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Adsorption of Congo red from aqueous solution using ZnO-modified SiO_2 nanospheres with rough surfaces

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ABSTRACT

As one of the toxic dyes, Congo Red (CR) is considered as emerging pollutant in surface water, thus, the development of novel adsorbent for its efficient removal is necessary. Here, ZnO/SiO_2 nanosphere composites with rough surfaces were synthesized by a facile wet impregnation method. The structure and morphology of as-prepared composites were characterized and their performances toward CR adsorption were evaluated. The ZnO/SiO_2-1 composite exhibited high adsorption capacity of ~83 mg/g and fast adsorption kinetic for removal of CR from aqueous solution. The adsorption kinetic and isotherm data could be well interpreted by the Pseudo-second-order rate equation and Langmuir adsorption isotherm, respectively. Moreover, the ZnO/SiO_2-1 could be easily regenerated by calcination and the adsorption capacity could be maintained at high level (up to 83%) for at least 4 adsorption-regeneration cycles.

1. Introduction

Organic dyes are extensively used in the textile, plastics, printing and cosmetic industries. The discharge of dye contaminants into natural or engineered water bodies has caused serious environmental problems in recent years, as many of the dyes are highly toxic to aquatic life and hard to be degraded in natural environments [1,2]. Therefore, it is essential to remove these dyes from wastewater.

The most commonly used techniques for dye removal are catalytic oxidation, ion-exchange and adsorption [3–6]. Among them, adsorption has become the most competitive method for wastewater treatment due to its easy and inexpensive operation, high efficiency and low energy consumption [7]. Various adsorbents, including activated carbon [8,9], clays [10,11], and metal oxides and hydroxides [12,13], have been studied for the adsorptive removal of dyes from contaminated water. However, many of these adsorbents fail to fully meet the requirements, such as good adsorption selectivity or high adsorption capacity. Thus, for the practical application of adsorption, exploring effective adsorbents is still needed.

As a common metal oxide, zinc oxide (ZnO) has been applied in many fields because of its low cost, good stability, nontoxicity and environmental-friendly properties [14–16]. To date, different methods have been used for the production of ZnO particles, such as precipitation [17,18], hydrothermal [19–21] and ultrasonic assisted methods [22,23]. In general, most of the methods have been developed for synthesis of ZnO nanoparticles, as nanomaterials often have larger specific surface areas and feature better adsorption performance than bulk materials. However, ultrafine particles tend to aggregate in water and are difficult to separate.

Dispersion of ZnO onto a substrate with relatively large size may solve the above problem. On one hand, impregnation of ZnO particles on a substrate with large internal surface area, such as porous material, may improve adsorption performance. However, introducing ZnO might occlude the pores of the substrate [24], which would be difficult to be used for the adsorption of large molecules. On the other hand, dispersion of ZnO onto a particle with large external surface, such as particles with rough surface, may be beneficial for adsorption of large molecules, but it has been rarely reported.

Recently, novel SiO_2 spheres with rough surfaces have been successfully synthesized and showed remarkable properties [25–27], which makes it possibly be a good substrate for ZnO dispersion. In this work, ZnO was dispersed onto SiO_2 spheres with rough surfaces by wet impregnation successfully. The ZnO-SiO_2 composites were characterized by different techniques and evaluated for the adsorption performances toward Congo red (CR). The results show that simple impregnation method led to good dispersion of ZnO onto the SiO_2 substrate. The adsorption capacities of the ZnO/SiO_2 composites for CR were as high as ~83 mg/g at 30 °C.

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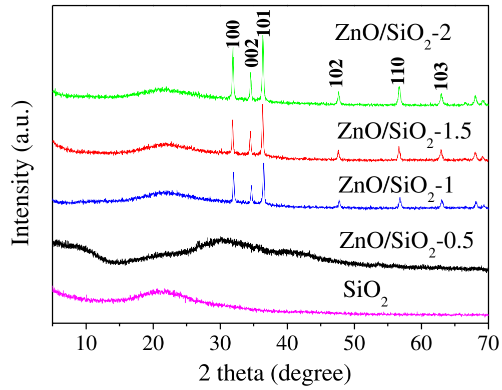

Fig. 1. XRD patterns of the pure SiO_2 sample and ZnO-SiO_2 samples.

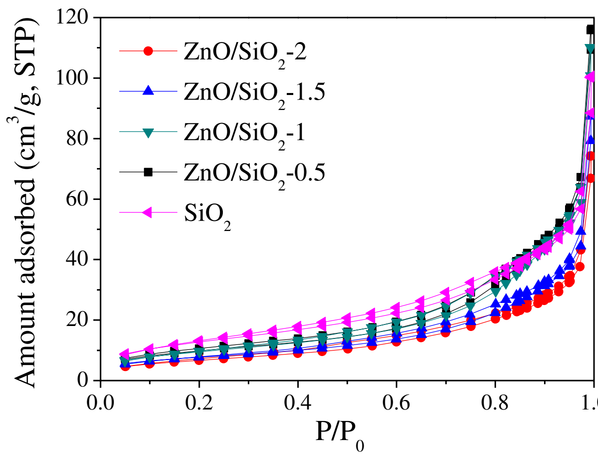

Fig. 3. Nitrogen adsorption-desorption isotherms of the pure SiO_2 sample and ZnO/SiO_2 samples.

2. Experimental

2.1. Materials

All reagents used were of analytical grade and were purchased from the Sino-reagent Company (Shanghai, China), including $Zn(NO_3)_2·6H_2O$ (>99%), ZnO (>99%), tetraethoxysilane (TEOS, >28.4% SiO_2), resorcinol (>99.5%), formaldehyde (>37%), ammonia aqueous solution (>28%), CR (>98%) and ethanol (>99.7%).

2.2. Preparation of silica spheres

The synthesis of silica spheres followed a reported procedure with minor revision [25]. Typically, 0.6 g of resorcinol, 0.84 mL of formaldehyde and 12 mL of aqueous ammonia solution were successively added into a solution composed of 140 mL of ethanol and 20 mL of water under stirring. The mixture was stirred continuously for 6 h at room temperature, followed by addition of 2.4 mL of TEOS and stirring for 8 min. Then 2.24 mL of formaldehyde and 1.6 g of resorcinol were added and the solution was stirred for another 2 h. Finally, the material was obtained by repeated filtration, washing with ethanol and subsequently drying in air at 50 °C overnight and calcination at 550 °C for 5 h.

2.3. Preparation of the ZnO-modified silica spheres

In a typical synthesis, 0.6 g of the dry silica spheres were suspended in 80 mL of $Zn(NO_3)_2$ solution with different concentrations (0.5, 1.0, 1.5 or 2.0 mol/L). Then, the suspension was treated by sonication for 30 min and the resulting paste was separated by centrifugation. Afterwards, the

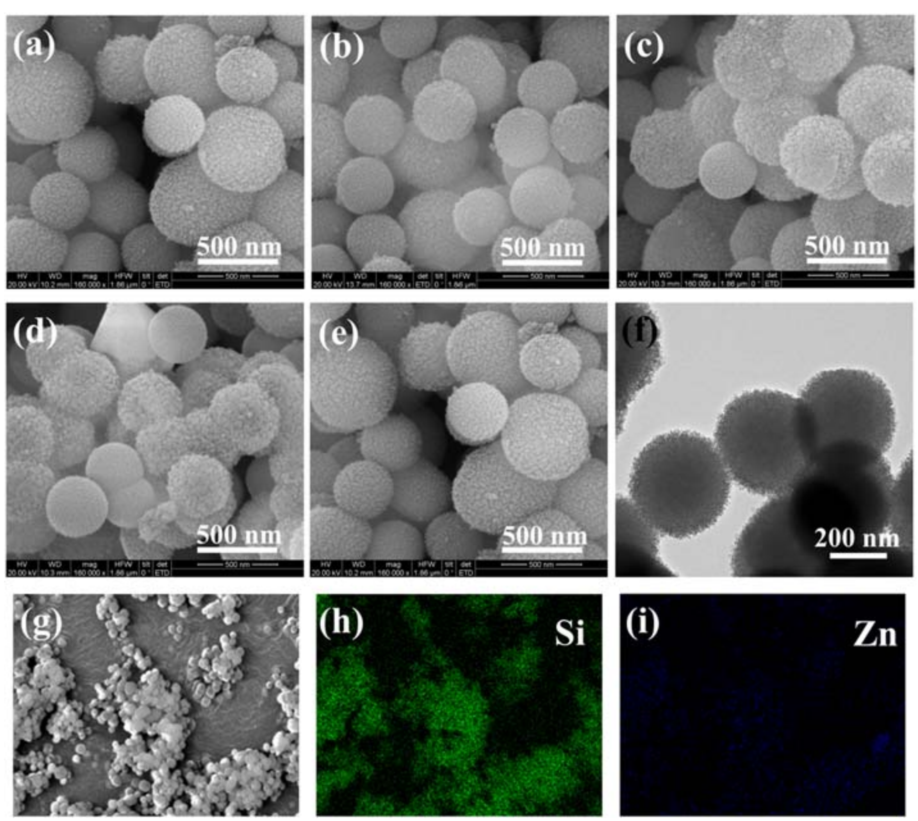

Fig. 2. SEM images of (a) SiO_2, (b) ZnO/SiO_2-0.5, (c) ZnO/SiO_2-1, (d) ZnO/SiO_2-1.5 and (e) ZnO/SiO_2-2. (f) TEM image of the ZnO/SiO_2-1.5 sample. (g–i) EDX mapping of the ZnO/SiO_2-1.5 sample (Magnification 7686).