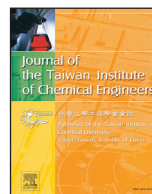




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Rapid, efficient and economic removal of organic dyes and heavy metals from wastewater by zinc-induced in-situ reduction and precipitation of graphene oxide

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ABSTRACT

A graphene oxide (GO) reduction-based method for rapid, efficient and economic removal of organic dyes and heavy metal ions is reported. This method is performed by adding GO, Zn powder and NH_4Cl into wastewater and stirring the solution at ambient conditions for a short period (< 10 min). During this process, NH_4Cl catalyzes the reduction of GO by Zn powder and causes the rapid in-situ adsorption and almost complete precipitation of pollutants by freshly reduced and nanoporous graphene oxide (rGO), therefore efficiently improving adsorption capacity and reducing adsorption time for water treatment. The adsorption capacities for organic dyes (methylene congo red, lemon yellow) and heavy metal ions (Cd^{2+} and Pb^{2+}) were 2.6, 7.6, 3.2, 8.4 and 17.9 g g^{-1} . The removal efficiencies are all above 98.46% and a maximum removal efficiency of 99.99% is obtained for Pb^{2+} . Moreover, the byproducts of water treatment, i.e., rGO with excessive Zn powder and NH_4Cl -containing water, can be further used in energy or agricultural fields. The present work establishes a new approach for the promising application of GO in the field of water treatment with high efficiency and good economic prospects.

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1. Introduction

The rapid development in industrialization, urbanization and population expansion has caused an increasing problem on environment water pollution [1,2]. Among water pollutants, organic dyes and heavy metals which are extensively used in human society from daily life to industrial production are generally non-biodegradable, highly toxic and carcinogenic, thus posing a grave threat to environment and human health [3–5]. Several methods, including membrane separation [6], adsorption [7], filtration [8] and ion exchange [9], have been adopted to alleviate water pollution. Therein, adsorption has been demonstrated to be an effective method due to availability of different adsorbents, simple preparation, low cost and high efficiency.

Graphene, an allotrope of carbon in the form of two-dimensional, atomic-scale and hexagonal lattices [10], have been widely employed as adsorbents in the field of water treatment be-

cause of their high surface area, tunable functionalities and good chemical stability [11–14]. Different from other types of adsorbents, graphene oxide (GO) and its reduced form (rGO) possess different surface functionalities and can absorb a variety of pollutants through interactions like hydrophobic, electrostatic, hydrogen bonding and π - π stacking interactions. For instance, efficient removal of organic dyes and heavy metal ions from wastewater by GO or rGO has been reported by several groups [15–18]. In addition, GO or rGO composites with polymers [19] and metal oxides [20–25] have also been developed to further improve the performance of graphene adsorbents in water treatment.

Recently, Sun et al. [26] reported a new method for removal of acridine orange by the in-situ reduction of graphene oxide with sodium hydrosulfite. This method not only enables the efficient adsorption of pollutants onto in-situ reduced GO with large surface areas and abundant active sites, but also facilitates the spontaneous separation of pollutants along with rGO from solution, thus greatly reducing cost and simplifying operations for water treatment. In-situ reduction of GO using Zn powder has been proved to be more economic and efficient because the used reagents are environmentally friendly, and the reaction can be triggered by various conditions such as pH/EDTA [27] and sonication [28]. However,

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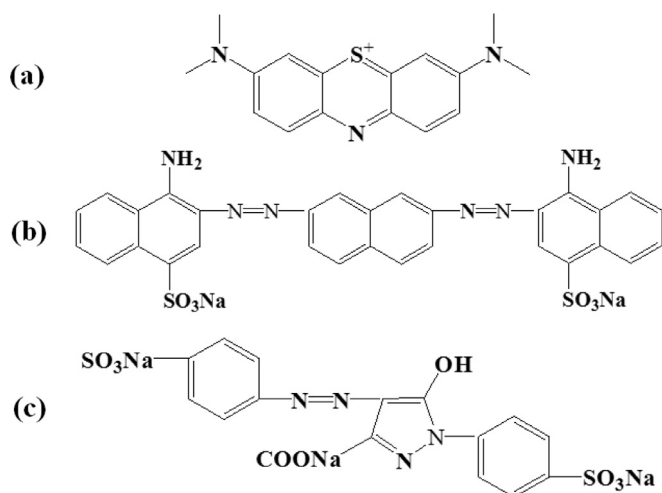


Fig. 1. The molecular structures of MB (a), CR (b) and LY (c).

the application of in-situ reduced GO by Zn powder is very rare, especially in the pollutant adsorption.

In this work, a new strategy for water treatment based on the in-situ reduction method of GO by Zn powder is developed. Five pollutants, methylene blue (MB), congo red (CR), lemon yellow (LY), cadmium ions (Cd^{2+}), and lead ions (Pb^{2+}) are used as example pollutants. In the course of in-situ reduction of GO, the removal efficiency of these pollutants is up to 98.46% within 10 min. Their adsorption capacities are up to 2.6, 7.6, 3.2, 8.4, and 17.9 g g^{-1} , respectively. This water treatment system utilizing Zn-induced in-situ reduction of GO has several advantages: (1) the in-situ reduction efficiency of GO is further facilitated by addition of NH_4Cl , and the removal efficiency is very high; (2) the reduction and precipitation of rGO can be finished within several minutes, which greatly reduces the period of water treatment and avoids additional separation operations; (3) the treatment cost is low and the environment problem is slight because the byproducts can be further used in energy or agricultural fields. In addition, this method has been successfully applied to the treatment of several real water samples including simulated wastewater samples, soil turbid water, milk and yogurt.

2. Materials and methods

2.1. Materials and reagents

Spectroscopically pure (SP) graphite, phosphorus pentoxide (P_2O_5), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), zinc (Zn) powder, ammonium chloride (NH_4Cl), calcium chloride (CaCl_2), methylene blue (MB), Congo red (CR), lemon yellow (LY), cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$) and lead nitrate ($\text{Pb}(\text{NO}_3)_2$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) (The molecular structures of the three dyes shown in Fig. 1). Technically pure (T.P.) manganese dioxide (MnO_2 , ~92%) was obtained from Adamas Reagent Co., Ltd. (Shanghai, China). Dimanganese trioxide (Mn_2O_3 , 99%) was purchased from Xiya Chemical Reagent Co., Ltd. (Chengdu, China). Potassium permanganate (KMnO_4) was purchased from Alfa Aesar. Qualitative filter papers (12.5 cm in diameter) were purchased from Hangzhou Wohua Filter Paper Co. Ltd., Hangzhou, China. Ultrapure deionized water (>18 $\text{M}\Omega\cdot\text{cm}$) was produced on a Milli-Q water purification system. Unless otherwise stated, all reagents were of analytical grade and used without further purification.

2.2. Instruments

Atomic force microscopic images (AFM) were obtained on a scanning probe microscope (SPM-9700) using the tapping mode at a scan rate of 0.5 Hz. Field emission scanning electronic microscope (FESEM) images were collected on JEOL-7600F with an acceleration voltage of 30 kV. Transmission electron microscopy (TEM) was performed on JEOL-2100. Raman spectra were carried out on DXR Confocal Raman microscopy (Thermo Scientific, excitation wavelength 532 nm). Fourier transform infrared spectra (FTIR) were performed on Equinox-55 FTIR (Bruker Company). X-ray diffraction (XRD) spectra were obtained on X' Pert PRO diffractometer (Panalytical Company, $\text{Cu } \alpha_1$ radiation 0.154 nm).

2.3. Synthesis of large GO sheets

GO was synthesis according to our previously reported modified Hummer method with slight modification, *i.e.*, a ball-milled mixture of T.P. MnO_2 and AR Mn_2O_3 was used to replace the widely used potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) or impure MnO_2 for the pre-oxidation of graphite.

Honey-like GO hydrogel with large sheets was synthesized according to previous report [29]. Briefly, a mixture of 1.84 g T.P. MnO_2 and 0.16 g AR Mn_2O_3 was ball-milled at ambient conditions for 2 h to prepare a preoxidant of graphite. This milled preoxidant and P_2O_5 (2.0 g) were gradually added to concentrated H_2SO_4 (10 mL) at 90 °C with stirring. After 10 min, the temperature was cooled to 80 °C and graphite (2.4 g) was slowly added. The mixture was allowed to react at 80 °C for 5 h, cooled to room temperature, carefully diluted with water (400 mL) and washed with abundant water on mixed cellulose ester filter membranes (diameter 50 mm, pore size 0.22 μm) until the filtrate became neutral. The resulting peroxidized graphite (POG) was dried at 60 °C for 6 h and added to concentrated H_2SO_4 (92 mL) in an ice-water bath. Then, KMnO_4 (12.0 g) was slowly added with stirring to control the temperature below 5 °C. The mixture was stirred at 35 °C for 4 h, diluted with ice water (200 mL) and heated to 48 °C for 2 h. Afterward, the mixture was cooled to room temperature and diluted with water (600 mL). Then, 30% H_2O_2 (10 mL) was added drop-wise with strong stirring. The brown sediment was washed by HCl (10 wt%, 300 mL) for at least six times to remove trace metal ions, each for 0.5 h. The mixture was allowed to stand overnight, washed with copious water and dialyzed in water for at least 7 days, producing a honey-like GO hydrogel.

2.4. Adsorption tests

Adsorption experiments without pH adjustment were carried out at room temperature in sample vials containing pollutants. The adsorption tests were performed by successively adding GO, Zn powder and NH_4Cl into pollutant solutions and stirring the solutions for 10 min. The reaction mixtures were then filtered on qualitative filter papers to separate the black precipitate from solution. The filtrate was further centrifuged at 12,000 rpm for 10 min to remove any solid products, which was used for detection of residual concentrations of dyes and heavy metal ions after water treatment. The residual concentrations of dyes were measured using a UV-Vis spectrophotometer (UV-2550, Shimadzu) at the corresponding maximum absorption wavelength (λ_{max} : MB 664 nm, CR 488 nm, LY 426 nm) and the concentration of metal ions were measured on a flame atomic absorption spectrometer (FAAS-ICE-3000, Thermo Fisher Scientific). Then, removal efficiency and adsorption

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