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Liquid phase adsorption of Indigo Carmine and Methylene Blue on Neem bark

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ABSTRACT

This research paper deals with the use of low-cost, easy obtained, high efficiency and eco-friendly adsorbents as an ideal alternative to the current expensive methods of removing dyes from wastewater. This study investigates the potential use of Neem bark powder (NBP) for the removal of Indigo Carmine (I.C) and Methylene Blue (M.B) dyes from simulated wastewater. The effects of different system variables, adsorbent dosage, initial dye concentration, pH and contact time were studied. The results showed that as the amount of the adsorbent increased, the percentage of dye removal increased accordingly. Optimum pH value for dye adsorption was different according to the nature of the dyes. The adsorption of both the dyes was found to be a pseudo-second-order rate equation and fit well with Langmuir equation, better than Freundlich equation. The maximum removal of I.C was obtained at pH 2 and M.B at pH 10. The maximum adsorption capacity obtained from Langmuir equation was 4.02×10^3 and 3.11×10^3 mol g^{-1} for I.C and M.B on NBP. Furthermore, adsorption kinetics of I.C and M.B were studied and the rate of adsorption was found to conform to pseudo-second-order kinetics with a good correlation ($R^2 > 0.99$) with intraparticle diffusion as one of the rate determining steps. Thus low-cost NBP can be an attractive option for dyes removal from diluted industrial effluents.

Keywords: Kinetics; Thermodynamics; Wastewater; Adsorption; Neem bark powder; Dyes

1. Introduction

Wastewater from textile and dyeing industries contains residual dyes, which are not readily biodegradable are the major contributors to water pollution and poses serious threat to the environment. Highly colored wastes are not only aesthetically displeasing but also hinder light penetration and may in consequence disturb biological processes in water bodies. Moreover, dyes itself are toxic to some organisms and hence disturb the ecosystem [1]. Many studies have been conducted on the toxicity of dyes and their impact on the ecosystem [2] as well as the environmental issues associated with the manufacture and subsequent usage of dyes [3,4]. Most of the used dyes are stable to photo-degradation, biodegradation and oxidizing agents [5]. Hence, investigations have been conducted on several physical or chemical methods of removing color from textile effluent. These studies include the use of coagulants [6] ultrafiltration [7] electro-chemical [8,9] and adsorption [10] techniques. The advantages and disadvantages of each technique have been extensively reviewed, among these methods, adsorption has been found to be an efficient and economic process to remove dyes, pigments and other colorants and also to control the biochemical oxygen demand [11]. Activated carbon (powdered or granular) is the most widely used adsorbent because it has

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Table 1. Literature review on the removal of I.C and M.B

Parameters	Values
NBP	
Ash content (%)	12.7
Bulk density (mg/m^3)	0.563
pH$_{ZPC}$	6.80
Volatile matter (%)	87.28
C (%)	43.23
H (%)	4.39
N (%)	0.93

excellent adsorption efficiency for organic compounds and heavy metals, but its use is somewhat limited due to its high cost which led to search for low-cost adsorbents [12].

In the present study Neem bark powder (NBP), a waste material obtained from wood industry have been used as adsorbent for the removal of Indigo Carmine (I.C) and Methylene Blue (M.B) from its aqueous solution. To develop the efficiency of the adsorbent, adsorption batch and kinetic studies were performed.

2. Literature review

Currently sorption process is proved to be one of the effective and attractive processes for the treatment of these dyes bearing wastewater. Also this method will become in expensive if the sorbent material used is of cheap or inexpensive material and does not require any expensive additional pre-treatment step. Below, a list of adsorbents are given (Table 1) which are successful in removing M.B and I.C dye from wastewater [13–41].

Continuing our effort in this direction we have utilized wood waste as a feedstock for the production of adsorbents. This provides a low-cost, environmental friendly precursor and it develops market for what is otherwise low-value waste materials. The present investigation deals with the preparation of adsorbents from Neem bark which is a waste/by product in the wood industry. The developed adsorbent is utilized for the remediation of I.C and M.Blue from wastewater/water successfully.

3. Materials and methods

3.1. Dye solution preparation

An accurately weighed quantity of the dyes, i.e. Indigo Carmine (IUPAC name = 3.3′-dioxo- 2,2′-bis-indolyden-5.5′-disulfonic acid disodium salt) and Methylene Blue (IUPAC name= 3,7 bis (dimethylamine phenazathionium chloride tetramethylthionine chloride) were dissolved in double-distilled water to prepare stock solution. Experimental solutions of the desired concentrations were obtained by successive dilutions. Dye concentration was determined using absorbance values measured before and after treatment using spectrophotometer (as discussed below). Experiments were carried out at initial pH values ranging from 2 to 10.

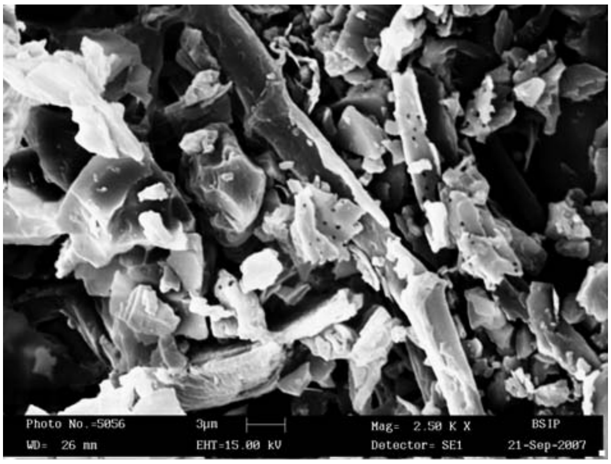

Fig. 1. (a,b). Scanning electron micrograph (SEM) of Neem bark powder at 2500×.

3.2. Sorbent

Neem bark used in the present work was collected from local wood shops. The collected barks were washed with permuted water several times to remove dirt particles and water soluble materials. The washed materials were then completely dried in an air oven at 105–110°C for 24 h till the barks could be grinded into fine powder by the local mixer grinder. The products so obtained were sieved to the desired particle sizes such as 150—212 μm. Finally, the product was stored in a vacuum desiccator until required. The developed powder is NBP. The powder having 150–212 mesh size was used in both the sorption and kinetic studies unless otherwise stated. The surface structure of NBP was analyzed by scanning electronic microscopy (SEM). SEM micrograph was obtained using model (SC 7640.U.K). The textural structure examination (Fig. 1) of Neem bark particles obtained from the SEM photographs at 2500 magnifications reveals that the bark exhibits a caves-like, uneven, and rough surface morphology.

3.3. Equipment

The pH of the solution was measured by using a pH meter (Model 744, Metrohm). Absorbance measurements were made on a GBC UV–visible spectrophotometer model Cintra-40. The spectrophotometer response time was 0.1 s and the instrument had a resolution of 0.1 nm. Absorbance values were recorded at the wavelength for maximum absorbance (λ_{max}), i.e. 610 and 660 nm for I.C and M.B, respectively. The agitation of the system under investigation was carried out on a thermostat-cum shaking assembly (model MSW 275).The zero point of charge (pHzpc) of NBP was estimated by using the alkalimetric titration method [42].

General characterization (Table 2) of NBP were obtained in the laboratory through various experimental set up. These characterizations help in understanding the physical nature of the bark powder.

3.4. General ranges of experimental parameters

Sorption studies were performed by the batch technique to obtain rate and equilibrium data. The batch technique was selected because of its simplicity. Batch sorption studies were performed at different temperatures, dye initial concentrations and adsorbent doses to obtain equilibrium isotherms. For isotherm studies, a series of 100 ml conical flasks were employed. Each conical flask was filled with 50 ml of dye solution of varying concentrations (mol $g^{-1} \times 10^{-6}$ mol $g^{-1} \times 10^{-4}$) separately and adjusted to the desired pH and temperature (43). The suspensions were stirred at 400 rpm at 25°C for 7 h until equilibrium was reached. Aqueous samples were taken from the solutions and the concentrations were determined (43). The contact time and other conditions were selected on the basis of preliminary experiments, which demonstrated that the equilibrium was established in 120 min for M.B and 150 min for I.C. The effect of pH was observed by studying the adsorption of dyes over a broad pH range of 2–10. The pH was adjusted using 0.1 N NaOH and 0.1 N HCl solutions. In this study 50 ml of dye solutions was agitated with 0.5 g of NBP for 24 h. The samples were then centrifuged and the left out concentration in the supernatant solution were analyzed using UV Spectrophotometer. The effect of temperature (at 283, 298, 313 K) on the sorption of I.C and M.B by NBP was studied at 0.5 g/50 ml with initial dye concentration of 10^{-5} mol L^{-1} (pH 2 and 10, respectively) for 7 h contact time to delineate the effect of temperature and to evaluate the sorption thermodynamic parameters.

A mass of 0.5 g of adsorbent (NBP) was contacted with 50 ml I.C and M.B solutions of dye concentrations mol $L^{-1} \times 10^{-4}$–mol $L^{-1} \times 10^{-6}$ at (pH 2 and pH 10) for I.C and M.B, respectively, using water-bath maintained at 25°C. The agitation speed was kept constant at 400 rpm. At predetermined intervals of time, samples were analyzed for the final concentration of I.C and M.B by a UV/Vis spectrophotometer. Samples of NBP (0.5, 1.0 and 2.0 g) were added to 50 ml of both the dye solutions. The initial dye concentration was 10^{-5} mol L^{-1} (pH 2 and pH 10 for I.C and M.B) at constant temperature (25°C) and stirring at the speed of 400 rpm to study the effect of sorbent dosage.

4. Result and discussions

4.1. Effect of contact time and initial concentration

The sorption efficiency of I.C and M.B increased gradually with increasing contact time. At this point, the amount of dye being sorbed onto the sorbent was in a state of dynamic equilibrium with the amount of dye desorbed from the sorbent. The contact time needed for I.C and M.B solutions to reach equilibrium at initial concentration of 1×10^{-5} mol L^{-1} was 150 and 120 min for I.C and M.B. It is also noticed that an increase in the initial dyes concentration leads to a decrease in the percentage of I.C and M.B removal. As the initial dye concentration increases from 10^{-6} mol L^{-1} to 10^{-4} mol L^{-1}, the equilibrium removal of both the dye solutions decreases from 69.76% to 40.89% for I.C and from 61.89% to 37.15% for M.B (Table 3). This effect can be explained as follows: at low dye/sorbent ratios, there are number of sorption sites in NBP structure. As the dye/sorbent ratio increases, sorption sites are saturated, resulting in decreases in the sorption efficiency. Thus it can be said that the sorption is increased instantly at initial stages (due to rapid attachment of dye to the surface of the sorbent), and then keeps increasing gradually until the equilibrium is reached and remains constant.

4.2. Effect of sorbent dosage

An increase in the Neem bark dose from 0.5 to 2 g/50 ml increases the percentage of dye removal from aqueous solution from 68.45% to 39.65% for I.C and 64.45% to 36.89% for M.B (Table 3). This may be attributed to increased sorbent contact area and availability of more sorption sites resulting from the increased dose of the sorbent. The increase in sorbent dose at constant dye concentration and volume will lead to unsaturation of sorption sites through the sorption process. At higher NBP to dye concentration ratios, there is a superficial sorption onto the sorbent surface that produces a lower dye concentration in the solution than when the sorbent to dye concentration ratio is lower. This is because a fixed mass of the adsorbents can only sorb a certain amount of dye. Therefore, the higher the sorbent dosage is, the larger the volume of effluent that a fixed mass of NBP can purify [44].

Table 2. Characteristics of NBP

Sl. No.	Adsorbate	Adsorbent	Comment	Ref. No.
Removal of Malachite green				
1	Methylene Blue	Rice husk	Monolayer capacity was found to be 40.5833 mg/g. Sorption process was found to be controlled by both surface and pore diffusion.	13
2		Jute fibre carbons	Activated carbon was prepared by treating jute fibre with phosphoric acid. Optimum pH was found to be between 5 amd 8.	14
3		Fuller's earth	Distribution co-efficient increased with an increased in the initial concentration of the dye, attained a maximum value and decreased again at a higher initial concent ration.	15
4		Cedar saw dust and crushed brick	Adsoption kinetic results indicated that both film and particle diffusion are effective adsorption mechanism. The extent of dye removal decreased with increasing the solution temperature and pH of solution.	16
5		Lemon peel	$Q_0 = 29$ mg/g. Adsorbent was effective enough for dye removal	17
6		Nitric acid treated water hyacinth.	The loading of MB onto (N-WH) was found to increase with increasing initial MB concentration, the resideual conc. Of MB also increased. Increase in temperature was found to increase the rate of adsorption process was diffusion controlled.	18
7		Cellulose based waste	Banana and orange peels were used as a low cost adsorbents. Banana peels are found to be more promising than orange peels.	19
8		Bamboo waste activated carbon	Bamboo an abundant & inexpensive natural resources in Malaysia was used to prepare carbon with KOH and CO_2 at an activating agent at 850°C for 2 hrs. $Q_0 = 454.2$ mg/g.	20
9		Posidenia Oceanica	It is a marine lignocellulosic biomass. The result showed that biosportion capacity was optimal using 6-9 range pH and increasing the concentration upto 1g/l of the biomass	21
10		Clay	Zeta potential and the conductivities of clay suspensions at various pH(1-11) & cation exchange capacity were measured. Adsorption increases with decrease in temperature and pH.	22
11		Fibrous clay minerals	The augmentation of clay contents or the methylene blue concentration reduced the adsorption capacity, because of clay particles micro aggregation. It may be due to electrostatic forces induced by the clay particles.	23
12		Giant duckweed	Percentage of dye sorption increases with increase in the amount of adsorbents.	24
13		Indian Rosewood Sawdust (IRS)	IRS is pretreated with formatdehyde and H_2SO_4. 1/6 removal increased with increase in adsorbent amount.	25
14		Neem leaf powder (NLP)	Adsorbent was prepared from mature leaves of neem tree. 93% of dye removed by 2 g of NLP. Reaction was endothermic	26
15		Acid Treated Carbon	Activated carbon was acid treated. Pore size distribution and surface chemical characteristic play an important role during adsorption.	27
16		Perlite	Extent of dye removal inc. in the initial concentration of the dye.	28
17		Ground nut hazelnut shell and sawdust of various woods	Reaction is endohermic in nature.	29

(continued)

Table 2 (continued)

Sl. No.	Adsorbate	Adsorbent	Comment	Ref. No.
18		Yellow passion fruit waste	In alkaline pH region the adsorption of dye was favourable. $Q_0 = 44.70$ mg/g.	30
19		Dehydrated peanut hulls	Peanut hulls were dehydrated with H_2SO_4. Intraparticle diffusion is becoming significantly controlling step.	31
20		Spent activated clay	It is a waste from edible oil manufacturer. $Q_0 = 0.94 \times 10^{-4}$ to 3.14×0^{-4} mol/g between 5 and 45°C	32
21		Peat	Peat was collected from peat land in south of Brazil. It should a successful adsorption percentage.	33
22		Dehydrated wheat bran carbon	Temperature maintained (25–45°C), initial concentration = 100–500 mg l^{-1}. Optimum pH = 2.5	34
23		Mango seed kernel powder	Waste generated from juie factories. Q^0 = 142.857–153.846 mg/g. Amount of dye uptake increase with increase in solution temperature.	35
24		Coirpith	$Q^0 = 5.87$ mg/g. Adsorption % increases with decrease in initial concentration of solution.	36
Removal of Indigo carmine				
Sl. No.	Adsorbate	Adsorbent/Methods	Comment	Ref. No.
1	Indigo Carmine	Chitin	No. of moles absorbed is $1.24–0.16 \times 10^{-5}$. Reaction shows to be exothermic enthalpic values of $-40.12–3.52$ KJ mol^{-1}.	37
2		Chitosan	No. of moles absorbed is $1.54–0.03 \times 10^{-4}$. Exothermic enthalpic values = 29.25–1.93 $KJmol^{-1}$ increase in entropy value .	37
3		Ultra filtration of aq. Solution	A low pressure membrane process was studied. The ultra filtration process used pressure of 0.1 and 0.2 MPa.	38
4		Photolytic degradation method.	The kinetics of reaction have been studied and were found to be zero or first order with respect to the dye.	39
5		Coffee beans	Reaction was found to be endothermic in nature as Gibbs free energy decrease with rise in temperature.	40
6.		Sewage sludge	The research work deals with potential application of adsorbent produced from sewage sludge in organic pollutant removal. After pyrolysis sewage sludge provide material of great porosity and high surface area.	41

4.3. *Effect of temperature*

The sorption studies were carried out at three different temperatures 10, 25 and 40°C. The removal percentage of I.C and M.B, increase with the increasing temperature, i.e. from 38.25% to 63.98% and 35.25% to 62.09% for adsorbent (NBP), indicating that the sorption is an endothermic process (Table 3). This may be a result of increase in the mobility of the dyes with increasing temperature. Furthermore, the enhancement in the sorption capacity might be due to the enhancement of sorptive interaction between the active sites of sorbent and sorbate ions, creation of some new sorption sites or the increased rate of intraparticle diffusion of I.C and M.B molecules into the pores of the sorbent at higher temperatures [45,46]. It can also be said that increasing temperature may also produce a swelling effect within the internal structure of the adsorbents enabling more dye molecules diffusion into the sorbents [47].

4.4 *Effect of pH*

The results of the experiments done at different pH values, which were conducted to determine the optimum pH range for dyes adsorption on NBP is shown in Fig. 2. The percentage removal of I.C and M.B by NBP was optimum at pH 2.0 and pH 10.0. Several reasons may be attributed to dye sorption behavior of the biosorbent relative to solution pH. The surface of bark powder may contain a large number of active sites and the solute (dye ions) uptake can be related to the active sites and also to the chemistry of the solute in the solution. This can be explained by considering the zero point charge of

Table 3. Percentage removal of I.C and M.B at different temperatures, dye concentrations and adsorbate doses

	Indigo Carmine			Methylene blue		
Time (min)	10	25	40	10	25	40
Effect of temperature °C (% Removal)						
0	0.13	0.23	0.44	0.11	0.18	0.35
30	15.89	22.87	27.63	12.34	19.64	25.74
60	23.65	40.75	45.54	20.20	37.82	41.65
90	30.11	47.83	53.90	30.59	51.43	59.61
120	35.09	55.44	60.01	35.25	56.66	62.09
150	38.25	59.78	63.98	35.55	56.75	62.19
Effect of concentration mol g^{-1} (% Removal)						
	10^{-4}	10^{-5}	10^{-6}	10^{-4}	10^{-5}	10^{-6}
0	0.11	0.24	0.45	0.09	0.22	0.42
30	13.67	23.66	25.65	10.74	21.12	24.74
60	25.63	37.89	43.90	18.54	36.63	41.63
90	33.72	46.83	57.83	31.54	48.88	58.93
120	38.53	52.09	64.21	37.15	52.07	61.89
150	40.89	58.76	69.76	37. 35	54.66	62.95
Effect of adsorbent dose g L^{-1} (% Removal)						
	0.5	1.0	2.0	0.5	1.0	2.0
0	0.08	0.25	0.39	0.06	0.21	0.40
30	11.11	21.98	24.34	10.56	18.63	22.65
60	23.67	35.62	44.87	17.86	39.48	42.74
90	34.85	47.32	55.31	33.95	46.84	58.45
120	37.55	51.67	65.45	37.15	51.35	61.89
150	39.65	57.75	68.45	37.65	51.55	61.93

the adsorbent. The pH at the pH_{ZPC} of the adsorbent (NBP) is 6.80. Thus it seems that for pH values below the zeta potential of adsorbents, positive charge density on the surface increases, the charge developed in the acid medium favors association of anionic dye, whereas negative charge density develops above zeta potential of the adsorbent. Thus, the positive charge density would be found more on the dye molecule at pH less than the zeta potential on adsorbent surface and this accounts for the higher uptake of I.C dye at pH 2.0 and higher uptake of M.B at pH 10.0 [47].

4.5. Isotherm analysis

The analysis and design of sorption process requires the relevant adsorption equilibria, which is the most important piece of information in understanding an adsorption process. Sorption equilibria provide fundamental physiochemical data for evaluating the applicability of sorption process as a unit operation. To facilitate estimation of the adsorption capacities the two well-known equilibrium adsorption models, Freundlich [48] and Langmuir [49] models were employed.

4.5.1 Langmuir isotherm

The Langmuir equation assumes that maximum adsorption occurs when the surface is covered by the adsorbate. The distribution of dyes between the solid-solution interface equilibrium has been described by the linear form of Langmuir equation given as follows:

$$(C_e/q_e) = (1/bQ^0) + (C_e/Q^0), \qquad (1)$$

where C_e is the concentration of the dye solution (mol L^{-1}) at equilibrium, q_e is the amount of dye adsorbed per unit weight of adsorbent (mol g^{-1}) and b is related to the energy of adsorption (L mol^{-1}).

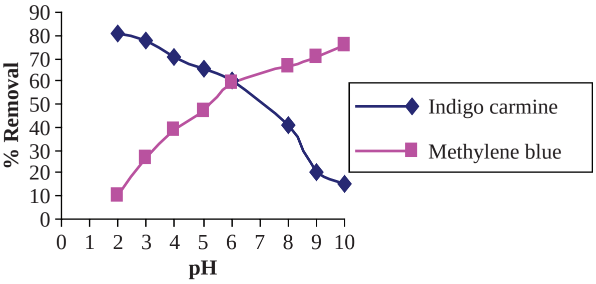

Fig. 2. Plot of pH vs. % removal of I.C and M.B over NBP.

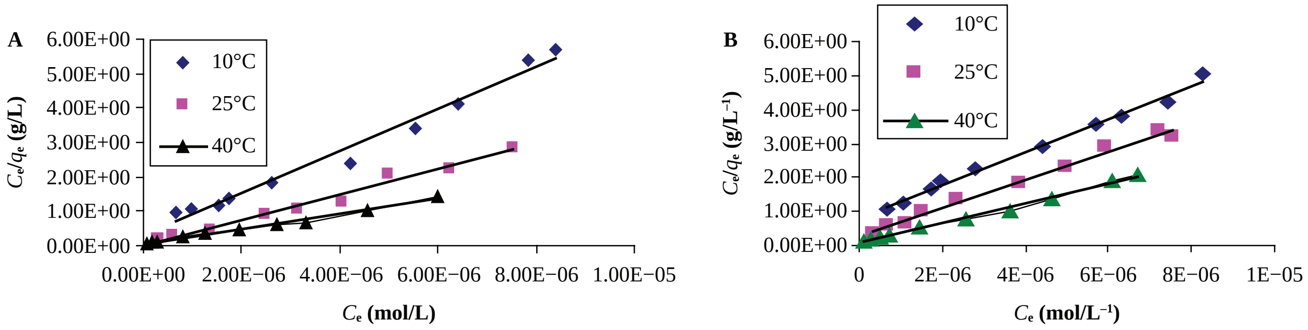

Fig. 3. Langmuir isotherm constants for the adsorption of (a) I.C and (b) M.B over NBP.

Values of Q^0 and b were calculated from the slope and intercept of the linear plot, C_e/q_e versus C_e. The isotherm was found to be linear over the entire concentration range studied with a good linear regression coefficient ($R^2 = 0.991$ and 0.993) for I.C and M.B. The fact that the Langmuir isotherm fits the experimental data may be due to homogeneous distribution of active sites (Figs. 3a and 3b) on the bark powder, since the Langmuir equation assumes that the surface is homogeneous. The values of monolayer saturation capacity Q^0 calculated from Langmuir equation was found to be 4.02×10^3 mol g^{-1} and 3.11×10^3 mol g^{-1} for I.C and M.B. The Langmuir parameters are tabulated in (Table 4).

The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor R_L [50]

$$R_L = 1/(1 + bC_0), \qquad (2)$$

where b is the Langmuir constant and C_0 is the initial concentration of the sorbate in solution. The values of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$).

4.5.2. Freundlich isotherm

The Freundlich expression is an exponential equation and therefore, assumes that as the sorbate concentration increases, the concentration of sorbate on the sorbent surface also increases. The linear form of the Freundlich isotherm is:

$$\ln q_e = \ln K_F + l/n \ln C_e, \qquad (3)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mol g^{-1}), C_e is the equilibrium concentration of the solute in the bulk solution (mol L^{-1}), K_F is the constant indicative of the relative adsorption capacity of the adsorbent (mol g^{-1}) and $1/n$ is constant indicative of the intensity of adsorption. The equilibrium data were further analyzed using the linearized form of Freundlich equation using the same set experimental data. The calculated Freundlich isotherm constants and the corresponding coefficient of determination values are shown in (Table 4). From Table 4, it was observed that both the Freundlich and Langmuir isotherms could well represent the experimental sorption data of I.C and M.B by NBP, but the Langmuir expression was better in both the cases. It is generally stated that values of n in the range 2–10

Table 4. Langmuir and Freundlich isotherm constants for the adsorption of I,C and M.B on NBP

Langmuir constants	10°C			25°C			40°C		
Adsorbate	Q^0 (×10^3 mol g^{-1})	b (×10^{-2} l mol^{-1})	R^2	Q^0 (×10^3 mol g^{-1})	b (×10^{-2} l mol^{-1})	R^2	Q^0 (×10^3 mol g^{-1})	b (×10^{-2} l mol^{-1})	R^2
I.C	3.25	5.76	0.99	3.78	6.22	0.99	4.02	7.01	0.99
M.B	2.55	3.73	0.99	3.01	5.34	0.99	3.11	5.65	0.99
Freundlich constants	K_f (×10^{2}mol g^{-1})			$1/n$			R^2		
Adsorbate	10°C	25°C	40°C	10°C	25°C	40°C	10°C	25°C	40°C
I.C	1.35	1.93	2.22	0.16	0.32	0.81	0.98	0.97	0.97
M.B	1.15	1.89	2.11	0.13	0.27	0.61	0.97	0.98	0.99

Table 5. Comparison of kinetic parameters for the adsorption of IC and M.B NBP

	$q_{e,exp}$ ($\times 10^4$ mol g^{-1})			$q_{e,cal-1}$ ($\times 10^4$ mol g^{-1})			$q_{e,cal-2}$ ($\times 10^4$ mol g^{-1})		
Adsorbate	10°C	25°C	40°C	10°C	25°C	40°C	10°C	25°C	40°C
I.C	2.51	3.11	3.51	1.41	2.18	2.77	2.45	3.01	3.25
M.B	2.19	2.98	3.12	1.28	2.19	2.51	2.08	3.03	3.09

represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics [51].

4.6. Adsorption kinetics study

Successful application of the adsorption demands innovation of cheap, non-toxic, easily available adsorbents of known kinetic parameters and adsorption characteristics. Adsorption kinetics can be modeled by applying pseudo-first-order Lagergren equation [52] and pseudo-second-order model [53].

Pseudo-first-order rate equation is presented as follows:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t, \qquad (4)$$

where q_e and q_t are the amounts of dye adsorbed at equilibrium and at time t, respectively, and k_1 is the rate constant of pseudo-first-order sorption (L min^{-1}). The parameters of the pseudo-first-order model are summarized in (Table 5). The values of determination coefficient for the plots were in the range 0.770–0.978 (fig not shown). This finding suggested that the sorption process does not follow the pseudo-first-order rate equation.

An expression of the pseudo-second-order rate is given below:

$$t/q_t = (1/k_2 q_e^2 t + 1/qe)t, \qquad (5)$$

where K_2 is the pseudo-second-order rate constant (g .mol^{-1} min^{-1}), q_e is the amount of dye sorbed at equilibrium (mol g^{-1}), and q_t is the amount of dye cation on the surface of the sorbent at any time t (mol g^{-1}). The plots of t/q_t versus t give a straight line for all the initial dye concentrations for both the dyes as shown in Figs. 4a and 4b, confirming the applicability of the pseudosecond-order equation. The parameters of the pseudo-second-order sorption kinetic model are summarized in Table 5. The determination coefficient values of the pseudo-second-order model exceeded 0.99 in both the cases (i.e. removal of I.C and M.B by NBP) and the calculated sorption capacity values determined from pseudo-second-order model were more consistent with the experimental values of sorption capacity. Therefore, the pseudo-second order model better represented the sorption kinetics for the removal of I.C and M.B on NBP.

4.7 Intraparticle diffusion

The variation in the extent of adsorption with time at different initial dye concentrations was processed for evaluating the role of diffusion in the adsorption system. Adsorption is a multi-step process, the three consecutive steps in the sorption of a sorbate by a sorbent are:

- Transport of sorbate molecules from the bulk solution to the external surface of the sorbent by diffusion across the liquid boundary layer (film diffusion).
- Diffusion of the sorbate within the pores of the sorbent (intraparticle diffusion).
- Sorption of the sorbate on the active sites [54].

It is generally accepted that the last step is usually very rapid in comparison to the first two steps. Therefore, the overall rate of sorption is controlled by either film or intraparticle diffusion [54]. The rate parameter of intraparticle diffusion can be defined as [55]

$$q = k_{id} t^{1/2} + C \qquad (6)$$

where q (mol g^{-1}) is the amount of I.C and M.B sorbed at time t, C (mol g^{-1}) the intercept, and k_{id} (mol g^{-1} $min^{-1/2}$) is the intraparticle diffusion rate constant. The kinetic results can be used to determine if particle diffusion is the rate-limiting step for dye sorption onto

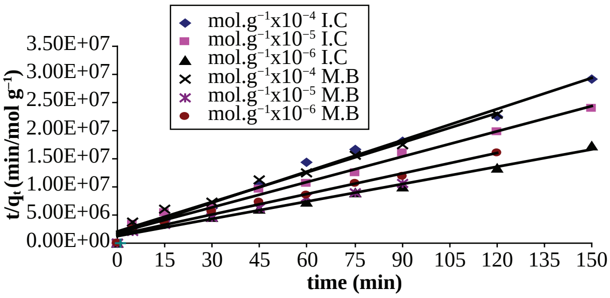

Fig. 4. Pseudo-second order reaction (t/qt) for removal of (a) I.C and (b) M.B over NBP at different initial dye concentration; sorbent dose = 0.5 g/50 ml, T = 25°C, optimum pH.

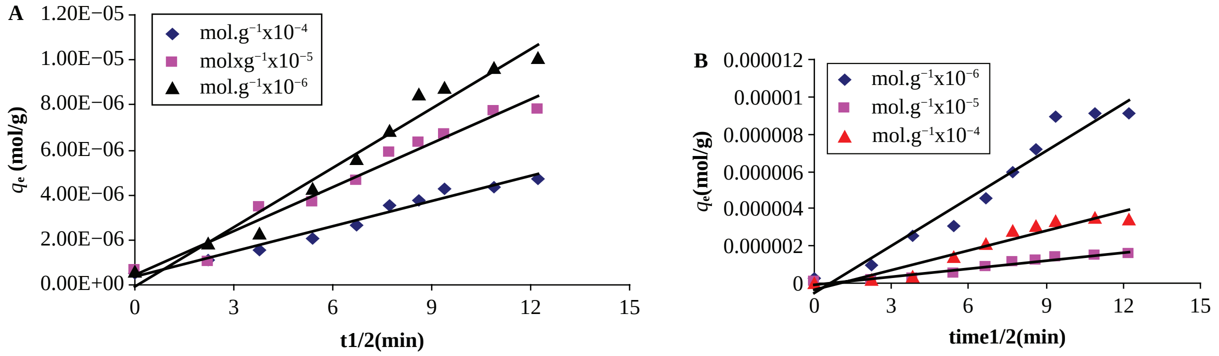

Fig. 5. Intraparticle diffusion for removal of (a) I.C and (b) M.B over NBP at optimum pH; Temperature = 25°C; dose = 0.5 g/50 ml.

material (Figs. 5a and 5b) shows the amount of dye sorbed vs $t^{1/2}$ for intraparticle transport of I.C and M.B by NBP at different initial dye concentrations. The intercept of the portion is proportional to the boundary layer thickness [56]. The determination coefficient values for this diffusion model are between 0.97 and 0.99.

4.8. Bangham's equation

Kinetic data can further be used to check by using Banghams equation [57].

$$\ln.\ln(C_0/C_0 - q_t m) = \log(K_b m/V) + a\ln(t). \qquad (7)$$

where C_0 is the initial concentration of adsorbate in solution (mg L^{-1}), V is the volume of the solution (L), m is the weight of adsorbent per liter of solution (g L^{-1}) q_t is the amount of adsorbate retained at time t, a and K_b are constants, values are summarizes in Table 6. The logarithmic plot (Fig. 6) according to above equation yielded perfect linear curves for adsorption of both I.C and M.B by NBP, showing that the diffusion of adsorbate into pores of the adsorbent is not the only rate controlling step [58].

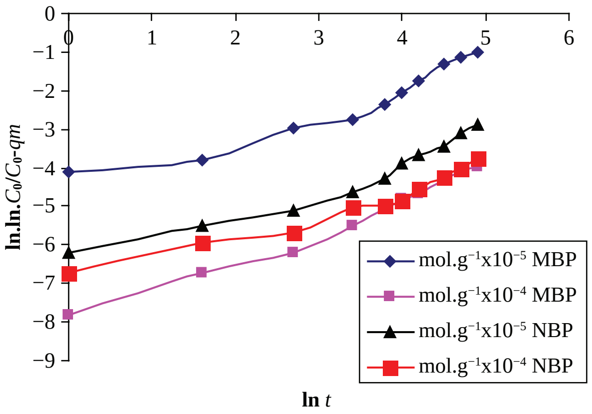

Fig. 6. Bangham's plot for removal of I.C and M.B onto NBP at different concentrations; optimum pH; Temperature = 25°C.

5. Conclusion

The results of this work suggest that the recycling of an agricultural waste byproducts as adsorbent for the treatment of dyeing industry wastewater.

1) NBP is a promising adsorbent for removal of dyes (I.C and M.B).
2) The experimental data produced perfect fit with the Langmuir isotherm for both the dyes, this suggest the monolayer coverage of I.C and M.B with adsorption capacity as 4.02 × 10^3 mol g^{-1} and 3.11 × 10^3 mol g^{-1}.
3) The kinetics of the adsorption of dyes (I.C and M.B) onto NBP reports to be pseudo-second-order chemical reaction kinetics. Pseudo-second-order kinetics is further supported by Bangham's equation.
4) The rate of adsorption of I.C and M.B onto NBP increased with increasing temperature. Thus suggesting the reaction to be spontaneous and endothermic in nature.

NBP act as a good adsorbent for removal of I.C and M.B from industrial and other effluents. However, the Q^0 values at different temperatures showed that NBP act as a better adsorbent for the removal I.C. Dyes are not found in a good degree of purity, even from good sources, as Merck. In general, water soluble mineral compounds are used in the dyes compositions. So, the average degrees of purity of the dyes are less then 70%.

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Table 6. Bangham's constants for adsorption of I.C and M.B three different adsorbate concentrations

	$2\ g\ l^{-1}$			$1\ g\ l^{-1}$			$0.5\ g\ l^{-1}$		
Adsorbate	K_b (ml/g/l)	a	R^2	K_b (ml/g/l)	a	R^2	K_b (ml/g/l)	a	R^2
I.C	3.19	0.45	0.99	2.29	0.64	0.99	2.59	0.68	0.99
M.B	3.11	0.14	0.99	2.79	0.69	0.99	2.71	0.71	0.99

Symbols

λ_{max}	wavelength for maximum absorbance
q_e	amount of dye adsorbed (mol g^{-1}),
C_0	the initial concentration of the solute in the bulk solution (mol L^{-1})
C_e	the equilibrium concentration of the solute in the bulk solution (mol L^{-1})
V	the volume of adsorbate (L)
W	the weight of the adsorbent (g)
Q^0	the monolayer adsorption capacity (mol g^{-1})
B	Langmuir constant related to the free energy of adsorption (L mol^{-1})
K_F	Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mol g^{-1})
$1/n$	Freundlich constant, indicative of the intensity of the adsorption
k_1	the first-order rate constant (min^{-1})
k_2	the pseudo-second-order rate constant (g mol^{-1} min^{-1})
k_i	the intraparticle diffusion rate constant (mol g^{-1} $min^{-0.5}$)
R_L	the parameter to indicate the shape of isotherm
r	coefficient of correlation
R^2	the correlation coefficient
C_0	the initial concentration of adsorbate in solution (mg L^{-1})
V	the volume of the solution (L)
m	the weight of adsorbent per liter of solution (g L^{-1})
q_t	the amount of adsorbate retained (mol g^{-1})
t	time (min)
K_b	Bangham's constant
a	Bangham's constant

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