Potential use of cotton plant wastes for the removal of Remazol Black B reactive dye

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ABSTRACT

In this study, the potential use of cotton plant wastes – stalk (CS) and hull (CH) – as sorbents for the removal of Remazol Black B (RB5), a vinyl sulfone type reactive dye, was investigated. The results indicated that adsorption was strongly pH-dependent but slightly temperature-dependent for each sorbent-dye system. The Freundlich, Langmuir, Redlich–Peterson and Langmuir–Freundlich adsorption models were used for the mathematical description of adsorption equilibrium and isotherm constants were evaluated at 25 °C. All models except the Freundlich model were applicable for the description of dye adsorption by both sorbents in the concentration range studied. According to the Langmuir model, CS and CH sorbents exhibited the highest RB5 dye uptake capacities of 35.7 and 50.9 mg g^{-1}, respectively, at an initial pH value of 1.0. Simple mass transfer and kinetic models were applied to the experimental data to examine the mechanisms of adsorption and potential rate-controlling steps. It was found that both external mass transfer and intra-particle diffusion played an important role in the adsorption mechanisms of dye, and adsorption kinetics followed the pseudo second-order type kinetic model for each sorbent. Using the Langmuir model parameters, thermodynamic constant $\Delta G°$ was also evaluated for each sorption system.

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1. Introduction

Dyes are widely used in textile, rubber, paper, plastic, and cosmetic industries for colouring purpose [1]. The discharge of coloured wastes into receiving streams causes serious environmental problems such as affecting photosynthetic activity in aquatic life due to reduced light penetration because of persistent and recalcitrant nature of various dyes. The presence of dyes in waterways is easily detectable and undesirable even when released in small concentrations. There are more then 100,000 commercially available dyes with 7×10^5 tons of dyestuff production annually. Due to their chemical structures, dyes are resistant to fading on exposure to light, water and many chemicals. Many dyes are difficult to decolourize due to their complex aromatic molecular structures and synthetic origin [2–7]. The main methods used for the treatment of dye-containing effluents are adsorption, oxidation–ozonation, biological treatment, coagulation/flocculation, and membrane processing. Although these methods may have certain efficiency in the removal of reactive dyes, their initial and operational costs are so great that they constitute an inhibition to dyeing and finishing industries [3,5,8].

Reactive dyes are typically azo-based chromophores combined with different types of reactive groups, e.g., vinyl sulfone, chlorotriazine, trichloropyrimidine, difluorochloropyrimidine. Azo reactive dyes are characterized by the presence of one or more –N=N– (azo) bonds. They have bright colour, excellent colour fastness, simple application techniques and low energy consumption. Almost 45% of all textile dyes produced annually belongs to the reactive class as a consequence of an intensive use of these dyes for colouring cellulose and viscose––rayon fibres. Reactive dyes have been identified as problematic compounds in textile wastewaters because they are water-soluble, are found in the wastewater at higher concentrations than other dye classes and mainly in their spent, hydrolysed form, and cannot be easily removed by conventional treatment systems [3–8].

Adsorption process is one of the most efficient methods used for the removal of pollutants from wastewaters. Activated carbon is the most widely used adsorbent for the removal of colour and treatment of textile effluents but due to its high price it is not used on a great scale [1,9,10]. In the past few years, extensive research has been undertaken to develop alternative and economic adsorbents. An economic sorbent is defined as one which is abundant in nature, or is a by-product or waste from industry, has little or no economic value, and requires little processing. Agricultural residues, also called lignocellulosic biomass resources, are defined as a biomass by-product from the agricultural sys-

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Nomenclature

a_{RP}	Redlich–Peterson adsorption constant $[(l\,mg^{-1})^{\beta}]$
A	Langmuir–Freundlich adsorption constant $(l^n\,mg^{1-n}\,g^{-1})$
A	specific surface area for mass transfer (cm^{-1})
b	Langmuir adsorption constant $(l\,mg^{-1})$
B	Langmuir–Freundlich adsorption constant $(l\,mg^{-1})^n$
C	residual dye concentration at any time $(mg\,l^{-1})$
$C_{ad,eq}$	adsorbed dye concentration at equilibrium $(mg\,l^{-1})$
C_{eq}	residual dye concentration at equilibrium $(mg\,l^{-1})$
C_0	initial dye concentration $(mg\,l^{-1})$
d_p	particle diameter (cm)
k_{ad}; $k_{o,ad}$	rate constants of saturation type adsorption $(l\,g^{-1}\,min^{-1}; l\,mg^{-1})$
$k_{1,ad}$	first-order rate constant (min^{-1})
$k_{2,ad}$	second-order rate constant $(g\,mg^{-1}\,min^{-1})$
k_L	external mass transfer coefficient $(cm\,min^{-1})$
K	intraparticular diffusion rate constant $(mg\,g^{-1}\,min^{-0.5})$
K_c'	apparent equilibrium constant of the adsorption system
K_c^o	standard thermodynamic equilibrium constant of the adsorption system
K_F	Freundlich adsorption constant $[(mg\,g^{-1})(mg\,l^{-1})^{1/n}]$
K_{RP}	Redlich–Peterson adsorption constant $(l\,g^{-1})$
m	Langmuir–Freundlich adsorption constant
n	Freundlich adsorption constant
q	amount of adsorbed dye per gram of cotton stalk or cotton hull sorbents at any time $(mg\,g^{-1})$
q_{eq}	amount of adsorbed dye per gram of cotton stalk or cotton hull sorbents at equilibrium $(mg\,g^{-1})$
Q^o	Langmuir adsorption constant $(mg\,g^{-1})$
r_{ad}	initial adsorption rate $(mg\,g^{-1}\,min^{-1})$
R	gas constant $(=8.314\,J\,mol^{-1}\,K^{-1})$
R^2	correlation coefficient
t	time (min)
T	solution temperature $(^{\circ}C, K)$
X	cotton stalk or cotton hull sorbent concentration $(g\,l^{-1})$

Greek symbols

β	Redlich–Peterson adsorption constant
ΔG°	the Gibbs free energy of adsorption $(kJ\,mole^{-1})$
ρ_p	particle density $(g\,ml^{-1})$

tem and include straws, husks, shells, and stalks. These wastes can be divided into two groups: crop residues, which remain in the field after harvest, for example, cotton; and agricultural residues, which are the by-products of the industrial processing of crops, for example, rice husk. Several million tons of agricultural wastes are being disposed in the world every year through different ways such as incineration, land applications and land filling. Dye adsorption by these wastes may provide an attractive alternative treatment due to their low cost and readily availability. Many workers have been studying the direct or activated use of these materials such as bagasse pith, carbonized bark, peat, tree and eucalyptus barks, chitin, rice husk, wood and sugar beet pulp, as cheap and efficient adsorbents for the removal of dye ions [4,11–19].

Cotton is the most abundant of all naturally occurring organic substrates and is being planted on a large scale in some countries such as United States, China, Brazil, India, Pakistan, and Australia. It is also a major crop in Turkey and Turkey is one of the eight countries producing 85% of world's cotton [20,21]. The cotton production in the world was approximately 140 million bales in 2004–2005 harvesting season. Due to this high production, the amount of cotton plant waste (cotton plant stalks, leaves and hulls) was also high. As the potential of the cotton waste started to draw researchers' attention, the usefulness and feasibility of using cotton waste for various applications became the subject of many studies in the last years. Various studies have focused on the use of cotton waste as livestock feed, composting, paper production and energy production. In spite of the new methods for its use, today much of the available cotton waste in the world is still disposed of by returning it back to the originating cropland, which may have a potential to be used as adsorbent.

Cotton plant wastes are composed primarily of cellulose (30–50%), hemicellulose (20–30%) and lignin (20–30%). Cellulose is a long linear-chain homo-polymer of glucose molecules, linked to one another primarily with β-(1–4) glycosidic and intramolecular and intermolecular hydrogen bonds with a large number of hydroxyl groups. Cellulose constitutes the most abundant and renewable polymer resource available worldwide. It is estimated that by photosynthesis, 10^{11} to 10^{12} tons of cellulose are synthesized annually in a relatively pure form, for example, in the seed hairs of the cotton plant, but more often are combined with lignin and other polysaccharides (so-called hemicelluloses) in the cell wall of cotton plant. Cellulose is insoluble in water. Hemicelluloses are complex branched polysaccharides containing primarily 5-carbon sugars such as xylose and arabinose with some glucose and mannose dispersed throughout. It forms a short-chain polymer that interacts with cellulose and lignin to form a matrix in the plant wall, strengthening it. Unlike cellulose, hemicelluloses in lignocellulosic materials are soluble in dilute alkali solutions and more easily hydrolyzed than cellulose. The lignins are highly branched, substituted, mononuclear aromatic polymers in the cell walls of the plant and are often bound to adjacent cellulose/hemicellulose fibres to form a lignocellulosic complex adding flexibility to the plant. The molecular structure of lignin polymers is very random and disorganized and consists primarily of carbon ring structures (benzene rings with methoxyl, hydroxyl, and propyl groups) interconnected by polysaccharides. The lignins alone are often quite resistant to conversion by microbial systems and many chemical agents. It is possible to break the lignin–cellulose–hemicellulose matrix and recover the lignin through treatment of the lignocellulosic material with strong sulfuric acid, however, lignin is insoluble in sulfuric acid [18,20–26]. The use of cotton wastes with these properties may be promising for dye removal due to excellent physical and chemical properties of cotton waste constituents in terms of stability, water absorbency, and surface functionalities with a wide variety of functional groups.

This study presents the first outcomes of the possible use of agricultural cotton plant wastes as RB5 reactive dye adsorbents as a function of initial pH, temperature and initial dye concentration. This material was chosen considering its large amount availability. Remazol Black B used in this study is one of the reactive dyes widely used in textile industries. Although some publications have recently suggested using activated cotton for removing of dye or heavy metal ions from aqueous solutions, there seems to be no study which reports all the equilibrium, kinetic and thermodynamic modelling of RB5 dye adsorption by cotton wastes in an batch system, which are important in the design of treatment processes in a wide range of dye concentration.

2. Mathematical description

Analysis of adsorption data is important for developing equilibrium, kinetic and thermodynamic equations that can be used for design purposes. Equilibrium data, commonly known as adsorption isotherms, provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions. The Langmuir and Freundlich are the most frequently used two-parameter models in the literature describing the non-linear equilibrium between adsorbed dye on the cells (q_{eq}) and dye in solution (C_{eq}) at a constant temperature. These models are simple, give a good description of experimental behaviour in a large range of operating conditions and characterized by a limited number of adjustable parameters.

The Langmuir equation which is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules, is given by the following equation:

$$q_{eq} = \frac{Q^o b C_{eq}}{1 + b C_{eq}} \tag{1}$$

where parameters Q^o and b are the Langmuir constants related to maximum achievable adsorption capacity (monolayer capacity) and bonding energy of adsorption (or affinity between the sorbate and sorbent), respectively, which are functions of the characteristics of the system [27].

The Freundlich isotherm model assumes neither homogeneous site energies nor limited levels of sorption. The Freundlich model is the earliest known empirical equation and is shown to be consistent with exponential distribution of active centres, characteristic of heterogeneous surfaces. It is expressed by the following equation:

$$q_{eq} = K_F C_{eq}^{1/n} \tag{2}$$

where K_F and n are the Freundlich constants characteristic on the system. K_F and n are indicators of adsorption capacity and adsorption intensity, respectively [28].

Despite the simplicity of these two-parameter models, some three-parameter models have also been widely used by researchers. Of these three-parameter models, the empirical Redlich–Peterson model has been developed by Redlich–Peterson to improve the fit by the Langmuir or Freundlich equation and is given by Eq. (3). It depends on concentration linearly in the numerator, but exponentially in the denominator.

$$q_{eq} = \frac{K_{RP} C_{eq}}{1 + a_{RP} C_{eq}^{\beta}} \tag{3}$$

where K_{RP}, a_{RP} and β are the Redlich–Peterson parameters. The exponent β lies between 0 and 1. For $\beta = 1$ Eq. (3) converts to the Langmuir form [29].

Langmuir–Freundlich model is another three-parameter empirical model for representing equilibrium adsorption data. It is a combination of the Langmuir and Freundlich isotherm type models. This model suggests that equilibrium data follow Freundlich isotherm at low sorbate concentrations and thus, do not obey Henry's law, and follow Langmuir pattern at higher sorbate concentrations. The following relation represents this model:

$$q_{eq} = \frac{A C_{eq}^m}{1 + B C_{eq}^m} \tag{4}$$

where A, B and m are the Langmuir–Freundlich parameters. Values for m (the heterogeneity factor) $\gg 1$ indicate heterogeneous adsorbents, while values for m closer to or even 1.0 indicate a material with relatively homogenous binding sites. In this case the model is reduced to the Langmuir equation.

Adsorption is a time-dependent process. In the removal of dyes from wastewater, it is necessary to know the rate of adsorption for design and evaluation of adsorbent. If the movement of dye ion from the bulk liquid to the liquid film or boundary layer surrounded the sorbent is ignored, the following sequence of steps can take place in the sorption process of porous sorbent: transport of solute ions from the boundary film to the external surface of the sorbent (film diffusion), transfer of ions from the surface to the intraparticular active sites by either pore diffusion and/or surface diffusion (intraparticular diffusion) and uptake of ions by the active sites on the surface of the adsorbent. The last step is considered to be an equilibrium reaction. Of the three steps, the third step is assumed to be rapid and considered to be negligible. The overall rate of sorption will be controlled by the slowest step, which would be either film diffusion or pore diffusion. However, the controlling step might be distributed between intraparticle and external transport mechanisms.

In the first step of adsorption, the film diffusion is an important rate-controlling step. The change of dye concentration with respect to time can be written as follows:

$$\frac{dC}{dt} = -k_L A(C - C_s) \tag{5}$$

where C is the bulk liquid phase concentration of dye at any time t, C_s the surface concentration of dye, k_L the external mass transfer coefficient and A the specific surface area for mass transfer. It is assumed that during the initial stages of adsorption, the intraparticle resistance is negligible and the transport is mainly due to film diffusion mechanism. At $t = 0$ the surface concentration of dye, C_s, is negligible and $C = C_0$. With these assumptions Eq. (5) can be simplified as:

$$\left[\frac{d(C/C_0)}{dt} \right] = -k_L A \tag{6}$$

Assuming the adsorbent particles are spherical, A is calculated from Eq. (7) as 1.26 and 2.70 cm^{-1} for cotton stalk and cotton hull, respectively:

$$A = \frac{6X}{d_p \rho_p} \tag{+7}$$

where X is the sorbent concentration in the solution ($1.0\,g\,l^{-1}$), d_p average particle diameter and ρ_p the density of the sorbent. By plotting C/C_0 against t, the value of k_L may be determined from the slope at $t = 0$ [10,12,30].

In the model developed by Weber and Morris [31] the rate of intraparticular diffusion is a function of $t^{0.5}$ and can be defined as follows:

$$q = f \left(\frac{Dt}{r_p^2} \right)^{0.5} = K t^{0.5} \tag{8}$$

where r_p is particle radius, D is the effective diffusivity of solutes within the particle, and K is intraparticular diffusion constant. According to this model, the plot of q versus $t^{0.5}$ should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the only rate-controlling step. Otherwise, some other mechanisms along with intraparticle diffusion are also involved. If such types of plots present multi-linearity, imply that two or more steps occur. The first, sharper portion is the external surface adsorption stage. The second linear portion is the gradual adsorption stage, where the intraparticle diffusion is rate-limited. The third portion is final equilibrium stage where the intraparticle diffusion starts to slow down due to extremely low solute concentration in the solution and surface. A good correlation of rate data in this model can jus-

tify the mechanism and K values can be obtained by linearization the curve $q = f(t^{0.5})$.

On the other hand three simplified kinetic models including pseudo first-order [32], pseudo second-order [33] and saturation type [10] were used to test the adsorption kinetics of cotton stalk and cotton hull sorbents. These three models basically include all steps of adsorption such as external film diffusion, adsorption, and intraparticle diffusion, so they are pseudo-models.

The pseudo first-order kinetic model based on solid capacity is generally expressed as follows:

$$\frac{dq}{dt} = k_{1,ad}(q_{eq} - q) \tag{9}$$

where $k_{1,ad}$ is the rate constant of first-order biosorption, respectively. After integration and applying boundary conditions, $t = 0$ to $t = t$ and $q = 0$ to $q = q$, the integrated form of Eq. (9) becomes a linear function and model parameters of q_{eq} and $k_{1,ad}$ may be obtained from the slope and intercept of $\log(q_{eq} - q)$ versus t plot. In order to fit the linear form of Eq. (9) to experimental data, the equilibrium sorption capacity, q_{eq}, must be known. In many cases q_{eq} is unknown and as adsorption tends to become immeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount. Furthermore in most cases the first-order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20–30 min of the sorption process in the region where rapid sorption takes place.

The pseudo second-order kinetic model is also based on the sorption capacity of the solid phase and on the assumption that the sorption process involves chemisorption mechanism and is expressed as:

$$\frac{dq}{dt} = k_{2,ad}(q_{eq} - q)^2 \tag{10}$$

where $k_{2,ad}$ is the rate constant of second-order adsorption. For the same boundary conditions the integrated form of Eq. (10) gives a linear relationship. The values of q_{eq} and $k_{2,ad}$ can be estimated from the slope and intercept of the t/q against t plot. For the application of this model there is no need to know any parameter beforehand. Contrary to the first-order model it predicts the behaviour over the whole range of contact time of adsorption.

On the other hand, the saturation type kinetic model derived from the relationship between initial adsorption rate and initial sorbate concentration can also describe the biosorption. The plot of q versus t can be used to find the initial biosorption rate (r_{ad}) by differentiating the plot at $t = 0$. From the experimental data, it was shown that the initial biosorption rate is proportional to the first power of the initial dye concentration at lower bulk dye concentrations (first-order kinetics) and at higher dye concentrations the rate becomes independent of initial dye concentration (zero-order kinetics). Eq. (11) can be used to describe the rate of biosorption very accurately in both situations. This kind of rate equation is defined as 'saturation type'.

$$r_{ad} = \frac{k_{ad}C_0}{1 + k'_{ad}C_0} \tag{11}$$

where k_{ad} is the first-order rate constant of saturation type adsorption. The zero-order rate constant ($k_{o,ad}$) is expressed as k_{ad}/k'_{ad}. A straight line of $1/r_{ad}$ versus $1/C_0$ suggests the applicability of this kinetic model and k_{ad} and k'_{ad} can be determined from the slope and intercept of the plot. This model predicts the adsorption behaviour over the whole studied concentration range of dye at a constant temperature.

The validity of all models was checked from the linear plots by studying the kinetics under different initial dye concentrations.

The thermodynamic parameter of standard free energy change ($\Delta G°$) reflects the feasibility and spontaneous nature of the process. This parameter can be estimated using equilibrium constant at 25 °C. The adsorption process of Remazol Black B dye can be summarized by the following reversible process, which represents a heterogeneous equilibrium.

$$\text{dye in solution} \leftrightarrow \text{dye-sorbent} \tag{12}$$

The apparent equilibrium constant (K'_c) of the adsorption is defined as:

$$K'_c = \frac{C_{ad,eq}}{C_{eq}} \tag{13}$$

where $C_{ad,eq}$ is the concentration of dye adsorbed on the sorbent at equilibrium. In this case the activity should be used instead of concentration in order to obtain the standard thermodynamic equilibrium constant ($K°_c$) of the adsorption system. By calculating the apparent equilibrium constant (K'_c) values at different initial concentrations of dye and extrapolating to zero, infinite dilute value of K'_c ($= K°_c$) can be found. When $1\,g\,l^{-1}$ of adsorbent is used, this parameter is equal to the reverse of intercept of C_{eq}/q_{eq} versus C_{eq} plot ($= bQ°$), which shows the linearized form of the Langmuir equation. Then the value of $K°_c$ may be used in the following equation to determine the free energy change of the adsorption reaction (Gibbs free energy) ($\Delta G°$) at 25°C.

$$\Delta G° = -RT \ln K°_c \tag{14}$$

where R is the universal gas constant and T is the absolute temperature.

3. Materials and methods

3.1. Sorbents

In this study, cotton stalk and hull, the agricultural cotton plant wastes, were used as adsorbents for the removal of RB5 dye. The raw cotton plant waste was supplied from Cukurova Region located in south of Turkey. Prior to use, the waste was extensively washed with tap water to remove the soil and dust, sprayed with distilled water and then dried in an oven at 60 °C to a constant weight. After peeling the hull part of waste cotton plant, one of the sorbents, the stalk part, was first cut into small pieces and pounded with a pestle. Next, they were grinded into small fine particles by a home type coffee grinder and then screened to give six fractions $d_1 < 75\,\mu m$, $75\,\mu m < d_2 \leq 150\,\mu m$, $150\,\mu m < d_3 \leq 250\,\mu m$, $250\,\mu m < d_4 \leq 355\,\mu m$, $355\,\mu m < d_5 \leq 500\,\mu m$, $d_6 > 500\,\mu m$ in particle sizes and stored in plastic bottles for further use. For cotton hull, only one size ($d_1 < 75\,\mu m$) was obtained after grinding and these particles were used for comparative adsorption studies. Both cotton waste sorbents were used directly for adsorption experiments without any pre-treatment.

The raw cotton plant waste materials were analyzed for α-cellulose, holocellulose, acid soluble and insoluble (Klason) lignins, and ash. For Klason lignin content estimation, the samples were firstly extracted with acetone, then, extracted with hot water to remove the water-soluble content. Klason lignin was estimated as the residue after sulfuric acid hydrolysis of the extracted sample according to TAPPI 93 standard method [34]. The acid-soluble lignin was determined spectrophotometrically. Holocellulose (cellulose–hemicellulose) and α-cellulose contents were determined according to method defined by Browning [35]. For this purpose holocellulose was isolated from the extracted sample by delignification for 4 h. The α-cellulose content was determined by removing the hemicelluloses from the holocellulose by alkali extraction. Ash content was estimated as the weight of residue after

6 h at 575 °C according to ASTM E 1755-01 standard method [36]. The results showed that cotton stalk contains about 38.3% cellulose, 24.2% hemicellulose, 22.2% lignin and 6.4% ash and cotton hull contains 37.9% cellulose, 23.1% hemicellulose, 17.3% lignin and 7.4% ash on a dry basis.

3.2. Chemicals

Remazol Black B (C.I. Reactive Black 5) (empirical formula $C_{26}H_{21}O_{19}N_5S_6Na_4$; molecular weight = 991.8), a commercial diazo reactive dye containing two vinyl sulfone as reactive groups, were kindly supplied by Gemsan, Turkey and used as received without further purification.

The test solutions containing required dye concentration were prepared by diluting $1.0\,g\,l^{-1}$ of stock solution of dye which was obtained by dissolving weighed quantity of RB5 dye in 1 l of double-distilled water. The range of concentrations of prepared dye solutions changed between 25 and $300\,mg\,l^{-1}$. The pH of each solution was adjusted to the required value with diluted or concentrated H_2SO_4 and NaOH solutions before contacting the sorbent. The preliminary studies showed that the initial pH value did not change considerably during the experimental period.

3.3. Sorption studies

Sorption studies were conducted in a routine manner by the batch technique. A number of plugged Pyrex glasses Erlenmeyer containing a definite volume (100 ml in each case) of solutions of RB5 dye of desired concentration, pH and temperature were placed in a thermostatic rotary shaker. For the studies, 0.1 g of adsorbent was treated with 100 ml of dye bearing solution. The flasks were agitated at a 150-rpm constant shaking rate for 24 h to ensure equilibrium was reached. Samples (3 ml) were taken before mixing the sorbent and dye bearing solution and at pre-determined time intervals. The dye solution was separated from the sorbent by centrifugation at 5000 rpm for 5 min. Uptake values were determined as the difference between the initial dye concentration and the one in the supernatant. All the experiments were carried out in duplicates and the average of the values were used for further calculations. For the calculation of average value, the percent relative standard deviation for samples was calculated and if the value of standard deviation for any sample was greater than 10% the data were not used.

3.4. Analysis of Remazol Black B

The concentration of unadsorbed RB5 dye in the adsorption medium was measured colorimetrically using a spectrophotometer (Spectro Double 8 Auto Cell UV–vis Spectrophotometer, Labomed, Inc., USA). The absorbance of the colour was read at 598 nm, where the maximum absorption peak existed.

4. Results and discussion

RB5 dye adsorption properties of two cotton plant wastes (cotton stalk and cotton hull) were investigated as a function of initial pH, particle size, temperature and initial dye concentration. The equilibrium, kinetic and thermodynamic results are given as the units of adsorbed dye quantity per gram of adsorbent at any time and at equilibrium $[q = (C_0 - C)/X$ and $q_{eq} = (C_0 - C_{eq})/X]$, respectively, unadsorbed dye concentration in solution at any time and at equilibrium (C and C_{eq}), respectively, and adsorption yield [% $Ad = 100x(C_0 - C_{eq})/C_0]$.

4.1. Effect of initial pH on Remazol Black B adsorption

An important influencing factor for dye adsorption has been referred to pH as discussed in most related studies published in the literature. To find a suitable pH for the effective adsorption of RB5 dye by the two sorbents, experiments were performed over a pH range of 1.0–4.0. The variation of equilibrium dye uptake with initial pH was given in Fig. 1 for each sorbent at about $100\,mg\,l^{-1}$ initial dye concentration. As seen, both the sorbents indicated similar binding patterns for RB5 dye. The highest uptake values were found at pH 1.0 and the adsorption of dye decreased significantly with further increase in pH for each sorbent. Data also showed that the cotton hull sorbent had a higher adsorption capacity than that of cotton stalk sorbent. At pH 1.0, the maximum equilibrium uptake of RB5 dye was $43.3\,mg\,g^{-1}$ for CH sorbent and $27.5\,mg\,g^{-1}$ for CS sorbent. The other adsorption experiments were also performed at pH 1.0.

Solution pH affects both aqueous chemistry and surface binding-sites of the adsorbents. It was verified that the cotton plant wastes mainly consist of natural cellulosic fibres and these fibres are negatively charged due to the presence of hydroxyl-groups of cellulose [18,23,25]. Depending on pH, these groups may change their valances. It is expected that at pH 1.0, most of the potential fixation sites on cotton plant wastes are protonated and the surface of sorbents are surrounded by hydronium ions. Reactive dyes are known to ionize to a high degree in aqueous solutions to form coloured anions due to the sulfonate group(s) in their structures. Two sulfonate ($-SO_3^-$) groups of RB5 dye are easily dissociated and have negative charges in the aquatic environment. The higher uptakes obtained at very acidic pH could be attributed to the electrostatic interactions between the positively charged sorbent and the negatively charged RB5 dye anions. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not favour the adsorption of dye anions due to the electrostatic repulsion. [25,30,37,38]. It seems very difficult to explain the adsorption mechanisms with respect to pH due to a large number of variables involved in the sorption of dye anions by the lignocellulosic sorbents and the complexity of the surface and water chemistry.
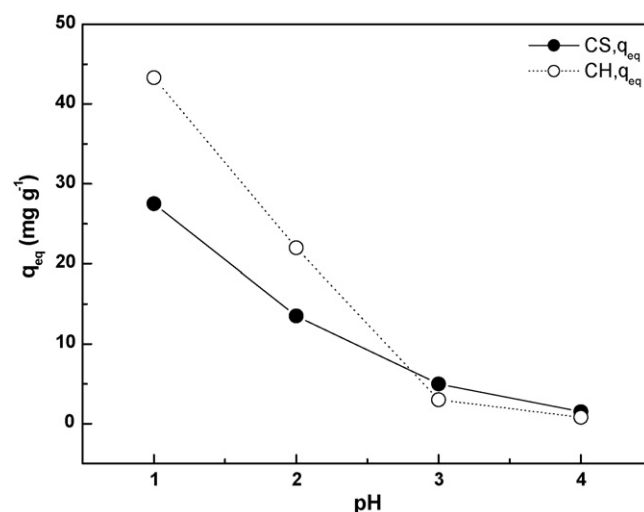

Fig. 1. Effect of initial pH on RB5 dye equilibrium uptake capacity of CS and CH sorbents (C_0: $100\,mg\,l^{-1}$, T: 25 °C, X: $1.0\,g\,l^{-1}$, agitation rate: 150 rpm).

Table 1
Effect of particle size of cotton stalk on RB5 dye equilibrium uptake capacity (C_0: 100 mg l^{-1}, T: 25 °C, X: 1.0 g l^{-1}, agitation rate: 150 rpm)

Particle size (μm)	q_{eq} (mg g^{-1})
$d_1 < 75$	27.5
$75 < d_2 \leq 150$	22.1
$150 < d_3 \leq 250$	16.5
$250 < d_4 \leq 355$	14.0
$355 < d_5 \leq 500$	13.8
$d_6 > 500$	10.3

4.2. Effect of particle size on Remazol Black B adsorption

The sorbent particle size is an important factor in adsorption kinetics because it determines the time required for transport of sorbate within the pore to adsorption sites. The diffusional resistance to mass transfer is greater for large particles but, the smallest size allows very fast removal kinetics if the adsorption is to be primarily a surface phenomenon. Moreover increasing the surface area due to small particle size also increases the number of sites, or indirectly increases the adsorption capacity. The studies carried out with six cotton stalk sorbents at different particle sizes ($d_1 < 75$ μm, 75 μm $< d_2 \leq 150$ μm, 150 μm $< d_3 \leq 250$ μm, 250 μm $< d_4 \leq 355$ μm, 355 μm $< d_5 \leq 500$ μm, $d_6 > 500$ μm) at pH 1.0 indicated that among the cotton stalk sorbents, the sorbent with a particle size of $d_1 < 75$ μm has the highest uptake capacity for Remazol Black dye as expected (Table 1). For cotton hull, as only one size ($d_p < 75$ μm) was obtained after grinding, the effect of size on RB5 dye adsorption by cotton hull could not be examined. However for both sorbents smallest sized particles were used for further comparative adsorption studies.

4.3. Effect of temperature on Remazol Black B adsorption

The effect of temperature on the equilibrium RB5 dye sorption capacity of both cotton sorbents was investigated in the temperature range of 25–45 °C and the results obtained for 100 mg l^{-1} initial dye concentration were indicated in Fig. 2. As seen for both sorbents the equilibrium dye uptake changed insignificantly by the temperature. An increase in the temperature from 25 to 35 °C lead to an increase in the sorption capacity from 27.5 to 30.7 mg g^{-1} for CS sorbent and from 43.3 to 45.1 mg g^{-1} for CH sorbent. When the temperature further increased to 45 °C, equilibrium uptake val-
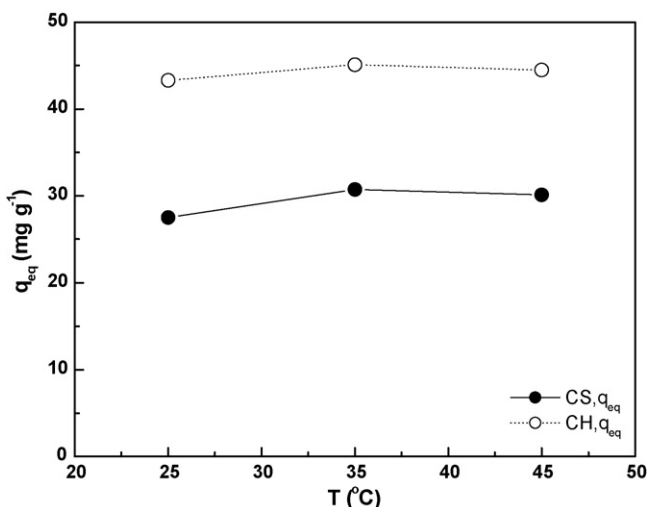
Table 2
Comparison of equilibrium uptakes and adsorption yields obtained at different initial RB5 dye concentrations (T: 25 °C, X: 1.0 g l^{-1}, agitation rate: 150 rpm)

C_0 (mg l^{-1})	q_{eq} (mg g^{-1})	Ad (%)
Cotton stalk		
25.5	13.7	54.9
54.1	21.9	40.7
78.8	25.5	32.4
104.8	27.5	26.2
216.7	32.5	15.0
314.7	34.1	10.8
Cotton hull		
23.9	19.1	79.6
50.0	32.9	66.0
75.8	39.0	51.4
100.3	43.3	42.9
200.0	48.4	24.0
299.0	50.0	16.7

ues were detected as 30.1 and 44.5 mg g^{-1} for CS and CH sorbents, respectively. The variations in adsorption capacity values due to temperature may be assumed negligible. Finally all other adsorption experiments were carried out at 25 °C.

4.4. Effect of initial Remazol Black B concentration on adsorption

The initial concentration provides an important driving force to overcome all mass transfer resistance of the dye between the aqueous and solid phases. Hence a higher initial concentration of the dye will increase the adsorption capacity. Such an effect was demonstrated in Table 2. The equilibrium sorption capacity of CS and CH for the dye enhanced with raising initial dye concentration up to 300 mg l^{-1} while the adsorption yield of dye showed an opposite trend. The amount of RB5 dye adsorbed increased from 13.7 to 34.1 mg g^{-1} for stalk sorbent and from 19.1 to 50.0 mg g^{-1} for hull sorbent with the change of initial dye concentration from 25 to 300 mg l^{-1} due to the increase in the number of ions competing for the available binding sites on both sorbents. RB5 dye removal yield was higher at low dye concentrations for both the sorbents due to availability of unoccupied binding sites on the adsorbents. However percent colour removal decreased with increasing dye concentration because of nearly complete coverage of the binding sites of sorbents at higher dye concentrations. As shown in Table 2, when the dye concentration increased from 25 to 300 mg l^{-1}, percent dye adsorption decreased from 54.9 to 10.8% for cotton stalk and from 79.6 to 16.7% for cotton hull.

4.5. Adsorption kinetics

Kinetics of sorption describing the solute uptake rate is one of the important characteristics defining the efficiency of sorption. Hence, the kinetics of RB5 dye removal has been carried out to understand the dye adsorption behaviour of the two cotton plant sorbents with respect to concentration. For this purpose, adsorption capacity (q) was plotted as a function of time for each sorbent at 25 and 300 mg l^{-1} of initial dye concentrations for the first 360 min (6 h) of adsorption (Fig. 3). For the given concentrations, the amount of dye adsorbed increased rapidly with time at the beginning, then non-linearly at a slower rate and finally attained saturation called the equilibrium time, which was dependent on time and concentration for each sorbent. The extent of dye removal enhanced with both raising initial concentration of the dye and contact time. The data showed that a contact time ranging from about 3 to 5 h depending on concentration was sufficient to achieve equilibrium and adsorption did not change subsequently up to 24 h (data not shown). From the figure, for all initial dye concentrations studied, initial sorp-
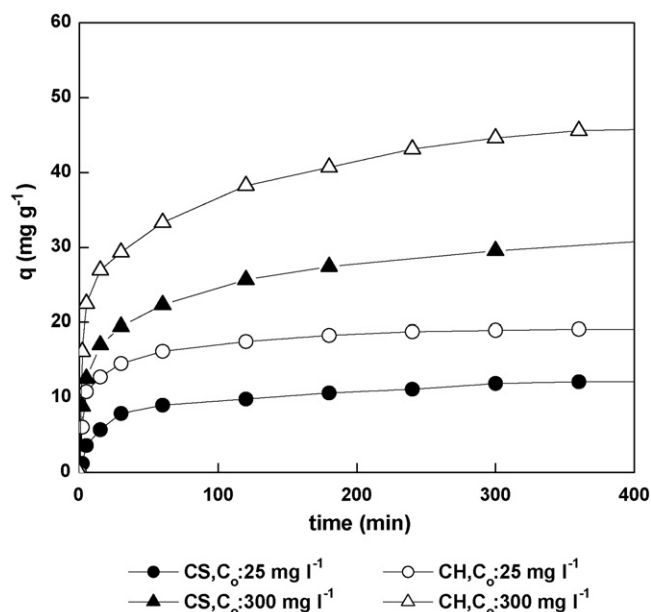

Fig. 2. Effect of temperature on RB5 dye equilibrium uptake capacity of CS and CH sorbents (C_0: 100 mg l^{-1}, initial pH: 1.0, X: 1.0 g l^{-1}, agitation rate: 150 rpm).

Fig. 3. Adsorption curves of RB5 dye adsorption onto CS and CH sorbents at 25 and 300 mg l^{-1} initial dye concentrations (initial pH: 1.0, *T*: 25 °C, *X*: 1.0 g l^{-1}, agitation rate: 150 rpm).

tion of dye occurred more rapidly and the majority of dye uptake took place within the first hour of contact for both sorbents. Such a rapid uptake of RB5 dye for both cases indicated that the sorbents have an affinity for the dye anions pointing towards physical adsorption, the uptake of dye occurs predominantly by surface binding and the structures of sorbents mainly consist of macropores and mesopores. The comparison of kinetic curves also showed that the rate of RB5 dye adsorption onto CH sorbent is higher than that of CS sorbent. Differences between adsorption rates seemed more marked at the beginning of adsorption, but the observed variation decreased with time. According to the results given in Fig. 3, it was also seen that the adsorption capacity of cotton hull sorbent is higher than that of cotton stalk sorbent. For example, the amount of dye adsorbed on hull sorbent (for 1.0 g l^{-1} sorbent concentration and 300 mg l^{-1} initial RB5 dye concentration) was 33.2 mg g^{-1} (63.2% of total adsorbed dye) at an adsorption time of 60 min. However, in a similar time period (60 min) the amount of RB5 dye adsorbed on stalk sorbent was only 22.3 mg g^{-1} (64.2% of total adsorbed dye).

Major constituents of lignocellulosic biomasses are cellulose, lignin, hemicellulose, ash and extractives. Sugar (xylose, arabinose, galactose, mannose, and glucose sugars), extractives and lignin (containing a variety of functional groups, such as, carbonyl, phenolic, amido, amino, sulphydryl, methoxyl, carboxyl, alcohol, and ester) contents of cotton wastes present active sites for binding process. Chemical dye sorption may occur by the polar functional groups. Moreover cellulose and hemicellulose components of cotton wastes provide abundant active hydroxyl groups. Functional groups on dye molecules may be attached to these hydroxyl groups through a variety of chemistries. Sulfonate groups of the dye molecules may attach covalently to the adsorbent by ion exchange [18,23,25]. Although the mechanism of each dye sorption process is not fully understood, ion exchange, complexation, co-ordination/chelation, electrostatic interactions, hydrogen bonding, hydrophobic interactions, and physisorption may be stated as fundamental interactions. It is possible that more than one of these factors can contribute to adsorption mechanisms, depending on the chemical and physical composition of the lignocellulosic biomass,

the nature of the dye and solution conditions such as pH, dye concentration, etc.

The structure, number and type of active sites and physical properties of sorbents also affected RB5 dye uptake capacity. Higher dye uptake capacity of cotton hull sorbent may be greatly due to the its lower lignin content (15 wt.%) and higher surface area. Low lignin content represents low density, loose structure when compared to more compact and less porous structure of stalk sorbent and easy accessibility of ions to active sites of hull sorbent.

4.6. Modelling of adsorption equilibrium

Fig. 4 indicates the experimental isotherm data of RB5 dye adsorption onto CS and CH sorbents at 25 °C. In the dye concentration range examined, the resulting isotherms were positive, regular, concave to the concentration axis, indicating an affinity for adsorption, and showed a saturation trend at higher dye concentrations; indicating a complete monolayer of dye covering the surfaces of both sorbents.

The criteria for selection of the most suitable isotherm model were average percentage error and deviation from experimental value. The corresponding Langmuir, Freundlich, Redlich–Peterson and Langmuir–Freundlich model parameters were estimated by non-linear regression analysis and listed in Table 3 along with the average percentage errors. The average percentage errors between the experimental and predicted values are calculated using Eq. (15). In Eq. (15), the subscripts 'exp' and 'calc' show the experimental and calculated values and *N* the number of measurements.

$$\varepsilon \ \% = \frac{\sum_{i=1}^{N} |(q_{eq,i,exp} - q_{eq,i,calc})/q_{eq,i,exp}|}{N} \times 100 \tag{15}$$

The Langmuir, Redlich–Peterson and Langmuir–Freundlich models fitted the experimental data reasonably well with an average percentage error in the range 0.61–4.13% and 2.96–5.50% for CS and CH sorbents, respectively. The validity of models in the concentration range studied was also checked by comparing the experimental and calculated equilibrium uptake values (q_{eq}). These values were predicted from the related model equations using
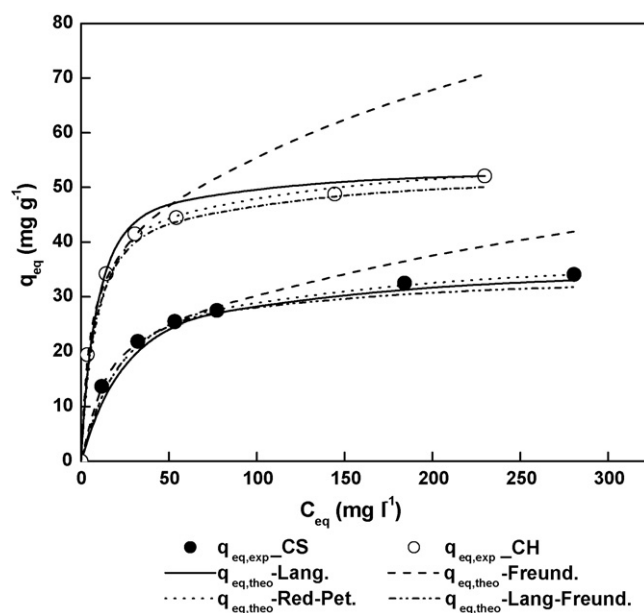

Fig. 4. Comparison of experimental and predicted equilibrium data of RB5 dye adsorption onto CS and CH sorbents (initial pH: 1.0, *T*: 25 °C, *X*: 1.0 g l^{-1}, agitation rate: 150 rpm).

Table 3
Comparison of the Freundlich, Langmuir, Redlich–Peterson and Langmuir–Freundlich adsorption constants of RB5 dye adsorption

Freundlich model	$K_F \ [(\mathrm{mg\,g^{-1}})\,(\mathrm{mg\,l^{-1}})^{-1/n}]$		n	$\varepsilon\,\%$
Cotton stalk	7.75		3.34	9.83
Cotton hull	15.24		3.69	14.95
Langmuir model	$Q^o \ (\mathrm{mg\,g^{-1}})$		$b \ (\mathrm{l\,mg^{-1}})$	$\varepsilon\,\%$
Cotton stalk	35.7		0.043	4.13
Cotton hull	50.9		0.126	2.96
Redlich–Peterson model	$K_{RP} \ (\mathrm{l\,g^{-1}})$	$a_{RP} \ [(\mathrm{l\,mg^{-1}})^\beta]$	β	$\varepsilon\,\%$
Cotton stalk	2.03	0.072	0.955	0.61
Cotton hull	4.27	0.084	0.994	5.50
Langmuir–Freundlich model	$A \ (\mathrm{l^m\,mg^{1-m}\,g^{-1}})$	$B \ (\mathrm{l\,mg^{-1}})^m$	m	$\varepsilon\,\%$
Cotton stalk	2.01	0.059	0.989	2.09
Cotton hull	4.85	0.092	0.948	4.85

the model parameters given in Table 3 and compared with the experimental equilibrium data in Fig. 4. The model curves also confirmed a good fitting of experimental equilibrium data to Langmuir, Redlich–Peterson and Langmuir–Freundlich models. This suggested that the monolayer sorption, mainly due to electrostatic attraction, would not be disturbed by lateral interactions between dye anions sorbed with similar sorption energies for both sorbents. The other two-parameter model of the Freundlich showed a poor fit the equilibrium data with an average percentage error of 9.83 and 14.95% for CS and CH sorbents, respectively.

Adsorption model constants, the values of which express the surface properties, adsorption mechanisms and capacity or affinity of the sorbent, can be used to compare the adsorptive capacity of CS and CH sorbents for RB5 dye.

K_F, one of the Freundlich constants has been used as a relative measure of adsorption capacity (K_F reaches the value of q_{eq} when the equilibrium concentration C_{eq} approaches to unity, thus can be considered as an indicative parameter of the adsorption strength). A greater value of K_F indicates a higher capacity for adsorption. From Table 3, the predicted values of K_F showed easy uptake of RB5 dye with high adsorptive capacity of each sorbent and significant differences in sorption capacities between the two sorbents. The n, the other Freundlich constant, is an empirical parameter that varies with the degree of heterogeneity indicating the degree of non-linearity between dye uptake capacity of biosorbent and unadsorbed dye concentration and is related to the distribution of bonded ions on the sorbent surface. In general $n > 1$ illustrates that adsorbate is favourably adsorbed on the adsorbent, corresponds to a normal an L-type Langmuir isotherm, and the higher the n value the stronger the adsorption intensity. Table 3 also indicated that n is greater than unity, indicating that RB5 dye is favourably adsorbed by both the sorbents.

Values of Q^o and b calculated from the Langmuir model are also tabulated in Table 3. While the Freundlich model does not describe the saturation behaviour of the sorbent, Q^o, the mono-component Langmuir constant represents the monolayer saturation at equilibrium or the total capacity of the adsorbent for the dye. The value of Q^o (50.9 mg g^{-1}) was found higher for the cotton hull-dye system in comparison with the maximum uptake of dye (35.7 mg g^{-1}) by the cotton stalk. The other mono-component Langmuir constant b is related to the free energy of adsorption, ΔG ($b \propto e^{-\Delta G/RT}$) and indicates the affinity of sorbent for the binding of dye. Its value is the reciprocal of the dye concentration at which half of the saturation of the adsorbent is attained (or RB5 dye amount of $Q^o/2$ is bound) so a high value of b, indicates a steep desirable beginning of the isotherm which reflects the high affinity of the sorbent for the

sorbate resulting in a stable adsorption product. The higher value of b obtained for cotton hull-dye system implied strong bonding of dye to cotton hull.

Related adsorption parameters were also calculated according to the three-parameter Redlich–Peterson model using non-linear regression method for RB5 dye and tabulated in Table 3. The model parameter K_{RP} also indicated that the relative RB5 dye adsorption capacity of CH sorbent is approximately two times higher than that of CS sorbent. The exponent β was nearly 1.0 for both cases, showing the closeness of the model to the Langmuir isotherm. It is noted that β normally lies between 0 and 1, indicating favourable adsorption.

The corresponding Langmuir–Freundlich parameters of A, B and m along with percentage errors are also presented in Table 3. The Langmuir–Freundlich constant A, also indicates a relative measure of adsorption capacity and affinity of each sorbent to RB5 dye, was found higher for cotton hull sorbent. Similar to Redlich–Peterson model, the values of Langmuir–Freundlich model exponent m were also close to unity for all cases studied (almost homogeneous sorbents).

4.7. Modelling of adsorption kinetics

Sorption kinetics shows a large dependence on the physical and/or chemical characteristics of the sorbent material, which also influences the sorption mechanism. Batch studies were carried out to identify the potential rate controlling steps for the RB5 dye sorption and to determine external film mass transfer coefficient and intraparticle diffusion coefficient. Moreover simple kinetic models have also been used to test the dynamics of sorption process and attempts were made to calculate the coefficients of these models for both sorbents.

External mass transfer is characterized by the initial rate of solute diffusion for the system studied. The effect of initial dye concentration on the external diffusion rate was given by a plot of C/C_0 versus time for 25 and 300 mg l^{-1} initial dye concentrations for both sorbents (Fig. 5). It was seen that the concentration of dye falls very fast during the initial uptake before intraparticle diffusion begins to control the adsorption kinetics for all cases. All the kinetic data were fitted to Eq. (6) for the initial uptake phase and the external mass transfer coefficients were determined from the slopes as $t \to 0$ and presented in Table 4 for each sorbent. The results showed that the increasing in initial dye concentration resulted in a decrease in the initial rate for both sorbents. It is clear that, as expected, external mass transfer cannot be neglected even for a high agitation speed, although this resistance is only significant for the initial period of adsorption time. Weber and Morris [31] have concluded that, for
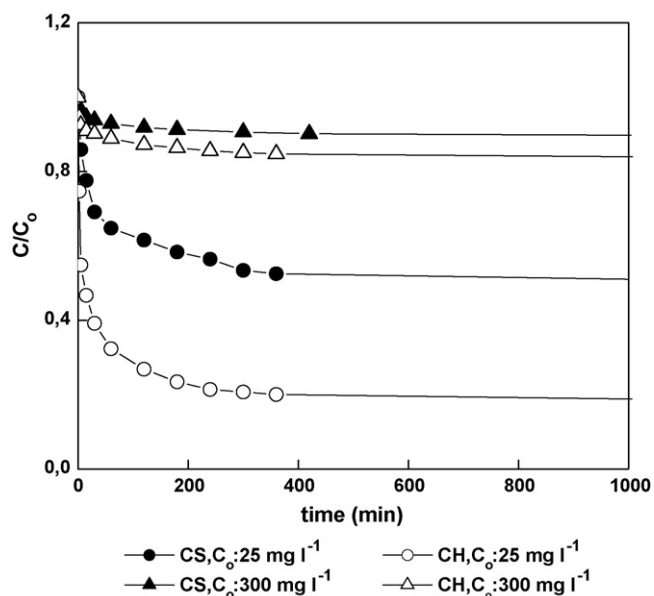
Fig. 6. Variation of k_L with C_0.

Fig. 5. C/C_0 vs. t plots of RB5 dye adsorption onto CS and CH sorbents obtained at 25 and 300 mg l^{-1} initial dye concentrations (initial pH: 1.0, T: 25 °C, X: 1.0 g l^{-1}, agitation rate: 150 rpm).

processes, which are controlled by external diffusion, the initial rate will be directly proportional to solute concentration. The non-proportionality shown in Fig. 6, therefore indicates that external mass transfer is not the rate controlling step.

Fig. 7 shows the effect of initial dye concentration on intraparticle diffusion at 25 and 300 mg l^{-1} initial dye concentrations for each sorbent. As seen from the figure all the plots have the same general feature. They all have initial curved portion, followed by an intermediate linear portion and a plateau. The initial portion of these plots which extent is related to initial dye concentration is due to external mass transfer and the intermediate linear part is due to intraparticle diffusion. The values of K evaluated from these intermediate linear parts of q versus $t^{0.5}$ plots are also tabulated in Table 4 for each sorbent. These are the rate parameters with the unit of mg g^{-1} min$^{-0.5}$ and as such, are not a direct quantification of the rate. Nevertheless, they can be interpreted in relative terms. Examined in this way, the data show that the rate of diffusion increased with a raise in initial dye concentration for both sorbents. This may be due to a greater driving force with increasing C_0. The linear plots at each concentration did not pass through the origin and this indicates that the intraparticle diffusion is not only rate controlling

step. Moreover, according to the theoretical equations for diffusion, when intraparticle diffusion is the only rate-determining step, the rate parameter is also directly related to the square root of the initial concentration ($C_0^{0.5}$). The plot of K versus $C_0^{0.5}$ given in Fig. 8 is not a linear plot. This means that intraparticle diffusion is not the only rate-limiting step; both the external and internal diffusions are taking place as controlling steps in adsorption of dye to CS and CH sorbents.

The first-order rate constants and predicted equilibrium uptakes determined from the plots of linearized form of the pseudo first-order model for the initial 30 min (data not shown) at all concentrations tested are summarized in Table 5 with the corresponding correlation coefficients for each sorbent. As seen in the table the model parameters partly depend on the type of biosorbent used and initial dye concentration. The first-order rate constants decreased slightly with increasing the initial concentration of dye

Fig. 7. q vs. $t^{0.5}$ plots of RB5 dye adsorption onto CS and CH sorbents obtained at 25 and 300 mg l^{-1} initial dye concentrations (initial pH: 1.0, T: 25 °C, X: 1.0 g l^{-1}, agitation rate: 150 rpm).

Table 4
Effect of initial dye concentration on external mass transfer and intraparticular diffusion coefficients

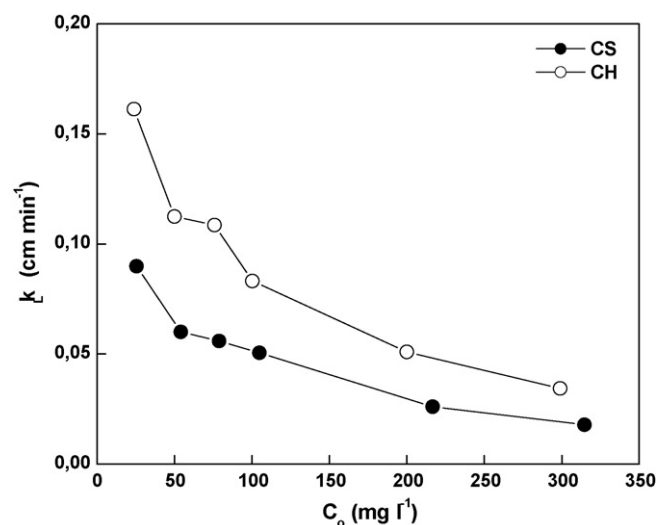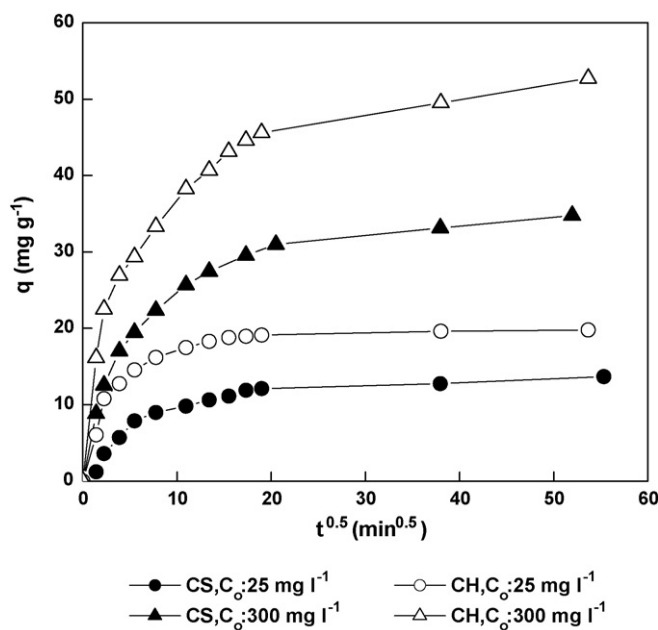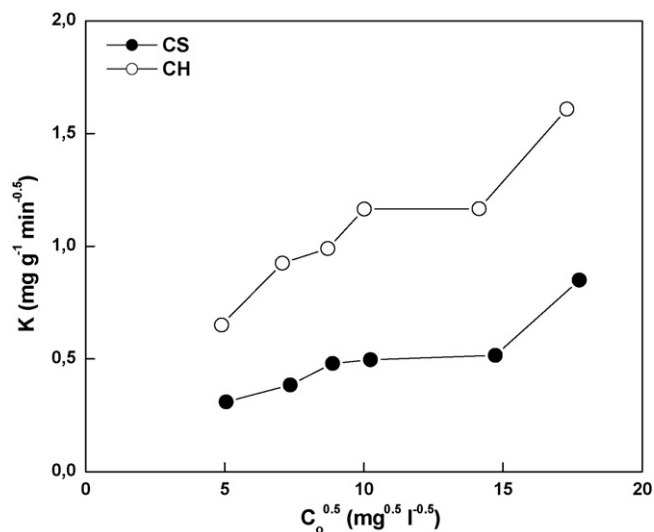| C_0 (mg l^{-1})	$k_L \times 10^2$ (cm min^{-1})	K (mg g^{-1} min$^{-0.5}$)
Cotton stalk		
25.5	8.81	0.31
54.1	5.89	0.39
78.8	5.48	0.48
104.8	4.96	0.50
216.7	2.56	0.52
314.7	1.75	0.85
Cotton hull		
23.9	15.81	0.65
50.0	11.03	0.93
75.8	10.64	0.99
100.3	8.16	1.16
200.0	5.00	1.17
299.0	3.38	1.61

Fig. 8. Variation of K with $C_0^{0.5}$.

Table 6
Comparison of saturation type kinetic rate constants

	$k_{ad} \times 10^1$ ($l\,g^{-1}\,min^{-1}$)	$k'_{ad} \times 10^2$ ($l\,mg^{-1}$)	$k_{o,ad}$ ($l\,mg^{-1}$)	R^2
Cotton stalk	0.39	0.96	4.06	0.948
Cotton hull	1.55	2.87	5.40	0.979

well-established models, pseudo-second-order model predicts the adsorption behaviour over the whole range of adsorption period and it is in agreement with the chemisorption mechanism being the rate controlling step.

The saturation type kinetic model was also applied to the experimental data to describe the batch adsorption kinetics over the whole concentration range of dye studied for cotton stalk and cotton hull sorbents. The values of k_{ad} and k'_{ad} were determined from the plots of linearized form of the saturation type kinetic model (data not shown) (Table 6). As seen from the table, the correlation coefficients were not as high as in pseudo-second-order kinetics. Applying the Weber and Morris principles to the variation in the initial rate with C_0 (Fig. 9) for both sorbents indicated that the rate was not directly proportional to C_0 and also confirmed that sorption process was not the only rate-limiting step.
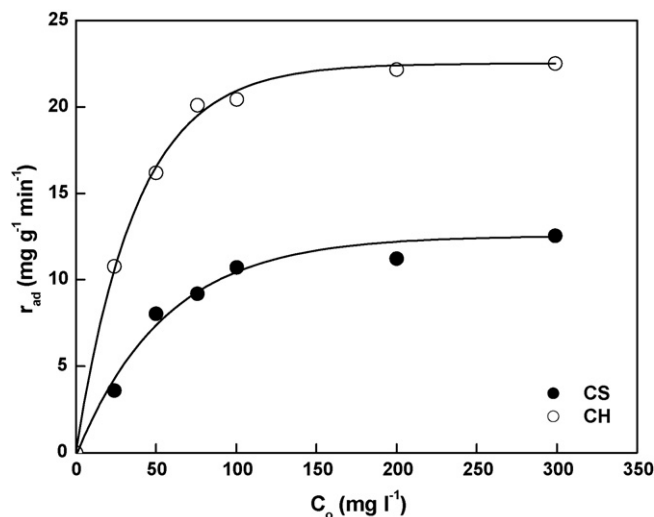
for both sorbents. The pseudo first-order kinetic model did not describe the sorption kinetics of each dye-sorbent system adequately because experimental q_{eq} values did not agree very well with q_{eq} values obtained from Lagergren plots and linear regression coefficients were lower than 0.956. A time lag, possibly due to a boundary layer or external resistance controlling at the beginning of the sorption process, is the reason for the differences observed in the q_{eq} values. In most cases, the Lagergren model did not fit the kinetic data well for the whole range of contact time, and generally underestimated the q_{eq} value.

Using the linearized form of the pseudo-second-order model, t/q was plotted against t and second-order adsorption rate constants ($k_{2,ad}$) and equilibrium uptake values (q_{eq}) were determined from the slope and intercept of the plots (data not shown). The values of parameters $k_{2,ad}$ and q_{eq} and of corresponding correlation coefficients are also presented in Table 5 for both sorbents. The results indicated that second-order rate constants were also affected by the initial dye concentration for both sorbents. Second-order adsorption rate constants diminished irrelevantly with increasing the initial dye concentration. For both sorbents the values of predicted equilibrium sorption capacities showed reasonably good agreement with the experimental equilibrium uptake values. Moreover the correlation coefficients obtained at all concentrations studied were found very high (>0.999). Contrary to other

Fig. 9. Variation of r_{ad} with C_0.

Table 5
Comparison of the pseudo first- and second-order kinetic constants and experimental and calculated q_{eq} values obtained at different initial RB5 dye concentrations

First-order kinetic model					Second-order kinetic model		
C_0 ($mg\,l^{-1}$)	$q_{eq,exp}$ ($mg\,g^{-1}$)	$k_{1,ad} \times 10^2$ (min^{-1})	$q_{eq,cal}$ ($mg\,g^{-1}$)	R^2	$k_{2,ad} \times 10^3$ ($g\,mg^{-1}\,min^{-1}$)	$q_{eq,cal}$ ($mg\,g^{-1}$)	R^2
Cotton stalk							
25.5	13.7	2.74	12.7	0.956	1.88	13.7	0.999
54.1	21.9	2.62	18.2	0.857	1.33	23.6	0.999
78.8	25.5	2.56	20.8	0.842	1.00	26.2	0.999
104.8	27.5	2.49	21.7	0.795	0.92	27.8	0.999
216.7	32.5	2.46	26.7	0.847	0.87	32.9	0.999
314.7	34.1	2.40	27.7	0.809	0.87	34.8	0.999
Cotton hull							
23.9	19.1	4.15	13.9	0.818	4.41	19.8	1.000
50.0	32.9	2.86	25.0	0.733	1.01	33.6	0.999
75.8	39.0	2.60	28.3	0.667	0.75	39.2	0.999
100.3	43.3	2.51	32.7	0.706	0.68	43.7	0.999
200.0	48.4	2.37	36.0	0.672	0.55	48.5	0.999
299.0	50.0	2.35	37.6	0.689	0.51	52.6	0.999

4.8. Modelling of adsorption thermodynamics

The values of K_c^o evaluated from the C_{eq}/q_{eq} versus C_{eq} plot (data not shown) at 25 °C as described in earlier pages of article, were found as 2.03 and 3.31 for CS and CH sorbents, respectively. Using Eq. (14), the values of $\Delta G°$ were determined as −1.76 and −4.56 kJ mol^{-1} for CS and CH sorbents, respectively. The negative values of $\Delta G°$ confirmed the feasibility of the each sorption process and spontaneous nature of adsorptions at 25 °C with an affinity of the dye molecules for each sorbent surface.

5. Conclusion

The aim of this work was to explore the possible use of cotton plant wastes, cotton stalk and hull, which are agricultural wastes available in large quantities in Turkey, as sorbents for the removal of textile dye Remazol Black B from aqueous solutions. For both sorbents adsorption at lower pH enhanced the efficiency of adsorption process, the effect of temperature on adsorption capacity was negligible and equilibrium uptake increased with increasing the initial dye concentration up to 300 mg l^{-1}. For cotton stalk sorbent decreasing particle size resulted in enhancement of adsorption. Adsorption of RB5 dye onto cotton hull sorbent occurred faster and reached higher equilibrium levels as compared to the cotton stalk sorbent.

Adsorption equilibrium data were correlated with the Langmuir, Freundlich, Redlich–Peterson and Langmuir–Freundlich isotherms and all models except the Freundlich model were found to provide the best fit of the experimental data in the concentration range studied. Assuming the batch adsorption as a single-staged equilibrium operation, the separation process can be mathematically defined using these isotherm constants to estimate the residual concentration of RB5 dye or amount of adsorbent for desired purification.

According to the Langmuir model, the maximum dye adsorption capacities of cotton stalk and cotton hull sorbents were 35.7 and 50.9 mg g^{-1}, respectively. When the RB5 dye adsorption capacities of CS and CH sorbents were compared to that of some other sorbents reported in the literature, it was seen that the biosorption capacities of dried fungus *R. arrhizus* [3] and *C. glutamicum* [33] for the same dye were 588.2 and 169.5 mg g^{-1}, respectively. Eren and Acar [34] determined the maximum adsorption capacity of powdered activated carbon and fly ash for RB5 dye as 58.8 and 7.9 mg g^{-1}, respectively. Morais et al. [15] found a 90-mg g^{-1} maximum RB5 dye uptake capacity with eucalyptus bark. The results indicated that the cotton plant wastes have also good adsorption capacities for RB5 dye but not as high as the microbial biomasses.

A film diffusion model and an intraparticle diffusion model developed by Weber and Morris [30] were used to find both the boundary and intraparticle diffusion rate constants. The sorption data indicated that the mechanism of dye adsorption by cotton waste sorbents is rather complex and is probably a combination of external mass transfer, intraparticle diffusion and sorption process. The suitability of the pseudo-first-order, pseudo-second-order and saturation type kinetic models for the sorption of dye onto cotton stalk and cotton hull sorbents were also used to test adsorption kinetics. It was shown that the adsorption of RB5 dye on to cotton stalk and cotton hull sorbents could be best fitted to the pseudo-second-order model. These kinetic parameters obtained can be used for reactor design.

Standard Gibbs free energy change during each adsorption process was negative, corresponding to feasible, spontaneous adsorption.

Results obtained from this study showed that cotton stalk or cotton hull can be used as an adsorbent for the removal of RB5 dye from the aqueous solution in a static batch system. Since cotton stalk and hull, the wastes of cotton plant, are freely, abundantly and locally available, they can be put in use as economical sorbents for the wastewater treatment.

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