



# Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles

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## ABSTRACT

Nano zerovalent iron (nZVI) is an effective adsorbent for removing various organic and inorganic contaminants. In this study, nZVI particles were used to investigate the removal of  $\text{Cd}^{2+}$  in the concentration range of 25–450  $\text{mg L}^{-1}$ . The effect of temperature on kinetics and equilibrium of cadmium sorption on nZVI particles was thoroughly examined. Consistent with an endothermic reaction, an increase in the temperature resulted in increasing cadmium adsorption rate. The adsorption kinetics well fitted using a pseudo second-order kinetic model. The calculated activation energy for adsorption was 54.8  $\text{kJ mol}^{-1}$ , indicating the adsorption process to be chemisorption. The intraparticle diffusion model described that the intraparticle diffusion was not the only rate-limiting step. The adsorption isotherm data could be well described by the Langmuir as well as Temkin equations. The maximum adsorption capacity of nZVI for  $\text{Cd}^{2+}$  was found to be 769.2  $\text{mg g}^{-1}$  at 297 K. Thermodynamic parameters (i.e., change in the free energy ( $\Delta G^\circ$ ), the enthalpy ( $\Delta H^\circ$ ), and the entropy ( $\Delta S^\circ$ )) were also evaluated. The overall adsorption process was endothermic and spontaneous in nature. EDX analysis indicated the presence of cadmium ions on the nZVI surface. These results suggest that nZVI could be employed as an efficient adsorbent for the removal of cadmium from contaminated water sources.

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## 1. Introduction

Cadmium is a toxic heavy metal of significant environmental and occupational concern [1]. It has been released to the environment through the combustion of fossil fuels, metal production, application of phosphate fertilizers, electroplating, and the manufacturing of batteries, pigments, and screens [2–4]. This heavy metal has resulted in serious contamination of both soil and water. Cadmium (Cd) has been classified as a human carcinogen and teratogen impacting lungs, kidneys, liver and reproductive organs [1,5]. The World Health Organization (WHO) has set a maximum guideline concentration of 0.003  $\text{mg L}^{-1}$  for Cd in drinking water [6]. Given pervasive cadmium contamination and the low drinking water guideline, there is considerable interest in the development of techniques to remove cadmium from contaminated water.

Adsorption has been developed as an efficient method for the removal of heavy metals from contaminated water and soil. A variety of adsorbents, including clays, zeolites, dried plant parts, agricultural waste biomass, biopolymers, metal oxides, microorganisms, sewage sludge, fly ash and activated carbon have been used for cadmium removal [2,7–20]. Nano zerovalent iron (nZVI), an emerging technology, is being used to successfully treat various

metallic ions in aqueous solutions (e.g.,  $\text{Cr}^{6+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{As}^{5+}$ , and  $\text{Co}^{2+}$ ) [21–25]. Nano iron particles are particularly attractive for remediation purposes due to their significant surface area to weight ratio leading to a greater density of reactive sites and heavy metal removal capacity [26,27]. Moreover, the magnetic properties of nano iron facilitate the rapid separation of nano iron from soil and water, via a magnetic field [28,29]. Heavy metals are either reduced at the nZVI surface (e.g.,  $\text{Cu}^{2+}$ ,  $\text{Ag}^{2+}$ ) or directly adsorbed to the nZVI surface where they are rendered immobile (e.g.,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ). The controlling mechanism is a function of the standard redox potential of the contaminant metal. The standard redox potential of  $\text{Cd}^{2+}$  (–0.40 V, 25 °C) is very close to that of zerovalent iron (–0.41 V, 25 °C), and thus, the removal of  $\text{Cd}^{2+}$  ions by nZVI is due to sorption [21].

Although previous research has investigated adsorption and redox processes as the removal mechanisms of metals by nano iron, comparatively little research has investigated the detailed adsorption characteristics and thermodynamics of metal removal by nano iron [21–25,27]. Çelebi et al. [23] indicated that the adsorption of  $\text{Ba}^{2+}$  on nZVI particles follows pseudo-second-order kinetics and the Dubinin–Radushkevich isotherm can be used to model the adsorption process. The Freundlich equation was used to model  $\text{Pb}^{2+}$  adsorption on amino-functionalized nZVI particles [29]. The adsorption of  $\text{As}^{3+}$  and  $\text{As}^{5+}$  on carbon supported nZVI showed two distinct linear sorption stages and were modelled using the Langmuir and Freundlich isotherms [27]. To our knowledge cadmium

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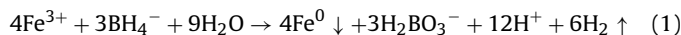
sorption onto nZVI particles has not been the subject of detailed study.

The objective of this research is to investigate the adsorption kinetics and isotherm models of cadmium removal by nano zerovalent iron at varying temperatures. Sorption kinetics is investigated to develop an understanding of controlling reaction pathways (e.g., chemisorption versus physisorption) and the mechanisms (e.g., surface versus intraparticle diffusion) of sorption reactions. Kinetic data can be used to predict the rate at which the target contaminant is removed from aqueous solutions and equilibrium adsorption isotherms are used to quantify the adsorptive capacity of an adsorbent (e.g., nZVI). Results from this study can be used to assess the utility of nZVI for heavy metal removal, in particular cadmium adsorption, at the field scale.

## 2. Materials and methods

### 2.1. Preparation of nZVI

nZVI particles were synthesized using the ‘bottom-up’ method of dropwise addition of 0.125 M NaBH<sub>4</sub> aqueous solution to 0.023 M FeCl<sub>3</sub> solution with continuous stirring. Ferric iron (Fe<sup>3+</sup>) was reduced to zerovalent iron (Fe<sup>0</sup>) by borohydride according to the following reaction:



Black nZVI particles appeared immediately after introducing the first few drops of NaBH<sub>4</sub> solution. After the addition of NaBH<sub>4</sub> solution, the mixture was stirred for an additional 20 min. nZVI particles were collected and washed thrice with iso-propanol to prevent oxidation. Deionized deoxygenated water (sparged with nitrogen) was used to prepare aqueous solutions. nZVI synthesis was conducted in an anaerobic chamber maintaining an O<sub>2</sub>-free environment by purging with O<sub>2</sub>-free Ar (95% Ar:5% H<sub>2</sub>).

### 2.2. Adsorption experiments

To study the temperature effect on the kinetics of Cd<sup>2+</sup> adsorption by nZVI, 0.5 g L<sup>-1</sup> nZVI was added to each glass vial containing 60 mL of 112.5 mg L<sup>-1</sup> Cd<sup>2+</sup> solution. The glass vials were capped with Teflon Mininert valves to minimize oxidation of nZVI particles during the equilibration period. Experiments were carried out at five temperatures (285, 297, 307, 313 and 333 K) by placing the glass vials on a temperature controlled shaker. Samples were collected at 0, 1, 3, 5, 8, 12, 24, 48, and 72 h for Cd<sup>2+</sup> analysis. Independent blank experiments (i.e., no nZVI) found that there was no Cd<sup>2+</sup> adsorption to the glass vials and valves.

Adsorption isotherms were obtained by varying the initial Cd<sup>2+</sup> concentration from 25 to 450 mg L<sup>-1</sup> in 60 mL vials with 0.5 g L<sup>-1</sup> nZVI at three temperatures (285, 297 and 307 K). The samples were collected at 0 and 72 h to quantify initial and final Cd<sup>2+</sup> concentrations. All experiments were performed in duplicate inside the anaerobic chamber.

Sample aliquots collected were filtered with 0.2 μm syringe filters. The filtrates were diluted with nitric acid and Cd<sup>2+</sup> concentrations determined by ICP-OES.

### 2.3. SEM/EDX and BET analyses

The surface morphology of nZVI was characterized by Scanning Electron Microscope (SEM, Hitachi S-2600N, 5.0 kV). The solid samples were sprinkled onto adhesive carbon tape supported on metallic disks. The elemental composition of nZVI before and after cadmium adsorption was determined by randomly selecting areas on the solid surfaces and analyzing by energy dispersive

X-ray (EDX) in conjunction with SEM. The specific surface area of nZVI particles was measured by Burnauer–Emmett–Teller (BET) N<sub>2</sub> method using a Micrometrics ASAP 2010 BET surface area analyzer.

## 3. Theory

### 3.1. Adsorption kinetics

Metal uptake  $q$  (mg metal ion per g nZVI) was determined by mass balance, as follows [8]:

$$q_t = (C_0 - C_t) \times \frac{V}{m} \quad (2)$$

where  $C_0$  and  $C_t$  are cadmium concentrations (mg L<sup>-1</sup>) at time 0 and  $t$ , respectively,  $V$  is the volume of the solution (mL), and  $m$  is the mass of nZVI (g).

Parameters from two kinetic models, pseudo first-order [30,31] and pseudo second-order [31,32], were fit to experimental data to examine the adsorption kinetics of cadmium uptake by nZVI.

#### 3.1.1. Pseudo first-order kinetics

The pseudo first-order equation (Lagergren's equation) describes adsorption in solid–liquid systems based on the sorption capacity of solids [30]. It is assumed that one cadmium ion is sorbed onto one sorption site on the nZVI surface:



where  $A$  represents an unoccupied sorption site on the nZVI and  $k_1$  is the pseudo first order rate constant (h<sup>-1</sup>).

The linear form of pseudo first order model can be expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

where  $q_e$  and  $q_t$  (mg g<sup>-1</sup>) are the adsorption capacities at equilibrium and at time  $t$  (h), respectively.

#### 3.1.2. Pseudo-second order kinetics

The pseudo second-order rate expression, which has been applied for analyzing chemisorption kinetics from liquid solutions [31,32], is linearly expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where  $k_2$  is the rate constant for pseudo second-order adsorption (g mg<sup>-1</sup> h<sup>-1</sup>) and  $k_2 q_e^2$  or  $h$  (mg g<sup>-1</sup> h<sup>-1</sup>) is the initial adsorption rate.

This model assumes that one cadmium ion is sorbed onto two sorption sites on the nZVI surface:



#### 3.1.3. Goodness of adsorption kinetic model fit

The best fit among the kinetic models is assessed by the linear coefficient of determination ( $r^2$ ) and non-linear Chi-square ( $\chi^2$ ).

The Chi-square test measures the difference between the experimental and model data. The mathematical form of this test statistic can be expressed as:

$$\chi^2 = \sum \frac{(q_{e,\text{exp}} - q_{e,\text{cal}})^2}{q_{e,\text{cal}}} \quad (7)$$

where  $q_{e,\text{exp}}$  is experimental equilibrium capacity data and  $q_{e,\text{cal}}$  is the equilibrium capacity from a model. If data from the model are similar to experimental data,  $\chi^2$  will be small and if they differ,  $\chi^2$  will be large.

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