Adsorption of toxic crystal violet dye using (Chitosan-OMWCNTs) from aqueous solution

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Abstract

Crystal Violet dye is a toxic organic pigment that has little solubility in water and causes serious health problems and environmental pollution. In the current study, a compound composed of multi-walled carbon nanotubes with chitosan was used. Experiments were conducted to adsorb the crystal violet dye for both the effect of the surface weight of the adsorbent and contact time. Dye with the CS-OMWCNTs. And the study of the effect of the pH and the study of the effect of ionic intensity in removing the dye. The results are shown. The best weight is obtained as an adsorbent surface was 0.035 g. The results showed the best contact time to reach a state of balance, which was 90 minutes. By studying the pH, the best acid medium was pH=4 and the percentage of deletion was 99% in the acidic medium with a concentration of 100 ppm. As for the ionic intensity study, each of the salts of sodium chloride and potassium carbonate are studied. The dye adsorption percentage decreases as the salt ions compete for the active sites of the adsorbent surface.

KEYWORDS: Chitosan-OMWCNT, Adsorption, Crystal Violet, Water Pollution

1-Introduction

Water Pollution: The increase in the population and consequently the increase in human activities leads to an increase in the percentage of water pollution[1][2]. The release of chemicals and household waste is pollution, whether intentionally or unintentionally[3][4]. Access to clean water is an imperative condition for the growth of healthy, disease-free organisms [5][6]. These pollutants are released mainly as (tanned leather, textiles, paint, dyes, petroleum refining, and wood and heavy metals processing) [7][8]. Among the health risks caused by pollution are (cancer, genetic damage, birth defects, damage to the immune system, and respiratory problems)[9][10][11]. Of the sources of water, pollution was either pollutants (organic or inorganic)[12][13][14]. There was many treatment methods, including (active carbon, thermal techniques, and electrical methods)[15][16].

Adsorption was a widely used method of removing pollutants, due to its low cost, high efficiency, and ease of operation [17]. The adsorption process depends on the physical and chemical properties of both the surface and the adsorbent on the surface[18][19]. The adsorption may be physical or chemical[20][21].
Crystal Violet It was the dye tri-phenylmethane, the name according to the IUPAC system N- [4- [bis (4-dimethyl-amino) -phenyl] -methene] -2,5-cyclohexadien-1-ylidine] -N-methyl- methanaminium chloride . It was considered a carcinogenic dye, but it is still used in commercial textile and biological coloring processes[22]. It causes (kidney failure, permanent blindness, skin irritation)[23]. The chemical formula (C25H30ClN3) has a wavelength of 586 nm [24]. As for the molar mass is (407.99) g / mol, while the chemical composition is in Table (1)

Table 1  

Properties of crystal violet dye and molecular structure

| Molecular formula | C_{25}H_{30}ClN_{3} |
|-------------------|---------------------|
| Molar mass        | 407.979 g /mol      |
| CL .number        | 548-62-9            |
| Type              | Cationic            |
| Maximum wavelength| 586 nm              |

Adsorbed carbon grafted onto chitosan[25][26], CS-OMWCNTs are nanomaterials of great interest due to their distinctive
properties, such as surface-to-volume ratio, high porosity, hollow structure, and presence of active groups on the surface [27].

2-Materials and experimental work

2-1. Materials

The adsorbent surface used is the compound manufactured in a laboratory (CS-0MWCNTs), Crystal violet (Avonchem, UK), HCl (HIMEDH), NaOH (Rasayan).

2-2. Experimental

Preparation of the adsorbents: The nanocomposite (CS-OMWCNTs) was prepared by taking 0.1 g of the activated OMWCNTs and mixing them with 20 ml of distilled water. Then this mixture was slowly added to 0.5 g of chitosan and 20 ml of DMF with continuous stirring for 6h at a temperature of 40°C. It is then dried to 50°C and is used in a crystal violet dye adsorption process.

Adsorbate solution: The stock solution of crystal violet was prepared from a solution of taking 0.01 g of the dye to 100 ml of distilled water. A series of solutions were prepared from the standard solution with appropriate dilution. The pH was adjusted using either 0.1 M of NaOH or 0.1 M of HCl.

Adsorption experiments: The experiments were conducted in a baker with a capacity of 250 ml, placed on mechanical vibrators at 150 rpm until equilibrium was reached at a temperature of 20°C. The weight effect of CS-MWCNTs was calculated by taking weights of (0.035-0.1) g from the adsorbed surface. The time effect was calculated by taking different times of (1-240) min. And with a certain weight of the adsorbent surface. The effect of the acidic function was studied by taking pH (2,3,4,6,8,10). The effect of ionic strength was studied by taking two salts, NaCl and CaCO3, with weights (0.001-0.05) g for both salts. The absorbance was measured by a UV-Visible device at a wavelength (586 nm). The amount of adsorbent is calculated by equation (1).

\[ q_e = \frac{(C_0 - C_e)v}{w} \quad 1 \]

Where \( C_0 \) and \( C_e \) are the initial and the equilibrium CV dye concentration (mg/L), \( V \) is the volume of solution (L), and \( W \) is the amount of CS-OMWCNTs used (g).

The percent removal (%) of dye was calculated using the following equation:

\[ \text{removal(\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad 2 \]

3-theory

3.1. Adsorption isotherm
Adsorption isotherms are essential for inferring the connection between the adsorbent surface and the adsorbent and to give an idea of the adsorption capacity through the number of layers that form on the adsorption surface can be equated to either a single layer or a multilayer.\(^5\)

\[
\text{Langmuir: } \frac{c_e}{q_e} = \frac{c_m}{q_m} + \frac{1}{K_L q_m} \tag{3}
\]

\[
\text{Freundlich: } \log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \tag{4}
\]

\[
\text{Temkin: } q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \tag{5}
\]

### 3.2. Kinetic modeling

Adsorption kinetics gives information about the adsorption mechanism and the adsorption pathways and also controls the rate of adsorption, which determines the time required to reach the equilibrium states of the adsorption process.\(^7\)

\[
\text{Pseudo-first order: } \log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \tag{6}
\]

\[
\text{Pseudo second-order: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}
\]

### 3.3 Thermodynamic parameters

Thermodynamic behavior of adsorption of CV on (CS-OMWCNTs) was evaluated by parameters –Gibbs free energy change (\(\Delta G^0\)), enthalpy (\(\Delta H^0\)) and entropy (\(\Delta S^0\)). These parameters were calculated using the following equations:

\[
\Delta G^0 = -RT \ln K_e \tag{8}
\]

\[
K_C = \frac{C_0}{C_e} \tag{9}
\]

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0 \tag{10}
\]

### 4. Results and discussion

#### 4.1. Effect of adsorbent weight

The surface quantity has a strong effect on the adsorption process. The effect of the surface(CS-OMWCNTs) weight on the dye adsorption and pulse was examined using weights of (0.035-0.1)g[28] (Fig 1). Dye concentration100ppm, And at a temperature of 20°C. Percentage of deletion (98.9%-99.9%) (Fig 2). The increase in the percentage of deletion is due to the increase in the percentage of removal of the dye. That is, the surface area decreases due to the accumulation of effective sites, which causes the impediment of the arrival of the dye and its attachment to the surface of which the weight was fixed for the conduct of experiments(0.035 g)[29][30]\(^1\)
Fig. 1. Effect of weight (CS-OMWCNTs) on CV dye removal (dye conc:100ppm, Tempe:20° C, 10ml,)

Fig. 2. Removal %0f CV

4-2 Effect of contact time of Crystal violet

The equilibrium time of the adsorption of the crystal violet dye with a concentration of 100ppm, a temperature of 20° C, and pH=7 were studied at different times (1-120)min (Fig. 2). The results showed that the adsorption rate of a dye is very fast in the first minutes of adsorption. This is due to the large surface area of the prepared compound (CS-OMWCNTs) available to absorb the dye particles [31]. The basic rate of dye removal is due to the presence of active groups on the surface. In general, the absorption of the dye increased with an increase in the time in the first minutes to reach the equilibrium state, at a time of 90 minutes, and the percentage of dye deletion was 99% [32].
Fig. 3. Effect of contact time of Crystal violet (CS-OMWCNTs:0.035 g , dye conc:100 ppm ,Tempe 20° C)

4-3 Effect of ionic strength

Ionic strength is important, it is the factor that regulates the adsorption. An increase in ionic strength can lead to an improvement or a decrease in the adsorption. The adsorption can be insensitive to the ionic strength of different ions. Decrease in the amount of crystal violet dye adsorbed on the surface of the compound with an increase in the concentration of salts in the solution. It is due to the effect of the competition between the cationic dye molecules and the positive ions of the salts on the active centers of the surface of the complex. Ions of small size can compete to bond with the active sites of the surface, while the negative ions form a double complex with the dye molecules[33] (Fig.4). The weights used for the salts were (0.001-0.05)g.

Fig.4. Effect of ionic strength (Dye conc:100 ppm , Tempe 20° C,CS-OMWCNTs:0.035 g)
4-4. Effect of \( \text{PH} \)

The \( \text{pH} \) is important in the adsorption process to control (the absorbent surface charge, the degree of ionization of the molecule, the extent of functional dissociation of groups on the active sites of the adsorbent)[34]. \( \text{pH}=(2,3,4,6,8,10) \), Fig 6. This is due to the increase in the negative charge density on the adsorbent surface in an \( \text{pH} = 4 \) and this, in turn, leads to the attraction between the positive charge of a dye and the surface of the adsorbent. It is observed that with the increase of the \( \text{pH} \), the surface charge density decreases, which leads to the repulsion of the dye molecule[35][36].

![Graph of \( Qe \) vs \( \text{pH} \)](image)

**Fig. 5.** Effect of \( \text{PH} \) on the removal of CV dye. (CS-OMWCNTs: 0.035 g, 10 ml, conc:100 ppm. Tempe 20 C)

5-Conclusion

The study revealed that the compound is a substance that absorbs the crystal violet dye from the contaminated wastewater by removing more than 98% of the dye. The studied results of the studied contact time, \( \text{pH} \), weight of the compound, and ionic intensity showed a varied effect on the adsorption process. Indication of suitable surface and structural properties for dye absorption. That is, linking structural features to absorption behavior.

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7- References

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