Hydrogel/Clay Nanocomposites for Removal of Cationic Organic Dye from their Aqueous Solutions

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Abstract

The hydrogel nanocomposite was prepared SA-g-poly (AAC-AAM)) /BC by free radical polymerization of acrylic acid (AAC) and sodium alginate (SA). The surface properties were studied using FT_IR technique, FE-SEM scanning electron microscope and X-ray diffraction. The thermodynamic functions, change in enthalpy, change in entropy, and change in free energy .The study showed that the dye was removed by adsorption process at different temperature (15,20,25,30℃).The adsorption process of the dye decreases when the temperature increases, meaning that the adsorption process is of the exothermic type.It showed the effect of salts on the adsorption process of the dye by using different weights of salt .The adsorption capacity of the dye decreases with the increase in the salt concentration.

Keyword: BC, hydrogel nano composites, sodium alginate, crystal violet.

1. Introduction

Pollution is a change in the environment and this change is physical, chemical or biological, as this change leads to the appearance of foreign and harmful substances in the environment as a result of industry and human activities, and pollution can affect the atmosphere, water and soil, The problem of pollution is one of the most important environmental problems at the beginning of the twentieth century, and pollution is one of the important problems facing man and nature together. Various types of natural materials and chemicals that the environment was not fully aware of before, so fumes and gases from the chimneys of hundreds of factories polluted the air and dumped their toxic and harmful residues in the sewage water. Water pollution is one of the most prominent problems, as water generally contains a lot of polluting substances such as organic and inorganic substances, with certain concentrations of a nature (dissolved, insoluble, suspended) and the concentrations of these substances vary depending on the nature of the water or where it is located and the percentage of increase or decrease of these Substances greatly affect the purity of the water and that water becomes polluted[1,2].There are a number of phenomena that indicate water pollution, including the lack of oxygen, thermal pollution, the presence of toxic waste, increased turbidity, dyes, pesticides, detergents, oil materials and other pollutants resulting from different industries [3,4].Water pollution due to the disposal of gaseous, liquid and solid wastes and radioactive materials leads to a change in the properties of general water such as its color, taste, turbidity, smell, change in the acidity function, density, viscosity and gaseous content, which makes the water unsuitable for human, agricultural and industrial uses[5,6]. The dyes present in water are among the most important water pollutants, and it is well known that manufactured dyes are widely used in dyeing, printing, paper, plastic, textiles, food and cosmetics for the purpose of coloring and enhancing the aesthetics of their products [7, 8].It is known that there are approximately more than 100,000 commercially available dyes, with more than 700,000 tons of dyes produced annually. Given the presence of this amount of dyes, they are discharged and liquid wastes are formed that change the color of water, and this is a clear evidence to distinguish it, detect it easily, and track its sources of generation. Therefore, it was necessary to search for the preparation of many physical and chemical techniques for the purpose of using them in water treatment, including (extraction, filtration and evaporation, Chemical and electrical precipitation, ion exchange) and despite the importance of these techniques, they are limited in uses due to the high economic cost and cannot be used effectively to treat a wide range of wastewater dyes. A large commercial [9-11]. Therefore, adsorption technology is considered one of the important ways to treat water because it is of low cost due to the availability of many natural resources that can be used as adsorbent surfaces such as clay, carbon, zeolite, organic blocks, agricultural residues and others [12].

2. Chemicals and Materials

Sodium alginate (SA), Bentonite (BC) Acrylic acid (AAC), Acryle amide (AAM), N, N'-Methylene-bis-acrylamide (MBA), NaOH, HCl, potassium persulfate (KPS), crystal violet (CV).NaCl,CaCl2,

Preparation of SA-g-P (AAC-AAM)/BC Hydrogel nano composite

The hydrogel nanocomposite was made by free radical polymerization, in which 1g of BC was dissolved in 20ml deionized water and stirred for 1hours before being placed in an ultrasonic device,

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with constant stirring, sodium alginate (0.5g) was progressively added to the prior mixture, and then (4ml) from AAC was periodically added to the solution. A solution (2.5g/5ml of AAM,0.05g/2ml MBA of the crosslinking agent) was prepared and added to the reaction mixture with continuous stirring for(15) a minute, and a solution (0.08g/2ml) of the initiator(KPS) was prepared and added to the reaction mixture with continuous stirring for(15) a minute. For 2 h, nanocomposite was immersed in deionized water to remove UN reacted monomers. Finally, it was dried in an electric oven at 50℃ to obtain a constant weight .The same steps are used to prepare the SA-g-P (AAC-AAM) Hydrogel without the use of bentonite. [13, 14]

3. Results and Discussion

FTIR, XRD and FESEM

FT-IR Spectrum

The infrared spectrum of the SA-g-P (AAC-AAM) hydrogel shows, and as shown in Figure 1 it showed at the range 3550-3210cm-1, broad absorption bands, which indicate the interference between the N-H band of the MBA crosslinker and the O-H band For bentonite, as for the C-H bonds present in the aliphatic compounds within the hydrogel composition, it showed absorption bands within the range 2600-2950cm-1, which represent the symmetric and asymmetric stretching vibrations of alkyl groups (-CH2) present in the hydrogel. As for the range 1460-1000 cm-1, the absorption bands that appeared in it showed the presence of the C-C, (C-N) and (C-O) bonds .As for the bands that appeared at 1400_1550 symmetric and asymmetric vibrations of the two Coo groups, which belong to the sodium alginate, and the lack of overlap of the acrylic acid and the sodium alginate is evidence of the absence of the Na-O band [15].The appearance of packages within the range 1013_1395 that belong to the O_H, C_H and N_H group

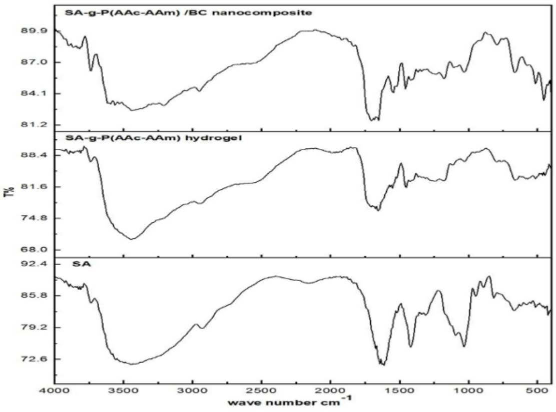

Fig 1 (a FT-IR of [SA-g-P(AAC-AAM]/BC (b) SA-g-P (AAC - AAM) (c) Sodium alginate (SA

FE-SEM

The FE-SEM scanning electron microscope technique was used to study the properties of the prepared surface and the nature of the surface as porous or smooth and to know the amount of homogeneity between the components and their distribution on the surface. Through this technique, it is possible to know the shape of the particles, the nature of their grouping and their size [16].The FE-SEM images shown in the figure2 showed that the surface of the hydrogel is smooth and porous and has a sponge-like structure as a monolithic network as a result of the strong bonding of the crosslinking agent with the polymeric chains. Regular After adsorption of cv dye on the surface SA-g-P (AAC-AAM)/BC the FE-SEM image shown in the figure revealed 2 The surface is smoother and firmer, as a result of filling the pores on the surface of the hydrogel overlay from the dye molecules, where dye molecules covered all the surface of the composite, which indicates the occurrence of a process adsorption [17, 18].

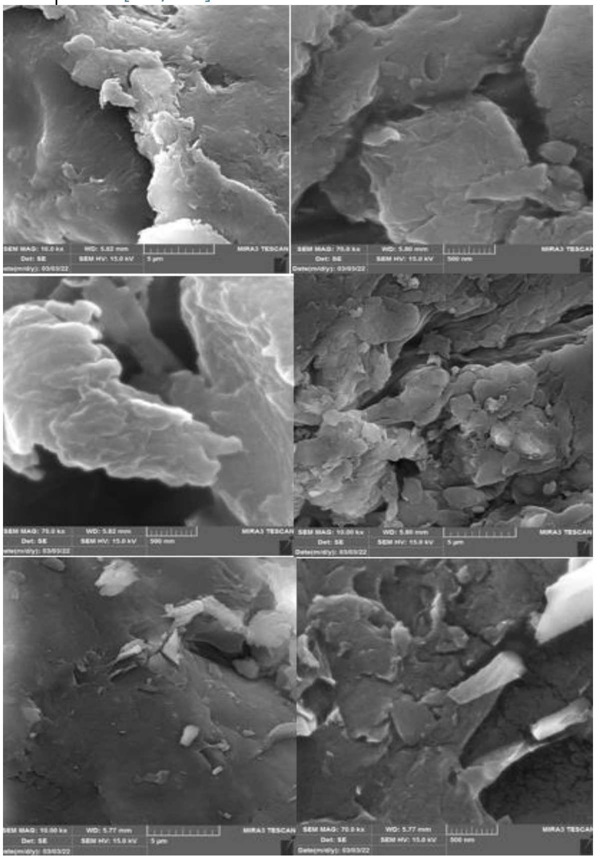

Fig 2 (a) FE-SEM image of [SA-g-P (AAC-AAM] (b) SA-g-P (AAC-AAM)/ BC (c)SA-g-P (AAC-AAM/BC after adsorption of CV

XRD

X-ray diffraction spectra were used to study the crystalline properties represented by the structure and crystal size of the SA-g-P(AAC-AAM) hydrogel and its BC/SA-g-P(AAC-AAM) hydrogel in the solid state using a single wavelength 1.5104Å light from Cu-kα source within The angular range 2θ is (0-80) degree It shows the spectrum XRD of hydrogel in the form 3.the presence of two beams, one of which is wide at 2θ=21.5◦ computed at a distance d =4.12591 Å and the other is less than it at the2θ= 37◦ computed at d= 2.45308 Å When, which indicates the non-crystalline nature of the hydrogel, as for the hydrogel nanocomposite and bentonite, it contains several crystalline peaks, and the appearance of these peaks is evidence of the crystalline nature of the hydrogel nanocomposite and bentonite.[19]

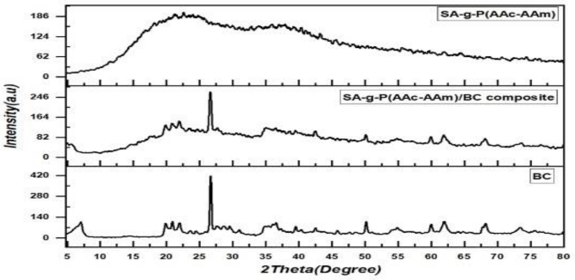

Fig 3 (a XRD of SA-g-P (AAC_AAM (b) SA-g-P(AAC-AAM)/BC (c) BC

Adsorption Isotherm

The adsorption isotherm is significant for the explanation of how the adsorbent will interact with the adsorbate and give an idea of adsorption capacity. they play an important role in understanding the mechanism of adsorption .the surface phase may be considered as a monolayer or multilayer ,Langmuir and Freundlich models are the most widely used to describe adsorption isotherms [20]. Different concentrations between 100 and 1000 were prepared to determine the CV dye's adsorption isotherms. 10 ml of these solutions were then put in conical flasks with 0.05g of the prepared adsorbent surface, shaken for 120 minutes at 25 C, and then separated using a centrifuge at 6000 for 15 minutes.

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

The following equations can be used to calculate the percentage of adsorbent removal:

$$\textbf{Adsorption}\ \% = \frac{(C_o - C_e)}{C_o} \text{ X } \mathbf{100} \text{ ------------------- } (2)$$

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

Effect of Temperature

The adsorption was studied at different temperatures and with a concentration of 100 for the dye and the change in temperature decreased or increased the ability of the adsorbent surface to adsorption of CV dye from aqueous solution .Through the results, the amount of stretched dye cv was shown with increasing temperature, meaning that the adsorption process is an exothermic process.

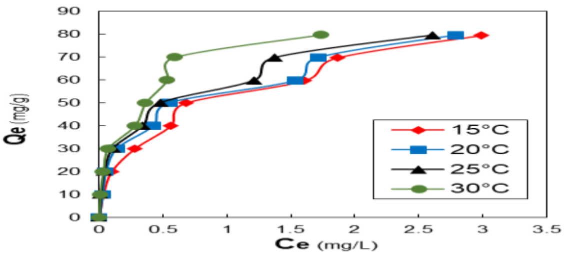

Fig 4: effect of Temperature for the dye adsorption.

The values of the thermodynamic functions were obtained for the Cv dye adsorption process,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[21].

Table (1): The Values of the Thermodynamic Functions				
Dyes	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (kJ/K.mol)	Euilibrium Constant (K)
CV	-18.677	-7.903	-36.155	6.071

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 CaCl2 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 of 120 minutes (contact time). As a result of competition between the positive ions of the salt and the dye molecules on the active sites of the adsorbing surface, where the salts increase the dye's solubility, the results demonstrated that as salt concentration increases, the adsorption of CV dye on the surface of the composite decreases. [22]

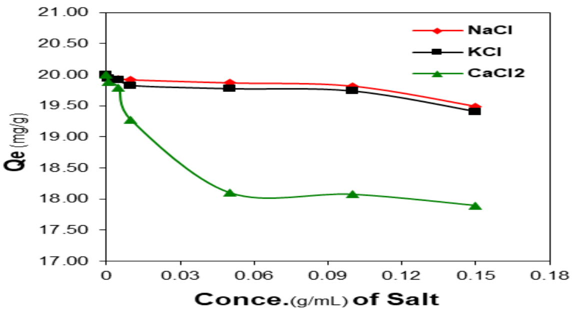

Fig 5: effect of of salts for the dye adsorption.

The adsorption isotherms

The adsorption isotherm on CV dye on the surface of the composite was studied at a temperature of 25℃ degrees and a concentration of 100ppm for the dye. The adsorption isotherms show the relationship between the amount of dye spread on the surface of the compound and Langmuir its concentration at equilibrium. From the table... The figure 3shows the Langmuir isotherm of a large match for the CV dye when compared with the Freundlich equation and Temken. This shows that the value of the correlation coefficient R2 equals 0.9785. The agreement of the Langmuir isotherm with the data of the adsorption process indicates the homogeneous nature of the adsorbing surface, equal energy and the formation of a single molecular monolayer of the adsorbed dye on the prepared surface [23, 24].

Table (2): isotherms of Langmuir- Freundlich and Timken of adsorption of CV adsorbed on the surface of the composite SA-g-poly (AAC-AAM)/BC

Adsorbate			Langmuir equation	Freundlich equation			Temken equation		
	KL	qm	R2	KF	n	R2	KT	B	R2
CV	4.32143	82.6446281	0.9785	74.165	3.244	0.8291	31.373	26.695	0.9434

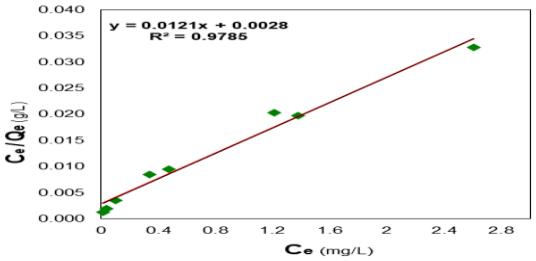

Fig 6: Langmuir isotherm for adsorption of CV dye adsorbed

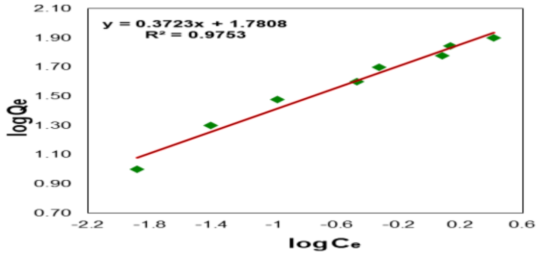

Figure (6): Freundlich isotherm for adsorption of CV dye adsorbed

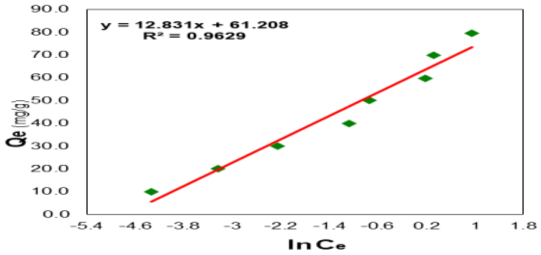

Figure (7): Timken isotherm for adsorption of CV dye adsorbed

Effect of pH on the Adsorption

The effect of pH in the adsorption process of CV dye on the surface of the prepared adsorbent compound was studied SA-g-poly (AAC-AAM)/ BC at specific pH values within the range (2_10) with stabilization of conditions from equilibrium time, temperature, dye concentration and weight of the adsorbent surface. From the results it was found that the adsorption of CV dye on the surface of the adsorbent composite Increases with increasing [26].

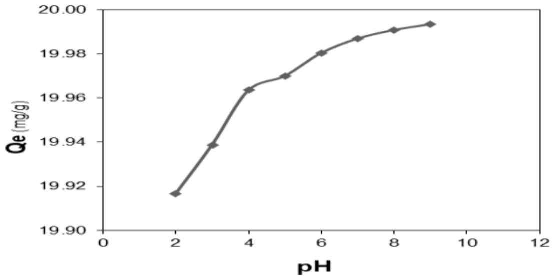

Fig 4: Effect of pH on the Adsorption for the dye adsorption.

4. Conclusions

1-SA-g-poly (AAC-AAM)/ BC had a high adsorption capability.

2- Thermodynamic experiments revealed that CV adsorption on SA-g-poly (AAC-AAM)/BC was exothermic, the system has positive G thermodynamic values, indicating a non-spontaneous process.

3- The adsorption of CV dye onto SA-g-poly (AAC-AAM)/BC was better represented by the Langmuir isotherm model.

4- CV can be removed from aqueous solutions using SA-g-(AAC-AAM) /BC as an adsorbent.

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