Surface Modification of Silica Fume and Adsorption Property of Pb (II) ions

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Abstract. In order to recycle the industrial waste, silica fume of industrial waste was modified with r-mercaptopropyltrimethoxysilane coupling agent (KH590). The adsorption of modified silica fume on lead ions (Pb²⁺) was studied. The structures were characterized by FTIR and X-ray photoelectron spectroscopy (XPS). FTIR showed that the surface of silica fume was successfully grafted with KH590. XPS showed that the Pb²⁺ adsorbed on the surface of modified silica fume with coordination Pb-S bond. The effects of reaction time, Pb²⁺ initial concentration, pH value and adsorbent dosage on the adsorption rate were investigated. The results showed that silica fume modified by KH590 was an efficient lead ion adsorbent and the absorption rate of modified silica fume was up to 96.7%.

1. Introduction
Waste silica fume is a by-product of ferroalloys in the smelting of ferrosilicon and industrial silicon (silicon). The main components are submicron silicon oxide spheres. The surface of silicon oxide contains a large amount of active silanol groups, and reactive functional groups can be introduced through chemical bonding. In recent years, to achieve the functional utilization of silica fume materials, it has become a research hotspot by introducing other groups on the surface of silica to make it more chemical selection [1, 2]. Heavy metals are difficult to degrade in the environment. Heavy metal pollution poses a serious threat to the environment, causing special attention. For example, Pb²⁺ has acute and chronic toxic effects on human health. It can cause anemia, headaches, and diarrhea, inhibit the production of heme, and cause serious damage to the kidneys, nervous system, reproductive system, brain and liver [3]. At present, methods for treating heavy metal wastewater include adsorption method, chemical precipitation method, ion exchange method, bio-adsorption method, electrochemical method, electrolysis method, membrane separation method, etc [4]. Adsorption method has certain advantages in the field of heavy metal wastewater treatment. Developing high-performance, low-cost adsorbents has been a research hotspot [5-7]. In this paper, the surface of silica fume was modified by KH590. The thiol group was introduced on the surface of silica fume, and the adsorption and separation of Pb²⁺ was realized by coordination reaction between thiol and Pb²⁺ in wastewater.
2. Experiment part

2.1. Reagents and instruments
Silica fume, r-Mercaptopropyltrimethoxysilane, toluene, acetone, lead nitrate, hydrogen diamine citrate, anhydrous sodium sulfite, hydroxylamine hydrochloride, dithizone, dichloromethane, ammonia, sodium hydroxide, hydrochloric acid. They are all analytical pure, all of the test water is distilled water.

Infrared spectrometer (IS10 model produced by Thermo Fisher Co., USA), nanoparticle size and zeta potential analyzer (ZEN3700 produced by Malvern, UK), and X-ray photoelectron spectrum analyzer (XSAM 800 model manufactured by Kratos, Shimadzu, Japan), Ultraviolet spectrophotometer (TU-1810 produced by Beijing General Analysis Instrument Co., Ltd.).

2.2. Silica fume modification experiment
In a three-necked flask equipped with a flashbang condenser, put 80 ml toluene and 6 ml r-mercaptoethyltrimethoxysilane, and then added 3 g silica fume. Under the protection of N2 and reacted at 70 ºC for 12 hours. After the reaction completed, acetone was used to wash for 3 to 4 times, vacuum-filtered, and dried in an electric thermostatic drying oven at 70 ºC for 12 hours, cooled to room temperature, and placed in a dry box for later use.

2.3. Adsorption experiment of Pb²⁺ on modified silica fume
In a 150 ml Erlenmeyer flask, added 50 ml of 10 mg/L Pb²⁺ simulated water sample, adjusted the solution to the desired pH, added 0.200 g of the modified silica fume, and placed the Erlenmeyer flask in a shaker. Adsorption at certain temperature, centrifugation at 8000 r/min for 10 min, supernatant was used to measure the remaining Pb²⁺ concentration in the solution by dithizone spectrophotometry. The adsorption rate of Pb²⁺ was calculated using equation (1). Use equation (2) to calculate the Pb²⁺ adsorption capacity.

$$\varphi = \left( \frac{c_0 - c}{c_0} \right) \times 100\%$$

Where: \( \varphi \) is adsorption rate; \( c_0 \) is initial concentration of lead ion, mg/L; \( c \) is residual concentration of lead ion in solution after adsorption equilibrium, mg/L.

3. Results and discussion

3.1. FTIR analysis
It can be seen from Figure 1a, the absorption peak at 1103 cm⁻¹ is the lateral and longitudinal symmetric stretching vibration peaks of Si-O-Si, the absorption peak at 806 cm⁻¹ is the symmetrical stretching vibration peak of Si-O-Si, and the absorption peak at 474 cm⁻¹ is the bending vibration peak of Si-O-Si. The absorption peak at 3377 cm⁻¹ is the stretching vibration peak of Si-OH, and the absorption peak at 1633 cm⁻¹ is the bending vibration peak of H-O-H. In Figure 1b, the methyl and methylene peaks appeared at about 2926 cm⁻¹ and about 2853 cm⁻¹, and the stretching vibration peak of C-Si in silane appeared at 813 cm⁻¹, which was overlapped with the symmetrical stretching peak of Si-O-Si, and the intensity of absorption peak was increased. In addition, the -SH stretching vibration peak should appear near 2550-2590 cm⁻¹, but it was not obvious in spectrum b. The reason may be that the amount of -SH on the surface of silica fume was small. The above showed that KH590 was successfully grafted to the surface of silica fume.
3.2. XPS analysis
In order to further explain the adsorption mechanism of Pb\(^{2+}\), the XPS spectra of samples KH590-silica fume and Pb-KH590-silica fume were determined.

**Figure 1.** FTIR of silica fume before and after modified with KH590 (\(^{a}\)unmodified silica fume; \(^{b}\)modified silica fume)

**Figure 2.** XPS spectra of KH590-silica fume and Pb-KH590-silica fume (\(^{a}\)overall spectra of KH590-silica fume and Pb-KH590-silica fume; \(^{b}\)Pb\(^{4f}\) spectrum of Pb-KH590-silica fume; \(^{c}\)C\(^{1s}\) spectra of \(^{b}\)KH590-silica fume and \(^{d}\)Pb-KH590-silica fume)
From Fig. 2a, there are six peaks in the entire spectrum before adsorption, which are O1s, C1s, S2s, S2p, Si2s and Si2p. The appearance of Pb4f peaks after adsorption indicates that Pb\(^{2+}\) was successfully adsorbed on the surface of KH590-silica fume. The doublet of 138.4eV (Pb4f\(_{7/2}\)) and 143.3eV (Pb4f\(_{5/2}\)) appeared in Fig. 2c, and the Pb4f\(_{7/2}\) binding energy of Pb(NO\(_3\))\(_2\) is approximately 139.1~139.5eV [8, 9]. The significant shift in chemical binding energy was attributed to the interaction between KH590-silica fume and Pb\(^{2+}\). Figures 2b and 2d are XPS spectra of C1s before and after adsorption. The C1s spectra of KH590-silica fume include three peaks, C-C and C-H (284.71eV), C-S (285.16eV) and C-O (286.23eV). In Pb-KH590-silica fume, C-C and C-H (284.78eV) did not change, C-O (286.19eV) did not change, C-S (283.77eV) binding energy decreased, due to the coordination reaction between Pb\(^{2+}\) and S, S shared electrons with lead ions, the electron density of adjacent carbon atoms increased and the binding energy decreased. Combined with the above analysis, it can be considered that KH590-silica fume adsorbed Pb\(^{2+}\) through its surface sulfur provided lone pair electrons and Pb\(^{2+}\) to react forms chelates.

3.3. Single factor experiment on adsorption of Pb\(^{2+}\) on modified silica fume

3.3.1. Effect of reaction time on adsorption rate. At 20 °C, according to the 2.3 method to test the adsorbed Pb\(^{2+}\) of modified silica fume. After 10, 20, 30, 60, 90 and 120 minutes of adsorption, the adsorption rate of Pb\(^{2+}\) was measured. The relationship between adsorption rate and reaction time was shown in Figure 3.

The figure shows that the modified silica fume and the unmodified silica fume have a very fast adsorption efficiency at first. After adsorption for 90 min, the adsorption equilibrium is basically reached, and the adsorption rate of modified silica fume can reach 96.41%. Compared with unmodified silica fume, the adsorption rate increased by 38.91%. This is due to the fact that the silica fume has a porous structure and has an adsorption effect on lead ions. The modified silica fume has an active group -SH on the surface, which can react with lead ions and increase the chelation and diffusion of silica fume and lead ions.
3.3.2. Effect of pH on adsorption rate. The pH of the Pb\(^{2+}\) simulated water sample was adjusted to 2, 3, 4, 5, and 6, and adsorbed on the shaker for 90 minutes. The relationship between the adsorption rate of Pb\(^{2+}\) and pH was shown in Figure 4.

When the pH of the solution is small, the H\(^+\) concentration is high. Lead of the lead solution is mainly in the form of Pb\(^{2+}\) and Pb (OH)\(^+\) [10]. H\(^+\) and Pb\(^{2+}\) and Pb (OH)\(^+\) compete for adsorption on the chelate adsorption sites on the surface of the adsorbent, which has a certain influence on the adsorption effect, and thus the adsorption efficiency is low. When the pH is large, Pb\(^{2+}\) will form a precipitate with the OH\(^-\) in the solution, and the adsorption reaction does not occur. When the pH was chosen as 5, the adsorption effect was better.

3.3.3. Effect of adsorbent dosage on adsorption rate. Adjust the pH of the solution to 5, keep other conditions unchanged, change the amount of adsorbent. The relationship between the adsorption rate and adsorbent dosage was shown in Figure 5.

As can be seen from the figure, with the increase of the dosage, the adsorption rate is also increasing. When the dosage is more than 0.200g, the adsorption rate basically reaches 100%. Although increasing the dosage can increase the adsorption rate of lead ions, considering the cost, choose the optimal dosage at the inflection point of the adsorption rate curve, that the best dosage is 0.200g. And the corresponding adsorption rates were respectively 96.7% and 75.9%.

**Figure 4.** The relationship of adsorption rate and pH

**Figure 5.** The relationship of adsorption rate and adsorbent dosage
3.3.4. Effect of initial concentration of Pb\(^{2+}\) on adsorption rate. The other conditions were unchanged. The initial solution of Pb\(^{2+}\) was 10, 20, 30, 50, and 70 mg/L. The relationship between the adsorption rate and the initial concentration of Pb\(^{2+}\) was shown in Figure 6.

As can be seen from the figure, with the increase of the initial concentration of Pb\(^{2+}\) in the solution, the adsorption rate of the modified silica fume and the unmodified silica fume gradually decreases. The initial concentration of Pb\(^{2+}\) is high, and at a certain adsorption capacity, the amount of Pb\(^{2+}\) that can be adsorbed is also constant. Therefore, the greater the total amount of Pb\(^{2+}\) is, the smaller the adsorption rate is.

4. Conclusion

(1) Using toluene as a solvent and KH590 as a modifier, silica fume was successfully modified by KH590, and its modification was confirmed by infrared spectroscopy.

(2) The adsorption mechanism of the modified silica fume was studied by XPS. It was studied that the modified silica fume through its surface sulfur provided a lone pair of electrons with Pb\(^{2+}\) and formed a chelate to adsorb Pb\(^{2+}\), belonging to chemical adsorption.

(3) The effects of reaction time, Pb\(^{2+}\) initial concentration, pH value and adsorbent dosage on the adsorption rate were investigated. When the Pb\(^{2+}\) initial concentration was 10 mg/L, the reaction time was 90 min, and the pH value was 5, the adsorption rate was the best.

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