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Use of agricultural waste sugar beet pulp for the removal of Gemazol turquoise blue-G reactive dye from aqueous solution

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Abstract

The potential use of dried sugar beet pulp, an agricultural solid waste by-product, as an biosorbent for Gemazol turquoise blue-G, a copper–pthalocyanine reactive dye commonly used in dyeing of cotton, was investigated in the present study. Batch adsorption studies were carried out to examine the influence of various parameters such as initial pH, temperature and initial dye concentration. The results indicated that adsorption was strongly pH-dependent and slightly temperature-dependent. At 800 mg l^{-1} initial Gemazol turquoise blue-G concentration, dried sugar beet pulp exhibited the highest Gemazol turquoise blue-G uptake capacity of 234.8 mg g^{-1} at 25 °C and at an initial pH value of 2.0. The Freundlich, Langmuir, Redlich–Peterson and Langmuir–Freundlich, the two and three parameters adsorption models were used for the mathematical description of the biosorption equilibrium and isotherm constants were evaluated depending on temperature. Both the Langmuir and Redlich–Peterson models were applicable for describing the dye biosorption by dried sugar beet pulp in the concentration (100–800 mg l^{-1}) and temperature (25–45 °C) ranges studied. Simple mass transfer and kinetic models were applied to the experimental data to examine the mechanisms of biosorption and potential rate controlling steps such as external mass transfer, intraparticle diffusion and biosorption 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 first-order, pseudo second-order and saturation type kinetic models described the biosorption kinetics accurately at all concentrations and temperatures studied. The thermodynamic analysis indicated that the sorption process was exothermic and the biosorption of dye on dried sugar beet pulp might be physical in nature.

Keywords: Agricultural waste; Biosorption; Gemazol turquoise blue-G; Reactive dye; Dried sugar beet pulp; Kinetics; Isotherms

1. Introduction

Because of their ease of use, inexpensive cost of synthesis, stability and variety of colours compared with natural dyes, synthetic dyestuffs have been increasingly used in the textile, paper, rubber, plastics, cosmetics, pharmaceutical and food industries. Today there are more than 10,000 dyes available commercially, most of which are difficult to biodegrade due to their complex aromatic molecular structure and synthetic origin [1,2]. The extensive use of dyes often poses pollution problems in the form of coloured wastewater discharge into water bodies. Even small quantities of dyes can colour large water bodies; colour not only affects aesthetic quality but also reduces sunlight penetration and photosynthesis. In addition, some dyes are either toxic or mutagenic and carcinogenic due to the presence of metals and other chemicals, in their structure. Colour removal has been the subject of increased attention in the last few years. Reactive dyes are typically azo-based chromophores combined with different types of reactive groups. They differ from all other classes of dyes in that they bind to the textile fibres such as cotton to form covalent bonds. They have the favourable characteristics of bright colour, water-fast, simple application techniques and low energy consumption and are used extensively in textile industries, but nearly 50% of reactive dyes may be lost to the effluent after dyeing of cellulose fibres. Reactive dyes cannot be easily removed by conventional wastewater treatment systems since they are stable to light, heat and oxidizing agents and are biologically non-degradable so they have been, therefore, identified as problematic compounds in textile effluents. Hence, their removal is of great importance [3–6]. Among the reactive dyes, copper–phthalocyanine dyes like Gemazol turquoise blue-G are preferred to direct dyes due

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Nomenclature

a_{RP}	Redlich–Peterson adsorption constant $[(l\,mg^{-1})^{\beta}]$
A	Langmuir–Freundlich adsorption constant $(l^{n}\,mg^{1-n}\,g^{-1})$
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_L	external mass transfer coefficient $(cm\,min^{-1})$
k_{ad}; $k_{0,ad}$	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	Intraparticular diffusion rate $(mg\,g^{-1}\,min^{-0.5})$
K'_c	apparent equilibrium constant of the biosorption system
K^0_c	standard thermodynamic equilibrium constant of the adsorption system
K_F	Freundlich adsorption constant $[(mg\,g^{-1})(mg\,l^{-1})^{n}]$
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 dried sugar beet pulp at any time $(mg\,g^{-1})$
q_{eq}	amount of adsorbed dye per gram of dried sugar beet pulp at equilibrium $(mg\,g^{-1})$
Q°	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	solution temperature (°C, K)
X	dried sugar beet pulp concentration $(g\,l^{-1})$
β	Redlich-Peterson biosorption constant
ΔG°	The Gibbs free energy of biosorption $(kJ\,mole^{-1})$
ΔH°	Enthalpy change of biosorption $(kJ\,mole^{-1})$
ΔS°	Entropy change of biosorption $(kJ\,mole^{-1})$
ρ_p	particle density $(g\,ml^{-1})$

to their brilliant hue, excellent light and wet fastness wherever high quality turquoises, greens and blues are desired and have a very large consumption rate in textile dyeing processes. These dyes appear in the washwater in their hydrolyzed or unfixed form at levels that depend upon the degree of fixation on the fabric and the type of dyeing process applied, and end up in the dyehouse effluent. While phthalocyanine-based textile dyes are of wide use and importance within the textile industry, little is known of removal of these compounds from wastewaters [4,7].

Although some existing technologies – conventional chemical coagulation/flocculation, ozonation, oxidation, adsorption – may exhibit removal of reactive dyes, their initial and operational costs are so high that they constitute an inhibition to dyeing and finishing industries. Activated carbon is the most popular and widely used adsorbent for the removal of colour in the treatment of textile effluents but due to its high cost, problems in regeneration or disposal of the spent carbon, it is not used on a large scale [5,6,8,9]. Therefore, there is a growing need to find low cost, renewable, locally available sorbent materials for the removal of colour.

Biosorption is an alternative technology to remove organic pollutants from dilute aqueous solutions using inactive and dead biomasses, such as agricultural and fermentation wastes, various kinds of microorganisms, to bind and accumulate these pollutants by different mechanisms such as physical adsorption, complexation, ion exchange and surface microprecipitation. The mechanism of binding by inactivated biomass may depend on the chemical nature of pollutant (species, size, ionic charge), type of biomass, its preparation and its specific surface properties and environmental conditions (pH, temperature, ionic strength, existence of competing organic or inorganic ligands in solution) [6,10].

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 and requires little processing. Agricultural waste biosorbents generally used in biosorption studies are also inexhaustible, low-cost and non-hazardous materials, which are specifically selective for organics and easily disposed by incineration. Agricultural by-products as a whole exceed 320 000 000 000 kg/year. Most of these by-products are considered to be low value products [11–15]. A number of agricultural waste and by-products of cellulosic or starch origin have been studied in the literature for their capacity to remove dyes from aqueous solutions, such as coir pith, bagasse pitch, eucalyptus bark, sugarcane dust, corncob, barley husk, sawdust, rice husk, powdered peanut hull, orange peel, etc.[3,9,16–22]. However, new, economical, locally available and highly effective dye biosorbents have been still needed.

The purpose of this work was to investigate the possibility of sugar beet pulp, a by-product of the sugar-refining factory as a biosorbent for removal of Gemazol turquoise blue-G anionic reactive dye from aqueous solution. Sugar beet pulp is an abundant and low cost agricultural waste residue mainly used as animal feed. Sugar beet pulp is a natural polysaccharide and is composed of 20% and more than 40% of cellulosic and pectic substances, respectively. The pectic substances, which account for more than 40% of the dry matter, are complex heteropolysaccharides containing galacturonic acid, arabinose, galactose and rhamnose as the major sugar constituents. The rest mainly constitutes proteins and lignin [23]. Due to the carboxyl functions of galacturonic acid, pectic substances, and protein structures are known to strongly bind heavy metal ions [23–26] and dyes [16,17,20].

This study presents the first outcoming results about the possible use of the agricultural solid waste of dried sugar beet pulp as Gemazol turquoise blue-G reactive dye biosorbent as a function of initial pH, temperature and initial Gemazol turquoise blue-G concentration. This material was chosen considering its large amount availability and the basic cellulosic structure, rich of possible binding active sites. Although a large number of publications have recently suggested using raw or activated sugar beet pulp for removing heavy metal ions from aqueous solutions, there seems to be no study which reports all the equilibrium, kinetic and thermodynamic modelling of Gemazol turquoise blue-G reactive dye adsorption due to temperature by dried sugar beet pulp in a batch system, which are important in the design of treatment processes in a wide range of dye concentration.

2. Materials and methods

2.1. Adsorbent

In this study, the waste pulp of sugar beet remaining from extraction of sugar was used as dye biosorbent. The pulp was obtained from the Ankara Sugar Mill, Turkey. The collected biomaterial was extensively washed with tap water to remove soil and dust, sprayed with distilled water and then dried in an oven at 100 °C to a constant weight. After grinding and dry sieving, three particle sizes were kept: 250, 350 and 500 μm.

The adsorbent 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 preliminary batch biosorption experiments were carried out using the three different beet pulp particle sizes of 250, 350 and 500 μm. Since the <250 μm particle size dramatically decreased the effectiveness of beet pulp for dye removal, the adsorbent particle size of 250 μm was selected for adsorption studies due to its higher adsorption rate and capacity. Higher removal with smaller particle size also indicated that the dye biosorption was a surface phenomenon.

2.2. Chemicals

The test solutions containing Gemazol turquoise blue-G dye were prepared by diluting 1.0 g l^{-1} of stock solution of dye which was obtained by dissolving weighed quantity of Gemazol turquoise blue-G, a copper–phthalocyanine reactive dye (Colour index name: Reactive Blue 21; molecular weight; 576.1; purity: not specified) (supplied from GEMSAN, TURKEY), in 1 l of double-distilled water. The range of concentrations of prepared dye solutions changed between 50 and 800 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 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 Gemazol turquoise blue-G dye of desired concentration, pH and temperature were placed in a thermostatic rotary shaker. For the studies, 0.1 g of biosorbent 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 (5 ml) were taken before mixing the biosorbent and dye bearing solution and at pre-determined time intervals. The dye solution was separated from the biosorbent by centrifugation (Nuve, TURKEY) 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 values were used for further calculations.

2.4. Analysis of Gemazol turquoise blue-G

The concentration of unadsorbed Gemazol turquoise blue-G dye in the biosorption medium were measured colorimetrically using a spectrophotometer (Bausch and Lomb-Spectronic 20D, Milton Roy Company, USA). The absorbance of the colour was read at 341 nm.

3. Results and discussion

Analysis of biosorption data is important for developing equilibrium, kinetic and thermodynamic equations that can be used for design purposes. The equilibrium, kinetic and thermodynamic results obtained in the biosorption of Gemazol turquoise blue-G on to dried sugar beet pulp 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 $q_{eq} = (C_0 - C_{eq})/X$] ($q$; q_{eq}: mg g^{-1}), respectively, unadsorbed dye concentration in solution at any time and at equilibrium (C; C_{eq}: mg l^{-1}), respectively, adsorbed dye concentration in solution at equilibrium ($C_{ad,eq}$: mg l^{-1}) and biosorption yield (Ad% = $100 \times (C_0 - C_{eq})/C_0$).

3.1. Effect of initial pH on Gemazol turquoise blue-G biosorption

An important influencing factor for dye biosorption on agricultural by-products has been referred to pH as in most studies published in the literature. The variation of equilibrium dye uptake with initial pH is given in Fig. 1 for an initial dye concentration of 100 mg l^{-1} at 25 °C for a contact time of 24 h. As seen from the figure, the biosorption of Gemazol turquoise blue-G was maximum at pH 2.0 (q_{eq} = 83.7 mg g^{-1}) and declined sharply with further increase in pH and reached to zero at pH 6, so the working pH value for Gemazol turquoise

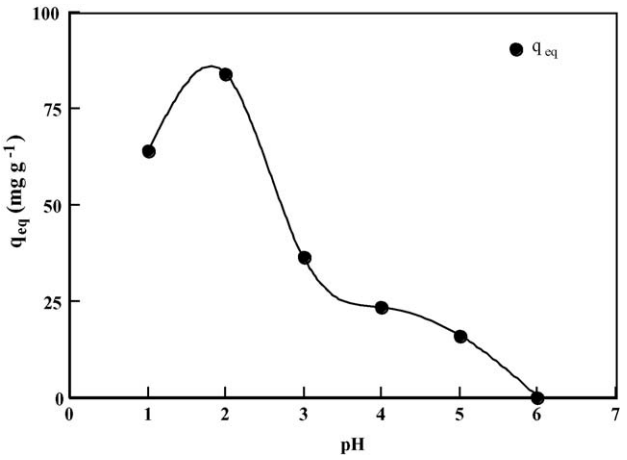

Fig. 1. The effect of initial pH on the equilibrium Gemazol turquoise blue-G dye sorption capacity of dried sugar beet pulp (T:25 °C, C_0:100 mg l^{-1}, X:1.0 g l^{-1}, Agitation rate:150 rpm).

blue-G biosorption was chosen as 2.0 and the other biosorption experiments were performed at this pH value.

The reactive dyes release coloured dye anions in solution. It was verified that the raw sugar beet pulp is dominated by negatively charged sites that are largely carboxylate groups together with some weaker acidic groups of heteropolysaccharides and nitrogen-containing functional groups of proteins [23]. At higher pH values, a negatively charged surface site on the biosorbent does not favour the adsorption of dye anions due to the electrostatic repulsion. The increase of OH^- ions with the increasing pH also cause a competition with the dye anions for the adsorption sites resulting in a decrease in biosorption. As the pH of the system decreases, the number of positively charged sites on the biosorbent surface increases so the dye uptake increases due to the electrostatic attractions between negatively charged dye anions and positively charged sorbent surface. It is expected that at pH 2, most of the potential fixation sites are protonated so the highest uptake was obtained at this pH value.

3.2. Effect of temperature on Gemazol turquoise blue-G biosorption

It has been found, in most cases, that the biosorption decreases with increasing temperature. The equilibrium uptake of Gemazol turquoise blue-G by dried sugar beet pulp was also affected by temperature due to the initial dye concentration and decreased slightly with increasing temperature up to 45 °C for all initial dye concentrations studied (Table 1). At 100 mg l^{-1} initial Gemazol turquoise blue-G concentration the equilibrium uptake capacity of sorbent decreased from 83.7 to 66.1 mg dye per gram of adsorbent with increasing temperature from 25 to 45 °C. Gemazol turquoise blue-G biosorption was exothermic thus the extent of biosorption increased with decreasing temperature so the sorption of dye by dried sugar beet pulp may involve mainly physical sorption. The decrease in biosorption capacity of dried sugar beet pulp at higher temperature may be attributed to the deactivation of the adsorbent surface.

3.3. Effect of initial Gemazol turquoise blue-G concentration on temperature-dependent Gemazol turquoise blue-G biosorption

The initial concentration provides an important driving force to overcome all mass transfer resistance of dye anions between the aqueous and solid phases. In addition, increasing initial dye concentration increases the number of interactions between dye anions and sorbent, which enhances the sorption process. Hence a higher initial concentration of Gemazol turquoise blue-G will increase the biosorption rate. The effect of initial dye concentration on the dye sorption capacity of dried sugar beet pulp biosorbent was investigated between 50 and 800 mg l^{-1} at three different temperatures and the results are presented in Table 1. The equilibrium sorption capacity of dried sugar beet pulp for Gemazol turquoise blue-G dye increased notably with increasing initial dye concentration up to 800 mg l^{-1}, and decreased with increasing temperature up to 45 °C. Then, the equilibrium uptake did not change with further increase in initial dye concentration at any of the temperature studied showing a saturation trend at higher Gemazol turquoise blue-G dye concentrations due to a finite number of surface binding sites. At 25 °C, when the initial dye concentration increased from 50.5 to 792.2 mg l^{-1}, the loading capacity of sorbent increased from 41.5 to 234.8 mg g^{-1}. The temperature also influenced equilibrium dye uptake as shown in Table 1. With the change in temperature from 25 to 45 °C, the uptake capacity decreased from 234.8 to 213.9 mg g^{-1} at 800 mg l^{-1} initial dye concentration. However, the removal percentage of Gemazol turquoise blue-G showed an opposite trend and decreased with increasing initial dye concentration. When the temperature was raised from 25 °C to 45 °C, the removal percentages of dye decreased from 82.2 to 70.4% and from 29.6 to 26.8% for 50 and 800 mg l^{-1}

Table 1
Effect of initial Gemazol turquoise blue-G dye concentration and temperature on the equilibrium uptake capacity and biosorption yield of dried sugar beet pulp

25 °C			35 °C			45 °C		
C_0 (mg l^{-1})	q_{eq} (mg g^{-1})	Ad%	C_0 (mg l^{-1})	q_{eq} (mg g^{-1})	Ad%	C_0 (mg l^{-1})	q_{eq} (mg g^{-1})	Ad%
50.5	41.5	82.2	50.9	39.0	76.7	49.9	35.1	70.4
110.0	83.7	76.1	95.7	71.3	74.5	100.2	66.1	65.9
206.7	142.2	68.8	214.3	133.0	62.1	199.6	122.2	61.2
416.3	208.7	50.1	407.0	194.8	47.9	417.4	180.9	43.3
602.2	228.7	37.9	613.0	212.0	34.6	581.5	204.4	35.1
792.2	234.8	29.6	787.5	223.4	28.4	798.3	213.9	26.8

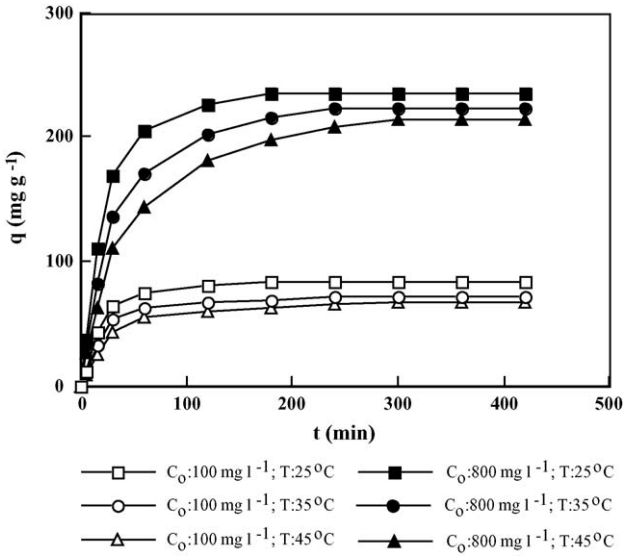

Fig. 2. The biosorption curves of Gemazol turquoise blue-G dye obtained at 100 and 800 mg l^{-1} initial dye concentrations and at different temperatures (initial pH 2.0, X:1.0 g l^{-1}, agitation rate:150 rpm).

initial dye concentrations, respectively. In the case of lower concentrations, the ratio of initial number of dye ions to the available sorption sites is low and subsequently the fractional biosorption becomes independent of initial concentration. At higher concentrations, however, the available sites of biosorption become fewer and subsequently the removal of dye depends on the initial concentration. As a result, the purification yield can be increased by diluting the wastewaters containing high dye concentrations.

3.4. Biosorption kinetics

Fig. 2 shows the adsorption kinetics of Gemazol turquoise blue-G dye at 25, 35 and 45 °C by plotting the dye uptake capacity, q, versus time for 100 and 800 mg l^{-1} of initial dye concentrations for the first 420 mins (7 h) of biosorption. Biosorption studies were carried out for 24 h in order to determine the effect of time on biosorption. For the given concentrations and temperatures, the amount of dye adsorbed increased linearly with time in the beginning, then non-linearly at a slower rate and finally attained saturation called the equlibrium time, was dependent on time and temperature. The data showed that a contact time ranging from about 2 to 4 h depending on temperature was sufficient to achieve equilibrium and biosorption did not change subsequently up to 24 h (Data not shown). Biosorption capacity was mainly dependent on initial dye concentration besides time and temperature parameters. In general, as the concentration of dye increased, although the time to reach equilibrium did not change notably, Gemazol turquoise blue-G removal increased without regard to temperature. For both initial dye concentrations, biosorption capacity of dried sugar beet pulp decreased with increasing temperature. Also, from the figure, it was observed that for all initial Gemazol turquoise blue-G concentrations and for all temperatures studied initial sorption of dye occurred more rapidly and the majority of dye uptake (66.7–89.1%) took place within the first hour of contact. Such rapid uptake of Gemazol turquoise blue-G and short times coupled with high removals in all cases indicate that the biosorbent has a high degree of affinity for the dye anions pointing towards physical adsorption and that the uptake of dye occurs predominantly by surface binding.

3.5. Modelling of biosorption equilibrium depending on temperature

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the analysis and design of adsorption systems. In order to discover the sorption capacity of beet pulp for Gemazol turquoise blue-G dye, the experimental data points were fitted to the Langmuir, Freundlich, Redlich–Peterson and Langmuir–Freundlich models which are the most frequently used two- and thee-parameters 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. These models were chosen since they are simple, give a good description of experimental behavior in a large range of operating conditions and recharacterized 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 Eq. (1).

$$q_{eq} = \frac{Q^{\circ} b C_{eq}}{1 + bC_{eq}} \quad (1)$$

where parameters Q° and b are Langmuir constants related to maximum adsorption capacity and bonding energy of adsorption, respectively, which are functions of the characteristics of the system as well as time. Q° represents a practical limiting biosorption capacity (monolayer capacity) when the surface is fully covered with dye and assists in the comparison of biosorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments [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:

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

where K_F and n are the Freundlich constants characteristic on the system. K_F and n are indicators of biosorption capacity and biosorption intensity, respectively. The Freundlich isotherm is also more widely used but provides no information on the monolayer biosorption capacity, in contrast to the Langmuir model [28].

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

Table 2
Comparison of the Freundlich, Langmuir, Redlich–Peterson and Langmuir–Freundlich adsorption constants of Gemazol turquoise blue-G biosorption by dried sugar beet pulp at different temperatures

Temperature (°C)	K_F (mg g^{-1})(mg l^{-1})$^{-1/n}$	n	ε (%)
Freundlich model			
25	20.02	2.40	11.98
35	15.89	2.26	4.57
45	11.43	2.05	6.86
Temperature (°C)	Q° (mg g^{-1})	b (l mg^{-1})	ε (%)
Langmuir model			
25	256.4	0.020	1.98
35	250.0	0.017	3.35
45	238.1	0.012	1.82

Temperature (°C)	a_{RP} [(l mg^{-1})$^\beta$]	K_{RP} (l g^{-1})	β	ε (%)
Redlich–Peterson model				
25	0.018	4.71	1.000	1.98
35	0.020	3.88	0.960	3.17
45	0.011	2.64	1.000	1.88

Temperature (°C)	A (l^{m}mg^{1-m} g^{-1})	B (l mg^{-1})^m	m	ε (%)
Langmuir–Freundlich				
25	2.14	0.0086	1.202	1.74
35	1.89	0.0074	1.088	2.75
45	1.89	0.0079	1.091	8.13

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 [29].

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 $m > 1$ [30].

Fig. 3 shows the experimental isotherm data of Gemazol turquoise blue-G on dried sugar beet pulp at three different temperatures. In the dye concentration range examined, the resulting isotherms were positive, regular, concave to the concentration axis, indicating an affinity for biosorption, and showed a saturation trend at higher dye concentrations; indicating a complete monolayer of dye covering the surface of biosorbent. The uptake of the dye anions decreased with an increase in temperature thereby indicating the process to be exothermic.

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 parameters at different temperatures are obtained by nonlinear regression analysis and listed in Table 2 along with the average percentage errors. The average percentage errors between the experimental and predicted values are calculated using Eq. (5). 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. 4 also depicted the comparison of experimental and predicted qeq values obtained from these adsorption models at the temperatures of 25, 35 and 45 °C. Basically, if most of the data are distributed around the 45° line, this indicates that the model

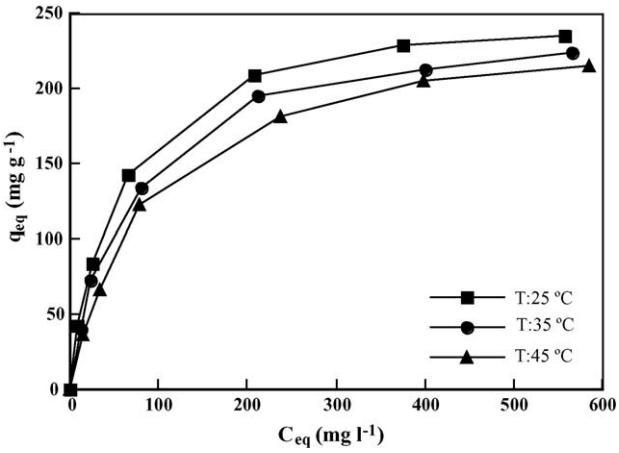

Fig. 3. Non-linearized adsorption isotherms (experimental equilibrium data) of Gemazol turquoise blue-G obtained at 25, 35 and 45 °C (initial pH 2.0, X: 1.0 g l^{-1}, agitation rate:150 rpm).

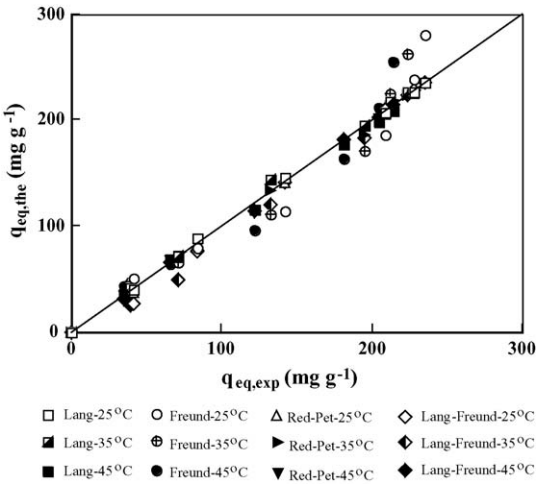

Fig. 4. Comparison of the experimental q_{eq} values with the theoretical q_{eq} values obtained from the Langmuir, Freundlich, Redlich–Peterson and Langmuir–Freundlich adsorption models at different temperatures for Gemazol turquoise blue-G biosorption.

represent well the experimental data of the system so as shown in the figure. On this basis, the Langmuir and Redlich–Peterson models fitted the experimental data reasonably well with an average percentage error in the range 2.49–3.61% suggesting that the monolayer sorption, mainly due to ion-exchange, would not be disturbed by lateral interactions between dye anions sorbed with similar sorption energies. The other two-parameter model of Freundlich could fit the equilibrium data with an average percentage error more than 12.99%. In view of the values of average percentage errors in the Table 2, the Langmuir–Freundlich model also exhibited a poor fit to the biosorption data of dye, especially at 35 °C.

Adsorption model constants the values of which express the surface properties and affinity of the biosorbent can be used to compare the adsorptive capacity of dried sugar beet pulp for Gemazol turquoise blue-G.

K_F, one of the Freundlich constants has been used as a relative measure of biosorption 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 2, the magnitude of K_F indicated a relatively easy uptake of Gemazol turquoise blue-G dye from aqueous solution with a high adsorptive capacity of dried sugar beet pulp at all temperatures studied. The highest K_F value was 20.02 at 25 °C and the value of K_F decreased with the rise in temperature which was consistent with the experimental observation. The n is an empirical parameter that varies with the degree of heterogeneity 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 2. also indicated that n is greater than unity, indicating that Gemazol turquoise blue-G is favourably adsorbed by dried sugar beet pulp at all the temperatures studied.

Values of Q° and b calculated from the Langmuir model at different temperatures are also tabulated in Table 2. While the Freundlich model does not describe the saturation behaviour of the biosorbent, Q°, the mono-component Langmuir constant represents the monolayer saturation at equilibrium or the total capacity of the adsorbent for dye. The biosorption capacity of sorbent also decreased with increasing the temperature. The value of Q° obtained at 25 °C (i. e. maximum uptake and equal to 256.4 mg g^{-1}) appears to be higher in comparison with the uptake obtained at the other temperatures. The other mono-component Langmuir constant b, is related to the free energy of biosorption, ΔG ($b \propto e^{-\Delta G/RT}$) and indicates the affinity 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 Gemazol turquoise blue-G amount of $Q^\circ/2$ is bound) so a high value of b, indicates a steep desirable beginning of the isotherm which reflects the high affinity of the biosorbent for the sorbate resulting in a stable adsorption product. The higher value of b obtained at 25 °C also implied strong bonding of Gemazol turquoise blue-G to the dried sugar beet pulp at this temperature.

Related biosorption parameters were also calculated according to the three-parameter isotherm of Redlich–Peterson using non-linear regression method for Gemazol turquoise blue-G and are tabulated in Table 2 at different temperatures. Redlich–Peterson constant K_{RP} indicated that the adsorption capacity of biosorbent also decreased with increasing temperature. It is noted that β normally lies between 0 and 1, indicating favourable biosorption. At 25 and 45 °C, the values of β are equal to 1.0 and for 35 °C β tends to unity, that is the isotherms approach the Langmuir form.

The corresponding Langmuir-Freundlich parameters of A, B and m for different temperatures along with percentage errors are also given in Table 2. Langmuir–Freundlich constant A indicated that the biosorption capacity and affinity of biosorbent to Gemazol turquoise blue-G ions also decreased with increasing temperature.

3.6. Modelling of biosorption kinetics depending on temperature

It is proved that adsorption on an adsorbent from the aqueous phase involves three steps: (1) the transport of the adsorbate from the bulk phase to the exterior surface of the adsorbent (film diffusion), (2) the transport into the adsorbent by either pore diffusion and/or surface diffusion (intraparticular diffusion), and (3) the adsorption on the surface of the adsorbent. The slowest of these steps determines the overall rate of the adsorption process. When removing Gemazol turquoise blue-G dye from aqueous solution by dried sugar beet pulp, these steps are possible. Sorption kinetics show 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 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 biosorption

process and attempts were made to calculate the coefficients of these models.

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:

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

where C is the bulk liquid phase concentration of dye at a time t, C_S the surface concentration of Gemazol turquoise blue-G, 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. (6) can be simplified as

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

Since it was not possible to determine the specific surface area A, due to the poor porosity of particles, it is approximated as the external surface area. Assuming the adsorbent particles are spherical, A is calculated from Eq. (8) as 0.2575 cm^{-1}.

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

where X is the sorbent mass concentration in the solution (1 $g\,l^{-1}$), d_p average particle diameter (0.025 cm) and ρ_p the density of the sorbent (932 $g\,l^{-1}$). By plotting C/C_0 against t, the value of k_L may be determined from the slope at $t=0$ [30] and [31].

External mass transfer is characterized by the initial rate of solute diffusion for the system studied. The effect of initial dye concentration and temperature on the external diffusion rate was given by a plot of C/C_0 versus time for 100 and 800 $mg\,l^{-1}$ initial dye concentrations and at 25, 35 and 45 °C temperature values (Fig. 5). It was seen 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 increased the mobility of dye during adsorption.The kinetic data presented in the figure were fitted to Eq. (7) for the initial uptake phase and the external mass transfer coefficients were determined from the slopes as tØ0 and presented in Table 3. The results show that both the increases in initial dye concentration and temperature resulted in a decrease in the initial rate, respectively. 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 biosorption time. Weber and Morris [31] have concluded that, for processes which are controlled by external diffusion, the initial rate will be directly proportional to the solute concentration. The non-proportionality shown in Fig. 6, therefore, indicates that external mass transfer is not the rate controlling step.

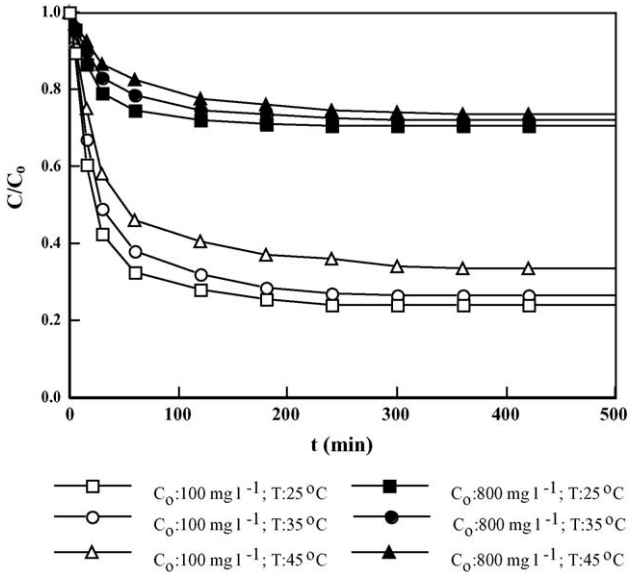

Fig. 5. C/C_0 vs. t plots obtained at 100 and 800 $mg\,l^{-1}$ initial Gemazol turquoise blue-G concentrations and at different temperatures (initial pH 2.0, X: 1.0 $g\,l^{-1}$, agitation rate: 150 rpm).

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:

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

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 a 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

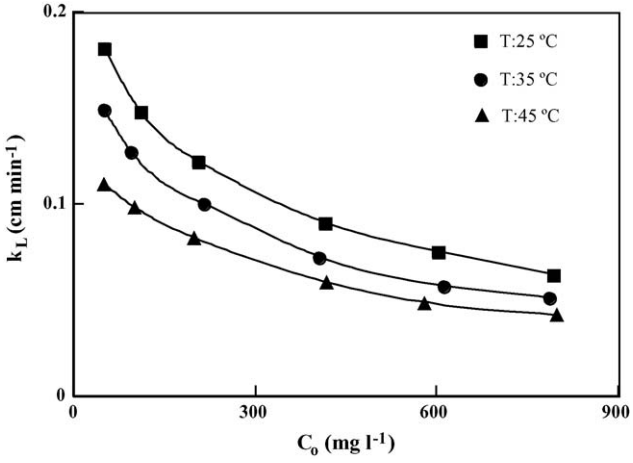

Fig. 6. Variation of k_L with C_0 with respect to temperature.

Table 3
Effect of initial Gemazol turquoise blue-G 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$^{0.5}$)
50.5	18.1	5.06	50.9	14.9	3.93	49.9	11.0	2.83
110.0	14.8	11.63	95.7	12.7	8.00	100.2	9.8	6.10
206.7	12.2	19.18	214.3	10.5	14.20	199.6	8.2	10.27
416.3	9.0	26.00	407.0	7.2	20.17	417.4	5.9	15.65
602.2	7.5	28.78	613.0	5.7	22.93	581.5	4.8	18.17
792.2	6.3	30.80	787.5	5.1	24.71	798.3	4.2	20.00

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

Fig. 7 shows the effect of initial dye concentration and temperature on intraparticular diffusion at 100 and 800 mg l^{-1} initial Gemazol turquoise blue-G concentrations and at 25, 35 and 45 °C temperatures. As seen from the figure all the plots have the same general feature presenting multilinearity, indicating that a few steps took place. The first, sharper portion which extent is related to initial dye concentration, 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. At a certain time limit (between 5–60 min at all initial dye concentrations and at all temperatures studied) the curves revealed a linear characteristic. The values of K evaluated from these linear parts of q versus $t^{0.5}$ plots are also tabulated in Table 3. 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 the rate of diffusion increased with a raise in initial dye concentration and decreased with increasing temperature of solution. This may be due to a greater driving force with increasing C_0. Increasing the dye concentration in the solution promoted the diffusion in the particles. At all temperatures when C_0 is increased from 50 to 400 mg l^{-1} there is a marked effect on the rate of intraparticular dye diffusion. Above C_0 400 mg l^{-1} the effect is small. It is also observed that the higher the value of K the more rapid is the uptake of Gemazol turquoise blue-G dye. The linear plots at each concentration and temperature did not pass through the origin and this indicated 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 ($C_0^{0.5}$). Such a plot given in Fig. 8 also confirmed that intraparticle diffusion is not the only operative mechanism. These two results show that increasing the Gemazol turquoise blue-G concentration in the solution seems to reduce the diffusion of dye anions in the boundary layer and to enhance the diffusion in the solid.

On the other hand, three simplified kinetic models including pseudo first-order [32], pseudo second-order [33] and saturation

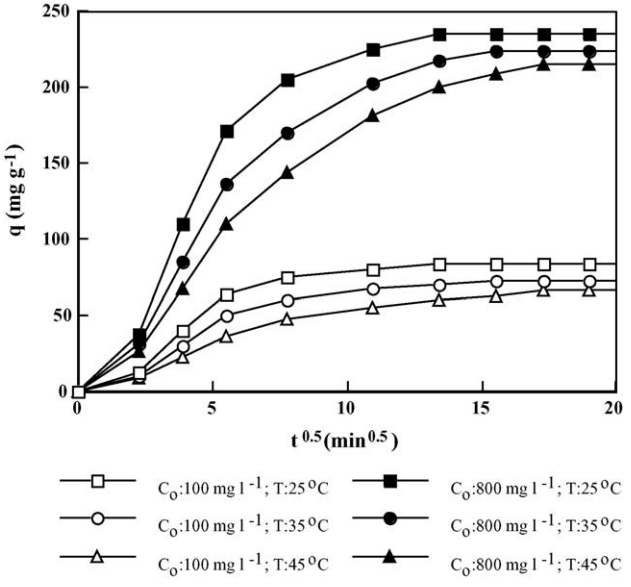

Fig. 7. q vs. $t^{0.5}$ plots obtained at 100 and 800 mg l^{-1} initial Gemazol turquoise blue-G concentrations and at different temperatures (initial pH 2.0, X: 1.0 g l^{-1}, agitation rate: 150 rpm).

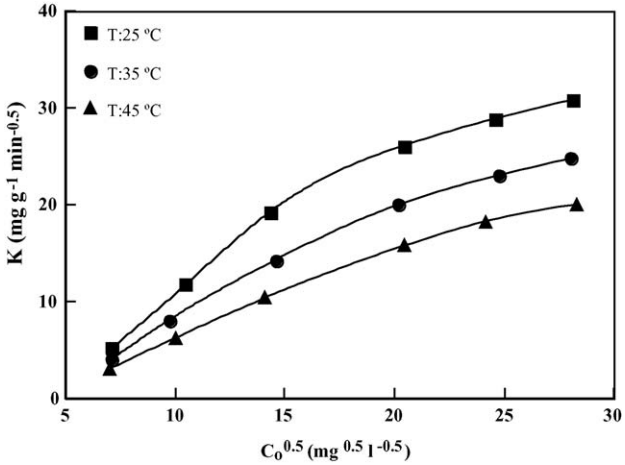

Fig. 8. Variation of K with $C_0^{0.5}$ with respect to temperature.

type [30] were used to test the biosorption kinetics. These three models basically include all steps of adsorption such as external film diffusion, adsorption, and internal particle diffusion, so they are pseudo-models.

The pseudo first-order rate expression based on solid capacity is generally expressed as follows:

$$\frac{dq}{dt} = k_{1,ad}(q_{eq} - q) \tag{10}$$

where $k_{1,ad}$ is the rate constant of first-order biosorption. After integration and applying boundary conditions, $t=0$ to $t=t$ and $q=0$ to $q=q_{eq}$; the integrated form of Eq. (10) becomes:

$$\log(q_{eq} - q) = \log q_{eq} - \frac{k_{1,ad}}{2.303}\, t \tag{11}$$

A straight line of $\log(q_{eq}-q)$ versus t suggests the applicability of this kinetic model. 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 equation 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:

$$\frac{dq}{dt} = k_{2,ad}(q_{eq} - q)^2 \tag{12}$$

where k_2,ad is the rate constant of second-order biosorption. For the same boundary conditions the integrated form of Eq. (12) becomes

$$\frac{t}{q} = \frac{1}{k_{2,ad}\, q_{eq}^2} + \frac{1}{q_{eq}} t \tag{13}$$

If second-order kinetics are applicable, the plot of t/q against t of Eq. (13) 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 applicability of saturation type kinetics in modeling the kinetic data was also discussed. The plot of q versus time can be used to find the initial biosorption rate (r_{ad}) by differentiating the plot at $t=0$ as defined in Eq. (14).

$$\left.\frac{dq}{dt}\right|_{t=0} = r_{ad} \tag{14}$$

From 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) (Fig. 9). Eq. (15) can be used to describe the rate of biosorption very accurately in both situations. This kind of rate equation is defined as 'saturation type'.

$$r_{ad} = \frac{k_{ad} C_0}{1 + k'_{ad} C_0} \tag{15}$$

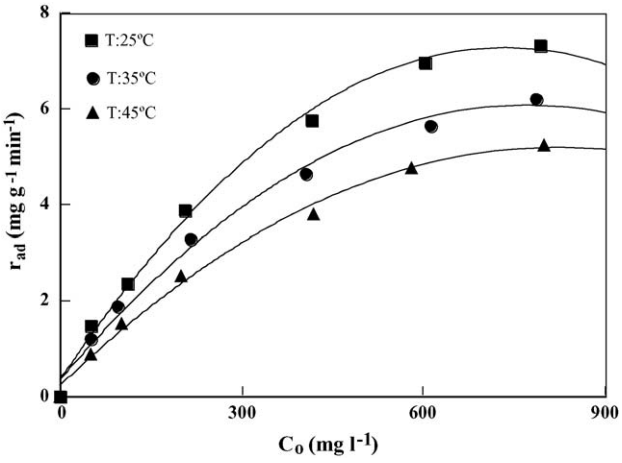

Fig. 9. Variation of r_{ad} with C_0 with respect to temperature.

where k_{ad} is the first-order rate constant of saturation type biosorption. The zero-order rate constant ($k_{0,ad}$) is expressed as k_{ad}/k'_{ad} and Eq. (15) becomes:

$$r_{ad} = \frac{k_{ad} C_0}{1 + k_{0,ad} C_0} \tag{16}$$

A straight line of $1/r_{ad}$ versus $1/C_0$ suggests the applicability of this kinetic model and k_{ad} and $k_{0,ad}$ can be determined from the slope and intercept of the plot. This model predicts the biosorption behavior over the whole studied concentration range of dye at a constant temperature.

The validity of all models can be checked from the linear plots.

The pseudo first-order rate constant ($k_{1,ad}$) and q_{eq} values were determined from the plots of linearized form of the pseudo first-order model (Eq. (11)) at all concentrations and at all temperatures studied for the initial 30 min (data not shown) and are presented in Table 4 along with the corresponding correlation coefficients. The first-order rate constants decreased slightly with increasing both the initial concentration of dye and temperature. As seen from the table, besides very high regression coefficients (>0.995), experimental q_{eq} values agreed very well with q_{eq} values obtained from Lagergren plots. This indicated that pseudo first-order kinetic model describes the kinetics adequately in the concentration and temperature ranges studied.

Using Eq. (13), t/q was plotted against t at 25, 35 and 45 °C, 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 the parameters $k_{2,ad}$ and q_{eq} and of corresponding correlation coefficients are also presented in Table 4. The results indicated that second-order rate constants were also affected by both the initial dye concentration and temperature and diminished with increasing these parameters. The correlation coefficients of all temperatures and concentrations studied were also found very high and equal to 1.000 in this case. Moreover the theoretical q_{eq} values found from the second-order kinetic model also agreed very well with the experimental q_{eq} values. This showed that the adsorption of Gemazol turquoise blue-G also follows the pseudo-second-

Table 4
Comparison of the first- and second-order reaction rate constants and experimental and calculated q_{eq} values obtained at different initial Gemazol turquoise blue-G concentrations and temperatures

Temperature (°C)	C_0 (mg l^{-1})	$q_{eq,exp}$(mg g^{-1})	First-order kinetic model			Second-order kinetic model		
			$k_{1,ad}$ ($\times 10^2$ 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
	50.5	41.5	3.66	41.4	1.000	13.09	41.8	1.000
25	110.0	83.7	3.18	86.6	0.995	1.36	84.0	1.000
	206.7	142.2	2.92	141.9	1.000	0.45	142.8	1.000
	416.3	208.7	2.49	213.8	0.998	0.11	208.3	1.000
	602.2	228.7	2.33	230.3	1.000	0.10	232.6	1.000
	792.2	234.8	2.21	239.3	0.999	0.07	238.1	1.000
	50.9	39.0	3.20	38.3	0.998	21.17	39.4	1.000
35	95.7	71.3	2.79	69.5	1.000	2.17	71.9	1.000
	214.3	133.0	2.56	132.2	1.000	0.65	135.1	1.000
	407.0	194.8	2.44	193.5	0.996	0.23	196.1	1.000
	613.0	212.0	2.28	211.5	1.000	0.18	212.8	1.000
	787.5	223.4	2.12	224.4	1.000	0.19	227.3	1.000
	49.9	35.1	2.81	35.0	0.997	28.36	35.5	1.000
45	100.2	66.1	2.65	67.4	0.999	3.39	66.7	1.000
	199.6	122.2	2.35	122.4	1.000	1.03	123.5	1.000
	417.4	180.9	2.23	179.6	0.999	0.43	185.2	1.000
	581.5	204.3	2.16	189.7	1.000	0.33	196.1	1.000
	798.3	213.9	2.05	213.5	0.999	0.23	217.4	1.000

order kinetic model. The values confirm that the sorption data are well represented by pseudo second-order kinetics for the entire sorption period suggesting chemisorption mechanism.

The saturation type kinetic model was also applied to the experimental data at different temperatures changing from 25 to 45 °C to describe the batch biosorption kinetics over the whole concentration range of dye studied. The values of k_{ad} and $k_{0,ad}$ were determined from the plots of linearized form of the saturation type kinetic model at all temperatures (data not shown). The plots indicated that such saturation type kinetic expression is also so valid to the present system ($R^2 > 0.997$ for all temperatures). Table 5 shows that both the biosorption rate constants were affected with increase in temperature and decreased notably with increasing temperature.

These suggest that the biosorption of Gemazol turquoise blue-G at 25, 35 and 45 °C may be best described by the pseudo first-order and pseudo second-order kinetics, following saturation type kinetic model, with fairly high correlation coefficients. The change of rate constant due to temperature also showed that one of the rate controlling steps is biosorption reaction. Applying the Weber and Morris principles to the variation in the initial rate with C_0 (Fig. 9) indicated that the rate was not directly proportional to C_0 and also confirmed that sorption process was not the only rate limiting step. The data also confirmed that both mass transfer and pore diffusion are important in determining the biosorption rates and that their relative significance depends on the initial Gemazol turquoise blue-G concentration, temperature and time.

Table 5
Comparison of the saturation type kinetic rate constants obtained at different temperatures

Temperature (°C)	k_{ad} ($\times 10^2$ l g^{-1} min^{-1})	$k_{0,ad}$ ($\times 10^2$ l mg^{-1})	R^2
25	3.30	0.35	0.989
35	2.66	0.32	0.998
45	1.95	0.26	0.994

3.7. Thermodynamic parameters of biosorption

The thermodynamic parameters reflect the feasibility and spontaneous nature of the process. Thermodynamic parameters of free energy change, enthalpy change and entropy change can be estimated using equilibrium constants changing with temperature. The biosorption process of Gemazol turquoise blue-G dye can be summarized by the following reversible process which represents a heterogeneous equilibrium.

$$\text{dye in solution} \leftrightarrow \text{dye} - \text{biosorbent} \quad (17)$$

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

$$K'_c = \frac{C_{ad,eq}}{C_{eq}} \quad (18)$$

where $C_{ad,eq}$ is the concentration of dye on the biosorbent at equilibrium. In this case the activity should be used instead of concentration in order to obtain the standard thermodynamic equilibrium constant (K^0_c) of the biosorption system. If infinite dilute value of K'_c can be found by calculating the apparent equilibrium constant (K'_c) at different initial concentrations of dye and extrapolating to zero, this value will give K^0_c. When 1 g l^{-1} of adsorbent is used, this value can be taken equal to the opposite value of intercept of C_{eq}/q_{eq} versus C_{eq} plot (=bQ°), 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 biosorption reaction (Gibbs free energy) (ΔG°) at 25 °C.

$$\Delta G^\circ = -RT \ln K^0_c \quad (19)$$

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

$$\ln K_c^0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{\mathrm{RT}} \quad (20)$$

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

The K_c^0 value at 25 °C evaluated from the $C_{aq,eq}/C_{eq}$ versus C_{eq} plot (data not shown) as 5.12 was used to find the ΔG° value. The standard Gibbs free energy for the biosorption process was obtained as $-4.05\,\mathrm{kJ\,mole^{-1}}$ using Eq. (19). A negative value of ΔG° confirms the feasibility of the process and spontaneous nature of biosorption at 25 °C with a high degree of affinity of the dye molecules for the biomass surface. The standard enthalpy and entropy changes of biosorption determined from the $\ln K_c^0$ versus $1/T$ plot ($R2 = 0.966$) were $-23.09\,\mathrm{kJ\,mole^{-1}}$ and $-0.064\,\mathrm{kJ\,mole^{-1}\,K^{-1}}$, respectively. The negative value of ΔH° indicates an exothermic biosorption reaction favorable at lower temperature while negative ΔS° confirms the decreased randomness at the solid–solution interface during biosorption.

4. Conclusion

An untried, low cost, locally available biosorbent was investigated for its anionic dye removal capacity from aqueous solution. Dried sugar beet pulp has been used successfully as an adsorbing agent for the removal of Gemazol turquoise blue-G dye from aqueous solution. Adsorption was influenced by various parameters such as initial pH, temperature and initial dye concentration. The maximum uptake of Gemazol turquoise blue-G by dried sugar beet pulp occurred at an initial pH of 2.0 and adsorption increased with increasing Gemazol turquoise blue-G dye concentration up to $800\,\mathrm{mg\,l^{-1}}$ and decreased with increasing temperature from 25 to 45 °C.

Adsorption equilibrium data were correlated with the Langmuir, Freundlich, Redlich–Peterson and Langmuir–Freundlich isotherms depending on temperature and the Langmuir and Redlich–Peterson models were found to provide the best fit of the experimental data in the concentration and temperature ranges 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 Gemazol turquoise blue-G or amount of adsorbent for desired purification.

According to the Langmuir model, the maximum dye biosorption capacity of biosorbent was $256.4\,\mathrm{mg\,g^{-1}}$ at 25 °C. The Gemazol turquoise blue-G adsorption capacity of dried sugar beet pulp was compared to the adsorption capacities of some other adsorbents reported in literature. Differences of dye uptake are due to the properties of each adsorbent such as structure, functional groups and surface area. Bustard et al. [34] examined the biosorption of Remazol turquoise blue-G by non-living *K. marxianus* IMB3 yeast and found a $98.0\,\mathrm{mg\,g^{-1}}$ maximum dye uptake capacity. Kargi and Ozmihci [35] studied the biosorption of the same reactive dye with powdered activated sludge and powdered activated carbon and determined the maximum biosorption capacity of each sorbent as 92.0 and $98.0\,\mathrm{mg\,g^{-1}}$, respectively. Aksu and Sen Cagatay [7] studied with the dried fungus *R. arrhizus* for the biosorption of Gemazol turquoise blue-G; the biosorption capacity of biosorbent was $625.0\,\mathrm{mg\,g^{-1}}$ at 45°. The comparison of results of this work with the others found in the literature showed that dried sugar beet pulp has a significantly high adsorption capacity for G(R)emazol turquoise blue-G dye.

The adsorption process rate and dynamic behavior of the system are very important factors for the process design and operation control. A film diffusion model and an intraparticle diffusion model developed by Weber and Morris were used to find both the boundary and intraparticle diffusion rate constants. Three simplified models including pseudo first-order, pseudo second-order and saturation type kinetic models were also used to test the adsorption kinetics. It was shown that the adsorption of Gemazol turquoise blue-G dye on to dried sugar beet pulp at 25, 35 and 45 °C is best described by all kinetic models with fairly high correlation coefficients with film and intraparticle diffusion being the essential rate controlling steps. The kinetic parameters obtained can be used for reactor design.

Thermodynamic constants were also evaluated using equilibrium constants changing with temperature. The negative value of ΔG° indicated the spontaneity and the negative values of ΔH° and ΔS° showed the exothermic nature and increase in order of Gemazol turquoise blue-G biosorption, respectively.

Results obtained from this study showed that dried sugar beet pulp was very effective at removing Gemazol turquoise blue-G dye to very high concentrations from the aqueous solution in a static batch system. Since sugar beet pulp, an agricultural solid waste, is freely, abundantly and locally available, the sorbent is expected to be economically viable for wastewater treatment. We believe that application of biosorption by dried sugar beet pulp in purification of waste water for the removal of Gemazol turquoise blue-G from industrial wastewaters can be suitable for the fabrication and designing of wastewater treatment plants by using these kinetic parameters.

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