Effect of Kaolin particle size on the removal of Pb(II) from aqueous solutions by Kaolin-supported nanoscale zero-valent iron

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Abstract

The removal of Pb(II) from aqueous solutions was investigated using kaolin with two different particle sizes (2.3 and 45 μm) with and without nanoscale zero-valent iron (nZVI, at a Fe content close to 30%). The experimental results show that 2.3 μm kaolin loaded with nZVI (K-nZVI) had the best Pb(II) removal performance under various test conditions. After 24 h, it removed 99.5% of Pb(II) ions in the solution, followed by 45 μm K-nZVI, 2.3 μm kaolin, and 45 μm kaolin (89.01%, 68.8%, and 65.8%, respectively). The removal rates by all four kaolin samples increased with increasing pH in the range of 2–6, and with increasing temperature between 30 °C–60 °C. The results show that using finer carrier particles improves the performance of K-nZVI for removing Pb(II) in aqueous solutions.

1. Introduction

With the global industrialization process, there is a growing concern for heavy metal pollution in wastewaters. Humans mostly ingest heavy metals by two routes: in the drinking water directly and by food ingestion. In many cases, these pollutants also bioaccumulate in the aquatic food chain [1–3]. Pb(II) is one of the most toxic heavy metal ions because it accumulates in the muscles, bones, kidneys, and brain tissues to cause various diseases. As a result, Pb is listed as a priority pollutant in many countries [4].

Over the last few years, use of adsorbent for the removal of different environmental pollutants [5–7]. And materials modified by nano-sized zero-valent iron (nZVI, with a size less than 100 nm) have attracted much attention for use in environmental remediation [8–10]. Various synthetic methods have been exploited to prepare iron nanoparticles [11–17]. Due to its considerable specific surface area, nZVI has a high surface energy and high reactivity [18], and therefore it is suitable for the removal of different environmental pollutants [19–26]. However, its efficiency is reduced by a strong propensity for aggregation [27]. Consequently, scholars have developed various supports for nZVI, such as layered double hydroxide (LDH)-intercalated cellulose nanocomposite [28], biochar-supported nZVI nanoparticles [29], clay-supported nZVI [30], and bentonite-nZVI (B-nZVI) [31, 32]. All these supports not only facilitate the dispersion of nZVI and stabilize it, but also allow easy adsorbent collection after use.

Kaolin is a common clay material known for its structural stability under geochemical conditions and good performance as an adsorbent. Therefore, it is suitable for carrying nZVI in osmotic reaction barriers or repair systems [33]. For examples, Uzüm et al (2009) synthesized and characterized Kaolin-supported nZVI (K-nZVI) [33], while Zhang et al (2010) demonstrated the removal of Pb(II) from water using K-nZVI [34]. However, the effect of kaolin particle size on the pollutant removal performance has not been well studied in the literature. The present authors believe that as the particle size of kaolin decreases, the specific surface area, the number of pores, and the pore volume will increase [35, 36]. The resulting increase in adsorption capacity will allow more nZVI to be loaded on the surface of kaolin, which should improve the removal efficiency for Pb(II) in water. Also, the present study examined the effects of solution pH, solution temperature, the presence of nZVI, and the initial Pb(II) concentration on Pb(II) removal.
2. Materials and methods

2.1. Chemicals

Kaolin samples (particle size of 2.3 and 45 μm) were purchased from Shanghai Yuanjiang Chemical Co., Ltd, and their chemical characteristics are shown in Table 1. Sodium borohydride, sodium hydroxide, ferrous chloride tetrahydrate, absolute ethanol, and lead nitrate, all of analytical purity, were purchased from China Pharmaceutical Chemical Reagent Co., Ltd (Beijing).

2.2. Preparation of K-nZVI

The two K-nZVI samples were prepared by adding 300 ml of high-purity water and 2.3 g of kaolin (2.3 or 45 μm) to a beaker and stirring for 30 min, followed by ultrasonic vibration for 30 min. Then, 5.343 g of FeCl₂·4H₂O was added into the beaker, and the mixture was subjected to 30 min of stirring and 30 min of ultrasonic vibration. Absolute ethanol (200 ml) was added, followed by another 30 min of stirring and 30 min of ultrasonic vibration. Next, 3.664 g of sodium borohydride solution (100 ml, pH = 11) was slowly added to the beaker under vigorous stirring, and this dropping process took approximately 15 min. After the reaction was completed, the mixture was stirred for 20 min and ultrasonically vibrated for 10 min. The supernatant was separated by centrifugation, and washed three times with high-purity water, and then twice with absolute ethanol. The sample was lyophilized in a freeze dryer, before being placed in a bag and stored in the refrigerator. The chemical reaction for the liquid-phase reduction of Fe is as follows [37]:

\[
\text{Fe}^{2+} + 2\text{BH}_4^- + 6\text{H}_2\text{O} \rightarrow 2\text{Fe(s)} + 2\text{B(OH)}_3^- + 7\text{H}_2\uparrow
\]

2.3. Surface properties of kaolin and K-nZVI samples

X-ray diffraction (XRD) analysis of the samples was carried out by a D8-Advance X diffractometer (40 kV, 40 mA; Bruker Company, Karlsruhe, Germany), and scanned at a rate of 0.15 s/step in the range of 5°–84°. Fourier transform infrared (FTIR) spectra were measured using a TENSOR27 instrument (Zhengzhou Great Wall Science Industrial Co., Ltd, Zhengzhou, China) with a scan range of 4000–400 cm⁻¹. The Brunauer–Emmett–Teller (BET) surface area was determined with an ASAP 2020 HD88 surface area tester (McMurray Tikem Instrument Co., Ltd, Shanghai). Lorentz transmission electron microscope (TEM) images were obtained on a 2100F device (JEM).

2.4. Effect of various parameters on Pb removal efficiency

For the effect of pH, a 200 mg l⁻¹ Pb(II) solution was adjusted to pH = 2, 3, 4, 5, and 6 using diluted hydrochloric acid. Then, 0.1 g of kaolin sample (2.3 μm K-nZVI, 2.3 μm Kaolin, 45 μm K-nZVI, or 45 μm Kaolin) was added to 100 ml of the solution and kept at room temperature (20 °C) for 16 h. The solution was then separated by centrifugation (5 min at 11 000 rpm) to remove the effect of the Kaolin. Afterwards, the concentration of Pb(II) in the solution was determined by atomic absorption method to calculate the removal rate of Pb. This method was used in all the other adsorption experiments.

For the effect of Pb concentration, Pb(II) solutions (200, 300, 400, and 500 mg l⁻¹) were added with 0.1 g of kaolin sample and stood for 24 h at 20 °C, before measuring the Pb removal efficiency.

For the effect of reaction time, a Pb(II) solution (200 mg l⁻¹, 100 ml) at 20 °C was added with 0.1 g kaolin sample. After give times (0.5, 1, 2, 3, 5, 7, 9, 11, 13, and 24 h), the Pb concentration in the solution was measured.

To measure the effect of reaction temperature on Pb removal, a Pb(II) solution (200 mg l⁻¹, 100 ml) was heated to 30 °C, 40 °C, 50 °C, or 60 °C. After adding 0.1 g of kaolin sample, the mixture was kept for 4 h at the respective temperature.

3. Results and discussion

3.1. XRD analysis of the kaolin and K-nZVI

The XRD patterns of four kaolin samples are presented in figure 1. A characteristic peak at 2θ = 44.8° confirmed the existence of zero-valent iron in the two K-nZVI samples (figures i(c) and (d)) [38], indicating that the Fe⁰...
nanoparticles were successfully loaded onto the kaolin surface. In addition, the Fe$^0$ peak was stronger in figure 1(d) than in figure 1(c), and so the iron content increases as the particle size of the kaolin carrier decreases.

3.2. FTIR spectra of the kaolin and K-nZVI

The amount of adsorption depends on the number of functional groups on the surface of adsorbent. When these functional groups are higher, the amount of adsorption increases [6, 39]. The FTIR spectra of all four kaolin samples in the range of 4000–400 cm$^{-1}$ are shown in figures 2(a)–(d). The spectra for kaolin in figures 2(a) and (b) show bands at 3628 and 3691 cm$^{-1}$, which correspond to O–H vibration of H$_2$O in the kaolin mesosphere [40], while the bands at 1038 and 1041 cm$^{-1}$ suggest the presence of Al–O–H structures [41]. After loading the nZVI, the O–H vibration peaks in the kaolin octahedra decrease significantly in intensity, due to the partial destruction of the Si–O and Al–O bonds when NaBH$_4$ reacts with H$_2$O [42]. In addition, new bands at 473, 474, 565, and 567 cm$^{-1}$ (corresponding to Fe–O stretch of Fe$_2$O$_3$ and Fe$_3$O$_4$) were observed in figures 2(c) and (d).
These results further demonstrate that nZVI was successfully loaded onto 2.3 and 45 μm Kaolin, and also that part of the nZVI surface was oxidized.

3.3. Specific surface area
Figure 3 shows the specific surface area of the samples. For kaolin particle sizes of 2.3 and 45 μm, the specific surface area of K-nZVI was 27.87 and about 20.01 m² g⁻¹, respectively, while that without loaded n-ZVI was 8.62 and 6.56 m² g⁻¹. Therefore, kaolin with a smaller particle size has a larger specific surface area, both before and after loading with n-ZVI.

3.4. Micro/nanostructures
The micro/nanostructures of the kaolin samples were observed by Lorentz transmission electron microscopy [43, 44], as shown in figures 4(a)–(c) and (b) for 2.3 μm Kaolin, 45 μm Kaolin, 2.3 μm K-nZVI, and 45 μm K-nZVI, respectively. Between figures 4(c) and (d), the finer kaolin particles were able to adsorb more nZVI than the 45 μm kaolin.

3.5. Effect of pH on Pb(II) removal rate
The effect of initial pH on the removal of Pb(II) from solution is shown in figure 5. Either with or without loaded n-ZVI, the 2.3 μm kaolin always had better performance than the 45 μm kaolin. With increasing pH, the Pb(II) removal rate by all four materials gradually increases. Hence, a higher pH value (4–6) is more favorable for Pb(II) removal. The reason is that zero iron catalyst’s level shows the most elimination at pH of 5–8 [7, 23]. At pH = 6, the removal rate by 2.3 and 45 μm kaolin is about 30% and 22%, while that for the corresponding K-nZVI was 98% and 91%, respectively. The main reason for this phenomenon is suggested that the H⁺ ions with iron solution in the acidic solution react to form a precipitate with Fe(III) in aqueous solutions and affect the removal of lead ions [45]. Moreover, when the kaolin is placed into the acidic condition, the lattice of the Si–O and Al–O bonds will be broken, and H⁺ ions will be adsorbed by bond breaking which will lead to an decrease rate of adsorptive removal [38]. Accordingly, the removal efficiency is low when the solution pH is less than 3. When pH = 2, the respective Pb(II) removal rates are about 14%, 9%, 29%, and 24%, suggesting a thicker interphase layer between the K-nZVI and solution [46]. These results support the previous finding that H⁺ competes with Pb(II) for active sites on the adsorbent surface, and hence a lower pH reduces the Pb(II) sorption [47].

3.6. Effect of initial Pb(II) concentration
When the Pb(II) concentration in the initial solution increased, its removal rates by kaolin and K-nZVI both decreased. From figure 6, when the initial Pb(II) concentration was 100 mg l⁻¹, the removal rates by all four materials were higher than 50%, in the order of 2.3 μm K-nZVI > 45 μm K-nZVI > 2.3 μm kaolin > 45 μm kaolin. When the initial Pb(II) concentration was 500 mg l⁻¹, the removal rates remained in the same order but all diminished greatly (55.8%, 45.6%, 13.9%, and 9.5%, respectively). The main reason for this phenomenon is that, the removal rate decreases with the increasing of concentrations of Pb(II), due to there is no sufficient
surface in adsorbent to remove all Pb(II). Oppositely, in low concentrations of the Pb(II), all of the molecules stick to the adsorbent surface, and then remove from the solution [5, 22, 25]. That being said, since the iron particles contain a finite number of adsorption sites, excess Pb(II) will saturate these sites before being fully adsorbed [48, 49].

3.7. Effect of reaction time
Figure 7 shows the Pb(II) removal efficiency in a 200 mg l⁻¹ aqueous solution using the four kaolin samples at pH = 5 and 20 °C for 30 min. The removal rates of 2.3 μm K-nZVI and 45 μm K-nZVI reached 40.7% and 32.1%, respectively, while those of 2.3 μm kaolin and 45 μm kaolin were lower, being only 23.0% and 19.2%. After the reaction time was extended to 24 h, the removal rates grew to 99.5%, 89.0%, 68.8%, and 65.8%, respectively. With increasing of the reaction time, the adsorbent has more time to eliminate Pb(II) [23]. Meanwhile, it can be seen that the loading of nZVI, especially when applied to finer kaolin particles, significantly

**Figure 4.** TEM images: (a) 2.3 μm Kaolin, (b) 45 μm Kaolin, (c) 2.3 μm K-nZVI, (d) 45 μm K-nZVI.

**Figure 5.** The removal efficiency of Pb(II) by materials with pH.
improves the removal rate of Pb(II). Therefore, the removal rate was ordered as 2.3 μm K-nZVI > 45 μm K-nZVI > 2.3 μm kaolin > 45 μm kaolin from 30 min to 24 h. On the other hand, the rate of removal is rapid at first, but gradually decreased with time until it reached equilibrium. It is due to fact that in early stages of absorption, a large number of vacant surface areas that can be adsorbed of adsorption, However, as time goes on, it is difficult for the vacancy remaining surface to adsorb pollutants [6, 24].

3.8. Effect of temperature
The removal rate of Pb(II) was found to increase with the increase of temperature (figure 8). When the temperature increased from 30 °C to 60 °C, the removal rate of Pb(II) by 2.3 μm K-nZVI increased from 50.7% to 69.4%. The same trend was observed for the other three materials, indicating a positive correlation between the temperature and the Pb(II) removal rate. The main reason for this phenomenon is that, the mobility and penetration of Pb(II) are enhanced by the increasing of temperature, that also caused an increase in adsorption [6]. At all temperatures, 2.3 μm K-nZVI showed better performance than 45 μm K-nZVI, further supporting the hypothesis that using smaller kaolin particles in the material synthesis could improve the removal rate of Pb(II) by K-nZVI.
4. Conclusions

This study examined the Pb(II) removal rate from aqueous solutions using kaolin particles of different sizes with and without loaded nZVI. The novelty of this manuscript lies in considering the influence of the particle size of nZVI carrier material particles on the adsorption performance. The results verified the previous finding that kaolin as a carrier could effectively hinder the agglomeration of nZVI. Microscopic observation confirmed that nZVI adhered well to the surface of kaolin.

The Pb(II) removal rate by K-nZVI synthesized from 2.3 μm Kaolin was higher than that synthesized from 45 μm Kaolin, in the order of 2.3 μm K-nZVI > 45 μm K-nZVI > 2.3 μm kaolin > 45 μm kaolin. This is true at different pH values, initial Pb(II) concentrations, reaction times, and solution temperatures. Under the acidic condition, the removal rate of lead ions with the increase of pH for kaolin and K-nZVI. When the pH was 6, the removal rate by 2.3 and 45 μm K-nZVI was about 98% and 91%. When the initial Pb(II) concentration was 500 mg l\(^{-1}\), the removal rates by 45 μm K-nZVI was 45.6% and by 2.3 μm K-nZVI was 55%. The removal rate of lead ions was enhanced by the increasing of time and temperature based on kaolin and K-nZVI. When the reaction time exceeded 24 h, the removal rates reaches 99.5%, 89.0%, 68.8%, and 65.8% corresponding to 2.3 μm K-nZVI, 45 μm K-nZVI, 2.3 μm kaolin and 45 μm kaolin, respectively. When the temperature was to 60 °C, the removal rates by 45 μm K-nZVI was 55.2%, and by 2.3 μm K-nZVI is more than 69%.

These findings confirm the author’s hypothesis that when used as a carrier for nZVI, smaller kaolin particles can increase the specific surface area, number of pores, and the pore volume, thereby effectively improving the Pb(II) removal rate by the synthesized K-nZVI.

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