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Evaluation of mesoporous bioactive glass (MBG) as adsorbent for removal of methylene blue (MB) from aqueous solution

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ABSTRACT

A series of mesoporous bioactive glasses (MBG) with excellent biosafety and hypotoxicity have been prepared and tested as adsorbent. It was aimed to evaluate the possibility of utilizing MBG for the adsorptive removal of methylene blue (MB) from aqueous solution and test the adsorption and desorption behavior of this new material. The process parameters affecting adsorption behaviors such as pH, contact time and initial concentration were systematically investigated. The result showed that MBG had excellent adsorption capacity (The adsorption capacity of MBG for MB is 157.3 mg/g). The maximum dye adsorption is at pH 10.0. The adsorption kinetics showed that the adsorption behavior followed the pseudo-second-order kinetic model and intraparticle diffusion model kinetics. The adsorption isotherm fit well to the Langmuir model. The MBG exhibited a good reusability after four consecutive cycles. Furthermore, the MB loaded MBG was easily desorbed with acid ethanol solution due to its electronegativity and mosoporous structure. The result indicated that these materials can be employed as candidates for removal of dye pollutant owning to its high adsorption capacity, excellent desorption performance and its biocompatibility and biosafety.

1. Introduction

It is known that mesoporous materials have attractive features of large surface area, ordered mesoporous structure, tunable pore size and volume, and well-defined surface property for modification [1–3]. Therefore, many potential applications of mesoporous materials have been widely investigated, such as catalysis, adsorption, separation, synthesis of nanomaterials, etc. [4–6].

A new kind of bioactive glass referred as mesoporous bioactive glass (MB), was first developed in 2004 [7]. This material has highly ordered mesoporous channel structure with pore size ranging from 5 to 20 nm. Compared to non-mesoporous bioactive glass, MBG possesses a more optimal surface area and pore volume [8,9]. For this reason, MBG has received much attention for applications in drug delivery and bone tissue engineering [10,11]. On the other hand, MBG is mainly silica based, surface active bone substitute which shows excellent biocompatibility with bones and soft tissues. Due to these remarkable properties, this material has been widely used in a variety of biomedical applications [12,13]. However, whether the biocompatible MBG has the potential to be utilized in the field of environmental protection and decontamination is rarely mentioned.

Effluents from the textile industry, which are dye-containing waste water, often cause serious environmental problems such as increasing the toxicity and chemical oxygen demand of the effluent [14–17]. Most of these dyes are synthetic and are composed by complex aromatic structures. Some of them can be carcinogenic and mutagenic, and they are inert and non-biodegradable when discharged into water [18,19]. Among them, methylene blue (MB) is a cationic dye, whose risk mainly arises from its harmful effect upon exposure to eyes, as well as possibility of nausea, vomiting and diarrhea [20,21].

Researches on control/removal of harmful dyes is being carried out by using different treatment technologies, e.g., chemical coagulation–flocculation, different type of oxidation processes, biological processes, membrane-based separation processes and adsorption [22–24]. Each of the above processes has their own benefits and limitations and adsorption techniques have been proven effective in removing colored organic species [25–27].

Due to the high biocompatibility and thermostability of the mesoproous bioactive glass (MBG), they will not cause secondary pollution and can be easily degraded when released into the environment. Therefore, we can use them as an absorbent in dye

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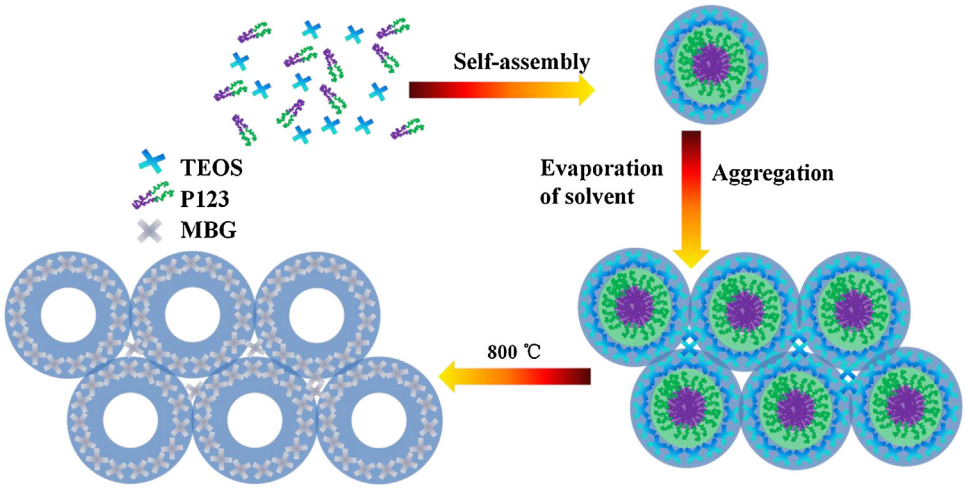

Fig. 1. Schematic of MBG synthesis mechanism.

removal. The objectives of this work are to evaluate the possibility of utilizing MBG for the adsorptive removal of methylene blue (MB) from aqueous solution and test the adsorption and desorption behavior of this new material.

2. Experimental

2.1. Materials and methods

A series of MBG (SiO_2–CaO–P_2O_5) sols with four different chemical compositions were prepared following a previously reported method [28]. Briefly, 4.0 g of P123 (Mw = 5800, Aldrich), predetermined amount of tetraethyl orthosilicate (TEOS, Tianjin Kermel Chemical Regent Co., Ltd.), $Ca(NO_3)_2{\cdot}4H_2O$ (Tianjin Kermel Chemical Regent Co., Ltd.), triethyl phosphate (TEP, Tianjin Guangfu Fine Chemical Research Institute) and 1.0 mL of 0.5 M HCl were dissolved in 60 mL of ethanol and stirred at room temperature for 24 h. Once the samples were completely dried, they were calcined at 800 °C for 10 h in a flow of air yielding the MBG. The synthesis mechanism is shown in Fig. 1. The amounts of reactants, final compositions and the sample names are listed in Table 1. The molar ratio (percentage) of SiO_2 (S) and CaO (C) were used to denote MBGs with different compositions and the P_2O_5 content was kept 5% in all the samples.

2.2. Characterization

The crystal phase and structure of the samples were identified by an X-ray powder diffractometer (XRD, D8-Advance, Bruker, Germany) using Cu Kα Radiation (λ = 1.54178 Å) and a fixed power source (40.0 kV, 40.0 mA). The surface functional groups of MBG were studied by Fourier transform infrared spectroscopy (FTIR, Necolet 6700, USA) in the wavennumber range of 600–4000 cm^{-1} under ambient condition. The morphology and microstructure of the samples were examined by a field emission scanning electron microscopy (SEM, Hitachi X-650B, Japan) and a high resolution transmission electron microscopy (TEM, JEM-2010, JEOL, Japan). N_2 adsorption–desorption isotherms were obtained on a Chemisorption–Physisorption Analyzer (Autosorb-1-C, Quantachrome, USA) at 77 K under continuous adsorption condition. BET and BJH analyses were used to determine the surface area, the pore size distribution and the pore volume. The zeta potentials of MBG at various values of pH were determined by a Zeta Meter System 3.0 (ZETA-METER Inc., USA).

2.3. Adsorption experiments

Adsorption experiments were carried out by contacting 0.30 g of MBG with 50 mL of MB solution of different initial concentrations (10–150 mg/L). A series of such conical flasks were then shaken at a constant speed of 150 rpm in a shaking water bath in 298 K. The solution was then centrifuged at 5000 rpm for 10 min and the initial (C_0) and equilibrium (C) concentrations were analyzed using a UV spectrophotometer (Shimadzu Brand UV-3000, Japan) by monitoring the absorbance changes at a wavelength of maximum absorbance (668 nm). The adsorption capacity was evaluated by the following formula:

$$q = \frac{V(C_0 - C)}{m} \quad (1)$$

where C_0 and C are, respectively, the initial and the final concentration (mg/L); V is the volume of the solution (L); m is the mass of adsorbent (g). Experiments were conducted at various time intervals to determine the kinetic parameters.

To study the effect of pH on adsorption capacity, the adsorption experiments were performed at various pH values. The pH of solution was controlled to 2.0–12.0 after the sorption equilibrium by adding HCl or NaOH solution.

Table 1
Chemical compositions and the amounts of the reactants of different MBG.

Sample name	Molar ratio Si:Ca:P	P123 (g)	TEOS (g)	$Ca(NO_3)_2{\cdot}4H_2O$ (g)	TEP (g)	HCl (0.5 M)	C_2H_5OH (mL)
MBG 100S	100:0:0	4.0	8.3	0	0	1.0	60
MBG 90S5C	90:5:5	4.0	7.5	0.5	0.73	1.0	60
MBG 80S15C	80:15:5	4.0	6.7	1.4	0.73	1.0	60
MBG 70S25C	70:25:5	4.0	5.8	2.4	0.73	1.0	60