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Surfactant modified tea waste as a novel adsorbent for the removal of Basic dye

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ABSTRACT

Textile industries consume large amount of water and generate highly dye contaminated effluent. The objective of present study was to examine the potential use of Tea waste and anionic surfactant modified house hold tea waste as a low cost sorbent for a basic dye removal from simulated textile effluent. The adsorbents were characterized by XRD, SEM and FTIR techniques. Batch adsorption experiments were carried out for the removal of Basic Red 12 from aqueous solution using tea waste and surfactant modified tea waste. This study examined the effects of parameters like contact time, pH, temperature, adsorbent dose, dye concentration etc. A fixed bed column was designed for the bulk removal of dye from simulated waste water. The effect of inlet flow rate, sorbent bed height and initial dye concentration was studied. The kinetic measurements helped in determining the specific rate constant for the process. Freundlich, Langmuir and Harkins Jura isotherm models were investigated. The values of thermodynamic parameters like ΔH^0 , ΔS^0 , ΔG^0 were calculated from the isotherm data. Our results reinforce the fact that structure and quantity of natural organic materials can control the sorption of organic pollutants from the water.

Key words: Surfactant modification, tea waste, adsorption, kinetics and thermodynamics.

INTRODUCTION

Dyes are discharged by many industries like textile, paper, cosmetics, leather, paints, pharmaceuticals etc. Release of many synthetic dyes in to waste water has many serious environmental effects. Many dyes cause health problems like allergic dermatitis, skin irritation, and mutations in human. Dyes affect aquatic flora by hindering their photosynthesis [1, 2] due to

reflection of sun light. Dye containing waste water offers considerable resistance to biodegradation due to their heat and light stability [3]. Hence conventional treatment methods like USAB are unsuitable. Activated carbon is the most successful adsorbent [4]. Due to its high cost attention is being paid to low cost adsorbents. Many Investigators have studied the feasibility of using low cost adsorbents such as bagasse fly ash{5, 6}, coir pith[7] , peat [8], orange and banana peel [9], saw dust , rice husk[10] , bark [11, 12], Deoiled soya and bottom ash[13], cotton waste[14] , slag [15] , sugar can stalk[16], dried mango seeds[17], ashoka leaf powder[18], activated carbon from low cost wood [19] and sewage sludge[20] etc. Consequently the interest in search for more economical and effective adsorbents has continued to grow.

Tea waste is a common house hold waste. Tea waste is rich in tannin and polyphenolic compounds thus biodegraded with difficulty and is an oxygen demanding pollutant [21] The objective of this study was to investigate the ability of Tea waste (TW) and Sodium dodecyl sulphate modified tea waste (SDS-TW) for the removal of basic dye, Basic Red-12 from an aqueous solution. In order to achieve this batch and column experiments were conducted. The effect of solution pH on Basic red 12 dye uptake was studied via isotherm experiment, and the effect of initial dye concentration on rate of sorption was investigated using different kinetic and isotherm models.

MATERIALS AND METHODS

Materials

Basic Red 12 (molecular weight 357.51), molecular formula $C_{25}H_{29}N_2Cl$ (1, 3, 3-Trimethyl-2-[3-(1, 3, 3-trimethyl-2-indolinyldene) propenyl]-3-indoliumchloride (Figure1) was procured from Thomas Baker chemicals. A stock solution of 1000 ppm was prepared in double distilled water and diluted as per requirement. Low cost adsorbent tea waste was collected from household. It was boiled with Tap water for 10 minutes. This was sieved and washed with deionized water till the filtrate was colorless. The material was then dried in hot air over at 80°C for 24 hours. The dried TW was crushed and passed through 100-170 BSS mesh screen i.e. particle size between 0.15-0.088mm. This was stored in air tight container for further use.

SDS was of analytical grade (Figure 2); the solution of SDS was prepared below its critical micellar concentration (CMC) as beyond CMC the surface modification was not effective. 100 ml of $10^{-3}M$ SDS solution was treated with 10.0 g. of Tea waste and shaken in a temperature controlled shaker at 180 rpm for 3 hours at 303 K. The modified TW was then filtered and washed with deionized water till conductance of filtrate was less than $0.05\mu S$. The surface modified TW was then dried in hot air oven at 80°C for 6 hours. This was then stored in air tight containers, for further use.

Equipments

The dye concentration was determined by finding out the absorbance $\lambda_{max} = 469 \text{ nm}$ by using & UV-Vis spectrophotometer (shimadzu, Japan). The pH measurements were made using microprocessor based pH meter by Toshnival India Ltd. Batch experiments were conducted by shaking solution in a temperature controlled (Labotec) shaker. Fourier Transform infrared spectroscopy carried out by using Perkin Elmer FTIR spectrophotometer in the range 400 – 4000

cm⁻¹. Scanning electron micrographs was carried out by using Zeol electron microscope. X-ray diffraction study was carried out by PANalytical X- ray diffractometer.

Methods

Batch experiments

The series of experiments were conducted by taking 50 ml of dye solution in Erlenmeyer flask and adding required amount of adsorbent in that. The pH of different solutions was adjusted with 0.1 N HCl and 0.1 N NaOH. The adsorbent dose was varied from 2.5 g L⁻¹ to 20.0 g L⁻¹. After attainment of equilibrium the aqueous phase was analyzed for residual dye concentration. From the absorbance data q_e (mg g⁻¹) was determined using Eq. (1)

$$q_e = \frac{(C_0 - C_e)V}{W} \text{----- (1)}$$

Where C_0 is initial dye concentration, C_e is final dye concentration and V is volume of dye in liters and W is mass of adsorbent in g. Duplicate experiments were performed to get concordant results. The results showed variation in the range $\pm 5\%$. The Kinetics of dye removal was studied by using 250 ppm dye concentration. The samples were withdrawn at regular intervals and residual concentration was analyzed after centrifugation. The isotherms were studied by using 50 ml of dye solution with in concentration range 100 ppm to 250 ppm for TW and 200-500 ppm for SDS-TW adsorbent at 303 K, 313 K and 323 K. After the attainment of equilibrium the residual dye concentration was analyzed spectrophotometrically.

Column experiments

Up flow columns; 50 cm long and 5 cm wide were used. 25 g of inert sand was mixed with 5.0 g of TW and SDS-TW respectively. The columns were packed with uniform slurry of sand and adsorbent. The particle size was < 500 μm with a bed depth of 20 cm and filling weight of 26.4 g in each column. The column had three 0.5 cm (internal diameter) septa ports through which the samples were collected at time intervals using a syringe with a needle. Before operation, the bed was rinsed with distilled water and left overnight to ensure a closely packed arrangement of particles with no void, channels, or cracks. The rate of flow was adjusted to 2 mL per minute and outflow was analyzed for residual dye.

RESULTS AND DISCUSSION

Adsorbent analysis

FTIR spectra (Figure not shown here) were carried out by encapsulating 0.5 mg of finely ground adsorbent with 400 mg of KBr to get a translucent disk. A broad absorption peak at 3448 cm⁻¹ is indicative of bonded hydroxyl group [22]. A peak observed at 1654.6cm⁻¹ can be assigned to >C=O group. A peak at 1560.1cm⁻¹ indicates secondary amino group. The peak at 1458.4 cm⁻¹ may be due to symmetric C-H stretching and C-O stretching of ether group is observed due to peak at 1093.3 cm⁻¹. After surfactant modification new peaks are observed at 1282.7 cm⁻¹and 1197.8 cm⁻¹ corresponding to C-C stretching in alkanes and at 1384.9 cm⁻¹ due to C-H deformations indicating surfactant modification of the TW [23]. The XRD spectra of TW revealed two main peaks at $2\theta = 21.50$ and 32.2 with d spacing 4.13\AA , 2.77\AA respectively (Figure3) The spectra revealed crystalline nature of TW, SEM (Figure 4a and 4b) revealed that

the surface of adsorbent is rough and almost non compact in nature. TW has considerable number of pores suitable for physisorption while after surfactant modification the pore gaps were almost filled with SDS and the surface becomes suitable for chemisorption of charged dye molecules.

Effect of pH

pHzpc for TW and SDS-TW was determined to investigate the surface charges by the method mentioned earlier [24]. At 298K the pH_{zpc} for TW was found to be 4.0 while for SDS-TW it was 4.5 indicating that after surfactant modification the potential developed on the surface increases due to electric double layer formation. At pH less than pH_{zpc} the adsorbent surface is positively charged while above its pH_{zpc} the surface acquires negative charge. The maximum adsorption of cationic dye BR-12 on TW and SDS-TW was observed at 3.0 and 4.0 respectively (fig 5). The percentage dye removal for the later is higher than the former though at pH greater than 7.0 cause's hydroxide ion binding with the cationic dye. There arises a competition between negatively charged adsorbent surface and OH⁻ ions for binding with dye but the net entropy increase decides the preferable dye binding with the adsorbent surface. At pH higher than 8.0 the adsorption decreases due to increase in concentration of OH⁻ ions which bind with the dye preferably in bulk solution.

Effect of adsorbent dose

The effect of adsorbent dose was studied at initial dye concentration of 250 ppm. This was observed that 94.48% dye was removed with 5.0 gL⁻¹ TW while 100% dye removal took place with same amount of SDS -TW under similar experimental conditions. The effect of adsorbent dose has been shown in Figure 6. The percentage removal of dye increased with the increase of adsorbent dose due to increase in availability of adsorption sites but the efficiency of chemisorptions is greater than physical binding of dye with adsorbent so higher adsorption capacity was observed for SDS-TW i.e. 97.28 mg g⁻¹ instead of 96.77 mg g⁻¹ for TW.

Effect of initial dye concentration

The effect of initial dye concentration was investigated on constant adsorbent dose of TW and SDS-TW at 303 K, 313K and 323K. The initial concentration of BR-12 was varied from 100 - 250 ppm with TW and 200-500 ppm with SDS-TW. It was observed that dye uptake increases with increase in concentration of dye as well as with the increase in temperature suggesting efficacy of the adsorbent and endothermic nature of the processes.

Adsorption isotherm study

The Freundlich, Langmuir and Harkins Jura isotherm models have been successfully applied to the above systems at various temperatures 303 K, 313 K and 323 K and the thermodynamic parameters were calculated accordingly. For the equilibrium concentration of adsorbate (C_e) and amount of dye adsorbed at equilibrium (q_e), the following linear forms of isotherms were studied.

Freundlich isotherm

The Freundlich isotherm [25], is the earliest known relationship describing the sorption isotherm, may be used in sorption from dilute solutions. Its sorption isotherm is expressed by the following equation.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{-----}(2)$$

Where q_e is amount of dye adsorbed at equilibrium in mg/g. C_e is concentration of dye at equilibrium and K_F is Freundlich constant and $1/n$ is a parameter related to sorption intensity. These parameters are calculated by plotting $\log q_e$ vs. $\log C_e$ (Figure 7a and 7b) for dye removal on TW and SDS TW respectively. The value of K_F and n are given in table 1 at 303 K, 313 K and 323 K. The value of $K_F > 1$ suggesting the favorable adsorption on both the adsorbents. The value of n goes on decreasing for SDS TW- BR 12 adsorption with the increase of temperature suggesting that with the increase of temperature the adsorption is becoming independent of concentration. The same is not true for TW- Basic Red 12 system where the value of n shows an increase due to heterogeneous surface which shows pore expansion with the increase of temperature. The Freundlich isotherm is more applicable on adsorption of Basic Red 12 TW than on SDS TW.

Langmuir adsorption isotherm

The linear form of Langmuir isotherm [26] is given in Eq. 3

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0 C_e} \quad \text{-----} (3)$$

Where q_e and C_e have their usual meanings and Q_0 and b are Langmuir constants determined from the plot of $1/q_e$ and $1/C_e$ from the intercept and slope respectively (Figure 8a and 8b) for dye removal on TW and SDS TW respectively. Straight lines are obtained for both adsorbents with basic dye. The values of Langmuir parameters are given in table 2. The values of Q_0 are found to increase with the increase of temperature suggesting endothermic nature of the ongoing processes. The increase in the value of Q_0 is more pronounced in adsorption of dye on TW than on SDS TW. This is probably due to the reason that interaction of charged dye and charged surfactant takes place on the surface and some amount of energy liberated during chemisorptions is used for counteracting disorder of dye molecules on the surface with ordered arrangement of surfactant molecules.

The essential characteristics of Langmuir isotherm are determined from a dimensionless separation factor R_L , a dimensionless factor [27] by using Eq. 4. The value of b was obtained from Langmuir isotherm.

$$R_L = \frac{1}{(1 + bC_0)} \quad \text{-----} (4)$$

The value of R_L for both adsorbents was less than unity suggesting favorable process at all temperatures (table 2)

Harkins Jura isotherm

Harkins Jura [28] accounts for multilayer adsorption and supports heterogeneous pore distribution.

$$\frac{1}{q_e^2} = \left[\frac{B}{A} \right] - \left[\frac{1}{A} \right] \log C_e \quad \text{----- (5)}$$

The values of constants B and A were obtained from linear plot of $1/q_e^2$ and $\log C_e$ at 303 K, 313 K and 323 K. The values of constants A and B along with regression coefficient are listed in table 3, suggesting preferable multilayer dye adsorption on TW than on SDS TW supporting our finding that TW adsorbs dye by physisorption while SDS TW adsorbs the same by chemisorption.

Thermodynamic studies

The changes in the reaction that can be expected during the process require the brief idea of the thermodynamic parameters which were also calculated from the above data. The Gibbs free energy, ΔG° was found to be negative at all temperatures, indicating spontaneous process at all the temperatures while enthalpy ΔH° , was positive suggesting endothermic nature of the process. The positive value of entropy, ΔS° suggests favorable randomness factor though its value is small. The thermodynamic parameters were calculated using following equations and the values of parameters are listed in Table 4.

$$\Delta G^\circ = -RT \ln b \quad \text{----- (6)}$$

$$\Delta H^\circ = -R \left(\frac{T_2 T_1}{T_2 - T_1} \right) \ln \left(\frac{b_2}{b_1} \right) \quad \text{----- (7)}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad \text{----- (8)}$$

Where b, b₁, b₂ are Langmuir constants at 303 K, 313 K and 323 K respectively.

Kinetic studies

First order kinetics

The rate of removal of basic Red 12 by TW and SDS TW has been studied as a function of time Adsorption rate constant study was carried out with the famous Lagergran rate equation. [29] as follows where q_e and q_t have their usual meanings and k_1 is pseudo first order rate constant and is determined from the slope of plot of $\log (q_e - q_t)$ vs. time (Figure9)

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303} \right) t \quad \text{----- (9)}$$

At equilibrium $q_e = q_t$ and q_e is determined from the intercept. The values of q_e and k_1 have been reported in the table 5. This is clear from the table that the adsorption of basic dye on both TW and SDS TW seems to follows pseudo first order kinetics.

Second order kinetics

The linear form [30,31] of second order rate equation (Eq. 10) is applied on the system and linear plot is drawn between $1/C_t$ and time, the slope gave the value of rate constant, the values are given in table 5.

$$\frac{1}{C_e} = k_{2s}t + \frac{1}{C_i} \text{----- (10)}$$

A linear plot is obtained for both the adsorbents suggesting the applicability of second order model on the data well (Figure10).

Pseudo second order kinetic model [32] was also applied on the data; Eq. 11

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \text{----- (11)}$$

A linear plot (Figure 11) is obtained and the values of Rate constant and q_e was calculated and has been given in table 5.

Column studies

The results show that the breakpoint is obtained earlier (Figure 12) after surfactant modification of TW. The steep breakthrough curve is seen followed with a broad tail after surfactant modification. The fluid velocity decreases with the increase of bed length. Similar results have been reported elsewhere (Ruthven, 1984). For higher dye concentration, steeper breakthrough curves are formed; due to lower mass-transfer flux from the dye solution to the particle surface due to the weaker driving force, thus the equilibrium is attained earlier for higher dye concentration on both adsorbents. The overall kinetics of the process is slow, because the time for molecules of dye to reach the adsorption site is more without surfactant modification.

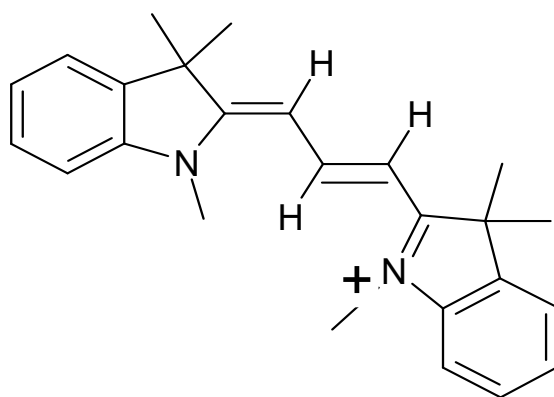


Figure 1 Structure of C.I. Basic Red 12 dye.

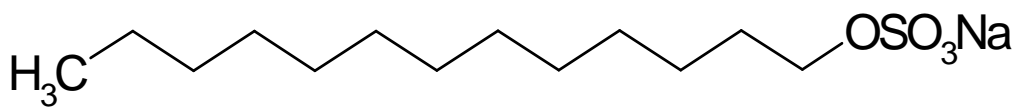


Figure 2 Structure of SDS (sodium dodecyl sulphate)

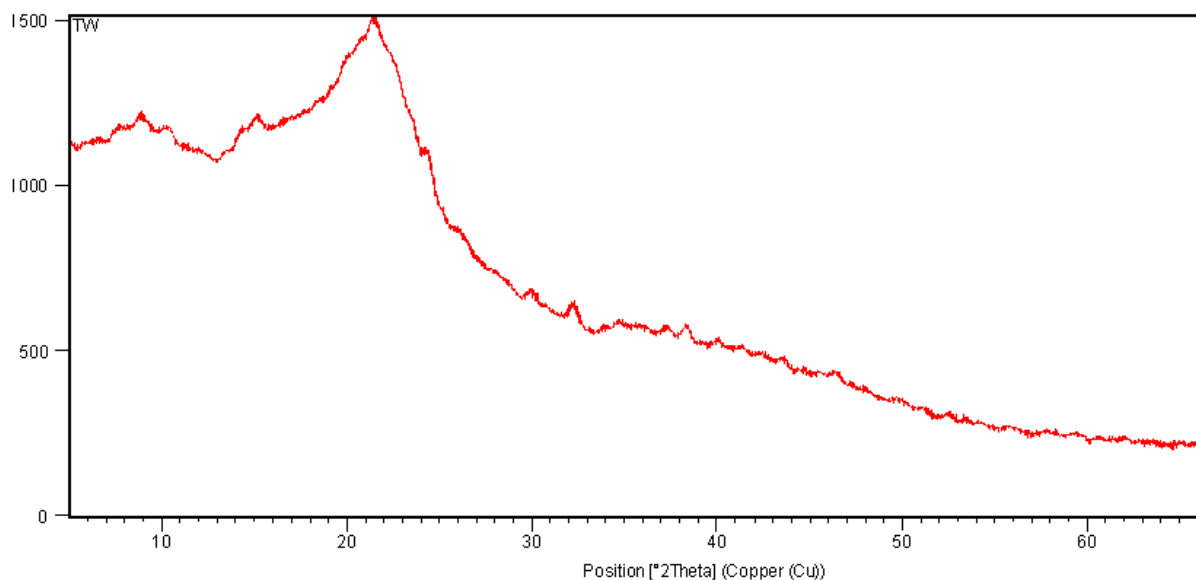


Figure 3 XRD of Tea waste.

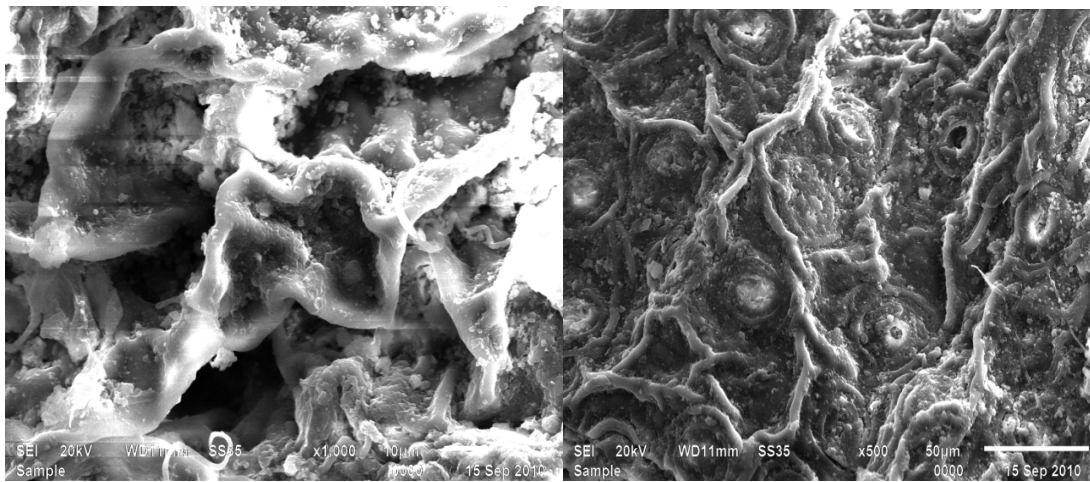


Figure4a

Figure 4b

4. a. Scanning electron micrograph of tea waste.
4. b. Scanning electron micrograph of tea waste after surfactant modification.

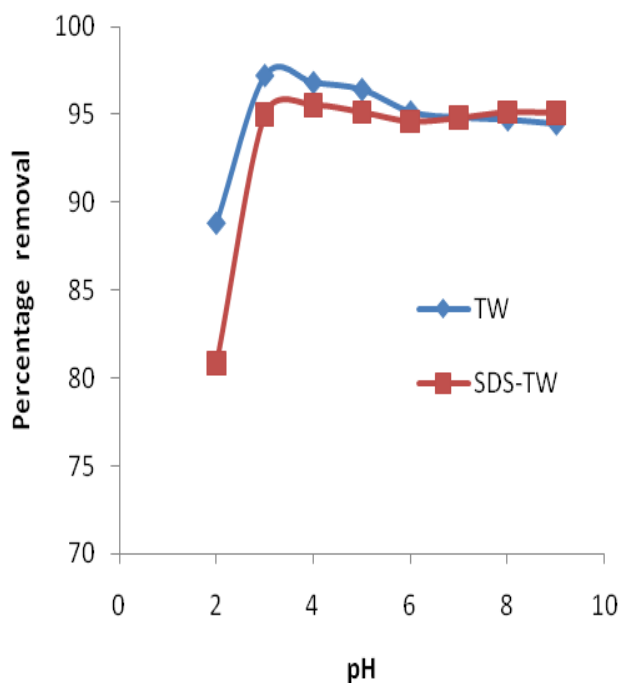


Figure 5. Percentage removal of Basic Red 12 by adsorption on TW and SDS TW upon change of pH at 303 K; Initial dye concentration 250 ppm.

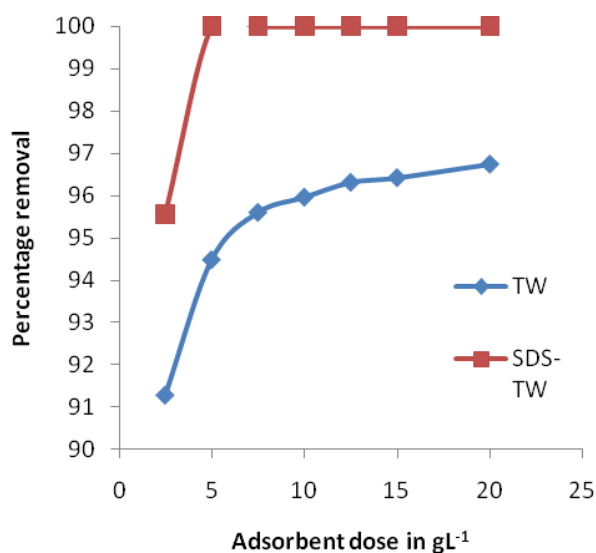


Figure 6. Effect of adsorbent dose on percentage removal of dye at 303 K; Initial dye concentration 250 ppm.

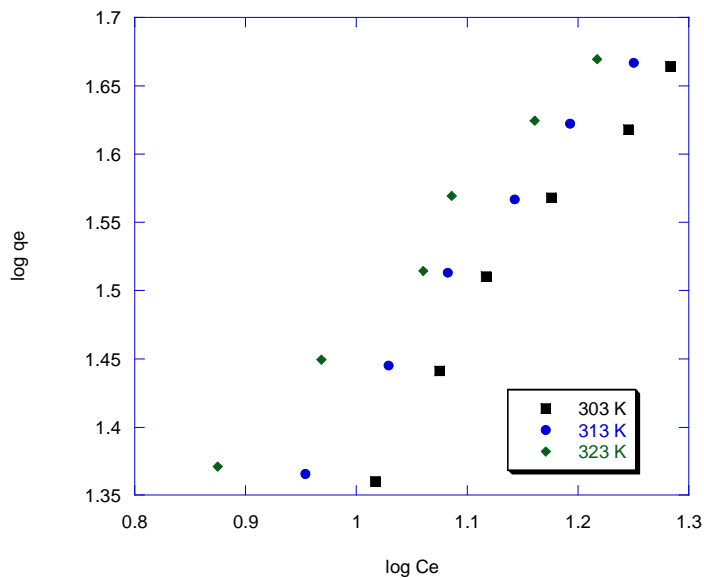


Figure 7a

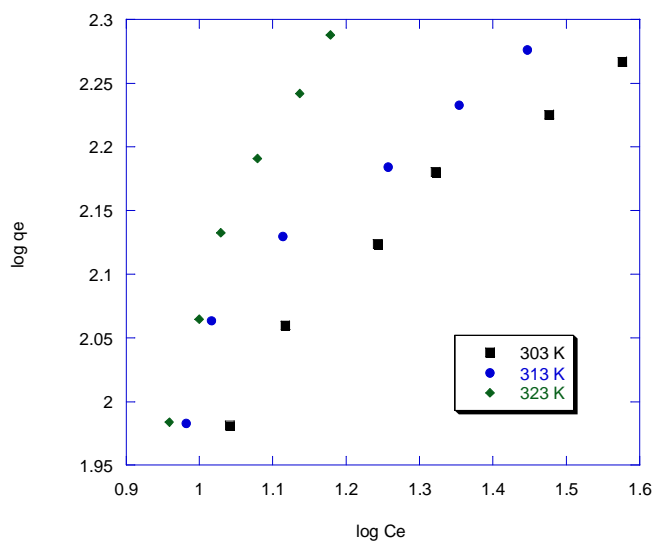


Figure 7b

7. a. Freundlich adsorption isotherm for the adsorption of Basic Red 12 over TW at different temperatures.

7. b. Freundlich adsorption isotherm for the adsorption of Basic Red 12 over SDS TW at different temperatures.

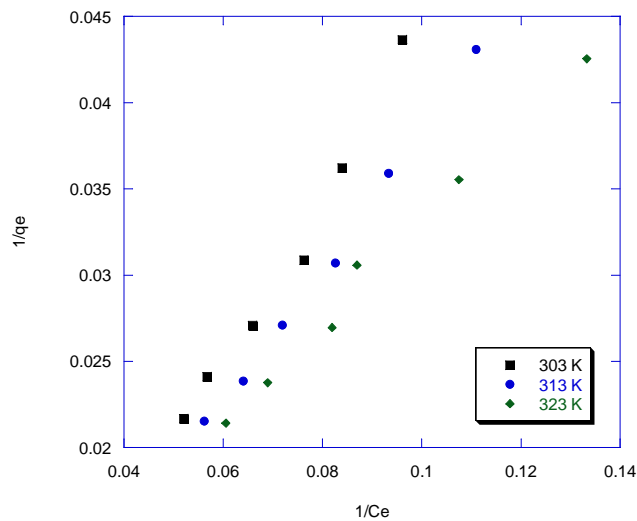


Figure 8a

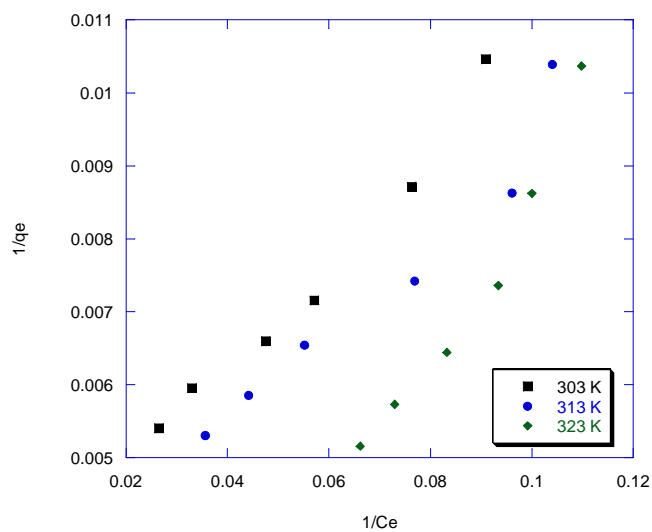


Figure 8b

8. a. Langmuir adsorption isotherm for the adsorption of Basic Red 12 over TW at different temperatures.

8. b. Langmuir adsorption isotherm for the adsorption of Basic Red 12 over SDS TW at different temperatures.

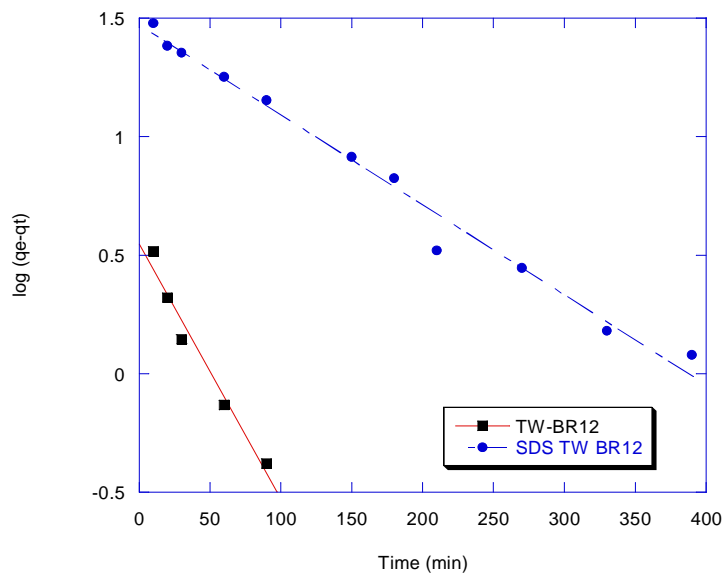


Figure 9. The fitting of Lagergren's Pseudo first order Eq. for adsorption of Basic Red 12 over TW and SDS TW at 303 K; Initial dye concentration 250 ppm

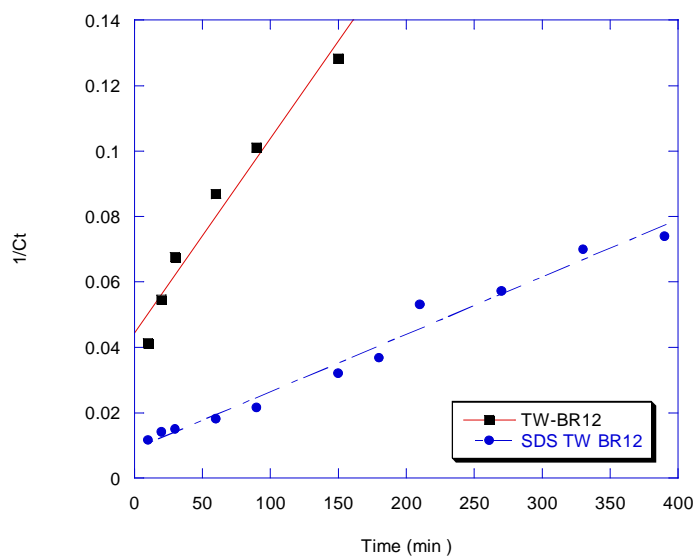


Figure10. The fitting of Pseudo second order Eq. for adsorption of Basic Red 12 on TW and SDS TW over 303 K; Initial dye concentration 250 ppm.

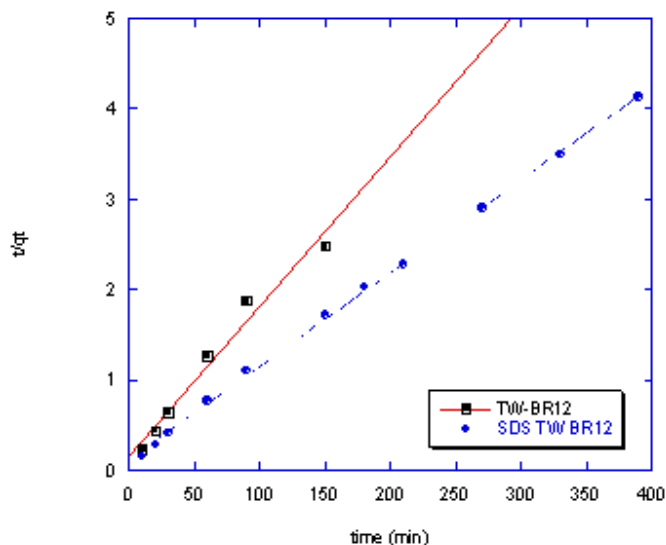


Figure 11. The fitting of second order Eq. for adsorption of Basic Red 12 on TW and SDS TW over 303 K; Initial dye concentration 250 ppm.

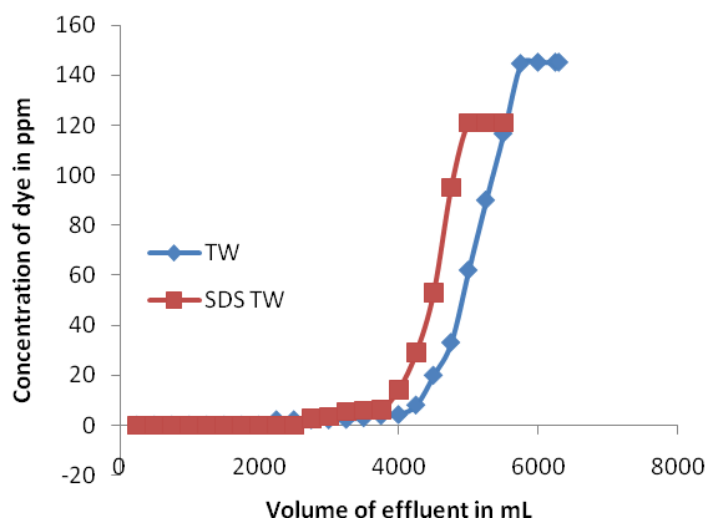


Figure 12. Breakthrough curves for Basic Red 12 through TW and SDS TW columns.

Table 1. Freundlich parameters for adsorption of Basic Red 12 over TW and SDS TW at different temperatures.

Temperature (K)	K_F	n	R
TW –BR 12			
303	1.8050	0.9071	0.9905
313	2.4389	0.9704	0.9980
323	3.9012	1.1307	0.9956
SDS TW-BR 12			
303	30.206	1.9650	0.9813
313	29.478	1.7699	0.9727
323	5.420	0.7506	0.9826

Table 2. Langmuir parameters for adsorption of Basic Red 12 over TW and SDS TW at different temperatures.

Temperature (K)	Q ₀ (mg/g)	b (L/mg)	R _L	R
TW –BR 12				
303	238.96	8.651X10-3	0.3161	0.9899
313	694.39	3.617X10-3	0.5251	0.9982
323	2696.8	1.261X10-3	0.7603	0.9956
SDS TW-BR 12				
303	308.83	0.0432	0.0442	0.9817
313	351.37	0.0655	0.0440	0.9708
323	358.80	0.0242	0.0762	0.9761

Table 3. Harkins Jura parameters for adsorption of Basic Red 12 over TW and SDS TW at different temperatures

Temperature (K)	A	B	R
TW –BR 12			
303	200.55	1.3504	0.9443
313	215.15	1.3189	0.9694
323	252.46	1.3038	0.9805
SDS TW-BR 12			
303	7363.77	1.7253	0.9302
313	6877.57	1.5887	0.9123
323	2960.33	1.2303	0.9303

Table 4. Values of thermodynamic parameters for adsorption of Basic Red 12 over TW and SDS TW

Temperature (K)	ΔG°(KJ mol ⁻¹)	ΔH° (KJ mol ⁻¹)	ΔS°(JK ⁻¹ mol ⁻¹)
TW –BR 12			
303	-28.443	+88.573	+0.386
313	-26.689		
323	-21.395		
SDS TW-BR 12			
303	-68.954	+49.849	+22.918
313	-61.568		
323	-58.011		

Table 5. Kinetic Model parameters for adsorption of Basic Red 12 over TW and SDS TW

Parameter	Value for TW	Value for SDS TW
Pseudo First order		
K_1 (min^{-1})	0.02468	0.00875
q_e (mg/g)	3.5154	29.723
R	0.9846	0.9926
Second order		
K_2 ($\text{L mg}^{-1} \text{min}^{-1}$)	5.927×10^{-4}	1.1757×10^{-3}
R	0.9804	0.9892
Pseudo second order		
K_2 ($\text{L mg}^{-1} \text{min}^{-1}$)	1.7459×10^{-3}	9.303×10^{-4}
q_e (mg/g)	60.419	96.805
R	0.9867	0.9995

CONCLUSION

Following conclusions are drawn from the present study:

- (1) The batch adsorption experiments show that the adsorption of the Basic Red 12 over TW and SDS TW is dependent on pH, amount of adsorbent, concentration, contact time, and temperature.
- (2) The adsorption of dye followed Freundlich, Langmuir and Harkins Jura isotherms on both adsorbents.
- (3) Pseudo first order kinetics seems to be more operative than other kinetic models.
- (4) The thermodynamic parameters obtained in both cases confirm the feasibility of the process at each concentration.
- (5) The column capacity for each process was found to be higher than the batch capacity.
- (6) From this study, it can be concluded that TW and SDS TW are inexpensive and can be used as excellent adsorbents for the removal of basic dyes.

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