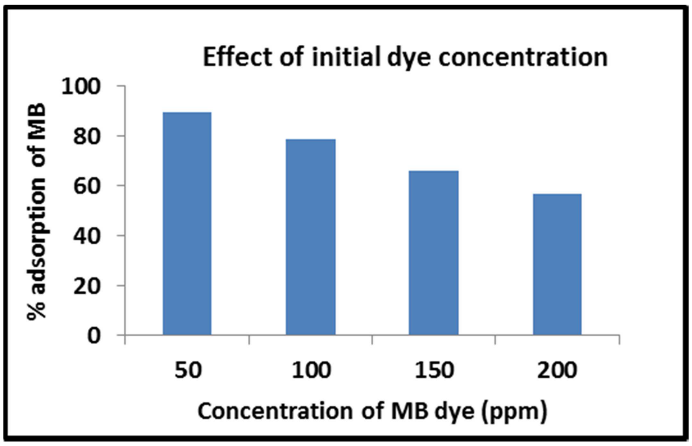


Figure 5. Effect of Initial dye concentration on the adsorption of MB onto CALRC

The increase in uptake capacity of the adsorbent with increasing dye concentration may be due to the increase of sorbate quantity. At lower initial dye concentration, sufficient adsorption sites are available for the adsorption of dye ions. Conversely, the numbers of dye ions at higher initial concentration are relatively more as compared to the available adsorption sites. Similar trends are reported by Atmani et al. [37] for CV onto almond waste. The percentage of dye adsorbed decreased with increasing the initial dye concentration of 50, 100, 150, and 200 mg/L.

Adsorption isotherm

In the present investigation, the equilibrium data were analyzed using the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. To optimize the design of an adsorption system, it is important to establish the most appropriate isotherm model. The mono-component equilibrium characteristics of adsorption of MB by CALRC were described by these four different isotherm models. The experimental equilibrium adsorption data were obtained by varying the concentration of MB with 0.2 g/50 mL of CALRC.

Table 2. Adsorption isotherm parameters for the adsorption of MB onto CALRC

Isotherm model	Parameters	
Langmuir	Q_m (mgg^{-1})	333.33
	b (Lmg-1)	0.0833
	R^2	0.9960
Freundlich	1/n	0.329
	K_f (mgg^{-1})	67.45
	R^2	0.9860
Temkin	α (Lg-1)	1.51
	β (mgL-1)	60.120
	b	41.90
	R^2	0.999
Dubinin-Radushkevich	Q_m (mgg^{-1})	245.67
	K (x10-5mol2kJ-2)	0.400
	E(kJmol-1)	1.118
	R^2	0.902

The adsorption data obtained by fitting the different isotherm models with the experimental data are listed in Table 2, with the linear regression coefficients, R^2. CALRC have a homogeneous surface for adsorption of MB. The Langmuir isotherm equation is therefore expected to best represent the equilibrium adsorption data. The R^2 values for the Langmuir model are closer to unity than those for the other isotherm models for CALRC ($R^2 = 0.9960$). Therefore, the equilibrium adsorption of MB dye on CALRC can be represented appropriately by the Langmuir model in the concentration range studied.

Adsorption Kinetics

The adsorption process of MB can be well fitted by use of the pseudo-second order rate constant for CALRC. The kinetic data are given in the Table 3. The q_e value (250) obtained from the second-order kinetic equation for CALRC was close to the experimental qe value (202.38) and the linear regression coefficient value R^2 value (0.999) obtained for pseudo-second-order kinetics was closer to unity than the R^2 value (0.804) for first-order kinetics. This indicates that adsorption of MB by CALRC follows pseudo-second-order kinetics.

Table 3. Comparison of the correlation coefficients of kinetic parameters for the adsorption of MB onto CALRC

Models	Parameters	
Pseudo first-order model	k_1 (min^{-1})	6.5957
	q_e (mg/g)	1.3803
	R^2	0.804
Pseudo second-order model	k_2 (g/mg/min)	0.0007
	q_e (mg/g)	250.0
	h	43.75
	R^2	0.999
Intra particle diffusion model	k_{dif} (mg/(g.min$^{1/2}$))	19.43
	C	87.47
	R^2	0.960
Elovich model	A_E (mg(g/ min))	0.0184
	b (g/ mg)	62.3027
	R^2	0.9830

In the intra particle diffusion model, the values of q_t were found to be linearly correlated with the values of $t^{1/2}$. The k_{dif} values were calculated by use of correlation analysis. $k_{dif} = 19.43$, $R^2 = 0.933$ for CALR. The R^2 values were closer to unity for CALRC, indicating the application of this model is a fit for CALRC.

CONCLUSION

Leaves of *Ricinus communis* were found to be a good raw material for developing activated carbon. The activated carbon produced has high surface area. The present investigation shows, the CALRC is an effective adsorbent for the removal of MB dye from aqueous solutions. The surface morphology and functional groups involved in the adsorbents were determined by analyzing through FTIR. Adsorption capacity of the adsorbents was highly dependent on the solution pH, initial dye concentrations and contact time. The optimum pH corresponding to the maximum adsorption was found to be 5 for CALRC. The maximum adsorption of MB onto CALRC from aqueous solution was 81.52 %. The efficiency of MB adsorption increased with an increase in the solution pH and contact time but it decreases with the increase in the initial concentration of the adsorbate solution. The adsorption data were well fitted by the Langmuir isotherm model; this is indicative of monolayer adsorption by CALRC. Among the kinetic models tested, the adsorption kinetics was best described by the pseudo-second order equation for the adsorption of MB onto CALRC. The leaves Of *Ricinus communis* used in this work are freely and abundantly available. The experimental studies showed that leaves of *Ricinus communis* could be used as an alternative, inexpensive and effective material to remove high amount of MB dye from aqueous solutions.

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