A Thermodynamic Study for the Removal of Crystal Violet (CV) Dye from Aqueous Solutions Using a Hydrogel Composite (SA-G-Poly (AAC-AAM)/Tio2.

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Abstract

In this study, adsorption technique was applied to remove crystal violet dye from aqueous solutions and the hydrogel composite SA-g-p (AAC-AA M) was used as adsorbent. The composite was diagnosed by FT- IR and FE-SEM methods, and the optimum conditions were determined to study the effect of pH, temperature and ionic strength on adsorption process. The thermodynamic functions (ΔH, ΔG and ΔS) were calculated and the reaction was found to be exothermic and consistent with the Langmuir Isotherm.

Keyword: TiO2 nanoparticles, hydrogel Nano composites, sodium alginate, crystal violet.

1. Introduction

Environmental contamination occurs when a chemical or substances, or any influence on an environmental component, renders it inappropriate for human use or limits its usage. Changes in energy patterns, radiation levels, chemical composition, and living organism abundance. Environmental pollution is a process of disrupting the natural equilibrium of the environment, which impacts the lives of living beings. Atmosphere, hydrosphere) [1, 2]. Because nature is constantly changing owing to subjective variables such as torrents, rain, volcanoes, earthquakes, tides, etc., pollution can be natural. However, man's technological advancement has led to a rise in population density at the expense of the natural environment [3, 4].

This has led to increased environmental pollution from anthropogenic sources, whereby various human activities have emitted many pollutants, including industrial chemicals such as dye, heavy metals, some toxic chemical compounds, and gaseous pollutants emitted from transportation activities (oil), thus contributing to what is known as chemical pollution [5, 6]. Chemical contaminants such heavy metals, dyes, and phenolic chemicals can induce lung and cancer disorders [7, 8].

Because chemical pollution has spread to every corner of the earth, removing organic and inorganic pollutants from the environment has become a great challenge, since the severe effects on the elements of the environment, which resulted from the great human intervention in the components of the environment, prompted environmentalists to consider regulating pollution and protecting the environment, as they ultimately hurt the human being [9]. Despite the benefits of adopting physical and chemical pollution treatment techniques such filtration, extraction, chemical and electrical precipitation, and ion exchange, their application has been limited due to their high cost and ineffectiveness in treating particular pollutants. Adsorption technique is a low-cost and effective way to remove toxins from the environment [10].

Water contamination is a severe environmental issue since water is the lifeblood of all living organisms and includes essential chemicals and compounds. Water is polluted before humans and aquatic organisms because it changes its physical and chemical qualities [11]. Dye is an organic chemical that can bond to the colored substance and give it color. The widespread usage of dyes has resulted in their presence in industrial wastewater and water bodies [8, 12, 13]. Dyes are a toxic pollutant that must be eliminated from water due to their harmful effects on aquatic species and humans alike. Toxic cationic dyes like CV dye cause serious ailments including kidney failure and can even cause cancer if used in large quantities. The best approach to remove colors from water is through adsorption [14, 15].

2. Material and Methods

Chemicals

Sodium alginate (SA), Titanium Dioxide (TiO2), Acrylic acid (AAC), Acryle amide (AAM), N, N'-Methylene-bis-acrylamide (MBA), NaOH, HCl, potassium persulfate (KPS), crystal violet (CV). All materials used in the study were of high purity, and were prepared using deionized water

Preparation of SA-g-P (AAc-AAM)/TiO2 Hydrogel Nano composite

The hydrogel nanocomposite was made by free radical polymerization, in which 0.12gram of TiO2 was dissolved in 20ml deionized water and stirred for 4hours before being placed in an ultrasonic device, With constant

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stirring, sodium alginate (0.5g) was progressively added to the prior mixture, and then (4g) from AAC was periodically added to the solution with stirring for (15) a minute. A solution (2g/2mlAAM, 0.05g/MBA of the crosslinking agent) was prepared and added to the reaction mixture with continuous stirring for (15) a minute, then (4) drops of (TEMED) were added to the solution intermittently for a period of (5 min.), and a solution (0.03g/2ml) of the initiator (KPS) was prepared and added to the reaction mixture with continuous stirring for(15) a minute. For two hours, the temperature was raised to (70ºC) to complete the reaction, nanocomposite was immersed in deionized water to remove un reacted monomers. Finally, it was dried in an electric oven at 50c to obtain a constant weight.

Adsorption Isotherm

To calculate the adsorption isotherms of CV a dye, different concentrations were prepared in the range of 100-1000, then 10 ml of the prepared solutions were taken and placed in conical flasks, and 0.05g of the prepared adsorbent surface was added to it, then placed in a shaker for 120 minutes at 25ºC, then separated using a centrifuge at 6000 for 15 minutes. The absorbance of the filtrate was measured by UV-VIS spectrum equipment, The amount of adsorbent was determined using the following law [16, 17]:-

$$Q_e = \frac{(C_o - C_e) * V_{sol}}{m} \quad (1)$$

Where:

Qe : denoted to the quantity of adsorbent material
Co and Ct: are the adsorbent solution's initial and equilibrium concentrations in mg/L,
M: denoted to the mass of hydrogel in mg
V: is refers to the total volume of solution (L)
The following equations can be used to calculate the percentage of adsorbent removal:

$$Re\,\% = \frac{(C_o - C_e)}{C_o} \text{ X } \mathbf{100} \quad (2)$$

Effect of Temperature

For study the effect of temperature on the adsorption of CV dye on the surface of the adsorbent composite, solutions (10-100) ppm was created to evaluate the essential thermodynamic functions of the process, the adsorption experiment was performed at varied temperatures of15, 20, 25 and 30 degrees Celsius.

Effect of PH

Solution with PH (2-10) was made, acidity function was organized by using standard solutions of NaOH and HCl using PH Scale, specific weight of CV dye was taken and added to the previous solutions with (0.05g) of surface of the adsorbent. The adsorption experiment was repeated using the shaker for 45 min. (contact time).

Effect of salts

To study the effect of ionic strength on the adsorption process of cv dye on the surface of the adsorbent composite, weights ranging between (0.001-0.15) were taken from KC l, NaCl, and CaCO3 salts, 10 ml of the dye solution was added to it at a concentration of 100 ppm, placed in conical flasks containing 0.05 g of adsorbent surface, and then returned adsorption experiment with constant temperature,pH and time.

3. Results and Discussion

Characterization

FTIR Spectrum

The P (SA-g-poly (AAC-AAM)/TiO2) was studied using FT-IR spectroscopy. In the mid-IR regions between 4000 and 400 cm-1, F.T-IR spectra with a resolution of 1 cm-1 were obtained. Figure (1) also shows the F.T-IR spectra of P (SA-g-poly (AAC-AAM)/TiO2) before and after CV absorption. The intensity of the bands in the F.T-IR pattern decreases after adsorption [17, 18]. Furthermore, before and after the expected CV interaction, an actual change between P (SA-g-poly (AAC-AAM)/TiO2) was identified. A phy-sorption process is produced by the data of attraction forces between the P (SA-g-poly (AAC-AAM)/TiO2 surface and the CV under investigation.

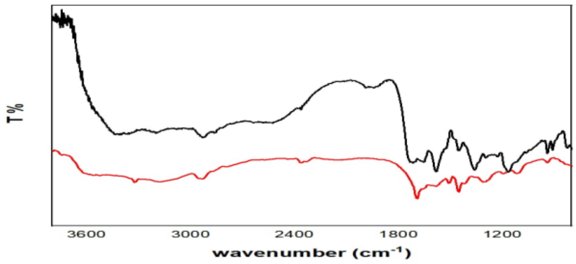

Fig. 1: FT-IR spectra of P (SA-g-poly (AAC-AAM)/TiO2) surface before, and after CV absorption.

FESEM Analyses

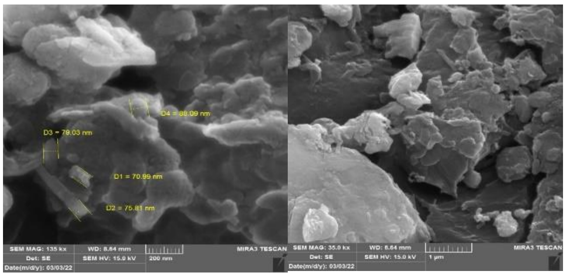

Fig. 2: FESEM Images of the Overlapping Surface of SA-g-poly (AAC-AAM)/TiO2 before Adsorption at Magnification Powers Vary

(SA-g-poly (AAC-AAM)/TiO2) revealed a smoother and more consistent surface. It has a lot of wrinkles that are clustered in an uneven way, as shown in Fig (2) following the adsorption of the particles on the composite surface, the FESEM picture shown in Figure (3) revealed that the surface is rough and porous, and that it is a sponge like compound with a mesh of compact layers. As a result, the aforementioned Particles have completely covered the surface of the combination, confirming the occurrence of the adsorption method [12, 19] [12, 20].

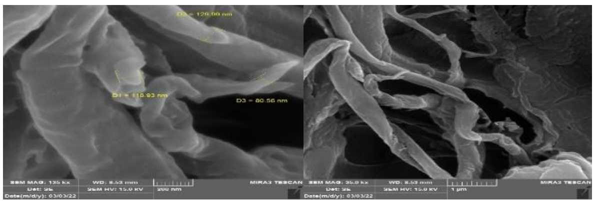

Fig. 3: FESEM Images of the Overlapping surface of SA-

g-poly (AAC-AAM)/TiO2 after Adsorption at Magnification powers vary

The adsorption isotherms of cv dye were calculated on the surface of the composite SA-g-poly(AAC-AAM)/TiO2, as the results showed, according to the classification of Gilles, that the adsorption process corresponds to the class L, in which the adsorption is single-layer so that the adsorbed molecules are horizontally oriented on the adsorbing surface, Langmuir,s isotherm showed more congruence than the two Freundlich and Temkin models, and it was possible, according to what was shown by the value of the correlation coefficient R2, which is 0.9721 as shown in table(1) that indicates the homogeneous nature of the adsorbent surface and that the active centers are equivalent energies and thus form a single molecular layer of the dye adsorbed on the surface superimposed [21-23].

Table (1): Correlation coefficients and isotherms of Langmuir- Freundlich and Timken of adsorption of CV adsorbed on the surface of the composite SA-g-poly (AAC-AAM)/TiO2

Langmuir equation			Freundlich equation			Timken equation		
KL	qm	R2	KF	N	R2	KT	B	R2
0.131	13.071	0.9721	3.411	3.073	0.9078	1.898	2.523	0.9297

Fig. 4: Langmuir isotherm for adsorption of CV dye adsorbed on the surface of the composite SA-g-poly (AAC-AAM)/TiO2

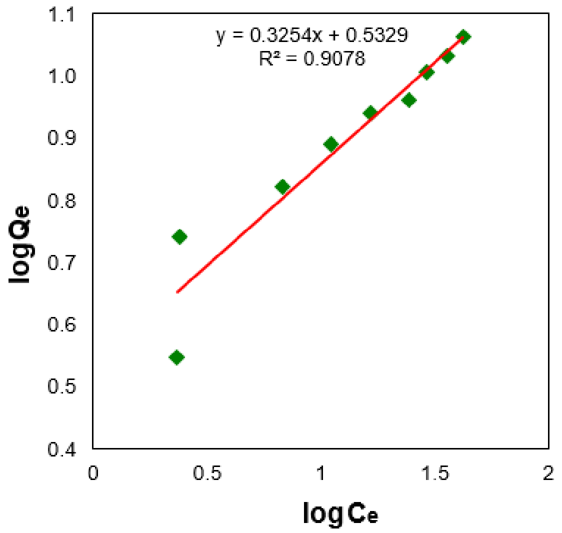

Fig. 5: Freundlich isotherm for adsorption of CV dye adsorbed on the surface of the composite SA-g-poly (AAC-AAM)/TiO2

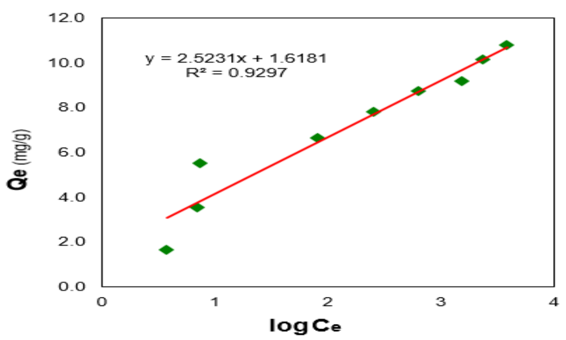

Figure (6): Timken isotherm for adsorption of CV dye adsorbed on the surface of the composite SA-g-poly(AAC-AAM)/TiO2

Effect of Temperature and Calculation of Thermodynamic Functions

The results showed that the amount of the adsorbent decreases with increasing temperature, as shown in Figure (7), which indicates that the process is exothermic, as the increase in temperature increases the solubility of the adsorbed dye particles, and this leads to a decrease in the affinity of the adsorbed particles towards the adsorbent surface, and the increase in temperature lead to an increase in entropy.

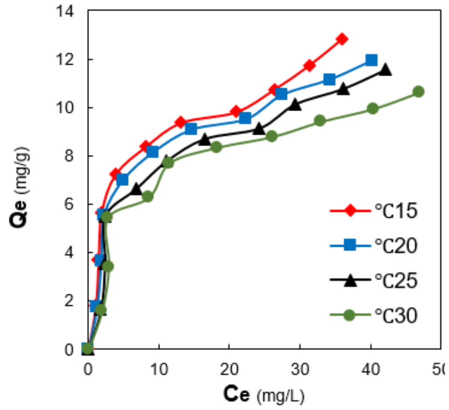

Figure (7): CV adsorption isotherms on the adsorbent composite surface SA-g-poly (AAC-AAM)/TiO2 at various temperatures

The values of the thermodynamic functions were obtained for the Cv dye adsorption process, as shown in the table (2), where the negative value of the enthalpy indicates that the process is exothermic and that adsorption decreases with increasing temperature, while the negative value of entropy refers to particles has low liberties and the value of the adsorption process's free energy is positive, indicating that the process automatically occurs.

Table (2): The Values of the Thermodynamic Functions

ΔH (kJ/mol)	ΔG(kJ/mol)	ΔS (kJ/K.mol)	Euilibrium Constant (K)
-13.210	1.260	-48.558	0.238

Effect of pH on the Adsorption

The effect of pH on the CV dye adsorption process was studied with a range of acidity functions ranging from (2-10) and constant temperature and time. It was observed from the results shown in the figure (8) that the adsorption process decreases at low pH due to competition between H ions and dye molecules. When the pH increases, the adsorption capacity increases due to ionization of the carboxyl and hydroxyl groups on the adsorbent surface, and thus it increases.

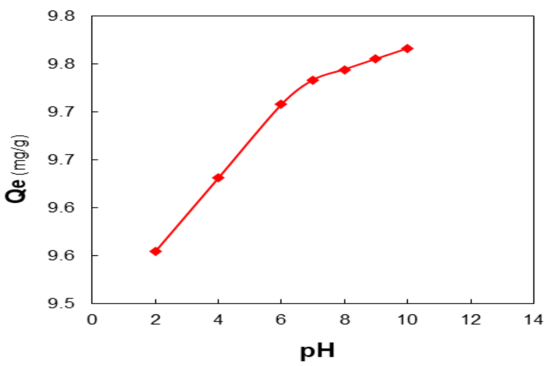

Figure (8) Effect of the acid function on the adsorption of CV dye at 25 C0

Effect of Ionic Force on Adsorption

The impact of ionic strength on the CV dye adsorption process on the adsorbent composite's surface was investigated. Different weights of KCl, Na Cl, and CaCO3 were utilized, with the rest of the variables of temperature, dye concentration, duration, and adsorbent compound weight being stable. The results showed that when the salt concentration increases, the adsorption of CV dye on the surface of the composite reduces due to competition between the positive ions of the salt and the dye molecules on the active sites of the adsorbing surface, where the salts improve the dye's solubility [23-26].

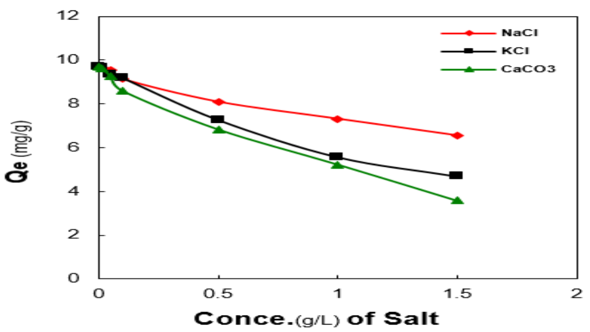

Figure (9) Effect of the acid function on the adsorption of CV dye at 25 C0

4. Conclusions

1-SA-g-poly (AAC-AAM)/TiO2 had a high adsorption capability.
2- CV can be removed from aqueous solutions using SA-g-(AAC-AAM) /TiO2 as an adsorbent.
3- The adsorption of CV dye onto SA-g-poly (AAC-AAM)/TiO2 was better represented by the Langmuir isotherm model.
4- Thermodynamic experiments revealed that CV adsorption on SA-g-poly (AAC-AAM)/TiO2 was exothermic, the system has positive G thermodynamic values, indicating a non-spontaneous process.

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