

# Synthesis and Characterization of Sodium Alginate-G-Poly (AAC-AAM)/BC Nanocomposite Hydrogel and its Application for Dyes Adsorption

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## Abstract

This study included the preparation of the SA\_g\_p (AAc\_AAM)/BC hydrogel nanocomposite by using the free radical copolymerization of acrylic acid (AAC), acryl amide (AAm), sodium alginate (SA) and bentonite (BC) where N, N\_Methylene diacrylamide (MBA) was used as crosslinking agent and potassium Persulfate (KPS) is a starter in the preparation of free radicals, as it studies the possibility of its use in the adsorption of crystal violet dye. The thermal, structural and surface properties of the prepared surface were diagnosed using several techniques such as FTIR spectroscopy. The adsorption isotherms according to the Giles classification were of class (L4) and that the adsorption isotherms of CV dye applied to the Lankmeier model. The results of the study of the adsorption kinetics of the dye on the surface of the adsorbent composite showed that the CV dye followed the false second order.

## 1. Introduction

Water pollution happens when pollutants are dumped into water bodies without being properly treated, either directly or indirectly. Water pollution is caused by marine dumping, industrial waste, home sewage, nuclear waste, oil pollution, subterranean storage leaks. Many businesses have the difficulty of disposing of huge amounts of wastewater containing potentially harmful organic solutes. These toxins in water are the leading cause of life-threatening diseases such as cancer, lung disease, skin problems, allergies [1]. Dyes are colored substances that can be used to color fabrics, wool, leather, paper, and other fibers. Natural colors like indigo, for example, have been used for over 5000 years. Due to their low cost and bewildering spectrum of new colors, synthetic dyes have overtaken natural dyes. More than 10,000 colors with varied chemical structures are available today. Synthetic dyes are now widely used in a variety of sectors, including textiles (textile industry, leather tanning industry, paper production, food technology, agricultural research, light-harvesting arrays, photoelectrochemical cells, hair colorings etc.) Every year, more than 10,000 tons of hues are estimated to be generated around the world. And the amount of dyes discharged into the environment is predicted to be 1-2 percent during production and 1–10 percent during use. It was recognized that effluents from the textile, paper and pulp, paint, printing, and cosmetic sectors include significant amounts of these dyes, which must be cleaned before being released into water bodies, as mandated by the environmental regulatory legislation [2]. It was discovered that colors with a

high solubility in water spread widely throughout the environment, posing a threat to agriculture, aquatic life, and human health. Because most dyes and their degradation byproducts are extremely toxic to living organisms, the value of using the adsorption method as one of the most productive methods of removing impurities from wastewater arose as a result of the alarming level of synthetic and natural organic substances in natural water [3]. Temperature, the composition of the adsorbate and adsorbent, and the presence of other contaminants, as well as the experimental conditions, are all factors to consider (pH, concentration of pollutants, contact time, particle size, stirring rate and temperature). When the concentrations of pollutant adsorbed and in water reach a constant level, an equilibrium is reached. An adsorption isotherm is a relationship between the amount of pollutant adsorbed and in water at equilibrium. Adsorption is a well-known commercial separation technique for purifying effluent media. Adsorption is now widely regarded as a cost-effective and efficient wastewater treatment technology. Removal of pollutants from contaminated waters using adsorbents has been proven to be a simple (in terms of operation), cost-effective, and efficient technique for the removal of both organic and inorganic contaminants [4, 5]. The removal of dye from aqueous medium is a common use for this separation process. Adsorption is used in the textile, leather, dyeing, cosmetics, plastics, food, and paper sectors, among others, where water recovery is critical. A careful selection of adsorbent is critical for achieving and maintaining efficient recovery of the required water quality. Different types of adsorbents have been utilized to remove

colors from wastewater throughout the last few decades [6].

## 2. Chemicals and Materials

Sodium alginate (SA), Bentonite Clay, Acryl amide (AAM), Acrylic acid (AAC), N, N'-Methylene-bis-acrylamide (MBA), potassium persulfate (KPS), crystal violet (CV). All compounds were of the highest analytical quality and were utilized after purification. All of the solutions were made with deionized water.

### Preparation of the SA-g-P (AAC-AAM)/BC Composite Clay

The SA -g-P (AAC-AAM)/BC Composite nano-hydrogel complex was prepared using aqueous free radical copolymerization, which ensured the dissolution of 0.5g of sodium alginate (SA) minutes in 20 ml of deionized water discontinuously to completely dissolved 5 ml of prepared Acryl amide (AAM) as 2.5g was added in 5ml of distilled water and Add 4ml of acrylic acid (AAc), administer to drops, then 1g of clay bentonite dissolved in 3ml was added gradually for 5 minutes with stirring Continuous for 1h 0,05 g of crosslinking agent MBA and 0.08 g of KPS dissolved in 2 ml of distilled water are added respectively through the separating funnel to the reaction mixture slowly with stirring for 30 minutes at 25°C and in the presence of nitrogen gas, then the temperature is raised to 60°C for 2 h to complete the polymerization process, then cut and immerse the hydrogel The compound SA-g-P (AAC-AAM) / BC Composite in deionized water to remove the unreactive monomers and after completing the washing process it is dried in an electric oven at 50°C to obtain a constant weight.



Fig 1: Photo of (a) preparing and cutting (b) drying (c) grinding of hydrogel Nano composite

### FTIR, XRD, FESEM

Infrared spectroscopy of the SA-g-P(AAC\_AAM)/BC .The infrared spectrum shown in the figure 2 of the superimposed showed a beam at the range (3600-3200) cm<sup>-1</sup> which indicates the interference that occurred between the two O-H beams in the carboxyl and hydroxyl group and the N-H group in the MBA crosslinker, and the appearance of a beam at the frequency of 2985 cm<sup>-1</sup> represents the vibrations The stretchiness of the symmetric and asymmetric CH<sub>2</sub>-groups in the aliphatic compounds that are present in the hydrogel structure[7, 8]where the C=O carbonyl group beam is shifted from 1734

cm<sup>-1</sup> to 1671 cm<sup>-1</sup>, as a result of the hydrogen affinity that occurs between the adsorbent surface and the dye molecules, and this indicates the adsorption of the dye on the surface of the composite [9, 10].

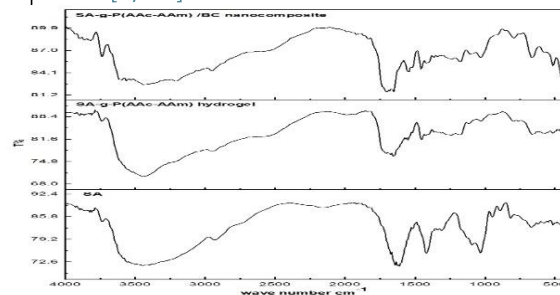


Fig 2: Infrared spectroscopy of the SA-g-P (AAC-AAM)/BC, SA-g-P (AAC-AAM) and SA

### 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 SA-g-P (AAC-AAM)/BC hydrogel in the solid state using a single wavelength 1.5104Å light from Cu- $\alpha$  source within the angular range  $2\theta$  is (0-80) degrees [11]. The XRD spectra of the hydrogel shown in Fig 3 show the presence of a wide band  $2\theta(13-30)$ , which indicates the amorphous nature of the hydrogel, as the (XRD) spectra showed that the hydrogel contains a wide band at  $2\theta=(21.5)$  At the calculated interlayer distance  $d=4.12591\text{\AA}$ . the SA-g-P (AAC-AAM)/BC hydrogel complex, XRD shows crystalline peaks .and the appearance of these peaks is evidence of the crystalline nature of the Composite nanohydrogel complex and bentonite [12,13]. And the XRD measurements of the composite materials are very different from the original materials from which they are formed due to the strong interaction between the materials that make up the composite.

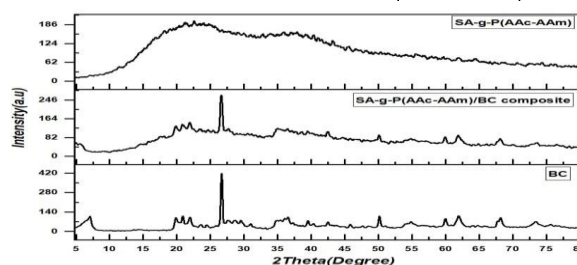


Fig 3 : (a) XRD spectrum of the hydrogel and) b) the nanocomposite hydrogel c) bentonite

The Debye-Scherrer equation was used to calculate the crystalline size of the prepared materials, as follows [14,15].  $D = \frac{K\lambda}{\beta \cos\theta}$

### Field Emission-Scanning Electron Microscopy (FE-SEM)

It is a common technique for identifying the porous or smooth SA-g-P (AAC-AAM) hydrogel and the SA-g-P AAC-AAM/ BC) nanocomposite hydrogel before and after CV dye adsorption, as well as in order to know the amount of homogeneity between the surface components and the size and shape of the particles. And the nature of its distribution on the

surface and how the interconnection between the polymer chains [17].The hydrogel has a very flat smooth surface in the form of more than one layer closely connected to each other and stacked as a thick layer that is not homogeneous in size and shape with edges containing unorganized corners and is attributed to the strength of Van Dervals that binds these layers among themselves .The surface of the SA-g-P (AAC-AAM)/BC hydrogel complex is rough and porous and is a nanocomposite with a sponge-like structure and a network of compact layers, containing many irregularly clustered wrinkles [18] Addition of BC to the SA-g-P (AAC-AAM) hydrogel improves the surface roughness, which is very beneficial for CV dye adsorption, as the inner pores of the SA-g-P(AAC-AAM)/BC nanocomposite can be seen after dye adsorption .

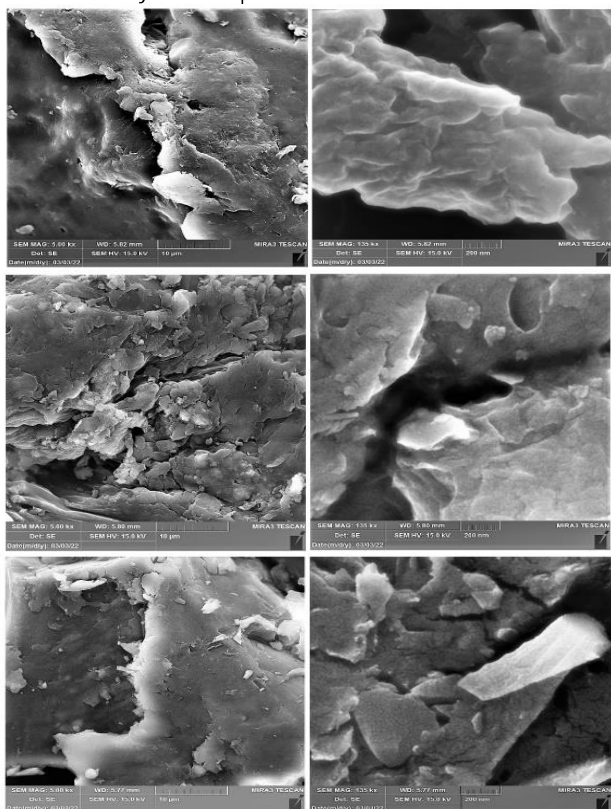


Fig 4 (a) FE-SEM image of [SA-g-P (AAC-AAM) Hydrogel (b) SA-g-P (AAC-AAM)/BC hydrogel composite (c) SA-g-P (AAC-AAM)/BC hydrogel Nano composite after adsorption of CV

### Equilibrium time

The appropriate equilibrium time was studied to remove a certain concentration of CV adsorbent dyes by the surface of the nano-hydrogel composite at a temperature of 25°C and pH = 7 and a constant weight of the hydrogel complex was 0.05 g at a concentration of 100 ppm for CV dye for different periods of time (1-180 min) and the results showed The time required to reach the equilibrium state for CV dye is 120 min, where the amount of adsorbed dyes increases remarkably and rapidly during the first minutes of the adsorption process, after which the increase is gradually until reaching the time required for equilibrium. At the beginning of the adsorption process, which is unoccupied and sufficient for the

adsorption of dyes, then the adsorption process becomes slow and more difficult due to the occupancy of all surface-active centers with dye molecules [19].

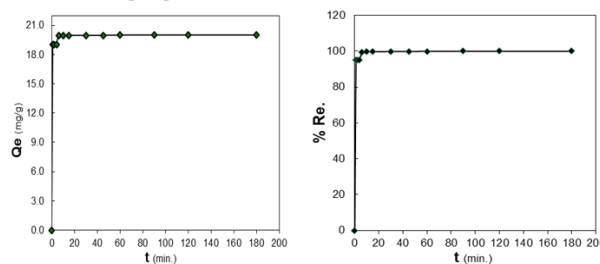


Fig 5: Effect of contact time of CV Adsorption at 25°C

### Effect of adsorbent weight on adsorption

A study was conducted on the adsorption of CV dye on the surface of the prepared compound by changing its weight. Different weight (0.001-0.15) g were used for the above compound, which are SA-g-P (AAC-AAM)/ BC with a fixed solution volume (10 ml) and a constant initial concentration of 100 mg/L. The experiments were conducted at a temperature of 25°C and it was shown from the results the study: Whenever the weight of the adsorbent surface increases, an increase in the amount of adsorption occurs. This is due to the fact that the adsorption process initially requires a balance between the adsorbent material and the adsorbent material, as all active size sites of the adsorbent material are occupied, which makes the adsorption process stable on the surface and the amount of adsorption reaches the highest value It represents the amount of adsorbent material in the saturation stage, However, the increase in the weight of the adsorbing surface after that may lead to an unstable spread of the large adsorbent surface compared to the amount of the adsorbent, and therefore the dissolution energy of the adsorbent will overcome the adsorption energy, on the surface, leading to a decrease in the amount of the adsorbent material on the surface [20]. As shown in the Fig7

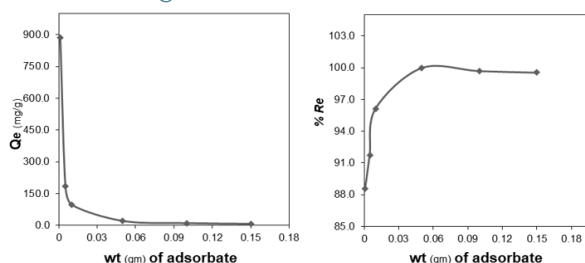


Figure 6: shows the effect of different weights on the adsorption process.

### Determination of the preferred weight of bentonite in the prepared compound of the adsorption system

A study was conducted on the effect of the prepared bentonite on the adsorption process and used in the preparation of the compound SA-g-P(AAc-AAM)/BC, as a group of different weights of bentonite (0.25\_ 1.75) g were used, then 10 ml of CV dye solution was added at a concentration of 100 ppm to a constant weight of 0.05 g of the compound and at a temperature of 25 °C and the results appeared in the

form of a gradual increase in the amount of adsorption by increasing the bentonite until it reaches a stage after which the amount of adsorption decreases and the reason for this is due to the excessive increase in the bentonite particles, which works to form These agglomerates weaken the interaction between the used bentonite and the hydrogel network.

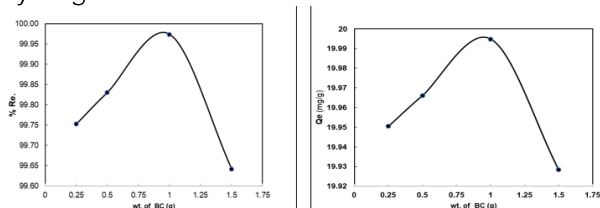


Figure 7: shows the determination of the preferred weight of bentonite in the prepared compound of the adsorption system

### Kinetic of adsorption

The study of adsorption kinetics is important in determining the time period during which the adsorption process occurs, as well as the extent of its impact on the efficiency of adsorption, as fixed concentrations of CV dye were used at a concentration of 100 ppm and a temperature of 25 °C where the adsorption rate decreases or rises with time.[21] In order to verify the effect of the surface of the adsorbent complex SA-g-P(AAC-AAM)/BC on the rate of adsorption, kinetic models were used to describe the experimental data. CV stain on the surface of the adsorbent composite was analyzed typical false first order and false second order [22]. The results showed that the value of the Correlation coefficient (R2) is relatively high for the pseudo-second-order model compared to the pseudo-first-order model, and we conclude from this that the adsorption process of CV dye on the surface of the adsorbent complex follows the pseudo-second-order model.[23].

Table (1) Kinetic adsorption coefficients of CV on SA-g-P(AAC-AAM)/BC at 25 C°				
Pseudo- first order CV on SA-g-P(AAC-AAM)/BC				
Slope	intercept	k1	qe	R <sup>2</sup>
-0.0216	0.2169	0.0216	1.24222	0.2778

Pseudo second order CV on SA-g-P(AAC-AAM)/BC				
Slope	intercept	k1	qe	R2
0.0499	0.025	20.04008	0.09881	0.999

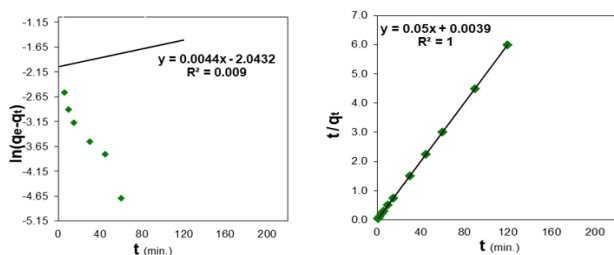


Fig8 a) A pseudo-first-order kinetic model for CV dye adsorption

b) Pseudo-second-order model for CV dye adsorption

### 3. Conclusion

In this study, we describe how to make SA-g-P (AAC-AAM) hydrogel and SA-g-P (AAC-AAM)/BC nanocomposite using a free radical grafting copolymerization. In contrast to many previously described adsorbents used for CV, the SA-g-P (AAC-AAM)/BC nanocomposite efficiently removes CV from a solution aqueous. The SA-g-P (AAC-AAM)/BC hydrogel nanocomposite has a greater adsorption capability. The insertion of BC nanocomposite into the hydrogel matrix of AAc and AAM grafting onto SA created a high pore depth and a distinct shape as a result, a hydrogel nanocomposite with high adsorption was developed. This means that the nanocomposite adsorbent SA-g-P (AAC-AAM)/BC can be employed for the selective removal of CV.

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