RESEARCH ARTICLE

Eco-friendly Synthesis of Hydrogel Nano-composites for Removal of Pollutants as a Model Rose Bengal Dye

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ABSTRACT

In this study, hydrogel Nano-composite was prepared by free radical polymerization in the presence of sodium alginate (SA) and TiO_2 nanoparticles (TiO_2 NPS) as a surface catalyst. Potassium per sulfate (KPS) was used as a reaction initiator. Crosslinking agent methylene bis-acrylamide, the structure and morphology its hydrogel Nano-composites were studied using Transmission electron microscopy (TEM), X-ray diffraction (XRD), Energy dispersive X-ray spectroscopy (EDX), and Field emission scanning electron microscopy (FE-SEM). Several factors that affected the adsorption process were studied, including effect of pH, effect of salt concentration and temperature. Also studied was the swelling behavior in two acidic mediums (pH=7, pH=1.2), the best surface swelling medium was at (pH=7). The adsorption isotherms were studied, and the result obeyed as favorable by Fruendlich isotherm depended on the value of (R^2= 0.9404).

Keywords: Removal, Adsorption, Dye, Hydrogel, Rose bengal dye, Sodium alginate, Titanium dioxide.

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INTRODUCTION

Water pollution is one of the most serious concerns living organisms have ever faced, if not the most challenging. Water quality is particularly important to human health. Based on the World Health Organization study, poor water quality is responsible for 2.2 million deaths occurring annually.[1-3] Moreover, more than two-thirds of infant deaths are caused by water-borne diseases. Hydrogel is a cross-linked polymeric network that swells with water, formed by the interaction of one or several monomers that are not soluble in water due to the presence of cross-linking between their polymeric chains. It is one of the types of hydrophilic polymers and possesses a 3D network structure able to absorb and retain large amounts of liquids such as water and biological fluids inside its pores.[4,5] Hydrogel is a polymeric material that can swell in water, which may be natural or synthetic. Because of its high water content and flexibility, it is similar to the natural biological tissue where the hydrogel retains large amounts of water within its structure without dissolution.[6,7] Hydrogels can swell and replenish water, and they are a soft material that can change its size and shape, and thus its composition can change its properties and respond to external environmental conditions such as temperature, pH, ionic strength, light, and change in concentration of chemicals. Specifically, as they are often called smart hydrogels.[8-10]

MATERIAL AND METHODS

Materials

Titanium dioxide (TiO_2), maleic acid (MAc), methylene bis-acrylamide(MBA), acrylic acid (AAc), sodium alginate (SA), NaOH, HCl, potassium persulfate (KPS), rose bengal (RB). All compounds were of the highest analytical quality and were utilized after purification.

Synthesis of TiO_2 Loading SA-g-p(AAc-MAc) Hydrogel Nanocomposite

Titanium dioxide loading SA-g-p(AAc-MAc) nanocomposite hydrogel is prepared using free radical copolymerization in the aqueous solution, which included dissolving the 0.1-g of TiO_2 NPs in 20 mL of DW with continuous stirring for 3 hours, after which it was transferred to the ultra-sonication for 4 hours. The reaction mixture transfer to a three-necked round bottom flask container condenser, funnel separated and nitrogen gas. Then, 0.5 gram, of SA was slowly added with stirring to the reaction mixture then added 4 mL AAc, and

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0.5 g MAc was slowly with stirring for 10 minutes after that added 0.05 g of MBA and drop by drop with stirring add the KPS (was prepared by dissolved 0.03 g in 2 mL deionized water) into the reaction mixture with 30 minutes of churning at room temperature. The temperature was raised to 70˚C for 2 hours to complete the polymerization reaction. To remove the unreacted from TiO_2 loading SA-g-p(AAc-MAc) hydrogel nanocomposite, it was immersed in deionized water. Finally, to produce a constant weight. In a hot oven, the product was dried at 50°C.

Preparation of Rose Bengel Solution

A stock solution of RB dye (100 mg/L) was prepared *via* dissolving (0.1-g) in 100 mL DW, the calibration curve can be prepared depending on the concentration RB dye range (2–16) mg/L, thus the data found conform law Lambert-Beer's.

Adsorption Studies

Adsorption of rose bengal **(**RB) dye on TiO_2 loading SA-g-P(AAc- MAc) hydrogel nano-composite was study in a batch mode system. Adsorption studies were conducted at 250 rpm by mechanical agitation for 1-hour at 20ºC. Several quantity in 100 mL about (0.02–0.12 g) solution initially include 60 mg.L^{-1} of dye RB were used in the experiment. The influence of solution pH on the efficiency of adsorption the beads is examined in pH (2–10) at 25ºC, the pH was varied without altering the concentration of RB dye significantly *via* utilizing small quantity of HCl and NaOH 0.1 N. Averages of triplicate experiments were reported for each adsorption studies, determined utilizing UV-visible spectrophotometer and the quantity of adsorbed RB and removal E% were calculate in equation 1,and 2:

$$\text{Removal Percentage E\%} = \frac{Co - Ce}{Co} \times 100 \ldots.(1)$$

$$\text{Adsorption capacity Qe} = \frac{(Co - Ce)Vsol}{W\,gm} \ldots.(2)$$

Factors Effect on the Adsorption Process

Influence of pH on Adsorption

The result of the solution pH it was investigated how pH affected the adsorption. A weight (0.05 g) of the hydrogel was taken to add to it a solution of RB dye (200 mg/L) at different pH (2–12) and with the stability of all other conditions (concentration, temperature and time), where solution pH was organized using a solution of HCl and NaOH, and the pH was measured using the pH meter.

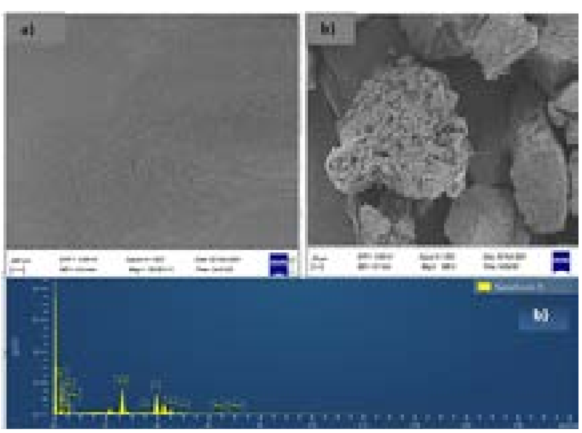

Figure 1: FESEM a) TiO2 loading SA-g-P(AAc- MAc) Nano-composite, b) after adsorption TiO2 loading SA-g-P(AAc- MAc) Nano-composite, c) EDX of TiO2 loading SA-g-P(AAc- MAc) Nano-composite.

Influence of Ionic Strength

By using various weights (0.001–0.051 g), the effect of ionic strength was examined of sodium chloride salt (NaCl), potassium chloride salt (KCl), calcium carbonate salt ($CaCO_3$), onto RB dye. with a concentration of (200 mg/L) into (0.05 g) of hydrogel in volumetric flasks at a temperature 25ºC, for a period of (120 minutes) for RB dye and at a speed of (150 rpm) until the state of equilibrium is reached and each is stable other conditions (temperature, time, and pH), and through the use of the UV-vis device, the absorbance of each solution was measured for all concentrations of the salts.

RESULTS AND DISCUSSION

Field emission scanning electron microscopy (FESEM) and Energy dispersive X-Ray (EDX)

The addition of TiO_2 into SA-g-P(AAc- MAc) nano-composite improves the surface roughness, which is very beneficial for the adsorption of RB dye, as the inner pores of the TiO_2 loading SA-g-P(AAc-MAc) nanocomposite can be seen in the morphology. As a result, TiO_2 NPS was sufficient to produce well-developed pores, resulting in a porous system with a high surface area, as shown in Figure 1 a. After RB dye adsorption on the surface of TiO_2 loading SA-g-P (AAc- MAc), revealed that the surface is smoother and more uniform as a result of filling the pores on the surface of the hydrogel. Which confirms the adsorption process as shown in Figure 1 b. The success of the adsorption process is verified by know the ratios of both oxygen and carbon of the TiO_2 loading SA-g-P(AAc- MAc) hydrogel nanocomposite before and after adsorption[11] as shown in Figure 1 (c).

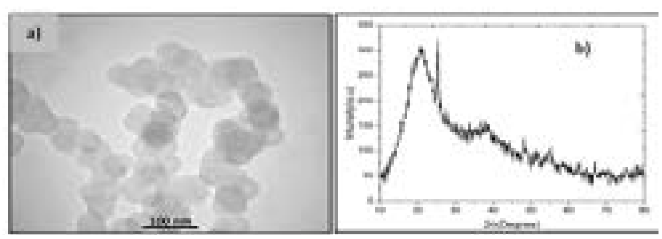

Figure 2: TEM (a) TiO_2 NPs, (b) TiO_2 loading SA-g-P(AAc- MAc) Nano-composite.

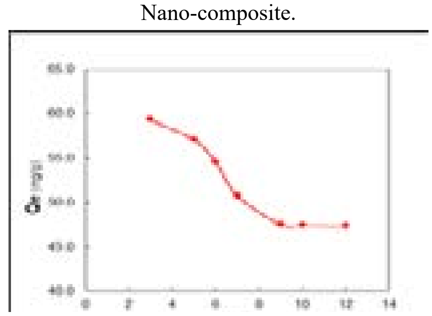

Figure 3: Effect of pH solution on the removal RB dye on to TiO_2 loading SA-g-P(AAc- MAc) nano-composite.

Table 1: Correlation coefficient and constant of langmiuir, freundlech, and timken of adsorption RB dye adsorbed on hydrogel

Langmuir model			*Freundlich model*			*Timken model*		
K_L	q_m	R^2	K_F	n	R^2	K_T	B	R^2
0.002	1000	0.059	4.965	1.312	0.945	0.865	75.134	0.798

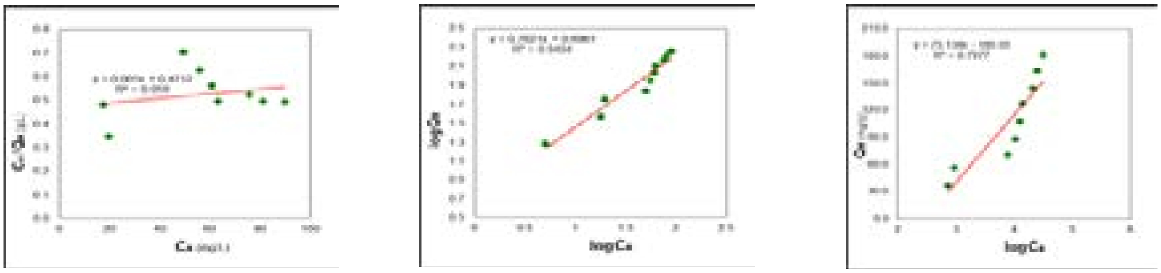

Figure 4: Isotherm Langmiuir (A), Isotherm Freundlech (B), and Isotherm Temken (C) of RB dye adsorption on hydrogrl.

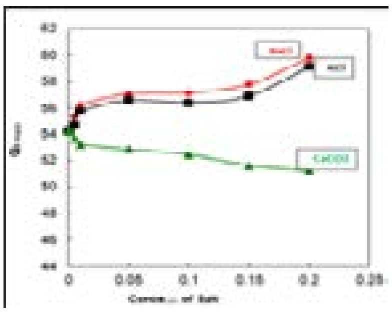

Figure 5: Effect of Salts on the Adsorption RB dye onto TiO_2 loading SA-g-P(AAc- MAc) nano-composite.

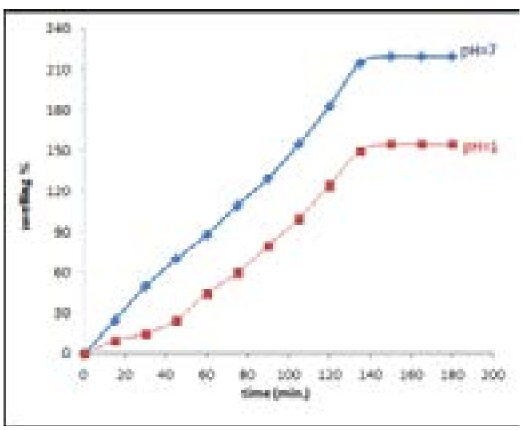

Figure 6: Effect of Swelling ratio on to hydrogel.

Transmission electron microscopy (TEM) and X-ray Diffraction (XRD)

The TEM image shown in Figure 2 (a) shows that the titanium dioxide nano-particles are mostly spherical. The obvious spherical and heterogeneous structures can be seen in the figure, indicating that the titanium dioxide is highly crystalline. The specific area diffraction pattern of the nano-particles indicates that the as-prepared TiO_2 nanoparticles are crystalline in nature.[12]

XRD of the TiO_2 loading SA-g-P(AAc- MAc) hydrogel nanocomposite shows crystalline peaks of 25, 392, 36, 485, 48.186, 53.685 and the appearance of these peaks is evidence of the crystalline nature of the complex as well as indicating the presence of TiO_2 NPs in the anatase phase,[13] as shown in Figure 2 (b).

Effect of pH Solution

One of the utmost important parameter affecting adsorption of solution pH. RB dye on to TiO_2 loading SA-g-P(AAc- MAc) hydrogel nano-composite among pH 2–12 as shown in Figure 3. This is explained by the fact that SA-g-P(AAc- MAc) hydrogel nano-composite loaded with TiO_2 can be removed by a variety of mechanisms in addition to electrostatic attraction. On the other hand, the SA-g-P(AAc- MAc) nano-composite with TiO_2 loading had more active sites on its surface, which may have reduced the competing adsorption of H^+ and RB dye ions and eliminated pH effects at low primary concentrations. Consequently, pH 2 yields the best results.[14]

Adsorption Isotherms

The most well-known isotherm equations for studying the adsorption equilibrium factor are the ones developed by Langmuir, Freundlich, and Temkin. The isotherm Langmuir (Figure 4A) is based on the idea that a set number of active sites are uniformly spread throughout the surface of the adsorbent; these sites have the same attractiveness for adhering a mono-molecular layer and do not have any interactions among adsorbed molecules. Also suitable for heterogeneous surface adsorption is the Freundlich isotherm (Figure 4B). This isotherm assumes a positive correlation between adsorbate concentration and adsorbent amounts on the surface. Similar to this, the energy sorption of the adsorbent correspondingly decreases near the end of the sorption centers. Isotherm Timken (Figure 4C) contains a component that takes adsorbent-adsorbate interactions into account. The model assumes the adsorption heat of all molecules in the layer will fall linearly rather than logarithmically with coverage since it disregards the meager and significant value of concentrations. The Langmuir, Freundlich, and Timken isotherms are used to match the experimental equilibrium finding for the dye-hydrogel system and calculate (R^2). The best correlation between Figures 4 and Table 1 and the Freundlich model is seen ($R^2 = 0.945$),[15,16]

Effect of Salts

The influence of salt intensity on the RB dye adsorption process on the nano-composite of the compound TiO_2 loading SA-g-P(AAc- MAc) nano-composite was studied, and different weights of salts $CaCO_3$, KCl, and NaCl were used in this study, with the optimum conditions of experimental. The adsorption of RB dye, the result shown in Figure 5 showed that the quantity of dye adsorption on the adsorbent increases with the increase in the amount of salts. The adsorption between the surface and the dye molecules increases.[17-19]

Effect of Swelling Ratio

The swelling ratios of the adsorbent compound were studied at an acidity function (7-1), which depends largely on the acidity function. The swelling rates increase with the increase in the acid function, where we notice that at pH = 7, the swelling rates are high compared to pH = 1 and the reason for this is due to the chemical composition of the adsorbent compound containing effective hydrophilic groups such as (COOH, OH, C = O), which in turn, it ionizes at an acidic function pH = 7 As appear in Figure 6.[20,21]

CONCLUSION

The TiO_2 loading SA-g-P(AAc- MAc) Hydrogel Nanocomposite shows a very high adsorption capacity in the rose Bengal dye RB adsorption. The best adsorption capacity at PH=2, the quantity of dye adsorption on the adsorbent increases with the increase in the amount of salts. The swelling rates increase with the increase in the acid function, where we notice that at pH = 7 the swelling rates are high compared to pH = 1. The Langmuir, Freundlich, and Timken isotherms are used to match the experimental equilibrium finding for the dye-hydrogel system. The best correlation with the Freundlich model is seen (R^2 = 0.945).

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