



# Co-polymerization of catechol and polyethylenimine on magnetic nanoparticles for efficient selective removal of anionic dyes from water



Yangke Long, Ling Xiao\*, Qihua Cao

Key Laboratory for Biomass-Resource Chemistry and Environmental Biotechnology of Hubei Province, School of Resource and Environmental Science, Wuhan University, Wuhan 430072, PR China

## ARTICLE INFO

### Article history:

Received 2 November 2016

Received in revised form 22 December 2016

Accepted 5 January 2017

Available online 6 January 2017

### Keywords:

Fe<sub>3</sub>O<sub>4</sub> nanoparticles

Catechol

Polyethylenimine

Anionic dyes

Selective adsorption

## ABSTRACT

In the present study, novel magnetic adsorbents Fe<sub>3</sub>O<sub>4</sub>@catechol/PEI were fabricated simply by co-polymerization of catechol and branched polyethylenimine (PEI) onto Fe<sub>3</sub>O<sub>4</sub> nanoparticles under alkaline condition, and characterized by transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and vibrating sample magnetometer (VSM). Adsorption of three different kinds of anionic dyes, methyl blue, orange G and amaranth, from aqueous solutions using Fe<sub>3</sub>O<sub>4</sub>@catechol/PEI was investigated. The adsorption results showed that the removal of anionic dyes by Fe<sub>3</sub>O<sub>4</sub>@catechol/PEI matched well with pseudo-second-order kinetic model and Langmuir isotherm model. The maximum adsorption capacities for methyl blue, orange G and amaranth were 344.8, 192.3, and 146.2 mg·g<sup>-1</sup>, respectively. Furthermore, the anionic dyes could be selectively adsorbed from dye mixtures containing anionic and cationic dyes. After adsorption, Fe<sub>3</sub>O<sub>4</sub>@catechol/PEI could be efficiently separated from the solution under the adsorbent magnetic field and could be easily regenerated. This novel magnetic adsorbent is a promising candidate for removal of anionic dyes in the wastewater.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

With the economic and social development, serious attentions have been paid to water pollution. Among various water contaminants, organic dyes are highly undesirable due to the highly intense colors and toxicity to human and other aquatic organisms even in low concentrations [1]. Organic dyes have been applied widely to various industries, such as the dye stuff, cosmetic, paper, leather, textile and printing industries [2–6]. Therefore, it is of significant importance to remove the dye from the dye-bearing industrial effluents before they are released into environment. In order to alleviate the contamination of industrial effluents containing organic dyes, a variety of techniques have been proposed, including biodegradation, advanced oxidation, adsorption, coagulation, flocculation, and membrane separation [7–11]. Owing to the advantages of easy operation, cost-effectiveness and high efficiency, adsorption is becoming increasingly popular in dealing with the dye-bearing wastewater. Recently, various adsorbents such as activated carbon [12], zeolite [13], silica [14], chitosan [15], carbon tube [16] and graphene [17], have been prepared to eliminate the dye pollution. Effective as they are, these adsorbents still suffered from some drawbacks. For instances, the synthesis process is complicated and time-consuming, raw materials are relatively costly, adsorbents are hard to

be collected, and so on. Thus, it is desirable to fabricate new promising adsorbents.

Inspired by the attachment of mussel adhesive proteins to wet surfaces, Lee et al. [18] pointed out that dopamine was a mimic molecular of adhesive protein found from the mussels. The dopamine monomers can be auto-polymerized to generate polydopamine (PDA) at alkaline pH values and easily deposited on virtually any surface of materials ranging from organic to inorganic without any surface pretreatment [19]. Owing to the excellent properties, polydopamine and its derivatives have received extensive attention in the field of environmental remediation [20–22]. Many PDA based materials were fabricated as novel adsorbents for the removal of pollutants from aqueous solutions [23–25]. Although these adsorbents are effective for the removal of pollutants, the main shortcoming of dopamine and its derivatives is that they are too expensive, which impedes their practical application. Most recently, the plant polyphenols, a kind of substance with very low cost, were used as coatings similar to dopamine [26,27], and these coatings retained most advantages of polydopamine. Lim et al. [28] demonstrated that polycatechol-amine coatings were much stable than polycatechol coatings and the presence of amine groups was vital for the development of mussel inspired catechol-based coating materials. Porous membranes modified by the co-deposition of catechol and polyethylenimine have been fabricated and applied in the treatment of wastewater [29,30]. However, these membrane techniques lacked of economic attraction because they are still confronted with high investment and maintenance costs.

\* Corresponding author at: The Luojia Mountain of Wuchang, Wuhan City, Hubei Province 430072, PR China.

E-mail address: [xiaoling9119@whu.edu.cn](mailto:xiaoling9119@whu.edu.cn) (L. Xiao).

In recent years,  $\text{Fe}_3\text{O}_4$  nanoparticles are gaining extensive attention in the field of wastewater treatment.  $\text{Fe}_3\text{O}_4$  nanoparticles based magnetic adsorbents have been widely studied because of their large surface area, low cost, and the unique superparamagnetism at room temperature [31]. After reaching saturated adsorption, the magnetic adsorbents could be simply separated from solution with the help of a magnet without requiring tedious filtration or centrifugation, and thus realize high efficiency in wastewater treating. To improve the adsorption performance of  $\text{Fe}_3\text{O}_4$  nanoparticles, the surface modification of  $\text{Fe}_3\text{O}_4$  nanoparticles is necessary.

In this study, novel magnetic adsorbents  $\text{Fe}_3\text{O}_4$ @catechol/PEI were fabricated via *co*-deposition of low cost catechol and branched polyethylenimine (PEI) onto  $\text{Fe}_3\text{O}_4$  nanoparticles in alkaline solution. The as-prepared adsorbents were characterized by various techniques and applied to selective removal of three anionic dyes, namely methyl blue, orange G, and amaranth, from aqueous solutions. The adsorption behaviors of the  $\text{Fe}_3\text{O}_4$ @catechol/PEI were systematically investigated.

## 2. Experimental

### 2.1. Materials and reagents

Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), iron(II) chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), ammonium hydroxide ( $\text{NH}_4\text{OH}$ , 28 wt%) and catechol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Trihydroxymethylaminomethane hydrochloride (Tris-HCl) was obtained from Sigma-Aldrich (USA). Polyethylenimine (PEI, Mw = 600) was supplied by Aladdin Chemistry Co., Ltd. (Shanghai, China). Three anionic dyes, methyl blue (MB), orange G (OG) and amaranth (AM), and a cationic dye, malachite green (MG) (chemical structures are shown in Fig. 1), were purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). All the reagents were used as received without further purification. Ultrapure water (18.25 M $\Omega$ ·cm) was used throughout the study.

### 2.2. Characterization

The transmission electron microscopy (TEM) imaging was performed on a Hitachi H-7000FA transmission electron microscope (Hitachi, Japan) with an accelerating voltage of 75 kV. Ultraviolet-visible (UV-vis) spectra were recorded using a UV-2700 spectrophotometer (Shimadzu, Japan) at room temperature. Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet 5700 FTIR spectroscope (Nicolet, USA). All pH values were measured with a Delta320 digital pH meter (Mettler-Toledo, Switzerland). The zeta potential was measured using a Malvern Zen 3600 Zetasizer (Malvern Instruments, United Kingdom) under various pH conditions. Powder X-ray diffraction (XRD) patterns were performed on a X'pert PRO diffractometer (PANalytical, Holland) using Cu K $\alpha$  radiation (wavelength  $\lambda = 1.5406 \text{ \AA}$ ) in the  $2\theta$  range of  $10^\circ$ – $80^\circ$ . X-ray photoelectron spectroscopy (XPS) measurements were analyzed using an ESCALAB 250Xi spectrometer (Thermo Fisher, USA). Magnetic properties (M–H curves) were evaluated using a PPMS-9T superconducting quantum interference device magnetometer (Quantum Design, USA) at 300 K. Thermogravimetric analysis (TGA) was conducted on a TG/DTA7300 thermogravimetric analyzer (Hitachi, Japan) at a heating rate of  $15^\circ\text{C}/\text{min}$  under a nitrogen purge.

### 2.3. Preparation of adsorbents

The magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles were synthesized via a chemical coprecipitation method with minor modification [32]. In a typical synthesis, 7.2 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 2.7 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 200 mL ultrapure water. The solution was transferred to a three-necked flask and was stirred vigorously for 1 h under pure nitrogen gas atmosphere. Subsequently, 28 mL  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (28 wt%) was added into the mixture dropwisely and the reaction temperature was elevated to  $60^\circ\text{C}$  and maintained for 2 h. Finally, the mixture was allowed to cool to room temperature. The black products were magnetically separated and washed with ultrapure water for several times. The as-prepared magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles were kept in water for further use.

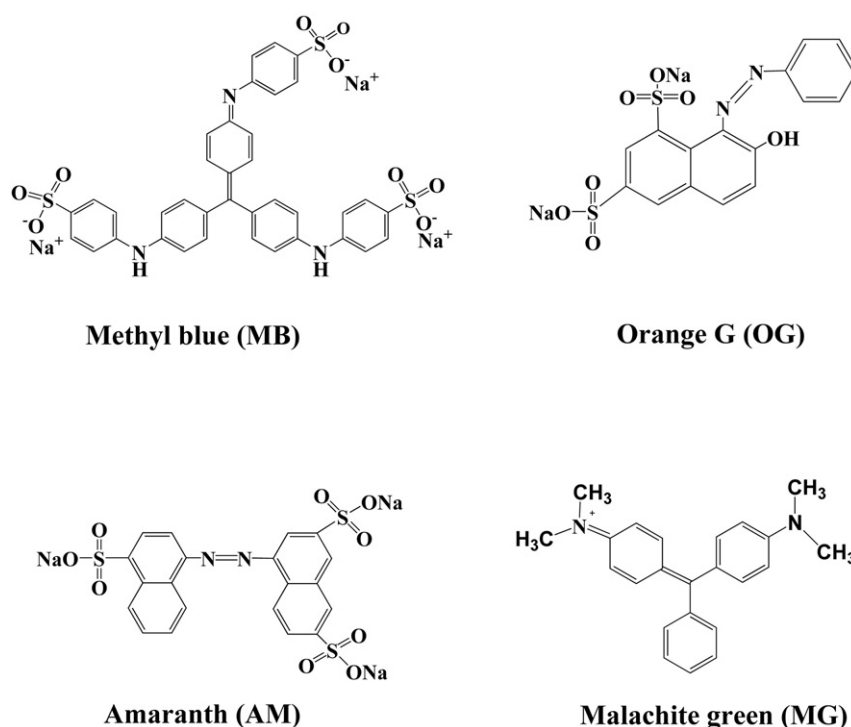


Fig. 1. Structures of MB, OG, AM and MG.

Download English Version:

<https://daneshyari.com/en/article/4915024>

Download Persian Version:

<https://daneshyari.com/article/4915024>

[Daneshyari.com](https://daneshyari.com)