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Research article

Adsorptive performance of MOF nanocomposite for methylene blue and malachite green dyes: Kinetics, isotherm and mechanism

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ABSTRACT

In the present study, Fe_3O_4@AMCA-MIL-53(Al) nanocomposite was utilized for the adsorptive removal of highly toxic MB and MG dyes from aqueous environment. The batch adsorption tests were performed at different contact time, pH, Fe_3O_4@AMCA-MIL-53(Al) dose, initial concentration of dyes and temperature. The maximum adsorption capacity of MB and MG dyes onto of Fe_3O_4@AMCA-MIL-53(Al) using Langmuir equation was 1.02 and 0.90 m mol/g, respectively. The isotherm and kinetic studies revealed that adsorption data were well fitted to Langmuir isotherm and pseudo-first-order kinetics models. Various thermodynamic parameters were also calculated and interpreted. The positive and negative values of ΔH° and ΔG° indicated that the adsorption was endothermic and spontaneous, respectively. The adsorptive binding of MB and MG on Fe_3O_4@AMCA-MIL53(Al) nanocomposite was directed by carboxylate and amide groups through electrostatic interaction, $\pi-\pi$ interaction and hydrogen bonding. The desorption of both dyes from Fe_3O_4@AMCA-MIL-53(Al) was also performed using mixed solution of 0.01 M HCl/ethanol. Thus, we conclude that the Fe_3O_4@AMCA-MIL-53(Al) was an outstanding material for the removal of dyes from aqueous environment.

1. Introduction

Nowadays, dyes are widely used in different industries as colorants, such as textile (Zhang et al., 2014), leather tanning (Ali, 2010), paper & plastics (Kabdaşli et al., 1999), cosmetics (Huang et al., 2017), pharmaceutical and foodstuffs (Batzias and Sidiras, 2007; Wróbel et al., 2001). It has become one of the most serious environmental issues to treat dyes-contaminated wastewater because dyes are toxic even at low concentration and create a serious hazard to the aquatic system and human health (Pathania et al., 2016). Many conventional techniques like electrochemical degradation of the color groups (Bekiari and Lianos, 2006; Salleh et al., 2011), chemical oxidation (Dutta et al., 2001), coagulation (Guibal and Roussy, 2007), photocatalytic (Muruganandham and Swaminathan, 2006), ion exchange (Liu et al., 2007) and adsorption (De Lisi et al., 2007) have been applied for the removal of dyes. Among these water treatment techniques, adsorption process provides an attractive method because of high efficiency, simplicity and cost efficiency (Albadarin et al., 2017; Naushad et al., 2018). A lot of adsorbents, for instance, carbon nanotubes (Jin et al., 2018; Xin et al., 2017), activated carbon (Sangon et al., 2018; Silva et al., 2018), activated diatomite, resin (Bayramoglu et al., 2009; Hu et al., 2013) have been applied for the adsorption of various dyes from aqueous solution (Baskaralingam et al., 2006; Yang et al., 2015). Recently, magnetic nanocomposites have gained much interest, because they not only have good removal capacity, fast kinetics and reactivity for pollutants removal, but also have high separation efficacy and reusability (Siddiqui and Chaudhry, 2017; Tang and Lo, 2013).

Metal-organic frameworks (MOFs) are a new class of microporous materials, that are consist of metals/metal clusters and organic ligands which linked to each other. MOFs have high chemical & thermal stability, high specific surface area and tunable pore size and these properties make them very promising for potential applications in a various fields such as storage of gas, drug delivery and adsorption (Camacho et al., 2015; Langmi et al., 2014). Several researchers have modified the MOFs by aziridine (Morris et al., 2011), amino group (Luo et al., 2015) and thiol group (Ke et al., 2011) for the removal of various types of organic and inorganic pollutants. Chen Li et al. (2015) have prepared two types of MOFs (MIL-53(Al)-NH_2 and MIL-53(Al)) and used for the removal of MG and MB through adsorption. Zhang et al. (Seoane et al., 2013) have synthesized a MNPC (g-Fe_2O_3/C) which was applied for the remove of MG dye from water. The combination of magnetic particles and MOFs has gained considerable attention for the wastewater treatment due to easy separation and recovery of adsorbents. Recently, some methods have been applied to develop the magnetic MOFs such as simply mixing the MOFs with Fe_3O_4 nanoparticles or encapsulating or embedding (Ricco et al., 2013).

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In the present study, by uniting the advantages of magnetic nanoparticle and the high adsorption capacity of MOF, a magnetic MOF (Fe_3O_4@AMCA-MIL-53(Al)) was developed and tested for the exclusion of MB and MG dyes from aqueous medium. The effect of various parameters on the adsorption of these dyes was optimized. Fe_3O_4@AMCA-MIL-53(Al) was also regenerated by using mixed solution of 0.01 M HCl/ethanol.

2. Experimental

2.1. Chemicals and reagents

Ferric chloride hexahydrate, ferrous chloride tetrahydrate, 2-Amino-1,4-benzenedicarboxylic acid, $AlCl_3{\cdot}6H_2O$, acetonitrile and methanol, MB and MG dyes were purchased from Sigma-Aldrich, Germany. N, N-dimethyl formamide was obtained from Panreac, England. Citric acid and 1,3-dicyclohexylcarbodiimide were purchased from Acros Organic, Ammonia solution (25% NH_4OH), hydrochloric acid, sodium hydroxide were procured from BDH, England.

2.2. Synthesis of Fe_3O_4@AMCA-MIL53(Al) nanocomposite

The magnetic MOF (Fe_3O_4@AMCA-MIL53(Al)) was prepared according to the method reported in the previous paper (Alqadami et al., 2017b). First, NH_2-MIL53(Al) was prepared and it was modified with citric acid to form AMCA-MIL53(Al). After that, Fe_3O_4@AMCA-MIL53(Al) was developed by adding 4.3 mmol of $FeCl_2{\cdot}4H_2O$ and 8.7 mmol $FeCl_3.6H_2O$ to an aqueous solution containing different masses of AMCA-MIL53(Al). The suspension mixture was then agitated and degassed for 3 h using N_2 gas, followed by adding 20 mL NH_3 solution to form black suspension. The resultant black solid was separated using external magnetic field, frequently washed with deionized water until the pH becomes neutral.

2.3. Adsorption studies

The adsorption of MB and MG dyes (Fig. S1) using Fe_3O_4@AMCA-MIL53(Al) nanocomposite was investigated by batch experiments. Typically 0.02 g Fe_3O_4@AMCA-MIL53(Al) adsorbent was dispersed in 25 mL of 25 mg/L dye solutions at 100 rpm for 24 h. After equilibration time, the samples were separated magnetically and analyzed by UV spectroscopy. The amount of the dyes adsorbed at equilibrium was computed as:

$$qe,mg/g = Co - Ce\frac{V}{m} \quad (1)$$

$$\%\ \text{adsorption} = \frac{Co - Ce}{Co} \times 100 \quad (2)$$

The influence of pH (pH: 1.5–11.5; adsorbent dose: 20 mg; dye solution 25 mL; Conc. 25 mg/L), Fe_3O_4@AMCA-MIL53(Al) dose (Dose: 20–100 mg; dye solution 25 mL; Conc. 25 mg/L) and temperature (Temp: 298–318 K; dye solution 25 mL; Conc. 25 mg/L, adsorbent dose: 20 mg, contact time: 210 min) on the adsorption of MB and MG was also optimized.

To achieve the effect of time on the adsorption of MB and MG dyes for kinetic studies, a series of conical flasks containing 20 mg of adsorbent was shaken with 25 mL of dye solution (Conc: 25 mg/L) at room temperature for different time (1–210 min). The flasks were removed from the shaker at different time intermissions and the remaining concentration of the dye was determined by UV–Vis spectrophotometer at 627 nm (MG) and 665 nm (MB).

To obtain the isotherm data, the adsorption of MB and MG dyes on Fe_3O_4@ AMCA-MIL53(Al) nanocomposite was accompanied with initial concentrations ranged from 25 to 400 mg/L at pH 8.9 and 6.8 respectively with 20 mg of adsorbent at the temperature ranging from 298 to 318 K. The thermodynamics studies were also performed in the temperature range between 25 and 45 °C.

For desorption study, 20 mg of Fe_3O_4@AMCA-MIL53(Al) nanocomposite was agitated with 25 mL of 25 mg/L dye solutions in the Erlenmeyer flask for 210 min under ambient temperature (298 K). After 210 min, Fe_3O_4@AMCA-MIL53(Al) nanocomposite was separated with external magnetic bar. Then, Fe_3O_4@AMCA-MIL53(Al) nanocomposite was washed and treated with 25 mL of different eluents in the Erlenmeyer flask under ambient temperature (298 K) conditions. After the equilibration time, the solutions were separated and the remaining concentrations of dyes in the solution phase were determined by UV spectroscopy. The % desorption of dyes was computed as:

$$\%\ \text{desorption} = \frac{\text{Conc·of dyes desorbed by eluent}}{\text{Conc·of dyes adsorbed on adsorbent}} \times 100 \quad (3)$$

3. Results and discussion

3.1. Characterization

The FTIR spectra of Fe_3O_4@AMCA-MIL53(Al) nanocomposite (Nicolet 6700, Thermo Scientific), before and after MB and MG adsorption are illustrated in Fig. 1. In the spectrum of Fe_3O_4@AMCA-MIL53(Al) nanocomposite, a peak at 576 cm^{-1} confirmed the existence of Fe_3O_4 in the nanocomposite (A. Alqadami et al., 2016a; A.A. Alqadami et al., 2017a). The peak at 3684 and 3425 cm^{-1} were allocated to hydroxyl groups of octahedral $AlO_4(OH)_2$ chains and hydroxyl (–OH) groups (Gascon et al., 2009). The bands at 1718 and 1399 cm^{-1} were matched to asymmetric and symmetric vibrations of carboxyl groups (C-O), the absorption bands at 1650 cm^{-1} was attributed to the formation of amide group CO-NH in the frameworks. The 1263 cm^{-1} frequency can be assigned to C-N vibrations. The FTIR spectrum of Fe_3O_4@AMCA-MIL53 (Al)/MG/MB showed slight shifting of peak positions and decrease in the intensity of the peaks in comparison to the free Fe_3O_4@AMCA-MIL53(Al). Due to the coordination of oxygen to the guest molecules, the double bond character of the C=O bond was reduced and the peaks were shifted (Abbasi et al., 2012). The adsorptive binding of MB and MG on Fe_3O_4@AMCA-MIL53(Al) nanocomposite was directed by carboxylate and amide groups through electrostatic interaction, hydrogen bonding and $\pi-\pi$ interaction (Fig. 2). The TEM and HRTEM (HRTEM JEOL 2100) of Fe_3O_4@AMCA-MIL53(Al) and Fe_3O_4 are also shown in Fig. 3. The TEM results indicated that Fe_3O_4 NPs were aggregated owing to the participation of −OH groups and

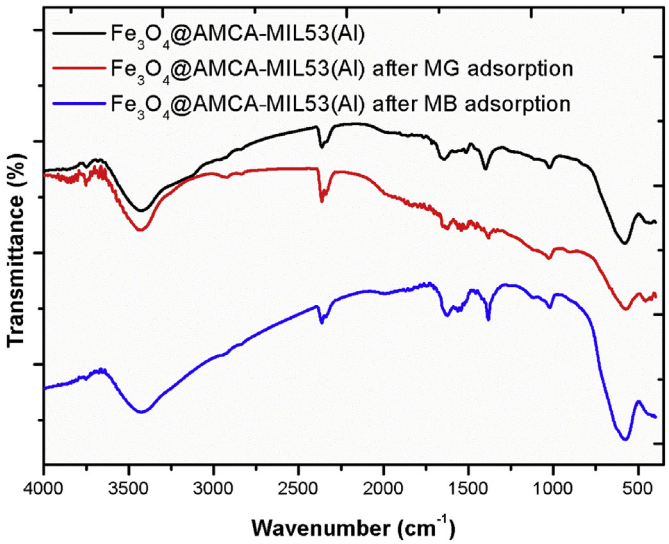

Fig. 1. FTIR spectra for Fe_3O_4@AMCA-MIL53(Al) nanocomposite before and after MB and MG adsorption.