J Nanostruct 15(1): 210-218, Winter 2025

RESEARCH PAPER

Eco-Friendly and Low-Cost Hydrogel Nanocomposite to Efficiently Remove Textile Dye from Aqueous Solution: Thermodynamics and Regeneration Study

Noor Alhuda Sabah [1], *Aseel M. Aljeboree* [2]*, *Khawla K. Jasim* [1]

[1] *Department of Chemistry, College of Sciences for Girls, University of Al-Muthanna, Al-Samawah, Iraq*

[2] *Department of Chemistry, College of Sciences for Girls, University of Babylon, Hilla, Iraq*

ARTICLE INFO

Article History:
Received 07 December 2024
Accepted 27 December 2024
Published 01 January 2025

Keywords:
Dye
Hydrogel
Maxilon blue (GRL)
Nanocomposite
Textile dyes

ABSTRACT

Maxilon blue (GRL), a widely used dye in various textile industries, has numerous harmful effects on humans, animals, and the environment. Therefore, it is essential to remove these dyes from drinking water to ensure the health and safety of the aquatic environment. In this study, an environmentally friendly and inexpensive hydrogel adsorbent based on gum (GG) with high adsorption efficiency was used. Three types of non-toxic monomers (N-isopropyl acrylamide, itaconic acid, and acrylic acid) were added to remove MB from aqueous solution. The CS-EGDE/TNP composite was characterized by SEM, EDX, TEM, XRD, FTIR, and BET techniques was applied to optimize the adsorption key parameters like contact time (5–60min), concentration of GRL dye (50–300 mg/L), adsorbent dose(0.02–0.08g/L), solution pH (3–10), temperature (10–40°C). The adsorption capacity of hydrogel nanocomposite for GRL dye was 575.55 mg/g at 30°C. Results supported the potential use of hydrogel nanocomposite as an effective adsorbent for the treatment of cationic dye. Hydrogel can be used as a promising material in many industries to reduce economic costs by regenerating more than four consecutive cycles.

How to cite this article
NSabah N., Aljeboree A., Jasim K. Eco-Friendly and Low-Cost Hydrogel Nanocomposite to Efficiently Remove Textile Dye from Aqueous Solution: Thermodynamics and Regeneration Study. J Nanostruct, 2025; 15(1):210-218. DOI: 10.22052/JNS.2025.01.020

INTRODUCTION

Water is considered one of the most important vital resources essential for the sustainability of life for humans, animals, and plants. In recent times, freshwater availability has been severely declining due to pollutants emitted by the textile industry, but also to human activities such as population growth. Industries such as paper, textiles, plastics, and pharmaceuticals are primarily responsible for releasing toxic and hazardous substances such as dyes, pharmaceuticals, heavy metals, radioactive waste, pesticides, and fertilizers into water [1]. The severity of this water pollution is exacerbated by emerging pollutants, such as pesticides, plasticizers, preservatives, personal care products, and food additives, which are constantly released into water. Living organisms are endangered by water pollution, harming the ecosystem and, ultimately, the global economy. Undoubtedly, drinking water pollution is one of the most significant problems facing humanity [2-4].

Textile dyes are a common hazardous

* *Corresponding Author Email: annenayad@gmail.com*

contaminant in water. The severity of these textile dyes is determined by their stability and resistance to temperature, light, chemicals, and bacteria. The harmful effects of dyes on living organisms and their inhabitants have been well documented. For example, dyes distort the aesthetics of the environment, reduce transparency, slow photosynthesis, impede sunlight penetration, and disrupt water quality parameters such as dissolved oxygen, pH, and water hardness [5]. They also negatively affect the growth and development of marine organisms such as algae and fish, as well as microbes. Humans are particularly susceptible to the effects of these hazardous and toxic dyes. Depending on their nature, concentration, and duration of exposure, they can cause both mild (such as allergies, skin irritation, vomiting, and nausea) and serious (such as genetic mutations and cancer). Therefore, it is imperative to develop methods to reduce water pollution [6-8].

Hydrogels, due to their highly porous nature, three-dimensional network, and finer, soft texture, are well suited for loading water-soluble materials. Furthermore, hydrogels, which are biodegradable and known as hydrogels, have interconnected pores that are very important for the adsorption process [9]. The porosity can be improved by the following methods: incorporation of nanomaterials, grafting, drying, cross-linking polymerization, and freezing and cryogenic applications. Synthetic hydrogels, with their excellent adsorption capacity, greater mechanical strength, and high swelling capacity, can be used instead of natural hydrogels [10-12].

This research focuses on preparing a highly porous hydrogel from environmentally friendly, non-toxic guar gum using ammonium persulfate as an initiator. The prepared hydrogel was characterized,, and its swelling behavior at different pH levels was tested using sorption experiments to determine its effectiveness.

MATERIALS AND METHODS

Preparation of nanocomposite hydrogel

The GG-grafted ITA in the loading NIPA was prepared using a graft-free radical co-polymerization method with the initiator KPS. In a reaction flask, 0.5 g of NIPA was dissolved in 20 mL of distilled water and sonicated for 30 minutes. Next, 0.5 g of GG and 0.5 g of ITA were added, each dissolved in 10 mL of distilled water, along with 0.05 g of MBA in 5 mL of distilled water. The initiator KPS, at a concentration of 0.005 g in 5 mL, was then added dropwise to the reaction mixture. Nitrogen gas was used to purge the system throughout the process. The copolymerization reaction proceeded for 120 minutes at 75 °C. Finally, the resulting powder was collected to form the hydrogel.

Adsorption Isotherm

Stander solutions of the GRL dye (1.0 g/1000 mL) were prepared, and the range of required concentrations was made by dilutions with distilled water. The conical flask contained an adsorbed concentration of GRL 300 mg/L, and the weight of hydrogel (0.02 -0.08 g) was maintained independently in a shaker water bath at a regulated temperature. The GRL dye concentration will be estimated spectrophotometrically using a spectrophotometer at the 599 nm wavelength equivalent to maximal absorbance, or max (UV–Vis 1700 Shimadzu). Samples are separated using centrifugation at different intervals. After 60 minutes, is established, the absorbance of the solution is measured, and the drug concentration is estimated.

$$R\% = \frac{C_o - C_e}{C_o} \times 100$$

$$Q_e(\frac{mg}{g}) = \frac{(C_o - C_e)Vml}{W(g)}$$

where C_o (mg/L) is the initial concentration of GRL, Ce (mg/L) is the concentration of GRL at equilibrium, V (mL) is the volume of the solution, and W(g) is the weight of the hydrogel.

RESULT AND DISCUSSION

FESEM

FESEM images of the hydrogel before and after adsorption are shown in Fig. 1. The hydrogel has a relatively smooth surface before adsorption, while the hydrogel after adsorption has rough surfaces due to crosslinking and polymerization. The structural morphology of the gel changes to a rough surface, appearing as a lumpy surface. This is due to the dye saturating the gel's active sites. The dye interaction leads to greater crosslinking, which increases the porosity of the polymer matrix. The surface morphology of any gel is highly

influenced by the chemical/physical interactions of the hydrogel surface [13].

TEM

Fig. 3 shows the TEM images of the nanocomposite. The hydrogel showed heterogeneous and irregular morphology within the surface, with some patchy shapes, and tended to form chain-like aggregates at 50 nm. Furthermore, the surface of the nanocomposite is covered with a transparent layer, where it is observed that the GG is embedded within the hydrogel. The GG plays a pivotal role in improving stability and increasing the surface area as an essential component for the synthesis [12].

TGA and XRD

Fig. 4 shows the hydrogel's thermograms. The hydrogel exhibited three distinct zones of weight loss. The initial weight loss of 9.78% occurred due to moisture loss between 29°C and 274°C. The second phase of weight loss, which accounted for 51.50%, took place within the temperature range of 274351°C , indicating the degradation of the hydrogel backbone[14].

Fig. 3c shows the hydrogel's XRD spectrum. The spectrum clearly shows a crystalline peak at 20.9° (2θ scale) corresponding to the [001] crystalline plane, confirming the hydrogel's formation [15].

BET analysis

BET experiments were carried out to determine the effects of hydrogel inclusion on the surface area and pore volume of the gel matrix of the hydrogel composite. The composite's BET surface area, pore volume, and pore diameter were 0.1544

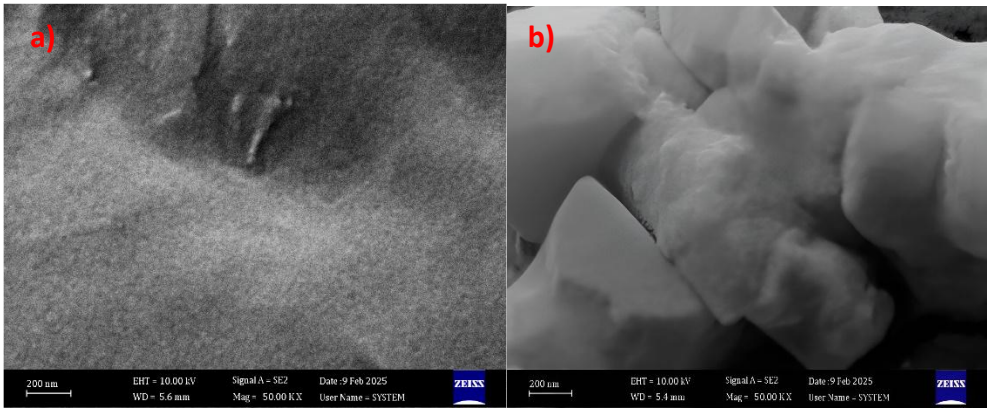

Fig. 1. FESEM image of a) hydrogel before adsorption, b) hydrogel after adsorption.

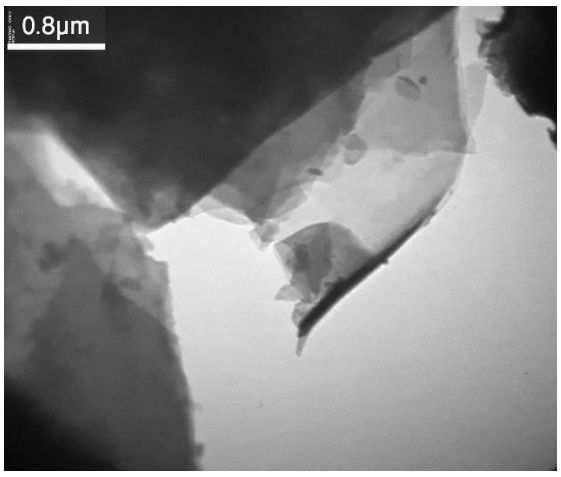

Fig. 2. TEM image of Hydrogel nanocomposite.

m^2/g, 0.00223 cm^3/g, and 294.42 Å, respectively [16].

Adsorbent dosage

The weight of hydrogel is one of the most important factors known to have the greatest impact on the adsorption process. Using different amounts of hydrogel (0.02-0.08 g) on the adsorption of a dye (300 mg/L dye solution at pH7), while keeping all other parameters constant, the effect of adsorbent dosage on dye removal from aqueous solutions was studied. The prepared solutions were then shaken for 120 minutes at 30 °C [17].

Fig. 4 shows that when the aqueous gel weight increased from 0.02 to 0.08 g, the adsorption efficiency decreased from 1083 to 318.31 mg/g. This was due to the increase in the number of active sites for adsorption into the solution, which led to competition between them and a decrease in adsorption efficiency. The dye removal efficiency increased from 72.3 to 98.6% as the aqueous

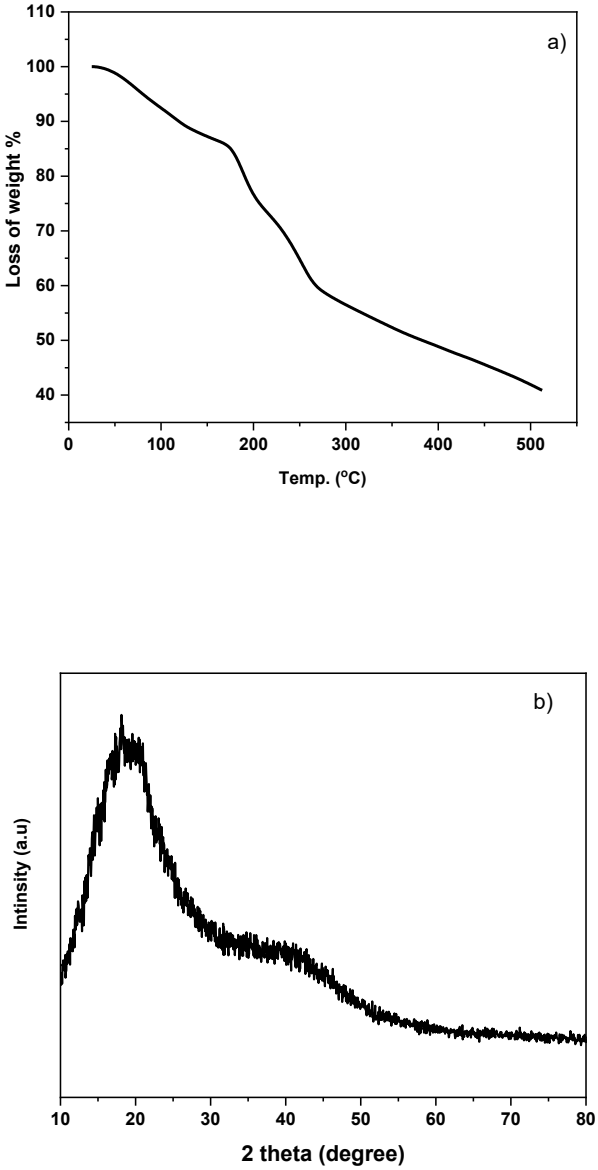

Fig. 3. a) TGA of hydrogel nanocomposite, b) XRD of hydrogel nanocomposite.

gel weight increased from 0.02 to 0.08 g. This is because the adsorbent surface contains more active sites that are available for dye adsorption. Therefore, the optimal adsorbent dosage at equilibrium was determined to be 0.05 g [18].

Effect of Contact Time

Equilibrium time is an important and fundamental parameter for water treatment. Fig. 5 illustrates the effect of equilibrium time on dye adsorption. Due to the abundance of

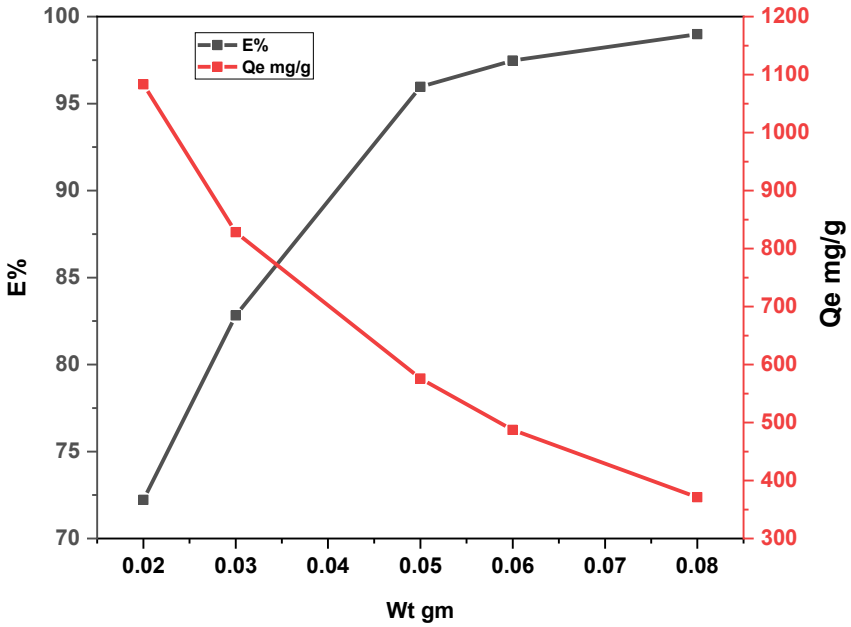

Fig. 4. Effect of the weight of hydrogel nanocomposite on the removal GRL dye.

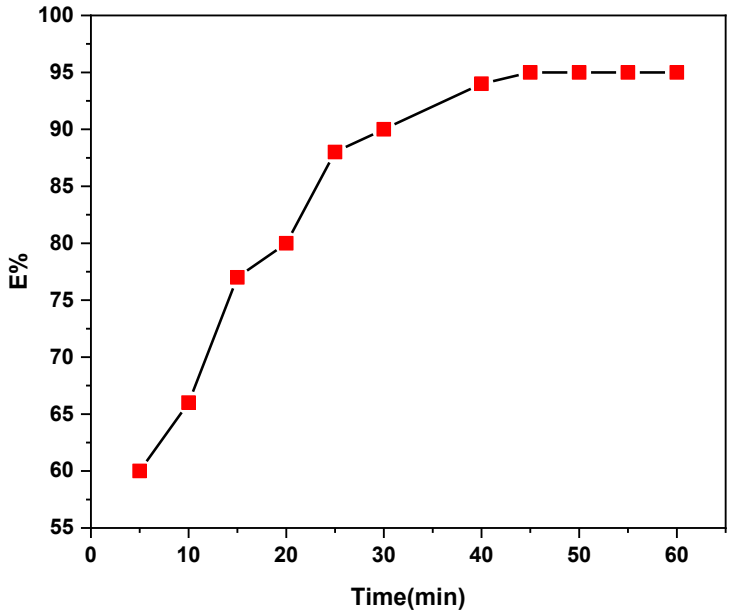

Fig. 5. Effect of Contact Time on the removal GRL dye by hydrogel nanocomposite.

unoccupied GRL dye adsorption sites, the dye was rapidly adsorbed during the first 10 minutes of equilibrium time. Rapid dye removal was observed during the first 30 minutes. After 60 minutes, the removal rate stabilized and reached its peak. This may be due to the lack of available active sites for dye adsorption. Therefore, 60 minutes was chosen as the optimal time period for the experiments

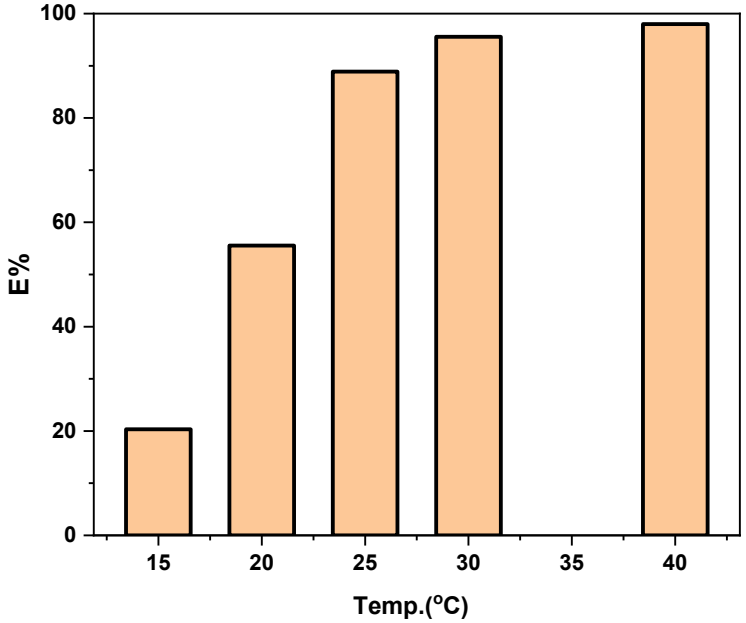

Fig. 6. Effect of Temperature on the removal GRL dye by hydrogel nanocomposite.

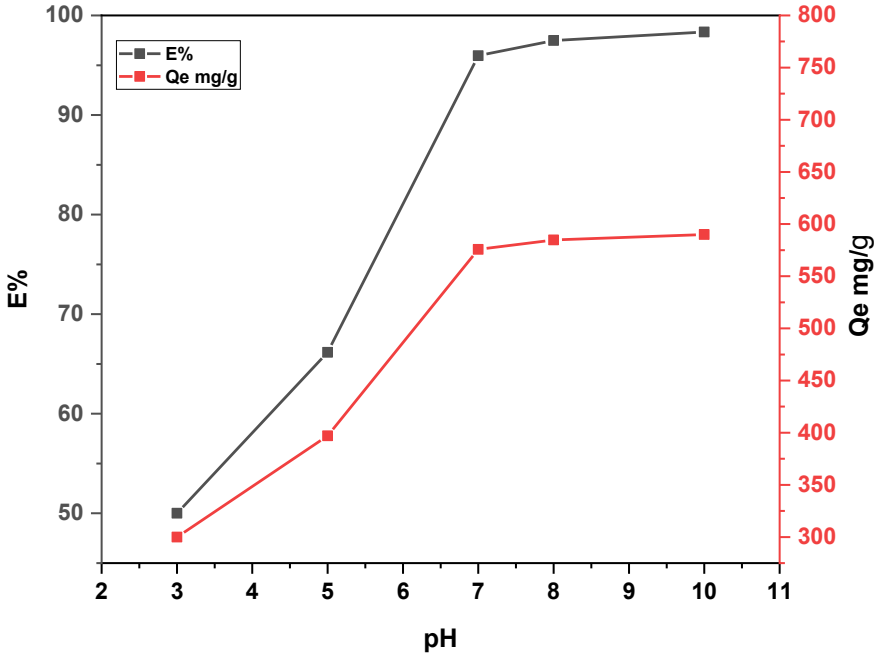

Fig. 7. Effect of pH solution on the removal GRL dye by hydrogel nanocomposite.

[19, 20].

Effect of Temperature

Temperature is a crucial factor in the adsorption process, as it significantly impacts adsorption properties. Generally, if the dye adsorption process increases with rising temperature, this indicates an endothermic reaction. This phenomenon can be explained by the fact that higher temperatures accelerate the diffusion rate of the dye and provide the dye molecules with adequate energy to interact with the adsorption sites. However, some research has shown that dye adsorption can also be exothermic, meaning that dye molecules adhere more effectively at lower temperatures. Therefore, a precise understanding of temperature is essential for designing an effective membrane. Studies investigating the effects of temperature on dye adsorption were conducted within a range of 15°C to 40°C, and the results are illustrated in Fig. 6. It is clear that as the temperature increased from 15°C to 40°C, the removal efficiency decreased from 20.76% to 95.53% [21-23].

Effect of pH

In aqueous solutions, the ionization of functional groups on the hydrogel surface (which represent the charges of the adsorption sites) is clearly affected by acidity (pH), an important parameter that influences dye adsorption behavior. This demonstrates that the dye removal efficiency increased from 50.66% to 98.5% with increasing pH. Hydrogen protons (H+) in the medium competed with the dye molecules for the same binding sites at lower pH, reducing the adsorption efficiency. However, the removal rate increased as the pH of the solution increased, due to the reduced competition between the dye molecules and hydrogen protons (H+) for the adsorption sites. Therefore, when the pH exceeds 8, the dye molecules begin to precipitate, which is important for dye removal [24, 25]

Experiments were conducted using 100 mL of dye solution (300 mg/L) containing 0.05 g of hydrogel over a pH range of 3 to 10 at room temperature for one hour, with other variables held constant[26]. The results are shown in Fig. 7.

Regeneration

Regeneration and recovery tests were performed on the hydrogel sample after washing it multiple times to measure the long-term effectiveness of the nano hydrogel adsorbent in removing dye from the aqueous medium. Four adsorption/stripping cycles were performed, and the dye extraction efficiency was evaluated after each cycle, as shown in Fig. 8.

The regeneration ability of any adsorbent is

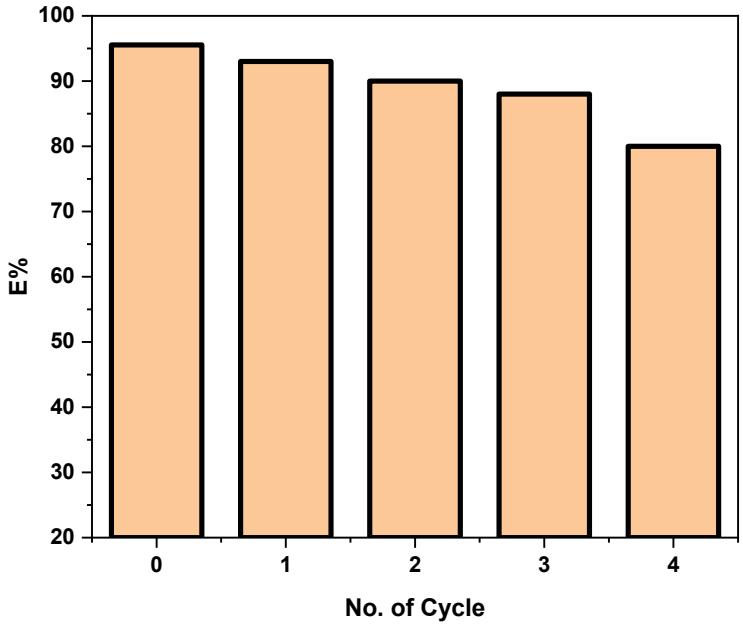

Fig. 8. Effect of Regeneration and recovery tests.

important and essential for its practical application in many industries. To test the reusability of the nano hydrogel, bound dye molecules were stripped in an acidic or basic solution. The adsorption rate was only 20% in the basic solution. However, the adsorption rate reached 95% when using the acidic solution. Consequently, we used the acidic solution to increase the adsorption of dye from the nano gel surface [9, 27, 28].

CONCLUSION

The prepared hydrogels are promising for the removal of basic dyes from aqueous solutions. Their high adsorption capacity, coupled with their ease of preparation and use, make them a valuable adsorbent for treating textile dye contamination. We thoroughly verified their preparation method and effectiveness using applied technology like FESEM, TEM, XDR, TGA, and BET. Our results indicate that the adsorption equilibrium increases with increasing dye concentration, especially at pH 7. After a contact time of 60 min, a 0.05 g dose of hydrogel showed the highest adsorption capacity at 575.66 mg/g. Furthermore, the success of reusing and regeneration of these granules for water treatment makes them a noteworthy addition to the field of adsorbents.

CONFLICT OF INTEREST

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

REFERENCES

1. Salleh MAM, Mahmoud DK, Karim WAWA, Idris A. Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. Desalination. 2011;280(1-3):1-13.
2. Makhado E, Hato MJ. Preparation and Characterization of Sodium Alginate-Based Oxidized Multi-Walled Carbon Nanotubes Hydrogel Nanocomposite and its Adsorption Behaviour for Methylene Blue Dye. Frontiers in chemistry. 2021;9:576913-576913.
3. Mittal H, Al Alili A, Morajkar PP, Alhassan SM. Graphene oxide crosslinked hydrogel nanocomposites of xanthan gum for the adsorption of crystal violet dye. J Mol Liq. 2021;323:115034.
4. Maryudi M, Amelia S, Salamah S. Removal of Methylene Blue of Textile Industry Waste with Activated Carbon using Adsorption Method. Reaktor. 2019;19(4):168-171.
5. Benkhaya S, M'Rabet S, El Harfi A. Classifications, properties, recent synthesis and applications of azo dyes. Heliyon. 2020;6(1):e03271-e03271.
6. Hong G-B, Yu T-J, Lee H-C, Ma C-M. Using Rice Bran Hydrogel Beads to Remove Dye from Aqueous Solutions. Sustainability. 2021;13(10):5640.
7. Zhao S, Zhan Y, Wan X, He S, Yang X, Hu J, et al. Selective and efficient adsorption of anionic dyes by core/shell magnetic MWCNTs nano-hybrid constructed through facial polydopamine tailored graft polymerization: Insight of adsorption mechanism, kinetic, isotherm and thermodynamic study. J Mol Liq. 2020;319:114289.
8. Adsorption and Removal of pharmaceutical Riboflavin (RF) by Rice husks Activated Carbon. International Journal of Pharmaceutical Research. 2019;11(2).
9. Liu L, Gao Q, Lu X, Zhou H. In situ forming hydrogels based on chitosan for drug delivery and tissue regeneration. Asian Journal of Pharmaceutical Sciences. 2016;11(6):673-683.
10. Dhiman J, Prasher SO, ElSayed E, Patel RM, Nzediegwu C, Mawof A. Heavy metal uptake by wastewater irrigated potato plants grown on contaminated soil treated with hydrogel based amendments. Environmental Technology & Innovation. 2020;19:100952.
11. Liang Y, Zhao X, Ma PX, Guo B, Du Y, Han X. pH-responsive injectable hydrogels with mucosal adhesiveness based on chitosan-grafted-dihydrocaffeic acid and oxidized pullulan for localized drug delivery. Journal of Colloid and Interface Science. 2019;536:224-234.
12. Kangwansupamonkon W, Klaikaew N, Kiatkamjornwong S. Green synthesis of titanium dioxide/acrylamide-based hydrogel composite, self degradation and environmental applications. Eur Polym J. 2018;107:118-131.
13. Thakur S, Pandey S, Arotiba OA. Development of a sodium alginate-based organic/inorganic superabsorbent composite hydrogel for adsorption of methylene blue. Carbohydr Polym. 2016;153:34-46.
14. Yi J-Z, Zhang L-M. Removal of methylene blue dye from aqueous solution by adsorption onto sodium humate/polyacrylamide/clay hybrid hydrogels. Bioresour Technol. 2008;99(7):2182-2186.
15. Han S, Wang T, Li B. Preparation of a hydroxyethyl–titanium dioxide–carboxymethyl cellulose hydrogel cage and its effect on the removal of methylene blue. J Appl Polym Sci. 2017;134(23).
16. Shirsath SR, Patil AP, Patil R, Naik JB, Gogate PR, Sonawane SH. Removal of Brilliant Green from wastewater using conventional and ultrasonically prepared poly(acrylic acid) hydrogel loaded with kaolin clay: A comparative study. Ultrason Sonochem. 2013;20(3):914-923.
17. Wang Y, Wang W, Wang A. Efficient adsorption of methylene blue on an alginate-based nanocomposite hydrogel enhanced by organo-illite/smectite clay. Chem Eng J. 2013;228:132-139.
18. Ahmed EM, Aggor FS, Awad AM, El-Aref AT. An innovative method for preparation of nanometal hydroxide superabsorbent hydrogel. Carbohydr Polym. 2013;91(2):693-698.
19. Pashaei-Fakhri S, Peighambardoust SJ, Foroutan R, Arsalani N, Ramavandi B. Crystal violet dye sorption over acrylamide/graphene oxide bonded sodium alginate nanocomposite hydrogel. Chemosphere. 2021;270:129419.
20. Jasim LS, Aljeboree AM, Sahib IJ, Mahdi MA, Abdulrazzak FH, Alkaim AF. Effective adsorptive removal of riboflavin (RF) over activated carbon. AIP Conference Proceedings: AIP Publishing; 2022. p. 030030.
21. El-Hamshary H, El-Sigeny S, Abou Taleb MF, El-Kelesh NA. Removal of phenolic compounds using (2-hydroxyethyl methacrylate/acrylamidopyridine) hydrogel prepared by gamma radiation. Sep Purif Technol. 2007;57(2):329-337.
22. Cass P, Knower W, Pereeia E, Holmes NP, Hughes T.

Preparation of hydrogels via ultrasonic polymerization. Ultrason Sonochem. 2010;17(2):326-332.
23. Aljeboree AM, Al-Baitai AY, Abdalhadi SM, Alkaim AF. Investigation Study of Removing Methyl Violet Dye From Aqueous Solutions Using Corn-Cob as A Source of Activated Carbon. Egyptian Journal of Chemistry. 2021;0(0):0-0.
24. Wang W, Wang A. Synthesis and swelling properties of pH-sensitive semi-IPN superabsorbent hydrogels based on sodium alginate-g-poly(sodium acrylate) and polyvinylpyrrolidone. Carbohydr Polym. 2010;80(4):1028-1036.
25. Bao Y, Ma J, Li N. Synthesis and swelling behaviors of sodium carboxymethyl cellulose-g-poly(AA-co-AM-co-AMPS)/MMT superabsorbent hydrogel. Carbohydr Polym. 2011;84(1):76-82.
26. Taifi A, Alkadir OKA, Aljeboree AM, Al Bayaa AL, Alkaim AF, Abed SA. Environmental Removal of Reactive Blue 49 Dye From Aqueous Solution by (Lemon peels as activated carbon): a Model of Low Cost agricultural waste. IOP Conference Series: Earth and Environmental Science. 2022;1029(1):012010.
27. Alidadi H, Dolatabadi M, Davoudi M, Barjasteh-Askari F, Jamali-Behnam F, Hosseinzadeh A. Enhanced removal of tetracycline using modified sawdust: Optimization, isotherm, kinetics, and regeneration studies. Process Saf Environ Prot. 2018;117:51-60.
28. Aljeboree AM, Alkaim AF. Removal of Antibiotic Tetracycline (TCs) from aqueous solutions by using Titanium dioxide (TiO_2) nanoparticles as an alternative material. Journal of Physics: Conference Series. 2019;1294(5):052059.