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Tea waste as adsorbent for ionic dyes

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ABSTRACT

Toxic dyes can be removed from textile effluents and recovered using dead biomass obtained, as waste from the food industry. In this work, tea waste (TW) was employed to assess its adsorptive capacity for the acidic and basic dyes that usually are present in textile industry waste water. Equilibrium and kinetic experiments were performed in batch and column mode. Adsorption equilibrium and fluid solid mass transfer constant data were analyzed through the concept of ion-exchange sorption isotherm. The equilibrium data were fitted with Langmuir and Freundlich models. Several operation variables, such as TW dosage, contact time, initial pH, and temperature, on the removal of dyes were investigated. The removal efficiency increased with increase in TW dosage. The adsorption process followed pseudo-first-order kinetics. Thermodynamic parameters like ΔH°, ΔS°, and ΔG° were analyzed. The processes were spontaneous for the acidic as well as basic dyes. These results suggest that TW is a potential low-cost food industry waste for textile industry waste water treatment. TW was characterized using Scanning electron micrograph and Fourier transform infrared spectroscopy and techniques.

Keywords: Tea waste; Biosorption; Kinetics; Thermodynamics; Column operation; Acidic and basic dye

1. Introduction

More than 10,000 dyes have been used extensively in textile, leather, paper, cosmetics, and pharmaceutical and food industries. These industries utilize a lot of water and generate huge volume of waste water every year [1]. The disposal of waste water containing dyes without color removal harms aquatic life. This makes penetration of sunlight through water difficult thus hampers the process of photosynthesis [2] by aquatic flora. Few dyes undergo decomposition in aqueous medium causing severe health problems for human [3]. Due to the complex molecular structure, the dyes are difficult to eliminate naturally. Dyes are highly soluble in water, and hence their removal by conventional physical treatment methods like froth floatation, chemical precipitation, reverse osmosis, ion exchange, membrane filtrations, and coagulation is difficult. It is worthwhile to consider adsorption for the removal of such hazardous organic compounds [4]. Activated carbon is a very efficient adsorbent due to large surface area and high adsorption capacity of organics [5].

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During the past decade, the focus of the research is to evaluate the use of agricultural and industrial waste as potential adsorbents. Several other low cost waste such as orange and banana peels [6], almond shells [7], corn cob [8], de-oiled soya [9], shale oil ash [10], sugarcane bagasse [11], coir pith [12], hazelnut shells [13], rice husk [14], wheat husk [15], sewage sludge [16], bark, [17,18] etc. have already been used. In the present adsorption studies, Tea waste (TW) is converted to cheap adsorbent and used for the removal of acidic and basic dye. TW has already been used as adsorbent only for basic dye [19,20], but batch mode of adsorption is evaluated. The present work reports the results of adsorption studies of TW for Acid orange-7; AO-7 (model acid dye) and basic yellow-2; BY-2 (model basic dye). The equilibrium data are attempted by adsorption isotherms like Langmuir and Freundlich. The kinetic study of adsorption process is also considered along with column mode separation of dye.

2. Materials

The TW was obtained from local tea shop. This was boiled in water for 15 min and was filtered, dried at 80°C for 24 h. The dried material was ground to a fine powder in electrical grinder. The crushed powder was washed with distilled water several times till the washings were colorless with neutral pH and negligible conductance. This was then dried in a hot air over at 80°C for 12 h and sieved to get the particle size less than 250 μm and was stored in an air tight container for further use. The dyes BY-2, C.I. 41,000 (303.8 g mol^{-1}), molecular formula $C_{17}H_{21}N_3 \cdot HCl$ {4,4′-Carbonimidoylbis(N,N-dimethylaniline) hydrochloride} and AO-7, C.I. 15,510 (350.32 g mol^{-1}), molecular formula $C_{16}H_{11}N_2NaO_4S$ {4-(2-Hydroxy-1-naphthylazo) benzenesulfonic acid sodium salt}, were procured from Qualichem India Ltd. and were used without further purification. The structure of dyes is given in Fig. 1(a) and 1(b). A stock solution of 1,000 mg L^{-1} of both dyes was prepared in double-distilled water and working solutions of desired concentrations were prepared from the stock solution. The microprocessor-based pH meter by Toshnival, India, was used to measure pH of the solutions. The dye concentrations in solution was monitored on UV–visible Shimadzu 2101 PC spectrophotometer at $\lambda_{max} = 481$ and 542 nm for BY-2 and AO-7, respectively. The Batch experiments were conducted by shaking solution in a temperature controlled (Labotec) shaker. Fourier transform infrared spectroscopy (FTIR) carried out by using Perkin Elmer FTIR spectrophotometer in the range 400–4,000 cm^{-1}. Scanning electron micrographs (SEM) was carried out by using Zeol electron microscope.

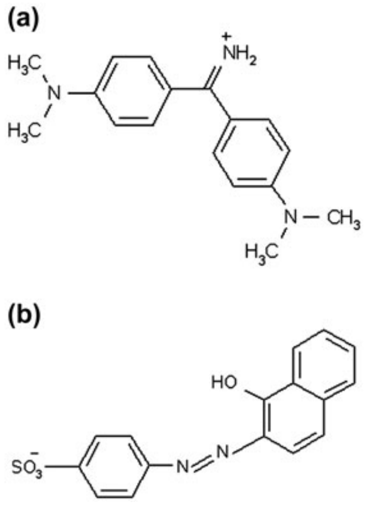


Fig. 1. (a) Molecular structure of basic yellow-2. (b) Molecular structure of acid orange-7.

3. Methods

3.1. Batch experiments

To study the effect of important parameters like initial concentration, pH, amount of adsorbent, temperature, and time for removal of dyes, a series of batch experiments were conducted. For each experiment, 50 mL of dye solution of known initial pH and amount of TW was taken in 100-ml stoppered glass bottle and was kept in temperature controlled water bath shaker till the attainment of equilibrium. The supernatant liquid was separated by centrifugation at 1,000 rpm using Remi ultracentrifugation machine, and amount of dye adsorbed was determined spectrophotometrically. The amount of dye adsorbed q_e in mg/g was calculated using the following equation.

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

where C_0 and C_e are the dye concentration in aqueous medium before and after the attainment of equilibrium, V is volume of solution in liters and W is the mass of adsorbent in g. The isotherms were studied by using 50mL of dye solution with in optimum concentration range (40–250 mg L^{-1}) at 303, 313, and 323 K. The kinetic measurements were carried out by shaking 250 mL of dyes with optimum dose of TW, and solutions were withdrawn at constant time intervals and analyzed spectrophotometrically after centrifugation.

3.2. Column studies

Up flow columns; 50 cm long and 5 cm wide were used. Twenty-five grams of inert sand was mixed with 5.0 g of TW. 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 AO-7 and BY-2 of concentration 100 and 250 mg L^{-1} respectively was fed through the fixed-bed column in an up-flow mode to avoid channeling of the simulated effluent and compaction. The roller pump (EYELA Roller pump RP-1,000) was used to control the flow rate at the inlet and the outlet. The effluent samples were collected at specified time intervals and measured for the remaining dye by a colorimetric method, which was spectrophotometrically analyzed. The flow to the column was continued until the effluent dye concentration (C_e) approached the influent concentration (C_0), $C_e/C_0 > 0.95$. The concentration of collected volume was determined spectrophotometrically.

4. Results and discussion

4.1. Analysis of TW

TW was analyzed using SEM and FTIR techniques. The TW was analyzed by SEM as shown in Fig. 2. SEM is widely used to study the morphological features and surface characteristics of the adsorbent materials. In the present study, SEM of TW reveals rough and porous surface texture. The pores are also seen for more effective interaction of dye in the aqueous phase with TW surface. FTIR spectra (Fig. 3) 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 3,448 cm^{-1} is indicative of bonded hydroxyl group [21]. A peak observed at 1,636.6 cm^{-1} can be assigned to $>C=O$ group. A peak at 1517.5 cm^{-1} indicates secondary amino group. The peak at 1,453.29 cm^{-1} may be due to symmetric C–H stretching and C–O stretching of ether group is observed due to peak at 1,036.9 cm^{-1}. The zero point charge of the activated TW and zderivatives was determined by solid addition technique. The surface area is an important parameter for the sorption capacity of adsorbents. The adsorption occurs at the liquid–solid interface, and the surface area available to the dye molecules determines the efficacy of the adsorbent. Generally, the larger the surface area, the higher the adsorbent's capacity is. However, the surface area must be available in certain pore sizes. According to IUPAC, the pores may be classified into three categories [22], that is, macropores (w >50 nm), mesopores (2–50 nm), and micropores (<2 nm). The large pores serve mainly as passageways to the smaller pores where the adsorption forces are stronger. The surface area of TW was found to be 196.25 m^{2}g^{-1} with the pore volume 9.88 cm^{3}g^{-1}. TW has pore size in the range 50–70 μm as is evident from SEM hence ionic dyes adsorbs on the TW after passing through the macropores on the surface. The surface area of dye molecules are measured using Marvin sketch software, and the dye dimensions are found to be 99.32 and 84.60 Å^2 for AO-7 and BY-2, respectively. TW was also was also analyzed for cellulose [23], hemicelluloses [24], and lignin [25]. The characteristics of TW are shown in Table 1.

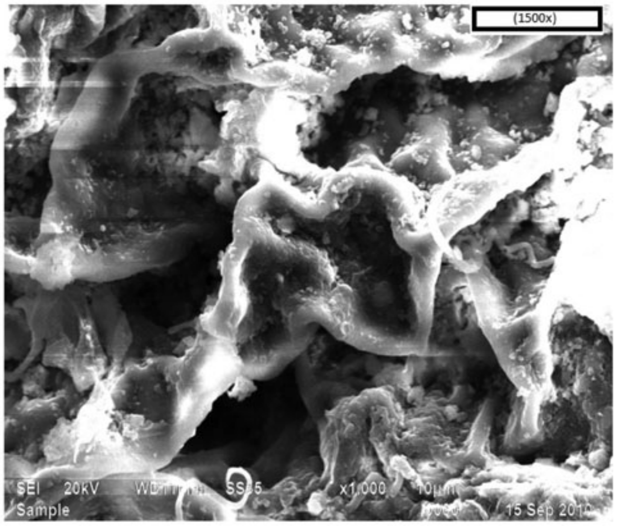
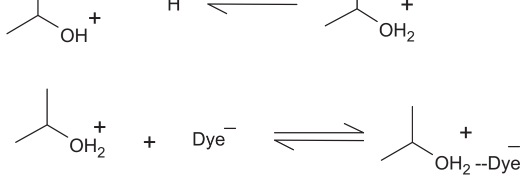


Fig. 2. Scanning electron micrograph of TW.

4.2. Effect of pH

To determine the effect of pH on the removal of the dyes, its adsorption was studied at varied pH range of 2.0–9.0 and is reported in Fig. 4. The Figure clearly indicates that maximum uptake of the AO-7 takes place at pH 2.0. At acidic pH, the phenolic and carboxylic groups are protonated, and thus, strong interactions exist among positively charged surface of adsorbent and anionic dye. It can be represented as follows.



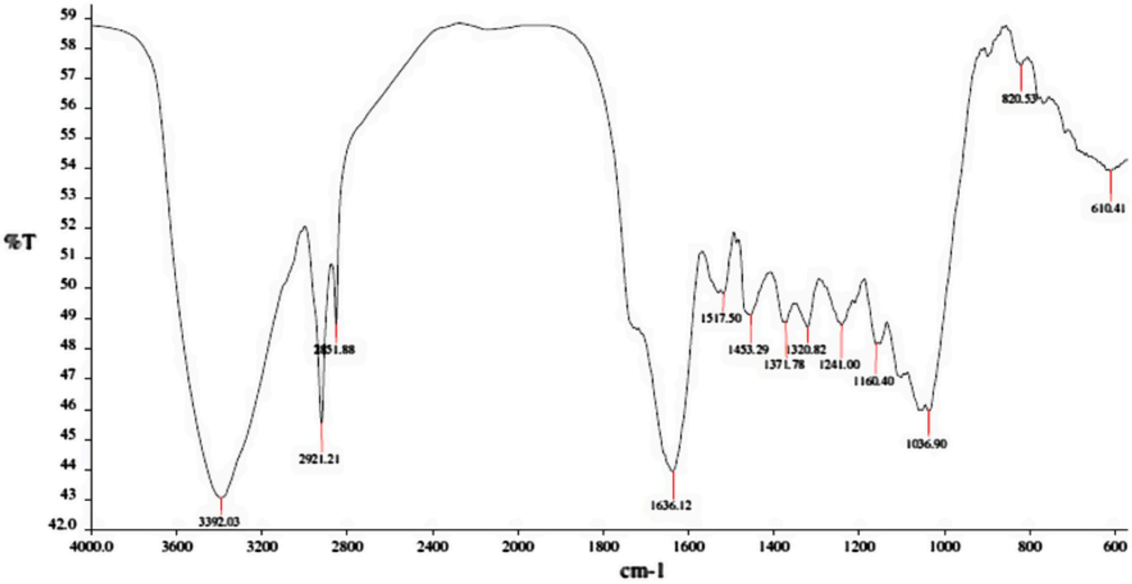


Fig. 3. FTIR spectra of TW.

Table 1
Characteristics of TW

Surface area (m^2g^{-1})	196.25
Bulk density ($g\,mL^{-1}$)	0.251
Pore volume ($cm^3\,g^{-1}$)	9.88
Zero point charge (pH_{zpc})	5.15
Total surface acidity ($mmol\,g^{-1}$)	0.683
Total surface basicity ($mmol\,g^{-1}$)	0.281
Cellulose (%age by wt)	21.5
Hemicellulose (%age by wt)	27.5
Lignin (%age by wt)	16.8
Ash (%age by wt)	5.1

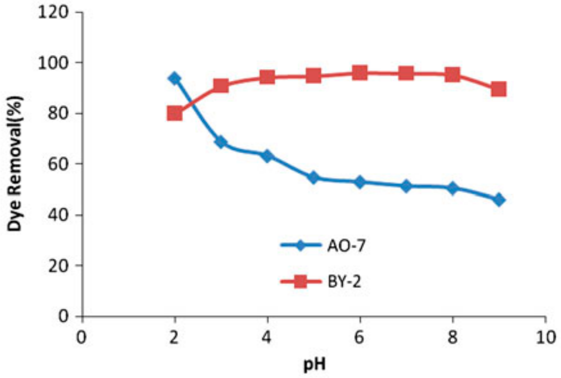
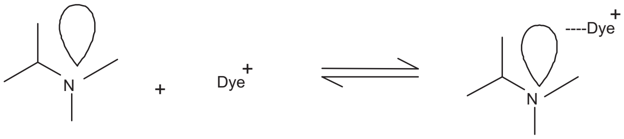


Fig. 4. Effect of pH on removal of acid and basic dye onto TW.

By increasing the pH, the ionization of phenolic groups takes place creating a negative charge on the adsorbent surface, thus due to equal electrical charges the dye molecules and adsorbent the repulsions comes into play. For BY-2, maximum removal of dye was obtained at pH 6, and this can be attributed to the fact that at slightly acidic pH the carboxylic group, amino groups, and phenolic groups are not ionized thus cationic dye adsorbs due to Vander Waals interactions with electron-rich adsorbent, and thus, the mode of adsorption is physisorption. This can be represented as follows.



Further, increase in pH causes ionization of carboxylate and phenolic group thus the surface gets negative charge and adsorption of cationic dye takes place through chemisorption. Due to this reason, the adsorption is almost constant in basic medium. The zero point charge measurement also suggests the same. pHzpc for TW is 5.15; the adsorbent carries negative charge beyond pHzpc so cationic dyes are best adsorbed above their pHzpc. The electrostatic attractions as well as the ionic properties and structure of dye molecules and TW surface could play very important roles in the dye adsorption. At pH below its zero point charge, a considerably high electrostatic attraction exists between the TW surface of the adsorbent and due to the ionization of functional groups of the adsorbent and negatively charged anionic dye molecules.

4.3. Effect of adsorbent dosage

To investigate the effect of adsorbent dose on adsorption of dyes, the experiments were conducted with different adsorbent doses and it was found that with an increase in the dose, the adsorption increases. A significant increase was observed at adsorbent dose of 0.100 g for basic dye and 0.200 g for acidic dye. The percentage removal of dye increased with the increase in adsorbent dose due to increase in availability of adsorption sites as indicated in Fig. 5. The study of effect of adsorbent dosage gives an idea of the effectiveness of the adsorbent and the ability of a dye to be adsorbed on adsorbent with minimum dosage, the percentage removal of BY-2 is more economical than AO-7 as the dye removal is high even at a low adsorbent dose.

4.4. Effect of initial dye concentration

The adsorption experiments were then conducted with varied adsorbate doses using different dye concentrations ranging from 40–100 mg L^{-1} for AO-7 and 100–250 mg L^{-1} for BY-2 at 293, 303, 313, 323, and 333 K temperatures and the behavior has been reported. It is apparent from the data that adsorption increases with an increase in the concentration of dye and with the increase with the temperature. This suggests that ongoing adsorptions are endothermic in nature.

4.5. Adsorption isotherms

The Freundlich and Langmuir isotherm models have been successfully applied to the above systems at various temperatures 303, 313 and 323 K. For the equilibrium concentration of adsorbate (C_e) and amount of dye adsorbed at equilibrium (q_e), the following linear forms of Langmuir [26] and Freundlich [27] isotherms were studied. Langmuir adsorption isotherm assumes monolayer adsorption of adsorbate on homogenous sites of adsorbent. The Langmuir parameters for the adsorption of BY-2 and AO-7 suggest that the value of b decreases with the increase of temperature for BY-2 and AO-7. Freundlich isotherm is the most primitive known relationship telling the non ideal and reversible adsorption. This isotherm model explains the multilayer adsorption on non uniform and heterogeneous surfaces. The strong active binding sites are occupied before other sites until the adsorption energy exponentially decreases upon the completion of adsorption process. If the slope $1/n$ ranges between 0 and 1, it implies chemisorption, and in the present study, its value is greater than 1 suggesting cooperative adsorption for BY-2 and AO-7 on TW. The values of Freundlich parameters are given in Table 2 suggesting that the value of n decreases for adsorption of AO-7 on TW, while it increases for the adsorption of BY-2 suggesting better adsorption of basic dye on TW than acidic dye. The regression analysis suggests that both Langmuir and Freundlich isotherm models are applicable as the adsorption sites may be heterogeneous with homogenous functional groups on the surface.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \tag{2}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

where Q_o and b are Langmuir constants, while K_F and n are Freundlich constants. The Freundlich and Langmuir isotherms gave straight lines and intercepts and slopes were used to determine the values of Langmuir and Freundlich parameters as indicated in Table 2, and the isotherms are presented in Figs. 6 (a), 7 (a) for AO-7 and Figs. 6 (b), 7(b) for BY-2.

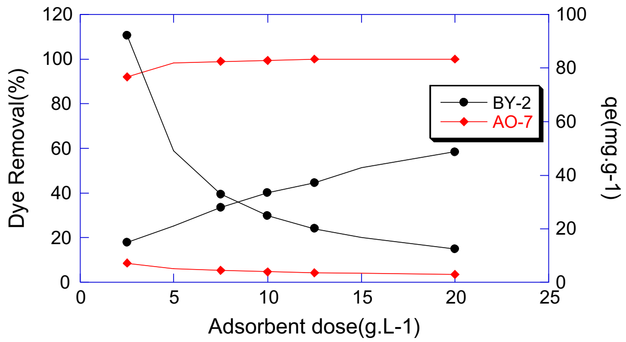


Fig. 5. Effect of adsorbent dose on percentage removal of acidic and basic dye on TW.

Table 2
Langmuir and freundlich parameters for the adsorption of dyes on TW

Temperature (*K*)	Q_0 (mg g^{-1})	b (L mol^{-1})	K_F (L g^{-1})	n
BY-2				
303	2.81×10^{-4}	4040.9	0.3305	0.7921
313	3.07×10^{-4}	3099.1	0.3969	0.7856
323	3.12×10^{-4}	2886.4	0.4784	0.7651
AO-7				
303	1.546×10^{-5}	6445.8	0.0082	0.7098
313	1.116×10^{-5}	5289.8	0.0372	0.7468
323	0.687×10^{-5}	5009.6	0.0335	0.8551

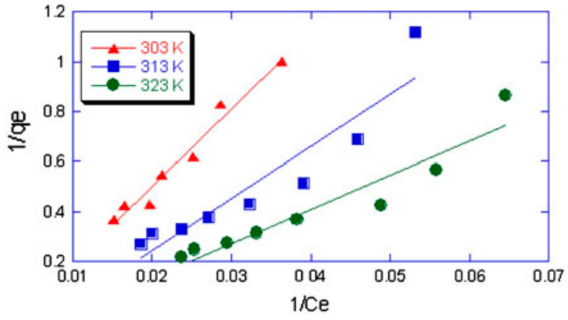


Fig. 6a. Langmuir adsorption isotherm of adsorption of AO-7 over TW at different temperatures ($1/C_e$ in L mg^{-1}and $1/qe$ in g mg$^{-1)}$.

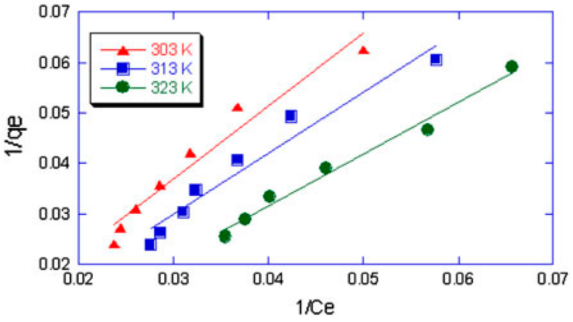


Fig. 6b. Langmuir adsorption isotherm of adsorption of BY-2 over TW at different temperatures ($1/C_e$ in L mg^{-1}and $1/q_e$ in g mg^{-1}).

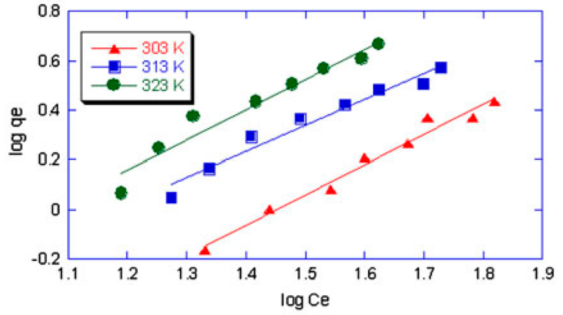


Fig. 7a. Freundlich adsorption isotherm for adsorption of AO-7 over TW at different temperatures.

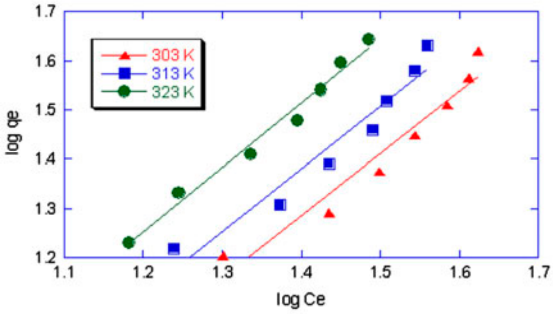


Fig. 7b. Freundlich adsorption isotherm for adsorption of BY-2 over TW at different temperatures.

4.6. Thermodynamic studies

The changes in the reaction that can be expected during the process require the brief idea of the thermodynamic parameters that 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 for both the dyes. The positive value of entropy, ΔS°, suggests favorable randomness factor though its value is small. The thermodynamic parameters were calculated by finding intercept and slope of the equation 5 to get the values of ΔH° and ΔS°. The plot is drawn between $1/T$ vs. $\ln b$ where b is calculated from Langmuir adsorption isotherm at 293, 303, 313, 323, and 333 K. The thermodynamic parameters were calculated using following equations and the values of parameters are listed in Table 3.

$$\Delta G^\circ = -RT \ln b \tag{4}$$

$$\ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \times \frac{1}{T} \tag{5}$$

Table 3
Thermodynamical parameters for the adsorption of dyes on TW

Temperature (*K*)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ K^{-1}mol^{-1})
BY-2			
293	−20.098		
303	−20.286	+7.332	+0.0919
313	−20.738		
323	−21.591		
333	−21.999		
AO-7			
293	−18.890		
303	−19.016	+78.2312	+0.3361
313	−22.160		
323	−23.022		
333	−23.143		

4.7. Kinetic studies

The rate of removal of AO-7 and BY-2 been studied as a function of time as can be seen in Fig. 8. The equilibrium was attained in 4 and 3 h, respectively, for AO-7 and BY-2. During the experiment, it was observed that initial phase of dye removal was quick for both dyes and half life of each adsorption decreases with the increase in temperature. Adsorption rate constant study was carried out with the Lagergran rate equation (Eq. (6))

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \qquad (6)$$

The time vs. log ($q_e - q_t$) plots as shown in Fig. 9 were found to be linear suggesting that the sorption followed the pseudo-first-order kinetics. The slope of the plots gave the value of rate constant and it was found to be $9.738 \times 10^{-3}$and 3.660×10^{-2} min^{-1}, respectively, for AO-7 and BY-2. The plot of q_t vs. $t^{1/2}$ was found to be linear with a slope $K_d = 0.2126$ mg g^{-1} min$^{-0.5}$ for AO-7 and 1.2915 mg g^{-1} min$^{-0.5}$ for BY-2, respectively (Fig. 10). The rate-determining step is either film diffusion or particle diffusion. Thus, particle diffusion process (Eq. (7)) is slow followed by fast steps like adsorption of dye on the surface of TW.

$$q_t = K_d\sqrt{t} + \text{Constant} \qquad (7)$$

The probable mechanism for these processes was diffusion film mechanism. The rate is therefore controlled by the step where equilibrium is attained between liquid film over the surface of TW and dye molecules.

The mechanism of dye adsorption on TW can be explained by assuming that dye molecules either cationic or anionic carries charge after ionization in aqueous medium but the mechanism as proposed by Boyd et al. [28] and Reichenberg [29] includes three main steps, that is, in the first step, the dye molecules are transferred from the bulk aqueous phase to the external surface of the adsorbent material. In the second step, the dye molecules disperse from the relatively small area of the external surface into the macropores, through which it passes into smaller pores within each adsorbent. In the third step, the dye molecule adsorbs to the surface in the pore. The adsorption process may be physisorption or chemisorption in nature. The main difference between two types includes strength of the bond between adsorbent and adsorbate. In physical adsorption, the dye molecules are held to the solid surface of TW by weak forces of intermolecular cohesion consequently, physical adsorption is a readily reversible process. In chemical adsorption, a strong chemical bond is formed between the dye molecule and adsorbent. Chemical adsorption, or chemisorptions, is not easily reversed. The forces in physical adsorption are electrostatic in nature and occur under suitable conditions. Physical adsorption is also referred to as Vander Waals' adsorption. Because of Vander Waals' forces, physical adsorption can form multiple layers of

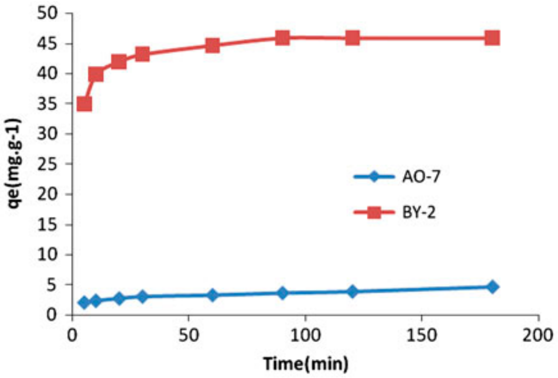


Fig. 8. Effect of contact time on adsorption of acidic and basic dye on TW.

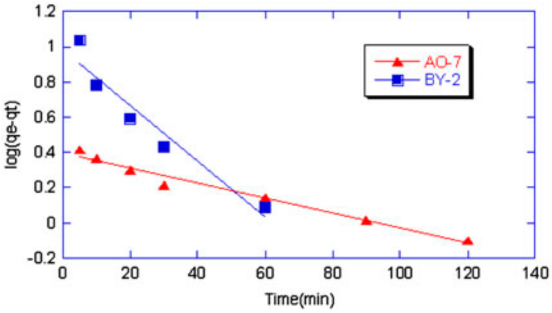


Fig. 9. Lagregran plot for the adsorption of acidic and basic dye on TW.

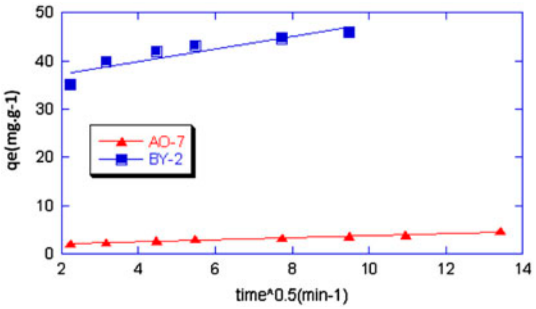


Fig. 10. Intraparticle diffusion film mechanism for adsorption of acidic and basic dye on TW.

Table 4
Comparison of different low-cost adsorbents for ionic dye removal

Adsorbent	Dye	$q_{\max}$ (mg g^{-1})	Reference
Spent brewary waste	Acid orange-7	30.5	[32]
Orange Peel	Acid violet-10	19.88	[33]
Blast furnance sludge	Acid yellow-36	1.4	[34]
Baggase pith	Acid red-114	20	[35]
Tea waste	Acid orange-7	5.73	Present study
Palm fruit bunch	Basic blue-3	92	[36]
Sawdust	Basic blue-9	9.78	[37]
Sawdust	Basic red-22	20.2	[37]
Beer brewary waste	Basic blue-9	4.92	[38]
Banana peel	Basic violet-10	20.6	[6]
Orange peel	Basic violet-10	14.3	[6]
Tea waste	Basic yellow-2	43.88	Present study

adsorbate molecules, one on top of another. The electrostatic effect that produces Vander Waals' forces depends on the polarity of both the dye and adsorbent surfaces. Molecules in any state are either polar or non polar depending on their chemical structure. Polar substances exhibit a partition of positive and negative charges within the compound, which makes it as a permanent dipole. Nonpolar substances have both their positive and negative charges in one midpoint, so they have no permanent dipole. Most organic compounds are nonpolar because of their symmetry. Physisorption can result from three different effects: orientation, dispersion, or induction, for polar molecules, attraction occurs because of the orientation effect. The negative charge of one molecule is attracted to the positive charge of the other. The adsorption of a non polar dye molecule onto a polar surface is accounted for by the dispersion effect. This effect is based on the fact that although non polar substances do not possess a permanent dipole, they do have a fluctuating or oscillating dipole [30] hence dispersion effect originates. The induction effect is very small when compared to the orientation or dispersion effects. Therefore, adsorption systems use polar adsorbents to remove polar dye molecules. TW has polar surfaces ideal for the removal of ionic dyes. TW is an excellent adsorbent for the removal of basic and acidic dye the $q_{\max}$ of different low-cost adsorbents is given in Table 4.

4.8. Column studies

The packed density or bulk density (ρ_s) of the adsorbent in the column was approximately 0.3103 g cm^{-3}. The breakthrough curves are of sigmoid type (Fig. 11). The area under the breakthrough curve gives an idea about amount of dye removed by the adsorbent. The adsorption of BY-2 suggests that the adsorption is mainly mass transfer controlled. The adsorption involves interface accumulation of dye making adsorption faster initially. Finally, the adsorption zone moves toward the exit point till the concentration of dye in inlet and outlet becomes almost same [31]. The column was assumed to be exhausted when 90% dye was obtained in output. The column was then regenerated with four aliquots of acetone (30 mL each). The column was finally washed with hot water and successfully used for removal of dye for six cycles. The acetone containing dye was recovered by distillation at 323 K using air condenser.

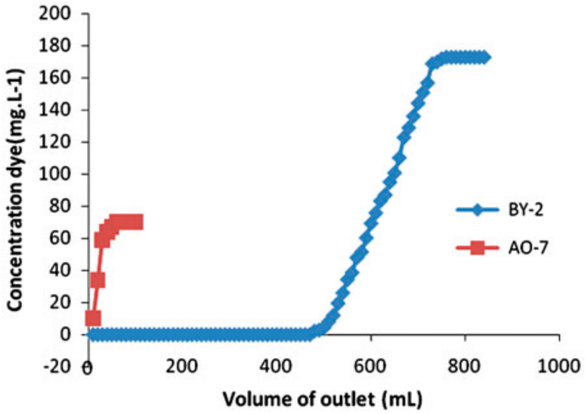


Fig. 11. Breakthrough curves representing removal of acidic and basic dye on fixed bed column of TW.

5. Conclusions

The research work presented here shows that anionic and cationic dyes can be effectively removed from the aqueous solution by adsorption on food industry waste. TW can serve as functional adsorbent for controlling water pollution due to dyes. The batch adsorption experiments show that the adsorption of the acidic and basic dyes over TW is dependent on pH, amount of TW, concentration, contact time, and temperature. The equilibrium between ionic dyes and TW was attained in 4 and 3 h for anionic and cationic dye, while optimum pH is 2 and 6. Langmuir and Freundlich isotherms fitted well on data suggesting that the adsorption sites are heterogeneous with homogenous functional groups. The thermodynamic parameters obtained in both cases confirm the feasibility of the process at each concentration. The results of kinetic experiments show that, for both adsorbates, the adsorption proceeds via film diffusion at higher and lower concentrations. The column capacity for basic dye removal was found to be higher than the batch capacity. Acidic dye removal was more successful in batch process. From this study, it can be concluded that TW is inexpensive and can be used as excellent adsorbents for acidic and basic dye removal from textile effluents.

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