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Studies on the Removal of Malachite Green from Its Aqueous Solution Using Water-Insoluble β-Cyclodextrin Polymers

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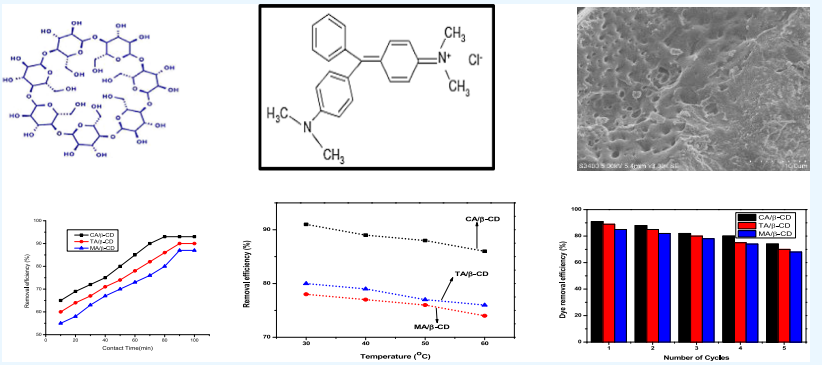

ABSTRACT: The rising global pollution of natural waters by dyes has brought to light the need for adaptable and efficient removal techniques. To create water-insoluble β-cyclodextrin (β-CD) polymers like CA/-CD, TA/-CD, and MA/-CD, several organic acids including citric acid (CA), tartaric acid (TA), and malic acid (MA) were cross-linked with β-cyclodextrin in this study. The obtained polymers were characterized by different advanced analytical techniques such as FTIR, SEM, and UV−vis spectrophotometry. Malachite green dye was removed from aqueous solutions using the synthesized polymers by adsorption. The adsorption investigation was conducted under several conditions, including pH, adsorbent mass, dye concentration, temperature, contact time, adsorption isotherm, and kinetics. The adsorbent CA/β-CD shows the highest adsorption of MG dye in all of the conditions because it contains a high number of carboxyl groups. The negatively charged carboxyl ions of CA/β-CD attract the positively charged MG dye electrostatically and remove MG from aqueous media with an efficiency of 91%. As a result, the findings indicated that water-insoluble polymers based on β-cyclodextrin are well-suited as inexpensive adsorbents to remove colors from aqueous media.

INTRODUCTION

One of the most vital resources for all life on earth to exist and flourish is water. Water quality, nevertheless, is consistently being compromised by heavy urban and industrial activities. A significant amount of organic dyes is used by the food, leather, paint, plastic, textile, and other sectors to color their products. As a result, the environment, especially the surface and underground water bodies, is seriously threatened by the effluents from such industries. Additionally, the dye waste prevents sunlight from penetrating the water, which impairs important biological activities.[1] The nature of organic dyes is poisonous, carcinogenic, mutagenic, and highly stable. Due to its great solubility in water, the cationic dye malachite green (MG), which is a member of the triphenylmethane family, is helpful for coloring a variety of industrial items. In some circumstances, the toxic effects of MG can cause developmental defects, organ damage, and mutagenesis or carcinogenic effects.[2] Thus, before releasing water into the environment, it is imperative to remove the excess MG from it. Photodegradation has been extensively employed; however, it has the limitation that degradation products are also toxic.[3] On the other hand, sophisticated oxidation processes are used for the degradation of organic pollutants in environmental remediation because they are economical and environmentally beneficial.[4,5] However, the processes almost create a lot of secondary and tertiary products, which most of the times are more hazardous than their precursors.[6] In the past, many techniques such as coagulation, ozonation, electrochemical, adsorption, microbial degradation, ion exchange, membrane filtration, and device development for harmful ion detection

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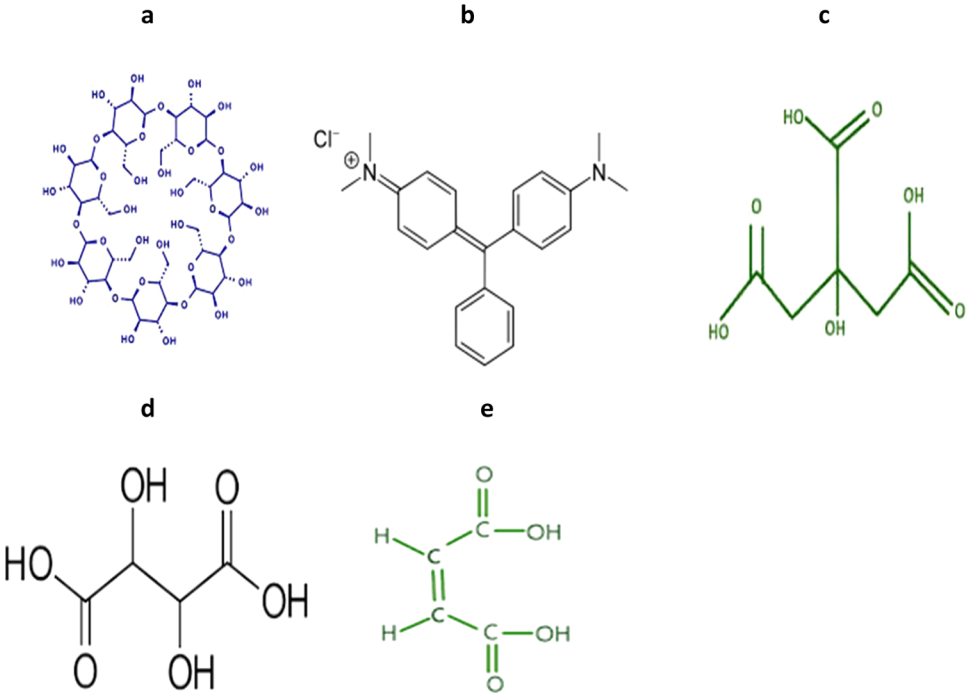

Figure 1. Structural formulas of (a) β-cyclodextrin (β-CD), (b) malachite green (MG), (c) citric acid (CA), (d) tartaric acid (TA), and (e) malic acid.

have been used to treat wastewater.[6] All of the techniques suffer from various disadvantages.[6] Of the many techniques proposed in the literature, adsorption is gaining importance as it traps the toxic molecules onto the surface of the adsorbent.[7−19] Additionally, the adsorption method of wastewater treatment is becoming more and more popular due to its ease of use, simplicity, viability from an economic standpoint, and high efficiency.[20] But creating adsorbent materials for the adsorption process that are effective, efficient, nontoxic, affordable, simple to use, and regenerate is a difficult task. Surface modification of naturally occurring, inexpensive materials can be utilized to remove organic pollutants from wastewater in order to solve this problem.[21−26] Despite the fact that these adsorbents produce solid waste, it can be greatly diminished by regeneration of the adsorbents.

A group of cyclic oligosaccharides known as cyclodextrins (CDs) is composed of six (α-CDs), seven (β-CDs), or eight (γ-CDs) anhydrous D-glucopyranose units (AGUs) linked together by $\alpha(1,4)$ glycosidic connections. Due to their use in the water purification process, as discovered by scientist Cyclodextrins Villiers, cyclodextrins have unique features. The glycosidic oxygens and methane proton groups that make up cyclodextrin's interior surface are hydrophobic and create complexes with noncovalent interactions.[27−29] Because of the hydroxyl groups in the cavity, the cyclodextrins' outside surfaces are hydrophilic. By changing the hydroxyl group, many cyclodextrin derivatives can be created, and these derivatives can be applied in the fields of pharmaceutics, separation, food, life, and environment research.[30−34] Because of their specific affinity, ease of use, and low cost, adsorption employing cyclodextrin-based polymers (CDPs) as adsorbents is a successful approach, particularly for the treatment of wastewater[35,36] and remediation of dyes.[37,38] In the current work, we offer a method for removing MG from aqueous solution that combines β-cyclodextrin (β-CD) with various organic acids, including citric acid (CA), tartaric acid (TA), and malic acid (MA). Cyclodextrin is a porous, low-cost substance having a large surface area. It is simple to synthesize, exhibits excellent thermal stability and straightforward chemical functionality, is biocompatible, and is naturally nontoxic. The −OH groups on the surface of β-cyclodextrin (β-CD) make it simple to combine it with various organic acids. Although the β-CD can be used to remove MG, this β-CD was functionalized with high surface area and porosity to increase the removal efficiency. To the best of our knowledge, the removal of MG from aqueous solution has not yet been investigated when β-cyclodextrin (β-CD) is combined with various organic acids.

MATERIALS AND METHODS

Without additional purification, all of the reagents were utilized after being acquired from SD Fine (India). Citric acid (CA) was 98+ % pure, and β-cyclodextrin (β-CD) was 99+ % pure. Malic acid (MA), malachite green (MG), tartaric acid (TA), and all other chemicals were of analytical quality. MA was 98+ % pure, MG was 99+ % pure, and TA was 95+ % pure (Figure 1). The correct volumes of dye powder were dissolved in deionized water to create stock solutions of 1000 mg L^{-1}. The stock solutions were diluted to create working solutions with concentrations ranging from 4 to 24 ppm. It was obvious to adjust the pH using 0.1 M HCl and 0.1 M NaOH.

SYNTHESIS OF β-CYCLODEXTRIN (β-CD)-BASED WATER-INSOLUBLE POLYMERS

Synthesis of Water-Insoluble Citric Acid-β-Cyclodextrin (CA-β-CD) Polymers. An 800 mL beaker had approximately 3 g of anhydrous citric acid, 6 g of β-cyclodextrin, and 1.5 g of KH_2PO_4 dissolved in deionized water and mixed together to achieve homogeneity. The beaker was then heated for 3.5 h at 140 °C without being stirred in a drying oven. The crude product was purified after reaching

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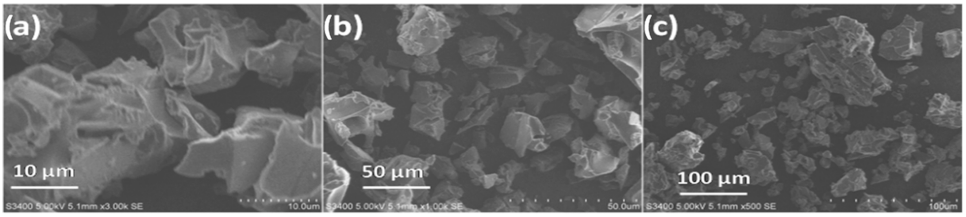

Figure 2. Scanning electron microscope images of (a−c) CA/β-CD MG dye adsorption in different magnifications.

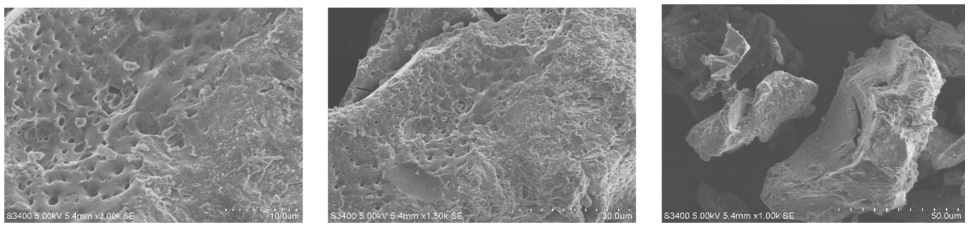

Figure 3. Scanning electron microscope images of (a−c) MA/β-CD MG dye adsorption at different magnifications.

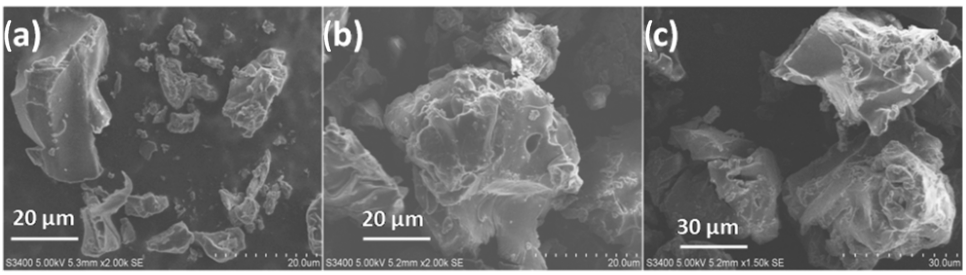

Figure 4. Scanning electron microscope images of (a−c) TA/β-CD adsorption in different magnifications.

room temperature by soaking in 500 mL of liquid for 5 min, followed by suction filtration and drying at 50 °C. The final CA-CD polymer product, 7.02 g, with a 66.86% yield, was later characterized[39] and stored at room temperature in a dry condition.

Synthesis of Water-Insoluble Malic Acid-β-Cyclodextrin (MA-β-CD) Polymers. With slight adjustments, the copolymerization of CD and MA was carried out in accordance with a scheme.[40] In an element, 3.82 g of MA (28 mmol), 3.8 g of $Na_2HPO_4.12H_2O$ (10 mmol), and 6 g of CD (4.75 mmol on a dry basis) were dissolved. The solution was heated for about an hour at 100 °C. The ground material was immediately put into a Petri dish and dried in a lab oven at 180 °C for 120 min. The raw material was weighed and pulverized.

Synthesis of Water-Insoluble Tartaric Acid-β-Cyclodextrin (TA-β-CD) Polymers. Similar to the previous method, using citric acid-CD polymers as a guide, TA-β-CD polymers were created by reacting β-CD with tartaric acid as a cross-linker and sodium dihydrogen phosphate (MSP) as a catalyst. 2.34 g of DL-tartaric acid, 6 g of β-CD, and 0.75 g of KH_2PO_4 were dissolved in 135 mL of ultrapure water and agitated to obtain a homogeneous solution in an 800 mL beaker. The beaker was switched into and heated for 3.5 h at 140 °C without being stirred. After cooling to room temperature, the crude product was purified by soaking and washing with deionized water several times, then suction-filtered and dried at 50 °C to a constant weight. Weight and % yield of purified products were recorded. The product was weighed, powdered, and finally characterized.

Adsorption Experiments. For adsorption investigations, the necessary concentration of MG in water (10−50 mg L^{-1}) was generated. In a 100 mL conical flask, 20 mL of a dye solution with a concentration of 10 mg L^{-1} was added, along with the dosages of 10−120 mg of CA/β-CD, TA/β-CD, and MA/β-CD. These conical flasks were shaken for 1 h in an incubator. Adsorbent type, pH effect, adsorbent dosage, initial dye concentration, temperature influence, and contact periods are only a few of the variables that were researched. Following dye removal, the effectiveness of dye removal was determined using the supernatant solution and a standard calibration curve that was examined by determining the absorption maxima values for MG using UV−vis spectroscopy at 617 nm. The dye removal procedure was carried out three times for each adsorbent in order to calculate the standard deviation.

RESULTS AND DISCUSSIONS

Characterization Techniques. *Surface Morphology Analysis.* The analysis of CA/β-CD surface morphology before and after adsorption was carried out by a scanning electron microscope and is shown in Figure 2. Analysis was done for the samples with different magnifications with different areas. Figure 2a shows the surface morphology of CA/β-CD in the range of 10 μm with a U-shaped structure. Figures 2b,c shows the surface morphology of CA/β-CD in the ranges of 50 and 100 μm with a spherical-shaped structure.

The analysis of MA/β-CD surface morphology before and after adsorption was carried out by a scanning electron microscope and is shown in Figure 3. Analysis was done for the

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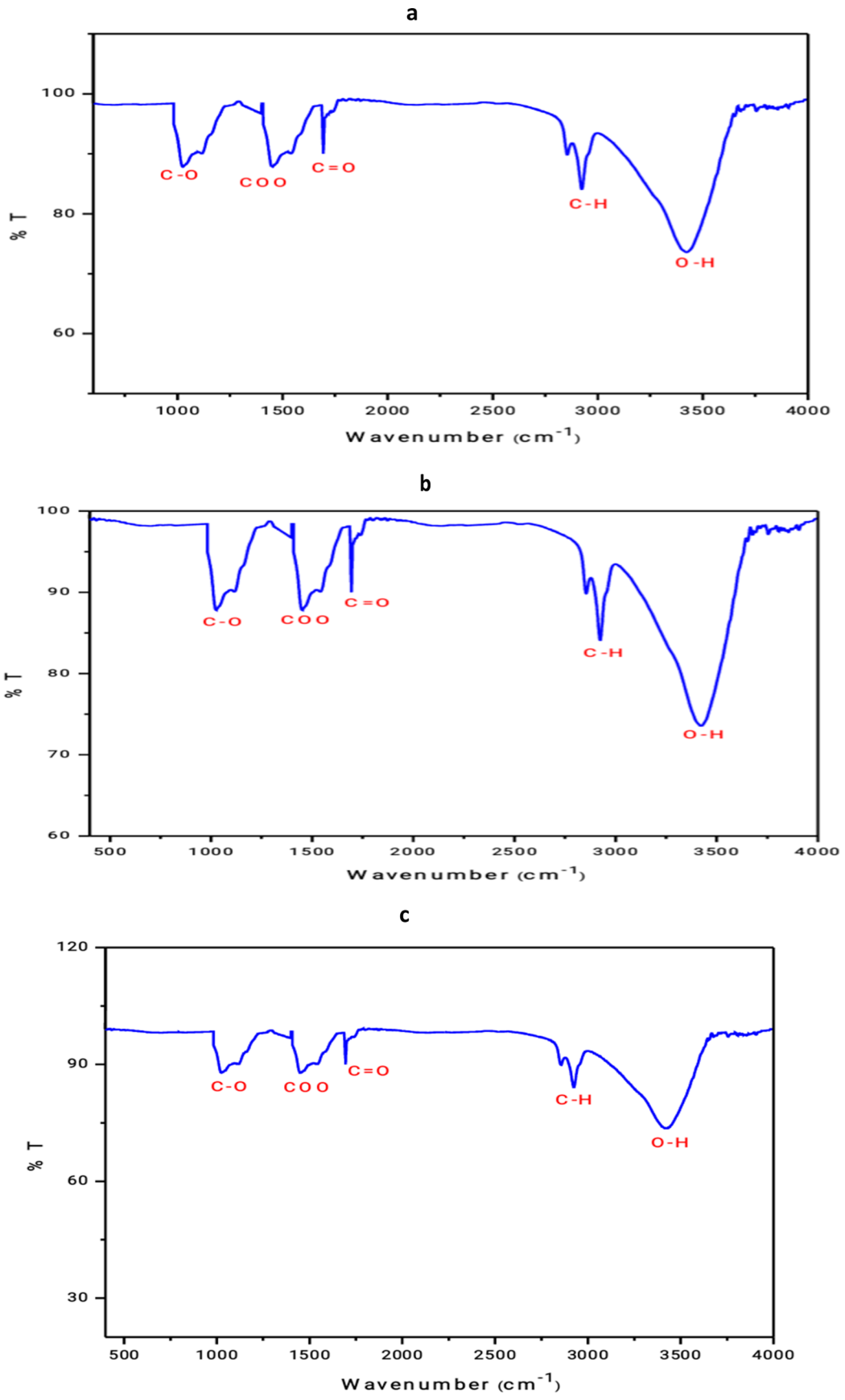

Figure 5. FTIR spectra of (a) CA/β-CD water-insoluble polymer, (b) TA/β-CD water-insoluble polymer, and (c) MA/β-CD water-insoluble polymer.

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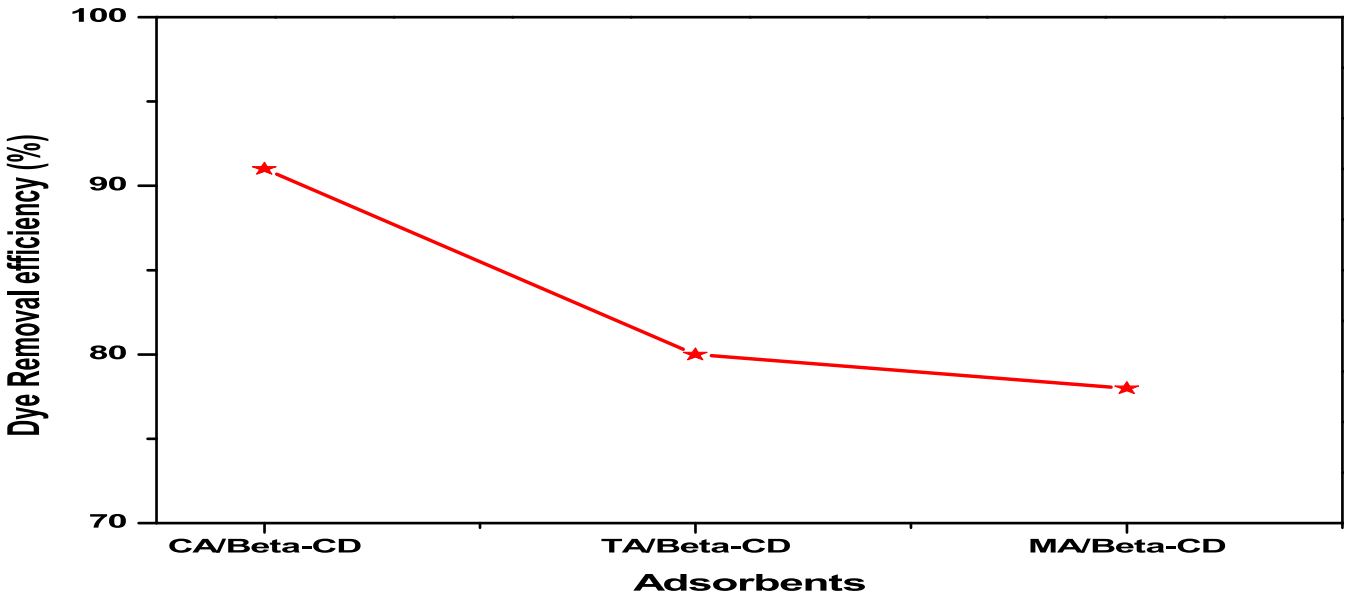

Figure 6. Effect of synthesized adsorbents on dye abolition efficiency.

samples with different magnifications with different areas. Figure 3a shows the surface morphology of MA/β-CD in the range of 30 μm with a leaf-like structure. Figure 3b,c shows the surface morphology of MA/β-CD in the range of 50 μm with a leaf-like structure containing different numbers of holes in its structure. It was observed from SEM images that the material has some porous-like structures also on its surface, which was useful for the adsorption experiments.

The analysis of TA/β-CD surface morphology before and after adsorption was carried out by a scanning electron microscope and is shown in Figure 4. Analysis was done for the samples with different magnifications with different areas. Figure 4a shows the surface morphology of TA/β-CD in the range of 20 μm in different areas of the sample, and it was observed that TA/β-CD has a porous-like structure in its morphology. Figure 4b,c shows the surface morphology of tartaric acid in the ranges of 20 and 30 μm with a porous structure. It was observed from the SEM images that the material has some porous-like structures also on its surface, which was useful for the adsorption experiments.

Overall, cross-linking agents like citric acid, tartaric acid, and malic acid have helped build porous and rugged structures, which helps in the adsorption process. SEM photographs qualitatively confirm the porosity of the adsorbents.[41−43] Moreover, the literature strongly suggests that the cross-linking agents enhance the mechanical properties such as strength, elongation at break, and toughness of the adsorbents.[44−46] However, quantitative measurements need to be performed to measure the actual porosity and hardness of the functionalized materials, which is beyond the scope of the current work to remediate the aqueous solutions.

Functional Group Analysis. Functional Group Analysis of CA/β-CD. The functional group analysis of CA/β-CD was characterized by FTIR analysis, and it is as shown in Figure 5a. It was observed that the broad absorption of IR radiation in the wavenumber region 3800−3200 cm^{-1} relates to the −OH groups of citric acid and β-cyclodextrin. The absorptions of IR radiation in the wavenumber regions 2900 cm^{-1} and 1750 cm^{-1} correspond to the −CH groups and C5O groups of citric acid, respectively. Further, the sharp absorption of IR radiation in the wavenumber region 1400 cm^{-1} corresponds to the COOH group of citric acid. However, the absorption of IR radiation in the wavenumber region 1090−1200 cm^{-1} corresponds to the C−O groups of citric acid and β-cyclodextrin.

Functional Group Analysis of TA/β-CD. The functional group analysis of TA/β-CD was characterized by FTIR analysis, and it is as shown in Figure 5b. It was observed that the broad absorption of IR radiation in the wavenumber region 3750−3150 cm^{-1} corresponds to the −OH groups of citric acid and β-cyclodextrin. The absorptions of IR radiation in the wavenumber regions 2850 and 1760 cm^{-1} correspond to the −CH groups and C5O groups of citric acid, respectively. Further, the sharp absorption of IR radiation in the wavenumber region 1460 cm^{-1} corresponds to the COOH group of citric acid. However, the absorption of IR radiation in the wavenumber region 1100−1250 cm^{-1} corresponds to the C−O groups of citric acid and β-cyclodextrin.

Functional Group Analysis of MA/β-CD. The functional group analysis of MA/β-CD was characterized by FTIR analysis, and it is as shown in Figure 5c. It was observed that the broad absorption of IR radiation in the wavenumber region 3850−3170 cm^{-1} corresponds to the −OH groups of citric acid and β-cyclodextrin. The absorptions of IR radiation in the wavenumber regions 2870 cm^{-1} and 1780 cm^{-1} correspond to the −CH groups and C5O groups of citric acid, respectively. Further, the sharp absorption of IR radiation in the wavenumber region 1440 cm^{-1} corresponds to the COOH group of citric acid. However, the absorption of IR radiation in the wavenumber region 1180−1230 cm^{-1} corresponds to the C−O groups of citric acid and β-cyclodextrin.

Effect of Adsorbents. The three adsorbents, together with CA/β-CD, TA/β-CD, and MA/β-CD, were used to carry out the removal of MG with the aid of an adsorption system. The MG removal efficiency with the aid of the adsorption technique was superior for CA/β-CD when compared to the other polymers. CA/β-CD has a 90% removal ability, as proven in Figure 6. The MG removal performance is more because of the presence of carboxyl groups. The MG with a net efficient rate has a higher electrostatic attraction with the CA/

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β-CD, which results in better adsorption. The MG performance is extensively greater in the case of CA/β-CD adsorbents because of the extra-wide variety of CA/β-CD that electrostatically draws undoubtedly charged MG molecules; therefore, MG molecules can have more electrostatic attraction with the CA/β-CD molecules. The MG was treated with CA/β-CD, TA/β-CD, and MA/β-CD, representing the adsorption of MG molecules from the CA/β-CD surface, thereby decreasing the concentration of MG inside the suspension. However, CA/β-CD shows better performance in comparison to TA/β-CD and MA/β-CD.

Effect of pH on the Removal of MG Using Synthesized Polymers. To test the pH effect in a batch setup, a specific pH range was used. The best pH for the elimination of MG was found using the procedure that is described below. With the use of HCl 0.1 N and NaOH 0.1 N solutions, the initial pH was altered. Each flask containing 20 mL of MG solution received 10 mg of adsorbent, which was added and then agitated until equilibrium was established. Below pH 4 and above pH 6, the absorbance of MG in the UV−visible spectrum significantly decreased. Similarly, when the pH was above 6 and below 4, the MG solution color depth diminished. Therefore, between pH values 4 and 6, the impact of pH on adsorption was investigated. In Table 1, the impact of pH on MG removal is shown.

Table 1. Effect of pH on the Removal Performance of the Adsorbent

	removal efficiency (%)		
pH	CA/β-CD	TA/β-CD	MA/β-CD
4	80.69	73.58	71.45
5	82.65	75.66	72.58
6	90.36	83.33	79.65
7	77.41	70.14	67.32

According to the values in Table 1, all adsorbents function optimally for removal at pH 6. The MA/CD implies significantly less elimination effectiveness at pH 6, with a best of 79.65%, while the CA/β-CD has excessive removal performance at pH 6 with 90.36%. UV−visible absorbance at pH 6 shows that the MG is more stable at this pH than it is at other pH levels, nonetheless. As a result, all of the many studies were carried out without altering the pH 6.

The removal efficiencies of the three adsorbents studied are in the order CA/β-CD > TA/β-CD > MA/β-CD. This is expected as there are four, four, and three −OH groups in CA, TA, and MA, respectively. Besides, CA has three electronegative oxygen groups compared to two oxygen groups in TA.

Effect of Adsorbent Mass on MG Elimination Performance. Figure 7 represents the MG performance with respect to the exceptional dosage (10−120 mg) of adsorbents. The MG elimination performance changed into a barely expanded dosage starting at 10−120 mg for all of the substances. The dye elimination performance faintly increased for dosages from 10 to 100 mg for CA/β-CD, TA/β-CD, and MA/β-CD. The elimination performance and adsorption potential increased with a rising dosage of adsorbents. It is evident that the percentage removal effectiveness of MG increased with increasing adsorbent dosage and reached saturation at 100 mg for CA/β-CD, TA/β-CD, and MA/β-CD when treated with various amounts of adsorbents.

Effect of MG Concentration on Elimination Performance. The elimination efficiencies of different adsorbents CA/β-CD, TA/β-CD, and MA/β-CD were evaluated with one-of-a-kind knowledge of MG. The exclusive concentrations of MG were 0, 10, 20, 30, 40, and 50 mg L^{-1}. During the experiment, 100 mg of adsorbent was brought to 20 mL of various concentrations of MG solutions and incubated for 1 h until reaching adsorption equilibrium. Later, the reaction mixture was centrifuged and the supernatant was analyzed through a UV−vis absorption spectrophotometer. Then, the removal performance of different organized samples CA/β-CD, TA/β-CD, and MA/β-CD was investigated, as shown in Figure 8. The elimination efficiency of adsorbents decreases as the concentration of MG increases. The elimination efficiency was high for all as-prepared adsorbents CA/β-CD, TA/β-CD, and MA/β-CD at an MG concentration of 10 mg L^{-1}. In addition,

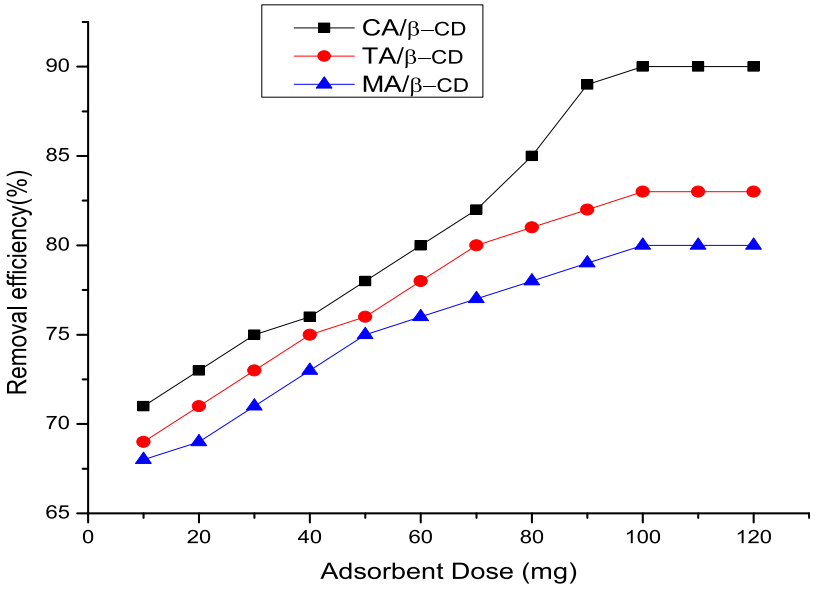

Figure 7. Effect of adsorbent mass on elimination performance.

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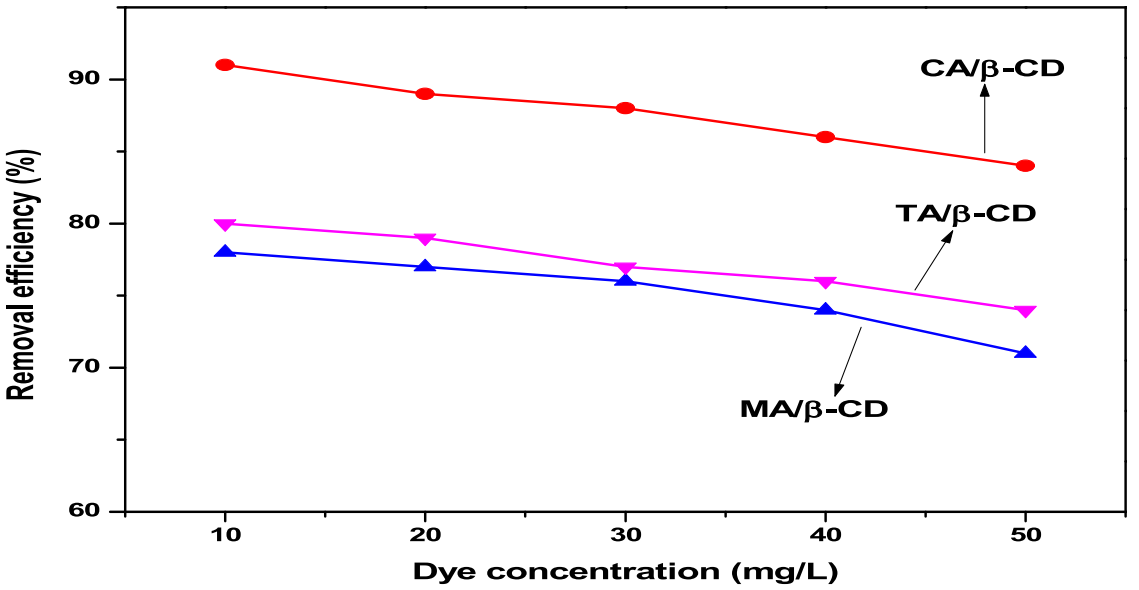

Figure 8. Effect of MG concentration on elimination performance.

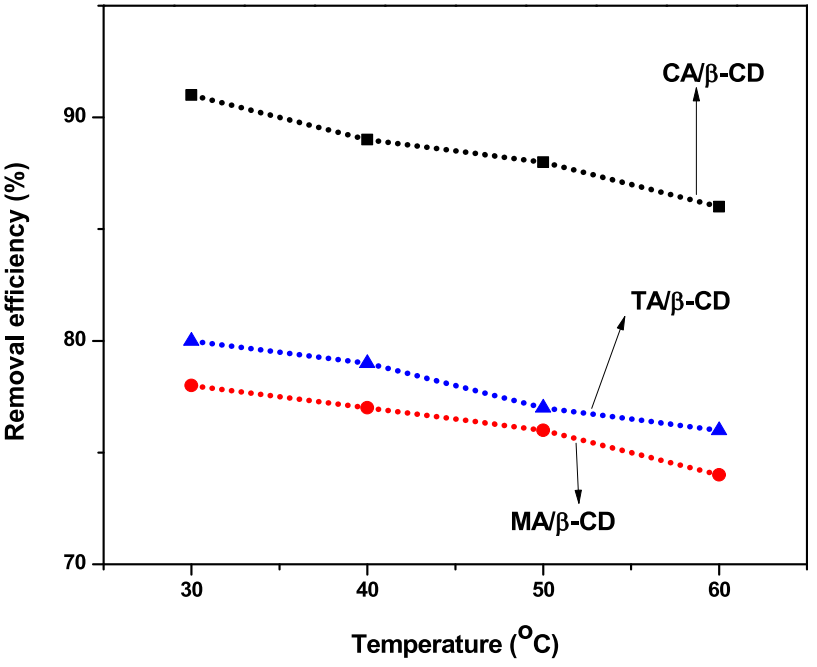

Figure 9. Effect of temperature on MG elimination performance.

as the MG concentration increases from 20 to 50 mg L^{-1}, the removal performance decreases. The decrease in elimination performance is due to the unavailability of the adsorbent surface at excessive MG concentrations for adsorption of dyes. However, the adsorption potential of CA/β-CD was excessive at an MG concentration of 10 mg L^{-1}, and the adsorption capability of MA/β-CD was low. Finally, it was found that the optimal concentration of MG was 10 mg L^{-1}, and this concentration was used for all of the experiments.

Effect of Temperature on Elimination Performance. The effect of temperature on an adsorbent's ability to eliminate MG was investigated using a temperature range of 30−60 °C, as depicted in Figure 9. As the temperature rose from 30 to 60 °C, the ability to remove MG decreased because at higher temperatures, the electrostatic attraction between the adsorbate and adsorbents tends to become more fragile. The adsorption process becomes exothermic with increasing temperatures, reducing the MG elimination performance. Similarly, the removal efficiency reduced on increasing the temperature from 30 to 40 °C, as opposed to at a higher temperature, where the elimination performance altered to improve at normal temperature. The experiment revealed that 30 °C is the ideal temperature for the elimination of MG via adsorption.

Effect of Contact Time on Elimination Performance. The process of time-bound adsorption was extensively investigated because, despite the possibility of having enough active sites on the adsorbent surface, the binding of the MG molecule on the adsorbent is not simultaneous. Figure 10 shows the evaluation of the removal effectiveness of MG by the adsorbents at the

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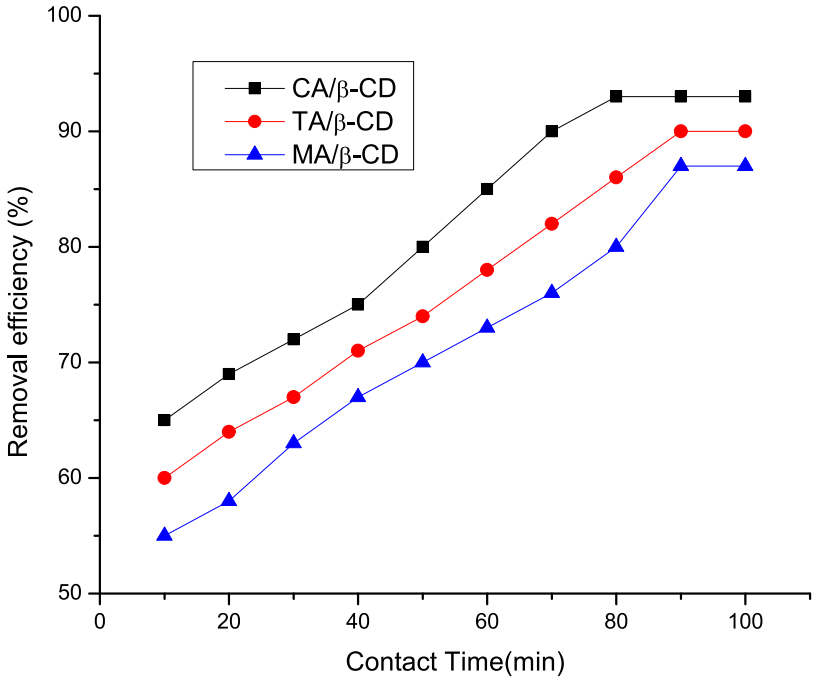

Figure 10. Effect of contact time on the elimination performance.

optimal adsorbent dosage of 100 mg, pH 6, and dye concentration 10 mg L^{-1}. The initial results indicated removal efficiencies for CA/*β*-CD, TA/ *β*-CD, and MA/*β*-CD of 90.39, 83.69, and 79.01%, respectively, during a contact duration of 80 min. Due to the abundance of active sites and the large surface area of the adsorbents, the MG adsorption process was greatly accelerated. Furthermore, because no adsorbent shows any preference, the saturation was changed to 80 min duration.

In brief, all four parameters have a profound influence on the removal efficiency of MG from the three adsorbents studied. However, pH plays a vital role in creating the ionic forms of the dye and the surface of the adsorbents, which forms the basis of the adsorption process through electrostatic forces of attraction. These results are in accordance with the other reported works on the removal of malachite green dye.[47,48]

Adsorption Isotherms. The Langmuir and Freundlich isothermal models were used to explore the equilibrium of dye adsorption via adsorbents.[49] Langmuir and Freundlich isotherm models were used to explore the equilibrium of dye adsorption using adsorbents. Studies on adsorption isotherms helped us understand the interaction of the MG dye, an adsorbate, and the adsorbent, namely, CA/*β*CD, TA/*β*CD, or MA/*β*CD. The data indicated that the correlation coefficient R^2 values using the Langmuir equation were higher for CA/*β*CD and TA/*β*CD, while a marginally higher value of 0.988 was obtained for MA/*β*CD using the Freundlich isotherm model. However, it may be mentioned that overall values of the Langmuir isotherm of 0.996 and 0.993 for CA/*β*CD and TA/*β*CD were higher than the 0.988 for MA/*β*CD obtained using the Freundlich isotherm model. Thus, it may be inferred that the Langmuir isotherm model is better suited for the adsorption process as shown in Figure 11a,b and stated in Table 2.

Studies on adsorption isotherms helped us understand the interaction of the MG dye, an adsorbate, and the adsorbent, namely, CA/*β*-CD, TA/*β*-CD, or MA/*β*-CD. The data indicated that the correlation coefficient R^2 values using the Langmuir equation were higher for CA/*β*-CD and TA/*β*-CD, while a marginally higher value of 0.988 was obtained for MA/*β*CD using the Freundlich isotherm model. However, it may be mentioned that overall values of the Langmuir isotherm of 0.996 and 0.993 for CA/*β*-CD and TA/*β*-CD were higher than the 0.988 for MA/*β*-CD obtained using the Freundlich isotherm model. Thus, it may be inferred that the Langmuir isotherm model is better suited for the adsorption process.

Adsorption Kinetic Study. Batch Kinetic Studies. The pseudo-first-order Lagergren model was used for describing adsorption/absorption kinetics.[50] The kinetic data were fitted with the nonlinearized pseudo-second-order kinetic model.[51] MG removal by using the polymer adsorbents seems to comply with the pseudo-second-order kinetics. The correlation coefficient, R^2, is determined to be higher for the pseudo-second-order kinetic response equation than for the pseudo-first-order kinetic equation, suggesting once more that the kinetic data agree well with the pseudo-second-order kinetic model in Figure 12a,b and Table 3. In brief, the Langmuir isotherm model and pseudo-second-order kinetics are more suitable to model the adsorption process of all three adsorbents to adsorb MG dye. These trends are in accordance with the other reported works on the removal of malachite green dye.[47,48]

The cross-linked citric acid on the *β*-cyclodextrin matrix proved to be an effective adsorbent to remove malachite green dye from the aqueous solution. There are several studies reported in the literature, and the current findings suggest a cheaper and sustainable alternative in the adsorption technologies. Table 4 compiles the literature along with the reported data in this work.

Reusability Studies. Stability, recyclability, and the economic aspect are essential characteristics for an adsorbent. For the resurrection of MG-loaded polymers in this investigation, 50 mL of 0.5 M HCl in water, 50 mL of 0.5 N HCl in ethanol, and 50 mL of 0.5 M HCl in water−ethanol were utilized individually. For the dye-loaded adsorbents in

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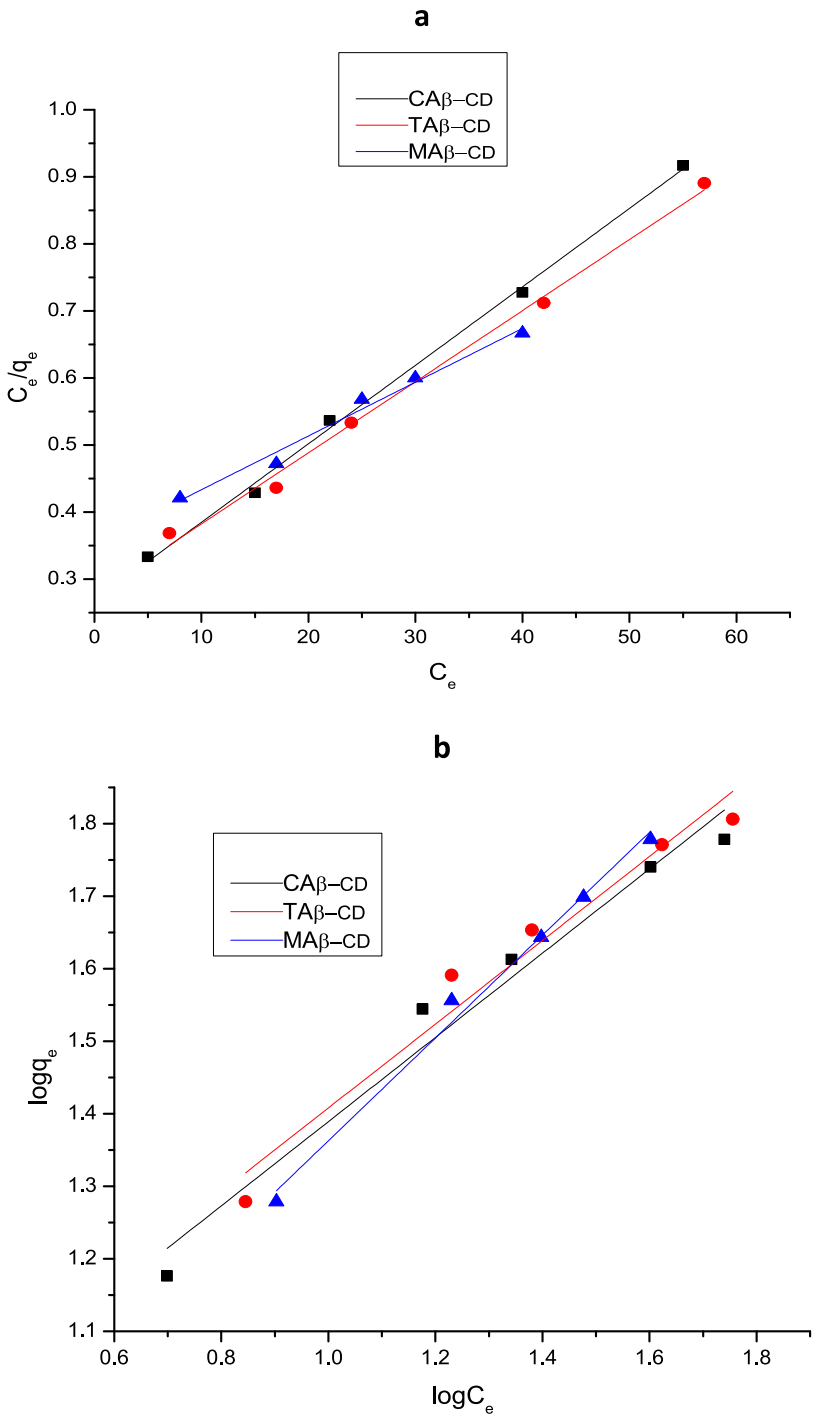

Figure 11. (a) Langmuir adsorption isotherm and (b) Freundlich adsorption isotherm of CA/*β*-CD, TA/*β*-CD, and MA/*β*-CD for the adsorption of MG.

Table 2. Adsorption Isotherm Model Constants and Correlation Coefficients for Adsorption of MG on Adsorbents

	Langmuir constants			Freundlich constants		
adsorbents	K_l	q_m	R^2	$1/n$	K_f	R^2
CA/*β*-CD	0.0436	85.47	0.996	0.58	3.801	0.962
TA/*β*-CD	0.0383	94.33	0.993	0.577	3.775	0.952
MA/*β*-CD	0.0226	124.84	0.978	0.709	5.116	0.988

Figure 13, the three regenerating solvents, each containing 0.5 M HCl in water, function better than any other. With various recycles, the MG removal efficiency gradually declined. With each cycle, this caused the elimination efficiency to gradually decline. Adsorbents can be employed up to 5 cycles with an elimination performance of 70−90% in the current design. Adsorbents may therefore be effective, efficient, and reasonably priced materials for the removal of MG from aqueous MG solutions.

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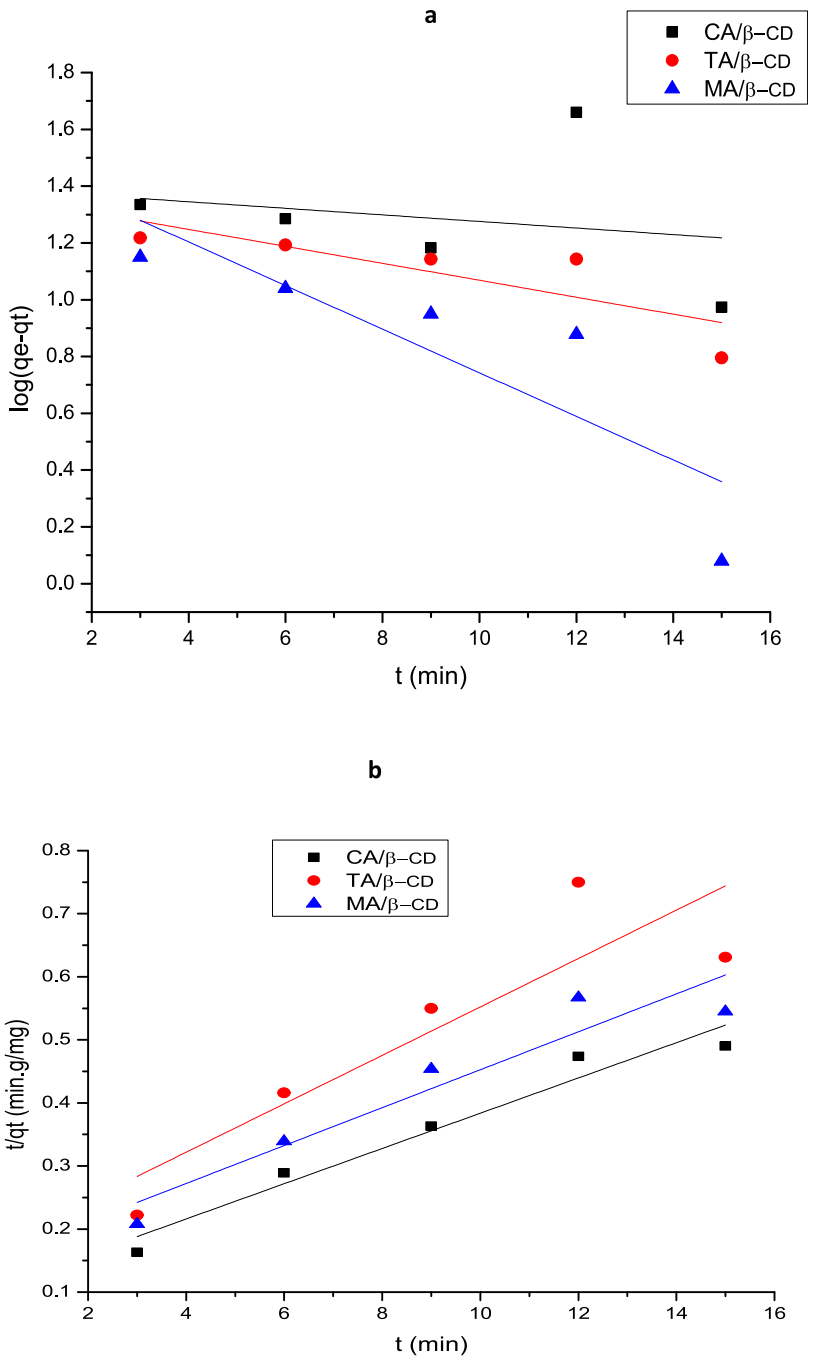

Figure 12. Adsorption kinetics of MG onto CA/*β*-CD, TA/*β*-CD, and MA/*β*-CD: (a) pseudo-first-order kinetics and (b) pseudo-second-order kinetics.

Table 3. Adsorption Kinetics of MG onto CA/*β*-CD, TA/*β*-CD, and MA/*β*-CD: (a) Pseudo-First-Order Kinetics and (b) Pseudo-Second-Order Kinetics

	pseudo-first-order					pseudo-second-order		
adsorbents	C_0 (mg L^{-1})	Q_e, exp (mg g^{-1})	K_1 (min^{-1})	Q_e, cal (mg g^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	Q_e, cal (mg g^{-1})	R^2
CA/*β*-CD	10	1.12	−0.0266	24.620	−0.26	0.00701	37.037037	0.94
TA/*β*-CD	10	1.04	−0.0686	23.291	0.56	0.0086	26.315789	0.73
MA/*β*-CD	10	0.98	−0.175	32.359	0.64	0.00596	33.333333	0.87

CONCLUSIONS

In this study, different organic acids such as citric acid (CA), tartaric acid (TA), and malic acid (MA) were cross-linked with *β*-cyclodextrin to synthesize water-insoluble *β*-cyclodextrin (*β*-CD) polymers like CA/*β*-CD, TA/*β*-CD, and MA/*β*-CD. The obtained polymers were characterized by different advanced analytical techniques. The synthetic polymers were employed to adsorb MG from aqueous solutions. The adsorption

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Table 4. Removal of Malachite Green from Various Adsorbents

adsorbents	pH	maximum adsorption capacity (mg g^{-1})	reference
carboxylate group-functionalized multiwalled carbon nanotubes	9	11.8	52,53
ZnO nanorod-loaded activated carbon	6	20	54
nickel hydroxide nanoplate-modified activated carbon	6.5	76.9	55
lignin sulfonate-based mesoporous materials	7	121	56
copper nanowires loaded on activated carbon	5	164	57
potassium salt-activated carbons from textile sludge	6	167	58
biobased magnetic activated carbon	6	218	59
zeolite nanostructures from waste aluminum cans		227	60
sulfonic acid-modified coal fly ash		233	61
starch-*graft*-poly(acrylamide) hydrogels	5.5	287	62
magnetic-cyclodextrin-graphene oxide nanocomposites	7	741	63
fibrous cellulose sulfate	6	960	64
oxidized mesoporous carbon	6.5	1265	65
citric acid cross-linked on *β*-cyclodextrin	**6**	**903.6**	**this work**

investigation was conducted in different conditions, and optimized conditions were investigated for the best adsorption of MG at pH = 6, adsorbent mass = 100 mg, MG concentration = 10 mg L^{-1}, temperature = 30 °C, contact time = 10−80 min, adsorption isotherm is the Freundlich isotherm, kinetics is the pseudo-second-order, and thermodynamics. The adsorbent CA/*β*-CD shows the highest adsorption of MG in all of the conditions because it contains a high number of carboxyl groups. The negatively charged carboxyl ions of CA/*β*-CD attracted positively charged MG electrostatically and removed MG from aqueous media with an efficiency of 90%. As a result, the findings demonstrated that water-insoluble polymers based on cyclodextrin might be employed as a cheaper alternative to expensive adsorbents for the removal of MG from aqueous solutions. The removal efficiency and reusability of the three adsorbents studied are in the order CA/*β*-CD > TA/*β*-CD > MA/*β*-CD. This is understandable as there are four, four, and three −OH groups, respectively. Besides, CA has an additional three electronegative = O groups, which helps enhance the adsorption process of the cationic MG dye in acidic pH.

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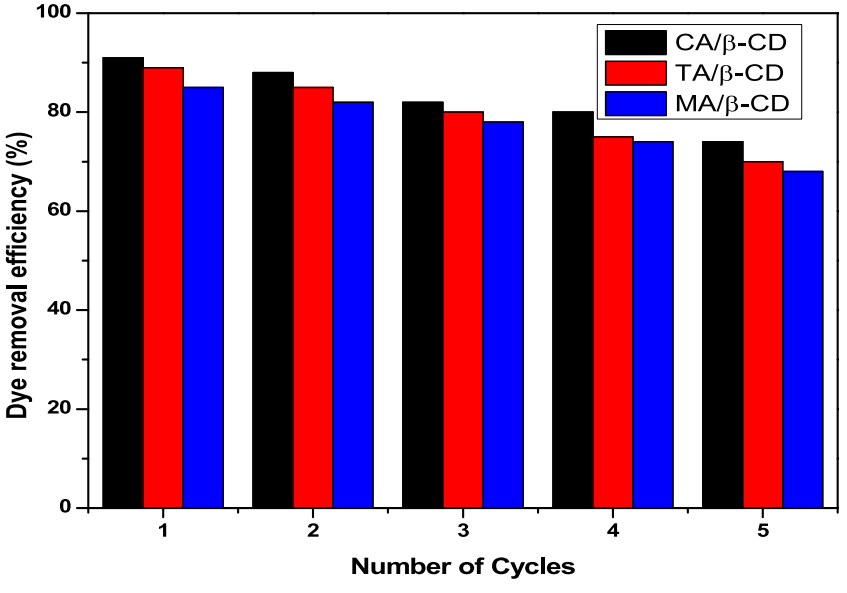

Figure 13. Reusability of adsorbents, CA/*β*-CD, TA/*β*-CD, and MA/*β*-CD.

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Notes

The authors declare no competing financial interest.

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