CELLULOSE CHEMISTRY AND TECHNOLOGY

EQUILIBRIUM STUDIES ON THE REMOVAL OF ACID GREEN 9 DYE FROM AQUEOUS SOLUTIONS BY CHITOSAN ADSORBENT: BATCH STUDIES

DOINA ASANDEI, VIORICA DULMAN,[*] TATIANA TODORCIUC and ELENA BOBU

"Gheorghe Asachi" Technical University, Faculty of Chemical Engineering and
Environmental Protection, 700050 Iasi, Romania
[*]*"Alexandru I. Cuza" University of Iasi, Faculty of Chemistry,*
11, Carol I Blvd., 700506 Iasi, Romania

Received May 30, 2012

Chitosan is a natural, renewable, nontoxic and biodegradable polymer. This unique natural cationic polymer has been evaluated as adsorbent for removing Acid Green 9 (AG9) dye from aqueous solutions. The experiments were performed in a batch system, at room temperature (20 ± 0.5 °C) and the effects of various experimental parameters (pH, contact time, initial dye concentration, adsorbent dosage, temperature, ionic strength) on adsorption capacity were investigated. The results have shown the effectiveness of dye removal is mainly dependent on the ratio between initial concentration of AG9 and chitosan dosage. At a given ratio of AG9: chitosan, an acid pH range of 4-6 was identified as optimal for dye removal. The temperature raising and presence of sodium sulphate (Na_2SO_4) resulted in a decrease of adsorption yield. The experimental data were analyzed for possible agreement with the Langmuir, Freundlich and Temkin isotherm equations. The Langmuir model was demonstrated to provide the best correlation with the experimental data.

Keywords: Acid Green 9, chitosan, adsorbent, isotherms, cationic polymer

INTRODUCTION

Among various aqueous pollutants generally present in wastewaters, the synthetic dyes are considered to constitute a distinct, wide and diverse group. These compounds are widely used in various industries, such as those producing textiles, foods, cosmetics and paper printing and are generally resistant to biodegradation due to their xenobiotic nature.[1, 2] The colored effluents of the textile industry cause serious environmental problems due to the structural variety of dyes and to the use of large amounts of water in the dyeing processes. These dyes have an anionic character and are used frequently for the dyeing of fibres within the cationic groups, such as wool, silk and polyamide.[3]

The removal of acid dyes from wastewaters is of great importance; likewise the soluble reactive dyes, they tend to remain in the medium during conventional treatment.[4] During the past years, several methods have been reported and attempted for the removal of dyes from textile effluents. Therefore, various physical or chemical treatment processes have been extensively tested.[5-9] Some of these techniques have been shown to be effective, although they have limitations.[4] Among various methods, adsorption occupies a prominent place in the removal of dye from textile wastewater. The use of low-cost adsorbents is recognized as an effective and economic method for textile water decontamination.[10] The adsorbents used include different agricultural wastes, such as rice hulls and coconut husk, industrial wastes as saw dust and lignin, and bio-sorbents as yeast, fungi, bacteria, chitosan, algae and peat mass.[7, 11-14] Special attention has been given to chitosan, a natural aminopolymer[15] with an extremely high affinity for many classes of dyes.[16]

The AG9 dye (Acid Green 9) is commonly used for textile fibre dyeing and its presence in effluents creates serious environmental problems. There are few studies mentioned in the literature on methods for AG9 dye removal from textile effluents. Some researches, which involve triarylmethane dyes as hydrological tracer, concern AG9 sorption onto a sandy soil.[17, 18] The adsorption and desorption of the AG9 on the acrylic weak base anion exchange resin with ethylenediamine functional groups has been also studied.[19] In this paper, chitosan is evaluated for its adsorption capacity and potential for application in the treatment of effluent containing AG9 dye. The effect of various experimental parameters, such as pH, initial dye concentration, contact time, adsorbent dosage and ionic strength, are investigated with the aim of identifying the best isotherm model and getting deeper knowledge on the adsorption mechanisms.

EXPERIMENTAL

Adsorbent characterization

Chitosan with an acetylating degree of 20.8%, loss on drying of 4.5% and a relative molecular weight (g/mol) of $4.15 \cdot 10^5$ was obtained from Vanson Co., Canada, and was provided in the form of powder with a particle equivalent diameter <0.200 mm. The chemical structure of chitosan is presented in Figure 1a.

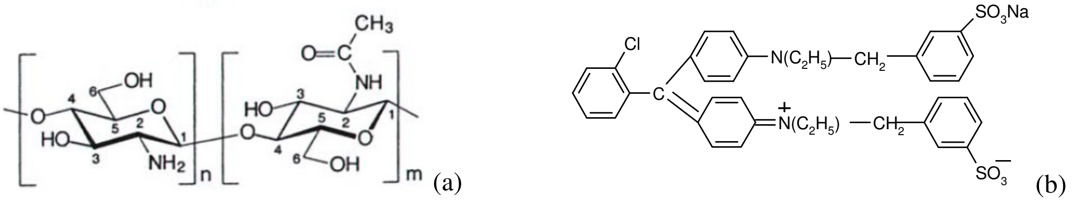

Figure 1: Chemical structures of chitosan (a) and Acid Green 9 (b)

Dye characterization

Acid Green 9 (AG9) with 72% dye content, a commercial product, was purchased from Bezema (Switzerland). It is also known under various commercial names, such as Benzanyl Grun F-2B (Bezema, Switzerland), Triacid Green 6B (Chemische Fabriek Triade, Netherlands), ORCOacid Fast Green B (Organic Dyestuffs Corporation, USA), Acid Green E-6B (Tianjin Dongpeng Industry and Trade). The structure of the dye is shown in Figure 1b. It can be seen that this triarylmethanic dye is in the form of a sulfonic acid salt, which determines its solubility in water. Aqueous solutions of 1000 mg L^{-1} textile dye (used without preliminary purification) were prepared using double distilled water and, subsequently, diluted when necessary.

Adsorption experiments

The change in the concentration of a pollutant (adsorbate) in the surface layer of the material (adsorbent), in comparison with the bulk phase with respect to unit surface area, is termed adsorption. The experiments only present data obtained using batch studies. The batch experiments were performed by adding chitosan to 20 mL solution containing AG9 dye, under intermittent stirring, at room temperature (20 ± 0.5 ºC), with the exception of one series, at a constant time of 24 hours. Five series of experiments were performed to evaluate the influence of the following variables: the pH value of the initial solution, contact time, adsorbent (chitosan) dosage, initial concentration of AG9 in solution and ionic strength of the solution. A constant volume of 20 ml dye solution was used for each experiment (batch).

The influence of the initial pH on the adsorption capacity of AG9 dye onto chitosan was investigated for the solutions with an initial concentration level of 125 mg AG9 /L, over the 2.0-7.0 pH range, at a constant dosage of chitosan (0.025 g chitosan/batch).

The influence of the initial AG9 dye concentration on chitosan adsorption capacity was studied at three different concentrations (130, 200, 270 mg AG9 /L), at a constant pH (pH = 5.5) of the initial solution and a constant dosage of chitosan (0.025 g chitosan/batch).

In order to evaluate the effect of chitosan dosage on AG9 dye adsorption, the AG9 solution of a constant concentration (200 mg/L) was treated with a variable dosage of chitosan (resulted chitosan concentrations in the mixture varied from 1.0 to 15 g/L), at a constant pH of the initial solution (pH = 5.5).

For each experiment, the phases were separated by 10 minute centrifugation at 5000 rpm. The adsorption procedure and AG9 concentration in aqueous solutions were analyzed spectrophotometrically, using UV-Vis 1700 Pharma Spec Spectrophotometer (Shimadzu, Kyoto, Japan) at $\lambda = 643$ nm.

Equilibrium studies

The adsorption isotherms were obtained using aqueous dye solutions of different concentrations and a constant dosage of 0.025 g chitosan in 20 mL solution. These solutions were stirred until adsorption equilibrium was reached and then processed as described previously. The amount of dye adsorbed per unit weight of adsorbent at equilibrium q_e (mg g^{-1}) was evaluated from Equation 1:

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

where: C_0 is initial concentration and C_e is the equilibrium concentration of dye in solution (mg L^{-1}); V – volume of solution used for each experiment (L^{-1}); m – chitosan dosage, in g.

RESULTS AND DISCUSSION

Effect of pH on AG9 dye adsorption

Most of the properties of chitosan as a natural aminopolymer can be related to its cationic nature, which is unique among abundant polysaccharides. Therefore, the ionic exchange and electrostatic attraction, as well as the structure of chitosan and dye molecules, could play a very important role in the adsorption of dye onto this biopolymer.[15] The initial pH (pH_i) of the dye solution is an important parameter affecting the adsorption process due to its influence on the chemistry of chitosan molecules. In acid medium, the chitosan undergoes the protonation of the nitrogen atoms, which favours the adsorption of the dye anion by the ion exchange process, according to the general equilibrium (Equation 2):

$$\mathrm{Chitosan}-\overset{+}{\mathrm{N}}\mathrm{H_3}\cdot \mathrm{Cl^-} + \mathrm{Dye}-\mathrm{SO_3^-}\cdot \mathrm{Na^+} \Leftrightarrow \mathrm{Chitosan}-\overset{+}{\mathrm{N}}\mathrm{H_3}\cdot {}^-\mathrm{O_3S}-\mathrm{Dye}+\mathrm{NaCl}$$

The preliminary tests have shown a low retention yield of the dye under basic medium. This result was expected, since the chitosan is fully protonated at pH = 4.2 and only partially protonated at pH = 6.5.[20] Therefore, the decrease of the adsorption capacity in basic medium can be explained by a reduction of cationic charged sites on the chitosan particle surface. For this reason, the effect of pH on chitosan adsorption capacity was studied in the pH domain from 2.2 to 7.0 (at constant values for: C_i = 125 mg/L, chitosan dosage = 0.025 g/batch). The acidity was corrected with sulphuric acid (H_2SO_4) solutions (10^{-1}-10^{-3} N), since other mineral or organic acids could produce partial or total solubilisation of chitosan particles.[20]

However, the graphs of Figure 2 show that the variation of initial pH (pH_i) in the range of 2.2-7.0 has no significant influence on AG9 dye removal by chitosan. The adsorption capacity increases only slightly, from 97.7% to 99.3%, in the pH_i domain 2.2-5.5 and then decreases to 97.4% around pH_i = 7. This evolution of dye adsorption as a function of the pH_i indicates that electrostatic interaction is not a single mechanism, since the adsorption decrease is very low comparatively with the pH increase and its influence on the cationic charge of chitosan surface particles. Toward neutral pH (5.5 → 6.5), the adsorption process is more complex and other interaction mechanisms could be involved, such as hydrophobic interactions, hydrogen bonding between chitosan and acid dyes and hydroxyl groups (especially in the C-3 position).[15,21] The final pH (pH_f) increases with the dye adsorption increase, especially when initial pH is in the range of 3.1-4.2, due to the neutralization of the anionic groups of the dye by chitosan groups. A similar behaviour was reported when Congo red dye was adsorbed by chitosan hydrogel beads impregnated with carbon nanotubes.[22] The adsorption of acid AR 37 and AB 25 dyes onto chitosan and cross-linked chitosan beads took place at pH 6.0 and 4.0, respectively.[23] The optimum pH range frequently reported in the literature for the removal of anionic dyes is pH 3.0-6.0.[12] Since the pH_i of 5.5 corresponds to an aqueous solution of dye and this value is in the optimum range of pH, all subsequent experiments were performed without pH adjustment.

Effect of initial dye concentration and contact time

The adsorption rates of AG9 from dye solutions of different concentrations (130, 200 and 270 mg /L) are shown in Figure 3. One can observe the dye uptake is dependent on initial dye concentration: at a dye concentration of 130 mg/L, about 55% of dye is adsorbed in the first 15 minutes and the equilibrium is attained within 240 minutes; at higher concentrations of 200 and 270 mg/L, about 60% dye is rapidly adsorbed after 45 and 90 minutes respectively, followed by a more gradual process.

A similar behaviour was noted by different studies concerning anionic compounds adsorption on chitosan, which are summarized in a review by Srinivasan and Viraraghavan.[12] At low concentrations, the mechanism of interaction may be explained by a possible formation of monolayer dye coverage of the molecules at the outer surface of chitosan. At higher concentrations however, the number of available adsorption sites becomes lower and subsequently the removal of dyes depends on the initial concentration. The diffusion of exchanging molecules within chitosan particles may govern the adsorption rate at higher initial concentrations, but this mechanism does not appear significant when the adsorbent concentration is constant. Thus, the adsorption rate of AG9 on chitosan powder and therefore the process effectiveness seems to depend strongly on the ratio of the initial concentration of dye to chitosan concentration (dosage).

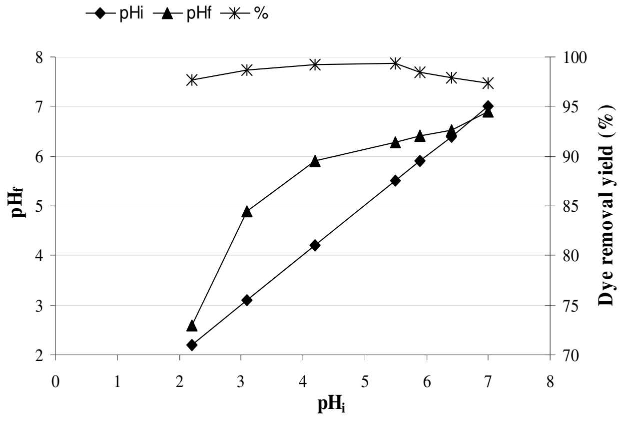

Figure 2: Effect of initial pH (pH$_i$) on AG9 dye adsorption and final pH (pH$_f$), at constant initial concentration (125 mg/L) and chitosan dosage (0.025 g/batch)

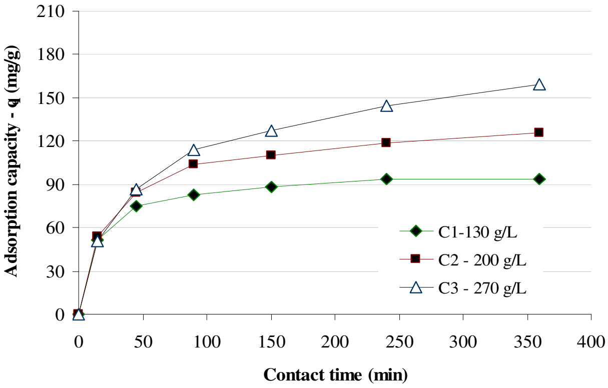

Figure 3: Effective adsorption (q$_e$) of AG9 dye as a function of contact time, at different initial concentrations and constant dosage of chitosan (0.025 g/batch)

Effects of adsorbent dosage on AG9 dye adsorption

The effect of chitosan dosage on the dye removal and adsorption capacity of chitosan was examined by varying the amount of adsorbent from 0.02 g to 0.3 g in a 20 mL solution volume used in each experiment (corresponding to the concentration variation from 1 to 15 g/L). Other experimental conditions were kept constant, as following: constant initial dye concentration of 200 mg /L, reaction time of 24 hours and 20 °C temperature. The graphs of Figure 4 evidence a fast increase of dye removal yield and a sharp decrease of the adsorption capacity of chitosan (q$_e$ – mg dye/g chitosan) for dosages increasing from 0.02 g to 0.07 g (chitosan concentration from 1 to 4 g/L). The adsorption yield increase could be explained by the increasing number of adsorption sites, respectively, active surface area available for adsorbent–dye interaction.[24] At the same time, the decrease of adsorption capacity may be attributed to the unsaturation of adsorption sites through the adsorption process (the dosage of chitosan was increased at constant dye concentration and volume). Another reason may lie in some secondary interactions, such as the aggregation of chitosan particles due to the high adsorbent dosage. Such aggregation would lead to a decrease in the total surface area of the sorbent and an increase in the diffusion path length.[25,26] These results show that high dosages of chitosan do not lead to a higher effectiveness of the adsorbent and could be cost-ineffective.

Effect of ionic strength on AG9 dye adsorption

The presence of different salts in textile wastewater should be taken into consideration, since different salts (sodium sulphate, sodium chloride) are used in industrial dyeing in order to obtain uniform colouration. Therefore, various salts and metal ions could exist in wastewater and their concentration (ionic strength) affects significantly the performance of the adsorption process. In this study, sodium sulphate was used in varying salt concentration from 10 to 30 g/L for dye solutions with an initial concentration of 200 mg/L. Figure 5 shows important reductions in the dye removal yield with the increase of solution ionic strength. The yield decreases almost linearly with the sodium sulphate concentration increase up to 17 g/L and then is stabilised at around 80%. The adsorption process is governed by electrostatic interactions between the cationic charged surface of chitosan particles and anionic dye. The decrease of dye removal could be due to an electrostatic screening effect, which is well-known in the presence of polyelectrolytes as chitosan, and to possible electrostatic interactions with SO_3^- ions. Such phenomena could be the result of the changes in dye activity (dissociation degree) or in the properties of the electric double layer on the surface of chitosan particles.[27] The structure of the diffuse layer is determined by electrostatic interactions described by the Gouy–Chapman theory and it is well known that the ionic strength increase produces a compression of the diffuse layer. These results are in agreement with those of other adsorption studies.[28, 29]

Adsorption isotherms

Adsorption properties and equilibrium data commonly known as adsorption isotherms describe the nature of interactions between the solute (AG9 dye) and the adsorbent material (chitosan powder). The decision about the most appropriate correlation for the equilibrium curve is significant for the optimization of the adsorbent system. The experimental data obtained for the adsorption equilibriums were analysed by applying three isotherm models: Langmuir, Freundlich and Temkin.

The *Langmuir isotherm* is characteristic of monolayer adsorption on a surface containing a limited number of identical sites. The following linearised form of the Langmuir equation (3) has been used: [30]

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \tag{3}$$

where: q_e – adsorption capacity ($mg \cdot g^{-1}$) at equilibrium; q_m – maximum adsorption capacity ($mg \cdot g^{-1}$) C_e – dye solution concentration at equilibrium ($mg \cdot L^{-1}$); b – adsorption coefficient ($L \cdot mol^{-1}$)

The Langmuir equilibrium constant K_L ($L \cdot mg^{-1}$) is obtained by the following relation (4):

$$K_L = q_m \cdot b \tag{4}$$

The plot of $1/q_e$ versus $1/C_e$, according to Equation 3, leads to a straight line with the slope $1/q_m b$ and an intercept with the ordinate equal to $1/q_m$. The essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L), which is given in Equation 5:

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

where: C_0 is initial dye concentration ($mol \cdot L^{-1}$).

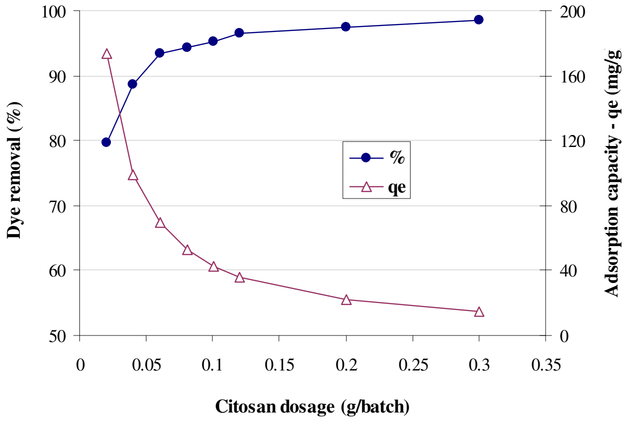

Figure 4: AG9 dye removal (%) and adsorption capacity (q_e) as a function of chitosan dosage, at constant initial concentration of the dye solution (C_i = 200 mg/L)

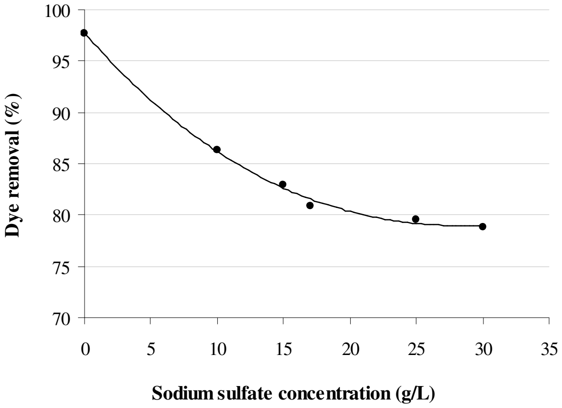

Figure 5: Effect of sodium sulphate concentration on the yield of dye removal, at constant chitosan dosage (0.025 g/batch) and initial dye concentration (200 mg/L)

The study of the *Freundlich isotherm* was performed using Equation 6:

$$\log q_e = \log K_F + 1/n \log C_e \tag{6}$$

where: q_e is the amount of dye adsorbed ($mg \cdot L^{-1}$) at equilibrium; K_F and n are constants that reflect adsorption capacity and intensity of adsorption, respectively; C_e – dye solution concentration at equilibrium ($mg\ L^{-1}$).

The K_F and n constants were calculated from the intercept and slope of the linear plots for log q_e versus $\log C_e$ (Figure 6b).

The *Temkin isotherm* constants were obtained from the plot of the q_e versus $\ln C_e$, as shown in Equation 7:

$$q_e = B \ln A + B \ln C_e \tag{7}$$

where: A ($L\ g^{-1}$) and B are the Temkin isotherm constants. The constant B (Equations 7 and 8) is related to the heat of adsorption, as follows:

$$B = RT/b \tag{8}$$

where: b is the Temkin isotherm energy constant ($J \cdot mol^{-1}$); R is the universal gas constant (8.3146 $J \cdot mol^{-1} \cdot K^{-1}$).

The Langmuir, Freundlich and Temkin plots are given in Figure 6 (a, b, c) for initial dye concentration in the range of 25-250 mg /L and at four different temperatures (281 K, 293 K, 308 K and 323 K). Other reaction conditions were kept constant as follows: solution volume per batch, V = 20 mL; chitosan dosage per batch – 0.025 g; reaction time – 20 hours). The parameters of the isotherms and correlation coefficients are presented in Table 3.

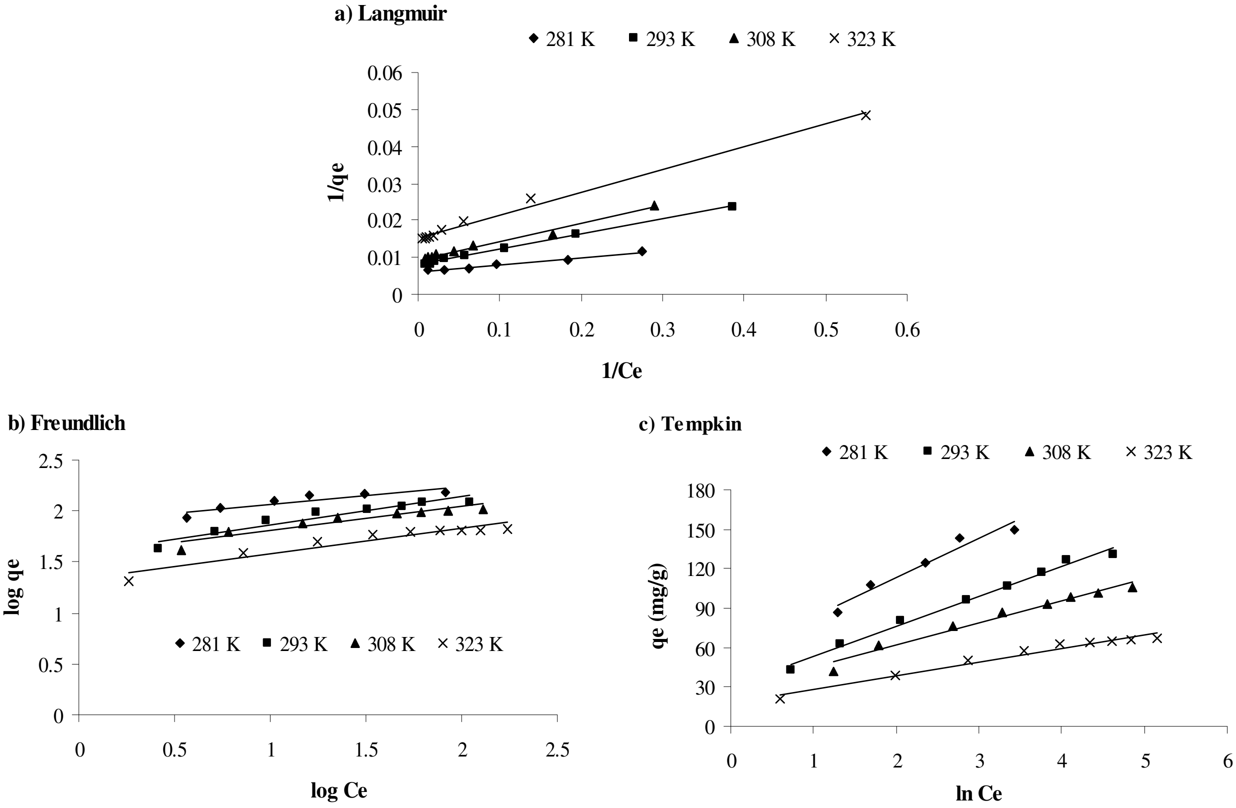

Figure 6: Langmuir (a), Freundlich (b) and Temkin (c) plots for AG9 dye adsorption on chitosan, at different temperatures

Table 3
Parameters of isotherm models for AG9 dye adsorption on chitosan at different temperatures

Isotherm model	Parameters	Temperature			
		281 K	293 K	308 K	323 K
Langmuir	$K_L (Lg^{-1})$	52.63	33.33	20.28	16.34
	q_m (mg g^{-1})	163.93	138.89	108.70	65.36
	b (L mg^{-1})	0.321053	0.24	0.186613	0.15
	R_L	0.0062	0.0083	0.0106	0.0079
	R^2	0.9829	0.9947	0.986	0.9906
Freundlich	K_F (mg/g)(L/g)^n	78.66834	38.34423	37.74853	21.51791
	n	5.77034	3.608805	4.310345	4.042037
	R^2	0.8063	0.9203	0.878	0.9067
Temkin	A (Lg^{-1})	0.2218	3.9542	5.2078	5.651
	B	29.72	22.634	16.871	10.352
	b (J mol^{-1})	78.59	107.6258	151.7819	259.4109
	R^2	0.9521	0.9879	0.9647	0.9628

Langmuir isotherm model

Langmuir equation is a frequently used isotherm model[15] based on three assumptions:

- the adsorption takes place at specific homogeneous sites (saturation of a fixed number of identical surface sites),

- the adsorption is limited to monolayer coverage of the adsorbent surface (all surface sites are alike),
- the ability of a molecule to be adsorbed on a given site does not depend on the neighbouring sites occupancy,
- the Langmuir isotherm respects the kinetic principle according to which the rates of adsorption and desorption from the surface are equal.

The values of the correlation coefficients (R^2) indicate that the AG9 dye adsorption onto chitosan is very well described by the Langmuir isotherm model, being much close to unit ($R^2 = 0.9947$) at room temperature and at the other tested temperatures ($R^2 > 0.98$).

The calculated values of R_L are situated in the range (0÷1), confirming that the process takes place spontaneously and there is a high adsorption affinity of chitosan for AG9 dye. The Langmuir model may be considered to be appropriate to the system, since it offers a representative description of the interaction between the components, which is leading to the assumption that the optimum retention takes place at monolayer coverage of the adsorbent surface.

As one can see from Table 3, all Langmuir parameters decreased with temperature rising, especially q_m. The maximum adsorption capacity (q_m) of AG9 onto chitosan was in the range 163.93÷65.36 $mg \cdot g^{-1}$ for the range of temperatures from 281 K to 323 K. The decrease of q_m with temperature increase suggests an electrostatic mechanism of dye retention on chitosan particles, which is not favoured by high temperature.

Freundlich isotherm model

The Freundlich equation is an isotherm model frequently applied for the characterisation of adsorption systems using chitosan as adsorbent. The Freundlich isotherm is an empirical equation based on the adsorption on a heterogeneous surface, when retention takes place on several layers.

The Freundlich isotherm is represented in Figure 6b as a linear dependence of lg q_e versus C_e. Considering the parameters calculated from the experimental data (Table 3), the linear Freundlich graph representation appears to offer a relatively good model of the AG9 dye adsorption by chitosan. According to the mathematical relation (Equation 6), the slope of plot represents the value of 1/n and the intercept gives the value of the Freundlich constant (K_F). The magnitude of the exponent 1/n is one of the parameters offering an indication of the favourability of adsorption. The value of 1/n indicates the curvature in the isotherm and may represent the energy distribution of the adsorption sites. The intensity of the interaction between the chitosan and the dye is strongly dependent on the value of constant n.

The relatively high value ($n > 1$) of constant n in the case of the studied system ($n = 3.60$) may suggest the existence of a significant affinity and a strong interaction between AG9 dye and chitosan. The Freundlich constant (K_F) is a relative measure of the adsorption capacity and its increase with temperature indicates that the interaction between the chitosan and the dye is an endothermic process.

However, the correlation coefficient (R^2) should not be neglected. Though R^2 is close to unity ($R^2 = 0.9203$), it is not high enough (at 281 K and 308 K, $R^2 < 0.90$). This evidence leads to the hypothesis that the Langmuir isotherm model is more appropriate than the Freundlich model.

Temkin isotherm model

The Temkin isotherm equation is a less frequently used model for the adsorption studies onto chitosan. The model is based on the following assumptions: [31]

- the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions,
- the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy,
- the effect of indirect adsorbate-adsorbate interaction on adsorption isotherm plays an important role: the heat of adsorption of all the molecules on the adsorbent surface layer would decrease linearly with coverage because of adsorbate-adsorbate interactions.

Figure 6c presents the Temkin linear plotting of adsorption capacity and concentration at equilibrium (q_e versus $\ln C_e$) for different temperatures. The value of constant B of about 20 $kJ\ mol^{-1}$ at room temperature suggests a strong interaction between the AG9 dye and chitosan.[32]

The Temkin model also shows a strong conformation to the experimental data, judging by the satisfactory values of the obtained linear regression coefficient, especially at room temperature ($R^2 = 0.98$). However, linear regression coefficients are lower at higher temperatures ($R^2 = 0.95$ and $R^2 = 0.96$), which is leading again to the conclusion that the Langmuir isotherm model describes better the adsorption mechanism of AG9 dye onto chitosan.

The comparison of R^2 values for the three isotherm models tested may suggest the following order: Langmuir > Temkin > Freundlich (Table 3).

The sorption of the solute on a sorbent can involve physical bonding, ion exchange, complexation, and chelation or a coalescence of these interactions. Taking in consideration the special features of chitosan and reasonable arguments of the appropriate isotherm model, one can conclude that the interaction between chitosan and AG9 dye involves different mechanisms, but the electrostatic interaction appears as a dominant one.

CONCLUSION

In this study, the adsorption of AG9 dye from aqueous solutions on chitosan was investigated with regard to the influence factors and potential mechanisms of interaction.

The effects of initial solution pH, contact time, chitosan dosage and initial AG9 dye concentration were evaluated by several series of experiments that were performed in batch system, at room temperature (20 ± 0.5 °C) and with a constant volume of dye solution (20 mL). The main conclusions of these experiments are summarised below.

- The initial pH (pH_i) of the dye solution has no significant influence in the studied pH range from 2.2 to 7.0, and was chosen around 5.5, which is the initial pH value of AG9 dye solution; the results have shown that the dye removal yield is maximum in the pH range of 4-6, when 99% of the dye is removed by adsorption on chitosan, and decreases slightly toward neutral conditions (pH 6 → 7). This influence of pH_i indicates that toward neutral pH, the adsorption process is more complex and other mechanisms than electrostatic interactions could be involved. Based on these results, all subsequent experiments were performed at the initial pH of the dye solution, without adjustment.
- At a constant concentration of chitosan, the time to reach an equilibrium state of the interaction between AG9 dye and chitosan surface increases consistently with the initial dye concentration increase. However, the initial dye concentration does not affect significantly the removal yield at equilibrium.
- The dye removal yield increases slightly with chitosan concentration, while the adsorption rate (mg dye/g chitosan) decreases strongly. Practically, the process effectiveness depends mainly on the ratio of initial concentration of the dye to chitosan concentration (dosage), which has to be optimized by a compromise between the removal yield and the process cost-effectiveness.

The application of the Langmuir, Freundlich and Temkin isotherm models for the mathematical description of AG9 dye adsorption on chitosan allows us the following remarks:

- Adsorption equilibrium data are very well fitted to the Langmuir isotherm with a high correlation coefficient (R2 > 0.99) and the maximum adsorption rate (q_{max}) of 138.89 mg/g, under the studied experimental conditions. The Langmuir model suggests a monolayer adsorption at specific homogeneous sites.
- The adsorption system may also fit the Temkin isotherm model (R2 > 0.98), suggesting that the effect of indirect adsorbate-adsorbate interaction on the adsorption isotherm plays an important role in the AG9 dye–chitosan adsorption system.
- The Freundlich equation fits poorly the experimental data, as compared to the other isotherm equations, with a low correlation coefficient (R2 < 0.92).

REFERENCES

[1] A. Pandey, P. Singh and L. Iyengar, *Int. Biodeter. Biodegr.*, **59**, 73 (2007).

[2] P. Kaushik and A. Malik, *Environ. Int.*, **35**, 127 (2009).

[3] Y. C. Wong, Y. S. Szeto, W. H. Cheung and G. McKay, *Process Biochem.*, **39**, 693 (2004).

[4] Z. Aksu, *Process Biochem.*, **40,** 997 (2005).

[5] A. Demirbas, *J. Hazard. Mater.*, **167**, 1 (2009).

[6] E. Forgacs, T. Cserháti and G. Oros, *Environ. Int.*, **30**, 953 (2004).

[7] G. Crini, *Bioresource Technol.*, **97**, 1061 (2006).

[8] Y. Anjaneyulu, N. S. Chary and S. S. D. Raj, *Rev. Environ. Sci. Biotechnol.*, **4**, 245 (2005).

[9] T. Robinson, G. McMullan, R. Marchant and P. Nigam, *Bioresource Technol.*, **77**, 247 (2001).

[10] V. K. Gupta and I. A. Suhas, *J. Environ. Manag.*, **90**, 2313 (2009)

[11] M. A. M. Salleh, D. K. Mahmoud, W. A. W. A. Karim and A. Idris, *Desalination*, **280**, 1 (2011).

[12] A. Srinivasan and T. Viraraghavan, *J. Environ. Manag.*, **91**, 1915 (2010).

[13] S. P. S. Syed, *Res. J. Chem. Sci.*, **1**, 88 (2011).

[14] P. J. M. Carrott and M. M. L. Ribeiro Carrott, *Bioresource Technol.*, **98**, 2301 (2007).
[15] G. Crini and P. M. Badot, *Prog. Polym. Sci.*, **33**, 399 (2008).
[16] A. Bhatnagar and M. Sillanpää, *Adv. Colloid Interfac.*, **152**, 26 (2009).
[17] J. Mon, M. Flury and J. B. Harsh, *Geoderma*, **133**, 217 (2006).
[18] J. Mon, M. Flury and J. B. Harsh, *J. Hydrol.*, **316**, 84 (2006).
[19] V. Dulman, C. Simion, A. Bârsănescu, I. Bunia and V. Neagu, *J. Appl. Polym. Sci.*, **113**, 615 (2009).
[20] R. A. A. Muzzarelli and B. Muzzarelli, in "Polysaccharides. Structural Diversity and Functional Versatility", edited by S. Dimitriu, Marcel Dekker Inc., 1998, pp. 569-594.
[21] D. Jocic, S. Vílchez, T. Topalovic, A. Navarro, P. Jovancic *et al.*, *Carbohyd. Polym.*, **60**, 51 (2005).
[22] S. Chatterjee, M. W. Lee and S. H. Woo, *Bioresource Technol.*, **101**, 1800 (2010).
[23] A. Kamari, W. S. Wan Ngah and L. K. Liew, *J. Environ. Sci.*, **21**, 296 (2009).
[24] S. S. Gupta and K. G. Bhattacharyya, *J. Colloid. Interf. Sci.*, **295**, 21 (2006).
[25] A. E. Ofomaja and Y.-S. Ho, *Dyes Pigments*, **74**, 60 (2007).
[26] G. Crini, F. Gimbert, C. Robert, B. Martel, O. Adam *et al.*, *J. Hazard. Mater.*, **153**, 96 (2008).
[27] T. S. Anirudhan and M. Ramachandran, *J. Colloid. Interf. Sci.*, **299**, 116 (2006).
[28] S. Chatterjee, S. Chatterjee, B. P. Chatterjee and A. K. Guha, *Colloid. Surface A.*, **299,** 146 (2007).
[29] A. K. Kushwaha, N. Gupta and M. C. Chattopadhyaya, *J. Saudi Chem. Soc.*, (2011), available at http://www.sciencedirect.com/science/article/pii/S131961031100130X
[30] G. McKay, H. S. Blair and J. R. Gardner, *J. Appl. Polym. Sci.*, **27**, 3043 (1982).
[31] S. Elbariji, L. N. Mounir, M. Elamine, H. Kabli, M. Bazzaoui *et al.*, *J. Environ. Chem.*, **2**, 52 (2010).
[32] A. T. M. Din and B. H. Hameed, *J. Appl. Sci. Environ.*, **5**, 161 (2010).