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Amit Bhatnagar[ab]; Eva Kumar[b]; A. K. Minocha[a]; Byong-Hun Jeon[b]; Hocheol Song[c]; Yong-Chan Seo[d]
[a] Environmental Science & Technology Division, CBRI, Roorkee, India [b] Department of Environmental Engineering (YIEST), Yonsei University, Wonju, South Korea [c] Environmental Hazards Division, KIGAM, Daejoeon, South Korea [d] Department of Environmental Engineering, Sangji University, Wonju, South Korea

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Removal of Anionic Dyes from Water using *Citrus limonum* (Lemon) Peel: Equilibrium Studies and Kinetic Modeling

Amit Bhatnagar,[1,2] Eva Kumar,[2] A. K. Minocha,[1] Byong-Hun Jeon,[2]
Hocheol Song,[3] and Yong-Chan Seo[4]
[1]Environmental Science & Technology Division, CBRI,
Roorkee, India
[2]Department of Environmental Engineering (YIEST), Yonsei University,
Wonju, South Korea
[3]Environmental Hazards Division, KIGAM, Daejoeon, South Korea
[4]Department of Environmental Engineering, Sangji University,
Wonju, South Korea

Abstract: The present study was undertaken to evaluate the adsorption potential of *Citrus limonum* (lemon) peel as an adsorbent for the removal of two anionic dyes, Methyl orange (MO) and Congo red (CR) from aqueous solutions. The adsorption was studied as a function of contact time, initial concentration, and temperature by batch method. The adsorption capacities of lemon peel adsorbent for dyes were found 50.3 and 34.5 mg/g for MO and CR, respectively. The equilibrium adsorption data was well described by the Langmuir model. Three simplified kinetic models viz. pseudo-first-order, pseudo-second-order, and Weber and Morris intraparticle diffusion model were tested to describe the adsorption process. Kinetic parameters, rate constants, equilibrium sorption capacities, and related correlation coefficients for each kinetic model were determined. It was found that the present system of dyes adsorption on lemon peel adsorbent could be described more favorably by the pseudo-first-order kinetic model. The results of the present study reveal that lemon peel adsorbent can be fruitfully utilized as an inexpensive adsorbent for dyes removal from effluents.

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Address correspondence to Amit Bhatnagar, Department of Environmental Engineering, Baekun Hall #332, Yonsei University, 234 Maeji Heungeop, Wonju 220-710, Gangwon-do, South Korea. Tel.: +82-33-760-2814; Fax: +82-33-760-2194. E-mail: amit_b10@yahoo.co.in

Keywords: Adsorbent, anionic dyes, equilibrium isotherms, kinetic modeling, Lemon peel waste

INTRODUCTION

Dyes are important water pollutants which are potentially toxic for the aquatic ecosystem (1). The major industries that contribute to water pollution by dyes are paper and pulp, textile and dyeing, leather, printing, tannery, food processing, cosmetics, and paint industries. Some dyes can cause allergy, dermatitis, skin irritation, mutations, and cancer in humans (2,3), therefore, their removal from industrial effluents is essential before they are mixed up with unpolluted natural water resources.

Various treatment technologies for dyes removal from water and wastewater have been reported in the past such as coagulation/flocculation (4), chemical oxidation (5), ozonation (6,7), ion exchange process (8), solvent extraction (9), photocatalytic degradation (10), and adsorption (11–13). Among the several treatment technologies mentioned above, adsorption is arguably one of the most suitable techniques for treating wastewater effluents containing toxic wastes including dyes.

Over the years, the adsorption process using activated carbon has been proved to be one of the most effective methods to treat wastewater containing dyes; however, use of activated carbon is sometimes restricted due to its higher cost. In view of the importance of water pollution control, efforts have been directed toward developing low cost alternative adsorbents.

Various low cost adsorbents derived from agricultural waste (14–17), industrial by-products (18–21) and natural materials (22–25) have been investigated so far for the removal of dyes from water. The utilization of agro-wastes as adsorbent is currently receiving wide attention because of their abundant availability and low-cost owing to relatively high fixed carbon content and presence of porous structure. In this perspective, we examined the use of citrus fruit peel i.e. lemon (*Citrus limonum*) as an adsorbent for the removal of two anionic dyes from aqueous solutions.

India is the largest producer of lemon in the world (an average of 1.5 million tons of lemon production per year). Lemon is of agronomic importance because the lemons are consumed as an ingredient in cooking, as garnish, and as juice in lemonade, carbonated beverages, and other drinks. To make better use of this cheap and abundant agricultural waste, lemon peel after juice extraction, can be utilized as an inexpensive adsorbent for dyes removal from water.

The objective of this study was to explore the potential use of lemon peel as an adsorbent for the removal of two important anionic dyes, Methyl orange (MO) and Congo red (CR) from water. Equilibrium and kinetic studies were performed to describe the adsorption process. Three simplified kinetic models including pseudo-first-order, pseudo-second-order, and the Weber and Morris model were tested to describe the adsorption process and the results have been discussed in this communication.

EXPERIMENTAL

Materials

Two anionic dyes viz. Methyl orange (MO) and Congo red (CR) were purchased from Aldrich Chemicals and used as adsorbates without further purification. Stock solutions of dyes were prepared by dissolving them in double-distilled water and were diluted further to obtain the lower concentration solutions. The dye solutions were kept at 4 ± 1°C and in the dark until used. All reagents used were of analytical reagent grade.

Preparation of Adsorbent Using Lemon Peel Waste

The used lemon peels were collected from the local fruit market. These were first washed with double distilled water three times and dried in an oven at 100 ± 2°C for 24 h. The dried lemon peels were ground and this material was then thermally activated at 500 ± 5°C in a muffle furnace for 1 h in the presence of air. After activation, the ash content was removed by washing it with distilled water and dried in an oven at 100 ± 5°C for 24 h. Different mesh sizes (BSS 100-250) were obtained after sieving and kept in a desiccator for further use. The particle size of BSS 150-200 mesh was used in the present study.

Adsorption Experiments

The adsorption of dyes on the prepared adsorbent was studied at room temperature (25 ± 2°C) by batch experiments. Ten mL of dyes solution of varying initial concentrations in 50 mL capped glass tubes was shaken with 0.1 g of adsorbent for a specified period of contact time in a temperature controlled shaking assembly. After equilibrium, samples were filtered using 0.45 µm filters (Whatman) and the concentration of the dyes was determined spectrophotometrically at $\lambda_{\max}$ of 465 nm for MO and 497 nm for CR. Reproducibility of the measurements was determined in triplicates and the average values are reported. Relative standard deviations were found to be within ±5.0%.

The amount of dye adsorbed (q_e in mg/g) was determined as follows:

$$q_e = (C_o - C_f)V/m \tag{1}$$

where C_o and C_f are the initial and final concentrations of the dye in solution (in mol/L), V is volume of solution (in L), and m is the mass of the adsorbent (in g). The pH of all solutions in contact with the adsorbent was found to be in the range 5.5–6.5. Kinetic studies of adsorption were also carried out at two initial dyes concentrations, where the extent of adsorption was investigated as a function of time.

RESULTS AND DISCUSSION

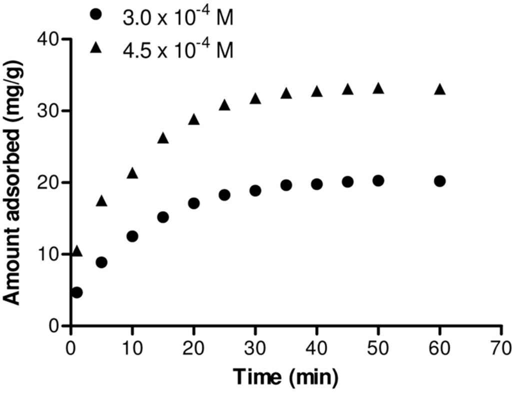
Effect of Contact Time and Initial Dye Concentration

In order to establish the equilibration time for maximum uptake of dyes and to know the kinetics, the adsorption of dyes on prepared lemon peel adsorbent was studied as a function of contact time and the results are shown in Fig. 1 (a and b). It is seen from the figure that the rate of uptake of both the dyes is rapid in the beginning and 50% adsorption is completed in 10 min and becomes constant after 50 min, which indicates that the equilibrium has been achieved. Thus, 60 min contact time was chosen in subsequent batch equilibrium experiments.

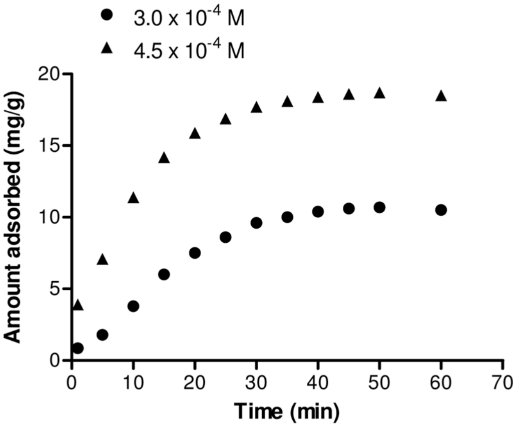
The effect of concentration on equilibrium time was also investigated at two different initial dyes concentrations and the results are also shown in Fig. 1 (a and b). It was found that the adsorption capacity at equilibrium increases from 20.2 mg/g to 33.1 mg/g in case of MO with an increase in the initial dye concentration from 3.0×10^{-4} M to 4.5×10^{-4} M. The same behavior was also observed for CR. This indicates that initial dye concentration plays an important role in the adsorption of dyes on prepared adsorbent.

Kinetic Modeling

Kinetics of adsorption is one of the important characteristics in defining the efficiency of adsorption. Various kinetic models have been proposed by different researchers. In the present study, we applied three important kinetic models viz. pseudo-first-order, pseudo-second-order, and an intraparticle diffusion model in order to investigate the mechanism of the adsorption of dyes on lemon peel adsorbent.



(a)



(b)

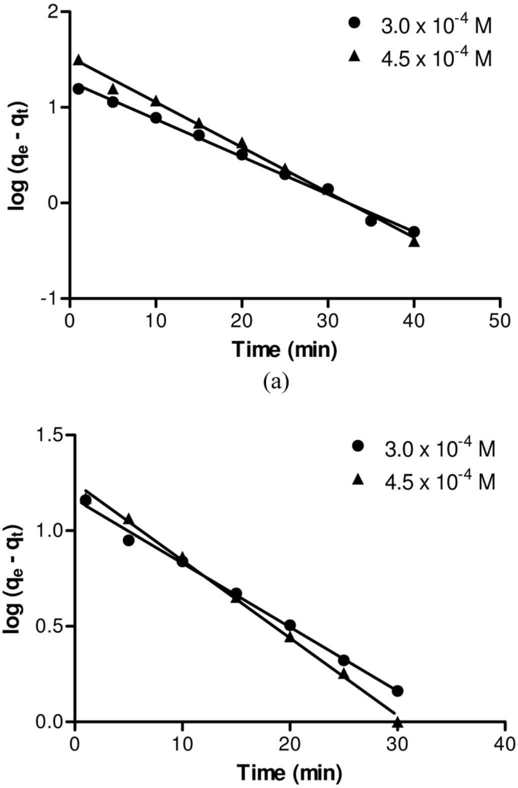
Figure 1. Effect of contact time and concentration on adsorption of dyes on lemon peel adsorbent (a) Methyl orange (b) Congo red [temperature = 25°C, adsorbent dosage = 0.1 g/10 mL, pH = 5.5–6.5].

Pseudo-First-Order Model

Various reports (26,27) exist where adsorption has been considered as pseudo-first-order. The Lagergren's rate equation (28) is the most widely used (29–31) for the sorption of a solute from a liquid solution. Thus this first order equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303}t \qquad (2)$$

where 'q_e' and 'q_t' are the amount of dye adsorbed (mg/g) at equilibrium and at time t, respectively, and k_f is the pseudo-first-order rate constant, was applied to the present study of dyes adsorption. Figure 2 (a and b) shows a plot of linearized form of the pseudo-first-order model at two concentrations studied. The slopes and intercept of plot of log $(q_e - q_t)$ versus t were used to determine the rate constants (k_f) and $q_{e(cal)}$ and are compiled in Table 1 alongwith the correlation coefficient (R^2) values. The plots were found linear with good correlation coefficients (R^2) for the pseudo-first-order kinetic model varying from 0.9943 to 0.9965 for both the dyes at two concentrations studied. Further, the theoretical $q_{e(cal)}$ values were also found in accordance with the experimental



(a)

(b)

Figure 2. Pseudo-first-order kinetic model plots of dyes adsorption on lemon peel adsorbent (a) Methyl orange (b) Congo red.

Table 1. Comparison of pseudo-first-order and pseudo-second-order model parameters, and calculated amount adsorbed, $q_{e(cal)}$ and experimental amount adsorbed, $q_{e(exp)}$ values for different initial dyes concentrations

			Pseudo-first-order			Pseudo-second-order		
Dye	C_o (M)	$q_{e(exp)}$ (mg/g)	k_f (1/min)	$q_{e(cal)}$ (mg/g)	R^2	k_s (g/ mg · min)	$q_{e(cal)}$ (mg/g)	R^2
Methyl orange	3.0×10^{-4}	20.3	0.90×10^{-1}	18.6	0.9943	6.36×10^{-3}	23.1	0.9894
	4.5×10^{-4}	33.2	1.09×10^{-1}	33.6	0.9950	5.37×10^{-3}	36.8	0.9876
Congo red	3.0×10^{-4}	10.7	0.77×10^{-1}	12.3	0.9955	5.73×10^{-3}	15.1	0.9600
	4.5×10^{-4}	18.7	0.93×10^{-1}	17.8	0.9965	3.42×10^{-3}	22.0	0.9710

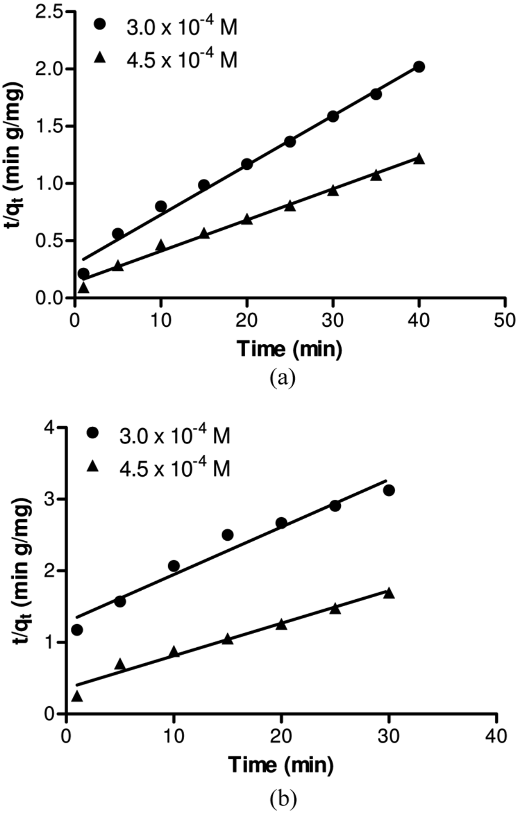
uptake values $q_{e(exp)}$. This suggests that the present adsorption system follows pseudo-first-order kinetics. It was also observed that rate constants (k_f) is a linear function of initial concentration of solute and a plot (not shown here) of k_f vs C_o gives a straight line, suggesting that sorption kinetics obeys the pseudo-first-order model (32).

Pseudo-Second-Order Model

The adsorption kinetics was also described as pseudo-second-order process (33–35)

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \tag{3}$$

where k_s is pseudo-second-order rate constant. The present data was also tested in the light of the pseudo-second-order kinetic model. The plots between t/q_t versus t were drawn and are shown in Fig. 3 (a and b). The slopes and intercept of plot of t/q_t versus t were used to determine the pseudo-second-order rate constants (k_s) and $q_{e(cal)}$ and are compiled in Table 1 along with the correlation coefficient (R^2) values. As can be seen from Table 1, the theoretical data $q_{e(cal)}$ slightly deviated from the experimental data $q_{e(exp)}$ in case of the pseudo-second-order kinetic model. Further correlation coefficient (R^2) values were lower than 0.99 (Table 1) suggesting that the present adsorption system is not a pseudo-second-order kinetics.



(a)

(b)

Figure 3. Pseudo-second-order kinetic model plots of dyes adsorption on lemon peel adsorbent (a) Methyl orange (b) Congo red.

It is well known that the adsorption kinetics is generally controlled by three consecutive mass transport steps associated with the adsorption of solute from the solution by an adsorbent. These are

1. film diffusion,
2. intraparticle or pore diffusion, and
3. sorption into interior sites.

The third step is very rapid and hence film and pore transports are the major steps controlling the rate of adsorption. In order to understand the diffusion mechanism, the intraparticle diffusion model was tested for the present dyes adsorption study.

Intraparticle Diffusion Model

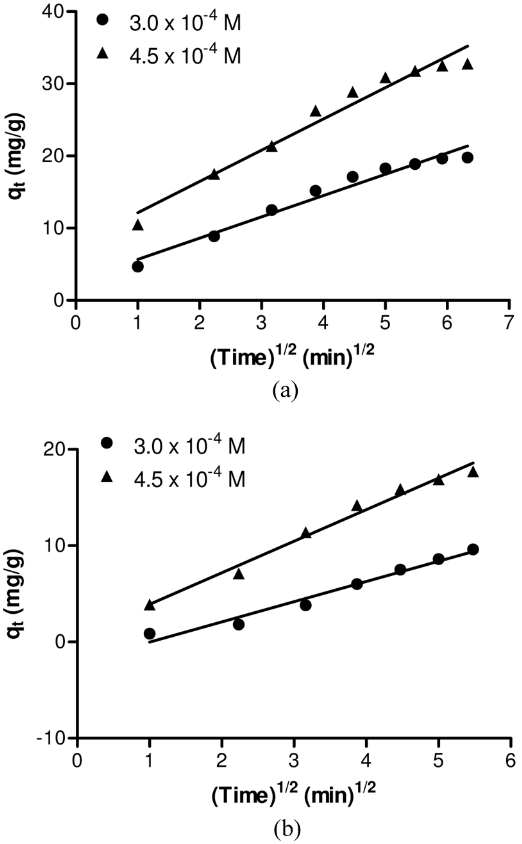
Kinetic data was analyzed in the light of the intraparticle diffusion model proposed by Weber and Morris (36):

$$q_t = k_{ip}t^{1/2} + C \tag{4}$$

where, C is the intercept and k_{ip} is the intraparticle diffusion rate constant. According to the above equation, a plot of uptake (q_t) versus the square root of t, ($t^{1/2}$) should be linear when adsorption mechanism follows the intraparticle diffusion process. Figure 4 (a and b) shows a plot of the linearized form of the intraparticle diffusion model. It is seen that the initial curves of the plot show the diffusion of dyes through the solution to the external surface of adsorbent. Further, a second linear portion of curves describe the gradual adsorption stage, where intraparticle diffusion of dyes on the adsorbent surface takes place. However, the intercept of the line fails to pass through the origin at each concentration which may be due to the difference in the rate of mass transfer in the initial and final stages of adsorption (37). Further, such deviation of the straight lines from the origin reveals that the pore diffusion is not the sole rate-controlling step (38). The results indicate that the mechanism of dyes adsorption onto the adsorbent is complex and both the surface adsorption as well as intraparticle diffusion contribute to the actual adsorption process.

Adsorption Isotherms

In order to determine the efficacy of the prepared adsorbent, the equilibrium adsorption studies were carried out with varying concentrations of the dyes and adsorption isotherms are shown in Fig. 5 (a and b). It is clear from the figures that initially isotherms rise sharply indicating that plenty of readily accessible sites are available in the beginning for the adsorption. However, after achieving equilibration, when the adsorbent becomes saturated, a plateau is reached indicating that no more sites are available for further adsorption. The adsorption capacities of lemon peel adsorbent for dyes were found 50 and 34.5 mg/g for MO and CR, respectively at 25°C. The adsorption potential of lemon peel adsorbent from the present study was compared with other adsorbents reported in previous studies for anionic dyes removal and are compiled in Table 2. It is evident that the prepared adsorbent, in the present study, shows efficient adsorption capacity for both the dyes removal from water.



(a)

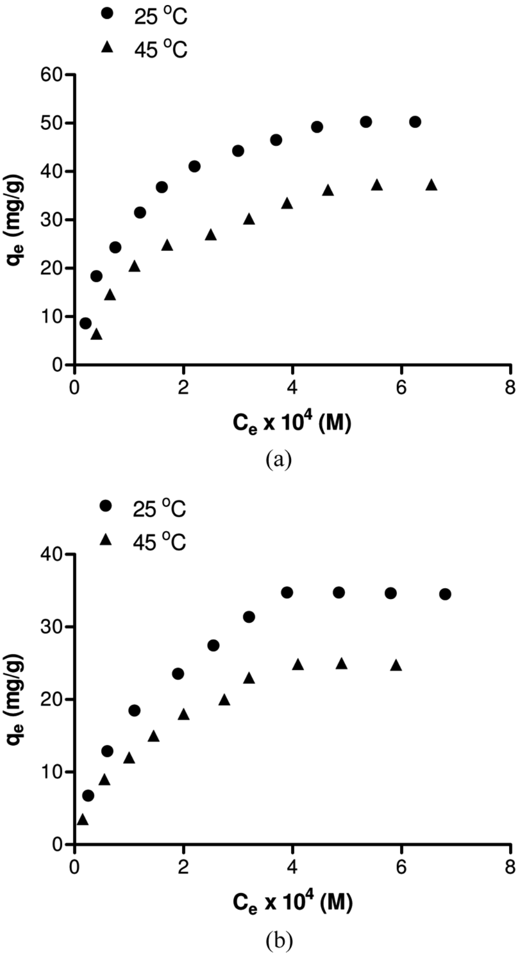
(b)

Figure 4. Weber & Morris intraparticle diffusion model plots of dyes adsorption on lemon peel adsorbent (a) Methyl orange (b) Congo red.

In order to understand the effect of temperature on the adsorption of anionic dyes, experiments were also conducted at 45°C and the results are shown in Fig. 5 (a and b). A comparison of adsorption isotherms at 25°C and 45°C shows that adsorption decreases with increase in temperature indicating that the process is exothermic in nature.

The most widely used isotherm equation, the Langmuir model, was used to describe the experimental data of adsorption isotherms and for the equilibrium modeling. The linearized Langmuir equation has the following form (39)

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \tag{5}$$



(a)

(b)

Figure 5. Adsorption isotherms of dyes on lemon peel adsorbent at different temperatures (a) Methyl orange (b) Congo red [adsorbent dosage = 0.1 g/10 mL, pH = 5.5–6.5].

where 'q_e' is the amount adsorbed at equilibrium concentration 'C_e', 'q_m' is the Langmuir constant representing maximum monolayer capacity, and 'b ' is the Langmuir constant related to the energy of adsorption. The plots between $1/q_e$ and $1/C_e$ for the adsorption of dyes are drawn in Fig. 6 (a and b). The values of the monolayer capacity (q_m) and Langmuir constant (b) have been evaluated from the intercept and slope of these plots and given in Table 3. A perusal of Table 3 shows that the

Table 2. Reported adsorption capacities of some anionic dyes on various adsorbents prepared from agricultural and industrial waste materials

Adsorbents	Anionic dyes	Adsorption capacity (mg/g)	Reference
Banana peel and orange peels	Methyl orange	20.5–21.0	Annadurai et al., 2002 (43)
Banana peel and orange peels	Congo red	14.0–18.2	Annadurai et al., 2002 (43)
Orange peel	Acid violet	19.88	Rajeshwarisivaraj et al., 2001 (44)
Sugarcane bagasse	Acid orange 10	5.78	Tsai et al., 2001 (45)
Wood sawdust	Acid blue 25	5.99	Ho and McKay, 1998 (46)
Egyptian bagasse pith	Acid blue 25	14.4	Ho and McKay, 2003 (47)
Red mud	Congo red	4.05	Namasivayam and Arasi, 1997 (48)
Coir pith	Congo red	6.72	Namasivayam and Kavitha, 2002 (49)
Coir pith	Acid violet	7.34	Namasivayam et al., 2001 (50)
Lemon peel adsorbent	Congo red	34.5	Present study
Lemon peel adsorbent	Methyl orange	50.0	Present study

monolayer capacity (q_m) of the adsorbent for the dyes is comparable to the maximum adsorption obtained from the adsorption isotherms.

The effect of the isotherm shape has been discussed (40) with a view to predict whether an adsorption system is “favorable” or “unfavorable”. The essential feature of the Langmuir isotherm can be expressed in terms of ‘R_L’, a dimensionless constant referred to as the separation factor or the equilibrium parameter. ‘R_L’ is calculated using the following equation

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

The values of ‘R_L’ calculated as per the above equation are incorporated in Table 3. As the ‘R_{L}’ values lie between 0 and 1, the adsorption isotherm is favorable (40).

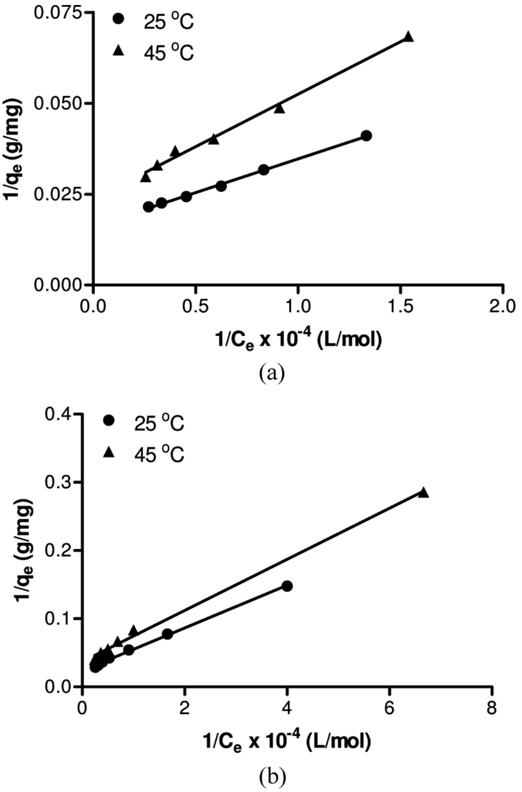


Figure 6. Langmuir plots of dyes adsorption on lemon peel adsorbent (a) Methyl orange (b) Congo red.

The values of free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) for the adsorption process were calculated using following equations (41)

$$\Delta G^\circ = -RTln(K) \tag{7}$$

Table 3. Langmuir constants and separation factor for the adsorption of dyes on lemon peel adsorbent at different temperatures

Dye	Temperature (°C)	q_m (mg/g)	b (L/mol)	R^2	R_L
Methyl orange	25	61.7	8.1×10^3	0.9978	2.3×10^{-1}
	45	42.0	7.8×10^3	0.9936	2.2×10^{-1}
Congo red	25	42.3	9.2×10^3	0.9977	2.1×10^{-1}
	45	27.1	7.9×10^3	0.9966	2.4×10^{-1}

Table 4. Thermodynamic parameters for adsorption of dyes on lemon peel adsorbent at different temperatures

Dye	Temperature (°C)	ΔG° (kJ/mol)	ΔS° (J/mol · K)	ΔH° (kJ/mol)
Methyl orange	25	−32.2	103.2	−1.4
	45	−34.3	103.2	
Congo red	25	−32.5	89.1	−6.0
	45	−34.3	89.1	

$$\ln\frac{K_2}{K_1} = \frac{\Delta \mathrm{H}^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{8}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{9}$$

where, '*b*' is a Langmuir constant (L/mol), temperature '*T*' in (K); R is an ideal gas constant (8.314 J/mol · K); ΔG° and ΔH° are in J/mol; ΔS° in J/mol · K and are summarized in Table 4. The negative ΔG° values indicate the spontaneous nature of the adsorption process. The values of the standard enthalpy change (ΔH°) for dyes adsorption are −1.4 kJ/mol (for Methyl orange) and –6.0 kJ/mol (for Congo red). It suggests that the interaction between the dyes and the adsorbent is exothermic in nature. In literature (42), when the value of ΔH° is lower than 40 kJ/mol, the type of adsorption can be accepted as the physical process. Since ΔH° values obtained in this study are lower than 40 kJ/mol, it would be claimed that physical adsorption occurs during the adsorption process. Further positive ΔS° values indicate the affinity of the adsorbent for dyes.

Treatment of Effluent of a Local Dyeing Unit

The adsorption studies of dyes on lemon peel adsorbent revealed that the prepared adsorbent adsorbs both dyes to an appreciable extent, and therefore, can be fruitfully used for their removal from wastewaters. The applicability of this adsorbent in the removal of dyes was further assessed by column operations on aqueous solutions of different dyes (including Methyl orange and Congo red dyes). It was thought desirable to treat the dye wastewater obtained from a local dyeing unit containing diverse types of dyes.

The effluent was obtained from a local dyeing factory using various commercial dyes for dyeing purposes of various textiles. This dye wastewater is characterized by a dark brown color, pH = 10.5 and

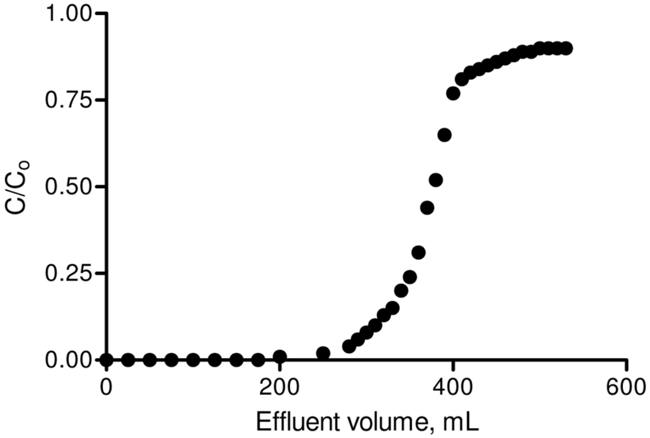


Figure 7. Breakthrough curve of dyeing wastewater on lemon peel adsorbent.

COD value (880 mg/L). The absorption spectra shows that the dye wastewater has four λ_{max} values at 267.0, 475.0, 560.0, and 835.0 nm with absorbance of 11.1, 25.7, 12.3, and 0.18, respectively. The treatment of this dye wastewater for dyes removal was carried out by passing it through a column (cross sectional area: 0.9 cm^2; height: 3.1 cm; mass: 1.0 g) of lemon peel adsorbent, of particles of size 50–200 mesh, at a flow rate of 2.5 mL/min. The monitoring of the column was done spectrophotometrically at λ_{max} values of the solution. For this purpose, 10 mL aliquot was collected and the absorbance was determined. It was observed that the effluent coming out of the column had almost nil absorbance at all the λ_{max} values upto a total volume of 240 mL. After that, the color started appearing and absorbance increased. The breakthrough curve obtained after passing this dye wastewater through the lemon peel adsorbent column is shown in Fig. 7. From the breakpoint of this curve, it can be seen that a column of 1 g of lemon peel adsorbent, as used by us can treat 240 mL of dye wastewater. The COD of the treated dye wastewater was within acceptable limits. Thus, the results show that 1 kg of the prepared adsorbent can treat 240 liters of the dye wastewater obtained from local dyeing factory. It is therefore reasonable to conclude that the prepared adsorbent can be fruitfully used as an alternative adsorbent for treating dye wastewater.

CONCLUSIONS

The results of the present study reveal that the lemon peel waste can be utilized as an effective adsorbent for the removal of Methyl orange and

Congo red dyes from aqueous solutions. The adsorption potential of lemon peel adsorbent was found to be 50.3 mg/g for Methyl orange and 34.5 mg/g for Congo red at 25°C. The adsorption data conformed best to the Langmuir model. The kinetic data were analyzed in the light of three simplified kinetic models viz. pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. It was found that theoretical $q_{e(cal)}$ values agreed well with the $q_{e(exp)}$ ones in case of pseudo-first-order kinetics suggesting that the present study of dyes adsorption on lemon peel adsorbent can be defined more favorably by the pseudo-first-order kinetic model. The intraparticle diffusion model suggests that the mechanism of dyes adsorption onto the adsorbent is complex and the surface adsorption as well as intra-particle diffusion contribute to the actual adsorption process. The results of the present study suggest that the adsorbent prepared from lemon peel can be fruitfully used as low-cost adsorbent for the removal of dyes from industrial effluents.

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