Crystal Violet Dye Removal by Low-Cost Nano-Superabsorbent Hydrogel: Thermodynamic and Isotherm Model

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ABSTRACT

Dye contamination is a major source of environmental pollution and health dangers practically in each section of the developing world, as people add color to textiles, paper, leather, and other materials to adorn and preserve them. Nowadays, green methods are considered the most important ways to solve environmental problems, especially the problems of the aquatic environment, and they fulfill the requirements of social, environmental, and economic guarantees. A new, environmental-friendly, and stable absorbent material has been prepared with absorbent properties based on biopolymers that have been successfully applied during the polymerization process with free radicals as a superabsorbent Ag-g-PAA/AC hydrogel. Many techniques were used to study the surface properties of the prepared hydrogel, including (FTIR, XRD, and FE-SEM). Several factors that affected the adsorption process were studied, including the effect of dye concentration, effect of hydrogel weight, effect of pH, and surface reactivation. Also, the adsorption isotherms of the Freundlich and Langmuir models were studied. Based on the findings, it was discovered that, depending on the R2 value, adsorption isotherms followed the Freundlich model.
Introduction
After industrial development and the increase in the population, the treatment of pollutants, liquid wastes resulting from factories of various industries and factories of pharmaceuticals and dyes has become an essential topic for solving the problem of pollution of the aquatic environment [1–3]. Therefore, there was an urgent need to produce an inexpensive absorbent material used in water treatment.
Activated carbon is one of the absorbent materials with a high efficiency in removing pollutants, especially dyes [4,5]. It is an available, inexpensive, and environmentally friendly material. Agricultural waste is one of the sources to obtain activated carbon, such as pomegranate peels, melon peels, coconut peels, date kernels, peels of oranges and lemons, cotton stalks, stems of cornflowers and plant stems, sunflower, and others [6,7].
Alginates, which are polysaccharide polymers of d-manuronic acid and guluronic acid extracted from brown seaweed, can broaden the field of applications. Alginate hydrogels are widely used in bio-medical applications like drug delivery, cell encapsulation, and tissue engineering [8–10]. However, these hydrogels are considered as a set of limited mechanical properties, and this causes an insufficient form of cellular interactions. It has been reported that hydrogels are so soluble that they cannot be controlled after calcium ion loss [11–14]. The aim of the present work concerns the feasibility of using activated carbon, through loading with hydrogel, for the removal of crystal violet dye, studying the factors affecting the adsorption process such as the effect of dye concentration, the effect of Ag-g-PAA/AC hydrogel weight, the effect of pH, and the effect of adsorption isotherms.

Materials and Method

Chemicals
Alginate of sodium (Ag), C₆H₉NaO₇, has a low viscosity (MW= 216.12 g/mol), acrylic acid (AAC) C₃H₄O₂ (MW= is 72.06 g.mol⁻¹). N, N'-methylene bisacrylamide C₇H₁₀N₂O₂ is a type of acrylamide (MBA) (MW = 154.17 g.mol⁻¹), sodium per sulfate (KPS) K₂S₂O₈ (MW = 270.31 g/mol), hydrochloric acid (HCl), hydroxide of sodium (NaOH), crystal violet (CV), C₂₅H₃₀N₃Cl (MW=407.98 g.mol⁻¹), and has the maximum wavelength of 565 nm, as displayed in Figure 1. After purification, all chemicals were of the highest analytical purity.

Adsorption experiments
The removal capacity of hydrogel-based absorbent for crystal violet dye was investigated via usual batch adsorption experiments. Standard solutions of crystal violet dye were prepared by dissolving 0.5 g of crystal violet in 500 ml of distilled water. Solution of pH was adjusted by 0.1 N HCl or NaOH. 100 mL of solution of CV dye was taken and put in Erlenmeyer flasks 100 ml at pH 7.6, and then several parameters were studied such as the equilibrium time, temperature, weight of adsorbent, and the initial concentration of CV dye. The adsorption experiments were conducted at 25°C and an agitation rate of 120 rpm on a shaking shaker water bath. After the contact time, the adsorbent was separated from aqueous solutions via centrifugation at 6000 rpm for 15 minutes. The CV residual concentration was estimated in each aliquot by using spectrophotometer UV-visible. The removal percentage% and adsorption capacity of CV dye were calculated by Equations 1 and 2:

Removal Percentage E% = \frac{C₀-Cₑ}{C₀} \times 100 \quad (1)

Adsorption capacity Qₑ = \frac{(C₀-Cₑ)Vml}{W gm} \quad (2)

Figure 1: Chemical structures of Crystal Violet (CV) dye
Preparation of Ag-g-PAA / AC hydrogel

Sodium alginate (Ag) by dissolving 2 gm in 40 ml of DW with continuous stirring until all the substance was dissolved in the distilled water at 1 hour. 0.5 gm of activated carbon (AC) was added to 20 ml of DW with continuous stirring to sodium alginate (Ag) solution at 1 hour after. Next, the amount of acryl acid (about 4 ml) was added to the reaction mixture with constant stirring, and then about 0.03 gm of potassium sulphate (KPS) in (1ml) of DW was added to the reaction mixture dropwise to the amount of N, N'-methylene bis-acrylamide (MBA). About 0.05 gm in 1ml of DW was added with continuous stirring until the substance was dissolved. To complete the polymerization reaction, the temperature was increased to 75°C for three hours. After being submerged in DW to remove unreached components, the Ag-g-PAA/AC hydrogel composite was dried at 60°C and used in experiment (Figure 2) [15].

Results

Characterization of the adsorbent

The AC presence in the hydrogel structure leads to fill up the pores of Ag-g-PAA/AC hydrogel and minimize the heterogeneity of the surface. Due to the fact that CV dye immobilization on hydrogel partially blocked surface porosity, the hydrogel preserved a porous nature for CV adsorption, as depicted in Figure (3b).

The IR spectra were utilized to characterize the Ag-g-PAA/AC hydrogel (Figure 3a) before and after the surface adsorption method on the CV dye, as shown in Figure 3c. Hence, due to the adsorption intensity, a clear and significantly more than a few CV dye was observed among Ag-g-PAA/AC hydrogel composite. In addition, the hydrogels before the adsorption method with the CV dye illustrated a clear decrease in the IR spectra in the intensity of the bands adjacent to the adsorption [16–18]. The surface contains the acidic group that leads to a difference in the intensity of absorption.

The X-ray diffraction patterns of hydrogel with AC are presented in Figure (3d), which indicates that Ag-g-pAA/AC is amorphous and no crystalline materials from the peaks are presented in the broad band in the case of Ag-g-PAA/AC hydrogel.

Figure 3: FESEM image: (a) Ag-g-PAA/AC, (b) Ag-g-PAA/AC loading CV, (c) FT-IR spectra of Ag-g-PAA/AC hydrogel surface before, and after adsorption of CV dye, and (d) XRD Ag-g-PAA/AC
Effect of different parameter

Effect of absorbent dosage

The effect of weight of Ag-g-PAA/AC hydrogel composite on the removal of CV dye is demonstrated in Figure 4. The data reveals that increase in the weight amount causes a decrease in the residual concentration of the CV dye at contact time, and thus it leads to an increase in the absorption removal capacity [19–23]. Certainly, the absorption values of the removal efficiency raised from 80.12 to 93.09% as the weight of Ag-g-PAA/AC hydrogel composite was increased from 0.01 to 0.08 g/100 ml. Such a trend is mainly attributed to an increase in the sorption, surface area, and the availability of more sorption sites. In contrast, the CV sorbed quantity per unit weight of Ag-g-PAA/AC hydrogel composite was decreased by the increase in absorbent dose. The values adsorption capacity was decreased from 801.12 to 116 mg/g as the weight of Ag-g-PAA/AC hydrogel composite was increased from 0.01 to 0.08 g/100 ml [24,25].

![Figure 4: The effect of weight of Ag-g-PAA/AC hydrogel surface on CV dye: Experimental conditions: pH 6.2, initial conc. 100mg/L, and 25°C.]

Effect of pH

The pH is an essential and important factor to determine the absorption efficiency of Ag-g-PAA/AC hydrogel composite at the optimum conditions of 25°C, the equilibrium time of 60 min, and the absorbent weight of 0.05 gm where it depends mainly on the pH of the CV dye and the hydrogel, as depicted in Figure 5. It was found that the adsorption efficiency increases with increasing pH from (148.1 to 190.34 mg/g), where the best pH solution was 10 in the basic medium [26,27].

![Figure 5: The effect of solution pH in CV adsorption uptake on (SA-g-PAAc)/AC hydrogel surface at 25°C]
Regeneration of Crystal Violet (CV)  
A study on the regeneration method carries out to see the re-activation of adsorbent and reuse potential of the adsorbate. If the CV desorption occurred via desorbing agents like (CH₃COOH, H₂SO₄, HCl, and NaOH at the concentration of 0.1 N), it was found the possibility of reactivating the surface and using it again, as indicated by the results in Table (1). The use of hydrochloric acid (0.1 N) was compared with the rest of the solutions, where the percentage of removal (90.012%) was through re-washing it only once [28,29].

**Table 1:** The desorption efficiency comparison of several types of solutions for the Crystal Violet (CV) on Ag-g-PAA/AC hydrogel

<table>
<thead>
<tr>
<th>Re-generation and Desorption</th>
<th>E%</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>90.012</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>80.874</td>
</tr>
<tr>
<td>acetone</td>
<td>60.66</td>
</tr>
<tr>
<td>NaOH</td>
<td>45.44</td>
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Adsorption Isotherm  
The values of isotherm constants and their respective R² correlation coefficients are given in Figure 6 and Table 2. The R2 calculated values suggested that the isotherm Langmuir and isotherm Freundlich models were fitted well with the result on adsorption equilibrium of Crystal Violet dye. The best (qₘₐₓ) according to the isotherm Langmuir model was found to be 180 mg/g at 25°C. In the isotherm Freundlich, the value of n (0.706) indicated the CV optimal adsorption on poly (Ag-g-AAc)/AC hydrogel by physical chemisorption on the heterogeneous surface of the hydrogel. It has been suggested that the n value between 1 and 10 represents an optimal sorption method. The KF calculated value in isotherm Freundlich was 33.574, suggesting the CV efficient adsorption by poly (SA-g-AAc)/AC hydrogel [30,31].

**Figure 6:** Nonlinear fitness of several adsorption models of CV adsorption dye on Ag-g-PAA/AC hydrogel, conc. = 100 mg L⁻¹, Temp. = 25°C, and mass of polymer (0.05 g/L)
Table 2: Freundlich and Langmuir Isotherms model parameter of Congo red adsorbed on Ag-g-PAA/AC

<table>
<thead>
<tr>
<th>Isotherm models</th>
<th>Parameters</th>
<th>Ag-g-PAA/AC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KF</td>
<td>33.574 ± 1.006</td>
</tr>
<tr>
<td></td>
<td>1/n</td>
<td>0.706 ± 0.015</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.9987</td>
</tr>
<tr>
<td>Langmuir</td>
<td>qm (mg/g)</td>
<td>392.445± 8.153</td>
</tr>
<tr>
<td></td>
<td>KL(L/mg)</td>
<td>0.0749 ± 0.0023</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.9912</td>
</tr>
</tbody>
</table>

Adsorption Thermodynamic Parameter

The spontaneity of the CV adsorption of Ag-g-PAA/AC hydrogel was evaluated by adsorption thermo-dynamics (Figure 7). Thermodynamics parameters counting change enthalpy ($\Delta H^\circ$), change entropy ($\Delta S^\circ$), and change free energy ($\Delta G^\circ$) were calculated by using the experimental result at several temperatures by Van't Hoff Equation (Eq. (3)).

$$\ln k = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$  \hspace{1cm} (3)

The negative value enthalpy of the CV adsorption on Ag-g-PAA/AC hydrogel indicated that the adsorption was endothermic and the positive value entropy suggested that the randomness raised as the adsorption proceed. The ($\Delta S^\circ$) was attributed to the liberation of water molecules from the hydrated shell of the absorbed species. The change free energy of the CV adsorption was estimated by using Eq. (4) and listed in Table (3), as follow:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$  \hspace{1cm} (4)

The values $\Delta G^\circ$ of the adsorptions under all testing conditions were negative, suggesting that the dye adsorption was a spontaneous process. Table (3) represents the CV adsorption thermodynamic factor on Ag-g-pAA/AC hydrogel.

Figure 7: The CV Adsorption isotherms on Ag-g-PAA/AC hydrogel at different temperatures

Table 3: Thermodynamic factors for CV dye adsorption on Ag-g-PAA/AC hydrogel

<table>
<thead>
<tr>
<th>Thermodynamic parameter</th>
<th>Delta H (kJ/mol.)</th>
<th>Delta G (kJ/mol.)</th>
<th>Delta S (kJ/K.mol.)</th>
<th>Equilibrium Constant (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20.688</td>
<td>-6.512</td>
<td>88.453</td>
<td>12.5</td>
</tr>
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</table>
Conclusion
In this study, the adsorption of crystal violet dye on Ag-g-PAA/AC hydrogel as a reactive surface was highly efficient in the color removal of the CV dye from an aqueous solution. The highest removal percentage of CV was (90.56%) at an equilibrium time of one hour, the dye concentration of (100 mg/L), and the weight of the hydrogel (0.05gm). Also, pH plays a key role in the color removal of the CV dye, as the greatest pH was in the alkaline medium. The process of reactivation of the surface Ag-g-PAA/AC hydrogel was applied and used again, as the hydrochloric acid gave the best removal efficiency when washing only once. The adsorption isotherms were studied, which matched the Freundlich model depending on the value of (R²).

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Authors' contributions
All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

Conflict of Interest
There are no conflicts of interest in this study.

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