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Characterization of the adsorption behavior of aqueous cadmium on nanozero-valent iron based on orthogonal experiment and surface complexation modeling☆



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ABSTRACT

Polyvinylpyrrolidone K-30 (PVP) was introduced into the preparation of nanozero-valent iron (nZVI) and the traditional liquid-phase reduction was improved. The introduction of PVP simplified the traditional method. The nZVI prepared with this new approach showed excellent surface characters and high performance on the removal of cadmium. TEM results showed that the aggregates of nZVI can reach to several micrometers in length but less than 100 nm in diameter. The iron particles that were enclosed by a layer of oxide film that is less than 10 nm, demonstrated that the nZVI possesses a core-shell structure. BET results indicate that the specific surface area of the nZVI was $20.3159 \text{ m}^2 \text{ g}^{-1}$. A three factor and three level orthogonal experiment was employed to find out the dominant factor that affects the removal rate of cadmium by nZVI. Based on the range values, the prominence order of each factor was: initial pH of the solution > initial concentration of cadmium > dosage of nZVI, the range was 96.453, 3.294 and 1.747, respectively. A simulation was performed under the same condition and a same conclusion was derived, this consistency confirmed the validity of the conclusion that pH is the most significant factor that affects the adsorption efficiency.

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1. Introduction

Cadmium (Cd) is a major environmental contaminant which is known to accumulate in rice plants [1]. Cd can be introduced into the environment through a combination of natural processes (volcanic eruptions and forest fires) as well as anthropogenic activities (non-ferrous metals production, electroplating, manufacturing of Ni–Cd batteries and pigments, application of phosphatic fertilizers, and burning of fossil fuels) [2,3]. The natural occurrence of Cd in groundwater is of great concern due to the toxicity of Cd and the potential for chronic exposure [4]. To address this problem, the World Health Organization (WHO) had set a maximum guideline concentration of $0.003 \text{ mg} \cdot \text{L}^{-1}$ for Cd in drinking water [5]. On this occasion many public water systems have to adopt cadmium removal processes in their water treatment systems in order to meet the stringent drinking water standards.

Various technologies are currently available to remove cadmium from water, such as chemical methods [6–8], membrane separation technique [9], ion exchange technique [10] and adsorption technique

[11–13]. Adsorption is a common practice for Cd removal from drinking water due to technological and cost advantages.

Nano zero-valent iron (nZVI) has been developed as an efficient adsorbent material to treat various heavy metals from contaminated water [14]. The specific removal mechanisms involved depend on the standard redox potential (E^0) of the target metal. The E^0 of Fe^0 is -0.44 V . Metals with E^0 s that are more negative or similar to -0.44 V will be removed by adsorption, others with E^0 s that are more positive than -0.44 V will be removed by reduction and precipitation. Metals with slightly more positive E^0 than Fe^0 will be removed by reduction, adsorption, oxidation or co-precipitation which depend upon the prevailing geochemical conditions [15,16].

As shown by several studies, factors such as aqueous phase pH, concentrations of contaminants and the presence of competitive ions have a significant effect on nZVI's reactivity with metals [17–21]. Although researches had investigated the factors that may have effect on the efficiency of nZVI, comparatively little research had studied which factor is the most significant one. Figuring out this factor will mean a lot on the application of nZVI.

Among all the nZVI synthesis methods, chemical reduction is widely used due to its simplicity and chemical homogeneity [22]. During the nZVI preparation, mechanical agitation needs to be employed to insure the size of ZVI at nanoscale [23]. Aggregation of nanoparticles was reported to be caused by the large surface area and magnetic dipole–

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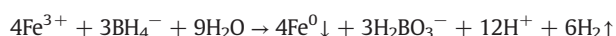
dipole interactions of the individual particles [24]. If the solution is stirred vigorously, the aggregation would be weakened to some extent. However, this mechanical stir method brings some questions (1) the waste of electricity, (2) some of the nanoparticles may stick to the agitator which are hard to clean.

The main objective of this study is to find out the most significant factor that affects the efficiency of nZVI. First, nZVI will be prepared by an improved liquid-phase reduction and characterized to verify this new method. Then an orthogonal experiment and simulation will be performed under the same conditions to find out the most significant factor.

2. Materials and Methods

2.1. Synthesis of nZVI particles

The nanoparticles were synthesized via the classical reaction as follows:



All the aqueous solutions were prepared with deionized deoxygenated water. Before the reaction begins, the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ($1 \text{ mol} \cdot \text{L}^{-1}$) was mixed with PVP ($1 \text{ g} \cdot \text{L}^{-1}$). Then the NaBH_4 ($1.6 \text{ mol} \cdot \text{L}^{-1}$) solution was added to the mixture mentioned above. The nitrogen was sparged into the solution during the whole process to maintain an anaerobic atmosphere.

2.2. Characterization of nZVI

Morphological analysis of the samples was performed by transmission electron microscopy (TEM) using a FEI Tecnai G2 F30 operated at 300 kV. Samples for TEM observation were suspended in ethanol and then supported on a double carbon membrane.

The specific surface area (SBET) of nZVI was calculated by Brunauer–Emmett–Teller (BET) N_2 method, and the pore size was measured by the BJH (Barrett, Joyner, and Halenda) N_2 adsorption/desorption isotherm method at 77 K using the automatic analyzer (ASAP 2020, Micromeritics, USA).

2.3. Orthogonal experiment

The experiments were based on an orthogonal array experiment design and the following three variables were analyzed: initial pH of the solution, dosage of nZVI and the initial concentration of cadmium. These three factors were identified to have significant impact on the efficiency of nZVI [25].

Other factors such as temperature and existence of other metal ions maybe as important as the parameters picked. But the effect of temperature had been studied by Boparai *et al.* completely so we didn't take this factor into account [26]. As for other metal ions, such as Pb(II) and As(III), although they may have significant effect on the adsorption of Cd^{2+} by nZVI, it is not appropriate to consider this factor in orthogonal experiment. Therefore, the effects of metal ions were excluded in our orthogonal experiment. Li *et al.* had studied the effect of pH in the range of 4–9 [27], and Zhang *et al.* had studied the effect of pH in the range of 3–8.6 [28]. But in actual project, the pH of effluents from chemical factory may beyond this range, so it is necessary to study the pH in a larger range. On this occasion, the range of pH used in our experiment was 2–10. Based on the waste water of metallurgical industry, the concentration of Cd(II) used in our experiment was 10, 20 and $40 \text{ mg} \cdot \text{L}^{-1}$. And the dose of nZVI was based on our earlier experiments. Above all, an $\text{L}_9(3^3)$ matrix, which is an orthogonal array of three factors and three levels, was employed to assign the considered factors and levels as listed in Table 1.

Data analysis would be carried out through the range analysis to reflect the magnitudes of the three factors.

Table 1

Levels and factors in orthogonal experiment design

Level	Factor		
	Dosage of nZVI $\text{A/g} \cdot \text{L}^{-1}$	Initial concentration of Ca^{2+} $\text{B/mg} \cdot \text{L}^{-1}$	Initial pH of the solution C
1	0.5	10	4
2	1	20	7
3	2	40	10

All the experiments were performed at ambient temperature and pressure using a 250.0 ml serum bottle. The pH values of the solutions were controlled and adjusted with the 0.02 M buffer as Boparai *et al.* had used [29].

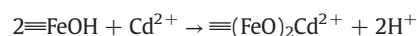
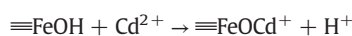
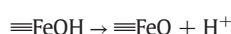
The contents were mixed on a thermostatic oscillator operated at $200 \text{ r} \cdot \text{min}^{-1}$. After 1 h an aliquot of supernatant was sampled and filtered using a $0.22 \mu\text{m}$ filter (Millipore), the samples were then transferred into clean falcon tubes and diluted using nitric acid (5%). The remaining concentration of cadmium in the filtrate was determined by means of inductively coupled plasma-optical emission spectroscopy (ICP-OES, AA 200, Agilent Technologies). Blank experiments with and without nZVI and without filtering were also performed to obtain the initial cadmium concentration prior to adsorption, as well as to rule out filtration as a reason for the decrease on the concentration of cadmium in the supernatant.

2.4. Surface complexation modeling

In aqueous solution, transition metals are known to assume different chemical forms that the formations depend on the pH of the solution. The speciation analysis of aqueous Cd^{2+} ions was performed at various initial concentration, temperature, pH, and ionic strength values using visual MINTEQ software.

In actual water, bare nZVI particles will react with water and oxygen to form outer iron (hydr)oxide layer [30]. On this occasion, the essence of the adsorption is the interaction between Cd and the outer layer. Based on this, a surface complexation modeling was carried out by Visual MINTEQ 3.0.

The iron oxide/hydroxide–water interface was represented by, for example, $\equiv\text{FeOH}$ and $\equiv\text{FeO}$, where the “ $\equiv\text{Fe}$ ” represents the solid–surface interface. Adsorbed materials are written as complexes of these surface oxides, for example, $\equiv\text{FeOCd}^+$. And the possible reactions are as follows:



Modeling was performed using the Diffuse Layer Model (DLM). This surface precipitation model can simulate the distribution of ions between adsorbed and dissolved phases based on the reactions as is mentioned above. Since the DLM model has been successfully used to describe metal ion adsorption on pure mineral materials [31], it is unnecessary to go into details about the theory. Parameters used in the modeling were based on experiment data and/or previous reports [29].

3. Result and Discussion

3.1. Characterization of nZVI

The microimages of the synthesized nZVI are shown in Fig. 1. As shown (Fig. 1(a) and (b)), the aggregates can reach to several micrometers in length but less than 100 nm in diameter (Fig. 1(c))

The result demonstrated that we can use N_2 bubbling and PVP to replace mechanical stirring in the preparation of nZVI. PVP, which is a kind of surfactant that has been widely used in the field of synthesizing nano-silver, can modify the surface properties of the particles [32]. The added PVP can effectively prevent the aggregation of ZVI particles by (1) reducing the specific surface energy of nZVI particles and (2) increasing the steric hindrance between nZVI particles.

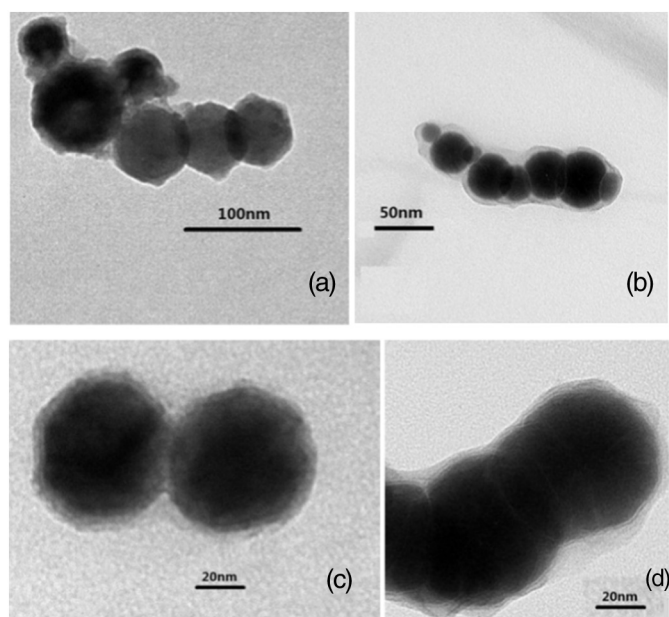


Fig. 1. TEM image of the nZVI.

The morphologies of nZVIs showed in Fig. 1(a) and (c) were fresh and those in Fig. 1(b) and (d) were placed for two months after preparation. As is shown in Fig. 1(b) and (d), there is a layer of semi-transparent film less than 10 nm thick around the black particle. It was reported that the exposure of nZVI to oxygen can lead the formation of iron oxide layer which contains Fe_2O_3 , Fe_3O_4 and $FeOOH$ [33]. The iron nanoparticles possessed a core-shell structure. The shell represented the oxidized part that surrounded the Fe^0 core and it can prevent the nZVI against further oxidation [34]. The addition of nZVI to aqueous systems usually generates OH^- by the reduction of water, resulting in the immobilization of metals by precipitation as hydroxides [35].

BET analysis indicated a specific surface area of $20.3159 \text{ m}^2 \cdot \text{g}^{-1}$. This data was used in the simulation later. Fig. 2 is the adsorption isotherm line, the trend of the plot indicated that nZVI is a typical material without holes or with macroporous.

The TEM and BET results showed that nZVI prepared with this new approach possessed excellent surface characters. With the presence of PVP, the size of ZVI can be insured to be in nanosize without mechanical stirring.

Compared to traditional methods (Fig. 3), this improved method has several advantages as follows.

- Compared with the three-necked flask, the serum bottle used as reactor is easier to clean and the solid-liquid separation is easier to achieve.

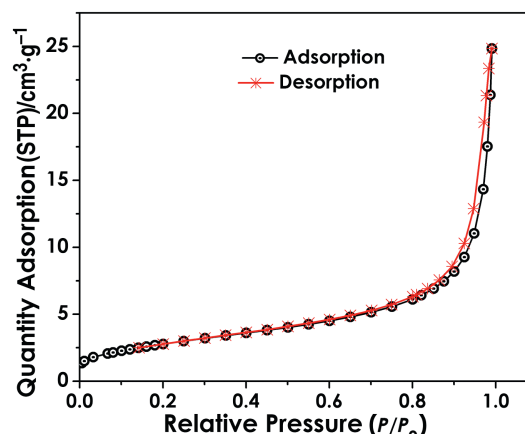


Fig. 2. BJH adsorption/desorption isotherm.

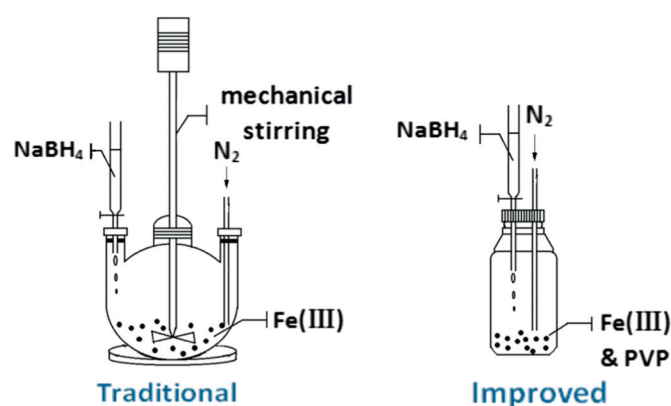


Fig. 3. Diagrammatic sketch of comparison between traditional method and new method in the synthesis of nZVI.

- In conventional approaches, negative pressure would be formed induced by rapid stirring, air will be introduced into the reaction mixture and the nZVI would be oxidized more easily.

3.2. Orthogonal experiment

An $L_9(3^3)$ orthogonal experiment was performed and the results are listed in Table 2. All the experiments were aimed at increasing the removal rate of cadmium by nZVI.

Table 2
Results of the orthogonal experiment

Trial number	Factor			Result (Y_i)
	Amount of nZVI, $A/\text{g} \cdot \text{L}^{-1}$	Initial concentration of Ca^{2+} , $B/\text{mg} \cdot \text{L}^{-1}$	Initial pH of the solution C	Removal rate of cadmium by nZVI/%
1	1	10	4	0.01
2	2	20	4	0.09
3	4	40	4	5.84
4	1	20	7	98.75
5	2	40	7	99.25
6	4	10	7	97.30
7	1	40	10	99.20
8	2	10	10	97.10
9	4	20	10	98.54

In order to figure out which factor is the most important, a range analysis is necessary. There are two parameters in a range analysis: K_{ji} and R_j . K_{ji} is defined as the sum of the evaluation indexes of all levels

($i, i = 1, 2, 3$) in each factor ($j, j = A, B, C$) and $\bar{K}_{ji}$ is the mean value of K_{ji} . R_j is defined as the range between the maximum and minimum value of $\bar{K}_{ji}$ and is used for evaluating the importance of the factors, i.e. Larger R_j value means a greater importance of the factor [36]. The calculation is displayed below (for the factor of A):

$$K_{A1} = Y_1 + Y_2 + Y_3 = 197.96;$$

$$K_{A2} = Y_4 + Y_5 + Y_6 = 196.44;$$

$$K_{A3} = Y_7 + Y_8 + Y_9 = 201.68;$$

$$\bar{K}_{A1} = \frac{K_{A1}}{3} = 65.987;$$

$$\bar{K}_{A2} = \frac{K_{A2}}{3} = 65.480;$$

$$\bar{K}_{A3} = \frac{K_{A3}}{3} = 67.227;$$

$$R_A = (\bar{K}_{Ai})_{\max} - \min(\bar{K}_{Ai})_{\min} = 67.227 - 65.480 = 96.453.$$

where K_{Ai} is the K value of the i level of the factor A; and Y_i is the value of the result of the trial number. Other K values of the factors can be determined by the same calculation steps. The mean values of K ($\bar{K}_{ji}$) for different factors at different levels in the range analysis were listed in Table 3.

Table 3
Range analysis data of the removal rate

Value name	Amount of nZVI, $A/g \cdot L^{-1}$	Initial concentration of Ca^{2+} , $B/mg \cdot L^{-1}$	Initial pH of the solution C
$\bar{K}_1$	65.987	64.803	1.980
$\bar{K}_2$	65.480	65.530	98.433
$\bar{K}_3$	67.227	68.097	98.267
R_j	1.747	3.294	96.453

As is mentioned above, R_j indicates the significance of a factor and a larger R_j means that this factor has a more significant impact on the removal rate. Based on the comparison of R_j , the prominence order of the factors was: initial pH of the solution (96.453) > initial concentration of cadmium (3.294) > amount of nZVI (1.747). R_C is the largest, which means a small change in the initial pH will have a significant effect on the removal rate of cadmium.

The mean value of each factor was displayed in Fig. 4. Based on the changes in the mean value of each factor, it can be speculated that the removal rate sharply increased from 1.98% to 98.267% with the initial pH increased from 4 to 10. When the amount of nZVI increased from $1 g \cdot L^{-1}$ to $4 g \cdot L^{-1}$, the removal rate increased steadily from 65.987% to 67.213%, which suggested that the amount of nZVI had a little effect on the removal efficiency of nZVI. Similarly, it can be speculated that the effect of the cadmium concentration ion is very small.

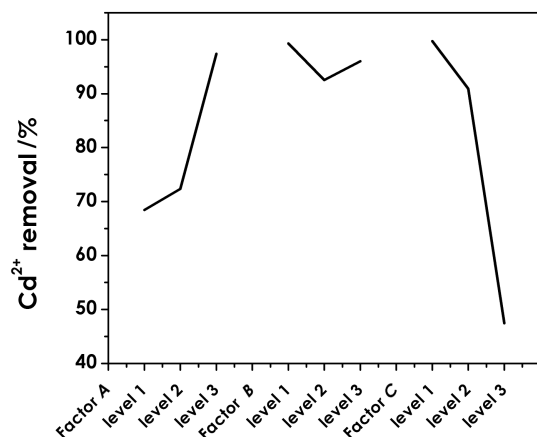


Fig. 4. Relationship between mean value of each factor and the removal rate.

Based on the orthogonal experiment and the range analysis, it can be speculated that the initial pH of the solution is the most significant factor that affects the adsorption performance of Cd^{2+} onto nZVI.

3.3. Surface precipitation modeling

In order to confirm that initial pH is the most significant factor, a simulation was performed. Parameters used in the modeling are as follows. The specific surface area of the iron (hydr)oxide shell was $20.3159 m^2 \cdot g^{-1}$ which was obtained from the BET analysis. The site density of type 1 sites (weak sorption sites) was $2.26 sites \cdot nm^{-2}$, and of type 2 sites (strong sites) was $0.056 sites \cdot nm^{-2}$ as recommended. The electrolyte was $0.01 mol \cdot L^{-1} NaNO_3$. After the adsorption equilibrium achieved, the result of the distribution of ions between adsorbed and dissolved phases is shown in Fig. 5. The tendency of the curve showed that in acidic condition most of the cadmium was dissolved and Cd^{2+} was found to be the dominant species. If the solution pH was higher, more cadmium would be adsorbed onto the nZVI and $(=FeO)_2Cd$ was found to be the dominant form.

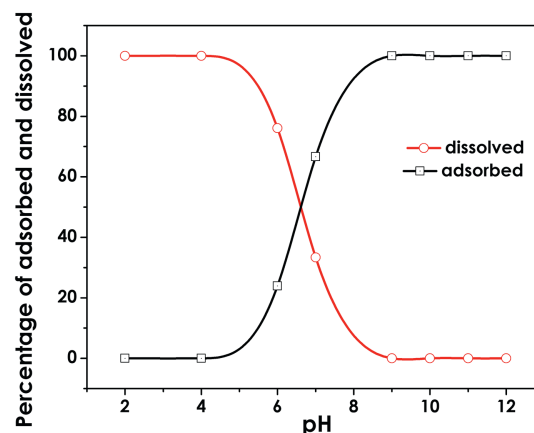


Fig. 5. Distribution of ions between adsorbed and dissolved phases in different pH.

Simulations were performed under the same condition and the range of each factor is illustrated in Fig. 6. The result showed that the range of factor C (99.99) is much larger than that of factor A (7.15) and factor B (7.16). The result is consistent with the conclusion we drew upon the orthogonal experiment: the initial pH is the most significant factor.

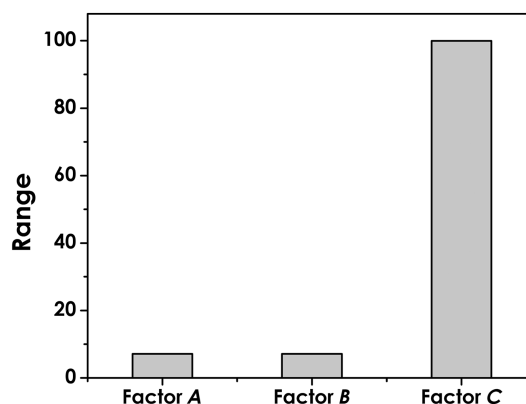


Fig. 6. Range of each factor calculated based on simulation.

Both the experiments and the simulations showed that pH has the most significant effect on the adsorption efficiency of the nZVI. In the range of 4–10, the higher the pH, the more cadmium is adsorbed. This

conclusion is important to maximize the adsorption rates and adsorption capacity of nZVI for cadmium.

As the E^0 of cadmium is -0.40 V, which is close to that of Fe^0 (-0.44 V), Cd will be removed by sorption and/or precipitation. The dominant adsorption mechanism and the existing form of cadmium in aqueous solutions are both related to the solution pH. At lower pH, Cd^{2+} is found to be the dominant species (Fig. 7). Since the isoelectric point (IEP) of nZVI was around 8.1–8.2 [37]. At pH values below the IEP, the surface is expected to possess a positive potential, this will decrease the adsorption of metal anions due to electrostatic repulsion. At higher pH, the abundant hydroxyl will result in the immobilization of metals in the form of hydroxides and precipitation is the dominant removal mechanism. Fig. 7 is the species distribution of cadmium over a pH range of 1 to 14. It can be seen that at pH 10, Cd^{2+} exists dominant as $\text{Cd}(\text{OH})_2$, and the percentage of $\text{Cd}(\text{OH})_2$ is about 85%, this means that the Cd^{2+} will be removed from water by precipitation without nZVI. But in the presence of nZVI, the removal rate of Cd^{2+} at pH 12 is 97.1–99.2 in our experiment, which means that nZVI can promote the removal of cadmium. In acidic conditions, the lower the pH, the stronger the repulsion. In alkaline conditions, the higher the pH, the easier the precipitation is to form.

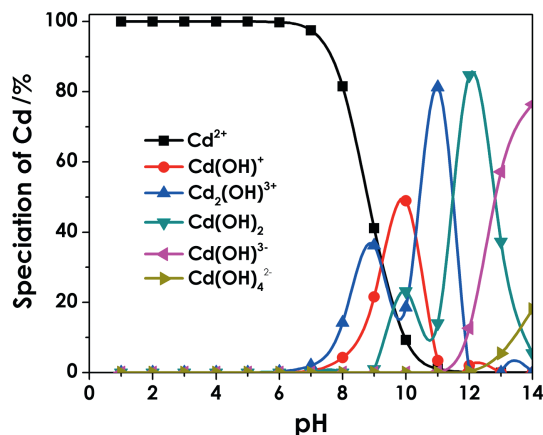


Fig. 7. The speciation of cadmium over a pH range of 1 to 14.

4. Conclusions

In this study, traditional liquid-phase reduction for preparing nZVI was improved by the introduction of PVP. TEM and BET analyses indicated that the improve method was better for nZVI preparation. An $L_9(3^3)$ orthogonal experiment was employed to find out the dominant factor that affects the removal rate of cadmium by nZVI. Three factors were examined: initial pH of the solution, concentration of cadmium and the dosage of nZVI, and initial pH was found to be the most significant factor. Surface precipitation modeling showed in different conditions, the Ca^{2+} was removed by nZVI in different mechanisms.

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