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

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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 (Na₂SO₄) 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. 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.

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. 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. Some of these techniques have been shown to be effective, although they have limitations. 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. 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. Special attention has been given to chitosan, a natural aminopolymer with an extremely high affinity for many classes of dyes.

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. The
adsorption and desorption of the AG9 on the acrylic weak base anion exchange resin with ethylenediamine functional groups has been also studied.\textsuperscript{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 \(4.15 \times 10^5\) 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)](image)

**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 Dyeestuffs 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 °C), 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:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]  \hspace{1cm} (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. 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):

$$
\text{Chitosan} - \text{NH}_3^+ + \text{Dye} - \text{SO}_3^- \leftrightarrow \text{NH}_2\text{C}^+ + \text{SO}_3^- + \text{Dye}^+ + \text{NaCl}
$$

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. 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$_2$SO$_4$) solutions (10$^{-1}$-10$^{-3}$ N), since other mineral or organic acids could produce partial or total solubilisation of chitosan particles.

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). 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. 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. The optimum pH range frequently reported in the literature for the removal of anionic dyes is pH 3.0-6.0. Since the pH$_f$ 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. 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).
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. 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. 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. 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.
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:

\[
\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m}
\]

(3)

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

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

\[
K_L = \frac{q_m b}{1 + b C_0}
\]

(4)

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

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

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

(6)

where: \( q_e \) is the amount of dye adsorbed (mg·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 In\( C_e \), as shown in Equation 7:

\[
q_e = B \ln A + B \ln C_e
\]

(7)

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

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:

\[
B = \frac{R T}{b}
\]

(8)

where: \( b \) is the Temkin isotherm energy constant (J·mol\(^{-1}\·K\(^{-1}\)); \( R \) is the universal gas constant (8.3146 J·mol\(^{-1}\·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, \( V = 20 \text{ mL} \); chitosan dosage per batch – 0.025 g; reaction time – 20 hours). The parameters of the...
isotherms and correlation coefficients are presented in Table 3.

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

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

**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·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:

- 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.

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 ($20\pm 0.5\, ^\circ C$) 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 $\rightarrow$ 7). This influence of pH 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 ($R^2 > 0.99$) 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 ($R^2 > 0.98$), 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 ($R^2 < 0.92$).

**REFERENCES**