Magnetically Recyclable Fe₃O₄/GO-NH₂/H₃PMo₁₂O₄₀ Nanocomposite: Synthesis, Characterization, and Application in Selective Adsorption of Cationic Dyes from Water

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Abstract

In this study, the PMo₁₂O₄₀³⁻ polyanion was immobilized chemically on amino functionalized magnetic graphene oxide nanosheets. The as-prepared ternary magnetic nanocomposite (Fe₃O₄/GO-NH₂/H₃PMo₁₂O₄₀) was characterized by powder X-ray powder diffraction (XRD), fourier transformation infrared spectroscopy (FTIR), Raman spectroscopy, energy dispersive spectroscopy (EDX), field emission scanning electron microscopy (FESEM), BET surface area measurements, magnetic measurements (VSM) and atomic force microscopy (AFM). The results demonstrated the successful loading of H₃PMo₁₂O₄₀ (~36.5 wt.%) on the surface of magnetic graphene oxide. The nanocomposite showed a higher specific surface area (77.07 m²/g) than pure H₃PMo₁₂O₄₀ (≤10 m²/g). The adsorption efficiency of this nanocomposite for removing methylene blue (MB), rhodamine B (RhB) and methyl orange (MO) from aqueous solutions was evaluated. The nanocomposite showed rapid and selective adsorption for cationic dyes from mixed dye solutions. The adsorption rate and capacity of Fe₃O₄/GO-NH₂/H₃PMo₁₂O₄₀ were enhanced as compared with GO, GO-NH₂, Fe₃O₄/GO-NH₂, and H₃PMo₁₂O₄₀ samples due to enhanced electrostatic attraction and hydrogen-bonding interactions. The nanocomposite is magnetically separated and reused without any change in structure. Thus, it could be a promising green adsorbent for removing organic pollutants in water.

Keywords: Graphene oxide nanosheets; Magnetic nanocomposite; Polyoxometalates; Organic dyes; Adsorption; Fe₃O₄ nanoparticles.

1. Introduction

Industrial activities release an increasing amount of contaminants, such as metal ions, organic dyes, and cleaning agents, which has raised public concern.¹² So, wastewater treatment has attracted much attention in the past decades because of grievous effluent discharge of some organic dyes from plating, textile, and printing paper, plastic, cosmetic, pharmaceutical, and food industries that are resistant to biological degradation, making them quite difficult to remove from the wastewater.³⁴ Organic dyes are not only highly visible and, even in a small amount, decrease gas solubility in water, but also toxic, carcinogenic, and mutagenic for human beings.¹⁻⁹ Owing to their complex aromatic molecular structures, dyes are generally stable to light, heat and oxidizing agents.¹⁰ Therefore, effective removal of dyes from dye-wastewater is essential. Among the various technologies such as photocatalytic degradation,¹¹ electrochemical degradation,¹² and adsorption,¹³ adsorption is considered one of the most efficient and economical methods for water purification.¹⁴ Many polymeric and inorganic adsorbents such as carbonaceous nanomaterials,¹⁵ porous metal oxides,¹⁶ clays,¹⁷ chitosan,¹⁸ zeolites,¹⁹ and so on²⁰,²¹ were developed for removing pollutants from aqueous solutions. However, such adsorbents are associated with certain problems that limit their practical applications, such as low adsorption capacity, slow adsorption rate, and difficult separation of the adsorbents.²² Furthermore, some of them are only effective for wastewater including low concentrations of dyes and they...
are generally poor at selectively removing the targeted organic dye wastes. Hence, in this regard, it is extremely imperative to find a new desirable adsorption material, which not only is capable of reducing the organic dyes in dye-wastewater with high efficiency and fast adsorption rate but also can achieve selective separation and recovery of raw materials.

Polyoxometalates (POMs), as an outstanding class of anionic metal oxide clusters, have attracted great attention due to their earth-abundant source, rich topology and versatility, controllable shape and size, oxo-enriched surfaces, high electronegativity etc., which have various applications in many fields, such as catalysis, optics, magnetism, biological medicine, and dye adsorption. The strong attraction of POMs to cationic dyes suggests that they are potential and suitable adsorbents for selectively capturing cationic dyes. However, there are still obvious disadvantages for POMs as adsorbents: (i) their relatively small surface area seriously obstructs the accessibility to the active sites and (ii) their excellent solubility in aqueous solution determines that they cannot be reused and recycled in the process of wastewater treatment. Therefore, plenty of remarkable work has been done to encapsulate POMs into porous solid matrices, such as activated carbon and silica for creating composite materials. Unfortunately, these methods sometimes lead to low POM loading; it is thus of vital significance to search for an applicable solid matrix to immobilize POMs, which might greatly improve their adsorption ability for target dyes.

Among various materials, graphene oxide (GO) has been proven as an effective sorbent for the removal of inorganic and organic pollutants owing to its large theoretical specific surface area (~2630 m²/g) and the presence of several active sites on its surface. In addition, in comparison with other carbonaceous nanomaterials, GO may be more environmental friendly and have better biocompatibility. However, it is difficult to separate it from aqueous solution because of its small particle size, causing serious health and environmental problems once it is discharged into the environment. The centrifugation method needs a very high rate and the traditional filtration method may cause blockages of filters. Compared with traditional centrifugation and filtration methods, the magnetic separation method is considered as a rapid and effective technique for separating nanomaterials from aqueous solution. Hence, magnetite/graphene composites with large specific surface area (enhancing the removal of water pollutants) and magnetic separation (facilitated by the recycling of the composites) have begun to be used in the field of environmental treatment.

On the basis of the above discussion, in this work, amino functionalized magnetic graphene oxide (Fe₃O₄/GO-NH₂) was synthesized by a facile method and used as a novel support for immobilizing Keggin-type PMo₁₂O₄₀⁻ anions. This magnetically recoverable ternary nanocomposite material (Fe₃O₄/GO-NH₂/H₃PMo₁₂O₄₀³⁻) was prepared by a simple acid-base electrostatic interaction between H₃PMo₁₂O₄₀³⁻ and amino groups of Fe₃O₄/GO-NH₂. For one thing, PMo₁₂O₄₀⁻ anion with highly electronegative and hydrophilic properties and structural stability could be utilized as a potential adsorbent for removal of the cationic dyes in dye-wastewater. For another, magnetic GO possesses outstanding porosity and extremely large surface area, and it is insoluble in water, which is an appropriate solid matrix to anchor Keggin-type PMo₁₂O₄₀⁻ anions. The combination of polyoxoanions and Fe₃O₄/GO-NH₂ could improve the surface area and avoid the dissolution of POM. The hybrid nanomaterial exhibited superior adsorption rate and selective adsorption ability for the cationic dyes. Remarkably, this material exhibited a large-scale adsorption capacity of 426.7 mg/g for MB. Hence, it is a promising and environmental friendly adsorbent for removing and separating organic pollutants in dye-wastewater.

2. Experimental

2.1. Materials and Characterization Techniques

Graphite powder (C, 99.95%), 3-aminopropyltriethoxysilane (APTES, 99%), phosphomolybdic acid (H₃P-Mo₁₂O₄₀, 98%), toluene, sulfuric acid (H₂SO₄, 98%), and potassium permanganate (KMnO₄, 98%) were purchased from Merck Chemical Co. All other chemicals were commercially purchased and used without further purification. The infrared spectra were recorded at room temperature using a Shimadzu FT-IR 160 spectrophotometer in the 4000–400 cm⁻¹ region with KBr pellets. Powder XRD patterns were recorded on a Rigaku D-max C III X-ray diffractometer using Ni-filtered Cu Kα radiation (λ = 1.54184 Å). The morphology of samples was studied using a MIRA3 TESCAN scanning electron microscope equipped with an energy dispersive X-ray analyzer (EDX) for the elemental analysis. AFM images were recorded by multi-mode atomic force microscopy (ARA-AFM, model Full Plus, ARA Research Co., Iran). Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM, Magnetic Daneshpajoh Kashan Co., Iran) with a maximum magnetic field of 10 kOe. Optical adsorption spectra were obtained using a Cary 100 Varian UV-Vis spectrophotometer in a wavelength range of 200–800 nm. The Brunauer–Emmett–Teller (BET) surface area was measured by N₂ adsorption measurements at 77 °K using a Nova 2000 instrument. The concentration of Mo in the composite was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, model OEC-730). A controllable Serial-Ultrasorics apparatus (James 6MD, England) operating at an ultrasonic frequency of 100 kHz with a nominal output power of 50 W was used to disperse samples.