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Original Article

Modification, Preparation, and Characterization, Low-Cost Hydrogel Nano/Micro Composite: Regeneration and Isotherm Models

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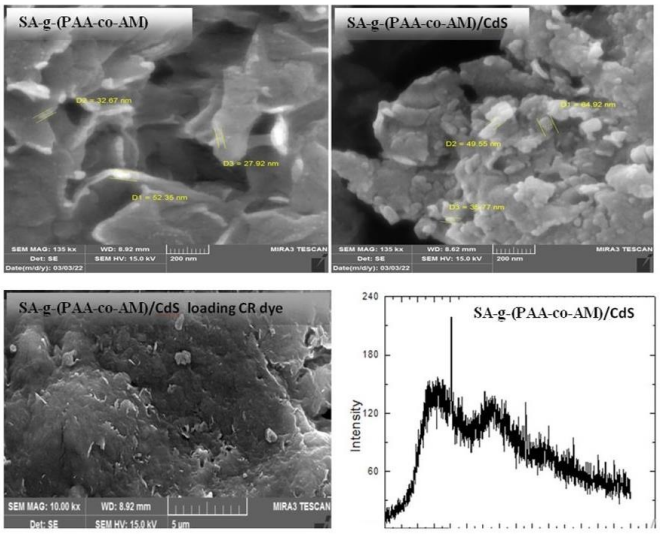
ABSTRACT

In this paper, a new method was used to prepare the SA-g-(PAA-co-AM)/CdS, which is an environmentally friendly, inexpensive, available, and highly efficient absorbent material in the removal of Congo red dye from an aqueous solution. It was based on developing sodium alginate (SA) modified with Cds nano/mico composite and evaluating chemical properties. CdS nano/micro composite was combined with SA, and their chemical properties were evaluated by FTIR spectroscopy and X-ray diffraction, FESEM. The Freundlich and Langmuir models of adsorption isotherms were studied, and through the results, it was found that it is applied to the Freundlich model depending on the value of (R^2=0.9895), compared with the Longmire model where the value of (R^2=0.9415), because physical adsorption depends on heterogeneous surfaces. This work developed a simple, eco-friendly, and practical preparation of a low-cost composite CdS/alginate hydrogel which can be used for the pollutants removal.

GRAPHICAL ABSTRACT



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Introduction

Adsorption is one of the utmost significant methods ever developed by researchers. Thus, adsorption is an extensively utilized technique to get rid of detrimental pollutants from the setting. Researchers clarify new ways and develop novel superabsorbents based on their better selectivity for a limited chemical species on a daily routine, among the pollutants removed by adsorption dyes industrial, drugs heavy metals. Therefore, confirmed, the dyes are very greatly poisonous and have a negative effect on animal and human health when discharged into aquatic solution preventing sunlight from penetrating, depleting dissolved oxygen, and damaging animals and humans [1–3]. Therefore, adsorption technology was adopted to remove textile dyes on the use of highly effective surfaces that are available and inexpensive, including agricultural waste, and converting them into activated carbon, including coconut peels, pomegranate peels, watermelon peels, orange peels, palm fronds, castor paper, date stone, pulp corn, and others. In addition, hydrogels are used as environmentally friendly absorbent materials. They have the ability to swell and retain contaminants inside, and their preparation depends on sodium alginate [4–7]. Sodium alginate (SA) is a naturally occurring polysaccharide that can be obtained from marine algae. It has the ability to biocompatibility and good biodegradability, and the low cost possesses a large number of free hydroxyl groups to make it widely used for chemical modification in most polymers, and as a super absorbent, it has many wide applications, such as wound healing, drug release, agricultural water retention [8–11]. In particular, the application and preparation of sodium alginate-based hydrogels to remove textile dyes have been extensively studied. This research was based on the preparation of hydrogels from sodium alginate by developing an alginate hydrogel (Ag) modified with nano-/micro of CdS.

Material and Methods

Dye adsorption properties of polymers SA-g-(PAA-co-AM)/CdS

The Congo red CR adsorption behaviors of superabsorbent polymers SA-g-(PAAC-co-AM)/CdS at several pHs 2-10 (adjusted by solutions 0.1N NaOH or 0.1N HCl) were estimated to evaluate their CR adsorption performance. Briefly, 0.03 g polymer 100 mg/L CR dye was put in a 100 mL solution and allowed to absorb CR for two hours at 25 °C. After the contact time, the adsorbent was separated from aqueous solutions via centrifugation at 6000 rpm for 15 minutes. The residual concentration of CR in each aliquot was estimated by using a UV-visible spectrophotometer. The removal percentage% and adsorption capacity of CR dye calculate by Equations 1 and 2:

$$E\% = \frac{Co - Ce}{Co} \times 100 \quad (1)$$

$$Qe = \frac{(Co - Ce)Vml}{M\ gm} \quad (2)$$

Preparation polymer SA-g-(PAA-co-AM)/CdS Nano-/Micro composite

Preparation of polymer SA-g-(PAA-co-AM)/CdS that have to dissolve 0.1 g of CdS in 2 mL DW and 0.5 g sodium alginate was dissolved in 20 mL and stirred for one hour at temperature 25°C. Next, the CdS solution was added to sodium alginate and 3 ml of acrylic acid was added to them. After that, 0.5 gm of acryl amide was added to 2 ml DW and it was stirred for 10 minutes at temperature 25°C, added KPS by 0.03 g in 1mL DW and MBA 0.05 g in 1 mL DW to solution alginate, processes took place in the N2 presence to form free radicals, and then it was put in water bath for 3 hours at a temperature of 70°C. The SA-g-(PAA-co-AM)/CdS composite was cut and washed several times to remove any uncreative materials. Next, it was dried in an oven at a temperature of 60 °C for a time of 24 hours, and then it was well ground. SA-g-(PAA-co-AM)/CdS composite (see Figure 1).

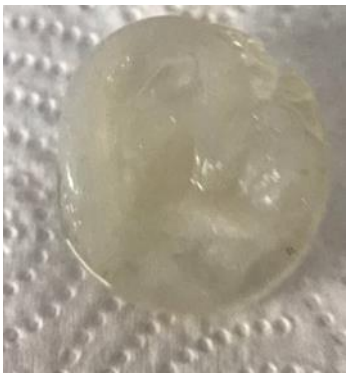

Figure 1: Image polymer SA-g-(PAA-co-AM)/CdS Nano-/Micro composite

Results and Discussion

Characterization of adsorbent polymers SA-g-(PAA-co-AM)/CdS

IR spectra wear were utilized to characterize the (SA-g-(PAA-co-AM)/CdS before and after the surface adsorption method on the CR dye, as displayed in Figure 2. Therefore, it was clear and significantly more than a few in the intensity of adsorption among SA-g-(PAA-co-AM)/CdS. The hydrogels before the adsorption method with the CR dye illustrate a clear decrease in the IR spectra in the intensity of the bands adjacent to the adsorption [12]. The surface contains the acidic group that leads to a difference in the intensity of absorption.

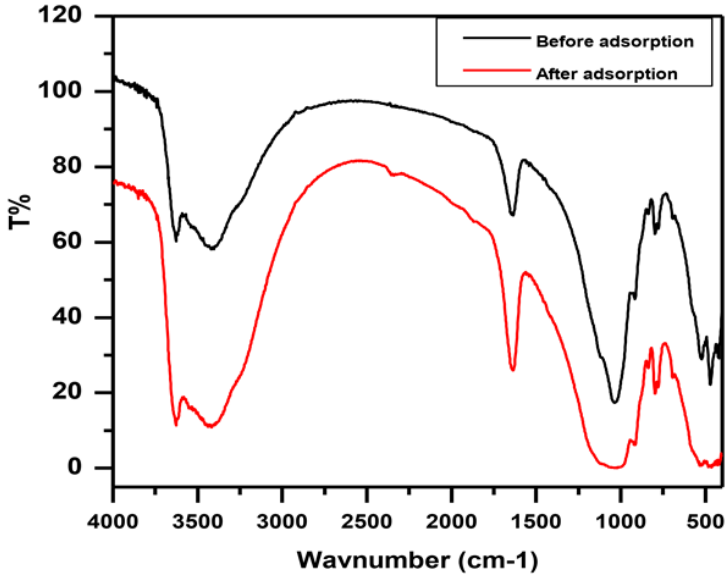

Figure 2: FTIR spectra of SA-g-(PAA-co-AM)/CdS surface before and after adsorption of CR dye

The Thermal Gravimetric Analysis reports of the as-obtained Architecture-like SA-g-(PAA-co-AM)/CdS composite, as depicted in Figure 3, provide an additional proof that CdS integrates into hydrogel [13,14]. A weight loss was found in the temperature range of 25–600°C, of which 4.914% occurred at temperatures lower than 200°C attributable to free water evaporation, and 29.6% occurred in the temperature range of 200-300 °C due to desorption of bound water and evaporation. The final one, at approximately 360-575 °C, is related to the reduction of CdS compounds, and the materials contain approximately 24.86 wt% of hydrogel [15–17].

The FESEM technique was used to study the properties of the prepared surface before and after the addition of (CdS), and also after the adsorption process, as indicated in Figure 3. It is observed that the surface (SA-g-(PAA-co-AM)) is smooth and cloud-like, while with the CdS introduction on the hydrogel, the surface shape becomes rougher, containing many aggregates, which is desirable to remove the CD dye. The Cds were sufficient to create well-developed pores

with uniform distribution leading to a large surface area and a high porous structure.

The crystalline of SA-g-(PAA-co-AM)/CdS composite was analyzed by (XRD). In the SA-g-(PAA-co-AM)/CdS, composite XRD pattern refers to the high crystalline of the SA-g-(PAA-co-AM)/CdS composite with one broad related peak at 2θ° =33.32 indicates the CdS dispersion into the polymeric network.

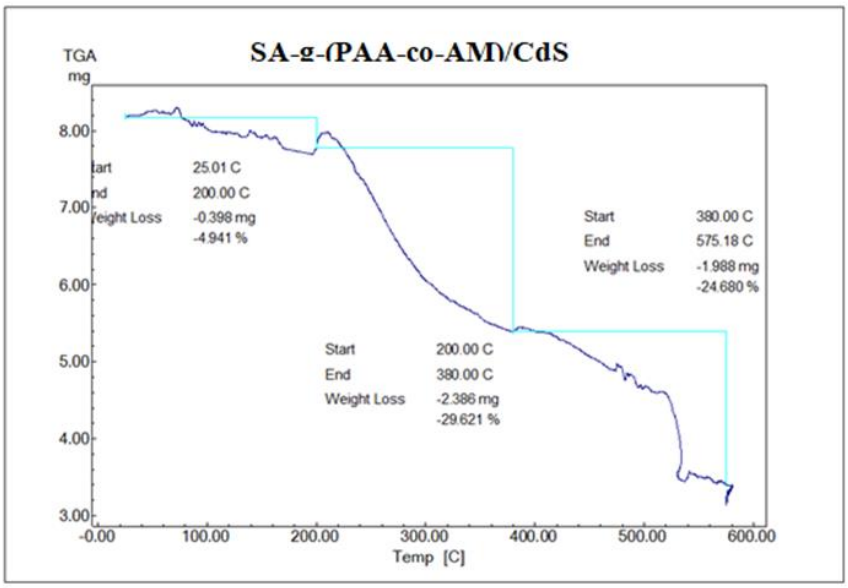

Figure 3: TGA curve of the SA-g-(PAA-co-AM)/CdS

Effect of different parameter

Effect of weight polymer SA-g-(PAA-co-AM)/CdS

The Removal percentage is greatly influenced by the weight of polymers SA-g-(PAA-co-AM)/CdS in the removal of Congo red dye from an aqueous solution. The quantity of CR dye adsorbed by polymers SA-g-(PAA-co-AM)/CdS was studied as a function of adsorbent dose (0.01-0.08 g) at a concentration of dye 100 mg/L. As illustrated in Figure 4, the dye uptake raised from 70.11 % to 94.21%, with the increase in the weight of polymers SA-g-(PAA-co-AM)/CdS from 0.015 to 0.08 g/100 mL. A rapid phase of weight-dependent rise in the removal of dye occurred up to 0.03 g/100 mL weight of polymers SA-g-(PAA-co-AM)/CdS, and this was followed by a sluggish phase removal of dye from 0.015 to 0.08 g/100 mL of the weight of adsorbent [18–20]. The better removal of dye, at an adsorbent amount of 0.03g/100 mL, was found to be 280, and 23 mg. g^{-1}.

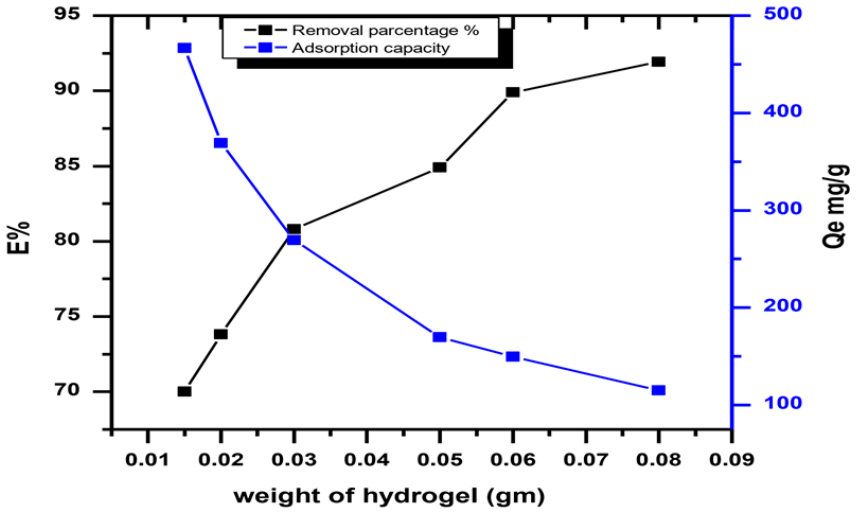

Figure 4: Effects of the weight SA-g-(PAA-co-AM)/CdS on the amount of adsorbed Congo red (Initial dye concentration = 100 mg. L^{-1}, equilibrium time 1hr and Temp = 25 °C)

Effect of pH

The pH mainly affects the dye solution as well as the surface of the absorbent material, where the effect of the pH range (2-10) was studied by using the polymers SA-g-(PAA-co-AM)/CdS on the absorption of the Congo red, under the experimental conditions of the dye concentration 100 mg/L, temperature 25°C and weight of the polymers SA-g-(PAA-co-AM)/CdS 0.03g [21]. As depicted in Figure 5, the adsorption efficiency increased from 210.23 to 310.65 mg.g^{1,} increasing pH from 2-to 10. The results showed the lowest adsorption efficiency in the acidic medium at pH 2 due to the lack of attractive force between the protons of the dye and the prepared surface. Furthermore, the high adsorption efficiency in the basic medium depends on the increased attraction between the dye protons and the hydroxyl group on the surface of the upper absorbent material [22,23].

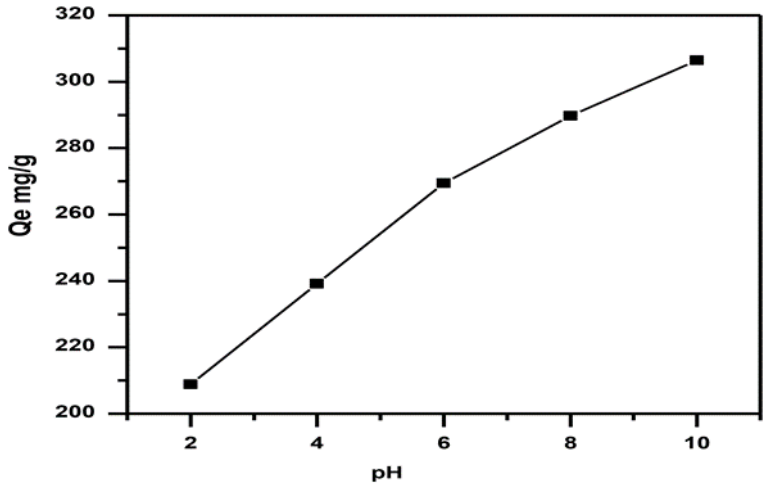

Figure 5: Effect of pH solution on the adsorption efficiency on to SA-g-(PAA-co-AM)/CdS (Exp. Condition: equilibrium time 1 hour, Temperature= 20°C, the quantity of hydrogel 0.05 g)

Re-generation of the polymers SA-g-(PAA-co-AM)/CdS

Re-activation of the sorbent may make processing more economical. Different experiments were conducted to remove the color from polymers SA-g-(PAA-co-AM)/CdS loaded with Congo red after the adsorption method utilizing different solutions (H_3PO_4, H_2SO_4, and HCl at concentration 0.1N), where the top solution to remove the CR loaded on polymers SA-g-(PAA-co-AM)/CdS was H_3PO_4, in which the effect of different acid concentrations (0.01-0.1N) was studied. It was noticed that the most excellent percentage removal was at the concentration (0.1 N), as presented in Table 1.

Table 1: Comparison of Re-activation of different kind type solution for the CR dye onto SA-g-(PAA-co-AM)/CdS

Reactivation (0.01N)	E%	Reactivation (0.05 N)	E%	Reactivation (0.1 N)	E%
H3PO4	72.32	H3PO4	77.77	H3PO4	80.41
H2SO4	66.67	H2SO4	70.51	H2SO4	79.99
HCl	60.76	HCl	67.76	HCl	77.53

Adsorption isotherms

The analysis of the adsorption model isotherm results by fitting them to two models is a significant step to find the suitable isotherm that can be utilized for design purposes. In this work, two sorption models, namely the isotherm Langmuir and Freundlich, in their nonlinear forms, were applied to the equilibrium data of CR dye sorption by polymers SA-g-(PAA-co-AM)/CdS [24,25].

The Langmuir model assumes uniform energies of sorption onto the surface and no sorbate transmigration in the surface plane [26, 27]. The equation non-linear of isotherm Langmuir model in Equation (3):

$$Q_e = \frac{Q_m K_L C_e}{1+K_L C_e} \quad (3)$$

Isotherm Freundlich model is an empirical equation based on adsorption on heterogeneous surface. The equation is usually calculated as follow:

$$Q_e = k_f C_e^{\frac{1}{n}} \quad (4)$$

In this work, two isotherms, namely isotherm Langmuir and isotherm Freundlich, were fitted to the experimental equilibrium result for CR dye at temperatures 25°C by nonlinear forms, and the obtained data are plotted in Figure 6. The isotherm factor values were indicated in Table 2.

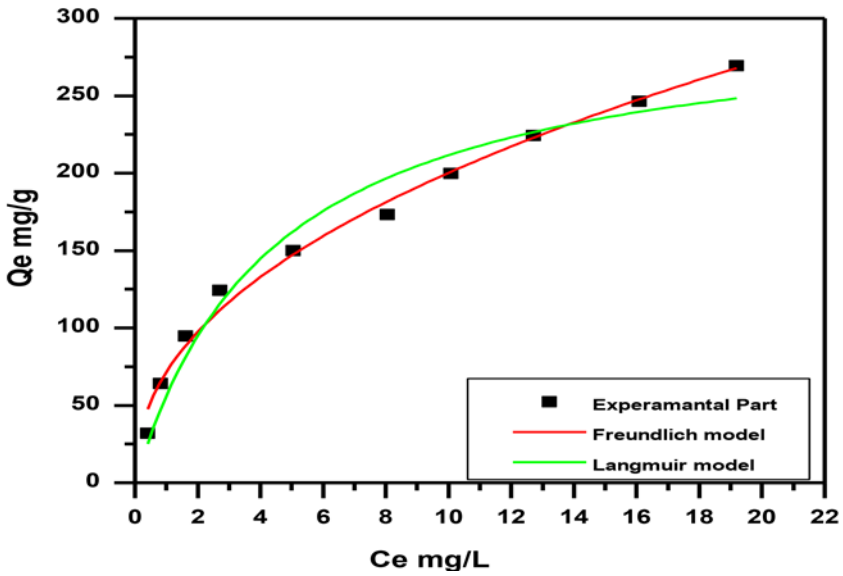

Figure 6: Several adsorption models nonlinear fit of adsorption Congo red on SA-g-(PAA-co-AM)/CdS, concentration = 100 mg/ L, Temperature = 25°C, and mass of polymer 0.03 g/L)

Table 2: Isotherms Freundlich and Langmuir model parameter Congo red adsorbed onto SA-g-(PAA-co-AM)/CdS

Isotherm models	Parameters	SA-g-(PAA-co-AM)/CdS
Freundlich	KF	71.445 ± 3.619
	1/n	0.447 ± 0.0205
	R2	0.9895
Langmuir	qm (mg/g)	306.005± 21.376
	KL(L/mg)	0.2241 ± 0.045
	R2	0.9415

Conclusion

In this paper, the adsorption of Congo red onto SA-g-(PAA-co-AM)/CdS as a surface reactive was highly efficient in the removal of the color CR dye from an aqueous solution. The highest E% of CR (80.16%) at a contact time of 1 hour and the concentration of dye (100 mg/L), the weight of SA-g-(PAA-co-AM)/CdS (0.03gm). Furthermore, solution pH plays a key role in the removal of the color of CR dye, as the greatest pH was in the alkaline medium. The process of re-activation of the SA-g-(PAA-co-AM)/CdS was applied and utilized again, as the H_3PO_4 gave the most excellent removal capacity when washing only once. The adsorption model was studied, which matched the model Freundlich, depending on the R^2 value.

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Authors' contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

Conflict of Interest

There are no conflicts of interest in this study.

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