RESEARCH PAPER

High-Efficient Adsorbent Based on Modified Guar Gum/ Acrylic Acid Micro/Nano Surface, Acrylamide for Removal of Methyl Violet Dye from Aqueous Solution

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ABSTRACT

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Keywords: Adsorption Dye Hydrogel Methyl violet Regeneration In this study, a biodegradable absorbent material based on guar gum (GG) was developed by grafting a copolymer mixture of acrylic acid (AA) and polyacrylamide (PAM), GG-g-poly (AC-co-PAM) was prepared using a free radical method with potassium persulfate (KPS) as the initiator and N, N-methylene diacrylamide (MBA) as the crosslinker. The hydrogel exhibited the highest swelling capacity when formulated with GG (1.0 g), PAM (0.5 g), and AC (0.05 g) as monomers, 0.08 g of MBA, and 0.05 g of KPS, at a pH of 7.0 and a reaction temperature of 75°C. The maximum swelling percentage achieved was 2200%. Hydrogel characterization involved several techniques, including transmission electron microscopy (TEM), field-emission scanning electron microscopy (FE-SEM) with energy-dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) analysis, and X-ray diffraction (XRD). The TEM image revealed a wrinkled morphology of the hydrogel, while FESEM analysis showed its porous nature, which is capable of accumulating a large number of water and dye molecules. The synthesized hydrogel exhibited high stability in aqueous solution and zero-point charge at a pH above 4.3. The hydrogel absorbent can be easily regenerated through a dilute acid wash, with minimal loss of absorbent performance even after four cycles of absorption and desorption. Therefore, this study confirms the effectiveness of using hydrogel as an effective absorbent for removing hazardous and toxic dyes.

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INTRODUCTION

Textile dyes are currently a source of concern for water pollution and pose a risk to all aquatic organisms. This is due to their widespread use in various textile industries, including plastics and paper, among others[1-3]. They pose a threat to human life because they block light, thus reducing the photosynthesis process in plants. Given these serious problems, it is essential to address them. Therefore, it is necessary to remove pollutants from wastewater for environmental, health, and economic reasons. Several technologies have been developed to remove contaminants from wastewater, including ozonation and oxidation, coagulation and flocculation, photolysis, and membrane separation. However, most of these

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COPY This work is licensed under the Creative Commons Attribution 4.0 International License. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/. traditional methods have begun to prove insufficient for simple and effective treatment and are expensive[4, 5]. This necessitates the consideration of effective and affordable technologies to remove various types of pollutants from water. Adsorption is one of the most important and effective methods for removing impurities. Inexpensive adsorbents, such as hydrogels, can effectively remove dyes from water [6, 7].

Hydrogels, classified as three-dimensional, hydrophilic polymers, are utilized in a wide range of hydrophilic applications and systems. The presence of hydrophilic groups on the hydrogel surface not only enables hydrogels to absorb large amounts of water but also influences their properties, including permeability, biocompatibility, and stability[8-10]. Due to their highly porous nature and smooth texture, hydrogels are highly suitable for loading water-soluble materials. Guar gum (GG) is a naturally occurring polysaccharide with high porosity and an active ingredient that promotes swelling. The use of guar gum has recently seen widespread interest, particularly in textile, paper, and medical applications for wound healing and pharmaceutical applications. It is also a natural sugar that retains its biodegradability due to its gummy nature while exhibiting enhanced properties suitable for various applications, most notably wastewater treatment[11-14].

In this study, a facile and inexpensive hydrogel based on guar gum (GG) was prepared using a graft co-polymerization method, incorporating a mixture of acrylic acid (AC) and acrylamide (AM) monomers. The adsorption efficiency of the synthesized hydrogel for removing the cationic methyl violet (MV) dye from aqueous solutions was investigated. Additionally, the effects of equilibrium time, hydrogel weight, MV dye concentration, pH, and zero-point charge (ZPC) on the dye removal efficiency were investigated. The regeneration process in relation to adsorption was also studied.

MATERIALS AND METHODS

Preparation of GG-g-poly(AC-co-PAM) Hydrogel

GG-g-poly (AC-co-PAM) hydrogel was prepared through a free radical grafting copolymerization process of acrylic acid (AC) and acrylamide (AM) using guar gum (GG) as a natural polymer. The preparation process involved dissolving 1.0 g of GG in 50 mL of distilled water to form a homogeneous solution, which was stirred continuously with a magnetic stirrer for 3 hours in a 100 mL beaker. A mixture of AM and AC was mixed in this solution (0.5 g). Potassium persulfate (KPS) was added at a concentration of 0.05 g as an initiator, and N, N-methylene-MBA diacrylamide (0.08 g) was used as a cross-linking agent. After 3 hours, the former gel was washed several times in distilled water to remove any unreacted monomers and then washed once with ethanol. Finally, the prepared hydrogel was dried for 2 days in an oven operating at 60°C.

Adsorption study

To prepare a standard solution of the dye with concentrations ranging from 10 to 100 mg/L, the stock solution of MV dye was diluted to the desired levels. For batch mode adsorption tests, 100 mL conical flasks were filled with 0.05 g of adsorbent and 100 mL of the prepared dye solution, maintaining an initial pH of 7. The flasks were shaken at 120 rpm for 1 hour at a temperature of 25±2°C using a mechanical shaker. After agitation, centrifugation was performed to separate the adsorbent from the adsorbate. The dye content in the supernatant was then measured using spectrophotometry at a wavelength of 586 nm.

Experiments were conducted at a constant dye concentration of 100 mg/L, with varying carbon dosages from 0.01 to 0.1 g per 100 mL, to investigate the effect of hydrogel dosage on the percentage of dye elimination. Additionally, the impact of dye concentration on the elimination percentage was investigated, with MV dye concentrations ranging from 10 to 100 mg/L, while maintaining a consistent adsorbent dosage of 0.05 g per 100 mL. The following equations calculate the adsorption efficiency and removal percentage:

 $adsorption\; capacity(Qe\frac{m}{g})\; = \frac{(C_o-C_e)V}{m(g)}$

removal effecincy E % =
$$\frac{C_o - C_e}{C_o} \times 100$$

RESULTS AND DISCUSSION

Fig. 1 presents the FTIR spectra of the hydrogel adsorbent before and after adsorption. The broad peaks observed around 3427 cm⁻¹ are indicative of O-H stretching vibrations from hydroxyl groups. Notably, the spectrum shows a significant presence

of peaks in the 3300–3500 cm⁻¹ range, a finding that aligns with previous studies on hydrogel. Additionally, the broad peak at approximately 3427 cm⁻¹ can be attributed to the stretching vibrations of -OH groups. The presence of these peaks suggests that the synthesized hydrogel is rich in functional groups, confirming the formation of hydrogen bonding between them, as demonstrated by the slight shifts observed in the N-H, O-H, and C-O functional groups[15]. The (FE-SEM) technique, as illustrated in Fig. 2a, is used to examine the properties of the hydrogel before and after the adsorption process. This technique provides valuable insights into the crystalline structure of the particles, their shape, the nature of their aggregation, and their surface area[16]. It also helps in evaluating surface porosity or smoothness, as well as the uniformity of hydrogel distribution on the surface. The FESEM images presented in Fig. 2b indicate that



Fig. 1. FTIR spectra of the hydrogel adsorbent before and after adsorption.



Fig. 2. FES-EM analysis of a) hydrogel before adsorption, b) hydrogel after adsorption.

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the hydrogel surface, after adsorption, appears smooth, clear, and flaky. Additionally, it exhibits a sponge-like porous structure characterized by a network of tightly packed layers and numerous irregularly arranged wrinkles. Notably, after the adsorption process, the sample's surface morphology undergoes significant changes, including a marked increase in surface roughness and porosity. This results in an irregular structure that binds the layers of hydrogel together through van der Waals forces [17].

Transmission Electron Microscopy (TEM) images reveal the morphology of the surface hydrogel. As shown in Fig. 3, the cloudiness of the surface is more pronounced, and a new geometry is created after decorating the hydrogel with GG. This change may be attributed to the amount of GG used. The imaging shows that GG exhibits a spherical shape, with irregular balls and some patchy shapes present. Additionally, a tendency



Fig. 3. TEM images of the hydrogel surface.



Fig. 4. X-ray diffraction (XRD) of hydrogel micro/nanosyrface.

to form chain-like structures is observed at a scale of 50 nm. Additionally, the hydrogel surface is covered by a transparent layer, within which GG is embedded [18].

X-ray diffraction (XRD) is employed to investigate the crystal phases and purity of nanomaterials. Fig. 4 shows the XRD patterns of the hydrogel. The results indicate a non-crystalline structure for the hydrogel. A broad peak at $2\theta = 22.141^{\circ}$ and another at $2\theta = 33.22^{\circ}$ suggest a transition from an amorphous state to a semicrystalline nature[19]. The TGA revealed a limitation in the thermal stability of the hydrogel (Fig. 5). A loss of weight in the hydrogel patterns was observed. A loss of weight from 60 to 200°C, equivalent to 12.133 %, occurred, consistent with the evaporation of water from the hydrogel. A significant weight loss of 43.677% was attributed to crosslink decomposition and the elimination of CO2 from the hydrogel structure at temperatures ranging from 300 to 560 °C. This also designated a loss of amide and hydroxyl groups in the structure. Final





Fig. 6. Effect of contact time on removal of MV dye by hydrogel.

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decomposition, occurring between 560 and 600 °C, resulted in a loss of weight[20].

BET experiments were conducted to investigate the impact of hydrogel inclusion on the surface area and pore volume of the gel matrix in the hydrogel composite. The composite's BET surface area, pore volume, and pore diameter were 0.233 $m^2/g,\ 0.00122\ cm^3/g,\ and\ 399.32$ Å, respectively. [21]

Effect of contact time

A 100 mL solution of methyl violet (MV) dye at a concentration of 100 mg/L is prepared and placed in a conical flask. The solution is mixed with



Fig. 7. Effect of weight of hydrogel on the removal of MV dye.



Fig. 8. Effect of pH solution on removal of MV dye by hydrogel.

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an adsorbent concentration of 0.05 g per 100 mL of hydrogel at a temperature of 25°C and shaken at a speed of 220 rpm. This setup is maintained in a temperature-controlled water bath. The concentration of the MV dye is measured spectrophotometrically at the wavelength corresponding to its maximum absorbance using a double-beam UV-visible (λmax) spectrophotometer. Samples are taken at various time intervals, ranging from 5 to 60 minutes, and a centrifugation process is used to separate them. The absorbance of each solution is measured, and the dye concentration is determined at intervals of 5 to 60 minutes until equilibrium is reached[22, 23] (Fig. 6).

Effect of weight of hydrogel

The increase in the removal percentage of MV dye removal with increasing hydrogel weight was primarily attributed to the rise in the surface area of the adsorbent, which enhances the number of active sites available for dye adsorption, as reported elsewhere. Dye removal increased with increasing hydrogel weight due to the introduction of more active sites on the surface. The primary influence explaining this property is that the adsorption sites remain unsaturated during the adsorption reaction, while the number of available adsorption sites increases with the weight of the hydrogel. As the weight increased from 0.01 to 0.1 g, the percentage of MV dye removal rose from 72.77% to 98.66% [24, 25]. Conversely, the adsorption capacity decreased from 350 to 1100 mg/g on the hydrogel after approximately one hour of adsorption time (Fig. 7).

Effect of pH

The equilibrium sorption capacity of methylene violet (MV) dye on hydrogel is minimal in basic conditions at pH 10. At this pH level, the adsorption capacity (Qe, mg/g) of the hydrogel is 32.44 mg/g, demonstrating that it is an effective adsorbent for removing MV dye from large volumes of aqueous solutions. As the pH increases beyond 7, the adsorption capacity (Qe, mg/g) of MV dye on the hydrogel rises with the increasing pH. The enhanced adsorption of the dye at acidic pH levels is likely due to the presence of excess H+ ions, which compete with the cationic groups of the dye for available adsorption sites. [26, 27]. At higher pH levels, the surface may become positively charged, enhancing the attraction of the negatively charged dye anion through electrostatic forces as shown in Fig. 8.

Effect of zero-point charge

The pH drift way was used for estimating the pH pzc. Typically, the pH pzc is the point where the curve of pH final versus pH initial intersects the line pH initial = pH final, with a value of 4.2 for the nanocomposite (Fig. 6). At pH < pH $_{pzc}$, the nanocomposite hydrogel displays a net positive charge, whereas at pH > pH $_{pzc}$ the surface is negatively charged. At alkaline pHs (pH > pH zpc), the amount of OH- ions in the aqueous solution increases, and the functional groups in



Fig. 9. Effect of zero-point charge of hydrogel surface.

the adsorber's structure have a negative charge, which can be effective in the process of eliminating pollutants. [28, 29](Fig. 9).

Effect of initial concentration

Effect of MV dye concentration at 10-100

mg/L at 25 °C to investigate the influence of concentration. The removal efficiency, E%, is plotted against the initial concentration in Fig. 10. After one hour, the equilibrium time was supposed to approach balance[30]. found that the adsorption efficiency increased from 92.88 to



Fig. 10. Effect of initial concentration of MV dye.



Fig. 11. Effect of regeneration and reuse of hydrogel.

99.88 % when the initial concentration of MV dye was increased from 10 mg/L to 100 mg/L at 25 °C and pH 7. In contrast, the clearance rate dropped as the concentration improved when it climbed sufficiently. Since an increase in concentration has a minor impact on the removal rate due to the filling, an acceptable efficiency was determined at a concentration of 100 mg/L and an equilibrium time of 60 min [31-33].

Recycling and recovery

Recovery and recycling tests were conducted on the same hydrogel samples to evaluate the long-term effectiveness of the hydrogel adsorbent in removing MV dye from water. Four cycles of adsorption and desorption were performed, and the efficiency of MV dye extraction was assessed after each cycle, as shown in Fig. 11. The reusability of an adsorbent is crucial for its practical application. To test the reuse of the hydrogel, we utilized a hydrochloric acid solution to examine the adsorption process of the bound dye molecules. With the application of hydrochloric acid, the adsorption rate reached 77.75%. Consequently, we utilized hydrochloric acid to further enhance the adsorption of MV dye from the surface of the hydrogel[34]

CONCLUSION

An active hydrogel surface is created using (GG) within hydrogel networks, which are effectively prepared through a copolymerization process. This method enhances the swelling of the hydrogels, resulting in a higher adsorption capacity. The surface demonstrated an impressive adsorption capacity of approximately 998 mg/g. Additionally, the surface charge of the hydrogel was determined to be 4.20, which describes the surface as acidic. To reduce economic costs, the prepared surface was recycled and reused over four consecutive cycles. The absorbent maintained a very high adsorption capacity, ranging from 90.11% in the first cycle to 88.89% in the fourth cycle. This indicates exceptional recovery of the hydrogel.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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