

Supporting information

Synthesis, characterization and application of chitosan/graphene oxide/copper ferrite nanocomposite for the adsorptive removal of anionic and cationic dyes from wastewater

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Materials

Graphite flakes (acid treated 99%), sodium nitrate, 30% hydrogen peroxide, 98%, ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), copper sulfate (CuSO_4) were purchased from Sigma-Aldrich. A high molecular weight 190,000 - 375,000 Da Chitosan (from shrimp shells, degree of de-acetylation $\geq 75\%$; viscosity >200 cP, 1 wt.% in 1% acetic acid), glacial acetic acid were purchased from Merck (Merck, Darmstadt, Germany). CTAB [Cetyltrimethyl ammonium bromide] (99%) was purchased Nentech, Hydrochloric acid (Chem-Supply), sodium hydroxide (Chem Supply), Indigo carmine dye was purchased from Aladdin (Shanghai, China). All reactions were carried out using double distilled deionized (DD) water.

Preparation of graphene oxide

GO was prepared as mentioned in our previous work (1), briefly, In 230 ml of H_2SO_4 (98%), 5.0 g of powdered graphite and 5.0 g of sodium nitrate were mixed together. and the temperature was maintained lower than 15°C for 4 hours. After that, 20.0 g of KMnO_4 were progressively added to the prior solution with stirring. Then the solution was diluted with water and the reaction temperature reaches around 98°C . In the following step, 30 ml of 30% H_2O_2 is gradually added with agitating until the yellow color appears. The obtained suspension was filtered, rained with 1.0 M HCl, water, and then dried at 50°C .

Preparation of spinel CuFe_2O_4 nanoparticles

The spinel CuFe_2O_4 was prepared by the coprecipitation strategy (2). Briefly, CuSO_4 and FeCl_3 were completely dissolved in 0.5 L water, in a 2: 1 molar ratio. Then, a 3.0 M NH_4OH was added progressively to form precipitates containing $\text{Cu}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$. The precipitate was then filtered and heated at 105°C . Finally, the obtained CuFe_2O_4 solid was calcined at 500°C for 2 hrs.

Preparation of magnetic chitosan-GO (MCGO)

A 0.80 g GO was dispersed in a 100 ml water with vigorous stirring. Then, a 0.30 g chitosan was dissolved in a 100 ml of 3% acetic solution with stirring and the obtained solution was then added to the previous GO suspension. The resulting mixture was then heated with constant stirring at 60 °C for 4 h before being cooled to room temperature. After that, a 0.20 g spinel CuFe_2O_4 NPs were added to the previously well-stirred suspension, the pH was adjusted to 8.0 by NaOH, and the reacting mixture was agitated in an ultrasonic bath for one hour. The resulting blackish solid was filtered and washed repeatedly with excess water to remove unbound particles before being dried at 60 °C overnight.

Materials Characterization

The crystallite size and phases of the as-synthesized nanoparticles were determined by Philips/PANalytical X'PERT-Pro MPD Powder Diffractometer using (Cu [$K\alpha_1/K\alpha_2$]) radiation; XRD peaks appeared with diffraction angle range of 5–100° with a step of 0.02° and integration time of 3 s/step. The surface area and the sample porosity were inferred from the N_2 -adsorption isotherms at 77 K using volumetric instruments connected to a vacuum for outgassing until reaching 10^{-5} Torr. Fourier-transform infrared (FTIR) spectra were recorded on an ATT Mattson series FTIR-TM spectrometer using the KBr disk technique. The samples were characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) to study the morphology of the samples using OXFORD INCA PentaFETX3-England. The shape and size of the particles were studied using a high-resolution transmission electron microscope (HRTEM) model (JEOL-2100). The magnetic properties of the prepared nanoparticles were determined using a vibrating sample magnetometer (MDK-VSM) at room temperature. Absorption

measurements were made with a Shimadzu UV1800 UV/Vis Molecular Absorption Spectrometer.

Adsorption studies in single pollutants systems

The elimination of anionic and cationic dye using MCGO composite was studied by adding the appropriate weight of MCSGO to a 100 ml of dye solutions with initial concentrations (1×10^{-5} - 1×10^{-4} M). The beaker containing the dye solution and MCGO was placed on a stirrer at a constant temperature and agitated for 1 hour at a constant speed of 400 rpm. Furthermore, with the exception of thermodynamic experiments, all batch adsorption was performed at 308 K. The beaker containing the dye solution and MCGO was placed on a stirrer at a constant temperature and agitated for one hour at a fixed speed of 400 rpm. Furthermore, with the exception of thermodynamic experiments, all the batch adsorption was performed at 308 K. Samples were drawn at indicated intervals, centrifuged to eliminate the adsorbed NPs, and analyzed by UV-vis spectrophotometer to assess remained dye concentrations.

To evaluate the effect of pH on the removal of contaminants (IC and SUF dye) by MCGO, batch experiments were performed by adjusting the pH of the solution with 0.1-1 mol/L NaOH or HNO₃ solution, wherein the range of pH value of 2.0-8.0 while keeping the other parameters are fixed.

The impact of MCGO dosages on the removal of cationic and anionic dyes was determined by adding various amounts of adsorbent (0.01, 0.02, 0.03, and 0.04 g) into 100 mL of dye solution.

The adsorption isotherms of IC and SUF dye were performed by adding 0.02 g of MCGO into a series of 100 mL of dye solution with an initial concentration in range (1×10^{-5} - 1×10^{-4} M) . The obtained data were fitted by using Freundlich, Langmuir, and Dubinin-Radushkevich (D-R) isotherm models.

To determine the impact of the presence of surfactant and ionic strength on the removal efficiency of contaminants by MCGO adsorbent, the adsorption experiments were performed over the NaCl and SDS concentrations in the range of 0-1000 ppm as NaCl and 0-10 ppm, respectively.

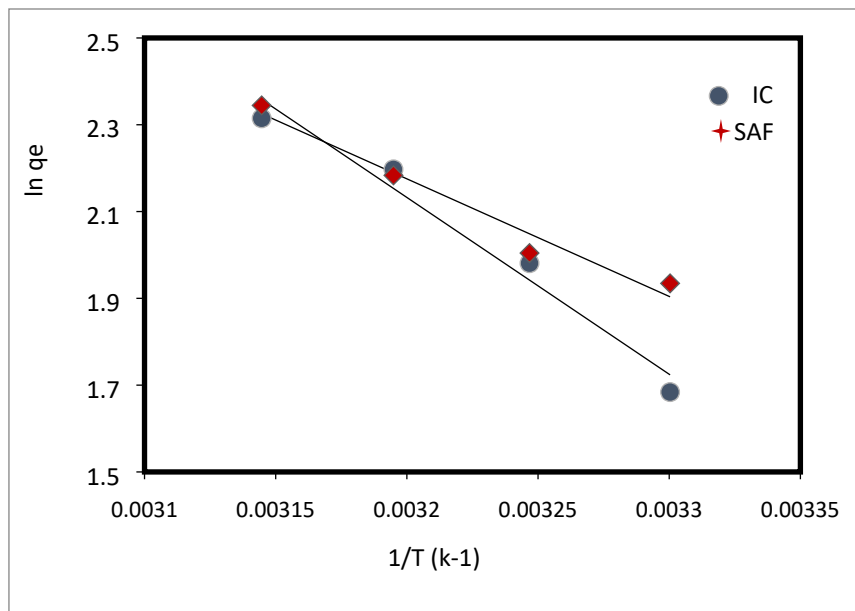


Figure S1 Effect of temperature on the adsorption capacity of IC and SAF dye removal onto MCSGO

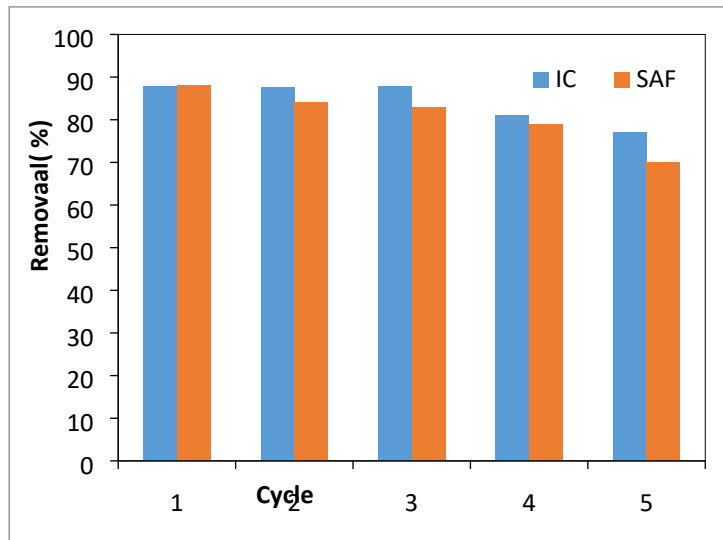


Figure.S2 Adsorption-desorption of IC and safranin dye on MCSGO.