



Preparation and characterization of sulfonated poly(styrene-alt-maleic anhydride) and its selective removal of cationic dyes



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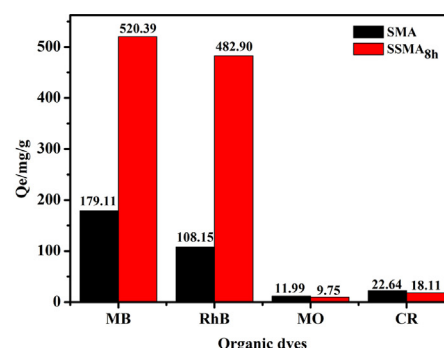
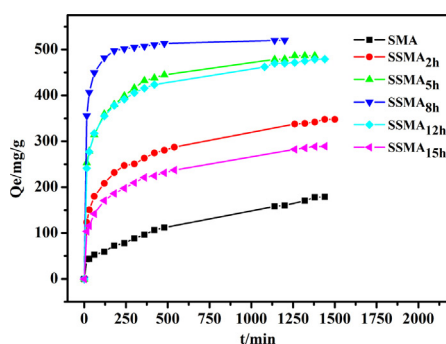
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HIGHLIGHTS

- SSMA microspheres were prepared from poly(styrene-alt-maleic anhydride) by sulfonation reaction.
- The presence of $-\text{SO}_3\text{H}$ on the surface of SSMA made it a possible candidate for the adsorption of positively charged dyes.
- SSMA was an adsorbent for selective removal of cationic dyes.
- The adsorption capacity of SSMA for cationic dyes was greatly increased compared to that of SMA.

GRAPHICAL ABSTRACT

After sulfonation, the adsorption capacity of SSMA for MB was enhanced significantly compared to that of SMA. And they showed great potential for selective removal of cationic dyes.



ARTICLE INFO

Article history:

Received 31 December 2015
Received in revised form 17 March 2016
Accepted 3 April 2016
Available online 4 April 2016

Keywords:

SMA
SSMA
Dyes
Sulfonation
Adsorption behavior
Adsorption kinetics

ABSTRACT

Sulfonated poly(styrene-alt-maleic anhydride) (SSMA) microspheres were prepared from poly(styrene-alt-maleic anhydride) (SMA) by sulfonation reaction and its adsorption behavior as an efficient adsorbent for the removal of organic dyes was systematically studied. The structure and morphology of SMA and SSMA were characterized by ^{13}C NMR, FTIR, EDS, XPS, SEM and TEM. The adsorption performance of SMA and SSMA toward organic dyes was investigated by batch mode adsorption experiments. Results indicated that the SSMA had much more adsorbability for cationic dyes such as methylene blue (MB) and Rhodamine B (RhB) compared to SMA. The adsorption capacity for MB of SSMA_{8h} which had been sulfonated 8 h was found to be 671.14 mg/g, while the adsorption capacity of SMA for MB was 344.83 mg/g at 25 °C, showing that the adsorption capacity for cationic dyes was enhanced 94.63% via the sulfonation. The kinetic studies revealed that the sorption followed a pseudo-second-order kinetic model which indicated that the adsorption interaction between adsorbent and adsorbate molecules was chemisorption. Moreover, adsorption isotherm mechanisms were analyzed by Freundlich and Langmuir models.

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1. Introduction

In recent years, the extensive use of synthetic dyes in manufacturing such as in textile, paper, paint, food, pharmaceutical

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and cosmetic industries, has led to an increased scientific interest in the field of dye wastewater treatment for the global society [1]. Synthetic dyes are difficult to degrade and generally stable to light, heat and oxidizing agents due to their complex aromatic structure [2,3]. Once these dyes degrade into toxic, mutagenic or carcinogenic compounds, they will have a huge impact on aquatic ecosystem and human health [4]. Therefore, effective removal of dyes from wastewater becomes very essential. Many techniques including flocculation, membrane separation, ion exchange, filtration, chemical oxidation, electrolysis, microbiological degradation, photocatalysis degradation and adsorption have been used till now [5,6]. Among these methods, adsorption takes advantages of low operating cost, high efficiency and low energy consumption, generally considered as the promising method for wastewater purification. To date, different conventional adsorbents such as activated carbon [7], clay [8], metal oxides [9,10], gel [11,12] and polysaccharide [13] have been studied extensively and systematically. However, the key problems are the low adsorption capability, difficult to recycle and unable to degrade which would cause secondary stress on the environment. Therefore, to develop biocompatible and biodegradable adsorbents for the removal of toxic dyes from effluents is very important.

Poly(styrene-*alt*-maleic anhydride) (SMA) is a well-known regular alternating combination of styrene and reactive anhydride group in its linear molecular chain copolymer with low toxicity, low cost, and good biocompatibility and biodegradation. Due to these excellent performances, the modified SMA copolymers have been introduced as surface active agents, microbicides, external dopant, drug carriers, and excellent sorbent for removal of heavy metal ions [14,15]. Our interest for the use of this copolymer is due to the fact that SMA is an inexpensive commercially available copolymer having good biocompatibility and biodegradation so that it could act as a potential adsorbent which would not cause the secondary pollution after removing dyes from aqueous solution.

To enhance the water-dispersibility of poly(styrene-*alt*-maleic anhydride) (SMA) copolymer for removal of dyes from aqueous solutions, it is sulfonated by concentrated sulfuric acid to get sulfonated poly(styrene-*alt*-maleic anhydride) (SSMA) [16]. The sulfonation process produces hydrophilic shells with sulfonic acid groups attached to SMA chains [17]. As the adsorption process is primarily driven by electrostatic forces, the effects of sulfonation will be an important factor on the adsorption capacity of SSMA toward dyes from aqueous solutions [18]. In fact, the SSMA microsphere is a kind of potential polymer adsorbents used in separation of cationic dyes from polluted water [19,20].

In this work, two kinds of adsorbents for the removal of organic dyes were successfully synthesized. Firstly, poly(styrene-*alt*-maleic anhydride) (SMA) spheres were prepared via precipitation polymerization method. Then, the as-prepared SMA microspheres were coated with sulfonic acid group by sulfonation with sulfuric acid as surface modification agent. Since various degrees of sulfonation may lead to some different electrical charges on adsorbent surfaces, the effect of sulfonation time on the adsorption capacity of SSMA was also studied. The resulting adsorbent microspheres were characterized by ^{13}C NMR, FTIR, EDS, XPS, SEM and TEM. As the H_2SO_4 -treated SMA were introduced negative charges on the surface of microspheres due to the formation of $-\text{SO}_3\text{H}$, the presence of negative charges on the surface of SSMA made it a possible candidate for the adsorption of positively charged dyes [20]. Hereon, MB and RhB were selected as two typical cationic dyes to evaluate the adsorption capacity of the adsorbents, while Methyl Orange (MO) and Congo Red (CR) selected as anionic dyes. Taking MB as a model dye, the adsorption properties such as adsorption kinetics and equilibrium isotherms of the adsorbents were investigated through the batch mode adsorption experiments.

Table 1
Recipes for the preparation of SSMA microspheres^a.

Sample identification	Samples	SMA (g)	Sulfonated time (h)
S1	SSMA _{0h} (SMA)	0.4	0
S2	SSMA _{2h}	0.4	2
S3	SSMA _{5h}	0.4	5
S4	SSMA _{8h}	0.4	8
S5	SSMA _{12h}	0.4	12
S6	SSMA _{15h}	0.4	15

^a The sulfonated temperature was 40 °C and the amount of concentrated sulfuric acid was 4 mL.

2. Materials and methods

2.1. Materials

Methylene blue (MB), Rhodamine B (RhB), Methyl orange (MO), and Congo Red (CR) dyes used in this study were supplied from Aladdin reagent Co., Ltd. (China). All dyes were analytical grade and used without further purification. Divinylbenzene (DVB, 80%) was supplied from Sigma–Aldrich Chem. Corp., USA. All of the other reagents were analytical-grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ethyl butyrate ($\geq 98.0\%$), sulfuric acid ($\text{H}_2\text{SO}_4 \geq 98.0\%$), ethanol ($\geq 99.0\%$), and other reagents were used as received. Styrene (St) was washed thrice with a 10% NaOH solution and thrice with water to remove inhibitor. It was stored at -10°C after drying over calcium chloride and then was freshly distilled under reduced pressure before use. Azobisisobutyronitrile (AIBN) was recrystallized twice from absolute methanol. Maleic anhydride (MAn) was recrystallized thrice from chloroform.

2.2. Methods

2.2.1. Synthesis of poly(styrene-*alt*-maleic anhydride) (SMA)

Poly(styrene-*alt*-maleic anhydride) (SMA) microspheres were prepared by precipitation copolymerization following the procedure described in the literatures [21,22]. Briefly, 30 mL of ethyl butyrate was added to a mixture of 1.56 g of styrene (St), 1.47 g of maleic anhydride (MAn), and 0.03 g of azobisisobutyronitrile (AIBN) in a three-necked round bottom flask at room temperature and deoxygenated by bubbling N_2 gas for 30 min. Then, the reaction mixture was heated to 80°C gradually. When the white precipitate appeared, 200 μL of divinylbenzene (DVB) was added. The flask was sealed and immersed in a water-bath for 5 h under N_2 protection. The white powder was collected by centrifugation and washed with ethanol for three times. The final product was dried under vacuum at 35°C for at least 24 h.

2.2.2. Preparation of SSMA microspheres

In a typical run for the preparation of sulfonated SSMA microspheres, the powder of the above prepared SMA microspheres (0.4 g) was dispersed ultrasonically in concentrated sulfuric acid (4 mL). The sulfonation reaction was carried out at 40°C under magnetic stirring for a certain time. After the reaction, the product was diluted and washed with deionized water for several times. The resulting sulfonated poly(styrene-*alt*-maleic anhydride) (SSMA) was put into a vacuum oven (0.01 MPa) to be dried at 35°C for 24 h. The detailed recipes were listed in Table 1.

2.2.3. Adsorption experiments for dyes

All adsorption experiments were carried out in a thermostatic shaker (Jin cheng Guo sheng, China) with a shaker speed of 150 rpm until the system reached equilibrium. Briefly, 20 mg of different as-prepared adsorbents powders were dispersed in 100 mL of aqueous solution containing various concentrations (100, 150, 200, 250, 300,

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