ELSEVIER

Chemical Engineering Journal 142 (2008) 23–39

Chemical Engineering Journal

www.elsevier.com/locate/cej

A comparative adsorption/biosorption study of Acid Blue 161: Effect of temperature on equilibrium and kinetic parameters

Zümriye Aksu *, Ayşe İdil Tatlı, Özlem Tunç

Department of Chemical Engineering, Hacettepe University, 06532 Beytepe, Ankara, Turkey

Received 2 May 2007; received in revised form 9 July 2007; accepted 6 November 2007

Abstract

In this study dried *Trametes versicolor*, a white-rot fungus and chitosan, a fungal component derivative were used for the removal of Acid Blue 161 (AB 161) acidic dye from aqueous solution and the results were compared with the outcomes of acid-washed powdered activated carbon (PAC). The influence of suspension pH, temperature, and initial dye concentration on AB 161 dye removal was investigated by conducting a series of batch adsorption experiments. All sorbents exhibited the highest dye uptake capacity at an initial pH value of 3.0. The effect of temperature on dye removal indicated that maximum capacity was obtained at 45 °C for each AB 161 dye–sorbent system. Sorption capacity of each sorbent increased with increasing initial dye concentration up to 500 mg l^{-1}. Among the three sorbents, chitosan was the most effectively sorbent showing a maximum acidic dye uptake of 471.6 mg g^{-1} at 45 °C. The Freundlich, Langmuir, Redlich–Peterson and Langmuir–Freundlich, the two- and three-parameter adsorption models were used for the mathematical description of the sorption equilibrium and isotherm constants were evaluated depending on sorption temperature. Equilibrium data of AB 161 sorption fitted very well to all models except that the Freundlich model for each acid dye–sorbent system in the concentration and temperature ranges studied. For each sorbent–dye system simple kinetic models were applied to the experimental data to examine the mechanisms of sorption and potential rate-controlling steps such as external mass transfer, intraparticle diffusion and sorption process. The sorption process was found to be controlled by both surface and pore diffusion with surface diffusion at the earlier stages followed by pore diffusion at the later stages. Pseudo-second-order kinetic model described the adsorption kinetics accurately at all concentrations and temperatures studied. The thermodynamic analysis indicated that the sorption process was endothermic and the sorption of dye on each sorbent might be chemical in nature.

Keywords: Adsorption; Biosorption; Powdered activated carbon; *Trametes versicolor*; Chitosan; Acid Blue 161; Isotherms; Kinetics; Thermodynamics

1. Introduction

Color is a visible pollution. Even a slight coloration of water sources could make them unacceptable to consumers though it may not be toxic to the same degree. The source of such pollution lies in the rapid increase in the use of synthetic dyes because of their ease of use, inexpensive cost of synthesis, stability and variety of color compared with natural dyes. More than 10,000 chemically different dyes are being manufactured. The world dyestuff and dye intermediates production is estimated to be around 7×10^8 kg per annum [1]. These dyes are mainly consumed in textiles, tanneries, pharmaceuticals, packed food industries, pulp and paper, paint, plastics, electroplating and cosmetics industries [1–8]. During processing, which include both dye manufacturing and dye application, up to 15% of the used dyestuff are released into the process water so the effluents from these industries are highly colored. Color acquired by receiving water bodies such as rivers or lakes inhibits growth of the desirable aquatic life necessary for self-purification by reducing penetration of sunlight, with a consequent reduction in photosynthetic activity. As all dyes used in the textile industry are designed to resist fading upon exposure to sweat, light, water, many chemicals including oxidizing agents, and microbial attack, dye-containing effluents are hardly decolorized by conventional physico-chemical and biological wastewater treatments. This led to the study of other effective methods, and many physical and chemical treatment methods including adsorption, coagulation, precipitation, filtration, electrodialysis, membrane separation and oxidation have been used for the treatment of dye-containing effluents. Some of these techniques have been

* Corresponding author. Tel.: +90 312 2977434; fax: +90 312 2992124.
E-mail address: zaksu@hacettepe.edu.tr (Z. Aksu).

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.11.005

Nomenclature

a_{RP}	Redlich–Peterson adsorption constant $((l\,mg^{-1})^{\beta})$
A	Langmuir–Freundlich adsorption constant in Eq. (4) $(l^m\,mg^{1-m}\,g^{-1})$
A	specific surface area for mass transfer in Eq. (6) (cm^{-1})
A_0	frequency factor of adsorption
b	Langmuir adsorption constant $(l\,mg^{-1})$
B	Langmuir–Freundlich adsorption constant $((l\,mg^{-1})^m)$
C	residual bulk 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_s	surface dye concentration $(mg\,l^{-1})$
C_0	initial dye concentration $(mg\,l^{-1})$
d_p	particle diameter (cm)
E_A	activation energy of sorption $(kJ\,mol^{-1})$
ΔG°	Gibbs free energy change of sorption $(kJ\,mol^{-1})$
ΔH°	enthalpy change of sorption $(kJ\,mol^{-1})$
k_L	external mass transfer coefficient $(cm\,min^{-1})$
$k_{2,ad}$	second-order rate constant $(g\,mg^{-1}\,min^{-1})$
K	intraparticular diffusion rate constant $(mg\,g^{-1}\,min^{-0.5})$
K_F	Freundlich adsorption constant $((mg\,g^{-1})(mg\,l^{-1})^n)$
K_{RP}	Redlich–Peterson adsorption constant $(l\,g^{-1})$
K_c^0	standard thermodynamic equilibrium constant of the adsorption system
m	Langmuir–Freundlich adsorption constant
n	Freundlich adsorption constant
q	amount of dye adsorbed per gram of sorbent at any time $(mg\,g^{-1})$
q_{eq}	amount of dye per gram of sorbent at equilibrium $(mg\,g^{-1})$
Q_{max}	Langmuir adsorption constant $(mg\,g^{-1})$
R	gas constant (=8.314 $J\,mol^{-1}\,K^{-1}$)
R^2	correlation coefficient
ΔS°	entropy change of sorption $(kJ\,mol^{-1}\,K^{-1})$
t	time (min)
T	solution temperature (°C, K)
X	sorbent concentration $(g\,l^{-1})$

Greek letters

β	Redlich–Peterson adsorption constant
ρ_p	particle density $(g\,ml^{-1})$

shown to be effective, although they have limitations such as, excess amount of chemical usage, or accumulation of concentrated sludge with obvious disposal problems, expensive plant requirements or operational costs, lack of effective color reduction, and sensitivity to a variable wastewater input [3–8].

Among these techniques adsorption has been shown to be an effective technique with its efficiency, capacity and applicability on a large scale to remove non-biodegradable dyes from aqueous streams. Activated carbons used in granular, powder or fiber forms, are the most common adsorbents in liquid-phase dye adsorption process. Activated carbons are usually produced from high carbon content materials and possess a great adsorption capacity due to their highly porous structure, extremely large surface area to volume ratio and high degree of surface reactivity. It is also known that acid treatment can modify the carbons' physical and chemical properties, influencing their adsorption behavior. The presence and concentration of surface functional groups plays an important role in the adsorption capacity and the removal mechanism of the dyes. In addition, the adsorption process is influenced by the nature of the dye and its substituent groups and pH of the aqueous solution. Although activated carbon has a good capacity for the adsorption of dyes, it suffers from a number of disadvantages. Activated carbon is quite expensive and the higher the quality the greater the cost. Both chemical and thermal regeneration of spent carbon is expensive, impractical on a large scale and produces additional effluent and results in considerable loss of the adsorbent [8–15]. This has led many workers to search for the use of cheap and efficient alternative materials [8,14–20].

Alternatively, the so-called biosorption, i.e. the passive uptake of organic and inorganic species including metals and dyes from aqueous solutions by the use of non-growing or non-living microbial mass or their derivatives, thus allowing the recovery and/or environmentally acceptable disposal of the pollutants, could also be considered [5,7,8,21]. The special surface properties of bacteria, algae and fungi as well as their cell components: alginic acid, chitin, cellulose, etc. enable them to adsorb different kinds of pollutants from solutions. The main attractions of biosorption are high selectivity and efficiency, cost effectiveness, good removal performance, possible regeneration at low cost, availability of known process equipment, sludge free operation and recovery of the sorbate; raw materials which are either abundant (sea weeds) or wastes from other industrial operations (fermentation wastes, activated sludge process wastes) can be used as biosorbents presenting performances often comparable with those of ion exchange resins [7,21]. Since fungal biomass is non-pathogen to humans and animals and it can be produced cheaply using simple fermentation techniques or obtained as a waste from various industrial fermentation processes, it is widely used for the biosorption of dyes [22–29]. However, a few studies have been focused on utilization of the white-rot fungus *Trametes versicolor* for dye biosorption so the adsorptive properties of the microorganism for acid dyes should be investigated.

Chitin is a natural polysaccharide found particularly in the cell walls of fungi. It is also a main component existing in the shells of crustaceans, such as crabs, shrimp, prawns, insects, and centipedes, and is easily prepared from their shells at low cost by removing other components, calcium and proteins, by treating with acids and alkalis, respectively. Consequently, it is one of the most abundant and cheapest forms of biomass, as well as cellulose. Chitosan is obtained on an industrial scale by the alkaline deacetylation of chitin, which is a linear polymer

of acetylamino-D-glucose [8,30,31]. This biopolymer represents an attractive alternative to other biomaterials because of its physico-chemical characteristics, chemical stability, high reactivity, excellent chelation behavior and high selectivity toward pollutants. Other useful features of chitosan include its abundance, hydrophilicity, biocompatibility, biodegradability and antibacterial property. Recently, the possibility of using chitosan as a material to remove dyes from water and wastewater has been received a great attention due to its low cost compared to activated carbon and its high contents of amino and hydroxy functional groups showing high potential for adsorption of dyes [8,32–36]. As the extension of chitosan as an adsorbent to remove acid dyes from water has seldom been explored, its acid dye removal properties should be investigated.

Acid dyes are sodium salts of organic sulfonic acids. Brightly colored, water soluble and reactive acid dyes are composed of ionizable anionic groups such as sulfonates, carboxylates or sulfates. Acid dyes have a direct affinity towards polyamide and protein fibers in an acidic dye bath so these dyes are commonly used for dyeing polyamide fibers as well as silk, wool and modified acrylics. Acid dye bath wastewaters are characterized by high chemical oxygen demand (COD), dissolved solids, high temperature and acidic pH. Moreover acid dyes are the most problematic with their high molecular weight, as they tend to pass through conventional treatment systems unaffected. The working conditions: acidic pH (pH 3–5) and high temperatures (95–105 °C) make acid dyes ideal candidates for adsorption/biosorption [13,20,37].

While acid textile dyes are of wide use and importance within the textile industry, little is known about the biosorption of these dyes by fungal and derivative biosorbents. The present investigation was an attempt to explore the possibility of using dried white-rot fungus *T. versicolor* and fungal component derivative chitosan to remove AB 161 acid dye from aqueous solutions. The efficacy of biosorbents in removing AB 161 was also compared with those of acid-washed powdered activated carbon.

2. Materials and methods

2.1. Biosorbents and adsorbent

The white-rot fungus *T. versicolor*, obtained from Hacettepe University, Biology Department, Turkey, was used as a biosorbent for this study. The microorganism was cultivated in liquid medium using the shake flask method. The growth medium consisted of (g l^{-1} of purified water); D-glucose (10.0); yeast extract (0.1); KH_2PO_4 (0.2); $NH_4H_2PO_4$ (0.5); $MgSO_4{\cdot}7H_2O$ (0.5) and 1 ml of $ZnSO_4$–$FeSO_4$ solution (prepared from 1.4 g l^{-1} $ZnSO_4{\cdot}7H_2O$ and $FeSO_4{\cdot}7H_2O$). The pH of the medium was adjusted to 4.5 with dilute H_2SO_4 and NaOH solutions before autoclaving. Once inoculated, 250 ml Erlenmeyer flasks containing 100 ml of sterile medium were incubated on an orbital shaker at 150 rpm for 7 days at 30 °C. After the growth period, the pellets were washed twice with distilled water and dried at 60 °C. For the biosorption studies, a weight amount of dried biomass was suspended in 100 ml of double-distilled water and homogenized in a homogenizer (Janke and Kunkel, IKA-Labortechnick, Ultra Turrax T25, Germany) at 8000 rpm for 20 min and then stored in the refrigerator. Ten milliliters of dried biomass suspension was contacted with 90 ml of solution containing a known concentration of dye in an Erlenmayer flask at the desired temperature and pH. Average cell size was found as 135 μm and cell density (ρ_p) was determined as 1045 g l^{-1}. Assuming spherical particles, the surface area per unit weight of dried cells which is equal to ($6X/\rho_p d_p$) (specific surface area) was calculated as 0.213 cm^{-1}.

Chitosan was the other biosorbent purchased from Fluka (84.9% deacetylated) (product number 22743). Chitosan flakes were used without further purification. The particle size, particle density and specific surface area of chitosan flakes were <335 μm, 1669 g l^{-1} and 0.107 cm^{-1}, respectively. For the biosorption studies, 0.1 g of biosorbent was contacted with 100 ml of dye bearing solution at a definite concentration, pH and temperature.

Acid (phosphoric and sulfuric acids) washed powdered activated carbon produced from peat bog (Sigma: product number C-5510) was used as the comparative acid dye adsorbent. It was oven-dried at 110 °C for 24 h and stored in a desiccator until used. The particle size, total surface area, specific surface area and particle density were <150 μm, 1400 cm^2 g^{-1}, 0.245 cm^{-1} and 1630 g l^{-1}, respectively. For the studies, 0.1 g of activated carbon was treated with 100 ml of known concentration dye containing solution at a definite pH and temperature.

2.2. Chemicals

For adsorption studies Acid Blue 161 (color index number: 15706; molecular weight: 394.4; molecular formula: $C_{20}H_{13}N_2O_5SNaCr_x$; dye content: 45%), a commercial monoazo dye, purchased from Sigma–Aldrich (catalog number A4770) was used as received without further purification. The test solutions containing AB 161 dye were prepared by diluting 1.0 g l^{-1} of stock solution of dye which was obtained by dissolving weighed quantity of acidic dye in 1 l of double-distilled water. The range of concentrations of prepared dye solutions changed between 50 and 500 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 mixing the sorbent or biomass suspension. The preliminary studies showed that the initial pH value did not change considerably during the experimental period.

2.3. Sorption studies

Sorption studies were conducted in a routine manner by the batch technique. A number of stoppered Pyrex glass Erlenmeyers containing a definite volume (100 ml in each case) of solutions of AB 161 dye of desired concentration, pH and temperature were placed in a thermostatic rotary shaker. All the final solutions contained 1.0 g l^{-1} of sorbent. The equilibrium and kinetic studies were done at the same time in the same apparatus. The flasks were agitated at a 150 rpm constant shaking rate for 48 h to ensure equilibrium was reached. Samples (5 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. The samples were disposed of in order not to change the solid/liquid ratio in the sorption medium. 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 values were used for further calculations.

2.4. Analysis of dye

The concentrations of unadsorbed AB 161 dye in the biosorption medium were measured colorimetrically using a spectrophotometer (Bausch and Lomb-Spectronic 20D, Milton Roy Company, USA). The absorbance of the color was read at 341 nm.

3. Results and discussion

3.1. Effect of initial pH on dye sorption

The effect of pH is an important factor on the dye-binding capacity of each sorbent. Fig. 1 shows the equilibrium dye uptake at various initial pH values ranging from 1.0 to 7.0 for *T. versicolor* fungal biomass and chitosan, and from 1.0 to 9.0 for PAC. For each pH value, the AB 161 concentration (50 mg l^{-1}), sorbent dosage (1.0 g l^{-1}) temperature (25 °C) and agitation speed (150 rpm) were kept constant. As seen from Fig. 1, the dye sorption was highly pH-dependent. For the biosorbent *T. versicolor*, equilibrium uptake of dye increased notably with raising the pH up to 3.0 and lessened sharply above pH 3.0. On the other hand for chitosan, as pH increased from 1.0 to 3.0, uptake percent increased from 5.1 to 97.8% and remained nearly constant up to pH 7.0. In the case of PAC, with raising the pH, adsorption capacity of PAC for AB 161 increased and reached to a maximum level at the pH range of 3.0–4.0, and uptake capacity did not change significantly up to pH 8.0 and then, the uptake was declined sharply with further increase in pH. Although the sorption of acid dye exhibited a different variation with pH for each sorbent, maximum uptake was obtained at pH 3.0 in each case. It was concluded that solution pH shows a significant influence on the biosorption of AB 161 by *T. versicolor*, but little effect on the sorption of AB 161 by PAC. Data also indicated that chitosan and PAC have higher adsorption capacities (48.5 mg dye g^{-1} of chitosan and 46.6 mg dye g^{-1} of PAC) compared with the biosorption potential of fungal biomass (26.0 mg dye g^{-1} of dried *T. versicolor*).

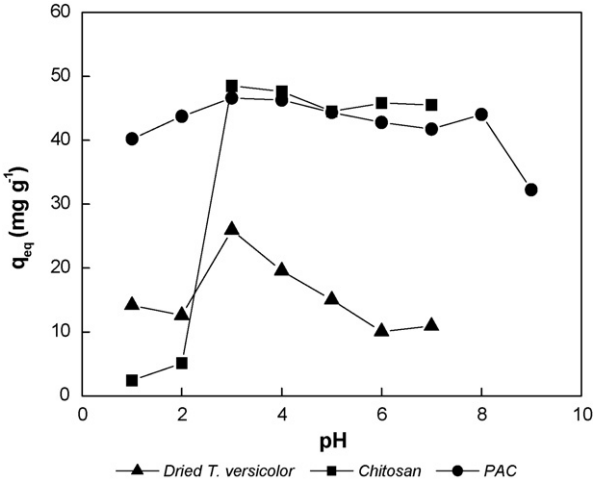

Fig. 1. Effect of initial pH on the equilibrium Acid Blue 161 dye sorption capacity of dried *Trametes versicolor*, chitosan and PAC (C_0: 50 mg l^{-1}, T: 25 °C, X: 1.0 g l^{-1}, agitation rate: 150 rpm).

The interaction between sorbate and sorbent is affected by the pH of an aqueous medium in two ways: firstly, since dyes are complex aromatic organic compounds having different functional groups and unsaturated bonds, they have different ionization potentials at different pH, resulting in the pH-dependent net charge on dye molecules. Secondly, the surface of sorbent include many functional groups, so the net charge on sorbent, which could be measured in the form of zeta potential or isoelectric point, is also pH-dependent. Therefore, the interaction between dye molecules and sorbent is basically a combined result of charges on dye molecules and the surface of sorbent. In the biosorption of AB 161 dye on fungal biomass, the fungal biomass is usually charged negatively on its surface. However at pH values below the isoelectric point (<4.0), the biomass will have a net positive charge due to protonation of nitrogen-containing functional groups such as amines or imadazoles which are the major biosorption sites for dye removal. AB 161 has its vital substituents, sodium sulfonate groups which ionizes into one sodium cation and one colored sulfonate anion in an aqueous solution. It is expected that positively charged functional groups on the sorbent surface will favor the adsorption of negatively charged dye anions due to electrostatic attraction which could be the primary mechanism [23,24,27,28]. In the case of chitosan, as the pK_a value of the amino group (R–NH_2) in the structure of chitosan is 6.3 [36], at lower pH values the deacetylated amino groups in the chitosan flakes will be protonated to form groups –NH_3^+ and subsequently interacted with the sulfonyl groups of acid dye to form the organic complex NH_3^+-OOOSR. In other words, at acidic pH values protonated amino groups will enhance electrostatic attractions between dye anions and adsorption sites of chitosan and increase dye adsorption [30–32]. The results also indicated that pH of dye solution between 3.0 and 7.0 is not a determining factor for the adsorption of this dye by chitosan. The complexes on carbon surface are generally classified as acidic, basic, or neutral. Carboxylic, anhydride, and lactone are acidic groups, while phenolic, carbonyl, quinone and ether groups are neutral or weakly acidic. Acid treatment produces more active acidic surface groups such as carboxyl and lactone, resulting in an increase in the adsorption of anionic dyes so for the PAC used in this study, at all solution pH values lower than pH_{ZPC} (7.4), higher removals of dye were observed. Since the dye species carry negative charge due to sulfonate groups, electrostatic attractions are expected to have a considerable contribution to the overall interactions. Furthermore, dispersive interactions, hydrophobic attraction, physical adsorption and some hydrogen bonding interactions should still be oper-

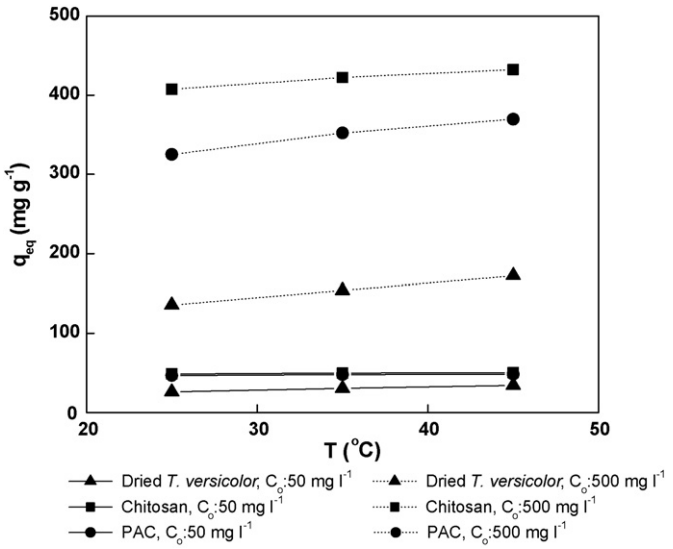

Fig. 2. Effect of temperature on the equilibrium Acid Blue 161 dye sorption capacity of dried *T. versicolor*, chitosan and PAC (initial pH: 3.0, *X*: 1.0 g l^{-1}, agitation rate: 150 rpm).

ative between dye species and PAC surface and can be acting simultaneously [8,11–13].

3.2. Effect of temperature on dye sorption

The effect of temperature on the equilibrium AB 161 dye sorption capacity of each sorbent was investigated in the temperature range of 25–45 °C at varying initial dye concentrations. The results obtained with 50 and 500 mg l^{-1} initial dye concentrations are presented in Fig. 2. As shown in Fig. 2, the adsorption of AB 161 dye enhanced with raising the temperature up to 45 °C for both concentrations studied indicating that a high temperature favored the dye removal by adsorption onto all these sorbents. The data also showed that the effect of temperature is significant at higher dye concentrations. At 50 mg l^{-1} initial dye concentration, the increase in equilibrium uptake capacity of fungal biosorbent, chitosan and PAC with increasing temperature from 25 to 45 °C were 8.2, 1.8, 1.7 mg dye g^{-1} of sorbent, respectively; while these increments raised to 36.9, 24.9, 44.7 mg g^{-1}, respectively, with increasing initial dye concentration up to 500 mg l^{-1}. The enhancement in adsorption with temperature may be attributed to increase in the number of active surface sites available for adsorption on each adsorbent, increase in the porosity and in the total pore volume of the adsorbent. The enhancement in adsorption could be also due to the decrease in the thickness of the boundary layer surrounding the sorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases. This may also be a result of an increase in the mobility of the dye molecule with an increase in their kinetic energy, and the enhanced rate of intraparticle diffusion of sorbate with the rise of temperature. It is clear that the sorption of AB 161 on the three sorbents is an endothermic process and AB 161 dye sorption may involve not only physical but also chemical sorption [22].

3.3. Effect of initial dye concentration on dye biosorption

A higher initial dye concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases, thus increases the uptake. In addition, increasing initial dye concentration increases the number of collisions between dye anions and sorbent, which enhances the sorption process. The effect of initial dye concentration on the dye sorption capacity of each sorbent was investigated between 50 and 500 mg l^{-1} at an initial pH value of 3.0 and at three different temperatures and the results are tabulated in Tables 6–8. Different binding capacities and yields depending on the sorbent, initial dye concentration and temperature were observed. Uptake of the AB 161 dye by the three sorbents enhanced notably with increasing the initial dye concentration tending to saturation at higher dye concentrations. At 45 °C, on changing the initial dye concentration from 50 to 500 mg l^{-1}, the amount sorbed increased from 34.2 to 172.4 mg g^{-1} for *T. versicolor*, from 50.3 to 432.3 mg g^{-1} for chitosan, and from 48.3 to 369.8 mg g^{-1} for powdered activated carbon. At all temperatures studied dye removal was higher for low dye concentrations for all sorbents because of availability of unoccupied binding sites on the sorbents. However color removal diminished with increasing the dye concentration due to nearly complete coverage of the binding sites of sorbents at high dye concentrations. The temperature also remarkably influenced the equilibrium dye uptake as shown in Tables 6–8. At 500 mg l^{-1} initial AB 161 dye concentration, with the raising temperature from 25 to 45 °C the uptake capacity of *T. versicolor* biomass, chitosan and PAC increased from 135.5 to 172.4 mg g^{-1}, from 407.4 to 432.3 mg g^{-1}, and from 325.1 to 369.8 mg g^{-1}, respectively. The results also indicated that the sorption capacity of fungal biosorbent appeared to be the lowest compared with the sorption capacities of other sorbents. At 500 mg l^{-1} initial dye concentration, biosorbent was only capable of removing 135.5 mg g^{-1} of dye from an aqueous solution at 25 °C.

3.4. Sorption behavior of dye

Kinetics of sorption describing the pollutant uptake rate is one of the important characteristics defining the efficiency of sorption and feasibility of adsorbent for its use in water pollution control. Hence, the kinetics of AB 161 dye removal has been carried out to understand the dye adsorption behavior of the three sorbents with respect to concentration and temperature. For this purpose, adsorption capacity (q) was plotted as a function of time for each sorbent at 50 and 500 mg l^{-1} of initial dye concentrations at 25, 35 and 45 °C (Fig. 3). Although the adsorption studies were carried out for 48 h in order to determine the effect of time on sorption, the data in Fig. 3 indicated that 24 h of adsorption is sufficient to reach equilibrium for dried *T. versicolor* and chitosan sorbents while the equilibrium is established within the first 4 h for PAC. For the given concentrations and temperatures, the amount of dye adsorbed was dependent on time, concentration and temperature for each dye–sorbent system. The extent of dye removal increased with increasing

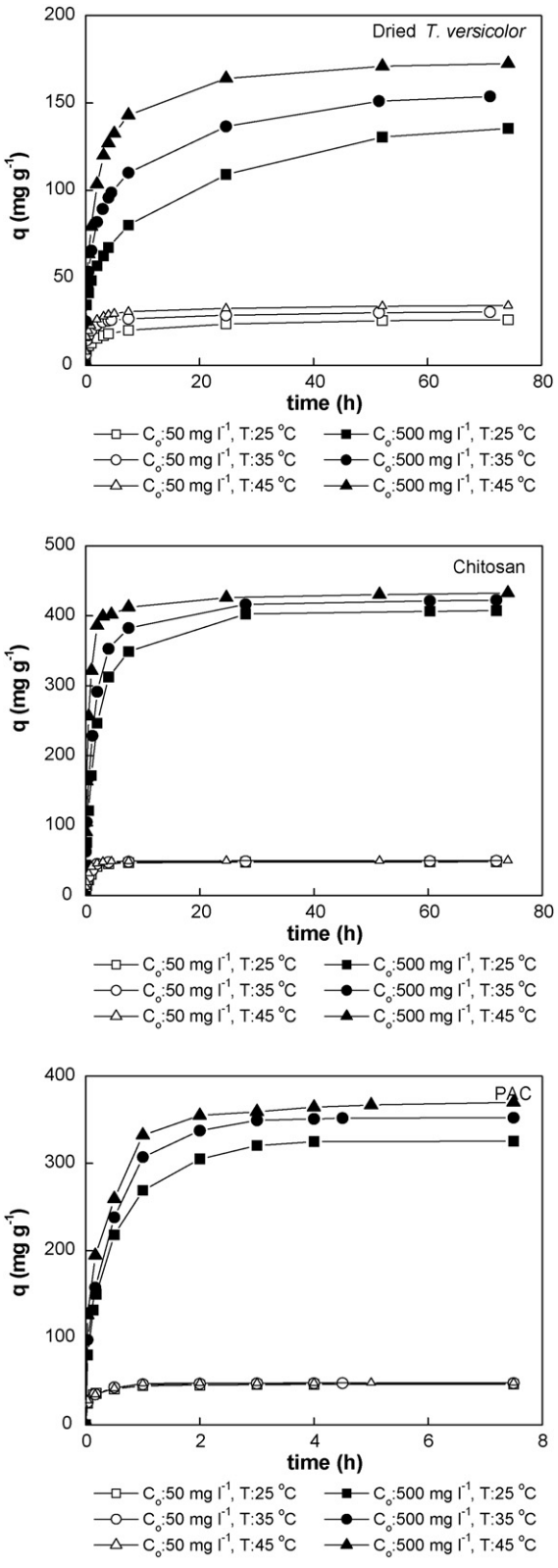

Fig. 3. The sorption curves of AB 161 dye obtained at 50 and 500 mg l^{-1} initial dye concentrations and at different temperatures (initial pH: 3.0, *X*: 1.0 g l^{-1}, agitation rate: 150 rpm).

contact time linearly in the beginning, then non-linearly at a slower rate and finally attained saturation called the equilibrium time (linear portions of the curves reflects surface layer diffusion while the plateau portions of the curves correspond to pore diffusion). The equilibrium time was influenced remarkably by the variation of concentration and increased with the increasing dye concentration for each sorbent. The data indicated that a contact time ranging from about 7.5 to 24 h for dried *T. versicolor*, from about 4 to 24 h for chitosan and from about 1 to 4 h for PAC depending on concentration was sufficient to achieve equilibrium and adsorption did not change subsequently up to 48 h. The time profiles of dye uptake are single, smooth, and continuous curves leading to saturation, suggesting the possible monolayer coverage of dye on the surfaces of the three sorbents.

The comparison of the kinetic curves showed that the initial rate of AB 161 dye sorption onto fungal biomass is relatively lower than that obtained onto other sorbents. Differences between adsorption rates seemed more marked at the beginning of adsorption; the observed variation decreased with time. In the case of PAC, for all initial dye concentrations and temperatures studied, initial sorption of dye occurred much more rapidly and the majority of dye uptake took place within the first hour of contact. For dried *T. versicolor* and chitosan sorbents the time required for the major dye uptake changed from 3 to 7.5 h and from 2 to 4 h, respectively, due to initial dye concentration. At 25 °C for 1.0 g l^{-1} sorbent and 500 mg l^{-1} initial AB 161 concentration, the amount of dye adsorbed on PAC sorbent was 269.0 mg g^{-1}, respectively (82.6% of total adsorbed dye) at an initial adsorption time of 1 h. However, in a similar initial time period (1 h) the amount of AB 161 adsorbed on dried fungus and chitosan were only 48.5 (35.8% of total adsorbed dye) and 171.3 mg g^{-1} (42.0% of total adsorbed dye), respectively. Such a rapid uptake of AB 161 by PAC indicates that this sorbent has an affinity for the dye anions pointing towards physical adsorption and that the uptake of dye occurs predominantly by surface binding and that available sites on the sorbents are the limiting factor for the sorption.

As seen from Fig. 3, at 25 °C AB 161 equilibrium dye uptakes by the sorbents of dried *T. versicolor*, chitosan and PAC increased from 26.0 to 135.5 mg g^{-1}, from 48.5 to 407.4 mg g^{-1} and from 46.6 to 325.1 mg g^{-1}, respectively, with the rise in initial concentration from 50 to 500 mg l^{-1}. It is clear that the adsorption capacity of chitosan and PAC sorbents are considerably higher than that of fungal biosorbent. According to data given in Fig. 3, AB 161 dye uptake capacity of all sorbents also increased with increasing the temperature from 25 to 45 °C. For 500 mg l^{-1} initial dye concentration 48.5, 65.5 and 79.2 mg g^{-1} dye was removed by fungal biomass in the first 1 h of contact time at 25, 35 and 45 °C, respectively. For the same initial dye concentration and time range, chitosan adsorbed up 171.3, 228.5 and 321.5 mg g^{-1} AB 161 dye at 25, 35 and 45 °C, respectively. The study also revealed that 269.0, 307.3 and 332.5 mg g^{-1} adsorption took place within the first hour of contact by PAC at 25, 35 and 45 °C, respectively. Removal of the tested dye exhibited that the sorbents have different capacities in the order chitosan > PAC > dried *T. versicolor*. This may due to the sur-

face and micropore–macropore areas, structure and active sites differences between the sorbents.

3.5. Equilibrium modelling

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, describe how adsorbates interact with adsorbents and so are critical in optimizing the use of adsorbents and provide information on the capacity of the adsorbent. In order to discover the sorption capacity of three sorbents for AB 161 acidic dye, the experimental data points were fitted to the Langmuir, Freundlich, Redlich–Peterson and Langmuir–Freundlich empirical models which are the most frequently used two- and thee-parameter equations in the literature describing the non-linear equilibrium between adsorbed pollutant on the cells (q_{eq}) and pollutant in solution (C_{eq}) at a constant temperature.

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:

$$q_{eq} = \frac{Q_{max} b C_{eq}}{1 + b C_{eq}} \quad (1)$$

where parameters Q_{max} and b are Langmuir constants related to maximum adsorption capacity and bonding energy of adsorption, respectively [38].

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:

$$q_{eq} = K_F C_{eq}^{1/n} \quad (2)$$

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 [39].

The further three-parameter empirical Redlich–Peterson model is widely used as a compromise between Langmuir and

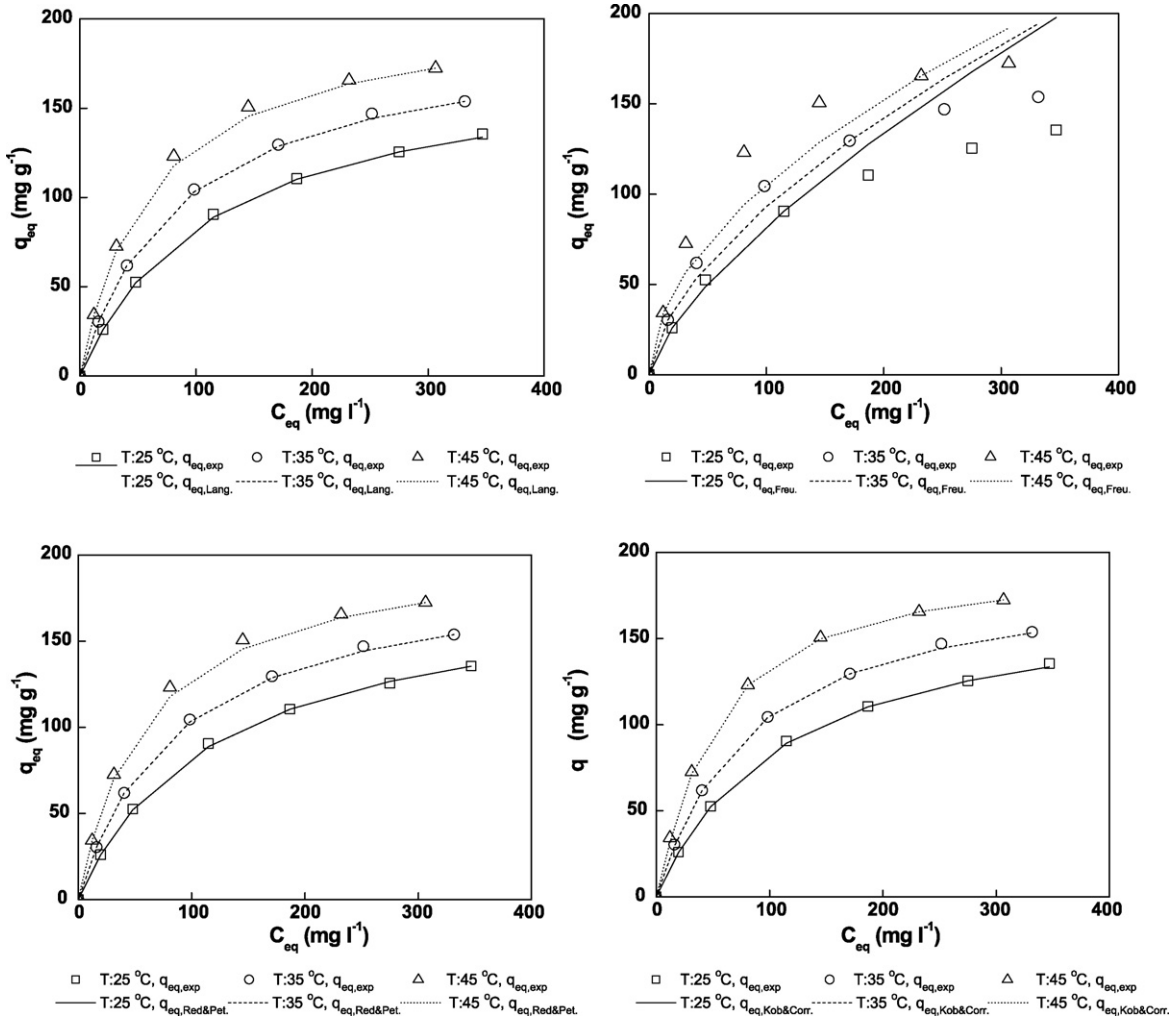

Fig. 4. The comparison of the experimental and estimated adsorption isotherms of AB 161 dye obtained at different temperatures for dried *T. versicolor* (initial pH: 3.0, *X*: 1.0 g l^{-1}, agitation rate: 150 rpm).

Freundlich systems and the non-linear form of the model is given by Eq. (3). It has a linear dependence on concentration in the numerator and an exponential function in the denominator:

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

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 [40].

Langmuir–Freundlich model is another three-parameter empirical model for the representing equilibrium biosorption data. It is a combination of the Langmuir and Freundlich isotherm type models and is given by

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

where A, B and m are the Langmuir–Freundlich parameters. This model is valid when $m > 1$.

The experimental equilibrium data of AB acidic dye on dried *T. versicolor*, chitosan and PAC obtained at three different temperatures were given in Figs. 4–6. All the isotherms are positive, regular and concave to the concentration axis (showing increasing the uptake of dye with increasing equilibrium dye concentration) indicating an affinity for sorption. The equilibrium uptake of the dye anions also enhanced with a rise in temperature thereby indicating the process to be endothermic. The isotherm curves of chitosan and PAC sorbents obtained at different temperatures indicated a limiting sorption capacity attained at initial concentrations of about 400–500 mg l^{-1}, respectively. *T. versicolor* exhibited the lowest uptake of AB 161 dye and adsorption equilibrium reached saturation at relatively lower concentrations (200–300 mg l^{-1}) over the concentration and temperature ranges involved. However all cases exhibited a complete monolayer of dye covering the surface of each sorbent.

The relative model parameters the values of which express the surface properties and affinity of each sorbent were estimated by non-linear regression analysis at different temperatures and are tabulated in Tables 1–4 with the average percentage errors. The average percentage error between the experimental and predicted values are calculated using Eq. (5) [41]. In Eq. (5), the subscripts 'exp' and 'calc' show the experimental and calculated values and N the number of measurements:

$$\varepsilon\,(\%) = \frac{\sum_{i=1}^{N} |(q_{eq,i,exp} - q_{eq,i,calc})/q_{eq,i,exp}|}{N} \times 100 \quad (5)$$

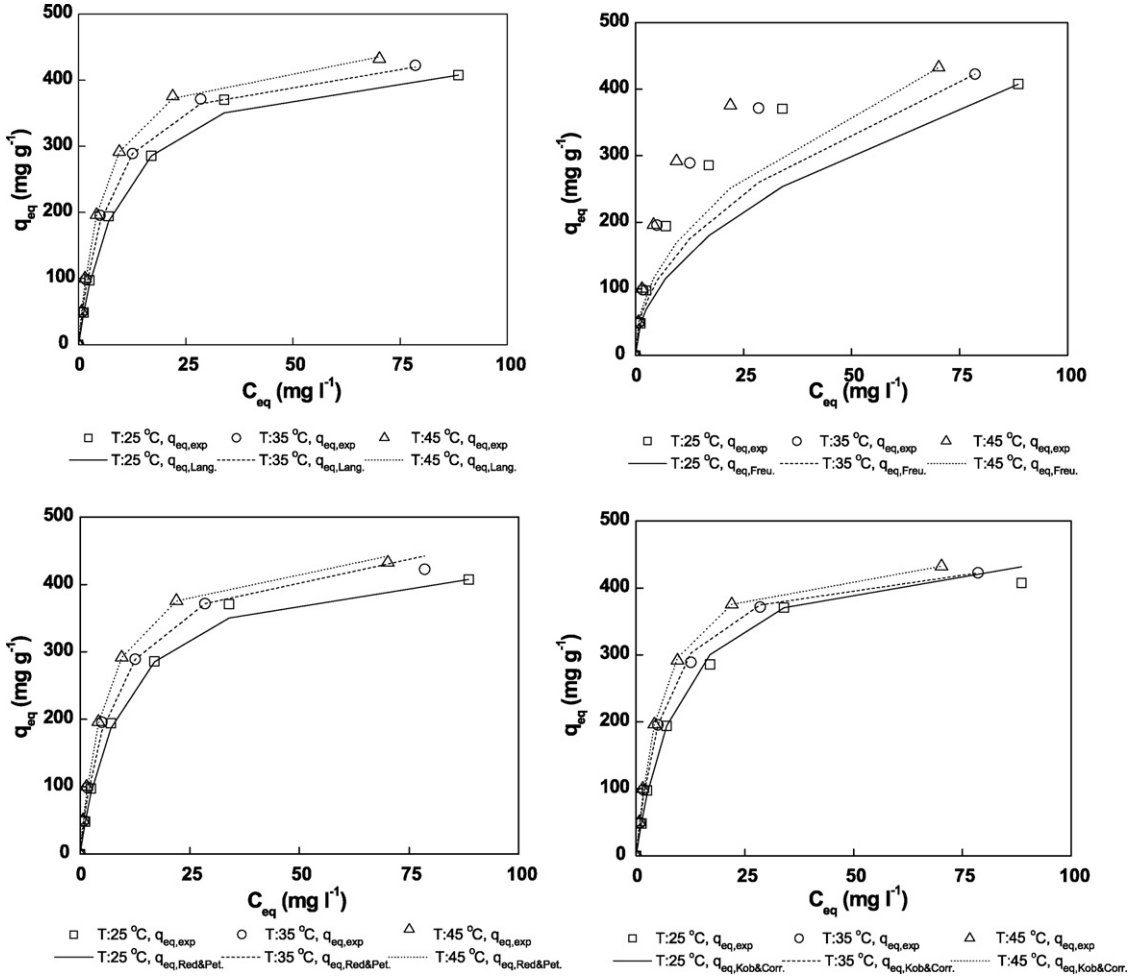

Fig. 5. The comparison of the experimental and estimated adsorption isotherms of AB 161 dye obtained at different temperatures for chitosan (initial pH: 3.0, X: 1.0 g l^{-1}, agitation rate: 150 rpm).

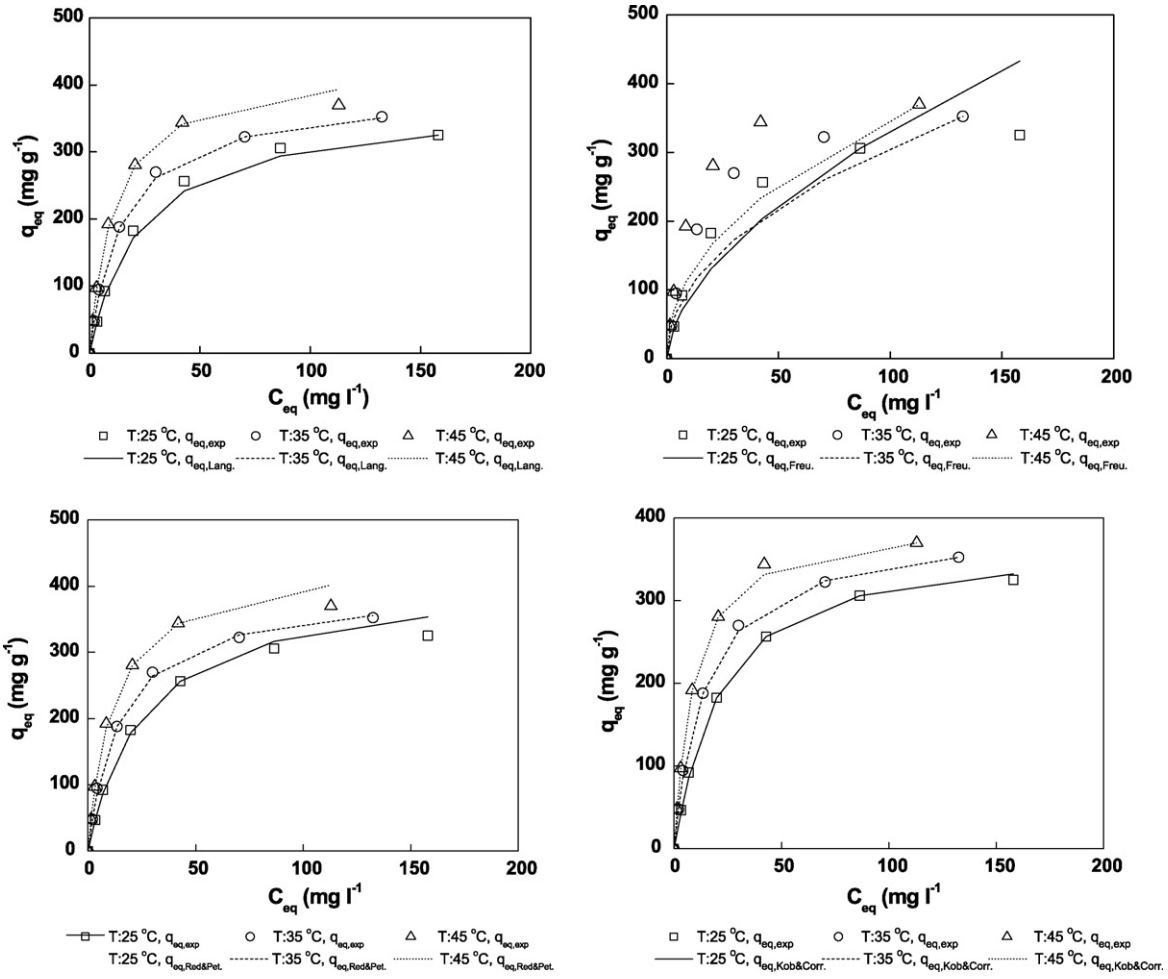

Fig. 6. The comparison of the experimental and estimated adsorption isotherms of AB 161 dye obtained at different temperatures for PAC (initial pH: 3.0, X: 1.0 g l^{-1}, agitation rate: 150 rpm).

The magnitude of average percentage errors was the criteria for the selection of the most suitable isotherm model. On the basis of average percentage errors in Table 2, the adsorption equilibrium data of AB 161 dye fitted very well to the Langmuir model in the concentration and temperature ranges studied for all sorbents. Moreover, the Redlich–Peterson and Langmuir–Freundlich models are also found to satisfactorily describe the adsorption isotherms of acid dye over the whole concentration and temperature ranges studied in all sorbent systems with the percentage error values lower than 4.14% in all cases. However the other two-parameter model of Freundlich exhibited a poor fit to the sorption data of AB 161 dye with an

Table 1
Comparison of the Freundlich adsorption constants of AB 161 dye adsorption on dried *Trametes versicolor*, chitosan and PAC at different temperatures

Temperature (°C)	K_F ((mg g^{-1})(mg l^{-1})$^{-1/n}$)	n	ε (%)
T. versicolor			
25	3.15	1.41	17.05
35	5.53	1.63	10.53
45	9.01	1.87	11.77
Chitosan			
25	44.32	2.02	22.86
35	52.17	2.09	23.92
45	59.36	2.14	24.22
PAC			
25	23.39	1.73	17.39
35	33.89	2.09	20.25
45	41.28	2.16	23.76

Table 2
Comparison of the Langmuir adsorption constants of AB 161 dye adsorption on dried *T. versicolor*, chitosan and PAC at different temperatures

Temperature (°C)	Q_{max} (mg g^{-1})	b ($\times 10^2$ l mg^{-1})	ε (%)
T. versicolor			
25	178.3	0.86	0.64
35	193.9	1.15	0.63
45	206.8	1.63	1.96
Chitosan			
25	454.0	9.97	2.74
35	459.8	13.44	3.57
45	471.6	17.04	1.40
PAC			
25	372.7	4.33	3.63
35	389.8	6.82	2.09
45	432.2	8.98	2.18

Table 3
Comparison of the Redlich–Peterson adsorption constants of AB 161 dye adsorption on dried *T. versicolor*, chitosan and PAC at different temperatures

Temperature (°C)	K_{RP} ($l\,g^{-1}$)	a_{RP} ($(\times 10^2\,l\,mg^{-1})^{\beta}$)	β	ε (%)
T. versicolor				
25	1.56	1.00	0.975	0.60
35	2.24	1.15	1.000	0.63
45	3.38	1.63	1.000	1.96
Chitosan				
25	45.25	9.97	1.000	2.75
35	62.55	14.94	0.966	4.14
45	77.93	16.21	1.000	2.42
PAC				
25	15.91	3.87	1.000	3.31
35	26.52	6.70	1.000	2.10
45	39.01	9.46	0.985	2.53

average percentage error more than 10.53%. The suitability of Langmuir model shows that the sorption process is monolayer and has a constant adsorption energy.

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 1, all measured values of K_F showed easy uptake of the acid dye with high adsorptive capacity of each sorbent and significant differences in sorption capacities among the three sorbents with respect to temperature. Although the value of K_F increased with the rise in temperature for each sorbent, the highest values of K_F were determined to be 9.01, 59.36 and 41.28 for *T. versicolor*, chitosan and PAC sorbents, respectively, at 45 °C. 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 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 favorably adsorbed on an adsorbent, corresponds to a normal an L-type Langmuir isotherm, and the higher the n value the stronger the adsorption intensity.

Table 4
Comparison of the Langmuir–Freundlich adsorption constants of AB 161 dye adsorption on dried *T. versicolor*, chitosan and PAC at different temperatures

Temperature (°C)	A ($l^m\,mg^{1-m}\,g^{-1}$)	B ($(\times 10^2\,l\,mg^{-1})^m$)	m	ε (%)
T. versicolor				
25	1.50	0.85	1.010	0.50
35	1.89	1.01	1.050	0.90
45	2.11	1.09	1.155	1.62
Chitosan				
25	44.81	9.35	1.020	2.78
35	62.31	13.78	1.062	2.75
45	73.77	16.02	1.073	3.77
PAC				
25	13.02	3.56	1.115	2.54
35	26.46	6.77	1.005	1.85
45	37.01	9.41	1.082	1.40

Table 2 also indicated that n is greater than unity, indicating that AB 161 dye is favorably adsorbed by all the sorbents at all temperatures studied.

Langmuir sorption model serves to estimate the maximum uptake value or the total capacity of the adsorbent for the dye (Q_{max}) where it could not be reached in the experiments. The constant b represents affinity between the sorbent and sorbate. Values of Q_{max} and b calculated from the Langmuir model at different temperatures are tabulated in Table 2. The Langmuir model parameters were largely dependent on the type of sorbent and temperature. Both Q_{max} and b increased with increasing temperature up to 45 °C for all sorbents. AB 161 dye uptake by chitosan at 45 °C was the greatest with a maximum value of 471.6 mg g^{-1}, while maximum uptake capacities of PAC and dried *T. versicolor* were 432.2 and 206.8 mg g^{-1}, respectively, at 45 °C. All the values of Q_{max} were higher for the chitosan–dye system in comparison with the maximum uptakes of other sorbents. The other 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 AB 161 amount of $Q_{max}/2$ is bound) so a high value of b, indicates a steep desirable beginning of the isotherm which reflects the high affinity of the sorbents for the sorbate resulting in a stable adsorption product. The higher values of b obtained for chitosan–dye system implied the most strong bonding of dye to chitosan.

Related Redlich–Peterson adsorption parameters calculated according to the three-parameter Redlich–Peterson isotherm model were listed in Table 3 for each sorbent at three different temperatures. The model parameter K_{RP} also indicated that the adsorption capacity of each sorbent increased with increasing temperature and reached maximum at 45 °C. The exponent β was approximately 1.0 for all cases, showing the closeness of the model to the Langmuir isotherm.

The corresponding Langmuir–Freundlich parameters of A, B and m for different temperatures along with percentage errors are given in Table 4 for each AB 161 dye–sorbent system. Langmuir–Freundlich constant A indicates the adsorption capacity and affinity of each sorbent to acidic dye, was found maximum at 45 °C for all the sorbents. The capacity constant of chitosan appeared to be significantly higher in comparison with the capacity constants of PAC and dried *T. versicolor* sorbents.

3.6. Kinetic modelling

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 surrounding 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. Batch studies were carried out to identify the potential rate-controlling steps for the acid dye sorption and to determine external film mass transfer coefficient and intraparticle diffusion coefficient. Moreover simple pseudo-second-order kinetic model has also been used to test the dynamics of sorption process and attempts were made to calculate the coefficients of this model.

In the first step of adsorption, the film diffusion (external mass transfer) is an important rate-controlling step and is characterized by the initial rate of solute diffusion for the system studied. The change of dye concentration with respect to time can be written as follows:

$$\frac{dC}{dt} = -k_L A(C - C_s) \quad (6)$$

where C is the bulk liquid-phase concentration of dye at a time t, C_s the surface concentration of dye, k_L the external mass transfer coefficient and A is 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. (6) can be simplified as

$$\left[\frac{d(C/C_0)}{dt}\right] = -k_L A \quad (7)$$

Assuming the adsorbent particles are spherical, A is calculated from Eq. (8):

$$A = \frac{6X}{d_p \rho_p} \quad (8)$$

where X is the sorbent concentration in the solution ($1.0\ g\ l^{-1}$), d_p the average particle diameter and ρ_p is the density of the sorbent. By plotting C/C_0 against t, the value of k_L may be determined from the slope at $t = 0$ [9,42].

The plots of C/C_0 versus t obtained at all initial dye concentrations and at 25, 35 and 45 °C temperature values for each sorbent (data not shown) indicated that the concentration of dye falls very fast during the initial uptake before intraparticular diffusion could begin to control the adsorption kinetics for all cases. Then, increase in contact time (or decrease in external diffusion rate) reduced the boundary layer resistance and thereby enhanced the mobility of dye during adsorption. For the initial uptake phase, the kinetic data were fitted to Eq. (7) and the external mass transfer coefficients were determined from the slopes as $t \to 0$ and presented in Table 5 for each case. The findings show that the increase in initial dye concentration resulted in a decrease in the initial rate while varying the temperature from 25 to 45 °C increased the external diffusion for all sorbents. In general the values of k_L shown in Table 5 suggest that in the acid dye adsorption by both chitosan and PAC sorbents, boundary layer effect was close to minimum values. It is clear that, as expected, external mass transfer resistance cannot be neglected even for a high agitation speed, although this resistance is only significant for the initial period of sorption time.

In the model developed by Weber and Morris [43] the rate of intraparticular diffusion is a function of $t^{0.5}$ and can be defined as follows:

$$q = f\left(\frac{Dt}{r_p^2}\right)^{0.5} = Kt^{0.5} \quad (9)$$

where r_p is the particle radius, D the effective diffusivity of solutes within the particle, and K is the 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. A good correlation of rate data in this model can justify the mechanism and K values can be obtained by linearizing the curve $q = f(t^{0.5})$ [44].

The plots of the amount of AB 161 dye per unit weight of sorbent (q) against the square root of time ($t^{0.5}$) at all initial AB 161 concentrations and at 25, 35 and 45 °C temperatures for each sorbent (data not shown) revealed that all the plots have the same general feature presenting multi-linearity, indicating that a few steps took place. The first, sharper portion obtained in very beginning period which extent is related to initial dye concentration and temperature, is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second linear portion describes the gradual layer adsorption stage, where intraparticle diffusion is rate limiting. The third portion is attributed to the final equilibrium stage for which the intraparticle diffusion started to slow down due to the extremely low dye concentration left in the solution. The linear plots of second portion at each concentration and temperature did not pass through the origin, this is indicative of some degree of boundary layer control and this shows further that the intraparticle diffusion is not only rate-controlling step. The values of K evaluated from these linear parts of plots are also tabulated in Table 5. These are rate parameters with units $mg\ g^{-1}\ min^{-0.5}$ and as such, are not a direct quantification of the rates. 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 and temperature of solution for all sorbents. This may be due to a greater driving force with increasing C_0 resulted in reducing the diffusion of dye anions in the boundary layer and enhancing the diffusion in the solid. At all temperatures when C_0 is increased from 50 to $400\ mg\ l^{-1}$ for chitosan and PAC, and from 50 to $200\ mg\ l^{-1}$ for dried fungus, there is a marked effect of concentration on the rate of intraparticular dye diffusion. Above these concentrations the effect is small. As shown in Table 5, increasing the temperature promoted the pore diffusion in all sorbent particles and resulted in an enhancement in the intraparticle diffusion rate. Weber and Morris [43] has also stated that, since diffusion is an endothermic process, the rate of sorption will increase with increased solution temperature when

Table 5
Effect of initial AB 161 dye concentration and temperature on the external mass transfer coefficients (k_L) and intraparticle diffusion rate constants (K)

25 °C			35 °C			45 °C		
C_0 (mg l^{-1})	k_L ($\times 10^2$ cm min^{-1})	K (mg g^{-1} min$^{-0.5}$)	C_0 (mg l^{-1})	k_L ($\times 10^2$ cm min^{-1})	K (mg g^{-1} min$^{-0.5}$)	C_0 (mg l^{-1})	k_L ($\times 10^2$ cm min^{-1})	K (mg g^{-1} min$^{0.5}$)
Dried *T. versicolor*								
45.8	25.7	0.86	46.5	30.3	1.14	46.3	38.1	1.29
100.5	15.2	1.92	102.5	19.5	3.00	104.0	21.5	3.93
205.5	12.0	2.43	203.0	13.1	3.97	203.9	13.3	5.67
297.5	11.7	2.80	300.5	12.9	4.65	295.6	13.1	6.14
400.5	11.1	2.86	398.7	12.1	5.13	397.5	12.4	7.03
482.5	10.9	2.89	485.5	11.9	5.19	479.0	12.3	7.29
Chitosan								
49.7	63.3	3.54	50.5	90.4	3.54	51.0	117.8	4.40
100.0	60.6	5.57	100.5	87.6	6.65	101.7	105.4	8.35
201.0	56.8	9.17	200.5	86.0	13.14	200.4	100.0	16.00
302.5	51.6	14.30	301.6	68.0	20.45	301.0	99.1	23.63
404.5	43.8	18.41	400.0	58.8	23.36	397.5	80.9	31.25
496.0	40.9	21.95	501.0	58.6	24.14	502.5	84.4	32.21
PAC								
49.9	89.1	2.41	49.9	94.6	2.49	49.7	103.9	2.75
99.1	88.2	3.78	99.0	89.1	4.02	100.5	101.6	4.08
202.3	55.9	16.32	201.5	59.4	17.00	200.5	66.0	17.30
299.4	41.6	24.73	300.0	48.1	25.04	301.1	54.2	25.53
392.5	33.6	31.09	392.8	39.2	31.34	386.0	48.3	32.05
483.5	30.4	32.33	485.0	36.9	32.68	483.0	47.3	33.25

Table 6
Comparison of the second-order rate constants and calculated and experimental q_{eq} values obtained at different initial AB 161 concentrations and at different temperatures for dried *T. versicolor*

Temperature (°C)	C_0 (mg l^{-1})	$q_{eq,exp}$ (mg g^{-1})	$k_{2,ad}$ ($\times 10^4$ g mg^{-1} min^{-1})	$q_{eq,calc}$ (mg g^{-1})	R^2
25	45.8	26.0	4.88	26.2	0.999
	100.5	52.5	2.63	52.9	0.999
	205.5	90.5	0.79	92.7	0.997
	297.5	110.5	0.53	113.4	0.993
	400.5	125.5	0.45	128.2	0.994
	482.5	135.5	0.44	137.5	0.993
35	46.5	30.4	8.29	30.5	1.000
	102.5	61.9	3.41	62.5	1.000
	203.0	104.5	0.94	106.4	0.999
	300.5	129.5	0.87	131.9	0.999
	398.7	147.0	0.60	149.7	0.998
	485.5	153.8	0.59	156.0	0.998
45	46.3	34.1	8.34	34.3	1.000
	104.0	72.5	3.59	73.0	1.000
	203.9	123.0	0.98	125.0	0.999
	295.6	150.5	0.91	152.7	1.000
	397.5	165.5	0.84	167.8	1.000
	479.0	172.4	0.82	174.8	1.000

intraparticle transport is the rate-limiting step. The higher values of K also indicate the more rapid uptake of AB 161 dye by PAC and chitosan sorbents. As a result it could be said that the sorption of AB 161 dye onto dried *T. versicolor*, chitosan and PAC particles was controlled due to film diffusion at earlier stages and as the adsorbent particles were loaded with dye ions, the sorption process was controlled due to intraparticle diffusion.

On the other hand pseudo-second-order kinetic model [45] can be used to test the adsorption kinetics. This model basically include all steps of adsorption such as external film diffusion, adsorption, and internal particle diffusion, so it is pseudo-model. The model is 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 biosorption. After integration and applying the boundary conditions of $t = 0$ to t and $q = 0$ to q; the integrated form of Eq. (10) becomes

$$\frac{t}{q} = \frac{1}{k_{2,ad}q_{eq}^2} + \frac{1}{q_{eq}}t \tag{11}$$

Table 7
Comparison of the second-order rate constants and calculated and experimental q_{eq} values obtained at different initial AB161 concentrations and at different temperatures for chitosan

Temperature (°C)	C_0 (mg l^{-1})	$q_{eq,exp}$ (mg g^{-1})	$k_{2,ad}$ ($\times 10^4$ g mg^{-1} min^{-1})	$q_{eq,calc}$ (mg g^{-1})	R^2
25	49.7	48.5	8.64	48.6	1.000
	100.0	97.5	2.45	98.4	1.000
	201.0	194.0	0.84	196.5	1.000
	302.5	285.5	0.55	289.8	1.000
	404.5	370.5	0.39	375.5	1.000
	496.0	407.4	0.35	413.2	1.000
35	50.5	49.6	11.94	49.7	1.000
	100.5	98.8	5.44	99.1	1.000
	200.5	195.5	2.08	196.6	1.000
	301.6	289.0	1.16	290.7	1.000
	400.0	371.5	0.56	375.9	1.000
	501.0	422.4	0.51	425.5	1.000
45	51.0	50.3	18.06	50.3	1.000
	101.7	100.2	8.17	100.3	1.000
	200.4	196.3	4.91	196.7	1.000
	301.0	291.5	2.57	292.4	1.000
	397.5	375.5	1.47	377.1	1.000
	502.5	432.3	1.33	432.9	1.000

If second-order kinetics are applicable, the plot of t/q against t of Eq. (11) should give a linear relationship, from which q_{eq} and $k_{2,ad}$ can be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand. The rate constant is also expressed as a function of temperature by the following Arrhenius type relationship:

$$k_{2,ad} = A_0 \exp\left(\frac{-E_A}{RT}\right) \quad (12)$$

where A_0 is the frequency factor of sorption and E_A is the activation energy of sorption. When $\ln k_{2,ad}$ is plotted versus $1/T$, a straight line with slope $-E_A/R$ is obtained. The magnitude of activation energy may give an idea about the type of sorption.

Using Eq. (11), t/q was plotted against t for all initial AB 161 concentrations at 25, 35 and 45 °C temperatures for each sorbent and second-order adsorption rate constant ($k_{2,ad}$) and equilibrium uptake values (q_{eq}) were determined from the slope and intercept of the plots (data not shown). The values of the parameters $k_{2,ad}$ and q_{eq} and of correlation coefficients are also presented in Tables 6–8 for each acid dye–sorbent system. As seen from the tables, all the second-order rate constants diminished with increasing initial dye concentration. As expected the rise in temperature up to 45 °C enhanced the second-order rate constants of AB 161 dye sorption to each sorbent. The results also show that PAC particles adsorbed the dye anions much more rapidly than that of other sorbents for all cases. The correlation coefficients for the second-order kinetic model are obtained greater than 0.993 for all sorbents studied. The theoretical q_{eq} values also agreed very well with the experimental q_{eq} values in the case of pseudo-second-order kinetics. These suggest that each of the sorption process may be best described by the pseudo-second order with intraparticle diffusion as one of the rate determining steps with fairly high correlation coefficients.

Dependence of adsorption rate constants on temperature gives valuable information about the activation energy of adsorption. Two main types of adsorption may occur: physical and chemical adsorption. In physical adsorption equilibrium is usually rapidly attained and easily reversible, because the energy requirements are small (usually no more than 4.2 kJ mol^{-1}), since the forces involved in physical adsorption are weak. Chemical adsorption is specific and involves forces much stronger than in physical adsorption. So the activation energy for chemical adsorption is of the same magnitude as the heat of chemical reactions (between 8.4 and 83.7 kJ mol^{-1}) in the Arrhenius equation. The activation energies of the sorption processes of AB 161 dye on dried *T. versicolor*, chitosan and PAC were found as 24.5, 52.4 and 8.6 kJ mol^{-1}, respectively, from the slopes of corresponding $\ln k_{2,ad}$ versus $1/T$ plots ($R^2 = 0.997$, 0.931 and 0.987, respectively) in the temperature range studied. The findings showed that acid dye sorption process is endothermic and involves chemical sorption for dried *T. versicolor* and chitosan sorbents. For PAC this value is of the same magnitude as the lower limit activation energy of chemical adsorption showing both mainly chemical and partly physical sorption.

3.7. Thermodynamic modelling of adsorption

Thermodynamic parameters of free energy change, enthalpy change and entropy change can be estimated using equilibrium constants changing with temperature. The sorption process of AB 161 dye can be summarized by the following reversible process which represents a heterogeneous equilibrium:

$$\text{dye in solution} \leftrightarrow \text{dye–sorbent} \quad (13)$$

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

$$K'_c = \frac{C_{ad,eq}}{C_{eq}} \quad (14)$$

Table 8
Comparison of the second-order rate constants and calculated and experimental q_{eq} values obtained at different initial AB161 concentrations and at different temperatures for PAC

Temperature (°C)	C_0 (mg l^{-1})	$q_{eq,exp}$ (mg g^{-1})	$k_{2,ad}$ ($\times 10^4$ g mg^{-1} min^{-1})	$q_{eq,calc}$ (mg g^{-1})	R^2
25	49.9	46.6	69.13	46.9	1.000
	99.1	93.0	35.59	92.5	1.000
	202.3	182.5	7.65	185.5	1.000
	299.4	263.9	3.71	258.1	1.000
	392.5	306.0	2.76	316.5	0.999
	483.5	325.1	2.51	335.6	0.999
35	49.9	47.8	75.25	48.1	1.000
	99.0	95.1	36.64	95.4	1.000
	201.5	188.0	8.83	190.8	1.000
	300.0	270.0	3.95	277.0	1.000
	392.8	322.5	2.98	331.1	1.000
	485.0	352.4	2.75	363.3	0.999
45	49.7	48.3	77.00	48.6	1.000
	100.5	97.4	45.23	97.9	1.000
	200.5	192.0	9.98	194.9	1.000
	301.1	280.5	4.12	286.5	1.000
	386.0	344.0	3.15	352.1	1.000
	483.0	369.8	3.12	377.4	1.000

where $C_{ad,eq}$ is the concentration of dye on the sorbent at equilibrium. When 1 g l^{-1} of sorbent is used, the value of $C_{ad,eq}$ will give the value of q_{eq} and the apparent equilibrium constant (K'_c) will be equal to

$$K'_c = \frac{q_{ad,eq}}{C_{eq}} \quad (15)$$

The standard thermodynamic equilibrium constant (K^0_c) of the sorption system can be obtained by calculating the apparent equilibrium constants (K'_c) at different initial concentrations of dye and extrapolating the data to zero. This value will be also equal to the opposite of intercept value of C_{eq}/q_{eq} versus C_{eq} plot ($=bQ_{max}$) at 25 °C, which shows the linearized form of Langmuir equation. The K^0_c value is used in the following equation to determine the free energy change of the adsorption reaction (Gibbs free energy) (ΔG°) at 25 °C:

$$\Delta G^\circ = -RT \ln K^0_c \quad (16)$$

where R is the universal gas constant and T is the absolute temperature. The free energy change indicates the degree of spontaneity of the sorption process and the higher negative value reflects a more energetically favorable adsorption. The equilibrium constant may be expressed in terms of enthalpy change of sorption (ΔH°) and entropy change of sorption (ΔS°) as a function of temperature. The relationship between the K^0_c and temperature is given by the van't Hoff equation:

$$\ln K^0_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (17)$$

ΔH° and ΔS° can be obtained from the slope and intercept of a van't Hoff plot of ln K^0_c versus $1/T$.

The values of K^0_c at 25 °C evaluated from the q_{eq}/C_{eq} versus C_{eq} plots for dried *T. versicolor*, chitosan and PAC sorbents (data not shown) as 1.54, 45.25 and 16.12, respectively, were used to find the ΔG° values of each dye–sorbent system. Using Eq. (16), the values of standard Gibbs free energy change (ΔG°) were calculated for each sorbate–sorbent system and presented in Table 9. The negative values of ΔG° confirm the feasibility of the processes and spontaneous nature of adsorptions at 25 °C with a high degree of affinity of the dye molecules for each sorbent surface. The standard enthalpy and entropy changes of each adsorption process were determined from the ln K^0_c versus $1/T$ plots (data not shown) and are also presented in Table 9. The positive values of ΔH° for all the processes suggest the endothermic nature of adsorption favorable at higher temperatures and possible strong bonding between dye and each sorbent while positive ΔS° values reflect the affinity of all sorbents to dye in solution and some structural changes in sorbate and sorbents.

Table 9
Comparison of the standard thermodynamic constants of AB 161 dye adsorption on dried *T. versicolor*, chitosan and PAC sorbents

Sorbent	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})
Dried *T. versicolor*	−1.07	30.94	0.107
Chitosan	−9.45	22.66	0.108
PAC	−6.89	34.67	0.139

4. Conclusion

Dried white-rot fungus *T. versicolor* and a fungal component chitosan have been utilized as biosorbents for the removal of Acid Blue 161 dye from aqueous solution and the results were compared with those obtained with acid-washed powdered activated carbon. Results show that a pH value of 3.0 is favorable for the adsorption of acid dye for the three sorbents. AB 161 dye removal is also temperature-dependent and found to be maximum at 45 °C for each sorbent. It was seen that sorption can be accomplished with a high uptake capacity by increasing the dye concentration up to 500 mg l^{-1} for all sorbents. For the three sorbents, the dye sorption occurred rapidly initially and then proceeded gradually to equilibrium in about 4–24 h suggesting very active surface phenomena of each sorbent. Although experimental equilibrium data obtained for all sorbent–sorbate systems were well described by Langmuir, Redlich–Peterson and Langmuir–Freundlich models, the Langmuir equation provided a better fit than the others in the temperature range studied. The Langmuir adsorption capacities of fungal biomass, chitosan and PAC for the dye were determined as 206.8, 471.6 and 432.2 mg g^{-1} of the sorbent, respectively, at 45 °C. Assuming the batch sorption as a single-staged equilibrium operation, the separation process can be mathematically defined using these isotherm constants to estimate the residual concentration of dye or amount of sorbent for the desired levels of purification. The isotherm constants obtained could also be used to find the stage number in multi-staged separation processes. Kinetic studies indicated that the adsorption process mechanisms are mainly dependent on diffusion and binding. Kinetic parameters of adsorption such as the external and intraparticle diffusion rate constants and pseudo-second-order constants obtained can be used to find equilibrium sorption capacity, percent dye removal and initial sorption rate to aid bioreactor design. Thermodynamic parameters such as change in free energy, enthalpy, and entropy were also determined for each sorbent–acid dye system indicating the spontaneous, endothermic and irregular nature of sorption in each case.

The performance of different adsorbents for the removal of miscellaneous acid blue dyes has been demonstrated and varying values of the Langmuir sorption capacity Q_{max} have been reported in the literature. Fu and Viraraghavan [24] investigated the biosorption of Acid Blue 29 anionic dye by live, dead and pretreated *A. niger* fungus and they reported a biosorption capacity changing from 6.6 to 13.8 mg g^{-1} due to pretreatment method. For the algae *A. filiculoides* and *A. rongpong*, the reported Acid Blue 15 sorption capacities were 116.3 and 66.2 mg g^{-1}, respectively [46,47]. Ozer et al. [48] determined the Q_{max} values as 1356.6 and 367.0 mg g^{-1} for the uptake of Acid Blue 290 and Acid Blue 324 by *S. rhizopus* alga, respectively. Choy et al. [44] used granular activated carbon type F400 for the adsorption of Acid Blue 80 dye and they determined the sorption capacity as 171.0 mg g^{-1}. Attia et al. [13] studied with a commercial acti-

vated carbon for the removal of Acid Blue 74 and they found a 230.0 mg g^{-1} adsorption capacity. Hoda et al. [12] investigated the removal of some acid dyes; Acid Blue 45, Acid Blue 92, Acid Blue 120 and Acid Blue 129 and they found 65.5, 49.5, 28.0 and 61.7 mg g^{-1} adsorption capacity values with activated carbon cloth, respectively. The adsorption capacity of granular activated carbon was determined as 57.47 mg Acid Blue 40 dye g^{-1} of sorbent by Ozacar and Sengil [11].

The results indicated that for the removal of Acid Blue 161, the Q_{max} values obtained by fungal biomass *T. versicolor* and fungal component chitosan are comparable with those reported in the literature and although the adsorption rate and capacity of dried *T. versicolor* was lower than that of chitosan and PAC, the fungal biosorbent could be an attractive adsorbent for the removal of acidic dye. As a result all these sorbents undoubtedly have the potential to rapidly, efficiently and effectively remove AB 161 dye to very low concentrations and to accumulate large amounts of dye. It may be concluded that white-rot fungus and chitosan can be efficiently used in wastewater treatment for the removal of acid dyes as abundant, renewable and biodegradable resources and low cost alternatives compared to commercial activated carbon and other adsorbents reported.

References

[1] H. Zollinger, Color Chemistry—Synthesis, Properties and Applications of Organic Dyes and Pigments, VCH, New York, 1987.

[2] E.A. Clarke, R. Anliker, Organic dyes and pigments Handbook of Environmental Chemistry, Anthropogenic Compounds, Part A, vol. 3, Springer, New York, 1980.

[3] Y.M. Slokar, A.M. Le Marechal, Methods of decoloration of textile wastewaters, Dyes Pigments 37 (1997) 335–356.

[4] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Biores. Technol. 77 (2001) 247–255.

[5] Y. Fu, T. Viraraghavan, Fungal decolorization of dye wastewater: a review, Biores. Technol. 79 (2001) 251–262.

[6] E. Forgacs, T. Cserhati, G. Oros, Removal of synthetic dyes from wastewaters: a review, Environ. Int. 30 (2004) 953–971.

[7] Z. Aksu, Application of biosorption for the removal of organic pollutants: a review, Process Biochem. 40 (2005) 997–1026.

[8] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, Biores. Technol. 97 (2006) 1061–1085.

[9] G. McKay, The adsorption of dyestuffs from aqueous solution using activated carbon: analytical solution for batch adsorption based on external mass transfer and pore diffusion, Chem. Eng. J. 27 (1983) 187–196.

[10] G.M. Walker, L.R. Weatherley, Adsorption of acid dyes on to granular activated carbon in fixed beds, Water Res. 31 (1997) 2093–2101.

[11] M. Ozacar, I.A. Sengil, Adsorption of acid dyes from aqueous solutions by calcined alunite and granular activated carbon, Adsorption 8 (2002) 301–308.

[12] N. Hoda, E. Bayram, E. Ayranci, Kinetic and equilibrium studies on the removal of acid dyes from aqueous solutions by adsorption onto activated carbon cloth, J. Hazard. Mater. 137 (2006) 344–351.

[13] A.A. Attia, W.E. Rashwan, S.A. Khedr, Capacity of activated carbon in the removal of acid dyes subsequent to its thermal treatment, Dyes Pigments 69 (2006) 128–136.

[14] G. McKay, G.R. Prasad, P.R. Mowli, Equilibrium studies for the adsorption of dyestuff from aqueous solutions by low-cost materials, Water Air Soil Pollut. 29 (1986) 273–283.

[15] S. Mukherjee, S. Kumar, A.K. Misra, M. Fan, Removal of phenols from water environment by activated carbon, bagasse ash and wood charcoal, Chem. Eng. J. 129 (2007) 133–142.

[16] S.S. Nawar, H.S. Doma, Removal of dyes from effluents using low-cost agricultural by-products, Sci. Total Environ. 79 (1989) 271–279.

[17] C. Namasivayam, K. Kadirvelu, Coir pith as an agricultural waste by-product, for the treatment of dyeing wastewater, Biores. Technol. 48 (1994) 79–81.

[18] G. McKay, M. El Geundi, M.M. Nassar, Equilibrium studies for the adsorption of dyes on bagasse pitch, Adsorp. Sci. Technol. 15 (1997) 251–270.

[19] P. Nigam, G. Armour, I.M. Banat, D. Singh, R. Merchant, Physical removal of textile dyes and solid state fermentation of dye-adsorbed agricultural residues, Biores. Technol. 72 (2000) 219–226.

[20] P.K. Malik, Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36, Dyes Pigments 56 (2003) 239–249.

[21] B. Volesky, Detoxification of metal-bearing effluents: biosorption for the next century, Hydrometallurgy 59 (2001) 203–216.

[22] Z. Aksu, S. Tezer, Equilibrium and kinetic modelling of biosorption of Remazol Black B by *R. arrhizus* in a batch system: effect of temperature, Process Biochem. 36 (2000) 431–439.

[23] T. O'Mahony, E. Guibal, J.M. Tobin, Reactive dye biosorption by *Rhizopus arrhizus* biomass, Enzyme Microb. Technol. 31 (2002) 456–463.

[24] Y. Fu, T. Viraraghavan, Dye biosorption sites in *Aspergillus niger*, Biores. Technol. 82 (2002) 139–145.

[25] D. Wesenberg, I. Kyriakides, S.N. Agathos, White-rot fungi and their enzymes for the treatment of industrial dye effluents, Biotechnol. Adv. 22 (2003) 161–187.

[26] Z. Aksu, S.S. Cagatay, Investigation of biosorption of Gemazol Turquise Blue-G reactive dye by dried *Rhizopus arrhizus* in batch and continuous systems, Sep. Purif. Technol. 48 (2006) 24–35.

[27] N.S. Maurya, A.K. Mittal, P. Cornel, E. Rother, Biosorption of dyes using dead macro fungi: effect of dye structure, ionic strength and pH, Biores. Technol. 97 (2006) 512–521.

[28] T. Akar, T.A. Demir, I. Kiran, A. Ozcan, A.S. Ozcan, S. Tunali, Biosorption potential of *Neurospora crassa* biomass for decolorization of Acid Red 57 (AR 57) dye, J. Chem. Technol. Biotechnol. 81 (2006) 1100–1106.

[29] G. Bayramoglu, G. Çelik, M.Y. Arica, Biosorption of Reactive Blue 4 dye by native and treated fungus *Phanerocheate chrysosporium*: batch and continuous flow system, J. Hazard. Mater. 137 (2006) 1689–1697.

[30] M.N.V.R. Kumar, A review of chitin and chitosan applications, React. Funct. Polym. 46 (2000) 1–27.

[31] E. Guibal, Interactions of metal ions with chitosan-based sorbents: a review, Sep. Purif. Technol. 38 (2004) 43–74.

[32] H. Yoshida, S. Fukuda, A. Okamoto, T. Kataoka, Recovery of direct dye and acid dye by adsorption on chitosan fiber-equilibria, Water Sci. Technol. 23 (1991) 1667–1676.

[33] F.C. Wu, R.L. Tseng, R.S. Juang, Comparative adsorption of metal and dye on flake- and bead-types of chitosan prepared from fishery wastes, J. Hazard. Mater. B73 (2000) 63–75.

[34] M.S. Chiou, P.Y. Ho, H.Y. Li, Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads, Dyes Pigments 60 (2004) 69–84.

[35] Y.C. Wong, Y.S. Szeto, W.H. Cheung, G. McKay, Adsorption of acid dyes on chitosan-equilibrium isotherm analyses, Process Biochem. 39 (2004) 693–702.

[36] I. Uzun, Kinetics of the adsorption of reactive dyes by chitosan, Dyes Pigments 70 (2006) 76–83.

[37] I.A. Alaton, S. Teksoy, Acid dyebath effluent pretreatment using Fenton's reagent: process optimization, reaction kinetics and effects on acute toxicity, Dyes Pigments 73 (2007) 31–39.

[38] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica, and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1368.

[39] H. Freundlich, Adsorption in solution, Phys. Chem. Soc. 40 (1906) 1361–1368.

[40] O.J. Redlich, D.L. Peterson, A useful adsorption isotherm, J. Phys. Chem. 63 (1959) 1024.

[41] J.C.Y. Ng, W.H. Cheung, G. McKay, Equilibrium studies of the sorption of Cu(II) ions onto chitosan, J. Colloid Interf. Sci. 255 (2002) 64–74.

[42] Z. Aksu, E. Kabasakal, Adsorption characteristics of 2,4-dichlorophenoxy-acetic acid (2,4-D) from aqueous solution on powdered activated carbon, J. Environ. Sci. Health B 40 (2005) 545–570.
[43] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. Am. Soc. Civ. Eng. 89 (1963) 31–39.
[44] K.K.H. Choy, J.F. Porter, G. McKay, Intraparticle diffusion in single and multicomponent acid dye adsorption from wastewater onto carbon, Chem. Eng. J. 103 (2004) 133–145.
[45] G. McKay, Y.S. Ho, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.
[46] T.V.N. Padmesh, K. Vijayaraghavan, G. Sekaran, M. Velan, Biosorption of Acid Blue 15 using fresh water macroalga *Azolla filiculoides*: batch and column studies, Dyes Pigments 71 (2006) 77–82.
[47] T.V.N. Padmesh, K. Vijayaraghavan, G. Sekaran, M. Velan, Application of *Azolla rongpong* on biosorption of Acid Red 88, Acid Green 3, Acid Orange 7 and Acid Blue 15 from synthetic solutions, Chem. Eng. J. 122 (2006) 55–63.
[48] A. Ozer, G. Akkaya, M. Turabik, Biosorption of Acid Blue 290 (AB 290) and Acid Blue 324 (AB 324) dyes *Spirogyra rhizopus*, J. Hazard. Mater. 135 (2006) 355–364.