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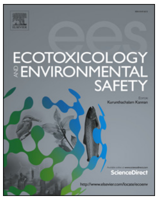

Removal of Cd(II) and Fe(III) from DMSO by silica gel supported PAMAM dendrimers: Equilibrium, thermodynamics, kinetics and mechanism

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ABSTRACT

A series of silica gel supported amino-terminated PAMAM dendrimers (SG-G1.0 - SG-G3.0) were used for the removal of Cd(II) and Fe(III) from dimethylsulfoxide (DMSO). Various parameters that influence adsorption behaviors including temperature, contact time, and initial metal ion concentration were studied. The adsorption mechanism was revealed by combining the results of experiment and density functional theory (DFT) calculation. It indicates that the adsorption capacities for Cd(II) and Fe(III) are largest among the metal ions tested. The adsorption capacity of SG-G1.0 - SG-3.0 for Cd(II) and Fe(III) follows the order of SG-G2.0 > SG-3.0 > SG-G1.0. The adsorption isotherm shows the adsorption capacities for both metal ions increases with raising the temperature and initial metal ion concentration. The adsorption isotherm is consistent with Langmuir model and the adsorption process is dominated by chemical adsorption mechanism. Thermodynamic parameters indicates that the adsorption for both Cd(II) and Fe(III) is spontaneous and endothermic. Kinetic adsorption indicates that the adsorption equilibrium times for Cd(II) and Fe(III) is about 200 and 350 min, respectively, which can be described by a pseudo-second-order model and controlled by film diffusion process. FTIR analysis and theoretical calculation revealed that the carbonyl O atoms, secondary amine N atoms, and primary amine N atoms are the primary factor responsible for PAMAM adsorption by forming tetra- and penta-coordinated chelates with metal ions.

1. Introduction

Dimethylsulfoxide (DMSO) is an important solvent that can dissolve a large number of compounds and polymers due to its high polarity (Chen and Tung, 2017; Jia et al., 2016). The excellent solubility, high boiling point, and low toxicity make it widely used in the fields of organic synthesis, polymer preparation, and pharmaceutical industry (Chen and Tung, 2017; He et al., 2016; Hann and Keserü, 2012). However, metal ions such as Fe, Cu, Zn, Cd, and Ni would be inevitably introduced during the production, transport and/or storage, distillation, and refinement process of DMSO (Yang et al., 2010). The quality of DMSO will deteriorate rapidly due to traces of metal ions. For example, a slight amount of metal ion would decrease the catalytic efficiency in organic synthesis and cause free radical inactivation in polymerization reaction (Eom and Kim, 2014; Wang et al., 2010). Moreover, toxic heavy metal ions in waste DMSO pose serious threats to human health and environmental safety (Burakov et al., 2018). Hence, the removal of metal ions from DMSO is of particular important.

Several techniques have been used for the removal of heavy metal ion, such as ion-exchange, chemical precipitation, membrane filtration, electrochemical method, and adsorption (Song et al., 2017a; Zong et al., 2011). Among these methods, adsorption has attracted considerable attention due to its high efficiency, convenience, and cost effectiveness (Song et al., 2017a). In the past decades, a number of functional groups have been adopted to construct novel adsorbents (Niu et al., 2013; Asiabi et al., 2017; Ko et al., 2017; Weidman et al., 2017), and the most important one is polyamidoamine (PAMAM) dendrimers as they contain a large number of nitrogen and oxygen functional groups that are easily functionalized to better chelate with metal ions (Kotte et al., 2015; Niu et al., 2014; Yen et al., 2017). However, both PAMAM dendrimers and their metal ion complexes are easily dissolved in aqueous solution and most of organic solvents, which make it hard to be recycled after adsorption (Zhao et al., 1998). In order to overcome this defect, it is essential to immobilize PAMAM dendrimer onto certain substrates such as silica gel (Niu et al., 2014; Wu et al., 2004; Jiang et al., 2007), chitosan (Qu et al., 2008a; Zarghami et al., 2016), hollow fiber membrane (Zhang et al., 2013), and grapheme oxide (Yuan et al., 2013; Ma et al., 2017).

Compared with other substrates, silica gel is considered to be a promising candidate due to its large surface area, unique chemical and

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thermal stability, and high mechanical strength (Niu et al., 2014; Jiang et al., 2007). The immobilization of PAMAM dendrimers onto silica gel have been widely used for the removal of metal ions from solution during the past years. Su et al. (Wu et al., 2004) reported the immobilization of amino-terminated PAMAM dendrimer (G4.0) onto silica gel for online preconcentration and separation of Pd(II) and Pt(IV). Gao et al. (Jiang et al., 2007) described the competitive removal of Cr(III), Cu(II), Pb(II), and Zn(II) from aqueous solutions by silica supported PAMAM dendrimers and their functional derivatives with EDTA. Qu et al. (2012) synthesized a series of silica gel immobilized PAMAM dendrimers for the removal of Cu(II) from ethanol. However, prior studies primarily focus on the removal of metal ions in aqueous and ethanol solutions, and there are currently no reports on its feasibility of removing metal ions from DMSO (Song et al., 2017a, 2017b; Niu et al., 2013; Jiang et al., 2007). Compared with aqueous solution, the PAMAM dendrimers would have different adsorption performance for extracting metal ions from DMSO (Madhusoodanan and Tembe, 1995; Chong et al., 2016; Tarazona-Vasquez and Balbuena, 2004). Therefore, it is necessary to investigate the adsorption property of silica gel supported PAMAM dendrimers for metal ions in DMSO to expand their application.

In our previous works, a series of silica gel supported PAMAM dendrimers were synthesized and used for the adsorption of metal ions from aqueous and alcoholic solutions (Song et al., 2017a; Niu et al., 2013; Qu et al., 2006). These adsorbents exhibited outstanding adsorption properties of metal ions such as Au(III), Pd(II), Pb(II), and Co (II). The aim of the present study is to investigate the feasibility of silica gel supported amino-terminated PAMAM dendrimers (SG-G1.0 - SG-G3.0) for the removal of metal ions from DMSO. The effects of temperature, metal ion concentration, and contact time for the adsorption of Cd(II) and Fe(III) were investigated using the batch method. The adsorption mechanism was revealed by combining the results of experiment and DFT calculation.

2. Experimental section

2.1. Materials and methods

SG-G1.0 - SG-3.0 that shown in Fig. S1 were synthesized by divergent method according to our previous report (Qu et al., 2006). The analytical grade metal chlorides, silver nitrate, and DMSO were obtained from Sinopharm Chemical Reagent Co., Ltd, China. The concentration of metal ions was determined by a GBC-932 atomic adsorption spectrophotometer (AAS, GBC Scientific Equipment Pvt. Ltd., Australia). Fourier Transform Infrared Spectroscopy (FTIR) was performed on a Nicolet iS50 (Thermo Fisher Scientific, USA).

2.2. Static adsorption

The static adsorption of SG-G1.0 - SG-3.0 was evaluated by adding 25 mg adsorbents and 20 mL of 0.001 mol L^{-1} metal ions (Ag(I), Cd(II), Co(II), Fe(III), Pb(II), Zn(II)) solution into 100 mL iodine flask, and the mixture was shaken for 12 h at 25 °C. After that, the concentration of metal ions was determined by AAS and the adsorption capacity was calculated using Eq. (1):

$$q = \frac{(C0 - C)V}{W} \tag{1}$$

where q is the adsorption amount (mmol g^{-1}); C_0 and C stands for the initial and equilibrium concentration of metal ions (mmol mL^{-1}), respectively; V denotes the volume (mL); and W represents the adsorbent weight (g).

2.3. Adsorption isotherm

Adsorption isotherm was obtained by the following procedure: 25 mg of adsorbent and 20 mL of Cd(II) or Fe(III) solution with different concentration were added to the iodine flask and shaken at different temperatures (20 °C, 30 °C, and 40 °C) for 12 h. After that, the concentration of metal ions was quantified by AAS and the adsorption capacity was calculated.

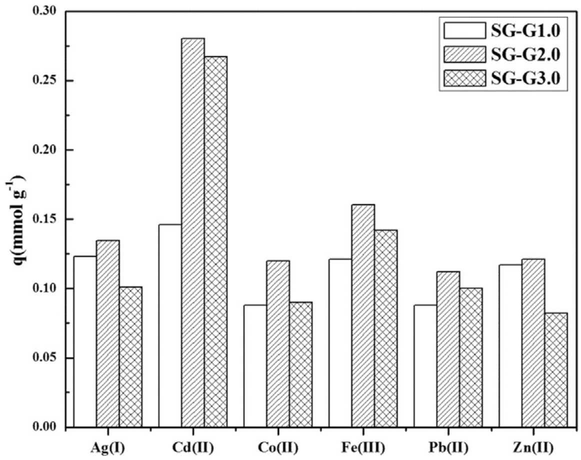

Fig. 1. Static adsorption property of SG-G1.0 - SG-G3.0 for metal ions.

2.4. Adsorption kinetics

Adsorption kinetics was measured by pouring 25 mg adsorbent and 20 mL of 0.001 mol/L Cd(II) or Fe(III) solution into the iodine flask. The mixture was shaken at 25 °C and the concentration of metal ion was determined at different time intervals. The adsorption capacity was calculated according to Eq. (1).

3. Results and discussion

3.1. Static adsorption

Fig. 1 shows the saturated adsorption capacity of SG-G1.0 - SG-3.0 for Ag(I), Cd(II), Co(II), Fe(III), Pb(II), and Zn(II) ions in DMSO solution. The adsorption capacities for Cd(II) are superior to other ones, which may be ascribed to the different interaction between the donor atoms of PAMAM dendrimer and metal ions. According to the Hard-Soft Acid-Base (HSAB) theory, Cd(II) is a soft acid, while other metal ions such as Fe(III), Zn(II), Co(II), and Pb(II) are hard and intermediate acid. $C{=}O$ group which is attributed to a soft base displays excellent binding ability to Cd(II) (Pearson, 1963), which indicates the $C{=}O$ groups of PAMAM dendrimer is responsible for the strong interaction with Cd(II). Similar phenomena were also observed for other adsorbents containing $C{=}O$ functional groups (Deng et al., 2017; Ezeokonkwo et al., 2018). As SG-G1.0 - SG-3.0 exhibited higher adsorption capacity for Cd(II) and Fe (III), the adsorption of these two metals were investigated to estimate the overall adsorption behavior of SG-G1.0 - SG-3.0. The adsorption capacity for both ions followed the order of SG-G2.0 > SG-G3.0 > SG-G1.0, which could be attributed to the intra- molecular crosslinking structure formed in higher generation PAMAM dendrimer during the propagation on the silica gel surface (Qu et al., 2006, 2008b). With the increase of dendrimer generation, the number of functional groups grows accordingly, resulting in the rise of adsorption capacity from SG-G1.0 to SG-G2.0. Though SG-G3.0 possesses the largest amount of functional groups, the steric hindrance of SG-G3.0 is also stronger than that of SG-G1.0 and SG-G2.0, leading to difficult diffusion of Cd(II) and Fe(III) into the interior of PAMAM dendrimer. Hence, the adsorption capacity of SG-G3.0 decreases compared with that of SG-G2.0. Similar phenomena were observed for the adsorption of metal ions from aqueous and ethanol solution (Song et al., 2017a; Niu et al.,