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Use of dried sugar beet pulp for binary biosorption of Gemazol Turquoise Blue-G reactive dye and copper(II) ions: Equilibrium modeling

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Abstract

In this study, simultaneous biosorption of Gemazol Turquoise Blue-G reactive dye anions and copper(II) cations to dried sugar beet pulp, an agricultural solid waste by-product, from binary mixtures was studied and compared with single dye and metal ion situation in a batch stirred system. The effects of pH and single and dual component concentrations on the equilibrium uptake of each component, both singly and in mixture were investigated. The working pH value for the biosorption of single Gemazol Turquoise Blue-G dye and single copper(II) was determined as 2.0 and 4.0, respectively. The equilibrium uptake of each component increased with increasing its initial concentration up to 750 mg l^{-1} for dye and up to 200 mg l^{-1} for copper(II) ions for both pH values. The presence of increasing concentrations of copper(II) ions increased the equilibrium uptake of dye anions while the adding of increasing concentrations of dye diminished the copper(II) ion uptake for both pH values studied. This situation showed the synergistic effect of copper(II) cations on dye biosorption and the antagonistic effect of dye anions on copper(II) biosorption. Adsorption isotherms were developed for single-dye, single copper(II) and dual-dye-copper(II) ion systems at these two pH values and expressed by the mono-component Langmuir model and multi-component synergistic and antagonistic Langmuir models and model parameters were estimated by the non-linear regression.

Keywords: Dried sugar beet pulp; Gemazol Turquoise Blue-G; Copper(II); Binary biosorption; Synergism; Antagonism; Equilibrium modeling

1. Introduction

Because of their ease of use, inexpensive cost of synthesis, stability and variety of colors compared with natural dyes, synthetic dyestuffs have been increasingly used in the textile, paper, rubber, plastics, cosmetics, pharmaceutical and food industries [1,2]. 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 [3]. The extensive use of dyes often poses pollution problems in the form of colored wastewater discharge into water bodies. Even small quantities of dyes can color large water bodies; color not only affects aesthetic quality but also reduces sunlight penetration and photosynthesis [4]. In addition, some dyes are either toxic or mutagenic and carcinogenic due to the presence of metals and other chemicals, in their structure [5–7]. Reactive copper phthalocyanine dyes like Remazol Turquoise Blue-G are the most important derivative of reactive dye class and are preferred due to their brilliant hue, excellent light and wet fastness, high tinctorial strength, remarkable chemical stability wherever high quality turquoises, greens and blues are desired. The dye appears in the washwater in its 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. Besides the difficulty to remove color from metallized dyes, the wastewater often contain metal ions such as copper released during process. While copper phthalocyanine dyes are of wide use and importance within the textile industry, little is known of removal of these compounds from wastewaters [8–10].

Although some existing technologies – conventional chemical coagulation/flocculation, precipitation, ozonation, oxidation, adsorption – may exhibit removal of reactive dyes and metal ions, their initial and operational costs are so high that they constitute an inhibition to dyeing and finishing industries. In the past few years, extensive research has been undertaken to develop alternative and economic adsorbents [11–13]. An economic sorbent is defined as one which is abundant in nature, or is a by-product or waste from industry and requires

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little processing [11,12,14,15]. Biosorption is an alternative technology to remove metal ions and 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 [17]. Agricultural waste biosorbents generally used in biosorption studies are also inexhaustible, low-cost and non-hazardous materials, which are specifically selective for heavy metal ions and organics, and easily disposed by incineration. Agricultural by-products as a whole exceed 320,000,000 tonnes/year. Most of these by-products are considered to be low value products. A number of agricultural waste and by-products of cellulosic origin have been studied in the literature for their capacity to remove metal ions and dyes from aqueous solutions, such as coir pith, bagasse pitch, eucalyptus bark, sugarcane dust, sugar beet pulp, corncob, barley husk, sawdust, rice husk, powdered peanut hull, orange peel, etc. [11–16,18–26].

Much of the work on the biosorption has focused on the uptake of single pollutants. In practice, wastewaters are polluted with multiple components. In addition, the equilibrium modeling of multi-component biosorption, which is important in the design of treatment systems, has largely been neglected. The examining of the effects of binary pollutants in various combinations is more representative, of the actual environmental problems, than single pollutant studies. Bioremoval of a single species of pollutants using biosorbents is affected by several factors. These factors include the chemical nature of pollutant (species, size, ionic charge), specific surface properties of the biosorbent and environmental conditions (pH, temperature, ionic strength, existence of other components) [13,17]. Many other parameters affect the capacity of biosorbents to bind more than one species simultaneously. The combined effects of two or more components also depend on the number of pollutants competing for binding sites, pollutant combination, levels of pollutant concentration, order of pollutant addition and residence time. While the knowledge of the general uptake of single and multi species is increasing, relatively little is known about the combined effects of two or more metal and organic dye pollutants and simultaneous removal of these species from their mixture [27–35].

At the first stage of biosorption, a rapid equilibrium is established between sorbed component on the surface and unadsorbed component remaining in solution at a constant temperature. This equilibrium can be represented by adsorption isotherms. The most widely used isotherm equation for modeling equilibrium is the Langmuir equation [36], based on the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface, these binding sites have the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules. The mathematical description of this model for a single component adsorption is:

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

where Q° is the maximum possible amount of component per unit weight of adsorbent to form a complete monolayer on the surface bound at high C_{eq}, and b is a constant related to the affinity of the binding sites. Another way of expressing Q° is as the maximum value of q_{eq}.

Since the interaction of one component with the other components in a mixture may be synergistic, antagonistic or non-interactive, the biosorption results cannot be predicted on the basis of single-component studies [35]. The equilibrium data obtained in a multi-component system indicate that how these components affected each other's biosorption equilibrium due to solution pH as compared with results from single-component adsorption situation. The prediction of multi-component equilibrium data has always been complicated due to the interactive and competitive effects involved. The behavior of each species in a multi-component system depends strongly on the physical and chemical properties of both sorbent and sorbate. This determines the sorbate–sorbent chemical relation which affects the equilibrium behavior hereafter. In addition, the number and kind of species present, concentration of each component, the pH of solution decide the shape and equilibrium constants of the isotherm. Nevertheless attempts are carried out to predict and correlate multi-component data from single-component data.

Several competitive multi-component adsorption models have been proposed to describe the antagonistic interaction between the adsorbed quantity of one component and the concentrations of all other components, either in solution or already adsorbed at equilibrium. These isotherms range from simple models related to the individual isotherm parameters only (non-modified adsorption models), to more complex models related to the individual isotherm parameters and to correction factors (modified adsorption models) [27–33]. The above monocomponent Langmuir model can be extended to describe a competitive multicomponent adsorption system [33]. In this case the Langmuir model can be written as:

$$q_{eqi} = \frac{Q_i^{\circ} b_i (C_{eqi}/\eta_i)}{1 + \sum_{j=1}^{N} b_j (C_{eqj}/\eta_j)} \tag{2}$$

where C_{eqi} and q_{eqi} are the unadsorbed concentration of i component in the mixture at equilibrium and the adsorbed quantity of i component per g of adsorbent at equilibrium, respectively. b_i and Q_i° are derived from the corresponding individual Langmuir isotherm equation and η_i is the Langmuir correction coefficient of the i component where estimated from competitive adsorption data. For binary mixtures, Eqs. (3a) and (3b) can be rewritten as for the first and the second component, respectively, and these two equations can be solved simultaneously to obtain the multi-component Langmuir adsorption constants of the first and the second components, respectively.

$$q_{eq1} = \frac{Q_1^{\circ} b_1 C_{eq1}/\eta_1}{1 + (b_1 C_{eq1}/\eta_1) + (b_2 C_{eq2}/\eta_2)} \tag{3a}$$

$$q_{eq2} = \frac{Q_2^{\circ} b_2 C_{eq2}/\eta_2}{1 + (b_1 C_{eq1}/\eta_1) + (b_2 C_{eq2}/\eta_2)} \tag{3b}$$

However, there is very limited data proposed a multi-component equilibrium model predicting the synergistic interaction between the adsorbed component and the concentrations of all other components. One of the proposed synergistic equilibrium model developed from the mono-component Langmuir adsorption model using the single component parameters and correction factors and has been proposed by Eq. (4).

$$q_{eqi} = \frac{Q_i^{\circ} b_i C_{eqi}}{1 + b_i C_{eqi}} [1 + F_i(C)]_i \quad (4)$$

where $F_i(C)$ represents the positive fractional deviation of the multi-component adsorption isotherm from the single-component Langmuir isotherm for component i. $F_i(C)$ assumed to be specific for each q_i is expressed by Eq. (5)

$$F_i(C) = \frac{\sum_{j=1, j\neq i}^{N} K_j C_{oj}}{\sum_{j=1}^{N} K_j C_{oj}} \quad (5)$$

where C_{oj} represents the initial concentration of j component in the mixture, and K_j is a modification coefficient for component j. According to Eqs. (4) and (5) the binary form of the modified synergistic Langmuir model for the first and the second components can be expressed as:

$$q_{eq1} = \frac{Q_1^{\circ} b_1 C_{eq1}}{1 + b_1 C_{eq1}} \left[1 + \frac{K_2 C_{o2}}{K_1 C_{o1} + K_2 C_{o2}}\right] \quad (6a)$$

$$q_{eq2} = \frac{Q_2^{\circ} b_2 C_{eq2}}{1 + b_2 C_{eq2}} \left[1 + \frac{K_1 C_{o1}}{K_1 C_{o1} + K_2 C_{o2}}\right] \quad (6b)$$

K_j values may be estimated from numerical simulations of two-component adsorption data [34,35].

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 simultaneous removal of Gemazol Turquoise Blue-G and copper(II) on dried sugar beet pulp in a batch stirred system. These components were selected as Gemazol Turquoise Blue-G is a typical dyestuff containing copper(II) in its structure with relatively higher consumption rates in the cotton dyeing process so they are frequently encountered together in textile wastewaters. 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 dye and dye-heavy metal biosorptions. The binding capacity of sorbent was shown as a function of pH, single and dual component concentrations. The mono- and multi-component Langmuir adsorption models used to predict and/or correlate mono- and multi-component equilibrium data were presented and applied to all combinations of two components in their aqueous solutions. Moreover a statistical comparison of the methods was carried out.

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 60 °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 [25,37]. 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 single copper(II) or single Gemazol Turquoise Blue-G dye were prepared by diluting 1.0 g l^{-1} of stock solution of each component to the desired concentrations. Stock solutions of copper(II) and Gemazol Turquoise Blue-G dye were obtained by dissolving the exact quantities of analytical grade $CuSO_4 \cdot 5H_2O$ (Merck) and Gemazol Turquoise Blue-G, a copper phthalocyanine reactive dye consists of a tetrasulfonated copper phthalocyanine (CuPc) with one to two of the sulfonate groups converted to linker arms [$CuPc(SO_3H)_{2-3}(SO_2NH\text{-}C_6H_4\text{-}SO_2\text{-}CH{=}CH_2)_{1-2}$], Color index name: Reactive Blue 21; molecular weight; 576.1; purity: not specified; (supplied from Gemsan, Turkey), in 1 l of double-distilled water, respectively. For binary mixture studies of copper(II) and dye ions, desired combinations of copper(II) and dye ions were prepared by diluting 1.0 g l^{-1} of stock solutions of components and mixing them in the test medium. Before mixing the biosorbent, the pH of each test solution was adjusted to the required value with diluted and concentrated H_2SO_4 and NaOH solutions, respectively. The range of concentrations of prepared solutions varied between 25 and 200 mg l^{-1} for copper(II) and between 25 and 750 mg l^{-1} for dye. Insignificant decreases in the final equilibrium pH were recorded, so during the uptake pH was assumed constant.

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 at desired level of each component were placed in a thermostatic rotary shaker at the desired temperature and pH. For the studies, 0.1 g of biosorbent was treated with 100 ml of single or binary mixture bearing solution. The flasks were shaken at

150 rpm for 24 h to ensure equilibrium was reached. Samples (5 ml) were taken before mixing the biosorbent and adsorption solution, at the beginning of adsorption and at definite times. The adsorption solution was separated from the biosorbent by centrifugation at 5000 rpm for 5 min and then the supernatant liquid was analysed for copper(II) and Gemazol Turquoise Blue-G dye. Uptake values were determined as the difference between the initial pollutant concentration and the one in the supernatant. Studies were performed at a constant temperature of 25 °C to be representative of environmentally relevant conditions. All the biosorption experiments were repeated twice to confirm the results and the average values were used for further calculations. A blank test without biosorbent was also performed for each case to evaluate possible color change and/or precipitation processes for both components and no color change and no precipitation were observed in biosorption medium due to the pH change, addition of second component, level of each component and adsorption time consumed.

2.4. Analysis of copper(II) and Gemazol Turquoise Blue-G dye

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 color was read at 341 nm. The concentration of residual copper(II) ions in the biosorption medium was determined in Hitachi Polarized Zeeman atomic absorption spectrophotometer with the detection limit of 0.05 ppm at the wavelength of 232.0 nm.

3. Results and discussion

Since real wastewaters will contain all kinds of pollutants, adsorption systems design must be based on multi-component effluents, making multi-component equilibrium data a necessity due to pH. In the mixtures of two or more species in a solution, the synergistic or antagonistic interaction occurring between the species might affect the individual uptake by the sorbent. On this basis simultaneous biosorption of Gemazol Turquoise Blue-G and copper(II) to dried sugar beet pulp from binary mixture was investigated and compared with single Gemazol Turquoise Blue-G or copper(II) situation in a batch system. The equilibrium results are given as the units of adsorbed copper(II) or dye quantity in single- or multi-component situation per gram of biosorbent at equilibrium (q_{eqi}, mg g^{-1}) and residual copper(II) or dye concentration in single or multi-component situation at equilibrium (C_{eqi}, mg l^{-1}). The adsorption yield is defined as the ratio of sorbed concentration of copper(II) or dye at equilibrium (this value is also equal to q_{eqi} value since the biomass concentration is 1.0 g l^{-1}) to the initial copper(II) or dye concentration for single component removal situation (Ad%). Individual and total adsorption yields in the simultaneous removal from the mixture of copper(II) and dye were also defined as the ratios of individual and total adsorbed concentrations of each component at equilibrium to individual and total initial component concentrations, respectively (Ad_i%, Ad_{Tot}%).

3.1. Effect of pH on the biosorption of Gemazol Turquoise Blue-G dye and copper(II)

pH is an important factor influencing dye or heavy metal biosorption on agricultural by-products. pH affects not only surface charge of the biosorbent, but also the degree of ionization of the species in solution so different species may have different pH optima [24,25]. Different functional groups with distinct acidities and the content of these functional groups present on the biosorbent surface can be determined by potentiometric titration. From the pH values deduced at the two-half equivalence points of the titration curves, it is possible to determine the global acidity (pK_a) of each functional group. The studies on the potentiometric titration of protonated beet pulp sample showed the presence of strong acidic groups, probably of carboxylic type according to their respective pK_a, 3.7 and 4.8. It was explained that each of these moieties is a potential ligand for metal ions and the difference in acidity of the carboxyl groups certainly induces a difference in metal ion reactivity [24]. The effect of pH on the equilibrium uptake of copper(II) and Gemazol Turquoise Blue-G dye was investigated between pH 1.0–6.0 since the precipitation by formation of copper(II) hydroxide ($Cu(OH)_2$) may occur above pH 6.0 and copper is mainly present in its free ionic form (Cu^{2+}) at pH values less than 5.0 [34,38]. As shown in Fig. 1 both the dye and copper(II) removals were strongly dependent on pH. At 100 mg l^{-1} initial ion concentration the uptake of free ionic copper(II) increased by increasing initial pH and was the greatest at pH 4.0 as 24.9 mg g^{-1}. The dye was more effectively adsorbed by the biosorbent than copper(II) at low pH values and found to be maximum at pH 2.0 as 83.7 mg g^{-1}.

The different pH binding profiles for these components could be due to the nature of the chemical interactions of each species with the sorbent. The reactive dyes release colored dye anions in solution. It is expected that at pH 2.0, most of the potential fixation sites are protonated. Higher uptakes of dye obtained at lower pH values may be due to the electrostatic attractions between these negatively charged dye anions and positively charged biomass surface [9]. The low level of copper(II) uptake

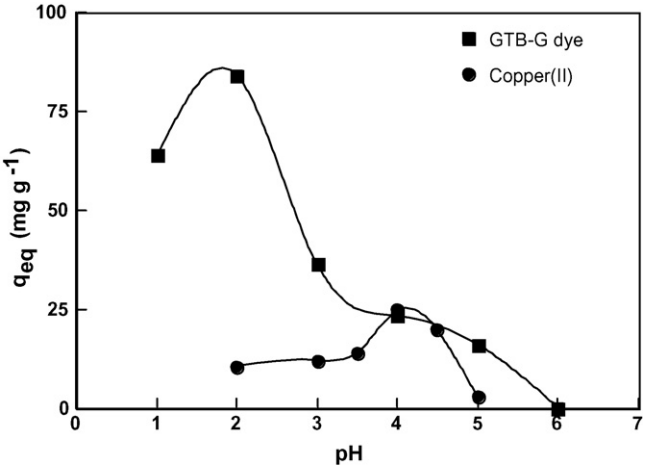

Fig. 1. Effect of pH on the equilibrium uptake of Gemazol Turquoise Blue-G dye and copper(II) ions in the single component situation (C_o: 100 mg l^{-1}, X: 1.0 g l^{-1}, T: 25 °C).

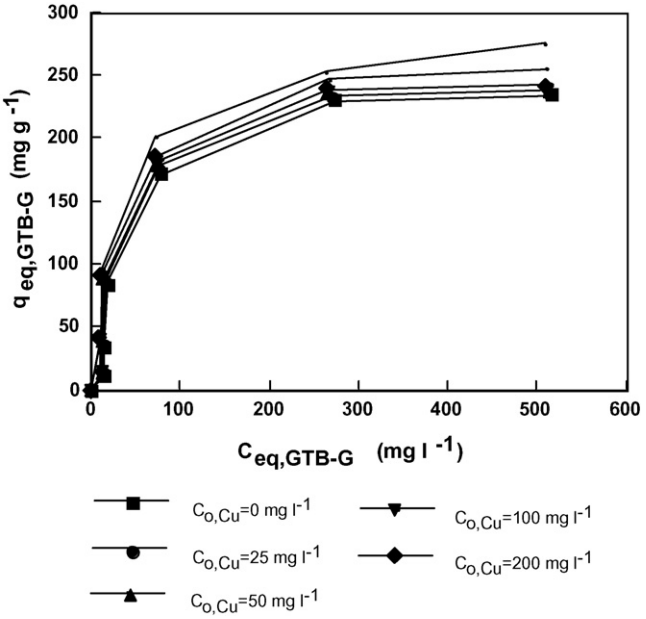

Fig. 2. The comparison of the experimental and estimated adsorption isotherms of Gemazol Turquoise Blue-G dye adsorption to dried sugar beet pulp with the Gemazol Turquoise Blue-G dye present as the single component and in the presence of increasing concentrations of copper(II) at pH 2.0 (X: 1.0 g l^{-1}, T: 25 °C) (lines represent model simulation, symbols represent experimental data).

at lower pH values could be attributed to the increased concentration of hydrogen (H^+) and hydronium (H_3O^+) ions competing for copper(II) binding sites on the biomass [39]. The smaller biosorption values observed at low pH have been attributed to the competition between the protons and the ions released, i.e., sodium(I), phosphorus(III), calcium(II), etc., by pulp into the solution. Moreover ion exchange with calcium(II) ions neutral-

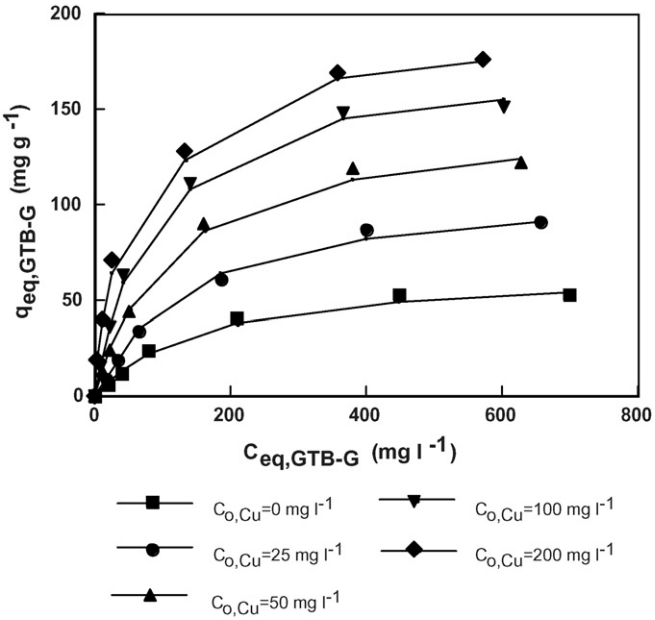

Fig. 3. The comparison of the experimental and estimated adsorption isotherms of Gemazol Turquoise Blue-G dye adsorption to dried sugar beet pulp with the Gemazol Turquoise Blue-G dye present as the single component and in the presence of increasing concentrations of copper(II) at pH 4.0 (X: 1.0 g l^{-1}, T: 25 °C) (lines represent model simulation, symbols represent experimental data).

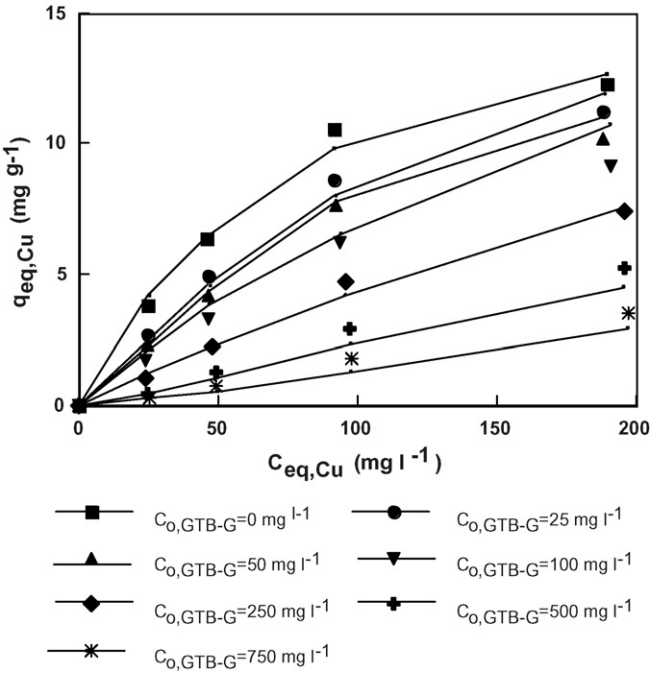

Fig. 4. The comparison of the experimental and estimated adsorption isotherms of copper(II) adsorption to dried sugar beet pulp with the copper(II) present as the single component and in the presence of increasing concentrations of Gemazol Turquoise Blue-G dye at pH 2.0 (X: 1.0 g l^{-1}, T: 25 °C) (lines represent model simulation, symbols represent experimental data).

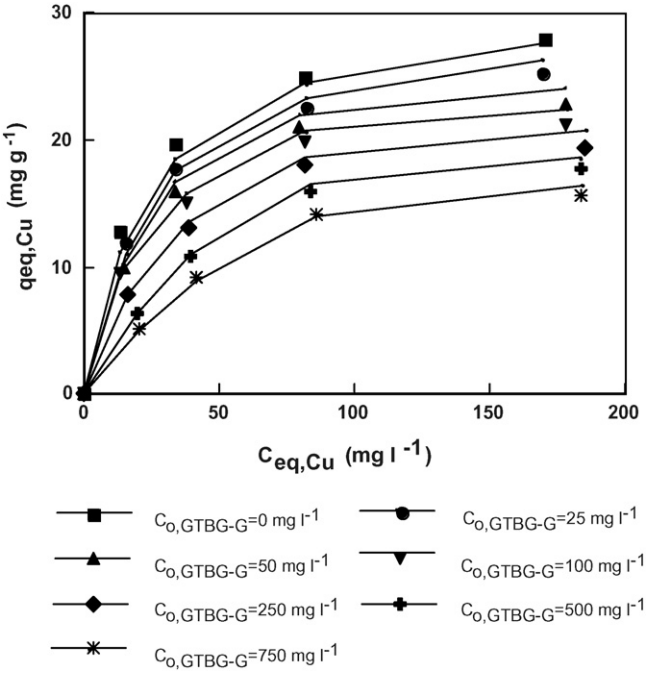

Fig. 5. The comparison of the experimental and estimated adsorption isotherms of copper(II) adsorption to dried sugar beet pulp with the copper(II) present as the single component and in the presence of increasing concentrations of Gemazol Turquoise Blue-G dye at pH 4.0 (X: 1.0 g l^{-1}, T: 25 °C) (lines represent model simulation, symbols represent experimental data).

izing the carboxyl groups of the polysaccharide may be the other predominant mechanism. As the pH of the system increases up to pK_{a1}, the number of negatively charged sites increases extremely and copper(II) ions are mainly fixed on related active sites in this case [4,7,14,17,18,40,41].

It is also obvious that the proposed biosorption mechanisms due to the pH are not sufficient to explain the biosorptions of both components observed at all the pH values studied. It is thought that additional types of biosorption mechanisms such as complex formation, chelation and microprecipitation or membrane transport and physicochemical forces such as van der Waals, H-binding are also important for the bioremoval of dye and copper(II) ions by the biomass, irrespective of initial pH [17,40]. However, the initial pH of wastewater could provide selectivity for the removal of the desired component in the mixture of Gemazol Turquoise Blue-G and copper(II) and this situation was observed in the simultaneous removal of these components studying at these two initial pH values.

3.2. Single and dual biosorption of copper(II) and Gemazol Turquoise Blue-G dye with respect to initial pH

The experimental equilibrium data (adsorption isotherms) of single copper(II) and single Gemazol Turquoise Blue-G dye biosorption at pH 2.0 and pH 4.0 are shown in Figs. 2–5. As seen from the figures, for both pH values the equilibrium uptake increased with increasing the initial pollutant concentration up to 750 mg l^{-1} for dye and up to 200 mg l^{-1} for copper(II) and maximum uptakes at these initial concentrations were determined as 234.8 and 52.2 mg dye g^{-1} biosorbent and as 12.3 and 28.5 mg copper(II) g^{-1} biosorbent at pH 2.0 and pH 4.0, respectively. The data also indicated that the uptake capacity of dried sugar beet pulp for copper(II) was generally less than that of the dye due to lower affinity of the sorbent for copper(II) for both pH values studied.

For binary sorption studies, while initial Gemazol Turquoise Blue-G dye concentration was changed from 25 to 750 mg l^{-1}, initial copper(II) concentration was held constant at 25, 50, 100, or 200 mg l^{-1} for each experiment set. The adsorption isotherms of dye obtained in the absence and in the presence of different concentrations of copper(II) at the two pH values are shown in Figs. 2 and 3. Equilibrium dye uptake increased with raising initial dye concentration up to 750 mg l^{-1} at all copper(II) concentrations studied for both pH values. The curvilinear relationship between the amount of dye adsorbed per unit weight of biosorbent and the residual dye concentration at equilibrium suggests that saturation of binding sites occurred at higher concentrations of this component. Higher dye uptakes were obtained

Table 1
Comparison of the individual and total equilibrium uptakes and individual and total adsorption yields found at different initial Gemazol Turquoise Blue-G dye concentrations at pH 2.0 in the absence and in the presence of increasing concentrations of copper(II)

C_{oGTB} (mg l^{-1})	C_{oCu} (mg l^{-1})	q_{eqGTB} (mg g^{-1})	%Ad_{GTB}	q_{eqCu} (mg g^{-1})	%Ad_{Cu}	$C_{o(GTB+Cu)}$ (mg l^{-1})	$q_{eq(GTB+Cu)}$ (mg g^{-1})	%Ad_{Tot}
25.4	0.0	11.8	46.4	0.0	0.0	25.4	11.8	46.4
48.4	0.0	33.9	70.1	0.0	0.0	48.4	33.9	70.1
101.8	0.0	83.7	82.2	0.0	0.0	101.8	83.7	82.2
251.0	0.0	172.3	68.6	0.0	0.0	251.0	172.3	68.6
502.1	0.0	230.3	45.9	0.0	0.0	502.1	230.3	45.9
750.0	0.0	234.8	31.3	0.0	0.0	750.0	234.8	31.3
26.7	27.4	13.0	48.7	2.7	9.8	54.1	15.7	29.0
50.2	26.7	35.4	70.5	2.3	8.5	76.9	37.7	49.0
101.0	25.3	85.2	84.4	1.8	6.9	126.3	87.0	68.8
249.6	25.1	174.4	69.9	1.0	4.1	274.7	175.4	63.9
502.5	26.0	232.5	46.3	0.4	1.7	527.6	232.9	44.1
749.0	25.3	234.5	31.3	0.2	0.9	774.3	234.7	30.3
25.3	51.4	13.3	52.6	4.9	9.5	76.7	18.2	23.7
50.2	50.3	37.7	75.1	4.2	8.3	100.5	41.9	41.6
99.4	49.8	87.6	88.1	3.3	6.6	149.2	90.9	60.9
251.2	50.0	177.6	70.7	2.1	4.1	301.2	179.7	59.6
500.0	50.1	235.0	47.0	1.2	2.4	550.2	236.2	42.9
750.8	49.9	236.3	31.5	0.7	1.1	800.7	237.0	29.6
25.0	100.4	13.7	54.8	8.6	8.6	125.4	22.3	17.8
50.3	100.7	39.5	78.5	7.6	7.5	151.0	47.1	31.2
103.8	100.4	89.6	86.3	6.5	6.4	204.2	96.0	47.1
252.0	99.9	178.4	70.8	4.2	4.2	351.9	182.6	51.9
502.5	100.0	236.3	47.0	2.5	2.5	602.5	238.7	39.6
749.0	99.6	238.0	31.8	1.8	1.8	848.6	239.8	28.3
25.5	199.8	14.3	56.1	11.2	5.6	225.3	25.5	11.3
50.6	199.5	41.7	82.4	10.3	5.2	250.1	52.0	20.8
100.8	200.6	90.6	89.9	9.7	4.8	301.4	100.3	33.3
257.6	203.2	185.6	72.1	7.4	3.6	460.8	193.0	41.9
501.3	200.9	238.8	47.6	5.2	2.6	702.2	244.0	34.7
750.8	200.8	241.5	32.2	3.6	1.8	951.6	245.1	25.8

at pH 2.0 as expected since the pH value of 2.0 had a selective effect for the removal of dye in the mixture of copper(II) and dye. The equilibrium uptake of dye also increased with the increasing initial concentrations of copper(II) indicating the synergistic effect of copper(II) on dye biosorption. As seen from Figs. 2 and 3, and Tables 1 and 2, the increase in equilibrium uptake of dye was insignificant at pH 2.0 while a regular and notable increase was observed at pH 4.0 with increasing copper(II) concentration. For example, at a 100 mg l^{-1} constant initial dye concentration, in the absence of copper(II) and in the presence of 100 mg l^{-1} of copper(II), equilibrium uptakes of dye were found as 83.7 and 89.6 mg g^{-1} at pH 2.0 and were found as 23.3 and 62.7 mg g^{-1}, respectively, at pH 4.0. The increase in the uptake of dye was 6.6% at pH 2.0 and was 62.8% at pH 4.0 in the presence of 100 mg l^{-1} of copper(II) concluding that pH 4.0 much more greatly affected the uptake of dye than that of pH 2.0. The reactive dye used in this study contains an azo linkage with hydroxy groups. These groups make a situation favourable for chelate formation with copper(II) ions at higher pH values and enhance the dye adsorption due to the possibilities of added bond formations with the biosorbent sugar beet pulp, a natural polysaccharide composed of 20% and more than 40% of cellulosic and pectic substances, respectively. As the stronger acidic conditions inhibited the formation of such a complex, the increase in dye uptake capacity due to copper(II) concentration was unimportant at pH 2.0 [42]. As seen from both the tables, in general the increase in initial Gemazol Turquoise Blue-G concentration up to 100 mg l^{-1} enhanced the individual adsorption yield of dye; further increase in dye concentration resulted in a decrease in dye uptake yield at pH 2.0. Although the addition of copper(II) increased the individual adsorption yield of dye slightly, total adsorption yield lessened while the concentration of copper(II) increased in the mixture for each experimental set at the same pH. At pH 4.0 individual adsorption yield of dye also increased with increasing initial copper(II) concentration, however, decreased with increasing initial dye concentration notably.

At this part of studies, this time, the uptake of copper(II) in the presence of changing concentrations of dye was investigated at the initial pH values of 2.0 and 4.0. Figs. 4 and 5 depict the variations of copper(II) uptakes at equilibrium with increasing initial copper(II) concentration (from 25 to 200 mg l^{-1}) at constant initial dye concentrations at the two pH values studied. Similar biosorption patterns were obtained both in the single-copper(II) and copper(II)-dye systems; copper(II) equilibrium uptake diminished with increasing initial copper(II) concentration up to

Table 2
Comparison of the individual and total equilibrium uptakes and individual and total adsorption yields found at different initial Gemazol Turquoise Blue-G dye concentrations at pH 4.0 in the absence and in the presence of increasing concentrations of copper(II)

C_{oGTB} (mg l^{-1})	C_{oCu} (mg l^{-1})	q_{eqGTB} (mg g^{-1})	%Ad_{GTB}	q_{eqCu} (mg g^{-1})	%Ad_{Cu}	$C_{o(GTB+Cu)}$ (mg l^{-1})	$q_{eq(GTB+Cu)}$ (mg g^{-1})	%Ad_{Tot}
25.0	0.0	6.0	24.0	0.0	0.0	25.0	6	24.0
49.5	0.0	11.8	23.8	0.0	0.0	49.5	11.8	23.8
102.9	0.0	23.3	22.7	0.0	0.0	102.9	23.3	22.7
250.0	0.0	40.6	16.2	0.0	0.0	250.0	40.6	16.2
500.0	0.0	52.2	10.4	0.0	0.0	500.0	52.2	10.4
750.0	0.0	52.2	7.0	0.0	0.0	750.0	234.4	52.2
24.3	27.4	8.6	35.4	11.9	43.3	51.7	20.5	39.6
52.8	24.4	18.5	35.0	10.0	40.8	77.3	28.5	36.9
96.3	24.9	33.2	34.4	9.7	38.7	121.3	42.8	35.3
245.3	24.2	60.7	24.7	7.9	32.8	269.5	68.6	25.5
486.5	25.4	86.5	17.8	6.2	24.4	511.9	92.7	18.1
746.7	25.1	90.4	12.1	5.1	20.4	771.7	95.5	12.4
22.1	51.4	12.8	57.7	17.8	34.6	73.5	30.5	41.5
44.4	50.3	23.7	53.3	17.0	33.7	94.7	40.6	42.9
95.3	53.3	43.8	46.0	15.7	29.4	148.6	59.5	40.1
250.7	52.3	89.3	35.6	13.7	26.1	303.0	103.0	34.0
497.9	50.7	118.8	23.9	11.2	22.1	548.6	130.0	23.7
749.6	50.2	121.0	16.2	9.2	18.3	799.8	130.2	16.3
23.2	104.9	14.4	54.8	22.6	21.6	128.0	37.0	28.9
56.4	100.7	35.1	78.5	21.1	20.9	157.1	56.1	35.7
103.7	102.2	62.7	86.3	20.4	19.9	205.8	83.0	40.3
250.0	99.4	110.7	70.8	18.0	18.1	349.4	128.7	36.8
513.5	100.3	147.9	47.0	16.9	16.9	613.8	164.8	26.9
752.5	100.1	150.2	31.8	14.5	14.4	852.6	164.7	19.3
21.4	194.8	18.3	85.6	25.2	12.9	216.2	43.5	20.1
50.7	200.8	39.3	77.6	22.9	11.4	251.5	62.2	24.8
94.3	200.1	70.3	74.6	21.8	10.9	294.4	92.1	31.3
259.3	204.7	127.3	49.1	19.4	9.5	464.0	146.7	31.6
526.0	201.6	168.8	32.1	17.8	8.8	727.6	186.6	25.6
746.7	199.8	173.5	23.2	15.6	7.8	946.5	189.1	20.0

Table 3
Comparison of the individual and total equilibrium uptakes and individual and total adsorption yields found at different initial copper(II) concentrations at pH 2.0 in the absence and in the presence of increasing concentrations of Gemazol Turquoise Blue-G dye

C_{oCu} (mg l^{-1})	C_{oGTB} (mg l^{-1})	q_{eqCu} (mg g^{-1})	%Ad_{Cu}	q_{eqGTB} (mg g^{-1})	%Ad_{GTB}	$C_{o(Cu+GTB)}$ (mg l^{-1})	$q_{eq(Cu+GTB)}$ (mg g^{-1})	%Ad_{Tot}
28.2	0.0	3.8	13.4	0.0	0.0	28.2	3.8	13.4
51.9	0.0	6.3	12.2	0.0	0.0	51.9	6.3	12.1
101.8	0.0	10.1	10.1	0.0	0.0	101.8	10.1	10.1
201.8	0.0	12.3	6.1	0.0	0.0	201.8	12.3	6.1
27.4	26.7	2.7	9.8	13.0	48.7	54.1	15.7	29.0
51.4	25.3	4.9	9.5	13.3	52.6	76.7	18.2	23.7
100.4	25.0	8.6	8.6	13.7	54.8	125.4	22.3	17.8
199.8	25.5	11.2	5.6	14.3	56.1	225.3	25.5	11.3
26.7	50.2	2.3	8.5	35.4	70.5	76.9	37.7	49.0
50.3	50.2	4.2	8.3	37.7	75.1	100.5	41.9	41.6
100.7	50.3	7.6	7.5	39.5	78.5	151.0	47.1	31.2
199.5	50.6	10.3	5.2	41.7	82.4	250.1	52.0	20.8
25.3	101.1	1.8	6.9	85.2	84.4	126.3	87.0	68.8
49.8	99.4	3.3	6.6	87.6	88.1	149.2	90.9	60.9
100.4	103.8	6.5	6.4	89.6	86.3	204.2	96.1	47.1
200.6	100.8	9.7	4.8	90.6	89.9	301.4	100.3	33.3
25.1	249.6	1.0	4.1	174.4	69.9	274.7	175.4	63.9
50.0	251.2	2.1	4.1	177.6	70.7	301.2	179.7	59.6
99.9	252.0	4.2	4.2	178.4	70.8	351.9	182.6	51.9
203.2	257.6	7.4	3.6	185.6	72.1	460.8	193.0	41.9
25.1	502.5	0.4	1.7	232.5	46.3	527.6	232.9	44.1
50.2	500.0	1.2	2.4	235.0	47.0	550.2	236.2	42.9
100.0	502.5	2.5	2.5	236.3	47.0	602.5	238.7	39.6
200.9	501.3	5.2	2.6	238.8	47.6	702.2	244.0	34.7
25.3	749.0	0.2	0.9	234.5	31.3	774.3	234.7	30.3
49.9	750.8	0.7	1.4	236.2	31.5	800.7	237.0	29.6
99.6	749.0	1.8	1.8	238.0	31.8	848.6	239.8	28.3
200.8	750.8	3.6	1.8	241.5	32.2	951.6	245.1	25.8

200 mg l^{-1} and increases in dye concentration lessened the equilibrium uptake of copper(II) considerably for both the pH values studied. The data in Tables 3 and 4 also indicated that extent of dye inhibition on copper(II) biosorption yield was dependent both on dye concentration as well as pH. The decrease in pH and the increase in dye concentration had a lessening effect on the individual uptake and uptake yield of copper(II). At 100 mg l^{-1} initial copper(II) concentration, in the absence of dye ions and in the presence of 100 mg l^{-1} Gemazol Turquoise Blue-G dye concentration, equilibrium uptakes of copper(II) were found as 10.3 and 6.2 mg g^{-1} at pH 2.0 and were found as 24.9 and 19.9 mg g^{-1}, respectively, at pH 4.0. The reduction of copper(II) uptake in the presence of 100 mg l^{-1} dye concentration was 39.8% at pH 2.0 and 20.1%, at pH 4.0. According to these results it can be said that the inhibitory effect of dye anions on the equilibrium copper(II) uptake is dominant at pH 2.0 due to selective and higher biosorption of dye anions at this pH value. As a result the copper(II) uptake by dried sugar beet pulp was reduced due to the presence of dye indicating the antagonistic effect of dye on copper(II) biosorption. As seen from the same tables, the individual adsorption yield of copper(II) lessened with raising the concentrations of both copper(II) and Gemazol Turquoise Blue-G at pH 2.0. In general total adsorption yield for each experimental set increased with the increase in Gemazol Turquoise Blue-G concentration up to 100 mg l^{-1}. However, further increase in dye concentration resulted in a decrease in total uptake yield at the same pH. At pH 4.0 the individual adsorption yield of copper(II) also diminished with increasing initial copper(II) and dye concentrations. Moreover total adsorption yield tended to decrease at higher initial dye concentrations in the mixtures.

For simultaneous biosorption of copper(II) and Gemazol Turquoise Blue-G dye, the data obtained in the single and dual systems indicated that the two ions affected each other's biosorption equilibrium due to solution pH and level of co-component. It was obvious that a significant part of uptake capacity of biosorbent was used for the dye adsorption for both pH values. It was seen that although the optimum pH was 2.0 for the Gemazol Turquoise Blue-G removal, the uptake of dye was significantly increased by the addition of copper(II) ions at pH 4.0 whereas the presence Gemazol Turquoise Blue-G ions decreased the adsorptive capacity of biosorbent for copper(II) ions notably and this effect increased as dye level increased for both pH values studied. The adsorption data for copper(II) approached the single-ion situation at lower concentrations of the dye component while the equilibrium uptake of Gemazol Turquoise Blue-G dye increased with raising the concentration of copper(II) ions for both pH vales studied.

Table 4
Comparison of the individual and total equilibrium uptakes and individual and total adsorption yields found at different initial copper(II) concentrations at pH 4.0 in the absence and in the presence of increasing concentrations of Gemazol Turquoise Blue-G dye

C_{oCu} (mg l^{-1})	C_{oGTB} (mg l^{-1})	q_{eqCu} (mg g^{-1})	%Ad_{Cu}	q_{eqGTB} (mg g^{-1})	%Ad_{GTB}	$C_{o(Cu+GTB)}$ (mg l^{-1})	$q_{eq(Cu+GTB)}$ (mg g^{-1})	%Ad_{Tot}
25.6	0.0	12.8	49.8	0.0	0.0	25.6	12.8	49.8
53.0	0.0	19.7	37.1	0.0	0.0	53.0	19.7	37.1
106.1	0.0	24.6	23.1	0.0	0.0	106.1	24.6	23.1
198.3	0.0	28.1	14.2	0.0	0.0	198.3	28.1	14.2
27.4	24.3	11.9	43.3	8.6	35.4	51.7	20.5	39.6
51.4	22.1	17.8	34.6	12.8	57.7	73.5	30.5	41.5
104.9	23.2	22.6	21.6	14.4	62.3	128.0	37.0	28.9
194.8	21.4	25.2	12.9	18.3	85.6	216.2	43.5	20.1
24.4	47.8	10.0	40.8	18.5	38.7	72.3	28.5	39.4
50.3	44.4	17.0	33.7	23.7	53.3	94.7	40.6	42.9
100.7	44.4	21.1	20.9	35.1	79.0	145.1	56.1	38.7
200.8	44.7	22.9	11.4	39.3	88.1	245.5	62.2	25.4
22.9	96.3	9.7	42.1	33.2	34.4	119.3	42.8	35.9
53.3	95.3	15.7	29.4	43.8	46.0	148.6	59.5	40.1
102.2	99.7	20.4	19.9	62.7	62.9	201.8	83.0	41.1
200.1	94.3	21.8	10.9	70.3	74.6	294.4	92.1	31.3
24.2	245.3	7.9	32.8	60.7	24.7	269.5	68.6	25.5
52.3	250.7	13.7	26.1	89.3	35.6	303.0	103.0	34.0
99.4	250.0	18.0	18.1	110.7	44.3	349.4	128.7	36.8
204.7	259.3	19.4	9.5	127.3	49.1	464.0	146.7	31.6
25.4	486.5	6.2	24.4	86.5	17.8	511.9	92.7	18.1
50.7	497.9	11.2	22.1	118.8	23.9	548.6	130.0	23.7
100.3	513.5	16.9	16.9	147.9	28.8	613.8	164.8	26.9
201.6	526.0	17.8	8.8	168.8	32.1	727.6	186.6	25.6
25.1	746.7	5.1	20.4	90.4	12.1	771.7	95.5	12.4
50.2	749.6	9.2	18.3	121.0	16.2	799.8	130.2	16.3
100.1	752.5	14.5	14.4	150.2	20.0	852.6	164.7	19.3
199.8	746.7	15.6	7.8	173.5	23.2	946.5	189.1	20.0

3.3. Equilibrium modeling of single and dual biosorption of copper(II) and Gemazol Turquoise Blue-G dye with respect to pH

As all determined biosorption isotherms exhibited a similar shape resembling that of Langmuir type isotherm of gas adsorption, it was decided to describe the available experimental biosorption data with Langmuir model(s). The mono-component Langmuir model was applied to the equilibrium data of single Gemazol Turquoise Blue-G dye and copper(II) biosorptions at the two pH values studied and individual adsorption constants are listed in Table 5 with the linear regression coefficients. In view of the values of linear regression coefficients, this model exhibited a good fit to the adsorption data of dye and copper(II) in the studied concentration range for both the pH values studied considering that obtained linear regression coefficients are greater than 0.984. 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 biosorbent for each component. Q°, one of the Langmuir constants, represents the monolayer saturation at equilibrium or the total capacity of biosorbent for each species. From Table 5, the values of Q° differed greatly from species to species due to pH. Dye uptake at pH 2.0 was greatest with a maximum value of 256.4 mg g^{-1}, while maximum uptake level of copper(II) was 31.4 mg g^{-1} at pH 4.0. The value of Q° tabulated in Table 5 (66.7 mg g^{-1}) also appeared to be significantly higher for dye in comparison with the uptake of copper(II) at the same pH value of 4.0. 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 of biosorbent for the binding of each component. Its value is the reciprocal of the concentration at which half of the saturation of the adsorbent is attained (or amount of $Q^{\circ}/2$ is bound). A high b value indicates a high affinity. The higher value of b implied the strong bonding of Gemazol Turquoise Blue-G to dried pulp at pH 2.0 and copper(II) ions at pH 4.0.

At a constant dye concentration the uptake of copper(II) ions at changing copper(II) concentrations, and at a constant copper(II) concentration the uptake of dye ions at changing dye concentrations on the dried sugar beet pulp were expressed by the multi-component antagonistic (competitive) and synergistic Langmuir adsorption models, respectively. Using the mono-component Langmuir constants for each species given in Table 5, the multi-component Langmuir constants were evaluated from the antagonistic and synergistic adsorption models at pH 2.0 and at pH 4.0. The relative model parameters are listed in Table 6. Using the individual and multi-component Langmuir adsorption constants, equilibrium uptake values of each component ($q_{eq,Cu}$; $q_{eq,GTB\text{-}G}$) were predicted from the related multi-component

Table 5
Mono-component Langmuir adsorption constants obtained for single copper(II) and single Gemazol Turquoise Blue-G dye biosorptions at pH 2.0 and at pH 4.0 with the linear regression coefficients

Component	pH 2.0			pH 4.0		
	Q° (mg g^{-1}) or [(mmol g^{-1})]	b (l mg^{-1})	R^2	Q° (mg g^{-1}) or [(mmol g^{-1})]	b (l mg^{-1})	R^2
GTBG dye	256.4 or [0.445]	0.020	0.999	66.7 or [0.116]	0.006	0.988
Copper(II)	18.2 or [0.286]	0.012	0.984	31.4 or [0.494]	0.043	0.999

Table 6
Multi-component Langmuir adsorption constants evaluated from the antagonistic (competitive) and synergistic Langmuir adsorption models for simultaneus biosorption of copper(II) and Gemazol Turquoise Blue-G onto dried sugar beet pulp at pH 2.0 and at pH 4.0

	Antagonistic Langmuir model (dye effect on copper(II) biosorption)		Synergistic Langmuir model (copper(II) effect on dye biosorption)	
	η_1	η_2	K_1	K_2
pH 2.0	1.181	1.136	0.699	0.442
pH 4.0	1.030	1.013	0.772	0.808

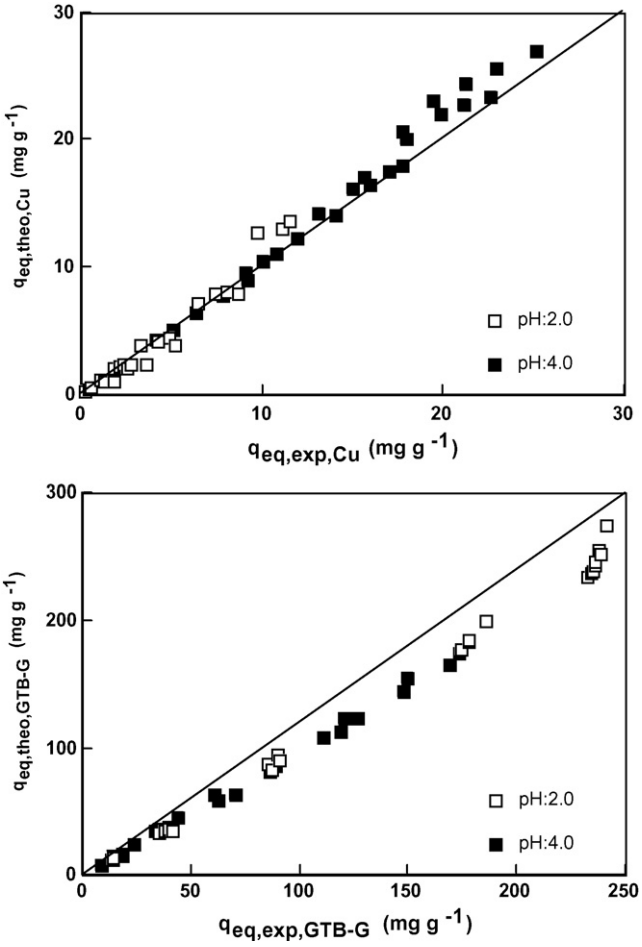

Fig. 6. The comparison of the experimental and calculated q_{eq} values of copper(II) and Gemazol Turquoise Blue-G dye ions in binary mixtures at pH 2.0 and at pH 4.0. (Antagonistic Langmuir model was used for the biosorption of copper(II) and synergistic Langmuir model was used for the biosorption of Gemazol Turquoise Blue-G from binary mixtures.)

Langmuir formula at both the pH values studied and compared with the experimental equilibrium data in Figs. 2–5. According to the theoretical base of multi-component antagonistic and synergistic Langmuir models, the adsorbed quantity of copper(II) decreased with increasing the dye concentration, and the adsorbed quantity of the dye increased with increasing the concentration of copper(II), respectively, depending on the values of the individual Langmuir constants of both the components at the two pH values studied. The comparison of the experimental and calculated q_{eq} values of dye and copper(II) in mixtures (scatter diagrams) is presented in Fig. 6 for both the pH values studied. Basically, if most of the data are distributed around the 45° line this indicates that both the models represent well the experimental data of the systems so as shown in Fig. 6. Both the multi-component Langmuir models fitted reasonably well the binary uptake data of copper(II) and dye ions in the studied concentration range, although significant deviations (the average percent deviation was changed from 0.0% to 33.3% in the models for the entire data set of copper(II) and dye ions) were observed between the experimental and calculated results from the models at higher concentrations of both components in the mixture. These results can be attributed to the insensitivity of models to interactive effects existing in multi-component systems and the characteristics of Langmuir model which is not valid for high concentrations assuming limited number of identical sites for sorption. It was concluded that although none of these predictive models confirms the non-ideal interactions occurring in the biosorption phenomenon, they are able to simulate adequately the copper(II)–Gemazol Turquoise Blue-G dye binary system behavior starting from the single system characteristic parameters.

4. Conclusion

The capability of the dried sugar beet pulp to bind Gemazol Turquoise Blue-G dye and copper(II) ions individually and simultaneously from aqueous solutions was examined and the mono- and multi-component synergistic and antagonistic Lang-

muir isotherm models were applied to experimental data to predict the equilibrium uptake of components, both singly and in combination with respect to pH. The obtained results showed that dried sugar beet pulp selectively adsorbed copper(II) ions at pH 4.0 while Gemazol Turquoise Blue-G ions were preferentially adsorbed by the biomass at pH 2.0. Although dried sugar beet pulp had a higher adsorption capacity for copper(II) at single component situation due to the pH of solution, the equilibrium uptake of copper(II) in the binary mixture was found to be decreasing due to the levels of Gemazol Turquoise Blue-G dye at both pH values studied because of the antagonistic effect of dye. However, the presence of copper(II) increased the equilibrium uptake of Gemazol Turquoise Blue-G dye and this efficacy increased as co-ion levels and medium pH were increased indicating the synergistic effect of copper(II). The proposed multi-component Langmuir models provided more realistic descriptions of the copper(II) or dye uptake at a level of co-ion and can be used to predict the uptake of copper(II) or dye ions in the binary system with more accuracy for each pH value studied.

This study has shown the convenience and effectiveness of dried sugar beet pulp, a widely available agroindustrial by-product for the single and binary removal of Gemazol Turquoise Blue-G dye and copper(II) ions from an artificial effluent with respect to pH. This work could also enable to extrapolate the prediction of adsorption equilibria of the single and binary system if experimental data are not available for a certain level of bisolute concentrations.

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