APPLICATION OF WOOD SAWDUST MODIFIED WITH CATIONIC SURFACTANTS FOR EFFICIENT REMOVAL OF ACIDIC DYES FROM AQUEOUS SOLUTIONS: KINETIC AND THERMODYNAMIC STUDIES

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In this paper, application of sawdust prepared from Narra wood (SD) modified with cationic surfactant of cetyltrimethylammonium bromide (SD/CTAB) was used for removal of two typical acid dyes commercially named as Acid Green 25 (AG25) and Acid Red 14 (AR14) from aqueous solutions. The effects of experimental variables, such as pH, initial dye concentration, adsorbent dose, contact time and temperature were investigated in order to find out the optimized conditions for removal of selected test dyes. Langmuir and Freundlich Isotherms were used to analyse the experimental adsorption data. Pseudo- first and second order models suggested by Lagergren, Ho & McKay were used for kinetic study. The van 't Hoff equation employed for obtaining of thermodynamic parameters. It was found that upon simple treatment of sawdust with a cationic surfactant, the adsorption capacity of sawdust for uptake of anionic dyes is improved considerably. The monolayer maximum adsorption capacity of SD/CTAB toward AG25 and AR14 dyes calculated using Langmuir isotherm model was 17.5 and 18.9 mg g^{-1} at 298 K, respectively. Based on kinetics and thermodynamic studies, it was found that adsorption process using SD/CTAB follows pseudo second-order rate equation and the adsorption investigated system is spontaneous and endothermic in nature. Exhausted adsorbent can also be regenerated for reuse with high performance. It was found that via simple treatment of agricultural wastes such as wood sawdust with cationic surfactants it is possible to improve the sorption capacity of sawdust for removal of anionic dyes from aqueous wastes considerably.

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Introduction

Dyes have been widely used in textile, paper, rubber, plastics, leather, cosmetic, pharmaceutical, and food industries, which generated huge volume of wastewater every year. The disposal of dye wastewater without proper treatment is a big challenge and has caused harms to the aquatic environment, such as reducing light penetration and photosynthesis.[1,2] Due to the complex molecular structure, dyes are usually very difficult to be biodegraded, making them hardly eliminated under natural aquatic environment [3]. Acid dyes are anionic compounds mainly used for dyeing nitrogen-containing fabrics like wool, polyamide, modified acryl and silk. Acid Green 25 (1,4-di-[(2-sulfono-4-methylphenyl) amino]-9,10-anthracenedione, disodium salt) (Fig. 1a) in particular belongs to the commercial acid dye often used in textile, hair dye formulation and cosmetic product.[4] Acid Red 14 (4-hydroxy-3-(4-sulfonato-1-naphthylazo)-1-naphthalenesulfonate disodium salt) (Fig. 1b) is a synthetic azo class of dye, imparting red color to foods. Being a typical azo dye the effluent containing AR14 dye is also difficult to treat in environmental systems due to the sulfonic group, which makes it polar and soluble in water. For many years it was used as coloring material for edibles like jams and preservatives; however, most of the developed countries finally prohibited its use in edibles due to the presence of β-naphthylamine, a well-known

carcinogen in it. These dyes also cause asthma or drug intolerance, including nettle rash and water retention to many people.[5,6] So its removal from wastewaters before its discharge in the environment seems to be very essential.
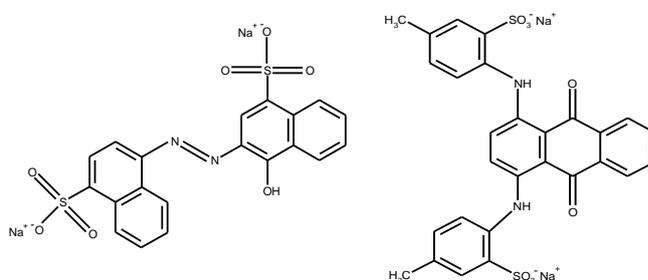
Figure. 1. Molecular structure of (a) AG25 and (b) AR14 dyes.

Several physical, chemical and biological treatment methods (e.g. adsorption, coagulation-flocculation, biodegradation, ion-exchange, chemical oxidation, ozonation, reverse osmosis, membrane filtration and electrochemical methods) have been applied to remove dye molecules from such effluent. However, these processes vary in their effectiveness, cost and environmental impact.[7-9] Adsorption has been found to be one of the promising techniques for dye wastewater treatment because of its simplicity, high efficiency, and wide-ranging availability. Different types of dye molecules can be removed very effectively by adsorption techniques and this process also removes the complete dye molecule, leaving no fragments in the wastewater. [10-13] In some recent publications, different low-cost adsorbents such as chitosan, seashells, soy meal hull, palm ash and chemically modified sawdust have been used for various dyes removal from aqueous solutions.[14-22] However, these adsorbents do not have good adsorption

capacities toward acid dye due to their negatively charged functional groups on their surfaces.[22] Therefore, to improve the adsorption capacity of these adsorbents, surface modification such as cationic surfactant treatment seems to be effective. Detergents or surface-active agents are organic molecules that, when dissolved in a solvent at low concentration, have the ability to adsorb (or locate) at interfaces, thereby altering significantly the physical properties of those interfaces. This adsorption behavior can be attributed to the solvent nature and to a chemical structure for surfactants that combine both a polar and a non-polar (amphiphilic) groups into a single molecule. It has been reported that the cationic surfactants mostly quaternary ammonium salts such as hexadecyltrimethylammonium (HDTMA) or cetyltrimethylammonium bromide (CTAB) provide potential positively charged active sites for efficient removal of anionic contaminants from aqueous solutions.[23] The same improvement in cationic dye removal was observed when sawdust modified with anionic surfactant of SDS.[19]

In this work, the removal of two acid dyes (AG25 and AR14) from aqueous solutions was investigated using cetyltrimethylammonium bromide modified sawdust (SD/CTAB) and adsorption capacity compared with untreated sawdust (SD). The study includes an evaluation of the effects of various operational parameters such as initial dye concentration, adsorbent dose, contact time, temperature and pH on the dye adsorption process. The adsorption kinetic models, equilibrium isotherm models, thermodynamic parameters and regeneration study related with the process were also performed and are reported.

Experimental and Measurements

Materials and methods

All chemicals used were analytical reagent grades and used without further purification. All experiments were carried out in aqueous solutions prepared with distilled water. Sawdust samples (SD) from Nara wood were obtained from a local carpentry workshop (North of Iran). AG25 ($C_{28}H_{22}N_2O_8S_2$ .2Na MW=622.59 g mol⁻¹), Acid red 14 dye ($C_{32}H_{22}N_6O_6S_2$. 2Na, MW=696.66 g mol⁻¹) and cetyltrimethylammonium bromide ($C_{19}H_{42}NBr$ MW=364.46 g mol⁻¹) were purchased from Merck chemical company. Solutions with concentration of 200 mg L⁻¹ for both dyes were prepared in distilled water as stock solution and the other working solutions were prepared by diluting the stock solution with distilled water to the needed concentration. AG25 and AR14 show intense absorption peaks in the visible region at 605 nm and 500 nm, respectively. A single beam Perkin-Elmer UV-Vis spectrophotometer with a glass cell (b=1.0 cm) was used for measuring all the absorption data at the maximum wavelength of each dye. A calibration curve based on Lambert-Beer law (A=εbc) obtained for each dye was used for quantitative analysis of the unadsorbed dye. The pH adjustments were carried out using dilute NaOH and HCl solutions (0.10 M). A pH meter (Metrohm, model 827) with a combined double junction glass electrode was used for pH measurements.

Preparation of sawdust modified by cetyltrimethyl-ammonium bromide (SD/CTAB)

Sawdust was first washed with distilled water in order to remove any dust or impurities and then dried at temperature of about 60 °C for 5 h in an air circulating oven. In order to have uniform modification and reproducible results, sawdust particles sieved pass through a 35-50 mesh (317-508 μm) screen before surfactant treatment. 35 g of sawdust was weighed and mixed with 500 mL of CTAB solution having a concentration of 4.0 g L⁻¹. The mixture was shaken for 5 h at room temperature. The aqueous samples were then filtered, washed with distilled water in order to remove any loosely adsorbed surfactant, dried about 50 °C and sieved before use.

Adsorption experiments

Batch mode studies were conducted with treatment of different amount of adsorbent in range of 0.20 to 1.0 g with 50 mL of aqueous dye solution of dyes having different known concentrations (50–200 mg L⁻¹). The mixtures were shaken using a mechanical shaker (150 rpm) for different periods of time exposures. At the end of each established contact time, the supernatant were analyzed for residual dye concentration. All experiments were carried out for at least three times with respect to each condition, mean values are presented. The amount of dye retained by the adsorbent (q_t) at each time interval t, was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (1)$$

where

q_t is the amount of dye adsorbed per unit weight of adsorbent at time t (mg g⁻¹);

C_0 and C_t are the initial and liquid-phase concentrations of the dye solution at time t (mg L⁻¹), respectively;

V is the volume of the dye solution (L); and

m is the amount of the adsorbent (g).

When t is equal to the equilibrium agitation time (i.e., $C_t=C_e$, $q_t=q_e$), then the amount of dye adsorbed at equilibrium, q_e (mg g⁻¹), was calculated using Eq.1.

Regeneration study

For regeneration study, 1.0 g of the selected adsorbent particles were packed into glass columns. Solutions of both dyes with constant concentration of 20 mg L⁻¹ and optimum pH values (pH 4 for AG25 and pH 6 for AR14 dye) were passed through the columns at a constant flow rate of 3.0 mL min⁻¹.

The exhausted or dye uploaded columns were regenerated using different washing solutions including NaOH, HCl, NaCl (0.10 M each) and commercial ethanol (96%) at the rate of 3 (mL min⁻¹).

The column adsorption capacity (q_c, mg g^{-1}) was estimated as follows: [22]

$$q_c = \frac{\Sigma \left(C_0 - C_i \right) V_{eff}}{m} \qquad (2)$$

where

    C_0 and C_i are the initial and effluent concentration of dye in the liquid phase (mg L^{-1}),

    V_{eff} is the volume of the effluent solution (L) and

    m is the mass of adsorbent (g).

The regeneration efficiency (*RE*) was subsequently calculated using the following equation:

$$\% RE = \frac{V_b{}'}{V_b} \times 100 \qquad (3)$$

where

    $V_b{}'$ is the breakpoint volume of the regenerated used column and

    V_b is the breakpoint volume of the virgin SD/CTAB column.

It might be needed to mention that a plot of effluent concentration vs. time or volume of effluent usually yields an S- shaped curve referred to as a breakthrough curve. The point on the S- shaped curve at which the effluent concentration reaches to 5% and 95% of the influent concentration are usually called breakpoint and point of column exhaustion, respectively.

Adsorption isotherms

Adsorption isotherms, describe how adsorbate molecules interact with adsorbent particles and are thus critical in optimizing the use of chemically modified solid materials.[25-27] It is possible to depict the equilibrium adsorption isotherms by plotting the concentration of the dye in the solid phase vs. that in the liquid phase. In the present study, experimental data were compared by using two well-known and widely applied isotherm models equations, namely Langmuir and Freundlich.[28-30] The application of the Langmuir isotherm model suggests that adsorption takes place as monolayer coverage on homogeneous surface containing a finite number of vacant sites energetically equivalent to each other in respect of adsorption phenomenon and with negligible interaction between adsorbed molecules. The energy of adsorption is constant and does not depend on the degree of occupation of the adsorbent active centers. The empirical non linear Langmuir equation is given by Eq. (4) as shown in the following:

$$\frac{q_e}{q_m} = \frac{K_L C_e}{1 + K_L C_e} \qquad (4)$$

where

q_e is the equilibrium dye concentration on the adsorbent (mg g^{-1});

C_e, the equilibrium dye concentration in solution (mg L^{-1});

q_m, the monolayer capacity of the adsorbent (mg g^{-1});

K_L, the Langmuir constant (L mg^{-1}) related to energy of adsorption.

The linearized equation of Langmuir is represented as follows (Eq.5):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \frac{1}{C_e} \qquad (5)$$

The values of K_L and q_m were determined from the slope and intercept of the representation $1/q_e$ versus $1/C_e$ of Eq. (5), respectively. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor (R_L) which is defined by Eq. 6.

$$R_L = \frac{1}{1 + K_L C_m} \qquad (6)$$

where C_m is the maximum initial dye concentration (mg L^{-1}).

The values of this parameter indicated the shape of the isotherm: for in which $R_L > 1$ is unfavorable, $R_L = 1$ is linear, $0 < R_L < 1$ is favorable, and $R_L = 0$ is irreversible. The Freundlich adsorption isotherm model can be applied for non-ideal adsorption on heterogeneous surfaces and multilayer adsorption. This model is the earliest known empirical equation and is shown to be consistent with exponential distribution of active centers, characteristic of heterogeneous surfaces. It is expressed by the following equation:

$$q_e = K_F C_e{}^{1/n} \qquad (7)$$

where

    q_e is the amount of dye adsorbed per unit of adsorbent (mg g^{-1}),

    C_e is the concentration of non-retained dye at equilibrium (mg L^{-1}),

    K_F (mg$^{(1-1/n)}$/g L$^{1/n}$) and $1/n$ are Freundlich empirical parameters relating to multilayer adsorption capacity and adsorption intensity, respectively.

For a suitable adsorption system $1/n$ value varies between 0 and 1.[31] Linear form of the Freundlich isotherm model is given by Eq. 8. The values of K_F and $1/n$ can be obtained from the linear plot of log q_e versus log C_e.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (8)$$

Kinetics study

Adsorption kinetic studies are significant since they not only provide valuable insights into the reaction pathways, but also describe the solute uptake rate which in turn controls the residence time of adsorbate at the solid–liquid interface. The experimental data were processed on the basis of three of the most commonly used kinetic models suggested by Lagergren, Ho McKay, Weber and Morris.[32-34] Pseudo-first order kinetic equation suggested by Lagergren shown by Eq. (9) is based on the assumption that the rate of change of adsorptive solute uptake with time is directly proportional to the difference in saturation concentration and the amount of adsorptive solid uptake with time.

$$\log\left(q_e - q_t\right) = \log q_{e1} - \frac{k_1}{2.303}t \qquad (9)$$

where

q_e and q_t is the amount of dye adsorbed per unit of adsorbent (mg g^{-1}) at equilibrium and at time t,

k_1 is the pseudo-first order rate constant (min^{-1}), and

t is the contact time (min).

The pseudo-first order rate constant (k_1) was calculated from the plot of log (q_e-q_t) against t. Another commonly used kinetic model is the pseudo - second-order kinetic model (McKay Ho model) which its linear form can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}^2} + \frac{1}{q_{e2}}t \qquad (10)$$

where k_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1}).

A plot of t/q_t against t provides second order adsorption rate constants k_2 and q_{e2} values from the slopes and intercepts. Both pseudo-first order equation or Lagergren's kinetics equation (Eq. 9) and pseudo-second order or HO and McKay (Eq.10) assume that adsorption rates are proportional to free available active sites on the surface of adsorbents for binding of adsorbate and Pseudo-second order equation which is based on the assumption that the adsorption process involves chemisorption mechanism. Weber and Morris proposed the intra-particle diffusion model to identify diffusion mechanisms of adsorption process. The effect of intra-particle diffusion resistance on adsorption can be determined by the following relationship.

$$q_t = k_{id}t^{1/2} + C \qquad (11)$$

where k_{id} is the intra-particle rate constant (g mg^{-1} min$^{-1/2}$), and the intra-particle rate constant k_{id} is a function of equilibrium concentration in solid phase q_e and intra-particle diffusivity. Adsorption mechanism follows the intra-particle diffusion model, a plot of q_t against $t^{1/2}$ should give a linear line with slope kid and intercept C. Values of C give information about the thickness of the boundary layer, i.e.

the larger intercept the greater is the boundary layer effect.[35] If the plot of uptake, q_t, versus square root of time, $t^{1/2}$ passes through the origin, the intra-particle diffusion will be the sole rate limiting process.

Thermodynamic study

The equilibrium constant (K_c) is a measure of adsorption which is defined as the ratio of the quantity of the adsorbate retained by the adsorbent to the amount of the adsorbate remaining in solution.[22,36,37] The equilibrium constant was calculated from the following equations (Eqs. 12-15):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (12)$$

$$\Delta G^0 = RT \ln K_C \qquad (13)$$

$$\ln K_C = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (14)$$

$$K_C = \frac{C_{Ae}}{C_e} \qquad (15)$$

where

ΔG^0, ΔH^0 and ΔS^0 are standard Gibb's free energy, enthalpy, and entropy changes, respectively.

R is universal gas constant (8.314 J mol K^{-1}),

T is absolute temperature (K),

K_c (L g^{-1}) is the adsorption equilibrium constant,

C_{Ae} is the amount of dye adsorbed on the adsorbent (mg g^{-1}),

C_e is the equilibrium or unadsorbed concentration of the dye in the solution (mg L^{-1}).

$\Delta G°$ is in fact the most fundamental criterion of spontaneity of any reaction. The slope and intercept obtained by the plot of ln K_c against $1/T$ were used to calculate the ΔH^0 and ΔS^0, respectively.[22] Gibbs free energy changes ($\Delta G°$) was then calculated from Eq. (12).

Results and Discussion

Effect of pH

The initial pH value of the solution is an important factor which can determine the surface charge of the adsorbent and the degree of ionization of the adsorbate.[21] The effect of pH on the uptake of dyes was analyzed over the pH range from 2 to 10. In this investigation, 0.40 g of adsorbent was treated with 50 mL of dye solution (100 mg L^{-1}) for 1 h at room temperature. It was observed that maximum adsorption for SD/CTAB occurred at pH value of 4 for AG25 and pH 6 for AR14. Therefore all of the next adsorption experiments for dye removal using SD/CTAB adsorbent were carried out at the optimum pH values of 4 (for AG25) and 6 (for AR14), respectively. The pH of dye solutions was adjusted to value of 2 in the case of untreated sawdust because of its maximum adsorption at this pH value.

Effect of initial dye concentration

For this investigation, the adsorption experiments were carried out with initial dye concentration range of 50-200 mg L^{-1}, 0.40 g adsorbent dose, 298 K and 60 min contact time. The Figure 2 show that the amount of dye adsorbed increased with increasing the initial dye concentration in the case of modified sawdust. At higher concentrations, more dye molecules were left in solution due to the saturation of the limited binding sites on the adsorbent.

As the results show, adsorption capacities (mg g^{-1}) of SD/CTAB toward uptake of AG25 increased from 6.1 to 20.0 (~ 3.5 times improvement) and for uptake of AR14 dye, it was increased from 5.5 to 17.3 (~3 times improvement). In the case of untreated sawdust (SD), the dye uptake was slow and gradually increased to the maximum adsorption values of 3.3 and 3.8 mg g^{-1} for AG25 and AR14, respectively.

As the data clearly show adsorption capacity of surfactant-modified sawdust (SD/CTAB) for both dyes is considerably higher than untreated sawdust (at least 5 times) especially at higher initial dye concentrations.

Effects of adsorbent dose

The effect of adsorbent dose on the removal of AG25 and AR14 at initial dye concentration of 100 mg L^{-1}, 298 K temperature and 60 min contact time for SD/CTAB and SD is shown in Fig. 3. Adsorbent dose was varied from 0.10 to 0.50 g for both adsorbents. The results obtained clearly indicate with increasing of adsorbent dose, the amount of dye uptake is increased and maximum adsorption of the dyes occurred by SD/CTAB at 0.40 g of adsorbent (Fig. 3). Therefore, further investigations were carried out using 0.40 g of adsorbent. SD/CTAB has also shows to be a more efficient adsorbent for the removal of acid dyes from aqueous solutions than the untreated SD. Increasing of adsorption with increasing of adsorbent dose can be due to the more availability of free binding sites with increasing of the amount of adsorbent.

Effect of contact time

In this investigation, fixed amounts of adsorbents (0.40 g) were agitated with constant volumes of dye solutions (50 mL) having initial dye concentration of 100 mg L^{-1} at established pH values. The mixtures were shaken at room temperature for different periods of contact times (5-60 min). The results obtained are presented in Figure 4. As the results show, the adsorption rate of acid dyes in the first 5 min for SD/CTAB is very fast. Highest amount of dye retained is occurred within the initial 10 minutes of contact time. After reaching the saturation value in 60 min of contact, a continuous and smooth curve is obtained for both adsorbents. Based on these results, 60 min was taken as the equilibrium time in batch adsorption experiments. Again as the results of this part of investigation clearly show, the uptake rate and adsorption amount of acid dyes onto SD/CTAB is much higher than that of SD at any contact time. The difference in the equilibrium time for both adsorbents may be due to strong attractive forces such as electrostatic between the dye molecules and the surfactant-modified sawdust.
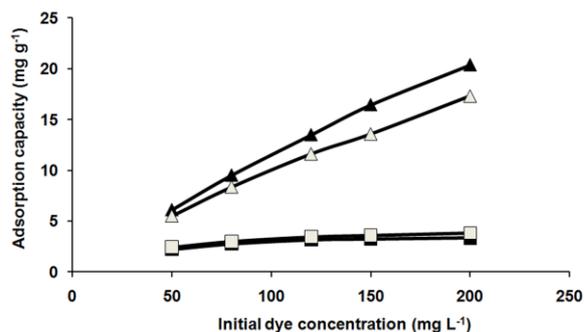
Figure 2. Effect of initial dye concentration on the adsorption of dyes by SD/CTAB (▲: AG25; Δ: AR14) and SD (■: AG25; □: AR14).
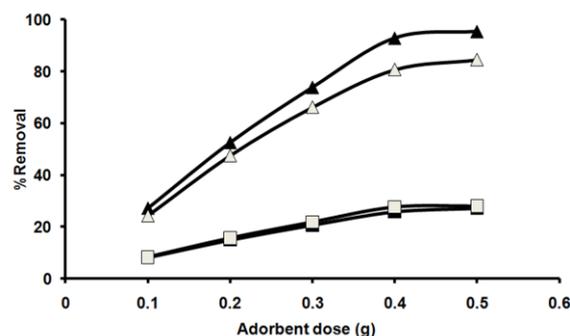
Figure 3. Effect of adsorbent dose on the adsorption of dyes by SD/CTAB (▲: AG25; Δ: AR14) and SD (■: AG25; □: AR14).
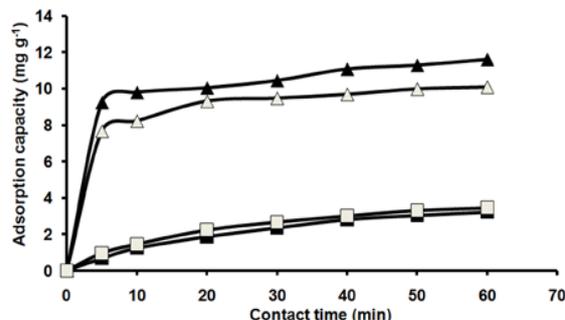
Figure 4. Effect of contact time on the adsorption of dyes by SD/CTAB (▲: AG25; Δ: AR14) and SD (■: AG25; □: AR14).

Effect of solution temperature

Investigation of temperature effect is very important from both kinetics and thermodynamic points of view. The effect of temperature (298-328 K) on adsorption of AG25 and AR14 by two selected adsorbents is illustrated in Fig. 5. In this investigation, constant amounts of adsorbents (0.40 g) were agitated with 50 mL of dye solutions with concentration of 100 mg L^{-1}. The results reveal (Fig. 5) that solution temperature does not affect the sorption efficiency. It might be concluded that the adsorption system investigated is not accompanied by considerable enthalpy changes. However, increasing of dye solution temperature seems to be more effective in the case of unmodified sawdust.

Table 1. Isotherm parameters obtained for adsorption of AG25 and AR14 dyes onto SD/CTAB and SD.

Adsorbent	Dye	Langmuir constants					Freundlich constants		
		q_m (mg g^{-1})	q_m (exp) (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2	K_F (mg$^{(1-1/n)}$/g L$^{1/n}$)	$1/n$	R^2
SD/CTAB	AG25	17.45	20.38	0.431	0.011	0.953	5.77	0.35	0.998
	AR14	18.87	17.30	0.066	0.070	0.986	2.33	0.48	0.997
SD	AG25	3.81	3.33	0.045	0.100	0.996	1.02	0.24	0.943
	AR14	4.33	3.83	0.041	0.108	0.999	1.00	0.27	0.979

Table 2. Kinetic parameters obtained for adsorption of AG25 and AR14 dyes onto SD/CTAB and SD.

Adsorbent	Dye	Pseudo first-order model			Pseudo second-order model				Intraparticle diffusion model	
		q_{e1} mg g^{-1}	k_1 min^{-1}	R^2	q_{e2} mg g^{-1}	q_e (exp) mg g^{-1}	k_2, g mg^{-1} min^{-1}	R^2	K_{id} g mg^{-1} min$^{-1/2}$	R^2
SD/CTAB	AG25	3.20	0.043	0.949	11.89	11.60	0.032	0.997	0.420	0.981
	AR14	3.46	0.064	0.945	10.42	9.43	0.040	0.999	0.435	0.935
SD	AG25	3.82	0.057	0.975	4.97	3.22	0.006	0.996	0.472	0.991
	AR14	3.92	0.061	0.956	4.65	3.45	0.010	0.997	0.463	0.976

*q_{e1} and q_{e2} stand for calculated q_e based on pseudo first and second-order models respectively.

Isotherm investigation

The adsorption isotherm based on linear form of Langmuir and Freundlich equations were plotted (not shown) and the estimated parameters obtained from intercepts and slopes of the corresponding linear plots (log q versus log C and $1/q$ versus $1/C$) are summarised in Table 1. Based on the regression analysis (value of R^2), adsorption data obtained for CRAB/SD is better fitted with Freundlich model. The R_L and $1/n$ values (between 0 and 1) obtained for both adsorbents revealing the favorable adsorption too.
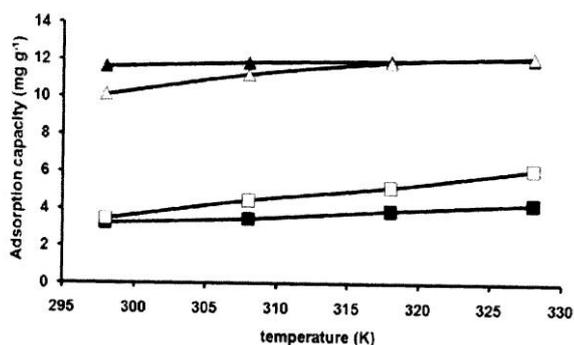
Figure 5. Effect of temperature on the adsorption of dyes by SD/CTAB (▲: AG25; △: AR14) and SD (■: AG25; □: AR14).

Kinetics investigation

The results of adsorption kinetics were processed based on the three kinetic models: pseudo-first order, pseudo-second and intraparticle diffusion models. The kinetic parameters related to each kinetic model were calculated from the intercepts and slopes of the corresponding linear plots (not shown) and the estimated parameters are summarised in Table 2.

The correlation coefficients (R^2) obtained for both adsorbents using pseudo-second-order model (0.996 and 0.999) are higher than those obtained for pseudo-first-order model (0.945-0.975). The calculated adsorption capacity value obtained from pseudo-second-order model (q_{e2}) agrees well with the related experimental value ($q_{e, exp}$). It could be concluded that the adsorption systems are fitted well to the pseudo-second-order model which confirms chemisorption mechanism. These results suggested that such adsorption of dyes might take place via surface ion exchange reaction until the surface function sites are fully occupied. The intra-particle diffusion plots for adsorption of AG25 and AR14 were linear but did not pass through the origin, indicated that the pore diffusion isn't the rate limiting step of the studied adsorption process.

Thermodynamic investigation

Thermodynamic study provides useful information about the spontaneity of a given adsorption processes point as well as calculating of fundamental thermodynamic parameters, such as $\Delta G°$, $\Delta H°$ and $\Delta S°$. The effect of temperature on the adsorption equilibrium constants and thermodynamic parameters of the adsorption equilibriums derived from the linear plot of ln K versus $1/T$ (not shown) deduced from Fig. 6 and van't Hoff equation (Eq. 14) are presented in Table 3.

As the data show (Table 3), the value of K_c increases with increasing temperature from 298 to 328 K, suggested the endothermic nature of adsorption process ($\Delta H^0 > 0$). The negative values of ΔG^0 indicated the spontaneous nature of the studied adsorption system. The more negative values obtained for ΔG^0 with increasing temperature indicates that the adsorption process is more favorable at higher temperature. The positive values of ΔG^0 obtained for untreated sawdust (SD) as adsorbent indicate the presence of an energy barrier in the adsorption process.

Table 3. Thermodynamic parameters obtained for adsorption of AG25 and AR14 dyes onto SD/CTAB and SD.

Adsorbent	Dye	T, K	K_c	ΔG^0, kJ mol^{-1}	ΔH^0, kJ mol^{-1}	ΔS^0, J mol^{-1} K^{-1}
SD/CTAB	AG25	298	12.97	-6.35	18.52	83.56
		308	17.15	-7.28		
		318	20.73	-8.01		
		328	26.00	-8.88		
	AR14	298	4.17	-3.54	55.96	199.61
		308	8.38	-5.44		
		318	18.02	-7.64		
		328	32.05	-9.45		
SD	AG25	298	0.35	2.68	10.83	27.38
		308	0.38	2.47		
		318	0.45	2.12		
		328	0.51	1.68		
	AR14	298	0.38	2.39	24.23	73.42
		308	0.55	1.53		
		318	0.70	0.95		
		328	0.95	0.14		

Regeneration investigation

For desorption study, various chemicals such as dilute solutions (0.10 M) of NaOH, HCl, and NaCl. The regeneration efficiency (%RE) was calculated using Eq. (3). The results indicate that among the tested washing solutions, NaOH (0.10 M) led to obtaining the best results. Before regeneration experiment, a glass column was first packed with SD/CTAB (1.0 g) and dye solutions (AG25 and AR14) with initial concentration of 20 mg L^{-1} were passed through the columns with flow rate of 3.0 mL min^{-1}. The dye uploaded columns were then washed with 0.10 M NaOH in order to regeneration and desorbing dyes. The results obtained for AG25 dye are illustrated in Fig. 6.
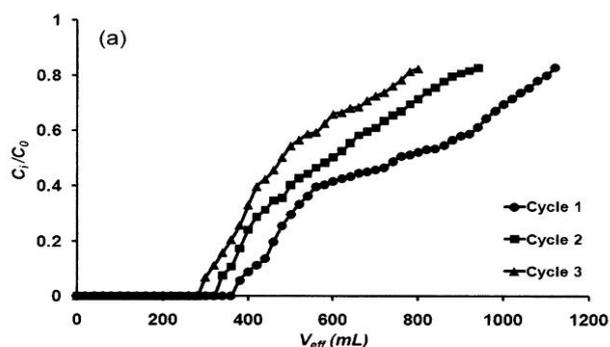
Figure 6. Breakthrough curves obtained for removal of AG25 by SD/CTAB regenerated column (●: Cycle 1; ■: Cycle 2; ▲: Cycle 3)

As the results represent the adsorption capacity of bed decreases as cycle proceeds and this is because of adsorbing sites, whose accessibility becomes difficult as the cycles progressed. Maximum decay observed after three run was about 20% of its initial performance. The results clearly indicate that both dyes retained good adsorption efficiency even after three runs. It was also found that simple pretreatment of the regenerated column with surfactant in each run leads to further improvement of sorption capacity of sawdust for dye removal.

Conclusion

Sawdust modified with cetyltrimethylammonium bromide (SD/CTAB) can be obtained by simple treatment of sawdust with surfactant solution and was proved to be an efficient low cost adsorbent for removal of AG25 and AR14 acid dyes. The adsorption process is influenced by some physical parameters such as solution pH, initial dye concentration, adsorbent dose, contact time and temperature. Adsorption capacity of the adsorbents increased with increasing initial dye concentration, contact time and temperature. The optimal pH of adsorption of AG25 and AR14 dyes onto SD/CTAB were found to be 4 and 6, respectively, while maximum adsorption capacity of these two dyes onto SD occurred at pH 2.

Freundlich isotherm described the equilibrium data of both dyes on SD/CTAB better than Langmuir isotherm, while Langmuir isotherm fitted better to the equilibrium data of dyes on untreated sawdust. The maximum adsorption capacity of SD/CTAB for AG25 and AR14 were found to be 17.5 and 18.9 mg g^{-1}, respectively, based on monolayer coverage of Langmuir model. Pseudo-second-order equation generated the best agreement with experimental data for adsorption systems for the two acid dyes. Thermodynamic analysis suggests that adsorption of dyes by SD/CTAB was a spontaneous and endothermic process.

High regeneration of the used SD/CTAB is quite possible using 0.01 M NaOH and the regenerated adsorbent can be reused without any considerable decay in its removal performance. Because of endothermic nature of the studied adsorption system, it may conclude that spontaneity is mainly governed by entropy factor ($\Delta S^0 > 0$). Upon simple treatment of agricultural wastes such as wood sawdust with cationic surfactants, it is possible to improve sorption capacity of sawdust toward anionic dyes from aqueous solution greatly. The same is true for removal of cationic dyes using sawdust pretreated with anionic surfactants as we have previously reported. The finding in this work seems to be a very important in order to be used in textile waste water treatment.

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