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## Removal of EDTA-chelated Cd<sup>II</sup> by sulfidated nanoscale zero-valent iron: Removal mechanisms and influencing factors

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#### ARTICLE INFO

ABSTRACT

Keywords: Sulfidated nanoscale zero-valent iron Cd<sup>II</sup>-EDTA Removal capacity Coupled effect Replacement In this study, the removal mechanisms of sulfidated nanoscale zero-valent iron (S-nZVI) toward EDTA-chelated Cd<sup>II</sup> (Cd<sup>II</sup>-EDTA) and the detailed effects of some critical factors on Cd<sup>II</sup>-EDTA removal by S-nZVI were systematically investigated. The results showed that the removal capacity of S-nZVI toward Cd<sup>II</sup>-EDTA within 90 min of reaction was 746.6 mg/g (when the initial concentration of Cd<sup>II</sup>-EDTA, the dosage of S-nZVI, and the initial solution pH were 300.0 mg Cd<sup>II</sup>/L, 0.3 g/L, and 2.6, respectively), which was 6.2 and 2.5 times higher than that of nZVI and Na<sub>2</sub>S, respectively, indicating that Fe and S had coupled effect on Cd<sup>II</sup>-EDTA removal. The removal mechanisms of Cd<sup>II</sup>-EDTA by S-nZVI consisted of two-step replacement reactions. In brief, Fe<sup>III</sup> generated from the corrosion of S-nZVI firstly replaced the Cd<sup>II</sup> in Cd<sup>II</sup>-EDTA, and then the decomplexed Cd<sup>II</sup> ions were immobilized by occurring the second-step replacement reaction with FeS in S-nZVI and forming CdS phase. Batch experiment results indicated that the removal of Cd<sup>II</sup>-EDTA by S-nZVI dosage (0.3 g/L) and initial Cd<sup>II</sup>-EDTA, concentration (300.0 mg Cd<sup>II</sup>/L), the acidic initial pH (pH<sub>0</sub> = 2.6) was favorable for the removal of Cd<sup>II</sup>-EDTA. This study demonstrated that S-nZVI could be a viable choice for the Cd<sup>II</sup>-EDTA-contaminated wastewater treatment.

## 1. Introduction

Ethylenediaminetetraacetic acid (EDTA) has been extensively applied in various industrial processes (e.g., electroplating, printing, metallurgy, etc.) due to its powerful chelating ability [1,2]. A large number of heavy metal ions such as  $Cu^{II}$ ,  $Ni^{II}$ ,  $Cd^{II}$ , and  $Pb^{II}$  always coexist with EDTA in the generated industrial effluent and can easily chelate with it to form strong heavy metal-EDTA complexes [1]. Because the solubility and stability of such type of heavy metals are higher than that of free heavy metal ions, some traditional techniques such as chemical precipitation, adsorption, and ion exchange widely used to remove free heavy metal ions are difficult to effectively treat heavy metal-EDTA complexes [3–5].

Until now, as for the treatment of industrial wastewaters containing heavy metal-EDTA complexes, the most commonly used effective technique is advanced oxidation technologies (AOTs), such as ultraviolet (UV)/H<sub>2</sub>O<sub>2</sub>, Fenton, photocatalytic, photoelectrochemical oxidation, and non-thermal plasma [2,3,6–12]. These decomplexation methods

aim to destroy EDTA ligand by some strong oxidants and release the central heavy metal ions from complexes [9,12]. Nevertheless, there are still some limitations related to these methods. For example, UV/H<sub>2</sub>O<sub>2</sub>, photoelectrochemical oxidation, and non-thermal plasma treatment process need extra energy consumption [2,5,11,12]. The treatment of Fenton toward contaminants is non-selective [3]. Moreover, traditional technique (such as precipitation) needs to be added to remove free metal ions after most of the above AOTs treatment [3,6,10], thus increasing the infrastructure expenditure and operating cost in practical utilization. In view of these limitations, it is necessary to explore some new cost-effective, time-saving, and simple techniques for the treatment of wastewater containing heavy metal-EDTA.

Nanoscale zero-valent iron (nZVI) has been extensively utilized to remove a variety of contaminants such as heavy metals, organic and inorganic compounds due to its high reactivity, large specific surface area, and environmentally friendly [13–15]. Previous study also showed that  $Cu^{II}$ -EDTA could be removed by nZVI. The removal mechanisms of nZVI toward  $Cu^{II}$ -EDTA included replacement, adsorption/precipitation

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or reduction [4]. During the removal of  $Cu^{II}$ -EDTA by nZVI, only one treatment unit was required, which could significantly save the treatment cost. However, nZVI was easily oxidized by some electron-acceptors such as water, oxygen, and protons, resulting in low electron efficiency of nZVI toward target pollutants [16]. Furthermore, as for other heavy metal-EDTA complex removal such as Cd<sup>II</sup>-EDTA, the complexation constant of Fe<sup>III</sup>-EDTA (log K = 25.2) is greatly larger than that of Cd<sup>II</sup>-EDTA (log K = 16.5) [1,17], consequently, Cd<sup>II</sup> in Cd<sup>II</sup>-EDTA can be replaced by Fe<sup>III</sup> generated from the oxidation of Fe<sup>0</sup>. Nevertheless, the standard potential of Cd<sup>II</sup> is close to that of Fe<sup>0</sup>, leading to free Cd<sup>II</sup> can be removed only via the adsorption of iron oxides layer [18]. With the temporal and spatial evolution, the adsorbed Cd<sup>II</sup> could release into aquatic environment again [19], causing potential secondary pollution.

Recent studies have found that the removal performance of nZVI toward both heavy metals (especially  $Cd^{II}$ ) and organic compounds has been greatly improved after sulfidation treatment [20–29]. The enhanced performance was ascribed to the formation of FeS<sub>x</sub> in sulfidated nanoscale zero-valent iron (S-nZVI), which has high hydrophobicity and conductivity, thus greatly inhibiting the side-reactions occurrence and improving the electron utilization efficiency [28,29]. As shown in previous study, both free Cd<sup>II</sup> ions and Cd<sup>II</sup>-EDTA could be effectively removed by S-nZVI [26], however, to our knowledge, the removal mechanisms of S-nZVI toward Cd<sup>II</sup>-EDTA and the detailed effects of some crucial factors (such as initial concentration of Cd<sup>II</sup>-EDTA, S-nZVI dosage, and initial pH (pH<sub>0</sub>) of solution) on Cd<sup>II</sup>-EDTA removal by S-nZVI are still unknown, which need further investigation.

Therefore, in this study, S-nZVI was used for the removal of  $Cd^{II}$ -EDTA. The specific objectives of this study were to (1) compare the performance of S-nZVI, nZVI, and Na<sub>2</sub>S toward  $Cd^{II}$ -EDTA removal; (2) elucidate the removal mechanism of S-nZVI toward  $Cd^{II}$ -EDTA; (3) explore the detailed effect of initial  $Cd^{II}$ -EDTA concentration, S-nZVI dosage, and pH<sub>0</sub> of solution on the removal of  $Cd^{II}$ -EDTA by S-nZVI. This study increases a viable choice for the  $Cd^{II}$ -EDTA-contaminated industrial wastewater treatment.

## 2. Material and methods

## 2.1. Chemical reagents

Iron trichloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O, >99.0%), sodium borohydride (NaBH<sub>4</sub>, >99%), ethylenediamine tetraacetic acid disodium salt dihvdrate (C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>8</sub>·2H<sub>2</sub>O, >99.0%), ammonium ferrous sulfate hexahydrate ((NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O,  $\geq$ 99.5%), 1,10-phenanthroline monohydrate ( $C_{12}H_8N_2 \cdot H_2O$ ,  $\geq 99.0\%$ ), ammonium acetate ( $C_2H_7NO_2$ ,  $\geq$ 98.0%), hydrochloric acid (HCl, 36.0–38.0%), nitric acid (HNO<sub>3</sub>, 65.0-68.0%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 95.0-98.0%), sodium hydroxide (NaOH,  $\geq$ 96.0%), ethanol (C<sub>2</sub>H<sub>6</sub>O,  $\geq$ 99.7%), and sodium dihydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>, ≥99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Sodium sulfide nonahydrate (Na<sub>2</sub>S·9H<sub>2</sub>O,  $\geq$ 98.0%) and cadmium chloride anhydrous (CdCl<sub>2</sub>,  $\geq$ 99.0%) were obtained from Aladdin Reagent Co., Ltd (Shanghai, China). Acetic acid glacial (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>, ≥99.5%) and cupric sulfate anhydrous (CuSO<sub>4</sub>,  $\geq$ 99.0%) were supplied by Macklin Biochemical Co., Ltd (Shanghai, China). All of the above chemical reagents were used directly as received without further purification. All solutions were prepared using deionized (DI) water from a Milli-Q system.  $Cd^{II}$ -EDTA stock solution (1.0 g  $Cd^{II}/L$ ) with a 1:1 molar ratio of  $Cd^{II}$ to EDTA was prepared by dissolving 1.6310 g CdCl<sub>2</sub> and 3.3118 g Na2EDTA2H2O in 500 mL DI water and boiling with a water bath at 90 °C for 1 h to gurantee the full complexation between Cd<sup>II</sup> and EDTA. After cooling to ambient temperature, the above solution was fixed to 1

## 2.2. Fabrication of S-nZVI and nZVI

S-nZVI (at a S/Fe molar ratio of 0.75) was fabricated according to a method reported by Liang et al. [26] with slight revision. In a word, the mixture (1.0 L) of NaBH<sub>4</sub> (0.25 M) and Na<sub>2</sub>S·9H<sub>2</sub>O (0.034 M) was dropwise added into 1.0 L FeCl<sub>3</sub> (0.045 M) solution by peristaltic pump and stirred with a mechanic stirrer at 600 rpm. The system was continually stirred for 15 min to ensure that the reactions were conducted fully. The resultant nanoparticles were collected in centrifuge tubes by centrifugation, and then washed three times by DI water followed with ethanol. The collected nanoparticles were filled with N<sub>2</sub>, sealed and stored in a refrigerator at 4 °C for subsequnet use. The moisture of the freshly prepared S-nZVI was measured by moisture analyzer (DSH-50A-1, YoKe, China). nZVI was fabricated in the absence of Na<sub>2</sub>S, however, the collection and storage of nZVI were identical to that of S-nZVI. The whole fabrication processes of S-nZVI and nZVI were conducted open to the air without N2 protection. Meanwhile, the DI water used to prepare the above reaction solutions also didn't need to purge N<sub>2</sub>.

## 2.3. Batch experiments

Cd<sup>II</sup>-EDTA removal experiments were performed in 100 mL glass bottle containing 100 mL 300.0 mg Cd<sup>II</sup>/L Cd<sup>II</sup>-EDTA solution with polyethylene screw cap. The reaction was initiated by adding 0.03 g SnZVI, nZVI, or Na<sub>2</sub>S into Cd<sup>II</sup>-EDTA solution. All of the reaction bottles were wrapped with aluminum foil to avoid the photodegradation of Cd<sup>II</sup>-EDTA and shaken on a shaker at a speed of 200 rpm and ambient temperature (25 °C). At pre-designed time intervals, 1.0 mL reaction suspension was withdrawn from reaction bottles and immediately filtered through a 0.22 µm syringe filter and acidified with concentrated HNO<sub>3</sub> for subsequent chemical analysis. Another batch experiments related to the effect of initial Cd<sup>II</sup>-EDTA concentration (50.0, 200.0, 300.0, 400.0 mg Cd<sup>II</sup>/L), S-nZVI dosage (0.1, 0.2, 0.3, 0.4 g/L), and solution pH<sub>0</sub> (2.6, 4.0, 6.0, 8.0) on the removal of Cd<sup>II</sup>-EDTA by S-nZVI were conducted. The desired pH<sub>0</sub> of reaction solution was adjusted by 1 M HCl or NaOH solution. Other experimental conditions and sampling methods were identical to the above description. All batch experiments were conducted in duplicate, and the results were averaged. The error bar of each data represents the standard deviation. At the end of reactions, the solids were collected for the following spectroscopic characterization and analysis of the adsorbed Cd<sup>II</sup>-EDTA by iron oxides during the reaction of Cd<sup>II</sup>-EDTA with S-nZVI according to the method developed by Nowack et al. [30]. In brief, 0.1 g reacted S-nZVI particles were treated by 20 mL 0.002 M phosphate solution in an ultrasonic bath for 10 min to desorb Cd<sup>II</sup>-EDTA at the surface of S-nZVI. After that, the suspension was filtered through a 0.22 µm syringe filter and acidified with concentrated HNO3 for the detection of total Cd. This part of Cd could be regarded as the adsorbed fraction by iron oxides.

#### 2.4. Chemical analysis and solid phase characterization

The concentrations of total Cd and Fe were measured by inductively coupled plasma optical emission spectrometer (ICP-OES-5110, Agilent, USA). Ferrous ion (Fe<sup>II</sup>) was analyzed with the phenanthroline spectrophotometric method using an UV–vis spectrophotometer (UV-1800, Shimadzu, Japan) at 510 nm. The concentration of dissolved Fe<sup>III</sup> in solution was the difference between total Fe and Fe<sup>II</sup>. The UV–vis spectrophotometer was also used to record the variation of Cd<sup>II</sup>-EDTA and Fe<sup>III</sup>-EDTA in solution at different reaction time. pH variation during reaction processes was monitored using a pH meter (SevenCompact-S210, Mettler Toledo, Switzerland). Total organic carbon (TOC) was detected by TOC analyzer (TOC-VCPN, Shimadzu, Japan).

The morphology and elements distribution of S-nZVI were obtained by transmission electron microscopy (TEM, FEI-TF20, Netherlands). Raman (Horiba Evolution, Japan) and Fourier transformed infrared (FTIR, Bruker-Tensor 37, Germany) were used to obtain the information of nanoparticles component. The Laser wavelength of Raman was 532 nm. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA) with an Al K $\alpha$  monochromatic source (1486.6 eV) was utilized to obtain the information of surface elements of S-nZVI. The XPS spectra data of each element were calibrated with the binding energy of C 1s (284.8 eV).

## 3. Results and discussion

## 3.1. Removal of Cd<sup>II</sup>-EDTA by nZVI, Na<sub>2</sub>S, and S-nZVI

The removal of  $Cd^{II}$ -EDTA by nZVI, Na<sub>2</sub>S, and S-nZVI was shown in Fig. 1. After 90 min of reaction, the removal of  $Cd^{II}$ -EDTA by nZVI and Na<sub>2</sub>S was ca. 12.1% and 29.6%, respectively. This result again verified the difficulty of the removal of  $Cd^{II}$ -EDTA by nZVI or traditional chemical precipitation alone. After sulfidation treatment, the removal performance of nZVI toward  $Cd^{II}$ -EDTA enhanced to 74.7% within 90 min, indicating that Fe and S had coupled effect on the removal of  $Cd^{II}$ -EDTA.

## 3.2. Removal mechanisms of Cd<sup>II</sup>-EDTA in S-nZVI system

## 3.2.1. Role of $Fe^{III}$ on $Cd^{II}$ decomplexation from $Cd^{II}$ -EDTA

As observed from Fig. S1, Cd<sup>II</sup>-EDTA has no absorption peak in UV–vis scanning spectra. According to the previous study, it was observed that Cu<sup>II</sup>-EDTA has an obvious peak in UV–vis scanning spectra. Moreover, the complexation constant of Cu<sup>II</sup>-EDTA (log K = 18.8) is larger than that of Cd<sup>II</sup>-EDTA (log K = 16.5) [1,17], thus resulting in Cu<sup>II</sup> can replace Cd<sup>II</sup> in Cd<sup>II</sup>-EDTA and form Cu<sup>II</sup>-EDTA. Therefore, after samples collection and filtration, a certain amount of Cu<sup>II</sup> was added into each sample and boiling for 1 h to ensure the full conversion of Cd<sup>II</sup>-EDTA into Cu<sup>II</sup>-EDTA (the added amount of Cu<sup>II</sup> in each sample was equal to the amount of Cd<sup>II</sup> in solution at 0 min). After the above treatment, the resulting samples at different reaction time were conducted UV–vis scanning test. The results were shown in Fig. 2. The variations of Cu<sup>II</sup>-EDTA and Fe<sup>III</sup>-EDTA in solution could be used to indirectly reflect the transformation between Cd<sup>II</sup>-EDTA and Fe<sup>III</sup>-EDTA.

The UV–vis scanning spectra (200–500 nm) of samples collected at different reaction time show that  $Cu^{II}$ -EDTA peak (at ca. 238 nm) disappeared and Fe<sup>III</sup>-EDTA peak (at ca. 256 nm) appeared after reacting with S-nZVI within 2 min [1], indicating that Fe<sup>III</sup> could realize the decomplexation of Cd<sup>II</sup> from Cd<sup>II</sup>-EDTA. Moreover, the intensity of Fe<sup>III</sup>-EDTA gradually increased during 2–10 min, and then began to weaken due to the adsorption or/and co-precipitation by S-nZVI corrosion products, in line with the results reported by Guan et al. [1] (Fig. 2). As



Fig. 1. Removal of  $Cd^{II}$ -EDTA by nZVI, Na<sub>2</sub>S, and S-nZVI. Experimental conditions:  $[Cd^{II}$ -EDTA]<sub>0</sub> = 300.0 mg  $Cd^{II}$ /L, solid dosage was 0.3 g/L, pH<sub>0</sub> = 2.6.



**Fig. 2.** UV–vis scanning spectra (200–500 nm) of samples (after adding  $Cu^{II}$  treatment) collected at different reaction time. Experimental conditions:  $[Cd^{II}-EDTA]_0 = 300.0 \text{ mg } Cd^{II}/L$ , [S-nZVI] = 0.3 g/L,  $pH_0 = 2.6$ .

shown in Fig. S2, the addition of 1 g/L 1,10-phenanthroline could significantly decrease the removal of  $Cd^{II}$ -EDTA from 74.7% to 12.6% within 90 min compared to that of the absence of 1,10-phenanthroline, suggesting that the oxidation of Fe<sup>II</sup> to Fe<sup>III</sup> is very crucial for the effective removal of  $Cd^{II}$ -EDTA by S-nZVI.

# 3.2.2. Role of S on $Cd^{II}$ immobilization after decomplexation from $Cd^{II}$ -EDTA

After reacting with Cd<sup>II</sup>-EDTA, the EDS elemental mapping of TEM shows that the distributions of Fe and S matched with O and Cd (Fig. 3c-f), respectively, indicating the oxidation of Fe and the formation of CdS on the surface of iron (hydr)oxides during reaction process. Fig. S3 depicted the Raman spectra of S-nZVI before and after reactions. No Raman bands corresponding to FeS (at 203 and 279 cm<sup>-1</sup>) were detected after reacting with Cd<sup>II</sup>-EDTA [31]. Instead, a significant characteristic peak corresponding to CdS was observed at ca. 305 cm<sup>-1</sup> [32], suggesting that Fe in FeS was replaced by Cd, thus resulting in the evolution of S species from FeS to CdS. In addition, Raman results verified the iron (hydr)oxides in S-nZVI after reacting with Cd<sup>II</sup>-EDTA were  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (at 656 and 1320 cm<sup>-1</sup>) and  $\gamma$ -FeOOH (at 243, 374, and 525 cm<sup>-1</sup>) [33,34]. A new characteristic peak corresponding to S<sup>0</sup> appeared at 480  $\text{cm}^{-1}$  [31], indicating that part of FeS also underwent oxidation when S-nZVI was reacting with Cd<sup>II</sup>-EDTA. XPS analysis was also conducted to obtain the evolution information of surface elements of S-nZVI before and after reactions, as shown in Fig. S4. The XPS spectra of Fe  $2p_{3/2}$  showed that the characteristic peaks corresponding to Fe<sup>0</sup> (706.1 eV), Fe<sup>II</sup>–S (707.3 eV), and Fe<sup>III</sup>–S (708.5 eV) detected in freshly prepared S-nZVI vanished after reacting with Cd<sup>II</sup>-EDTA (Fig. S4a) [22,35]. The disappearance of Fe<sup>0</sup> was attributed to the oxidation of SnZVI during reaction process. Furthermore, these results also suggested that Fe<sup>II</sup>–S and Fe<sup>III</sup>–S on the surface of S-nZVI might participate in the reaction of Cd<sup>II</sup>-EDTA with S-nZVI. Combining with the spectra of S 2p and Cd  $3d_{5/2}$  (Fig. S4b and c), it was further confirmed that Fe in Fe<sup>II</sup>-S and Fe<sup>III</sup>–S could be replaced by Cd<sup>II</sup> and forming Cd<sup>II</sup>–S, consistent with the results of TEM and Raman. According to the results of TEM, Raman, and XPS, it was found that S is an important reactive site for the immobilization of Cd<sup>II</sup> after decomplexation from Cd<sup>II</sup>-EDTA.

## 3.2.3. TOC removal

As shown in Fig. S5, ca. 30% TOC was removed within 90 min during the reaction of Cd<sup>II</sup>-EDTA with S-nZVI. The results of FTIR show that some characteristic peaks corresponding to the vibrations of  $v_{as}CO_2^-$ (1589 cm<sup>-1</sup>),  $v_{sym}CO_2^-$  (1403 cm<sup>-1</sup>),  $-COO^-$  (1321 cm<sup>-1</sup>), vC-C(CH<sub>2</sub>COO<sup>-</sup>) (925 cm<sup>-1</sup>), and Fe—O (476 cm<sup>-1</sup>) were detected in S-nZVI after reacting with Cd<sup>II</sup>-EDTA (Fig. 4) [36–39]. In addition to Fe—O



Fig. 3. HAADF and TEM-EDS mapping images of S-nZVI after reacting with Cd<sup>II</sup>-EDTA (a) HAADF, (b) Fe + O + S + Cd overlay, (c) Fe K $\alpha$ , (d) O K $\alpha$ , (e) S K $\alpha$ , and (f) Cd K $\alpha$ . Experimental conditions: [Cd<sup>II</sup>-EDTA]<sub>0</sub> = 300.0 mg Cd<sup>II</sup>/L, [S-nZVI] = 0.3 g/L, pH<sub>0</sub> = 2.6.



Fig. 4. FTIR spectra of S-nZVI before and after reacting with Cd<sup>II</sup>-EDTA. Experimental conditions:  $[Cd^{II}-EDTA]_0 = 300.0 \text{ mg Cd}^{II}/L$ , [S-nZVI] = 0.3 g/L,  $pH_0 = 2.6$ .

band, other bands were all originated from EDTA. Combining with the results of FTIR, it was confirmed that the decrease of TOC in reaction solution was ascribed to the adsorption or/and co-precipitation of EDTA by S-nZVI oxidation products (iron (hydr)oxides). This result is in agreement with the elimination of TOC during the removal process of  $Cu^{II}$ -EDTA by Fe<sup>0</sup> coupled with a weak magnetic field [1].

According to the above discussion, it was summarized that the removal mechanisms of S-nZVI toward  $Cd^{II}$ -EDTA included two-step replacement reactions. First, Fe<sup>III</sup> generated from the corrosion of S-

nZVI replaced the chelated  $Cd^{II}$  in  $Cd^{II}$ -EDTA, making  $Cd^{II}$  released from  $Cd^{II}$ -EDTA and existed as the form of free ions (Eq. (1)). Subsequently, the decomplexed  $Cd^{II}$  ions were removed by taking place the replacement reaction with FeS in S-nZVI, forming CdS (Eq. (2)). Meanwhile, the whole process of  $Cd^{II}$ -EDTA removal by S-nZVI also accompanied with TOC elimination. The removal mechanisms of  $Cd^{II}$ -EDTA removal by S-nZVI are different from that of free  $Cd^{II}$  ions removal, where the major reaction mechanism is only one-step replacement between FeS and  $Cd^{II}$  [26].

$$Fe^{III} + Cd^{II}$$
-EDTA  $\rightarrow Cd^{II} + Fe^{III}$ -EDTA (1)

$$Cd^{II} + FeS \rightarrow Fe^{II} + CdS$$
 (2)

3.3. Effect of factors (initial  $Cd^{II}$ -EDTA concentration, S-nZVI dosage, and solution  $pH_0$ ) on  $Cd^{II}$ -EDTA removal by S-nZVI

## 3.3.1. Effect of initial Cd<sup>II</sup>-EDTA concentration

The effect of initial  $Cd^{II}$ -EDTA concentration on the removal of  $Cd^{II}$ -EDTA by S-nZVI was depicted in Fig. 5a. The removal of  $Cd^{II}$ -EDTA by S-nZVI could reach up to ca. 97.7%, 89.8%, 74.7%, and 44.2% within 90 min for 50.0, 200.0, 300.0, and 400.0 mg  $Cd^{II}$ /L  $Cd^{II}$ -EDTA, respectively. Moreover, after 90 min of reaction, the phosphate desorption experiment shows that the removal of S-nZVI toward  $Cd^{II}$ -EDTA was mainly dependent on the replacement between FeS and  $Cd^{II}$  rather than adsorption by iron (hydr)oxides (Fig. 5c), indicating that replacement was the major removal mechanism of  $Cd^{II}$ -EDTA by S-nZVI, in agreement with the characterization results in Section 3.2. Meanwhile, the results of the phosphate desorption experiment (Fig. 5c) also confirmed that the adsorbed EDTA to S-nZVI (the results in Section 3.2.3) primarily



**Fig. 5.** Effect of initial Cd<sup>II</sup>-EDTA concentration on (a) Cd<sup>II</sup>-EDTA removal, and (b) the pseudo-second-order rate constant  $k_2$  and the removal capacity of Cd<sup>II</sup>-EDTA by S-nZVI within 90 min. (c) The amount of removed Cd<sup>II</sup>-EDTA by adsorption and replacement within 90 min at different initial Cd<sup>II</sup>-EDTA concentration. Experimental conditions: [S-nZVI] = 0.3 g/L, pH<sub>0</sub> = 2.6.

originated from Fe<sup>III</sup>-EDTA rather than Cd<sup>II</sup>-EDTA. Compared to the removal of Cd<sup>II</sup>-EDTA by TiO<sub>2</sub> (Cd<sup>II</sup> in Cd<sup>II</sup>-EDTA was mainly removed by adsorbing onto the TiO<sub>2</sub> after decomplexation) [40], the removal stability of Cd<sup>II</sup> in Cd<sup>II</sup>-EDTA by S-nZVI was significantly enhanced. These results also demonstrated that S-nZVI is an excellent candidate for the treatment of Cd<sup>II</sup>-EDTA-polluted wastewater.

Fig. S6 shows that the removal of Cd<sup>II</sup>-EDTA at different initial Cd<sup>II</sup>-EDTA concentrations could be fitted well with a pseudo-second-order model (Eq. (S1)). With the increase of initial Cd<sup>II</sup>-EDTA concentration from 50.0 to 300.0 mg Cd<sup>II</sup>/L, the corresponding pseudo-second-order rate constant  $k_2$  significantly decreased from 7.09 × 10<sup>-3</sup> to 0.73 × 10<sup>-3</sup> g/(mg·min), and  $k_2$  kept almost stable when initial Cd<sup>II</sup>-EDTA concentration further increased from 300.0 to 400.0 mg Cd<sup>II</sup>/L (Fig. 5b). The decreasing effect of an increased initial Cd<sup>II</sup>-EDTA concentration on Cd<sup>II</sup>-EDTA removal rate was ascribed to the formation of more CdS during the reaction of Cd<sup>II</sup>-EDTA with S-nZVI. As shown in Fig. S7, the characteristic peak of CdS became sharpened as initial Cd<sup>II</sup>-EDTA concentration increased from 50.0 to 300.0 mg Cd<sup>II</sup>/L, which could accelerate the passivation of S-nZVI and inhibit the contact between Cd<sup>II</sup>-EDTA and the reactive sites on S-nZVI [26]. Thus, resulting in the decrease of  $k_2$ . However, the trend of Cd<sup>II</sup>-EDTA removal capacity variation was opposed to that of  $k_2$ . The removal capacity increased with increasing the initial Cd<sup>II</sup>-EDTA concentration. As the initial Cd<sup>II</sup>-EDTA concentration increased to 300.0 mg Cd<sup>II</sup>/L, the removal capacity of SnZVI toward  $Cd^{II}$ -EDTA was 746.6 mg/g, reaching up to the maximum within the concentration investigated (Fig. 5b). Because the removal of Cd<sup>II</sup>-EDTA by S-nZVI is a surface-mediated process [26], the reactive sites are limited. An increased initial Cd<sup>II</sup>-EDTA concentration would promote the reactive sites to be progressively occupied and reaching up to saturation.

Before the reactive sites fully occupied by  $Cd^{II}$ -EDTA ([ $Cd^{II}$ -EDTA]\_0  $\leq$  300.0 mg  $Cd^{II}$ /L), Fig. 6a shows that the removal capacity of  $Cd^{II}$ -EDTA within 90 min by S-nZVI had a significantly positive relationship with the initial  $Cd^{II}$ -EDTA concentration (p < 0.05). Meanwhile, there was also a significantly negative linear correlation between the removal capacity of  $Cd^{II}$ -EDTA and  $k_2$  (p < 0.05) (Fig. 6b). Therefore, it is possible to predict the removal capacity and  $k_2$  of S-nZVI toward other arbitrary initial  $Cd^{II}$ -EDTA (<300.0 mg  $Cd^{II}$ /L) concentration removal



**Fig. 6.** Relationships between the removal capacity of Cd<sup>II</sup>-EDTA by S-nZVI within 90 min and (a) the initial Cd<sup>II</sup>-EDTA concentration, and (b) the pseudo-second-order rate constant  $k_2$ . Experimental conditions: [S-nZVI] = 0.3 g/L, pH<sub>0</sub> = 2.6.

that was not included in the experimental data, once the initial  $Cd^{II}$ -EDTA concentration was known.

## 3.3.2. Effect of S-nZVI dosage

Fig. 7a shows the effect of S-nZVI dosage on the removal of Cd<sup>II</sup>-EDTA by S-nZVI. The removal of Cd<sup>II</sup>-EDTA at different S-nZVI dosage could be divided into two stages, namely a fast stage and a slow stage. The fast stage of Cd<sup>II</sup>-EDTA removal at low (0.1 and 0.2 g/L) and high (0.3 and 0.4 g/L) S-nZVI dosage was achieved in 2 and 30 min, respectively. At fast stage, only 23.6% Cd<sup>II</sup>-EDTA was removed by 0.1 g/ L S-nZVI, with increasing the S-nZVI dosage to 0.2, 0.3, and 0.4 g/L, the removal of Cd<sup>II</sup>-EDTA increased by 7.6%, 49.2%, and 62.0%, respectively. A slight amount of Cd<sup>II</sup>-EDTA was removed at slow stage, indicating that the reactions reached up to equilibrium. The whole process of Cd<sup>II</sup>-EDTA removal at different S-nZVI dosage also followed pseudosecond-order model (Fig. S9). The removal rate constant  $k_2$  decreased from  $3.53 \times 10^{-3}$  to  $0.76 \times 10^{-3}$  g/(mg·min), as the S-nZVI dosage increased from 0.1 to 0.2 g/L. Further increasing the S-nZVI dosage to 0.4 g/L,  $k_2$  increased to  $1.79 \times 10^{-3}$  g/(mg·min) because sufficient reactive sites were supplied for  $Cd^{II}$ -EDTA removal. The highest  $k_2$  was obtained when S-nZVI dosage was 0.1 g/L (Fig. 7b). This result was attributed to the pH change during reaction process. As observed from Fig. S10, the addition of S-nZVI particles into Cd<sup>II</sup>-EDTA solution could enhance the solution pH. However, the increase degree of solution pH was slight in the 0.1 g/L S-nZVI reaction system (from 2.6 to 2.9) compared to that of other S-nZVI dosage systems. As depicted in Fig. S11, compared with other S-nZVI dosage, there were no obvious



**Fig. 7.** Effect of S-nZVI dosage on (a) Cd<sup>II</sup>-EDTA removal and (b) the pseudosecond-order rate constant  $k_2$ . Experimental conditions:  $[Cd^{II}-EDTA]_0 = 300.0 \text{ mg Cd}^{II}/L$ ,  $pH_0 = 2.6$ .

characteristic peaks corresponding to Fe—O vibration detected in 0.1 g/L S-nZVI after reacting with Cd<sup>II</sup>-EDTA. Moreover, the amount of dissolved Fe<sup>III</sup> released in the solution by per gram of S-nZVI during the removal of Cd<sup>II</sup>-EDTA with 0.1 g/L S-nZVI was higher than that with other S-nZVI dosage (Fig. S12). Lower solution pH would accelerate the dissolution of the passive oxide layer at the surface of S-nZVI and increase the release amount of dissolved Fe<sup>III</sup>, which are beneficial to the mass transfer and the occurrence of the first-step replacement reaction (Eq. (1)) [16,41], thus resulting in higher  $k_2$ .

## 3.3.3. Effect of solution $pH_0$

The solution pH is an important factor, which has great influence on the surface charge of materials and relative distribution of heavy metal-EDTA complexes species [1,39,42,43]. Therefore, the effect of pH<sub>0</sub> on the performance of Cd<sup>II</sup>-EDTA removal by S-nZVI was conducted at different pH<sub>0</sub> levels (i.e., 2.6, 4.0, 6.0, and 8.0). As illustrated in Fig. 8a, 74.7% Cd<sup>II</sup>-EDTA was removed after 90 min of reaction at pH<sub>0</sub> 2.6. With increasing the  $pH_0$  to 6.0, the removal of Cd<sup>II</sup>-EDTA decreased by 43.4%, and the removal of Cd<sup>II</sup>-EDTA changed negligibly as the pH<sub>0</sub> further increasing from 6.0 to 8.0. The influence of  $pH_0$  on Cd<sup>II</sup>-EDTA removal by S-nZVI is greatly different from that of free Cd<sup>II</sup> ions removal due to different removal pathways [26]. Based on the visual MINTEQ 3.0 analysis, it was known that the predominant Cd<sup>II</sup>-EDTA species were CdHEDTA<sup>-</sup> and/or CdEDTA<sup>2-</sup> over the pH range from 2.5 to 14.0, when the initial Cd<sup>II</sup>-EDTA concentration was 300.0 mg Cd<sup>II</sup>/L (Fig. S13). As shown in previous study, the isoelectric point (IEP) of S-nZVI was 6.01 (at S/Fe molar ratio of 0.75) [26], resulting in S-nZVI positively charged when pH was below IEP, which might be one of the possible reasons for the high removal of Cd<sup>II</sup>-EDTA by S-nZVI under acidic  $pH_0$  ( $pH_0 = 2.6$ ). However, the Raman spectra of S-nZVI (Fig. S14) and the results of phosphate desorption experiments (Fig. S15) after reacting with Cd<sup>II</sup>-EDTA at different pH<sub>0</sub> show that pH<sub>0</sub> had no impact on the removal mechanisms of S-nZVI toward Cd<sup>II</sup>-EDTA.

The variations of dissolved total Fe concentrations and pH with time in the process of Cd<sup>II</sup>-EDTA removal by S-nZVI at different pH<sub>0</sub> were also detected. As shown in Fig. 8b and c, both total Fe and pH appeared an increasing trend as the reaction time prolonging at all investigated pH<sub>0</sub>. The dissolution of anodic Fe<sup>0</sup> always accompanies with the consumption of cathodic H<sup>+</sup> [44], which rationalized the variations trend of total Fe and pH with time.

The release amount of dissolved Fe<sup>III</sup> was 117.0, 26.0, 12.1, and 10.7 mg/L within 90 min, respectively, when  $pH_0$  was 2.6, 4.0, 6.0, and 8.0 (Fig. S16), indicating that  $pH_0$  has great influence on Fe<sup>III</sup> release. Moreover, after 90 min of reaction, it was observed that there was a strong positive relationship between the release amount of dissolved Fe<sup>III</sup> and the removal capacity of S-nZVI toward Cd<sup>II</sup>-EDTA at different pH<sub>0</sub> (Fig. 8d), suggesting that the decomplexation of Cd<sup>II</sup> from Cd<sup>II</sup>-EDTA by Fe<sup>III</sup> is indispensable for the effective removal of Cd<sup>II</sup>-EDTA by S-nZVI.

Based on the above discussion, it was concluded that under the same S-nZVI dosage and initial  $Cd^{II}$ -EDTA concentration, lower solution  $pH_0$  is favorable for the adsorption of  $Cd^{II}$ -EDTA on the surface of S-nZVI through electrostatic interaction, and can promote the corrosion of S-nZVI, resulting in more dissolved Fe<sup>III</sup> released, which is beneficial to the occurrence of the first-step replacement (Eq. (1)), consequently, the removal capacity of S-nZVI toward Cd<sup>II</sup>-EDTA increased.

#### 4. Conclusion

This study unraveled that the removal of  $Cd^{II}$ -EDTA by S-nZVI was significantly enhanced compared with that of nZVI and Na<sub>2</sub>S under the same reaction conditions (when the initial concentration of  $Cd^{II}$ -EDTA, the dosage of S-nZVI, nZVI, or Na<sub>2</sub>S, and the solution pH<sub>0</sub> were 300.0 mg  $Cd^{II}$ /L, 0.3 g/L, and 2.6, respectively), indicating that Fe and S had coupled effect on the removal of  $Cd^{II}$ -EDTA. The UV–vis scanning spectra indicated that Fe<sup>III</sup> generated from the corrosion of S-nZVI could



**Fig. 8.** Effect of  $pH_0$  on (a)  $Cd^{II}$ -EDTA removal, (b) Fe dissolution, and (c) pH variation. (d) Relationship between the dissolved Fe<sup>III</sup> and the removal capacity of  $Cd^{II}$ -EDTA within 90 min in different S-nZVI systems at pH<sub>0</sub> 2.6–8.0. Experimental conditions:  $[Cd^{II}$ -EDTA]<sub>0</sub> = 300.0 mg  $Cd^{II}/L$ , [S-nZVI] = 0.3 g/L.

realize the decomplexation of Cd<sup>II</sup> from Cd<sup>II</sup>-EDTA. The characterization results of TEM, Raman, and XPS demonstrated that the decomplexed Cd<sup>II</sup> ions were immobilized by occurring the replacement reaction with FeS in S-nZVI and forming CdS with  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -FeOOH as the final corrosion products of S-nZVI. Meanwhile, the removal process of Cd<sup>II</sup>-EDTA by S-nZVI also accompanied with the elimination of TOC due to the adsorption or/and co-precipitation of EDTA by the above corrosion products. Batch experiment results showed that the initial Cd<sup>II</sup>-EDTA concentration, S-nZVI dosage, and pH<sub>0</sub> had significant influence on the removal of Cd<sup>II</sup>-EDTA by S-nZVI. In practical scenarios, some ions always co-exist with target pollutants, which have great influence on contaminants removal. Therefore, it is necessary to conduct further study in future to elucidate the superiority of S-nZVI toward Cd<sup>II</sup>-EDTA removal in the presence of different background ions.

#### CRediT authorship contribution statement

Li Liang: Conceptualization, Methodology, Investigation, Data curation, Visualization, Writing - original draft, Writing - review & editing. Weiying Li: Funding acquisition, Supervision. Yue Li: Writing - review & editing. Wei Zhou: Writing - review & editing. Jiping Chen: Writing - review & editing.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary material

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