



Synthesis of metal-organic framework hybrid nanocomposites based on GO and CNT with high adsorption capacity for dye removal

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HIGHLIGHTS

- The nanocomposites of Zeolitic imidazolate framework (ZIF) were synthesized.
- The prepared nanomaterials were used to remove malachite green from wastewater.
- Adsorption capacities were 1667, 2034 and 3300 mg g⁻¹ for ZIF, ZIF-CNT and ZIF-GO.
- The data are fitted the Langmuir isotherm model and pseudo-second order kinetics.
- The hybrid nanocomposite exhibited stable and high reusability over four cycles.

ARTICLE INFO

Article history:

Received 13 April 2017

Received in revised form 11 June 2017

Accepted 12 June 2017

Available online 15 June 2017

Keywords:

Metal organic framework
Zeolitic imidazolate framework
Graphene oxide and carbon nanotubes
Hybrid nanocomposites
Adsorption process
Colored wastewater

ABSTRACT

In this study, zeolitic imidazolate framework (ZIF-8) as a metal-organic framework (MOF) and its hybrid nanocomposites based on graphene oxide (GO) and carbon nanotubes (CNTs) were synthesized by facile method at an ambient temperature. The sufficiency of GO and CNT substrates as the main components of the composites to grow nanoscale MOFs and increase dispersive forces were investigated. The characteristics of the MOF and hybrid nanocomposites were studied using FTIR, SEM, XRD, BET and TGA techniques. The prepared nanomaterials applied as adsorbents to remove malachite green (MG) as a cationic dye from colored wastewater. The removal rates of the hybrid nanocomposites were greater than that of the sole MOF. The maximum adsorption capacities were 1667, 2034 and 3300 mg g⁻¹ for ZIF-8, ZIF-8@CNT and ZIF-8@GO respectively at 20 °C, which could be enhanced at the higher temperatures. The effect of several influential parameters such as MOF loading dosage, adsorbent dosage, solution pH, initial dye concentration and temperature were well studied and optimized using batch adsorption study. The adsorption kinetics, isotherm, activation and thermodynamics were also determined. ZIF-8 and its hybrid nanocomposites were regenerated by a simple ethanol-washing method. The hybrid nanocomposites exhibited stable and high reusability over four cycles. Overall, the simple synthesis, highly-effective, regenerable and stability in aqueous phase features enable prepared hybrid nanocomposites as excellent candidates to adsorptive removal processes.

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1. Introduction

Dyes are basically chemical compounds that can connect themselves to surfaces or fabrics to impart color. Synthetic dyes are widely used in many fields of advanced technology, e.g., in different kinds of the textile, paper, leather tanning, food processing, plastics, cosmetics, rubber, printing and dye manufacturing industries. [1]. In up-to-date data, more than 100,000 commercially

available dyes with the rate of 7×10^5 tons per year are produced and usually two percent of the products are discharged into water systems as waste [2]. Their discharges into hydrosphere can cause carcinogenesis, mutagenesis, chromosomal fractures, teratogenicity and respiratory toxicity and this is a major threat to human health and greatly contributes to the global shortage of clean water. Malachite green (MG) is a cationic dye and a biocide. It is used in various industries including textile, paper, and silk, etc. However, it can cause toxicity. Due to the environmental persistence and acute toxicity, the removal of MG from wastewater is essential to prevent the environmental pollution.

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Several methods have been used for treating colored wastewater [3–8]. In the meantime, the most important methods include: solvent extraction, micro and ultrafiltration, gravity separation, flotation, sedimentation, coagulation, oxidation, evaporation, distillation, reverse osmosis, adsorption, ion exchange, electrodialysis and electrolysis. Among the above procedures, the adsorption process is one of the easiest and most effective methods. Because of relatively low cost, simple design, easy operation, small amounts of harmful byproducts, the availability of wide range of adsorbent and easy retrieval of them, and the adsorption process is one of the striking techniques for treating wastewater. In addition, the adsorption method can be used to remove soluble and insoluble organic, inorganic and biological contaminants in water for domestic, industrial and other purposes [9,10]. Considering these issues, adsorption seems to be a more feasible method to remove MG.

Porous materials are considered as good adsorbents which have a major role in the adsorption separation or purification; for this reason, in the past few decades there has been a lot of attention over the advanced porous materials. About two decades ago, a fascinating and relatively new class of highly porous crystalline materials named metal-organic frameworks (MOFs) emerged and its various applications in different areas of research, especially adsorption removal, separation and purification have been proven [11]. On the other hand, porous metal-organic frameworks are considered according to their various applications, including capture and storage of gas, separation of chemicals, catalysis, etc. [12–14]. These crystalline materials have a relative advantage compared to the other porous materials due to the specific surface area, tunable and high porosity, performance of pores, different composition and structure of pores and open metal sites [15,16]. Recently, extensive studies have been carried out on the capture and separation of various hazardous compounds from the liquid phase by MOFs [1]. In addition to the mentioned features, MOFs can be easily used for specific purposes through surface modification, immobilization of functionalized materials, replacing or grafting appropriate functional groups to the metal sites or organic ligands [17,18], changing or mixing metal sites and construction of composite with suitable materials. Lately, hybrid composites of MOFs have attracted considerable attention for various applications including adsorption process. This field is relatively new and recently several reports on the synthesis and promising applications of the MOF composites are provided. [19,20] By combining MOFs and appropriate materials, kinetics of synthesis, morphology, physical and chemical properties, stability and potential usage of MOFs can be greatly improved [21]. However, the synthesis of MOF-based composites using suitable raw materials is crucial. Graphene oxide (GO) and carbon nanotubes (CNTs) are appropriate materials for synthesis of MOF composites. They suppress MOF aggregation, and control MOF properties including morphology, structure, etc. [22,23]. Therefore, MOFs@GO and MOFs@CNTs composites were hoped to be good adsorbent materials for wastewater.

In this work, several hybrid nanocomposites based on ZIF-8 MOF, GO and CNT were synthesized using a simple, facile, and ambient temperature method. The sufficiency of GO and CNT substrates as the main components of the composites to grow nanoscale MOFs were investigated. The properties of synthesized materials were characterized by FTIR, XRD, SEM, TGA and BET, and were used as adsorbents in removal of MG as target organic pollutant. Then the prepared hybrid nanocomposites were utilized as adsorbents. The effect of several influential parameters such as MOF loading dosage, adsorbent dosage, solution pH, initial dye concentration and temperature were well studied and optimized using batch adsorption study. Moreover, mechanisms with kinetic, thermodynamic models and MG adsorption isotherm were measured and discussed. The regenerability and reusability of the nanocomposites was assessed via cycling experiment.

2. Experimental

2.1. Materials

Malachite Green (MG) were obtained from Ciba Company. Methanol, Zinc nitrate ($\text{Zn}(\text{NO}_3)_2$), H-methylimidazole (H-MIM), n-butylamine, H_2SO_4 , NaNO_3 , KMnO_4 , H_2O_2 , graphite powder and carbon nanotubes were purchased from Merck company. Diluted NaOH and HCl solution was used to adjust the pH value at desired level for all experiments where it needed. All aqueous solutions were prepared using doubly distilled water. Deionized (DI) water was provided to show less than 18 MOhm-cm. All Chemicals were of analytical grade and used as received without any purification.

2.2. Synthesis of materials

2.2.1. Graphene oxide (GO)

GO was synthesized from graphite powder according to the Hummer's method as described in our previous work [24].

2.2.2. ZIF-8

Zeolitic imidazole framework-8 was provided according to the reported procedure with modification [25]. Briefly 10 mmol of H-methylimidazole (H-MIM) and 2 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved separately in 40 mL of methanol. ZIF-8 crystal size can be controlled by the addition of a modulator agent into the organic ligand solution. Following this approach, 1 mL of n-butylamine was added to the H-MIM solution. The solution containing the organic ligand was poured, drop by drop, into the other one under stirring at ambient temperature. The solution mixture was left, without stirring, at room temperature for 24 h. Next, the white precipitate was separated by centrifugation, washed several times with fresh methanol and DI water and dried at room temperature. The yield of the final product was 65% based on the amount of zinc salt added in the synthesis.

2.2.3. ZIF-8@GO hybrid nanocomposites

At first, a suspension of GO was prepared in 30 mL methanol by sonicating for 30 min. Meanwhile, different amounts of H-MIM was dissolved in 30 mL of methanol. Then, the zinc solution with various amount of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to the GO suspension and sonicated for 15 min. Afterwards, the 2-methylimidazolate solution containing 1 mL n-butylamine was slowly added to the solution of zinc nitrate hexahydrate with GO under constant stirring at room temperature. The final mixture was left, without stirring, at room temperature for 24 h. Next, the hybrid nanocomposite was collected by centrifugation, washed several times with fresh methanol and DI water and dried at 50 °C in the vacuum oven for 12 h to get the final product. Finally, according to the ratio between ZIF-8 MOF and GO, four different types of ZIF-8@GO hybrid nanocomposites (50–90 wt% ZIF-8 content based on final product) were synthesized.

2.2.4. ZIF-8@CNTs hybrid nanocomposites

The same procedure was followed for preparation of ZIF-8@CNT hybrid nanocomposites, but instead of GO, CNTs were utilized. The pure CNTs were dispersed in PVP methanol solutions (in a mass ratio of CNTs: PVP = 1:4) and stirred for an hour to obtain well disperse CNTs. Finally, according to the ratio between ZIF-8 MOF and CNTs, four different types of ZIF-8@CNT hybrid nanocomposites (50–90 wt% ZIF-8 content based on final product) were synthesized.

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