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Stepwise grafting polyethyleneimine onto silica surface for Cu(II) removal

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Abstract

Polyethyleneimine (PEI) is a novel polymer that contains multiple amine groups that are suitable for chelation with many heavy metal ions (HMI). Anchoring PEI onto the surface of a solid substrate has been widely adopted to develop adsorbent materials with the hope of combining the HMI chelating ability of PEI with the heterogeneity of the substrate. Herein, the preparation of PEI grafted SiO2 (PEI/SiO2) has been demonstrated by a stepwise method in which SiO2 nanoparticles were functionalized with 3-glycidoxypropyltrimethoxysilane (KH560) followed by refluxing with PEI. The method could provide PEI/SiO2 material with 23.4% of PEI by weight. Studying the adsorption properties of PEI/SiO2 with Cu(II) revealed that the adsorption of Cu(II) ions on PEI/SiO2 followed Langmuir and Dubinin-Radushkevich models and included both chemisorption and physisorption. The adsorption capacity was about 25.3-27.3 mg/g. The stepwise method demonstrated in this study may be adopted to fabricated PEI based materials for HMI removal.

Keywords: Polyethyleneimine, PEI, silica, clean water, adsorption

1. Introduction

Heavy metal ions (HMI), microorganisms, and organic compounds are the main pollutants in water. At the same time, organic and microorganism pollutants are biodegradable and can be removed by aerobic or anaerobic processes. Meanwhile, HMI are indestructible and have to be removed artificially. The presence of HMI in water arises from both industry and human activities, such as

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plating, metal smelting, mining, and tanning industries [1]. Due to the toxic and non-biodegradable properties, the concentration of HMI has to be detected and controlled at a proper limit [2]. Copper is a typical example that its concentration in water needs to be controlled below 3 mg/L, although it is an essential element to the human body [3]. Today, there are four main strategies for HMI removal including adsorption, membrane, chemical, electric, and photocatalytic methods. Each method has distinct advantages and is used in different scenarios, depending on the targeted wastewater. Among the available methods, adsorption is advanced by low-costs, technical maturity, and environmentally friendly [1]. Adsorption removal of HMI is based on the physicochemical interactions between an adsorbent and HMI which could involve ion exchange, electrostatic attraction, complexation, and precipitation [4]. Therefore, adding functional groups that could form coordination linkages to HMI onto the surface of activated carbon or silica is a significant strategy to increase the removal capacity of the adsorbent with high efficiency [5], [6].

Silica is a conventional substrate that can be fabricated in different forms including nanoparticles and porous materials. Because native silica has inactive Si–O–Si groups and relatively active Si–OH groups on the surface the post-functionalization of silica relies on the reactions of the silanol groups. Conventionally, alkoxylsilane containing the target functional group, e.g. H2N-R-Si(OCH3)3, is refluxed with silica to perform a condensation reaction between the as-formed R-Si-OH and the surficial Si-OH [7], [8], equation (1)

$$\begin{aligned} &\left(CH_3O\right)_3 Si-R-NH_2 + H_2O \rightarrow \left(HO\right)_3 Si-R-NH_2 \\ &SiO_2-OH + \left(HO\right)_3 Si-R-NH_2 \rightarrow SiO_2-O-Si-R-NH_2 \end{aligned} \quad (1)$$

Practically, due to the surface hindrance, the density of grafted functional groups is relatively low so the absorption of HMI onto the surface of adsorbent depends on the individual groups. Alternatively, grafting polymer chains that involve dense functional groups onto silica has emerged as an effective method to enhance the adsorption capacity of silica-based materials [6]. To this strategy, polyethyleneimine (PEI) has been used widely because it contains multiple amine groups in repeating (-NHx-CH2-CH2-) units that could chelate to various HMI [6], [9]–[12]. Herein, we have demonstrated the preparation of PEI grafted silica (PEI/SiO2) via a stepwise method using 3-glycidoxypropyltrimethoxysilane (KH560) as a surficial linker. Cu(II) was selected as a typical HMI to evaluate the adsorption properties of PEI/SiO2.

The results revealed that the adsorption of Cu(II) onto PEI/SiO2 involved both chemical and physical adsorption with an adsorption maximum of 27.2 mg/g according to the Langmuir adsorption isotherm.

2. Experimental section

2.1. Chemicals

Chemicals including PEI (99%, MW = 600 Dalton, Aladdin Chemials), KH560 (97%, Aladdin Chemicals), silica particles (SiO_2, Macklin), copper sulfate pentahydrate (99.9%, Xilong), and HPLC grade solvents were purchased and used without purifications.

2.2. The stepwise synthesis of PEI/SiO_2

A three-neck flask containing 5 g of freshly oxidized SiO_2, 150 ml toluene, and 36 mmol of KH560 was connected to a Schlenk line system and a temperature-controlled heating stirrer. Under Ar (99.98) atmosphere, the mixture was refluxed for 24 hours. After that, the solid was filtrated and washed with

ethanol to remove unreacted KH560. The solid was dried at 60°C to obtain KH560 grafted SiO_2, which was then added to a flask containing 100 ml methylenechloride and 1 g of PEI. The mixture was refluxed for 6 hours, filtrated, and washed with ethanol to obtain PEI/SiO_2.

2.3. Characterizations

Thermogravimetric analysis (TG) was conducted on a Thermo Plus EV02 (Rigaku, Japan) while an FT/IR-4600 spectrometer (Jasco, Japan) was used to perform infrared spectra. A nova touch 4xl was used to conduct the nitrogen adsorption – desorption isotherm for PEI/SiO_2 at -196°C.

2.4. Batch adsorption

In each Erlenmeyer flask, 0.1 g of PEI/SiO_2 and 50 ml of Cu(II) solution having a concentration ranging from 10 to 90 mg/L was added, closed, and shaken at a speed of 140 cycles per minute for 6 hours. The mixture was filtered by a syringe filter having a pore size of 0.21 μm to remove the adsorbent. The concentration of Cu(II) before (C_o) and after adsorption (C_e) was determined by a UV-Vis absorption method that was described by D. Guspita [13]. The absorbance of samples at 615 nm (*Abs*) was carried out on a UV-2450 spectrometer (Shimadzu, Japan). The correlation between *Abs* and Cu(II) concentration (C) was determined to be as in equation (2) with an R^2= 0.9998:

$$C = 1320.8 \times Abs - 36.334 \text{ (mg/L)} \quad (2)$$

Cu(II) adsorption quantity (q_e) was determined by equation (3):

$$q_e = \frac{50 \times 10^{-3} \left(C_0 - C_e\right)}{0.1} \text{ (mg/g)} \quad (3)$$

The adsorption of Cu(II) on PEI/SiO_2 was studied using different models including Langmuir (equation 4), Freundlich (equation 5), and Dubinin-Radushkevich (equation 6) [14].

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{q_{\max} K} \quad (4)$$

$$\ln\left(q_e\right) = \frac{1}{n} \ln\left(C_e\right) + \ln\left(K_F\right) \quad (5)$$

$$\ln\left(q_e\right) = -\beta\varepsilon^2 + \ln\left(q_m\right); \varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (6)$$

In the above equations, q_{max} is the maximum adsorption capacity (*mg/g*); K is Langmuir isotherm constant (L/mg); K_F is Freundlich isotherm constant (*mg/g*); n is adsorption intensity; β is Dubinin-Radushkevich isotherm constant (mol^2/kJ^2); R is the gas constant (J/molK); and T is the temperature (K).

3. Results and discussion

3.1. The structural properties of PEI/SiO_2 material

The stepwise synthesis of PEI/SiO_2 is schematically illustrated in Figure 1. SiO_2 was oxidized by a piranha solution containing concentrated H_2SO_4 and H_2O_2 with a volumetric ratio of 7/3 at 80°C to increase the density of surficial silanol groups. Upon refluxing in toluene, the methoxy (-OCH_3) groups of KH560 were slowly hydrolysis to form silanol groups which condensed with the surficial silanol to graft KH560 onto the surface of SiO_2. The bearing oxiranyl group of KH560 reacted with an amine group of PEI to anchor PEI chains onto the surface of SiO_2. The grafting of KH560 and PEI on the surface of SiO_2 was validated by FTIR spectra shown in Figure 2a. Two characteristic absorption peaks

of SiO_2 are seen at 1060 and 800 cm^{-1} which are assigned to Si-O-Si anti-symmetric stretching and Si-O bending vibrations, respectively [15]. Additionally, a broad absorption band around 3360 cm^{-1} is due to the stretching of the O-H bond in adsorbed water or silanol groups. After KH560 grafting, an absorption shoulder appeared at 2800-3000 cm^{-1}, which is attributed to the stretching vibration of C-H bonds in the methylene groups of the KH560. In the IR spectrum of KH560/SiO_2 sample, the characteristic absorption peaks originating from the C-O-C bond were not observed in the 1000-1200 cm^{-1} region because they were likely overlapped by the vibrational absorption of Si-O-Si bonds. The existence of PEI in PEI/SiO_2 was confirmed by two characteristic peaks at 1640 and 1475 cm^{-1}, which are attributed to the bending vibration of N-H bonds in secondary amine groups and the stretching vibration of N-H bonds in primary amine groups, respectively [16], [17].

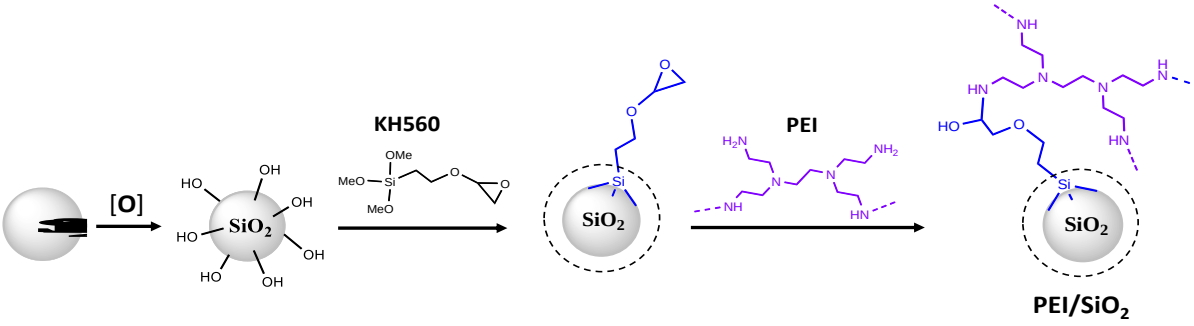

Figure 1. The stepwise synthesis of PEI grafted silica (PEI/SiO_2).

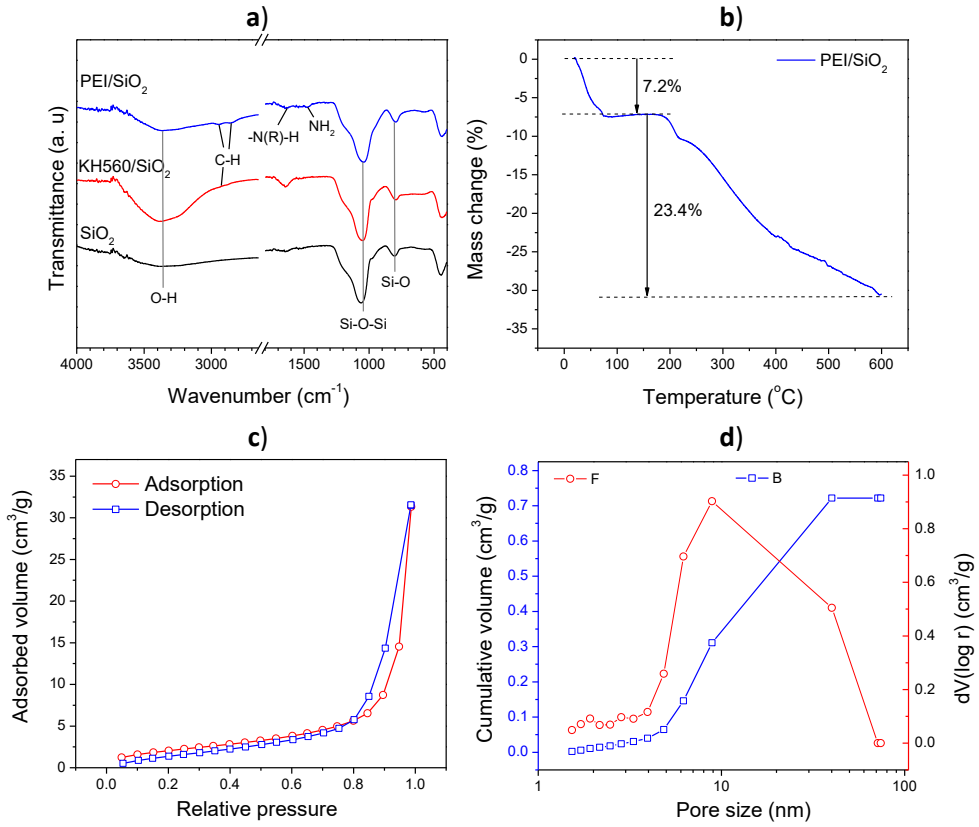

Figure 2. a) FTIR spectrum of PEI/SiO_2 in comparison with SiO_2 and KH560 grafted SiO_2 (KH560/SiO_2); **b**) TGA curve of PEI/SiO_2 in air conditions; **c**) nitrogen adsorption – desorption isotherm of PEI/SiO_2; **d**) pore size distribution of PEI/SiO_2.

TGA curve of PEI/SiO_2 conducted in air conditions, Figure 2b, involves two distinct mass-losing regions. The first mass loss at 80^{o}C could be attributed to the desorption of water. After this temperature, PEI/SiO_2 is stable to about 200^{o}C. At higher temperatures, the mass decreased gradually according to the thermal decomposition of organic components, which accounted for 23.4% by the mass of PEI/SiO_2. It is reasonable to take this value as the mass component of PEI in PEI/SiO_2.

3.2. The adsorption of Cu(II) ions on PEI/SiO_2 material

Nitrogen adsorption-desorption isotherm of PEI/SiO_2 shown in Figure 2c could be classified as an H3 type isotherm that has a narrow hysteresis loop and fast gradient changing in adsorption or desorption at high relative pressure [18]. Based on the adsorption data, the Brunauer-Emmett-Teller (BET) surface area of PEI/SiO_2 was determined to be 6.9 m^2/g, which is comparable to silica nanoparticles [17]. Pore size distribution according to the Barrett-Joyner-Halenda (BJH) method of PEI/SiO_2 is shown in Figure 2d. The total volume of PEI/SiO_2 was about 0.72 cm^3/g. Pores in PEI/SiO_2 were mesopores with a diameter ranging from 4 to 70 nm whereas pores of ~9 nm mostly accounted for the volume of PEI/SiO_2.

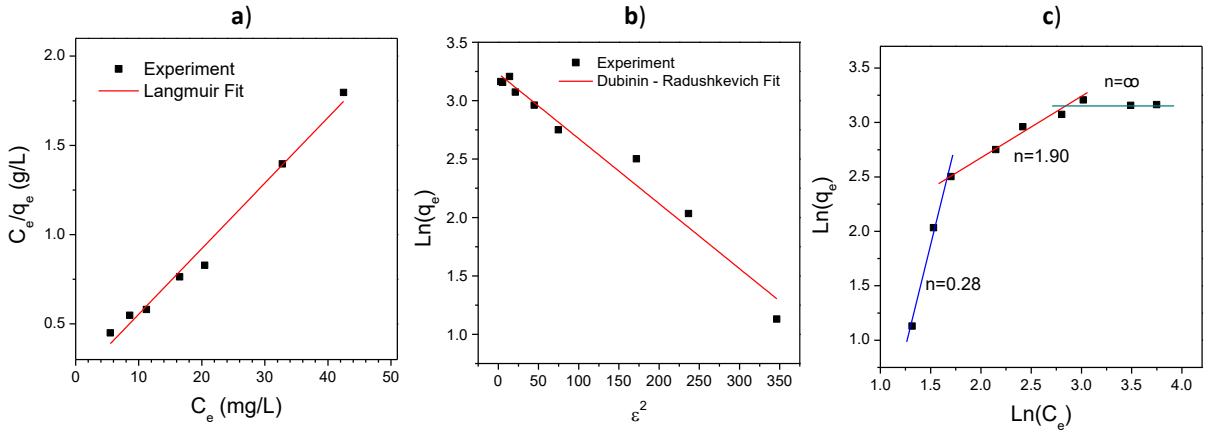

Figure 3. Fitting the Cu(II) adsorption of PEI/SiO_2 using different models: **a**) Langmuir, **b**) Dubinin – Radushkevich, and **c**) Freundlich.

To evaluate the HMI adsorption capability of the PEI/SiO_2 we used Cu(II) as an HMI model and the adsorption results were summarized in Figure 3. As shown in Figure 3a, the experiment data was fairly fitted with the Langmuir adsorption isotherm according to equation (4) with an R^2 value of 0.983. Consequently, the maximum adsorption capacity was estimated to be 27.2 mg/g. Additionally, the adsorption data was also well fitted with the Dubinin-Radushkevich model (equation 6) with an R^2 value of 0.967. The corresponding adsorption capacity was determined to be 25.3 mg/g, which is very close to the Langmuir adsorption maximum. For comparison, the adsorption capacity of PEI/SiO_2 in this study is higher than that of 3-aminopropyltriethoxysilane (19.2 mg/g) [19] or triethylenetetramine (23.9 mg/g) [20] functionalized mesoporous silica SBA-15) but it is relatively lower than PEI functionalized wheat straw (48.6 mg/g) [21] or mesoporous silica KIT-6 (36.43 mg/g) [22]. As shown in Figure 3a the adsorption data was well fitted by the Langmuir model revealing that the adsorption of Cu(II) ions onto PEI/SiO_2 was limited to a monolayer [23]. In addition, the adsorption energy was Gaussian distribution because the adsorption data also followed the Dubinin-Radushkevich model [14]. To study the type of adsorption, we plotted in Figure 3c the dependence of $ln(q_e)$ on $ln(C_e)$ according to the Freundlich model. In a low-concentration regime, the Freundlich adsorption intensity was 0.28, which is smaller than 1, indicating that the adsorption of Cu(II) ions onto PEI/SiO_2 was a chemisorption. When the

concentration was in the range of 5.5 – 20 mg/L, the adsorption intensity (n= 1.9), which is greater than 1, indicates that the adsorption was physical adsorption [24]. At higher concentrations (C_e> 20 mg/L), the adsorption reached infinitive. The concentration dependence of the adsorption shown in Figure 3c could be due to the coexistence of different amine groups in PEI. There are amine groups in close proximity that could chelate to Cu(II) to perform chemisorption. After chemisorption sites are occupied the remaining Cu(II) ions tend to interact with individual amine groups of PEI. This single amine – Cu(II) interaction is weaker than the multiple amine groups – Cu(II) chelation interaction so the adsorption of Cu(II) was a physisorption. Those interactions are schematically illustrated in Figure 4.

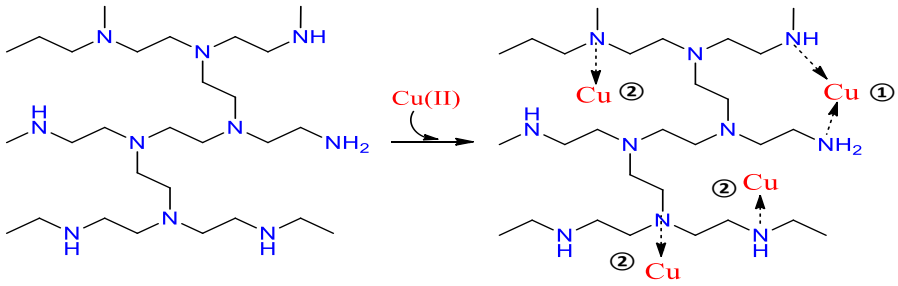

Figure 4. Representative chemisorption ① and physisorption ② of Cu(II) ions on PEI/SiO_2.

4. Conclusions

Polyethyleneimine (PEI) chains were grafted successfully on the surface of SiO_2 by a two-step procedure using KH560 as a linker. PEI was about 23.4% by mass in the final PEI/SiO_2 adsorbent. PEI/SiO_2 has mesopores whose diameter ranges from 3 to 70 nm with the accumulative volume of 0.72 cm^3/g. By using Cu(II) as a model of heavy metal ions to study the adsorption properties of PEI/SiO_2, it has been demonstrated that the adsorbent has an adsorption capacity of 25.3-27.2 mg/g. The adsorption of Cu(II) ions onto PEI/SiO_2 followed Langmuir and Dubinin-Rudushkevich models and involved both chemisorption and physisorption. The stepwise preparation of PEI grafted SiO_2 demonstrated in this report could be adopted for the development of heavy metal ions adsorbents.

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