Materials and Design 135 (2017) 333–342

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Synthesis and application of sulfonated polystyrene/ferrosoferric oxide/diazoresin nanocomposite microspheres for highly selective removal of dyes

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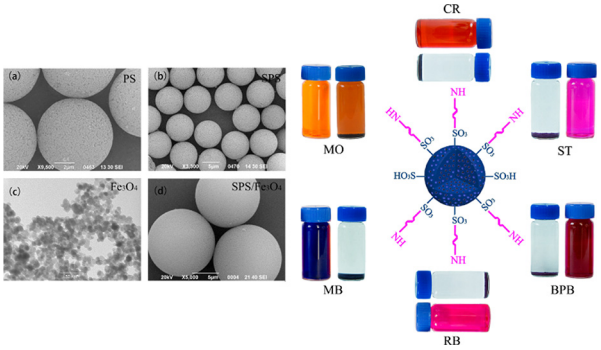
HIGHLIGHTS

- SPS/Fe_3O_4/DR microspheres were synthesized by seeded polymerization, surface modification and self-assembly.
- Large surface area, several acidic/basic groups and magnetic properties of microspheres could be obtained.
- SPS/Fe_3O_4/DR microspheres were applied as sorbents for removal dyes with good adsorption performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 July 2017
Received in revised form 16 September 2017
Accepted 18 September 2017
Available online xxxx

Keywords:
Sulfonated polystyrene
Ferrosoferric oxide
Diazoresin
Adsorption
Dyes

ABSTRACT

A versatile porous adsorbent of sulfonated polystyrene/ferrosoferric oxide/diazoresin (SPS/Fe_3O_4/DR) nanocomposite microspheres with magnetic property and acidic/basic groups was prepared and applied for removal of different dyes from water. The adsorbent showed good adsorption performance due to its functional groups and strong adsorption forces. The selective removal of methylene blue (MB) from MB/methyl orange (MO) mixture can be realized using this adsorbent. The adsorption uptake capacity of the adsorbents was 223.71 mg/g and the removal efficiency was more than 90% even after five adsorption-desorption cycles. This adsorbent could be readily separated from solution within 2 min using a magnet. Furthermore, adsorption kinetics for SPS/Fe_3O_4/DR followed by the pseudo-second order model. Isothermal equilibrium data were fitted with Langmuir model, which indicated the adsorption process is the monolayer adsorption. This novel, low cost and high effective adsorbent possesses great potential in environmental pollution cleanup.

1. Introduction

To date, the rapid development of various industries, for example textile, food, cosmetics, pharmaceuticals, leads to the increasing in amount of dyes and other colored contaminants. Dye stuff has becoming a global environmental issue owing to its carcinogenic and mutagenic effects to human and other living organisms. Long-term exposure to dyes can seriously affect bodily functions. Besides, most dyes are non-biodegradable due to their complicated aromatic structure. Thus, it is important to remove dyes from wastewater before discharging. Many technologies for removing toxic dye stuffs from aqueous solution have been developed, including ion exchange [1], adsorption [2,3], electrochemical treatment [4], biological treatment [5], chemical oxidation [6] and degradation [7]. Among the above mentioned technologies,

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https://doi.org/10.1016/j.matdes.2017.09.039
0264-1275/

adsorption is considered to be one of the most effective and competitive method, owing to its operational simplicity, wonderful adsorption performance and regeneration of the adsorbents [8]. The core of adsorption is the choice of the adsorbents. Various adsorbents have been invented for adsorption of organic dyes, such as poly(cyclotriphosphazene-*co*-4,4′-sulfonyldiphenol) nanotubes, silica hybrid membrane, montmorillonite, activated carbon and nanocomposite hydrogel, graphene oxide and so on [9–14].

However, there are still some problems to be handled: many adsorbents can only adsorb the specific dye molecule; the aim of selective adsorption is hard to be achieved; the adsorption capacity is relatively low. All these factors seriously limit the applications of the adsorbents. Thus, it is highly imperative to develop eco-friendly materials with low-cost, multiple groups and good adsorption capacity.

To solve these above problems, a novel multifunctional magnetic SPS/Fe_3O_4/DR nanocomposite microspheres were prepared and investigated in this work, which possessing sufficient acidic and basic functional groups simultaneously. Highly selective adsorption of cationic dyes except for anionic dyes were realized using this adsorbent. In addition, the magnetic material of Fe_3O_4 could promote the rapid separation of the adsorbents from the dye solution. Diazoresin (DR) is a positive-charged nontoxic photoactive polyelectrolyte. Under the action of light, diazo groups can undergo photolysis reactions to form positive carbon ions (in polar media) or neutral radicals. Generally, sulfonated polystyrene (SPS) microspheres are prepared by three steps, i.e. the preparation of polystyrene seed by using dispersive polymerization, then synthesis of polystyrene particles with larger particle size by seed emulsion polymerization [15–18], subsequently the sulfonation reaction are processed on the basis of polystyrene particles. However, there may be some difference, when it comes to the type of the reaction reagents, dosage, temperature and reaction time, and so on. Some commonly used sulfonation reagents, include sulfuric acid, acetyl sulfate, chlorosulfonic acid [19–21]. Youn-Sik Lee and coworkers synthesized sulfonated SPS particles by taking dispersed highly porous hypercrosslinked polystyrene into the acetyl sulfuric acid, which was prepared by thoroughly mixing sulfuric acid and acetic anhydride in the presence of 1,2-dichloroethane [22]. Lincheng Zhou team prepared porous SPS Microspheres by using H_2SO_4 and Ag_2SO_4 as the sulfonation reagents on the basis of porous PS Microspheres. They poured porous PS microspheres into the mixture of H2SO4 and Ag_2SO_4. After reaction under 80 °C for 2 h, the products were washed using distilled water and then dried at 40 °C for 24 h, thus SPS microspheres were obtained [23]. Sulfuric acid is the most direct method to achieve the goal without any extra steps. Tariq M. Bhatti team also fabricated sulfonated PS-DVB microspheres. After obtaining PS polymer support, the product was reacted with the concentrated sulfuric acid (98%), in 1:5 ratios (w/v). Herein, the solid materials were sulfonated directly with acid solution at 98 °C for 2 h, without other regents [19]. Porous SPS possesses many properties, for example, excellent mechanical performance, porous structure, large surface area, sufficient functional groups (–SO_3H). Basic functional groups makes highly selective adsorption ability for the dyes [19].

MB was utilized as the model dye to assess the adsorption capacity of the adsorbents and to study the adsorption kinetics and isotherm models. The influence of MB initial concentration, pH, dose of the adsorbents and contact time toward adsorption efficiency were investigated. The regeneration of the dye-adsorbed SPS/Fe_3O_4/DR was also discussed.

2. Experimental

2.1. Materials

Congored (CR), safranine T (ST), bromophenol blue (BPB), rhodamine B (RB), methylene blue (MB), methyl Orange (MO), ethanol, polyvinylpyrrolidone (PVP), 2,2′-azobis (isobutyronitrile) (AIBN), sodium dodecyl sulfate (SDS) were purchased from Aladdin industrial corporation. Toluene, dibutyl phthalate (DBP), benzoyl peroxide (BPO), divinylbenzene (DVB, 80%), poly(vinyl alcohol) (PVA), tetrahydrofuran (THF), $FeCl_3$, $FeCl_2$, H_2SO_4 (98%) and NaOH were obtained from Tianjin Xingfu Fine Chemical Research Institute. Styrene (St) was distilled to remove the inhibitor before use. Other reagents were used as-received without further purification.

2.2. Preparation of SPS/Fe3O4/DR

Firstly, polystyrene (PS) seeds and cross-linked polystyrene particles were synthesized via dispersion polymerization and seeded swelling polymerization. Monomers were consisted of St and DVB. DVB contains 80% pure DVB isomers (a mixture of o-, m-, p-isomers) and 20% impurities. Cross-linking can be controlled and calculated by adjusting the mass of St as well as DVB. Then, the porous polystyrene particles with different degree of cross-linking were directly sulfonated by using concentrated sulfuric acid as the sulfonation reagent. As a consequence, $-SO_3H$ will be grafted onto the polymer networks by sulfonic acid reacted with benzene ring. It is noteworthy that the collapse and rearrangement of porous structure will be occurred once sulfonation time is too long. Finally, a self-assembled DR monolayer coating was completed on the surface of SPS/Fe_3O_4 microspheres. The coating cycle was repeated 15 times to obtain a multilayer coating. After drying, the microspheres were exposed to 365 nm ultraviolet (UV) light for 1 h in order to form the covalently linked DR coatings on the surface. The detail preparation methods of the magnetic SPS/Fe_3O_4/DR nanocomposite microspheres and procedure for characterization methods are described in the Supporting Information.

2.3. Adsorption experiments

Six kinds of dyes were selected as the target adsorbates in a series of adsorption experiments, which are Cong Red (CR), Safraninc T (ST), Bromophenol Blue (BPB), Rhodamine B (RB), Methylene Blue (MB), Methyl Orange (MO). The adsorption kinetics experiments were optimized with 50 mL dyes solution (different concentration) at room temperature and the agitation at 150 rpm for desired time. After adsorption, the adsorbent was separated from solution by an external magnet. The concentration of dyes molecule remained in the aqueous solution was measured via UV–Vis spectroscopy (Germen) for three times to make sure accuracy of the results.

When it comes to MB dye, the standard curve was obtained using standard solutions with concentration ranging from 0.2 to 10.0 mg/L. The MB dye concentration was determined via UV–vis spectroscopy at $\lambda_{max} = 664$ nm. The effect of initial concentration on the adsorption performance was obtained by adding adsorbent into 50 mL MB solutions with different initial concentrations (50–240 mg/L) at room temperature (25 °C). The pH value was adjusted by using HCl or NaOH ranging from 2 to 12. The effect of contact time and amount of the adsorbents were also discussed. The amount of MB adsorbed (Q_e in mg/g) and the adsorption efficiency of the adsorbents are calculated as following Eqs. (1) and (2), respectively:

$$Q_e = \frac{(c_0 - c_e)v}{M} \tag{1}$$

$$\text{Adsorption effeciency } (\%) = \frac{(c_0 - c_e)}{c_0} \times 100\% \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentrations of MB (mg/L), M represents the mass of the adsorbents (g), and V is the volume of the aqueous solution (L), Q_e is the adsorption capacity of MB at equilibrium state.