Cucurbituril-Functionalized Nanocomposite as a Promising Industrial Adsorbent for Rapid Cationic Dye Removal

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ABSTRACT: A supramolecular cucurbit[6]uril (CB[6])-enriched magnetic montmorillonite (CBCM) nanocomposite was prepared and characterized. CB[6] played a prominent role as a capping agent, helping in better distribution of the nanoparticles, and as a binder between nanoparticles. Montmorillonite provided structural stability and fortified ultrafast adsorption toward dyes. Its application in the removal of cationic dyes from wastewater was systematically assessed. Process parameters such as pH, initial dye concentration, dosage, temperature, and time were optimized. Kinetics and isotherms of the process were described using pseudo-second-order kinetics and the Langmuir isotherm, respectively. CBCM exhibited rapid dye removal capacity in short reaction times with $q_{\text{max}}$ of 199.20, 78.31, and 55.62 mg g$^{-1}$ and $K_2$ of 0.0281, 0.0.0823, and 0.0953 L mg$^{-1}$ min$^{-1}$ for crystal violet, methylene blue, and rhodamine B, respectively. Benefiting from the synergetic effects of montmorillonite surface hydrophobicity, abundant carbonyl groups of CB[6], and magnetic properties of copper ferrite, CBCM demonstrated outstanding dye removal capacity, negligible leaching at saturation, and high tolerance toward harsh conditions. This intrinsic nature is expedient in prolonged industrial operations. To demonstrate industrial viability, syringe filtration and continuous flow fixed-bed column operations were validated. The CBCM fixed-bed column demonstrated stable dye removal efficiency with 10–100 mg mL$^{-1}$ dye at 10–50 mL min$^{-1}$ flow rates. Utilizing the magnetic and catalytic activities of the copper ferrite nanoparticles, CBCM was recycled using a magnet, regenerated, and reused for several cycles. CB[6] remarkably improved the performance of the nanocomposite and made it suitable for different effluent treatment techniques. This may pave a sustainable way toward the efficient onsite treatment of effluent at the industrial scale.

1. INTRODUCTION

Dyes have been extensively used in textile industries and are the foremost source of severe water pollution. More than 1 00 000 types of dyes are available in the market, and each year, about 7 00 000 tons of dyes are prepared globally, leading to severe health hazards. Numerous methods such as adsorption, membrane filtration, coagulation, distillation, oxidation, ion exchange, electrolysis, precipitation, photochemical degradation, and reverse osmosis have been used to treat dye-contaminated water. Among these, adsorption is a widespread method used for industrial-scale effluent treatment. Based on targeted pollutants, these methods utilize different adsorbents such as activated carbon, clay, ion-exchange materials, biosorbents, zeolite, biodegradable composites, and hybrid materials. Nevertheless, adsorption over clay minerals and modified clay-based materials have been proven to be highly favored over other adsorbents due to their process simplicity, cost-effectiveness, commercial availability, good efficiency, and eco-friendly nature. However, these adsorbents suffer from common operational issues such as reusability, stability in long-duration operations, and dye leaching after saturation. Clays were modified with different materials to overcome these operational issues. In this direction, montmorillonite (MMT) clay applicability in dye removal at a larger scale was improved by enriching with cucurbit[6]uril (CB[6]) and copper ferrite nanoparticles. Cucurbit[6]urils (CB[6]s) are cage-shaped supramolecules known for their host–guest complex formation ability, especially with cationic molecules, through noncovalent, electrostatic interactions. The inner cavity of CB[n] is hydrophobic and accessible through two identical carbonyl portals to form inclusive complexes with the cationic guests. CB[n]s are also unique candidates for nanoparticle-capping, where they bind over the nanoparticle surface and also provide an available cavity for guest binding. The complexation of CB[n] with azo dyes, textile dyes, and reactive dyes was studied by Buschmann and Karcher to understand the binding mechanism and its probable application in wastewater treatment. Among homologues of CB[n], CB[6] is a suitable adsorbent for wastewater treatment due to its better thermal
stability, good binding nature, and poor solubility in water. Moreover, CB[6] is insoluble in water and can be recovered by simple filtration after the experiment, whereas CB[5] and CB[7] are soluble in water. When CB[6] was directly used as an adsorbent, it was only able to remove a minimum quantity of dyes but exhibited exceptional binding with greater selectivity. To utilize the advantages of CB[6] dye-binding capabilities, Karcher et al. suggested coating CB[6] over a solid support material to prevent leaching of CB[6] into the effluent. Jin and group have implemented a similar strategy to prepare a CB[7]-modified polymer for adsorption of methylene blue (MB) and CB[6]-anchored silica for adsorption of an antibiotic sulfonylmethoxime. Lazzara et al. have employed halloysite as solid support for CB[8] to adsorb toluene vapors. CB[6] possesses a lower equilibrium association constant when complexed with a larger dye molecule, but it does exhibit shallow interactions with large positively charged moieties. Similarly, researchers have reported the use of CB[6]-based composites for different applications. This phenomenon could greatly improve traditional clay-based adsorbents in terms of selectivity and reusability. Therefore, utilizing the nanoparticle-capping ability and complexation phenomenon of CB[6], we have synthesized an improved CB[6]-capped magnetic cobalt ferrite nanoparticle-enriched montmorillonite (CBCM) clay nanocomposite for wastewater treatment. Since the separation, regeneration, and reusability of the adsorbent material are crucial concerns needed to be addressed, the magnetically separable montmorillonite composite by introducing magnetic nanoparticles into clay sheets makes adsorbent separation easy, rapid, and suitable for bulk solutions in heterogeneous systems. On the other hand, copper ferrite nanoparticles possess unique properties such as moderate saturation magnetization, high coercivity, chemical stability, mechanical hardness, and magnetic crystalline anisotropy. Owing to these interesting properties, we used CoFe2O4 nanoparticles to induce magnetism in the CBCM nanocomposite. The CBCM composite aimed to provide enhanced, rapid dye adsorption; good reusability; and selectivity for wastewater treatment. Since the separation, regeneration, and reusability of the adsorbent material are crucial concerns needed to be addressed, the magnetically separable montmorillonite composite by introducing magnetic nanoparticles into clay sheets makes adsorbent separation easy, rapid, and suitable for bulk solutions in heterogeneous systems. On the other hand, copper ferrite nanoparticles possess unique properties such as moderate saturation magnetization, high coercivity, chemical stability, mechanical hardness, and magnetic crystalline anisotropy. Owing to these interesting properties, we used CoFe2O4 nanoparticles to induce magnetism in the CBCM nanocomposite. The CBCM composite aimed to provide enhanced, rapid dye adsorption; good reusability; and selectivity for wastewater treatment, and it was synthesized by an ultrasonication-assisted co-precipitation method and characterized using adequate analytical techniques. Comprehensive dye removal studies using the CBCM nanocomposite have been conducted for the removal of selected dyes, crystal violet (CV), methylene blue (MB), and rhodamine B (RhB), from aqueous solutions (Figure S1, Supporting Information (SI)). Large-scale industrial applications of CBCM was also demonstrated through syringe filters and continuous flow fixed-bed column operations.

2. MATERIALS AND METHODS

Iron(III) chloride hexahydrate, cobalt(II) chloride hexahydrate, and sodium hydroxide were purchased from Merck Inc. Glycoluril, montmorillonite K10 (Sigma-Aldrich), crystal violet (CV) (Sigma-Aldrich, C16H18ClN3S.3H2O, 373.9 g mol$^{-1}$), methylene blue (MB) (Sigma-Aldrich, C16H18ClN3S.3H2O, 373.9 g mol$^{-1}$), and rhodamine B (RhB), from aqueous solutions (Figure S1, Supporting Information (SI)). Large-scale industrial applicability of CBCM was also demonstrated through syringe filters and continuous flow fixed-bed column operations.

2.1. Synthesis of the CBCM Nanocomposite. CoFe2O4 nanoparticles, exfoliated montmorillonite (ex-MMT), and CB[6] were prepared according to previously reported methods. An aqueous solution containing 1.0 g of as-prepared CoFe2O4 nanoparticles was taken in a beaker, and 0.6 g of CB[6] was added to the solution and then sonicated for 1 h. The resulting suspension was further stirred at room temperature for 1 h; then, solid CB[6]-capped cobalt ferrite nanoparticles (CB[6]-CoFe2O4) were isolated using a magnet, washed with DI water, and dried at 100 °C for 3 h. Solid, dried CB[6]-CoFe2O4, was added to a 5.0% aqueous suspension of ex-MMT. The suspension was sonicated for 1 h and stirred overnight at room temperature. The suspended solid was separated using a magnet, washed several times with DI water, and dried at 100 °C in an oven, followed by calcination at 200 °C for 2 h to obtain a black CBCM nanocomposite (Figure S1, SI), which was characterized and used as such for dye removal studies.

2.2. Characterization of the CBCM Nanocomposite.

Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) surface area measurements, thermogravimetric analysis (TGA), and diffuse reflectance UV–visible (DR UV–vis) spectroscopy were used to characterize morphological, optical, and structural properties of the CBCM nanocomposite. The FTIR spectrum was obtained in the range of 4000–400 cm$^{-1}$ using a PerkinElmer spectrum-II infrared spectrophotometer with an attenuated total reflectance (ATR) accessory. XRD analysis was carried out using a PANalytical X’pert-pro X-ray diffractometer in the 2θ range of 10–80° using Cu Kα radiation. FE-SEM images were acquired using a LEO 1550 Gemini (Zeiss) scanning electron microscope. TEM imaging was carried out on a TEI, Tecnai G2, F30 (300 kV potential) instrument. TGA was performed on a NETZSCH TG 209F1 Libra TGA209F1D-0105-L instrument in the temperature range of 50–1000 °C at a 10 °C min$^{-1}$ step size in an argon atmosphere. Solid-state diffuse reflectance UV–vis spectra were recorded on a Shimadzu UV-2600 spectrophotometer in the range of 200–900 nm at a 1 nm step size. Nitrogen adsorption–desorption-based five-point BET surface area measurement was carried out on a Quantachrome Autosorb-IQ instrument. ζ Potential was measured using a Malvern Zetasizer Lab instrument by dispersing 2 mg of CBCM in 2 mL of DI water. In dye removal studies, the dye concentration was determined by the Beer–Lambert method using a UV–vis spectrophotometer (Labindia, model: UV-3000+). The pH of the solutions was measured using a Hanna edge pH meter equipped with a HI111310 electrode calibrated with a three-point method using standard buffer solutions. The point of zero charge (PZC) was determined by the standard solid addition method.

2.3. Dye Adsorption Studies. 2.3.1. Batch Experiments. A set of experiments was carried out to determine the effect of varying pH, temperature, adsorbent loading, and dye concentration on the dye removal efficiency of CBCM. Adsorption isotherms were plotted by experimentally determining the relationship between the dye concentration and the amount of dye adsorbed. The kinetics of adsorption was determined by performing experiments with respect to time. All dye stock solutions were prepared by dissolving a definite amount of solid in deionized water to obtain the desired concentration. Working solutions of dyes were prepared from the stock solution (200 mg L$^{-1}$) to the desired concentrations (10–100 mg L$^{-1}$). All of the experiments were carried out at a constant speed on a slow-moving platform shaker. The initial pH value of the dye solutions was adjusted with 0.1 M HCl or 0.1 M NaOH solution in pH studies.
Adsorption experiments were carried out typically by adding a definite amount of the CBCM nanocomposite to 3 mL of the dye solution in 5 mL polypropylene vials. The adsorption studies were carried out at different pH values (2, 4, 7, 8, and 10), temperatures (35, 45, and 55 °C), adsorbent dosages (0.03–0.2 mg mL⁻¹), and initial dye concentrations (10–100 mg mL⁻¹). UV–vis analysis of all adsorbed samples was performed after reaching equilibrium at the maximum absorption wavelength (λmax) of the dye (CV, MB, and RhB exhibited maximum absorbance (λmax) at 585, 665, and 554 nm, respectively). The absorbance of the dye solution from batch experiments was measured after magnetic separation of CBCM to avoid turbidity. The amount of the dye adsorbed per unit mass of the adsorbent at time t and equilibrium are qt (mg g⁻¹) and qe (mg g⁻¹), respectively, calculated using eqs 1 and 2

\[ q_t = \frac{(C_0 - C_t)V}{W} \]  
\[ q_e = \frac{(C_0 - C_e)V}{W} \]  

where \(C_0\) (mg L⁻¹), \(C_t\) (mg L⁻¹), and \(C_e\) (mg L⁻¹) are the initial dye concentration and remaining dye concentration after adsorption at time t and equilibrium, respectively. V is the liquid volume (L) and W is the dosage of the solid adsorbent (g).

2.4. Recovery and Regeneration of the CBCM Nanocomposite. After completion of dye adsorption, the CBCM nanocomposite was recovered with a magnet and was regenerated by the catalytic reduction method using 0.1 M sodium borohydride. Since the dye adsorbed on the CBCM composite was difficult to desorb using DI water, electrolyte, or mild acid washes due to resilient adsorption, the catalytic reduction method was adopted to regenerate the nanocomposite quickly and to reduce secondary dye effluent generation. In a typical procedure, the CBCM nanocomposite was treated with a 0.1 M sodium borohydride aqueous solution until complete decolorization was achieved and collected with the help of a magnet, washed with deionized water, dried in an
oven at 110 °C for 3 h, and reused in subsequent adsorption experiments.

2.5. Dye Removal Using CBCM-Loaded Syringe Filters. Commercial nylon syringe filters with a 0.22 μm pore size were loaded with the CBCM nanocomposite. Then, 20 mg of the CBCM nanocomposite was dispersed uniformly in 5 mL of DI water and injected into the syringe filters; then, they were dried at 60 °C in a hot air oven. These CBCM-loaded syringe filters were used for the demonstration of instant dye removal on a small scale. The dye-contaminated water was filtered through the CBCM-modified syringe filter using a syringe to obtain decolorized water instantly (Figure S5, SI). The saturated CBCM-modified syringe filter was regenerated by passing 10% sodium borohydride solution until complete removal of color. Then, it was washed with DI water and dried completely in a hot air oven. The regenerated syringe filter was again used for instant dye removal (SI).

2.6. Dye Removal Using a Continuous Flow CBCM Fixed-Bed Column. A continuous flow fixed-bed column was prepared by loading a polycarbonate column with the CBCM nanocomposite, with a 1.8 cm distance in between sand layers and the polymer mesh separator. Dye effluent was fed from the top of the column using a rotary drive pump. The flow rate was adjusted using a flow-regulating knob fitted before the inlet. Influent and effluent dye concentrations were determined using UV–visible spectra by collecting at least 2 mL of the solution at definite time intervals. Complete details of the study with photographs, graphs, and a representative video are available in the Supporting Information (SI).

3. RESULTS AND DISCUSSION

3.1. FTIR. Formation of the CBCM nanocomposite was determined using FTIR spectra by comparing with spectra of its constituents (Figure 1A,B). Cobalt ferrite exhibited two characteristic peaks at 588 and 416 cm⁻¹ in the FTIR spectrum, which were assigned to metal–oxygen intrinsic vibrations of tetrahedral and octahedral sites in the spinel ferrite structure, respectively.55,46 These characteristic vibrational peaks shifted to 590 and 420 cm⁻¹, respectively, in CBCM due to different metal–oxygen bond lengths. The spectrum of pure CB[6] exhibited peaks at 1713, 965, and 799 cm⁻¹ assigned to carbonyl stretching, mixed vibrations of C–C and C–N bonds, and the rocking of CH₂, respectively (Figure S2C, SI). A minor shift was observed for CB[6] carbonyl peaks when splitting into two at 1726 and 1628 cm⁻¹.

3.2. XRD. A comparison of the powder XRD diffractogram of CoFe₂O₄ with that of the CBCM nanocomposite is presented in Figure 1C. Intense diffraction peaks of CoFe₂O₄ at 2θ = 18.0, 30.1, 35.4, 43.1, 53.4, 57.0, and 62.6° were ascribed to the reflection of 111, 220, 311, 400, 422, 511, and 440 planes of CoFe₂O₄, which were well-indexed to the cubic spinel structure (JCPDS card no. 22-1086).47 Peaks at 2θ = 19.8, 26.6, 34.9, and 50.138° represent the characteristic peaks of MMT (JCPDS file no. 29-149848 (Figure S2B). CB[6] merely showed a broad hump in XRD spectra and did not have any distinct effect on XRD due to its amorphous nature. Diffraction peaks of the CBCM nanocomposite were obtained at 2θ = 17.7, 19.8, 26.6, 30.2, 34.9, 35.5, 43.3, 50.138, 52.6, 57.1, and 62.8° (Figure 1C). All characteristic diffraction peaks of CoFe₂O₄ and MMT were indexed in the CBCM nanocomposite diffractogram, which confirmed the presence of CB[6]-capped CoFe₂O₄ within the MMT clay lamella. The average crystallite size of CoFe₂O₄ nanoparticles in the CBCM nanocomposite was found to be 26.2 nm, calculated using the Scherrer equation with respect to the most intense peak at 2θ = 53.5° (311) corresponding to nanoparticles.

3.3. TGA. Thermogravimetric analysis of the CBCM nanocomposite resulted in three distinct weight-loss regions (Figure 1E,F). The first weight-loss region due to moisture loss was observed below 180 °C with a total 6.0% weight loss. CBCM exhibited a major weight loss of 23.1% from 280 to 450 °C attributed to the presence of CB[6]. A similar weight-loss region was also observed in CB[6] (Figure S2C). The third small weight-loss region near 800 °C specified the phase shift of MMT. These insights confirmed the incorporation of cobalt ferrite and CB[6] within the MMT lamella. Onset temperature shifts for CB[6] indicated the improved thermal stability of CB[6] in the CBCM nanocomposite. Moreover, the absence of the peak representing deformation of cobalt ferrite at around 800 °C in the CBCM thermogram confirmed the nanoparticle-capping of CB[6] via noncovalent interactions discussed in the Section 3.1. These interactions were instrumental in providing stability and preventing the deformation of nanoparticles at higher temperatures.

3.4. Solid-State DR UV–Vis Spectroscopy. Diffuse reflectance UV–visible (DR UV–vis) spectra of CoFe₂O₄ and CBCM are shown in Figure 1D. Adsorption of CBCM unveiled the combined nature of CB[6], CoFe₂O₄, and MMT (Figure 1D). Optical adsorption of CB[6] and MMT occurred in the UV region below 400 nm, whereas optical adsorption of CoFe₂O₄ took place majorly in the UV region then gradually reduced toward the near-infrared region with band-edge adsorption at 1090 nm19,49 (Figures 1D and S2E, SI). Similarly, CBCM exhibited a broad absorption band in the UV region, which extended toward the visible region. Band-edge adsorption at 1049 nm was noted with a blue shift compared to bare CoFe₂O₄ nanoparticles. Broad absorption in the UV–vis region of CBCM confirmed the exfoliation of MMT and specified the interaction between CoFe₂O₄ and MMT.

3.5. FE-SEM and TEM. The morphology of the CBCM nanocomposite was studied using FE-SEM and TEM (Figure 2). The original structure of exfoliated MMT covered with...
CB[6]-capped CoFe2O4 in the CBCM nanocomposite confirmed the modification of the clay lamella (Figure 2A, B). MMT was used as a solid medium for supporting CB[6]-capped CoFe2O4 nanoparticles to improve the stability and applicability of the particles. Correspondingly, the TGA of the CBCM nanocomposite also confirmed the higher thermal and structural stability of nanoparticles within the CBCM nanocomposite. Energy-dispersive X-ray (EDX) spectra of the composite established the presence of all of the individual components in the nanocomposite (Figure 2C). The average particle size of CoFe2O4 in CBCM was determined to be about 26 nm. Similar observations were made by TEM micrographs (Figure 2E–H). CB[6]-capped CoFe2O4 nanoparticles were distributed over exfoliated MMT layers, creating void spaces. The CoFe2O4 nanoparticles appeared to be densely anchored on the surface of exfoliated MMT, implying the strong interaction between CB[6]-capped CoFe2O4 nanoparticles and MMT. More importantly, even after prolonged sonication, the nanoparticles were strongly bound to the MMT lamella with the help of magnetic dipolar interactions among nanoparticles and noncovalent interactions induced by CB[6]. EDX spectra recorded from the selected points of the CBCM nanocomposite also confirmed the presence of CB[6], MMT. The organic matter surrounding the nanoparticles was attributed to the capping of CB[6]. The selected area electron diffraction (SAED) pattern of the nanoparticle region in the CBCM nanocomposite exhibited a multicrystalline nature with visible diffraction bright spots and diffuse circles (Figure 2F, inset). The first two sets of diffuse circles indicating 220 and 311 planes correspond to the most intense peaks of CuFe2O4 nanoparticles. Likewise, the SAED image of the clay region exhibited mostly a diffuse circle without notable bright spots, indicating the presence of the amorphous MMT clay (Figure 2H, inset). SAED patterns confirmed the presence of nanoparticles and clay, indicating the formation of the CBCM nanocomposite. Insights gained from electron microscopic images indicate that the CBCM structural framework could be determined as CB[6]-capped CoFe2O4 decorated over the clay lamella. CB[6]-capped CoFe2O4 nanoparticle aggregates comprised even smaller subunits, indicating that nanoparticle assemblies formed first and then agglomerated over the MMT clay lamella. Finally, the CBCM nanocomposite surface area determined by the five-point BET method was found to be 71.87 m² g⁻¹, suitable for adsorption experiments (Figure S2F). Based on structural and morphological topographies of the CBCM nanocomposite, its

Figure 2. (A, B) FE-SEM images, (C) EDAX spectra from FE-SEM, (D) EDAX spectra from TEM, (E–H) TEM images, and SAED diffraction patterns (inset) of the CBCM nanocomposite. Here, the inset in (F) represents the SAED pattern recorded from the nanoparticle region and the inset in (H) shows the SAED pattern taken from the clay region of the CBCM nanocomposite.

Figure 3. (A) Comparison of the dye removal efficiency of the CBCM nanocomposite with CB[6] and CuFe2O4 nanoparticles to understand the synergetic effects and (B) point of zero charge plot of the CBCM nanocomposite.
application was explored in dye removal from aqueous solutions using three different dyes, CV, MB, and RhB, in batch and continuous flow experiments, envisaging the CBCM nanocomposite use in industrial effluent treatment.

3.6. Dye Removal Studies. The CBCM nanocomposite was investigated for the removal of selected dyes [CV, MB, and RhB] from water by performing batch and continuous flow experiments. Initial dye removal experiments were conducted to evaluate the synergetic effects of CBCM in comparison with its constituents. Under identical experimental conditions, maximum dye adsorption for all three dyes was observed in the following order: CBCM > CoFe₂O₄−CB[6] > CB[6] > CoFe₂O₄ (Figure 3A). Thus, CBCM exhibited the maximum adsorption, revealing synergic effects between its constituents. Capping CoFe₂O₄ with CB[6] eventually amplified the adsorption capacity of the nanoparticles due to partially negative carbonyl portals of CB[6] and increased affinity toward cationic dye molecules. When these CB[6]-capped CoFe₂O₄ nanoparticles were intercalated into the MMT lamella, they created a similar effect and helped to achieve more adsorption. With these results in hand, comprehensive dye removal batch experiments were conducted, and adsorption isotherms and kinetics were determined. Further, studies on the versatile applicability, regeneration, and reusability of CBCM were also performed systematically. CBCM-loaded syringe filters and continuous flow fixed-bed columns were fabricated for instant treatment of wastewater at the industrial scale.

3.7. Effect of pH. pH is an essential aspect that gives an understanding of dye–adsorbent interactions and the ionic form of the dye that is favorable for higher adsorption.⁵⁰ To understand the effect of pH on the dye removal efficiency, different dye solutions with varying pH values from 2 to 10 were studied (Figure 4A–C). The maximum dye removal percentages for CV (90%) and MB (52%) were recorded at pH 7 and that for RhB (34%) was observed at pH 2 under

Figure 4. Effect of various parameters on the adsorption of CV (purple), MB (blue), and RhB (pink) dyes from aqueous solutions using the CBCM nanocomposite. (A–C) Effects of pH, (D–F) temperature, (G–I) adsorbent dosage, and (J–L) initial dye concentration. Here, the red line with the triangle symbol (△) represents color removal efficiencies and the black line with the sphere symbol (●) represents the adsorption capacity at equilibrium (qₑ).
identical experimental conditions. The dye removal percentage of CV and MB increased with pH until pH 8 and thereafter remained unchanged, whereas, in the case of RhB, the dye removal percentage decreased with the increase in the solution pH. This behavior based on electrostatic interactions was explained by the point of zero charge (PZC). The PZC is defined as the point where the surface charge of the adsorbent material is zero. Accordingly, if the pH is less than the PZC, the adsorbent surface is positively charged, and if the pH is greater than the PZC, then the adsorbent surface is negatively charged. The PZC of the CBCM nanocomposite was determined as 7.3 using the solid addition method (Figure 3B). Hence, below pH 7.3, CBCM acquires a positive surface charge. In this condition, both H⁺ ions and the dye cations compete for positively charged adsorption sites on the CBCM surface, resulting in a decreased adsorption capacity. If the pH was more than 7.3, the CBCM surface would have been predominated by a negative charge; therefore, electrostatic interactions occur between the dye and the negatively charged adsorption sites, resulting in higher dye adsorption. RhB exhibited maximum adsorption between pH 2 and 3. In RhB, the COOH group exists in the protonated form below pH 3, thus leading to the formation of RhB⁺ ion, whereas at pH above 3, the dye exists in the zwitterion form. The zwitterion increases the aggregation of RhB and also leads to dimer formation. Due to its bulky nature, it was difficult to accommodate the dimeric form of RhB in CBCM pores, but the monomeric form was suitable for adsorption. Moreover, CB[6] also ideally favored the host–guest type of binding with the RhB monomer, and the protonated form of RhB was more favorable than the zwitterion form, which resulted in higher RhB removal at lower pH.

3.8. Effect of Temperature. Temperature is another crucial factor that influences adsorbent behavior. Adsorption studies were carried out by the CBCM nanocomposite at 25, 35, 45, and 55 °C (Figure 4D–F). The dye removal percentage was increased from 90 to 93 for CV, from 52 to 58 for MB, and from 34 to 40 for RhB when the temperature was increased from 25 to 45 °C, indicating the endothermic adsorption nature. This behavior occurred due to the lowered viscosity of the dye solution at a higher temperature, which facilitated faster diffusion of the dye into the nanocomposite. Beyond 45 °C, the dye removal percentages remained constant, which could be due to weak physical interaction between the dye molecules and the nanocomposite. To attain ease of process and energy efficiency, all dye removal experiments of MB and CV were carried out above the PZC (pH 7) and RhB removal was performed at pH 2–3 at ambient temperature.

3.9. Effect of CBCM Nanocomposite Dosage. The effect of CBCM dosage (from 0.03 to 0.2 mg mL⁻¹) on the dye removal capacity is presented in Figure 4G–I. With the increase in the CBCM dosage from 0.03 to 0.2 mg mL⁻¹, the dye removal percentage was increased from 48 to 100% for CV, 26 to 95% for MB, and 18 to 85% for RhB. With the increase in the CBCM dosage, the availability of adsorption area/sites was increased, leading to complete decolorization. On further increasing the nanocomposite concentration to 0.26 mg mL⁻¹, the removal efficiency of MB and RhB reached 100%, whereas CV attained complete removal efficiency with only 0.20 mg mL⁻¹ CBCM dosage. However, adsorption capacity (qₑ) values decreased simultaneously with increased CBCM loading.

3.10. Effect of Dye Concentration. The adsorption capacity of CBCM was evaluated at the equilibrium state by varying the dye concentration while keeping the CBCM dosage constant, and the results are presented in Figure 4J–L. The CBCM qₑ value gradually increased with increasing dye concentration, and the highest qₑ values of 218 mg g⁻¹ for CV, 80 mg g⁻¹ for MB, and 79 mg g⁻¹ for RhB were exhibited. Higher dye concentrations amplified the concentration gradient and developed a driving force between the dye solution and CBCM adsorption sites, resulting in maximum adsorption capacity. At lower dye concentrations, the maximum amount of dye molecules was adsorbed on the nanocomposite, attaining higher dye removal efficiency. In contrast, at higher dye concentrations, the active adsorption sites became saturated and lower removal efficiency was observed. On increasing the dye concentration from 10 to 100 mg mL⁻¹, the dye removal percentage decreased from 100 to 44 for CV, 95 to 16 for MB, and 85 to 16 for RhB, due to adsorbent saturation. The adsorption process was less effective by dye concentration and demonstrated decent adsorption capacity.

3.11. Effect of Time. Within the initial 5–10 min, the dye adsorption process was quick, and maximum adsorption occurred at this stage. In the later stage when the process...
approached equilibrium, the adsorption process became slower due to the interparticle diffusion of the dye within the pores of the CBCM nanocomposite. After 30 min, the adsorption and desorption processes reached an equilibrium where the dye solution in the bulk was in a dynamic balance with the nanocomposite.\textsuperscript{56} CBCM exhibited very rapid dye adsorption, removing the maximum dye in less than 5 min, which could be advantageous for continuous flow dye removal applications. Kinetics and adsorption isotherm parameters of the process were calculated based on time-dependent adsorption studies.

### 3.12. Adsorption Kinetics

Kinetic plots of CV, MB, and RhB removal using CBCM were shown in Figure S, and the obtained rate constant values are listed in Table 1. Experimental data were fitted into nonlinear pseudo-first-order and pseudo-second-order kinetics models (Figure S). The nonlinear pseudo-first-order kinetics was expressed by eq S\textsuperscript{57}

$$q_t = q_e (1 - e^{-kt})$$  \hspace{1cm} (5)

where $q_t$ and $q_e$ are the amounts of dye (mg g$^{-1}$) adsorbed on the adsorbent at equilibrium and at a given time $t$ (min), respectively, and $k_t$ is the rate constant of adsorption (g mg$^{-1}$ min$^{-1}$).

The nonlinear pseudo-second-order kinetics were plotted using eq S\textsuperscript{60}

$$q_t = \frac{k_d q_e^2 t}{1 + k_d q_e t}$$  \hspace{1cm} (6)

where $k_d$ is the rate constant for the pseudo-second-order adsorption process. The values of $k_d$ and $q_e$ were determined using eq 6.

According to kinetic plots, the CBCM nanocomposite followed pseudo-second-order kinetics for the dye adsorption process on the CBCM nanocomposite (Table 1 and Figure S). The correlation factors for pseudo-first-order kinetic plots were less than 0.854, whereas pseudo-second-order kinetic plots exhibited correlation factors above 0.950 for all dyes used in the experiment. Pseudo-second-order rate constants were calculated to be 0.0281 L mg$^{-1}$ min$^{-1}$ (CV), 0.0823 L mg$^{-1}$ min$^{-1}$ (MB), and 0.0953 L mg$^{-1}$ min$^{-1}$ (RhB) under experimental conditions (Table 1). The CBCM nanocomposite followed the pseudo-second-order kinetic model for cationic dye adsorption. This implies that adsorption could be dominated by chemisorption rather than physical adsorption. Chemisorption could be a result of host-guest interactions between cationic dyes and CB[6] or ionic interactions with the negatively charged surface of the CBCM nanocomposite.

### 3.13. Adsorption Isotherms

Adsorption isotherms provide valuable information about adsorption behavior, surface properties, and affinity of the dye toward the adsorbent. The amount of dye adsorbed on the nanocomposite surface and the amount of dye remaining in the solution at a fixed temperature and pH at equilibrium can be evaluated by isotherms.\textsuperscript{54} The equilibrium adsorption of the CBCM nanocomposite was analyzed using Langmuir, Freundlich, and Temkin adsorption isotherms.\textsuperscript{58}

The Langmuir isotherm assumes that the monolayer of dye molecules is adsorbed at definite homogeneous sites on the surface of the adsorbent and that these sites cannot be further occupied by another dye molecule, which can be expressed using eq 7\textsuperscript{89}

$$q_e = \frac{q_m K_l C_e}{1 + K_l C_e}$$  \hspace{1cm} (7)

where $q_e$ is the adsorbed amount of dye at equilibrium (mg g$^{-1}$), $C_e$ is the equilibrium concentration of the dye in solution (mg L$^{-1}$), $q_m$ is the maximum adsorption capacity (mg g$^{-1}$), and $K_l$ is the Langmuir constant.

The Freundlich adsorption isotherm assumes that dye adsorption takes place at heterogeneous sites on the surface of the adsorbent and that the adsorption capacity of an adsorbent depends on the concentration of the dye, which can be expressed using eq 8\textsuperscript{60}

$$q_e = K_f C_e^{1/n}$$  \hspace{1cm} (8)

where $K_f$ is the adsorption capacity and $\frac{1}{n}$ is the adsorption intensity.

The Temkin isotherm discusses the effect of indirect interactions of the dye and the adsorbent in the process. It assumes that the heat of adsorption of all molecules in the layer linearly decreases with an increase in surface coverage, which can be expressed using eq 9\textsuperscript{61}

$$q_e = \frac{RT}{b} \ln(K_t C_e)$$  \hspace{1cm} (9)

where $b$ (kJ mol$^{-1}$) is the Temkin constant associated with sorption enthalpy, $K_t$ (L g$^{-1}$) is the Temkin equilibrium binding constant, $R$ (kJ mol$^{-1}$ K$^{-1}$) is the gas constant, and $T$ is the absolute temperature in Kelvin.

In this study, Langmuir, Freundlich, and Temkin isotherm models were fitted with experimental data and then the isotherm constants and correlation factors were calculated and are listed in Table 2. Based on the correlation factor ($R^2$) values, it can be deduced that the adsorption process of cationic dyes on the surface of CBCM follows the Langmuir isotherm model owing to high correlation values of 0.999, 0.962, and 0.985 for CV, MB, and RhB, respectively (Figure S and Table 2). This implies that monolayer adsorption took place over the CBCM nanocomposite. Freundlich and Temkin isotherm models did not correlate with the experimental data. The maximum adsorption capacities ($q_{max}$) of the CBCM nanocomposite for CV, MB, and RhB dyes calculated using the Langmuir model were 199.20, 78.31, and 55.62 mg g$^{-1}$, respectively. A high adsorption capacity indicates that good coverage of cationic dyes over the

### Table 1. Kinetic Parameters of CV, MB, and RhB Adsorption onto the CBCM Nanocomposite

| dye      | $C_0$ (mg mL$^{-1}$) | $q_{(emp)}$ (mg g$^{-1}$) | $q_{(cal)}$ (mg g$^{-1}$) | $k_1$ (min$^{-1}$) | $R^2$ | $q_{(emp)}$ (mg g$^{-1}$) | $K_2$ (L mg$^{-1}$ min$^{-1}$) | $R^2$ |
|----------|----------------------|---------------------------|---------------------------|-------------------|-------|---------------------------|-------------------------------|-------|
| CV       | 10                   | 50.00                      | 49.06                      | 0.432             | 0.663 | 50.9                      | 0.0281                        | 0.963 |
| MB       | 10                   | 47.52                      | 47.85                      | 0.907             | 0.854 | 48.7                      | 0.0823                        | 0.987 |
| RhB      | 10                   | 42.58                      | 41.60                      | 0.932             | 0.697 | 42.4                      | 0.0953                        | 0.951 |

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adsorbent surface could be due to the abundant negatively charged adsorption sites induced by the presence of CB[6].

3.14. Recycling and Reusability. Adsorbent regeneration studies were performed to establish the reusability of the CBCM nanocomposite. Due to the presence of magnetic cobalt ferrite nanoparticles, recycling of the CBCM nanocomposite from the reaction mixture was much easier and the removal of surface-bound dye was crucial. In the case of common adsorbents, surface-bound dyes were extracted using mild acidic or solvent washes for a prolonged time. Similarly, CBCM was soaked and stirred in various desorption-initiating media, such as acidic (aqueous HCl, pH 3–4) and basic (aqueous NaOH, pH 8–9) solutions, deionized water, and organic solvents (acetone), and compared with MMT (Figure 6D). Almost negligible desorption was exhibited by CBCM in all conditions, whereas MMT readily desorbed dyes when basic and organic solvents were used. Even after soaking and stirring under harsh conditions, the dye did not desorb from the CBCM surface, showing superstrong surface-binding in comparison with MMT. This higher stability was observed in CBCM due to strong binding between dyes with increased interactions induced by CB[6] and the nanocomposite or due to the ultrafast adsorption−desorption cycles. This behavior is highly helpful in long-duration and extreme operational conditions observed in the industry. For example, the textile industry effluents often reach a pH of 8–10 and effluent treatment operations require longer durations. In this scenario, the pristine MMT adsorbent is not beneficial as it may gradually desorb all adsorbed dyes. Therefore, with conventional adsorbents, effluent treatment must be completed within the speculated time or repeated often. Under these extreme conditions, the CBCM nanocomposite serves better to treat the effluent as such without worrying about dye desorption. It is also important to develop a suitable regeneration method to reuse the CBCM nanocomposite. Utilizing the catalytic activity of cobalt ferrite nanoparticles, we have developed an efficient catalytic reduction method to rapidly regenerate the CBCM nanocomposite and simultaneously degrade the adsorbed dye. Catalytic degradation in the presence of nanoparticles and a mild reducing agent is widely used for the removal of many pollutants. Here, the same phenomenon was utilized for faster regeneration of the CBCM nanocomposite after dye removal experiments. The CBCM nanocomposite was regenerated using the sodium borohydride-based catalytic reduction method and reused for several consecutive dye removal cycles (Figure 6A). This method offered easy, cost-effective, and fast regeneration of the

| model   | parameters | CV      | MB      | RhB     |
|---------|------------|---------|---------|---------|
| Langmuir | $K_L$ (L mg$^{-1}$) | 0.999   | 2.233   | 2.736   |
|         | $q_m$ (mg g$^{-1}$) | 199.20  | 78.31   | 55.62   |
|         | $R^2$      | 0.999   | 0.962   | 0.985   |
| Freundlich | $K_f$ (L g$^{-1}$) | 98.47   | 54.03   | 45.20   |
|         | $n$        | 5.20    | 10.63   | 19.70   |
|         | $R^2$      | 0.847   | 0.921   | 0.837   |
| Temkin  | $K_T$ (L mg$^{-1}$) | 28.71   | 4475.40 | 2.56    |
|         | $b$ (kJ mol$^{-1}$) | 0.079   | 0.357   | 0.863   |
|         | $R^2$      | 0.932   | 0.939   | 0.853   |

“Bold values indicate the highest correlation factor values obtained for isotherms, based on these values, it is concluded that the CBCM dye removal process followed the Langmuir isotherm model.

Figure 6. (A) Reusability cycles of the CBCM composite, (B) FTIR spectra, (C) Fe-SEM image of the recycled CBCM nanocomposite after five cycles, and (D) digital photographs of dye desorption studies with MMT (vials labeled X) and the CBCM nanocomposite (vials labeled Y) performed in DI water (neutral, pH 7) and acidic (pH 3–4), basic (pH 8–9), and acetone solutions.
nanocomposite along with efficient dye degradation with minimal secondary effluent generation compared to desorption. Typically, the CBCM nanocomposite was treated with a definite amount of a 0.1 M sodium borohydride aqueous solution until complete decolorization, followed by washing with deionized water. It was separated using a magnet, then dried at 110 °C in an oven and reused for the next consecutive cycle. The regenerated CBCM nanocomposite exhibited excellent dye removal efficiency for at least five cycles without any loss in adsorption capacity (Figure 6A). A slight reduction in the dye removal percentage in the fifth cycle was observed merely due to the loss of catalyst during handling. The regenerated CBCM nanocomposite was characterized by FTIR and FE-SEM, which confirmed that there was no significant structural or morphological deformation during dye removal or the regeneration process (Figure 6B). This study confirmed that the CBCM nanocomposite indeed exhibited an ultrastrong binding nature and low-desorption behavior, which is quite useful for treating real-time industrial effluent where the process is lengthy and the effluent condition is uncertain. The catalytic degradation method for regeneration of the adsorbent also provided new insights for future use.

3.15. Mechanism. FTIR analysis was performed to determine the mechanism for adsorption of dye on the surface of the CBCM nanocomposite. Figure 7A shows the FTIR spectra of CV, MB, and RhB after being adsorbed on the surface of the CBCM nanocomposite in the 2000–4000 cm⁻¹ range. A complete spectrum is provided in Figure S3, SI. Before adsorption, the surface of the CBCM nanocomposite has characteristic peaks at (a) 590 and 420 cm⁻¹ (Co−O), (b) 1726 and 1628 cm⁻¹ (C=O), and (c) 528 and 468 cm⁻¹ (Si−O). After dye adsorption, a new peak at around 1593 cm⁻¹ distinctly appeared and a more broadened peak was observed in the case of CV adsorption (Figure 7A). This peak can be assigned to the vibration of the aromatic ring owing to the C=C bond, indicating that all of the three dyes are anchored on the surface of the CBCM nanocomposite. A minor peak shift was observed in the peaks associated with the Co−O, C=O, and Si−O bonds in the CBCM nanocomposite after dye adsorption. The peaks corresponding to Co−O were shifted to 577 and 413 cm⁻¹, those corresponding to C=O were shifted to 1720 and 1647 cm⁻¹, and those corresponding to Si−O were shifted to 524 and 464 cm⁻¹. This peak shift is attributed to the electrostatic interactions between cationic dyes and the negatively charged surface of the CBCM nanocomposite. This behavior has been supported by ζ potential analysis. The ζ potential of the CBCM nanocomposite was −32.5 mV at the experimental pH, indicating good emulsion stability and dispersion. At the same pH, MMT and CuFe₂O₄ NPs exhibited ζ potentials of −9.16 and −16.2 mV, respectively. Hence, the incorporation of CB[6] helped to attain better emulsion stability. This also confirms that the surface of the composite becomes more negatively charged than those of pristine nanoparticles and MMT clay due to the presence of abundant CB[6] carbonyl portals. This negatively charged surface can actively adsorb cationic dyes, which improved the dye removal capacity of the CBCM nanocomposite. Moreover, CB[6] is also capable of forming host–guest complexes and external binding complexes with dyes, leading to an increased dye uptake. Based on this, different types of possible molecular interactions over the surface of CBCM with cationic dyes are illustrated in Figure 7B. Overall, the CBCM nanocomposite was sturdily bound with the dye molecules through strong hydrogen bonding with carbonyl portals of CB[6], weak H-bonding, and electrostatic interactions with the MMT lamella and the nanoparticles, resulting in rapid cationic dye adsorption.

3.16. Versatile Application of the CBCM Nanocomposite for Dye Removal. 3.16.1. Treatment of a Mixture of Dyes (Model Effluent). Industrial effluent often contains more than one dye. Individually measuring the adsorption capacity for each dye may not be conclusive enough to understand its practical application. Hence, we have prepared a model industrial effluent with a mixture of CV, MB, and RhB dyes in three different acidic (2−3), neutral (7), and basic (11−12) pH ranges, and the model industrial effluent was treated with the CBCM nanocomposite. Figure S4 shows the change in absorbance with increasing CBCM quantity. All of the pH absorbances for CV and MB in water decrease consistently, whereas for RhB, the absorbance

![Figure 7](https://dx.doi.org/10.1021/acsomega.0c05400)

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**Figure 7.** (A) FTIR spectra of CBCM after adsorption of (a) RhB, (b) MB, and (c) CV for mechanistic investigation. (B) Probable mechanism for adsorption and (C) the continuous flow column.
increasing the initial dye concentration to 100 mg mL$^{-1}$, the breakthrough point early due to adsorbent overloading. On observing within a short contact time, but the column reached a breakthrough point after 1400 min (Figure S6, SI). Even with an increased flow rate up to 50 mL min$^{-1}$, complete dye removal was observed within a short contact time, but the column reached a breakthrough point early due to adsorbent overloading. On increasing the initial dye concentration to 100 mg mL$^{-1}$ with a higher flow rate, color removal was persistent until reaching the breakthrough point, and the dye adsorption capacity of CBCM remained unchanged. This study ensured that CBCM nanocomposite can be used for the treatment of real effluent.

3.16.2. Syringe Filtration Method. CBCM exhibited rapid and stable adsorption performance under ambient conditions for the removal of selected dyes. To widen the practical applicability of the material, we have also prepared syringe filters loaded with the CBCM nanocomposite for fast, inline water treatment, as shown in Figure S5. The syringe filter method provided conceptual proof that CBCM could be used for inline operations due to its rapid, irreversible adsorption behavior. Commercially available syringe filters with the CBCM nanocomposite and the dye-contaminated water is passed through the modified filters using a syringe. To our delight, CBCM-modified filters rapidly trapped all dyes from wastewater and instantly produced decolorized clean water (Video S1, SI). The rapid adsorption with a minimum contact time of CBCM enables its possible application in household effluent treatment where rapid removal of contaminants is required. Further, CBCM application was also evaluated under industrial conditions using continuous flow fixed-bed column operations.

3.16.3. Continuous Flow Fixed-Bed Column for Rapid and Large-Scale Operations. To investigate the applicability of the CBCM nanocomposite in industrial-scale effluent treatment, a tubular polycarbonate column was prepared sandwiching CBCM between sand beds (Figure 7C). The dye-contaminated water was pumped using a rotary pump and collected instantaneously from the bottom tap (Figure S5). The CBCM-loaded fixed-bed column exhibited rapid dye removal efficiencies at higher flow rates from 10 to 50 mL min$^{-1}$ under testing conditions. The dye removal efficiency in the continuous flow fixed-bed column was investigated by varying dye concentrations and flow rates. With a 10 mL min$^{-1}$ flow rate using 50 mg mL$^{-1}$ CV, the CBCM column reached a breakthrough point after 1400 min (Figure S6, SI). Even with an increased flow rate up to 50 mL min$^{-1}$, complete dye removal was observed within a short contact time, but the column reached a breakthrough point early due to adsorbent overloading. On increasing the initial dye concentration to 100 mg mL$^{-1}$ with a higher flow rate, color removal was persistent until reaching the breakthrough point, and the dye adsorption capacity of CBCM remained unchanged. This study ensured that CBCM was quite beneficial for industrial-scale effluent treatment with continuous feed. We fed the influent from the top of the column to ensure that CBCM-based fixed-bed columns can also be used in gravity-driven wastewater treatment operations where electricity is not available.

Further, the CBCM nanocomposite efficiency was compared with a few similar adsorbents reported in the literature (Table S1, SI). CBCM displayed a relatively high adsorption capacity, rapid adsorption, and good reusability than many other adsorbents reported. Due to its magnetic nature and good in-process stability, the CBCM nanocomposite could be recycled conveniently and reused, which is beneficial over traditional adsorbents like clay and activated carbon. Additionally, the CBCM nanocomposite proved to be suitable for different types of application techniques, and the continuous flow and batch methods are advantageous over traditional adsorbents. Moreover, CB[6] presence improved desorption behavior and selectivity, thus making it suitable for extreme industrial conditions such as long-duration operations.

4. CONCLUSIONS

A functional CBCM nanocomposite where the supporting montmorillonite clay sheets are decorated with CB[6]-capped magnetite CoFe$_2$O$_4$ nanoparticles has been synthesized through a simple ultrasonication-assisted solution process. In the CBCM nanocomposite, CB[6] provided additional selectivity, improved dye removal efficiency owing to its negatively charged carbonyl portals, and strong molecular interactions with dyes. It also helped in better distribution of the nanoparticles and acted as a binder between MMT and CoFe$_2$O$_4$, providing additional stability to the CBCM nanocomposite. The adsorption performance of this nanocomposite has been tested for several parameters such as pH, temperature, CBCM concentration, adsorbate concentration, and time on a series of cationic dyes, CV, MB, and RhB, by monitoring the fingerprint spectral changes in the solutions. It is confirmed that the nanocomposite has excellent adsorption capabilities toward the tested dyes. Also, it can be quickly separated from water with the help of a magnet due to the integrated magnetic nanoparticles. Adsorption over the CBCM nanocomposite was so strong that it was stable even in higher and lower-pH solvents, including solvents such as acetone. Once the nanocomposite attains saturation, simple catalytic reduction treatment at moderate conditions can easily and efficiently regenerate it at almost no expense to its adsorption capacity in the consecutive cycles. More importantly, the nanocomposite shows satisfactory tolerance against the variations in pH conditions/dye concentrations. Even in a more realistic condition where mixtures of dyes are involved, the nanocomposite shows extremely good multiplex absorbability without decreasing the adsorption capacity for each of the dyes as compared with those adsorbed individually. CBCM worked well in the syringe filtration method and fixed-bed column applications even at higher flow rates, reaching up to 50 mL min$^{-1}$ with dye concentrations ranging from 10 to 100 mg mL$^{-1}$. Taking advantage of the simple preparation, quick adsorption, rapid extraction, and easy regeneration of the nanocomposite, this new type of adsorbent is very promising for high-efficiency and low-cost real-time wastewater treatment at the industrial scale.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomga.0c05400.

Method to determine the point of zero charge; FTIR, XRD, TGA, DTG, and DR-UV spectra of CB6 and MMT; comparative FTIR spectra of dyes before and after adsorption; UV–vis spectra of the removal of a mixture of dyes; graphs and images of continuous flow fixed-bed removal of dyes; and comparison table of CBCM performance with reported adsorbents (Table S1) (PDF)

Representative video of continuous flow fixed-bed removal of dyes using the CBCM nanocomposite (Video S1) (MP4)
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C.K.P. and M.U.T. contributed equally to this work. C.K.P. and M.U.T. conceptualized the research, performed experimental work, and wrote the original manuscript. K.P. assisted in dye removal experiments. N.M.M. helped in conceptualization, data interpretation, and manuscript writing. M.K.P. acquired funding and supervised the work. All digital photographs and videos were taken by M.U.T. The final manuscript was reviewed and approved by all authors.

Notes
The authors declare no competing financial interest.

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