Radiation synthesis and characterization of 3-(trimethoxysilyl) propyl methacrylate silanized silica-graft-vinyl imidazole for Hg(II) adsorption (Postprint)

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Abstract

Silica-based adsorbent was prepared by radiation induced grafting of vinyl imidazole (VIM) onto the silanized silica, which was silanized by 3-(trimethoxysilyl) propyl methacrylate. The effects of monomer composition and absorbed dose on the grafting yield were investigated to optimize the reaction conditions. The results showed that a VIM concentration of 2.5 mol • dm 3 and an absorbed dose of 50 kGy were the optimal reaction conditions. FT IR and XPS spectra manifested that VIM was successfully grafted onto the silica surface. The SS-g-VIM adsorbent had excellent selectivity for Hg(II) adsorption in mixture divalent cationic metal solution and a maximum adsorption capacity of ca. 78 mg/g to Hg(II) at pH 5. The adsorption isotherm was investigated and the adsorption of Hg(II) fitted well with Langmuir mode. These results suggested that SS-g-VIM adsorbent has potential application for the removal of Hg(II) from wastewater.

Full Text

Abstract

A silica-based adsorbent was prepared by radiation-induced grafting of vinyl imidazole (VIM) onto silanized silica that had been functionalized with 3-(trimethoxysilyl) propyl methacrylate. The effects of monomer composition and absorbed dose on grafting yield were investigated to optimize the reaction conditions. The results showed that a VIM concentration of 2.5 mol • dm^{-3} and an absorbed dose of 50 kGy were optimal. FTIR and XPS spectra confirmed that VIM was successfully grafted onto the silica surface. The SS-g-VIM adsorbent exhibited excellent selectivity for Hg(II) adsorption in mixed divalent cationic metal solutions, with a maximum adsorption capacity of approximately 78 mg/g for Hg(II) at pH 5. The adsorption isotherm was investigated, and

Hg(II) adsorption followed the Langmuir model well. These results suggest that the SS-g-VIM adsorbent has potential application for Hg(II) removal from wastewater.

Key words: γ Radiation, Grafting, Silica, Vinyl imidazole, Adsorbent

Introduction

Mercury contamination in water sources represents a critical environmental concern, as mercury is an extremely toxic metal that can cause irreversible neurological damage in humans [**?**]. Poly(N-vinyl imidazole) and its copolymer hydrogels have been found capable of chelating a wide variety of metal ions, including Cu^{2+}, Cd^{2+}, Hg^{2+}, $UO_2{}^{2+}$, and others \cite{2 5}. Therefore, adsorbents functionalized with poly(N-vinyl imidazole) are expected to be effective for Hg^{2+} removal from wastewater. Silica is chemically inert and possesses excellent mechanical properties, and surface modification via reaction of surface silanol groups makes it an excellent base material for adsorption applications [**?**, **?**]. 3-(trimethoxysilyl) propyl methacrylate, which is widely used as a carbonyl source [**?**, **?**], was employed to modify the silica surface [**?**]. Graft polymerization is an effective method for preparing adsorbents with desired ion-exchange and chelating capacity for specific targets, and can be initiated using gamma rays, electron beams (EB), UV radiation, plasma treatment, or chemical initiators.

In our previous work, DMAEMA was grafted onto a silica matrix by radiation grafting using γ-rays and electron beams, revealing the potential of synthesized silica-based adsorbents for heavy metal ion removal from wastewater. These adsorbents showed particular advantage in adsorbing heavy metal ions such as Cr(VI), As(V), and Hg(II), especially in strongly acidic environments [**?**]. Additionally, AAM/VIM was successfully cografted onto chlorotrimethylsilane (TMCS) silanized silica by pre-radiation grafting using electron beam irradiation [**?**].

In this work, VIM was grafted onto 3-(trimethoxysilyl) propyl methacrylate silanized silica via radiation-induced grafting. The effects of reaction conditions, including monomer composition and absorbed dose, were investigated to optimize the reaction conditions and characterize the adsorbent properties. The Hg(II) adsorption properties, including selective adsorption and adsorption isotherm behavior, were systematically investigated.

Experimental Methods

Materials

Column chromatography silica gel (particle size 0.15–0.30 mm, average pore size 10 nm, Branch of Qingdao Haiyang Chemical Co. Ltd., China) was used as the substrate. 3-(trimethoxysilyl) propyl methacrylate and VIM (>98%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China and used without purification. All other chemicals were analytical reagent (AR) grade.

Preparation of Adsorbent

The silica was first washed with 1.0 $\mathrm{mol \cdot dm^{-3}}$ HNO_3 at 70°C to remove impurities. After washing with distilled water and drying in vacuum at 80°C, the silica (5.0 g) was silanized with 5.0 g of 3-(trimethoxysilyl) propyl methacrylate in 80 mL xylene at 80°C for 72 h. Unreacted trimethylchlorosilane was removed by xylene washing, and the silanized silica was then dried in vacuum at 60°C.

For grafting, silanized silica (SS) and VIM aqueous solution were sealed in polyethylene bags purged with nitrogen gas. The samples were irradiated to the desired absorbed dose by γ-rays at room temperature with a dose rate of 300 $\mathrm{Gy \cdot min^{-1}}$. The homopolymer and unreacted monomer were removed by washing with distilled water and ethanol. Finally, the SS-g-VIM adsorbent was dried in vacuum at 50°C.

Characterization

Grafting Yield. The grafting yield (GY) was determined gravimetrically using Eq.(1):

$$GY = \frac{W_1 - W_0}{W_0} \times 100\%$$

where W_1 is the weight of SS-g-VIM and W_0 is the initial weight of silanized silica.

FTIR Spectroscopy. FTIR analyses of SS and SS-g-VIM were performed using a Fourier Transform Infrared Spectrometer (NICOLET750) with MCT/A attachment. Spectra were measured in transmittance mode over a wavenumber range of 4000–600 $\mathrm{cm^{-1}}$.

XPS Analysis. X-ray photoelectron spectroscopy (XPS) analysis was performed with an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charging effects, binding energies were calibrated using the C 1s hydrocarbon peak at a binding energy (BE) of 284.80 eV. The data were converted into VAMAS file format and imported into the CASAXPS software package for manipulation and curve fitting.

Adsorption Experiments

Selective Adsorption. For selective adsorption studies, aqueous solutions containing Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Hg^{2+} were prepared with each metal at a concentration of 100 ppm. Approximately 30 mg of adsorbent was immersed in 50 mL of the mixed solution with continuous stirring for 8 h. The solution pH was adjusted using HNO_3.

Hg(II) Adsorption Capacity. For Hg(II) adsorption studies, approximately 30 mg of adsorbent was immersed in 50 mL of Hg(II) solution with continuous stirring for 8 h.

The adsorption capacity of metal ions per unit weight of adsorbent at time t, q_t ($\mathrm{mg \cdot g^{-1}}$), was calculated from mass balance using Eq.(2):

$$q_t = \frac{(C_0 - C_t)V}{m}$$

where C_0 is the initial concentration of adsorbate ($\mathrm{mg \cdot L^{-1}}$), C_t is the concentration at time t ($\mathrm{mg \cdot L^{-1}}$), V is the volume of adsorbate solution, and m is the mass of adsorbent.

Metal Ion Concentration Measurement. For selective adsorption studies, the concentrations of various heavy metal ions in the supernatant were measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (PROFILE SPEC, Leeman, USA). For Hg(II) adsorption studies, Hg(II) concentration was measured by colorimetry using a UV-Vis Spectrophotometer (UV-3010, Hitachi, Japan) [**?**]. For this measurement, 1 mL of sample solution was placed in a beaker and the pH was adjusted to 2 with HNO_3 for mercury-dithizone complex formation. A saturated solution of dithizone in ethanol (9 mL) was then added, and the solutions were allowed to equilibrate for 1 min before recording the absorbance at 495 nm. The calibration curve was established using Hg(II) standard solutions from 5 to 40 ppm under identical experimental conditions.

Results and Discussion

Optimization of Reaction Conditions

The effects of absorbed dose and monomer composition on the grafting yield of SS-g-VIM were investigated to determine optimal reaction conditions for adsorbent preparation. A dose rate of 300 $\mathrm{Gy \cdot min^{-1}}$ was adopted for all grafting reactions.

Effect of Absorbed Dose. Figure 1 [Figure 1: see original paper] shows the effect of absorbed dose on grafting yield at a fixed VIM concentration of 1.5 $\mathrm{mol \cdot L^{-1}}$. VIM successfully grafted onto SS even at a low absorbed dose of 10 kGy. The grafting yield increased with absorbed dose, reaching approximately 23% at 70 kGy. However, the rate of increase slowed after 50 kGy, and significant homopolymer formation occurred at doses exceeding 70 kGy. Therefore, an absorbed dose of 50 kGy was selected for subsequent experiments.

Effect of Monomer Composition. The effect of VIM concentration on grafting yield is shown in Figure 2 [Figure 2: see original paper]. The grafting yield increased with VIM concentration, reaching 35% at a VIM concentration of 2.5 $\mathrm{mol \cdot L^{-1}}$. However, the rate of increase slowed beyond 2.5 $\mathrm{mol \cdot L^{-1}}$, making higher concentrations economically unfavorable. Therefore, the optimal reaction conditions were determined to be an absorbed dose of 50 kGy and a VIM concentration of 2.5 $\mathrm{mol \cdot L^{-1}}$, which yielded a grafting efficiency of 35%.

Characterization Results

FTIR Analysis. FTIR spectra of silica and SS-g-VIM are presented in Figure 3 [Figure 3: see original paper]. In the silica spectrum, characteristic peaks at approximately 1095, 955, and 800 cm^{-1} were assigned to the asymmetric stretching vibrations of Si-O-Si, stretching vibration of free Si-OH groups on the amorphous solid surface, and symmetric stretching vibrations of Si-O-Si bonds, respectively [?]. In the SS-g-VIM spectrum, peaks at 3112 and 2950 cm^{-1} corresponded to stretching vibrations of =CH in the VIM ring and CH_2 in the polymer backbone, respectively. The absorption band at 1712 cm^{-1} was attributed to C=O stretching vibrations [?], while bands at 1417 and 1506 cm^{-1} corresponded to CH_2 bending vibrations and C=C/C=N stretching vibrations in VIM [?]. The appearance of these characteristic VIM peaks in the SS-g-VIM FTIR spectrum confirmed successful silanization of silica and grafting of VIM onto the silanized surface.

XPS Analysis. XPS spectra of SS and SS-g-VIM adsorbents are illustrated in Figure 4 [Figure 4: see original paper]. The appearance of the N 1s peak confirmed successful grafting of VIM onto the silanized silica [?]. The Si 2p and O 1s binding energies remained essentially unchanged before and after grafting, indicating that the grafting reaction had minimal effect on the silica backbone and occurred primarily at silanol groups via free radicals generated from the alkyl groups of the silanization reagent [?]. These results further corroborated the successful grafting of VIM onto silanized silica.

Adsorption Behavior of Hg(II)

The SS-g-VIM adsorbent prepared under optimal conditions (50 kGy absorbed dose, 2.5 $mol \cdot L^{-1}$ VIM) was used to investigate Hg(II) adsorption behavior.

Selective Adsorption. Selective adsorption is crucial for separating target metal ions from wastewater. Table 1 lists the adsorption capacities of various heavy metal ions from a mixed solution at pH 5. The results demonstrate that SS-g-VIM exhibits excellent selectivity for Hg(II) adsorption in mixed divalent cationic metal solutions.

Adsorption Isotherms. The adsorption behavior of Hg(II) onto SS-g-VIM at pH 5 is shown in Figure 5 [Figure 5: see original paper], with initial Hg(II) concentrations ranging from 10 to 200 ppm. The Langmuir isotherm model (Eq.3) and Freundlich model (Eq.4) were applied to analyze the adsorption mechanism and calculate theoretical maximum adsorption capacity [?]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

where C_e is the equilibrium concentration of ions ($\mathrm{mg \cdot L^{-1}}$), q_e is the amount adsorbed per gram of adsorbent ($\mathrm{mg \cdot g^{-1}}$), q_m is the theoretical maximum adsorption capacity ($\mathrm{mg \cdot g^{-1}}$), K_L is the adsorption energy ($\mathrm{L \cdot g^{-1}}$), K_F is the Freundlich constant, and n is the heterogeneity factor.

Table 2 lists the corresponding Langmuir and Freundlich constants along with correlation coefficients (R^2). The Langmuir equation provided a better fit to the experimental data than the Freundlich equation, with a correlation coefficient of 0.999. This indicates that Hg(II) adsorption by SS-g-VIM follows monolayer adsorption behavior [?]. Under the experimental conditions (initial Hg(II) concentration of 10–200 ppm), the theoretical maximum adsorption capacity was calculated to be 78 $\mathrm{mg \cdot g^{-1}}$.

Conclusion

A silica-based adsorbent (SS-g-VIM) was successfully prepared by γ-radiation-induced grafting of vinyl imidazole (VIM) onto silica that had been silanized with 3-(trimethoxysilyl) propyl methacrylate. FTIR and XPS results confirmed successful grafting of VIM onto the silica surface. Under optimal reaction conditions (2.5 $\mathrm{mol \cdot L^{-1}}$ VIM concentration and 50 kGy absorbed dose), the grafting yield was 35%. The SS-g-VIM adsorbent demonstrated excellent selectivity for Hg(II) adsorption in mixed divalent cationic metal solutions, with a considerable Hg(II) uptake of approximately 78 $\mathrm{mg \cdot g^{-1}}$ at room temperature and pH 5. The adsorption behavior followed the Langmuir model, indicating monolayer adsorption. The SS-g-VIM adsorbent shows promise for Hg(II) removal from wastewater.

References

[?] Zhu J Z, Yang J, Deng B L. J Hazard Mater, 2009, 166: 866 872. [?] Li J N, Wang L N, Qi T, et al. Microporous Mesoporous Mater, 2008, 110: 442 450. [?] Pekel N, Guven O. Colloids Surf, A, 2003, 212: 155 161. [?] Ajji Z, Ali A M. J Hazard Mater, 2010, 173: 71 74. [?] Salih B, Pekel N, Guven O. J Appl Polym Sci, 2001, 82: 446 453. [?] Ngeontae W, Aeungmaitrepirom W, Tuntulani T. Talanta, 2007, 71: 1075 1082. [?] Zhang Y, Qu R J, Sun C M, et al. Appl Surf Sci, 2009, 255: 5818 5826. [?] Bourgeat-Lami E, Lang J. J Colloid Interface Sci, 1998, 197: 293 308. [?] Joseph R, Zhang S M, Ford W T. Macromolecules, 1996, 29:1305-1312. [?] Phuong T T T, Hang T D, Hung N P, et al. J Porous Mater, 2012, 19: 295 300. [?] Zhao L, Sun J, Zhao Y H, et al. Chem Eng J, 2011, 170: 162 169. [?] Xu L, Sun J, Zhao L. Radiat Phys Chem, 2011, 80: 1268 1274. [?] Dias N L, Gushikem Y. Sep Sci Technol, 1997, 32: 2535 2545. [?] Qiu J, Wang Z, Li H, et al. J Hazard Mater, 2009, 166: 270 276. [?] Joon-Yong S, Hae-Jun S, Joo-Myung S, et al. Radiat Phys Chem, 2012, 81: 923 926. [?] Pekel N, Sahiner N, Guven O. Radiat Phys Chem, 2000, 59: 485 491. [?] Ang A K S, Kang E T, Neoh K G, et al. Polymer, 2000, 41: 489 498. [?] Yang G H, Kang E T, Neoh K G. IEEE T Adv Packaging, 2002, 25: 365 373. [?] Ma F, Qu R, Sun C, et al. J

Hazard Mater, 2009, 172: 792 801. [?] Sun C, Qu R, Ji C, et al. Talanta, 2006, 70:14 19.

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