Adsorption of Crystal Violate (Cv) Dye in Aqueous Solutions by using Zno/P (Aa-Ca) Composite as Adsorbate Surface Characterization, Thermodynamics And Equilibrium Evaluation

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Abstract
Toxic dyes in water have put human health at risk all around the world. We used biodegradable polymers such as ZnO/Poly (Acrylic acid-Crotonic acid) hydrogel (ZnO/P(AA-CA)) to make an excellent absorbent hydrogel for the removal of pollutant crystal violet dye (CV) from aqueous solutions. Diagnostic methods such as FT-IR, FE-SEM and XRD were used to examine the produced materials. Tests on CV dye adsorption via hydrogel and the influence of different parameters such as temperature, CV dye concentration and isotherm modules were conducted. The correlation coefficient (R2) indicated that the adsorption process followed the Langmuir model, which was confirmed by the data. It is clear from these results that hydrogels are a cost-effective and efficient biomaterial for eliminating CV dye from water.

1. Introduction

Many facets of human existence are affected by the availability or scarcity of water. Inadequate sanitation and water supply could have environmental, economic, and social repercussions. Access to clean water is essential for the wellbeing of the poor and vulnerable, especially children [1, 2]. Each year, 10–20 million people die from waterborne disease, and more than 200 million people die from nonfatal infections. Most people in the world have no safe drinking water at this time [3]. Creating severe health problems within a few decades, the current water supply will be reduced by one-third, and more than a billion people will lack access to potable water. Toxic heavy metals [4], oils and dyes [5]. Organic dyes are utilized in textiles, paper, plastics, leather, food, and cosmetics [6, 7]. It doesn't matter how small the amount of textile dye is, it still has a bright color [8, 9]. Bioaccumulative these dyes are non-biodegradable and don't break down in the environment. They don't break down when they are exposed to light, biological, or chemical treatments. Another thing that makes them dangerous is that they can be mutagenic and cancerous to people [10, 11]. Dyes in water make it harder for light to penetrate, which has a major impact on photosynthesis, and conventional treatment methods are unable to remove them fast enough[12, 13]. Electrochemical and chemical procedures, photo catalysis and other approaches can be used to effectively remove these hues [14, 15]. Comparing nanotechnology to traditional water treatment approaches, it is a superior platform for the treatment and remediation of microorganisms and organic dyes in drinking water[16]. Adsorption is a cost-effective and efficient innovation among these technologies because of its high efficiency, simple design, and ease of operation[17]. The hydrogels adsorb crystal violet dye quickly and effectively with the help of a ZnO/poly (AA-CA) nanocomposite. The primary focus of this study is to characterize the binding of Rhodamine B from aqueous solution to the surface of composites under different temperature. Calculation of thermodynamic functions.

2. Experimental

Preparation of ZnO/P (AA-CA)

A ZnO, AA and CA of solutions were prepared, starting with the preparation of crotonic acid (1 g in 10 ml of water), the solution remains on the magnetic stirrer after adding 8 ml of acrylic acid for 15 minutes. The second solution includes the preparation of ZnO (0.2g in 10 ml of water), with stirring, then transferred to the (sonicator) and gradually added to the above solution. After that, a solution of MBA (0.1g in 4 ml of water) and a solution of KPS (0.06g in 4 ml of water) were prepared, then these solutions were mixed with each other and the final solution was transferred to glass tubes and placed in the water bath at 70°C for 3 hours. The washed polymer was dried in Oven at 70°C for 6 hours.

Adsorption studies

The isotherm adsorption model of the reactions was used to analyze the effect of various parameters such as temperature solution, primary concentration of CV and contact time, on the adsorption of CV dye in batch form. For 60 min., a shaker water bath was used to add the appropriate amount of (ZnO/P (AA-CA)) to the CV dye solutions made at various concentrations. Temporary conditions in which equilibrium can be achieved. The small amount of CV was remaining in the filtered solutions. The maximum wavelength absorbance (λ_{max}) of

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CV dissolved in aqueous solutions was determined using an atomic adsorption spectrophotometer (UV-Vis-spectrophotometer, Shimadzu, PC-1800). An absorbent was used to agitate CV solutions of various concentrations until equilibrium was reached in order to evaluate the isotherms adsorption model. ZnO/P (AA-CA) adsorption capacity and CV elimination percentage were determined using Eq. (1), (2)

$$Q_e = \frac{V(C_o - C_e)}{m} \quad (1)$$

$$Re\% = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

qe (mg.g-1) represents the amount of the CV absorbed over the absorbent at equilibrium. Co (mg.L-1) and Ce (mg.L-1) refer to the initial and equilibrated concentrations of CV. Moreover, m (g) implies the absorbent mass and V (L) represents the content of the added solution.

Results and discussion

Characterization

Fourier Transform Infrared Spectroscopy (FTIR)

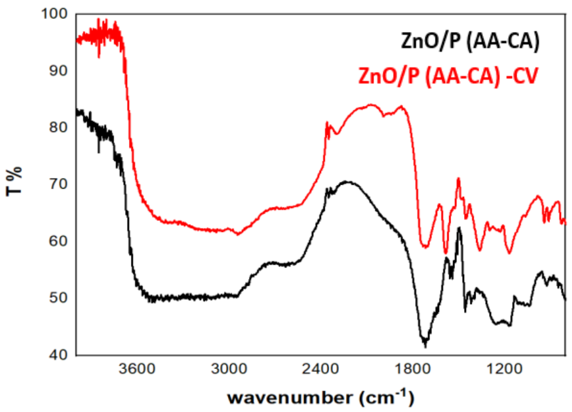

Fig. 1: FTIR spectrum of Nano composite before and after CV adsorption

The infrared spectra of the composite before and after the adsorption were recorded in Figure (2) show the belong of a wide adsorption band at ranges 3187–3510 cm-1, suggesting that the O–H band overlapped with the N–H band. In addition, the presence of bands. There was also a band at 1735 cm-1 that belonged to the carbonyl group C = O in the carboxylic acid, 1630 cm-1 for C=N of CV dye. A shift occurred in the IR spectrum of the CV dye[18].

Femes

The scanning electron microscope technique was used to study the surface properties of the prepared composite and to know the shape of the particles, their size, the nature of their aggregates and the nature of the surfaces if they are porous or smooth (Figure (2), as well as knowing the amount of homogeneity between the compon [19].

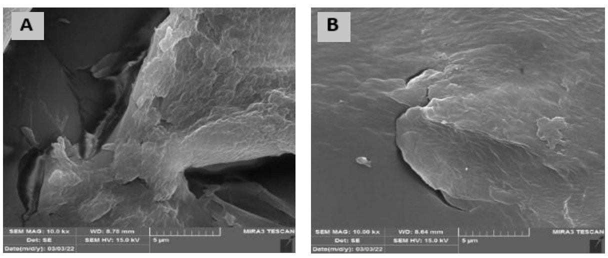

Fig. 2: FESEM image of ZnO/P (AA-CA). (A) before and (B) after adsorption of CV

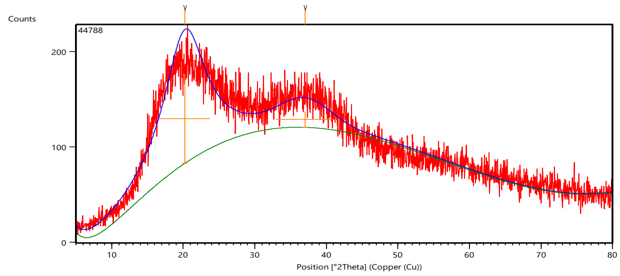

Fig 3. XRD diffraction of ZnO/P(AA-CA) nanocomposite.

X-ray diffraction spectra were used to study the structural properties represented by the structure and crystal size of ZnO/P(AA-CA) composite in their solid state using a single light of wavelength 1.5104 A0 from Cu-Kα source within the angular range 2θ is (0-80) degrees [20, 21]. Figure (3) and Table (1).

Table (1): Characteristics and X-ray diffraction values of the prepared nanocomposite ZnO/P (AA-CA) XRD

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip Width	Matched by
20.22(8)	94(4)	7.1(3)	4.38808	100.00	8.5123	
37.0(2)	17(2)	8(1)	2.42688	17.99	9.8472	

Table (1): Characteristics and X-ray diffraction values of the prepared nanocomposite ZnO/P (AA-CA)

Effect of contact time

Figure (4) shown how the contact time affects the CV adsorption on the ZnO/P (AA-CA) surface. Adsorption reached equilibrium in one hour, and the adsorption capacity CV (capacity for adsorption) went up with the amount of time it was together. In the first few minutes, adsorption increases [20]. After the fifth minute, the changes in adsorption capacity were more gradual, and equilibrium was reached in about an hour with 9.707mg/g CV in about an hour

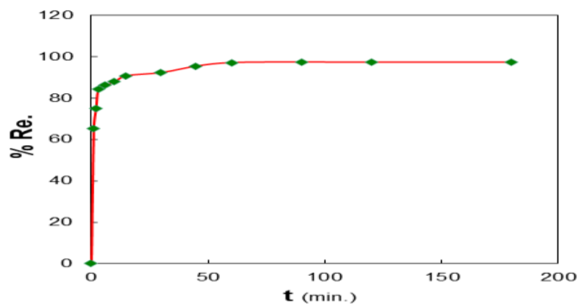

Fig. 4: Effect of contact time on the CV adsorption. Condition: CV: 50ppm, 25 °C, adsorption dosage 0.05 g/10 mL

Effect of temperature

At different temperatures (15-30°C), it has been shown how this affects how much absorbate there is in the solution [22]. This means that the method is exothermic, which means that the molecules are able to get more kinetic energy by heating them up, which is why there is less adsorbate in higher temperatures (Figure (5).

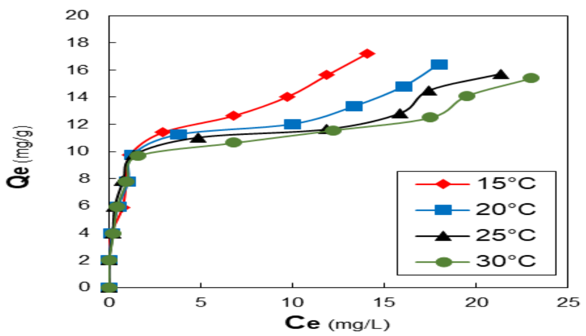

Fig 5. Isotherm of adsorption for CV on [ZnO/P (AA-CA)] at different temperatures, adsorbent mass 0.05 g/L and constant time

Thermodynamic parameters such as (ΔHo) enthalpy, (ΔGo) Gibbs free energy, and (ΔSo) entropy were calculated using equations (3 and 4). These estimates are shown in Table (2) and Figure (6).

$$\ln_{xm} = \frac{-\Delta H}{RT} + \text{constant (3)}$$

$$\Delta G = -RT\ln K \text{ (4)}$$

Table (2): Effect of temperature on the maximum amount of CV dye adsorbed at constant time onto [ZnO/P (AA-CA)] at 25℃ temperature			
T(K)	1000/T(K-1)	Ce = 2.1	
		Xm	ln Xm
283	3.5335	12.7	2.541
293	3.4129	11.6	2.451
298	3.3557	11.2	2.415
303	3.3003	10.6	2.360

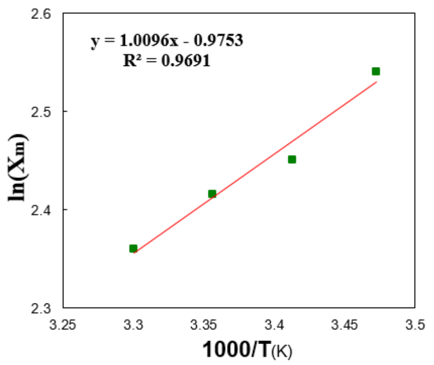

Fig. 6: The maximum adsorption amount lnXm of CV dye at different adsorption temperatures

Table (3) shows the thermodynamic factors computed for the CV adsorption on [ZnO/P(AA-CA)]. Adsorption is exothermic if the enthalpy value is high enough. One probable description of the endotherm city of heats of adsorption is that CV and the [ZnO/P(AA-CA)] have been solvated in the water. The negative ΔG value indicates that the adsorption process was spontaneous, and the positive ΔS value indicates the high randomness of the system and that the molecules are free to move[22].

Table (3): Thermodynamic factors for the CV adsorption onto ZnO/P(AA-CA)			
ΔG (kJ/mol)	ΔH (KJ/mol)	ΔS (J.mol-1. K-1)	Equilibrium constant
-8.394	-5.224	17.529	8.235

Adsorption isotherm

Freundlich isotherm

The Freundlich equation (Figure (7)), which defines physical adsorption from a liquid, is one of the brief empirical equations typically used to represent adsorption data. We provide here the empirically obtained Freundlich coefficient:

$$q_e = K_f C_e^{1/n} \text{ (5)}$$

qe is the mass of the absorbent absorbed in each unit weight (mg/g), (mol/g)C_e refers to the Equilibrium concentration of adsorbate in the solution following the adsorption (mol/L), Kf denotes the empirical Freundlich's constant (L/gm) or the capacity factor (L/gm), 0.1/n: Freundlich exponent[23].

Langmuir isotherm

The Langmuir isotherm is a well-known technique for removing impurities from liquid solutions [24]. One of the other equations was obtained using Langmuir to describe the nature of the adsorption process from solutions in a particular scenario. The Langmuir adsorption isotherm is next shown; the Langmuir adsorption isotherm is illustrated in equation [6].

$$Q_e = \frac{q_0 . K_L . C_e}{1 + K_L . C_e} \text{ (6)}$$

q_e refers to the amount absorbed in each unit weight of the absorbent at equilibrium (mg/g), q_0 implies the Empirical Langmuir constant representing the greatest adsorption capacity (mg/g), C_e represents the Equilibrium concentration of the adsorbent in the solution following adsorption (mg/L). Moreover, K_L represents the empirical Langmuir constant (L/mg) Figure (7).

Temkin and Pyzhev Isotherm

Temkin isotherm contains a factor that explicitly takes into the account adsorbing species-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The Temkin isotherm is given as:

$q_e = B \ln (K_T C_e)$ (7)

Where;

K_T: is the equilibrium binding constant ($L.g^{-1}$), B: is the Temkin isotherm constant.

Langmuir isotherm model reflected the best fit to absorb the CV on hydrogel as seen in the R^2 (0.9762) values[25]. Now, values of our model parameters provided from the diagram of q_e against C_e Figure (7) and Table (4).

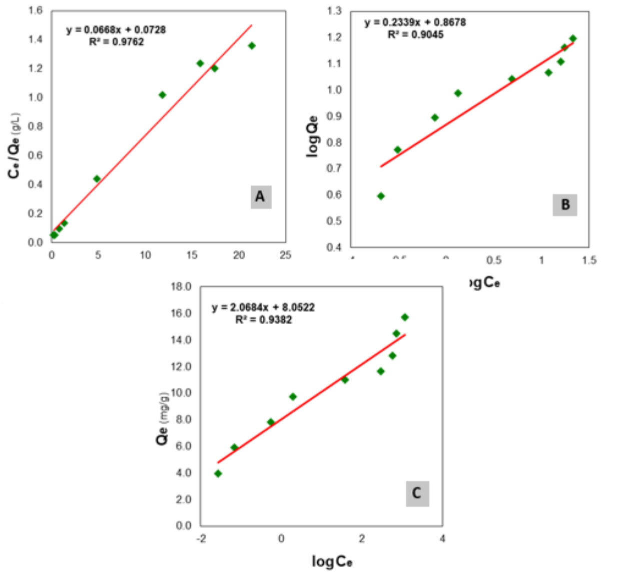

Fig. 7: Various adsorption isotherm patterns nonlinear fit for adsorbing the CV on ZnO/P(AA-CA), (A)Langmuir (B), Freundlich, initial concentration = 100 mg/L, Temperature = 25℃, the adsorbent = 0.05 g/L and contact time = one hr.

Table (4): The Freundlich, Langmuir, the isotherms parameters for CV absorbed on ZnO/P(AA-CA) at 25ºC								
Langmuir equation			Freundlich equation			Timken equation		
KL	qm	R2	n	KF	R2	KT	B	R2
14.97	0.918	0.9762	4.275	7.376	0.9045	2.068	49.056	0.9382

3. Conclusion

In this study, the nanocomposite ZnO/P (AA-CA) was prepared and used as an adsorbent. It was noted that the use of ZnO/P (AA-CA) is an effective, fast and cheap adsorption method to remove CV dye from its aqueous solutions. The effect of other conditions on the adsorption process was studied, such as CV concentration, equilibrium time, temperature and the effect of the acidity function. The results showed that the equilibrium data fit well with the Langmuir isothermal equations. The kinetic data were installed using different models, as it turned out that the adsorption process follows a false second order, and that the amount of adsorbent (CV) increases with the increase of pH for the solution

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