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Removal of Pb(II) from water using synthesized kaolin supported nanoscale zero-valent iron

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ABSTRACT

Nanoscale zero-valent iron (nZVI) used to remediate contaminated groundwater is limited due its lack of durability and mechanical strength. To address these issues, synthesized kaolin supported nanoscale zero-valent iron (K-nZVI) was used to remove Pb(II) ion from aqueous solution. This study has demonstrated that synthesized K-nZVI was efficient in removing Pb(II) from aqueous solution containing 500 mg L^{-1} of Pb(II), where 90.1% of Pb(II) was removed within 60 min using 5 g L^{-1} of K-nZVI having a nZVI mass fraction of 20% at pH 5–6. Ni(II) and Cd(II), as co-existent ions, were also removed by the synthesized K-nZVI. This however had little effect on the removal of Pb(II) from solution. The synthesized K-nZVI could be reused more than 5 times when applied to remove Pb(II) from solution with concentrations of 50 mg L^{-1}. Additionally, synthesized K-nZVI was efficient in removing Pb(II) (98.8%) and total Cr (99.8%) from an electroplating wastewater, indicating that the synthesized nZVI is a potential remediation material when used for the treatment of electroplating wastewater containing metal ions.

1. Introduction

The presence of heavy metal ions in aquatic environments is of concern due to the harmful effects on human and animal health. Two main methods of ingestion are direct drinking water and food while bioaccumulation can occur in aquatic food chains [1]. Pb(II) ion is one of the most poisonous heavy metal ions that accumulates in muscles, bones, kidney and brain tissues and has the potential to cause various disorders, and is regarded as the priority controlled pollutant in many countries [2]. Elevated Pb(II) ion concentration in surface water and ground water can be caused by the discharge of untreated effluents from battery manufacturing, electroplating industry and the combustion of automobile petrol [3]. Methods used to remove Pb(II) from wastewater mainly involve chemical precipitation [4], chemical reduction [5], ion exchange [6], membrane separation [7], mineral adsorption [8], and biosorption [9]. However, most of these methods are only suitable for the removal of Pb(II) in low concentrations and often require extensive processing and high cost. It is therefore necessary to develop more efficient remediation strategies that are able to removal Pb(II) from contaminated water in high concentrations.

In recent years, materials modified with nanoscale zero-valent iron with size of <100 nm have attracted attention. Nanoscale zero-valent iron (nZVI) has high surface energy and reaction activity due to its large specific surface area [10]. The physicochemical properties of nZVI and its reductive capacity [11] allow its application in the rapid decontamination of many aqueous pollutants. However, nZVI is often aggregates and decrease in its efficiency [12]. Consequently, various immobilization technologies are being developed for nZVI stabilization, such as starch-stabilized nZVI [12], using sodium carboxymethyl cellulose (CMC) as a stabilizing agent to immobilize nZVI [13], zeolite-supported nZVI [14], guar gum-stabilized nZVI [15] and bentonite/iron nanoparticles [16], all of which decrease aggregation and improve dispersion as well as stabilization. Kaolin is chemically stable [17], inexpensive and is an ideal support material for nZVI. However use of kaolin as a support material is not well researched in the literature. We present a method of synthesizing kaolin supported nanoscale zero-valent iron (K-nZVI) and demonstrate its use in removing Pb(II) from aqueous solutions.

K-nZVI has a relatively low standard potential allowing it to efficiently donate electrons to pollutants, converting them into their reduced forms. In the process, Fe is transformed from Fe^0 to Fe^{2+} as expressed in following equation [18]:

$$Fe^0 \rightarrow Fe^{2+} + 2e^-; \quad \Phi^0_{Fe^{2+}/Fe^0} = -0.440\,V \tag{1}$$

Therefore, theoretically Fe^0 can reduce any pollutant that has a higher reduction potential than −0.440 V. Additionally K-nZVI has a good dispersive properties and is able to absorb pollutants in aqueous suspensions.

The aim of the study was to optimize the efficiency of removal of Pb(II) from aqueous solution using K-nZVI. Hence, we report

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here: firstly the synthesis and characterization of the K-nZVI; and secondly investigation of removal of Pb(II) from aqueous solution using the use of K-nZVI to remove Pb(II) from aqueous solution under various conditions. Variables tested were the mass fraction of nZVI, contact time, the concentration of Pb(II), pH, ionic strength and dosage; thirdly an examination of reusability of K-nZVI and the removal of Pb(II) from wastewaters containing a mixture of co-contaminating metals ions. The study also conducted a practical demonstration in the removal of Pb(II) from an electroplating wastewater.

2. Materials and methods

2.1. Pretreatment of kaolin clay

Natural kaolin provided by Longyan Kaolin Co., Ltd. (Fujian, China) is composed of 88% of kaolinite and 12% of quartz and has a specific surface area of $3.67\,m^2\,g^{-1}$ measured using BET-N_2 adsorption method (Micromeritics' ASAP 2020MC, U.S.A). The kaolin used as a support material was oven dried at 110 °C for 3 h and then ground to pass through a 0.135 mm (110 mesh) sieve. All reagents including iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, Sigma–Aldrich), sodium borohydride ($NaBH_4$), and lead (II) nitrate ($Pb(NO_3)_2$) were analytical grade.

2.2. Preparation of K-nZVI and characterization

Kaolin-loaded nanoscale zero-valent iron (K-nZVI) was prepared using Fe(III) reduction method described elsewhere [19]. Briefly, 100 mL 0.179 M of Fe(III) solution was prepared by dissolving $FeCl_3 \cdot 6H_2O$ into a mixture of ethanol and water (30%, v/v). The solution was added to a three-necked flask containing kaolin (4 g) and the contents were mixed uniformly under nitrogen using an eclectic stir bar. Then equal volume of $NaBH_4$ (1.610 M) was added dropwisely into the stirred mixture. The reduction reaction is given in Eq. (2). The black solid produced was vacuum filtrated (Buchner funnel, Whatman filter paper, grade No. 1) and washed three times with 50 mL of 0.1 M HCl, distilled water and acetone, respectively. The solid was then dried under N_2 atmosphere overnight [5].

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0_{(s)} \downarrow + 3B(OH)_3 + 9H^+ + 6H_{2(g)} \uparrow \quad (2)$$

Theoretically (Eq. (2)), kaolin could be modified to contain 20% (w/w) nZVI to produce K-nZVI. The particles of nZVI loaded on the kaolin surface had an average size of 44 nm and a specific surface area of $26.11\,m^2\,g^{-1}$ (measured with the BET-N_2 adsorption method). The ESEM images (Philips-FEI XL30 ESEM-TMP, Philips Electronics Co., Eindhoven, Netherlands) obtained from kaolin and K-nZVI in Fig. 1a and b show nZVI dispersed well with little aggregation in the kaolin and confirm the successful attachment of nZVI to the kaolin.

K-nZVI containing 5, 10, 15 and 25 wt% of nanoscale Fe^0 was prepared. In this study, nZVI in K-nZVI material used in all the following experiment was 20% unless otherwise indicated.

2.3. Batch experiments for uptake of Pb(II) by K-nZVI

A stock solution of Pb(II) was prepared by dissolving 1.60 g of $Pb(NO_3)_2$ into distilled water and then diluted to 1000 mL, acquired a $1000\,mg\,L^{-1}$ of Pb(II) solution. Working solutions of Pb(II) were prepared from the stock solution by dilution. Similarly, working solutions of heavy metals [Ni(II), Cd(II), Zn(II), Cu(II) and Cr(VI)] were prepared from their respective stock solutions ($1000.0\,mg\,L^{-1}$).

In the following experiments, various grades of K-nZVI and metal ion solutions were well mixed prior to placement on a rotary shaker with 250 rpm at 30 °C. The mixed solutions were periodically sampled ($n = 3$) using a syringe to withdraw aliquots which were then filtered using a 0.45 μm CMC membrane (cellulose membrane) filter to separate the solid particles and solution. Residual concentrations of metal ions in the filtrates were diluted with distilled water and concentrations were determined by atomic absorption spectrometer (AAS; VARIAN AA240, USA) [20].

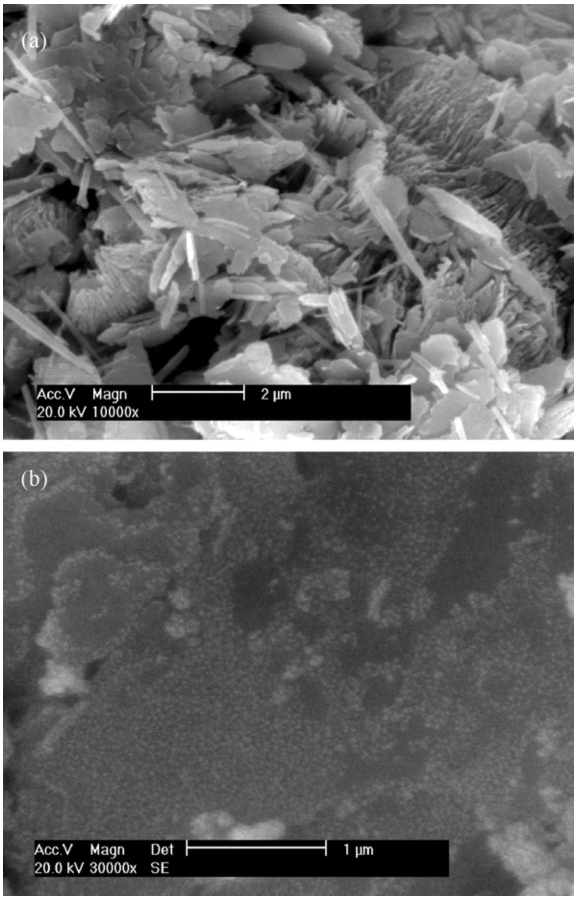

Fig. 1. SEM images: (a) kaolin and (b) K-nZVI.

The rate of Pb(II) (10 mL of 50.0, 250.0, 500.0 and $1000.0\,mg\,L^{-1}$) removal from solutions containing 0.1 g of K-nZVI was monitored as a time course at 5, 10, 15, 20, 30, 45, 60, 75, 90, 120 and 150 min of reaction intervals. Residual concentrations of Pb(II) in mixed solutions were measured by AAS.

A direct comparison was made between K-nZVI, nZVI and kaolin in their abilities to remove Pb(II) from solution. The efficiency of K-nZVI in removing Pb(II) from solution were conducted using different initial concentrations of Pb(II). 10 mL of 50.0, 100.0, 250.0, 500.0, 750.0 or $1000.0\,mg\,L^{-1}$ Pb(II) solutions were added to separate serum bottles containing 0.10 g of K-nZVI individually. At the same time, 0.02 g of nZVI or 0.1 g of kaolin used as contrasting removal reagents were added to 10 mL of 50.0, 100.0, 250.0, 500.0, 750.0 or $1000.0\,mg\,L^{-1}$ Pb(II) solutions, respectively.

To examine the effect of nZVI contents in K-nZVI on the removal of Pb(II) from solution, 0.10 g of K-nZVI loaded with 5%, 10%, 15%, 20% and 25% of nZVI was added to 10 mL of $500\,mg\,L^{-1}$ Pb(II) solution, respectively. These series of mixtures were replaced on a rotary shaker with 250 rpm at 30 °C for 30 min. Samples were then collected and centrifuged at 3000 rpm for 5 min. The supernatants were separated and the concentration of residual Pb(II) were determined.

The effect of pH value on removal of Pb(II) solution from the mixed solutions for 500 mg L^{-1} of Pb(II) was studied at pH 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0. pH was adjusted using 0.1 M of HNO_3 and NaOH solution. The K-nZVI was held constant at 0.10 g in a sample volume of 10 mL.

The effect of ionic strength on the removal of Pb(II) by K-nZVI from solution containing different concentrations of sodium nitrate was also studied. The concentrations of Na^+ in 500 mg L^{-1} Pb(II) solution were adjusted to 0.00, 0.01, 0.10 and 1.00 M with sodium nitrate. 0.10 g of K-nZVI was then added into 10 mL of 500 mg L^{-1} Pb(II) solution with different concentrations of sodium nitrate, which reacted under the same conditions described previously. Samples were centrifuged at 3000 rpm at ambient temperature in high rotary centrifugation for 5 min, and Pb(II) in supernatant were determined with AAS methods.

The effect of K-nZVI dose on removal of Pb(II) was studied for the initial Pb(II) concentration of 500.0 mg L^{-1}. 0.10 g of K-nZVI was added into a batch of 10, 20, 30 and 40 mL of Pb(II) solutions where the doses of K-nZVI added were 10.0, 5.0, 3.3 and 2.5 g L^{-1}, respectively. Samples were collected and were then centrifuged at 3000 rpm for 5 min.

Experiments on the reuse of K-nZVI were also performed. Firstly, 10 mL of 50.0 and 250.0 mg L^{-1} Pb(II) solutions were separately mixed into serum tubes containing 0.10 g of K-nZVI, respectively, and these mixtures were reacted on a rotary shaker with 250 rpm at 30 °C for 30 min; secondly, all supernatant were removed with pipette and were used to determined Pb^{2+}; then the K-nZVI left in serum tubes were mixed with another new 10 mL of 50.0 and 250.0 mg L^{-1} Pb(II) solutions on the same reaction condition. At this step the reusability of K-nZVI was achieved.

To investigate the effect of co-contaminating heavy metal ions on the efficiency of removal of Pb(II) from solution, 0.10 g of K-nZVI was added to serum tubes with 10 mL of 250 mg L^{-1} Pb(II) solution containing 50 mg L^{-1} of Ni(II) and Cd(II) individually. Samples were collected at 0, 2, 4, 6, 8, 10, 12, 14, 16, 20 and 30 min and were then centrifuged at 3000 rpm for 5 min.

Batch experiments were run in duplicate, and mean values were used to fit curves. The uptake amounts of Pb(II) by the tested materials were calculated using the following formula:

$$Q_t\ (\mathrm{mg/g}) = \frac{(C_0 - C_t)V/1000}{W} \quad (3)$$

where Q_t is the uptake amount of Pb(II) onto the kaolin, nZVI and K-nZVI at time t, C_0 is the initial concentration of Pb(II) (mg L^{-1}), C_t is the concentration of Pb(II) at time t (mg L^{-1}), V is the volume of Pb(II) solution used (mL), and W is the weight of the tested materials used (g).

2.4. Removal of metal ions from an electroplating wastewater

To study the capacity of the synthesized K-nZVI to remove heavy metal ions from electroplating wastewater collected from an electroplating factory's drainage, pH value and concentrations of main heavy metal ions in the wastewater were measured first. Then 10 mL of this wastewater was added to 50 mL of the serum tubes with 0.10 g of K-nZVI. The mixtures reacted on a rotary shaker at 30 °C with 250 rpm for 60 min, and the residual concentrations of these metal ions after the reaction was determined by AAS.

3. Results and discussion

3.1. Removal of Pb(II) from aqueous solution

Fig. 2 shows the residual concentrations of Pb(II) as a function of reaction time for batch serum tubes containing 0.1 g of K-nZVI, and kaolin in the absence of loaded nZVI (shown in the insert figure) and 10 mL of different initial concentrations of 50.0, 250.0, 500.0 and 1000.0 mg L^{-1} Pb(II). The results demonstrate that the equilibrium for Pb(II) removal from solution was reached within the first 30 min using K-nZVI and 10 min using the kaolin in the absence of nZVI despite the different initial Pb(II) concentrations. In addition, the results also indicated that the rate for removal of Pb(II) from solution using K-nZVI was much higher than using kaolin. Results demonstrate that K-nZVI used in this study has a larger specific surface area of 26.11 $m^2\ g^{-1}$ compared to standard kaolin with 3.67 $m^2\ g^{-1}$. K-nZVI consequently has a higher capacity for Pb(II) uptake from solutions. This is likely due to the kaolin support preventing agglomeration of iron and therefore presenting a higher specific surface area of available iron to the aqueous phase [5]. The observation was similar to Cr(VI) reduction by resin-supported nZVI [5] and to Cu(II) and Co(II) removal using Turkey kaolinite-supported nZVI [19]. Results are consistent with the kaolin support preventing agglomeration of the iron in aqueous solution.

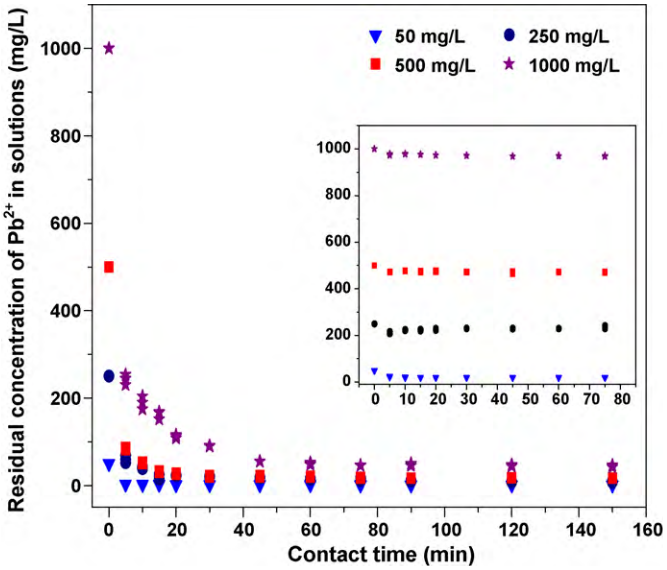

Fig. 2. Relationship of Pb(II) concentration versus time for initial concentrations of 50, 250, 500, 1000 mg L^{-1} Pb(II) removal by K-nZVI and kaolin (insert represents Pb(II) removal by kaolin).

The accumulation of Pb(II) after 30 min by K-nZVI, kaolin or nZVI varied with the equilibrium concentrations of Pb(II) and is presented in Fig. 3 (the insert summarizes the accumulation by separate quantities of nZVI or kaolin). K-nZVI was more efficient than kaolin in the removal of Pb(II) from aqueous concentrations within the range 50.0–1000.0 mg L^{-1}. However, nZVI also showed a similar or higher removal capability when the initial concentrations of Pb(II) were less than 250 mg L^{-1} since the mechanisms of Pb(II) reduction by both K-nZVI and nZVI were likely similar. This result is supported by the literature [5] in which the kinetics of Pb(II) reduction by both nZVI and resin-supported nZVI were investigated. However, nZVI had a poor removal efficiency when it was used to remove Pb(II) with a concentration greater than 250 mg L^{-1}, which may have been caused by the aggregation of nZVI decreasing its specific surface area and reaction activity [21]. Kaolin supported nZVI is a stable material and dispersed nZVI in aqueous solution increasing the activity of nZVI [19]. The removal percentage of Pb(II) using K-nZVI, nZVI and kaolin was 97%, 51.2% and 6.7%, respectively where initial concentration of Pb(II) was 50 mg L^{-1}. When initial concentration of Pb(II) was 500 mg L^{-1}, the removal percentage of Pb(II) was 96.7% for K-nZVI, 15.8% for nZVI and 8.6% for kaolin. These results suggest that K-nZVI could efficiently remove Pb(II) from solutions at elevated concentrations.

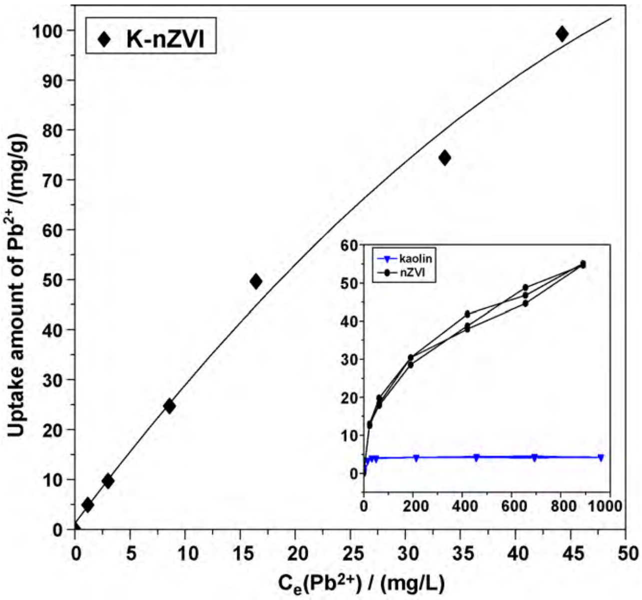

Fig. 3. Relationship between the equilibrium concentration of Pb(II) in solutions and uptake amount of Pb(II) on different solid uptake materials (insert represents uptake of Pb(II) by nZVI and kaolin individually).

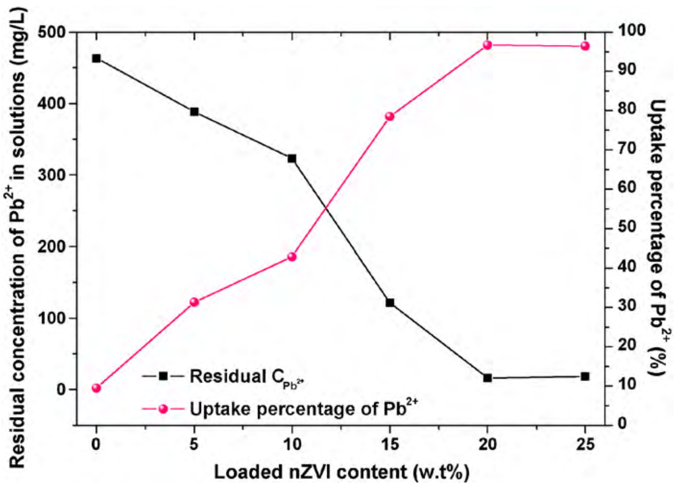

Fig. 4. Effect of nZVI loadings on removal of Pb(II).

Fig. 4 shows the effect of loading amounts of nZVI on removal of Pb(II) from solutions by K-nZVI. When the loading amounts of nZVI were changed from 0% to 20%, the removal percentage was subsequently increased. This could explain the increasing nZVI loadings would increase the specific surface area of K-nZVI [10], and was also supported by specific surface area measurement using BET-N_2 analysis technique, which showed that an increase in loading amounts of nZVI from 0%, 5%, 10%, 15% to 20% led to an increase in specific surface areas from 3.67, 6.14, 7.93, 18.16 to 26.11 $m^2\,g^{-1}$, respectively. A concomitant increase in the surface area of exposed iron was apparent with an increased loading of nZVI thereby increasing the efficiency of removal of Pb(II). When the loadings were within the range from 20% to 25% the removal efficiency remained constant. The specific surface areas decreased slightly from 26.11 $m^2\,g^{-1}$ for 20% to 25.62 $m^2\,g^{-1}$ for 25% of nZVI. This may have been caused by aggregation in the 25% of nZVI loadings causing a decrease in specific surface area and a reduction in the removal capacity of Pb(II). Similar observations were reported in removal of nitrate using nanoscale zero-valent iron loaded on exfoliated graphite [22].

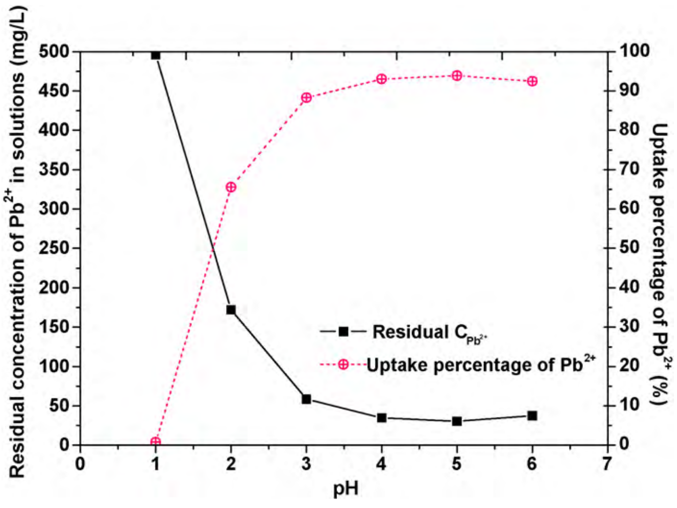

Fig. 5. Effect of initial pH value of mixed solutions on removal of Pb(II).

The effect of initial pH on removal of Pb(II) from solution is shown in Fig. 5. Results indicated that Pb(II) was removed less efficiently at low pH. The more favorable pH values were within the range from 4 to 6. It can be seen that the pH solution did not significantly impact on the removal of Pb(II) in pH range of 4–6. Only 94% of Pb(II) in solution was removed in pH range of 4–6. This could have resulted from the formation of a Fe(II) and Pb(II) oxyhydroxide layer coating on the surface presumably decreasing Pb(II) uptake by K-nZVI [5]. In addition, the iso-electric point (IEP) of K-nZVI surface was in the pH range of 6.5–7.2 [17]. When the pH of mixed solution exceeded to 7.2, concentration of hydroxyl (–OH) was increased in solution, which resulted in either K-nZVI surface to become negatively charged or caused precipitation of $Pb(OH)_2$ in solution as well on the surface of K-nZVI. Conversely results also indicated that removal efficiency was poor when the pH of a mixed solution was <3, suggesting an increase in the thickness of double layer at the interphase between the K-nZVI and solution [10,19]. Results support the notion that there was competition between protons and Pb(II) for the active sites on the surface of K-nZVI which reduced Pb(II) sorption [23]. Results indicate that optimal sorption occurs within the pH range 5–6 in aqueous solutions containing a solution of co-contaminating heavy metals.

The effect of ionic strength on uptake of Pb(II) by K-nZVI is listed in Table 1, from which it could be found that concentration of $NaNO_3$ has little effect on Pb(II) uptake by K-nZVI. These results are consistent with the hypothesis that the removal of Pb(II) from solution is not merely an adsorption process, but also a reduc-

Table 1
Effects of ionic strength and K-nZVI dose on removal of Pb(II) from solutions.

C_0 (Pb^{2+})	Ionic strength/C_{NaNO_3} (mol L^{-1})				Uptake agent concentration (gL^{-1})			
500.0 mg L^{-1}	0.00	0.01	0.10	1.00	10.0	5.0	3.3	2.5
Uptake amount (mg Pb^{2+} g^{-1} K-nZVI)	48.4	48.2	48.4	48.0	48.0	88.1	91.9	87.9
Uptake amount (mg Pb^{2+} g^{-1} loaded nZVI)	242.0	241.0	242.0	240.0	240.0	440.5	459.5	439.5
Uptake percentage (%)	98.9	98.7	98.9	98.2	95.9	90.4	61.3	44.0

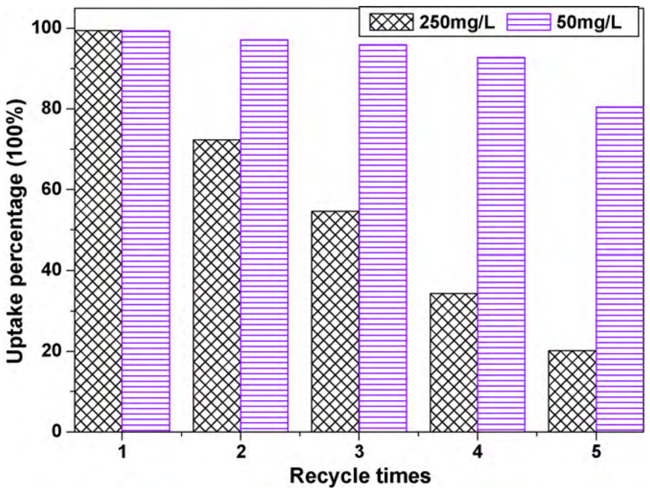

Fig. 6. Removal percentage of Pb(II) in solutions varied with recycle of K-nZVI. (⊠ the change in uptake percentage of initial 250 mg L^{-1} of Pb(II) with recycle time; ▤ : the change in uptake percentage of initial 50 mg L^{-1} of Pb(II) with recycle time)

tion process in which Pb(II) ion is reduced concomitantly by K-nZVI [18,24]. Results also suggest that Na$^+$ ion would not only compete with Pb(II) for the active sites on the surface of K-nZVI, but also had an adverse influence on the quantification of aqueous Pb(II) using AAS method. Nevertheless, the uptake of Pb(II) by K-nZVI was efficient in the presence of NaNO$_3$ suggesting that K-nZVI would be useful in the removal of Pb(II) from electroplating wastewater.

In addition, the effect of K-nZVI dosage was also investigated at mass concentrations of 10.0, 5.0, 3.3 and 2.5 g L^{-1} on Pb(II) removal. The results from Table 1 indicated that high uptake amount together with an efficient removal percentage for 500.0 mg L^{-1} of Pb(II) could be achieved when the dose of K-nZVI with 5.0 g L^{-1} was used in the solution, where, 440.5 mg Pb(II) was uptaken by per nZVI.

In summary, the general reduction of Pb(II) by K-nZVI are thought to be [5]

$$2Fe^0 + 3Pb^{2+} + 4H_2O \rightarrow 3Pb^0 + 2FeOOH + 2H^+ \quad (4)$$

However, other additional processes operate in Pb(II) reduction when K-nZVI is used which result in the formation of oxidized surface species [5,19]. Additionally K-nZVI is believed to produce a partial decrease in the extent of aggregation resulting in the dispersed ZVI having the characteristic core–shell structure [10,11].

3.2. *Reuse of K-nZVI*

The experimental results of evaluating reusability of K-nZVI for removing Pb(II) from solution are shown in Fig. 6, which indicated that 10 g L^{-1} of K-nZVI could be reused at least 5 times for every initial concentration of 50 mg L^{-1} of Pb(II) in solution. The removal percentage of Pb(II) that could be reached is as high as 80.5% even at the fifth reuse. However, compared with 50 mg L^{-1} of Pb(II), reusability of K-nZVI was low for removal of Pb(II) from solution with the initial concentration of 250 mg L^{-1}, indicating that this synthesized K-nZVI could be reused for the removal of Pb(II) from wastewater with lower concentrations of metal (e.g., Pb(II) ≤ 50 mg L^{-1}). Similar result was reported for the removal of Cu(II) and Co(II) ions from aqueous solutions [19].

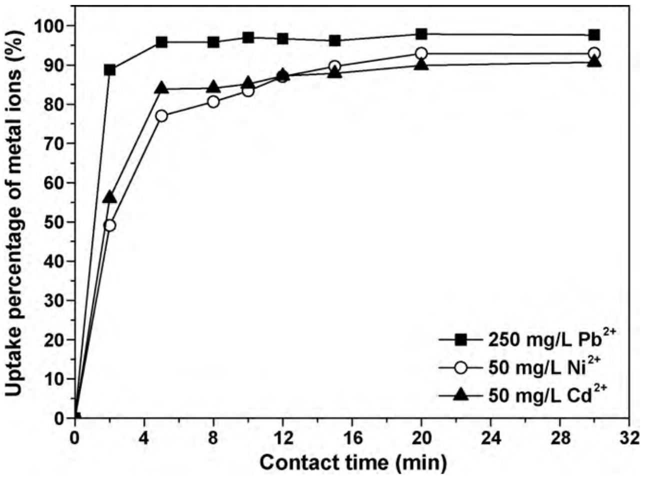

Fig. 7. Effect of co-existence heavy metal ion on removal of Pb(II).

3.3. *The effect of co-contaminating metal ions on the efficiency of Pb(II) removal*

Fig. 7 shows the uptake percentage and residual concentrations of Pb(II) as a function of contact time in the presence of co-contaminating Ni(II) and Cd(II) ions. K-nZVI was more efficient at removing Pb(II) from solution than Ni(II) or Cd(II)· This was probably the result of the standard reduction potentials of Ni(II) and Cd(II) ($\Phi^0_{Ni^{2+}/Ni^0} = -0.257\,V$, $\Phi^0_{Cd^{2+}/Cd^0} = -0.352\,V$) being more negative than $\Phi^0_{Pb^{2+}/Pb^0} = (-0.126\,V)$. However, K-nZVI was still capable of removing Ni(II) and Cd(II) from aqueous solution due to their higher standard reduction potentials compared with that of $\Phi^0_{Fe^{2+}/Fe^0}$. The uptake percentages obtained within 30 min for initial 250 mg L^{-1} of Pb(II), 50 mg L^{-1} of Ni(II) and 50 mg L^{-1} of Cd(II) were 97.8%, 92.9% and 90.7%, respectively.

3.4. *Remediation of electroplating wastewater*

An electroplating wastewater with pH at 1.8 containing primarily Zn(II), Cr(VI) and Cr(III), Cu(II), Pb(II) and Ni(II) ions was measured by AAS. The corresponding metal concentrations are listed in Table 2. After 10 mL of the wastewater reacted with 0.10 g of K-nZVI under the same experiment conditions described above for 60 min, residual concentration, uptake amount and uptake percentage of these metal ions were determined as listed in Table 2. The results showed that 99% of Pb(II), 99.8% of total Cr, 69.5% of Cu(II), 28.1% of Zn(II) and 23.0% of Ni(II) were removed, where Pb(II) and total Cr were well removed but Zn(II) and Ni(II) were less efficiently removed. Since the standard reduction potential of Zn(II) ($\Phi^0_{Zn^{2+}/Zn^0} = -0.76\,V$) was more negative than that of Fe(II) [24], Zn(II) was mainly adsorbed onto the K-nZVI surface without reduction of Zn(II) to Zn^0 by Fe^0. The possible reason that Ni(II) had a low

Table 2
Remediation of actual electroplating wastewater by K-nZVI.

Wastewater	Pb^{2+}	Total Cr	Cu^{2+}	Zn^{2+}	Ni^{2+}	pH
C_0 (mg L^{-1})	12.75	71.00	27.25	216.45	8.00	1.8
C' (mg L^{-1}) after reaction	0.15	0.12	8.31	155.68	6.16	4.5
Uptake amount (mg Pb^{2+} g^{-1} K-nZVI)	1.26	7.09	1.89	6.08	0.18	
Uptake percentage (%)	98.8	99.8	69.5	28.1	23.0	

removal efficiency could attributed that both Cu(II) ($\Phi^0_{\mathrm{Cu}^{2+}/\mathrm{Cu}^0} = 0.337\,\mathrm{V}$) and total Cr ($\Phi^0_{\mathrm{Cr(VI)/Cr(III)}} = 1.23\,\mathrm{V}$) had positive reduction potentials and would be reduced prior to Ni(II) reduction [24]. Synthesized K-nZVI provides a promising environmental remediation material employed to treat electroplating wastewater and possibly other wastewaters containing Pb(II) and Cr(VI).

4. Conclusions

In this study, investigations of removal of Pb(II) from aqueous solution using synthesized K-nZVI demonstrated that, 91% of Pb(II), 440.5 mg Pb(II) g^{-1}, was removed from 500 mg L^{-1} of Pb(II) in solution under the conditions of 5 g L^{-1} of K-nZVI with 20% of nZVI loadings. The optimal pH range was from 4 to 6 in the absence of electrolytes within a reaction time of 60 min. K-nZVI could be reused more than 5 times when dose of 10 g L^{-1} loading in the removal of Pb(II) from aqueous solutions having concentrations of <50 mg L^{-1}. The results demonstrated that K-nZVI could useful in the removal of Pb(II) from electroplating wastewater containing Pb(II), Cr and some other co-contaminating metal ions. Kaolin is inexpensive, readily accessible and a useful support material for nZVI. Kaolin modified with nZVI was easily dispersed in water and efficiently removed Pb(II). K-nZVI is an efficient and promising remediation material for the removal of Pb(II) from electroplating wastewater and possibly from other heavy metal-containing wastewaters.

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