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Kinetics of selenite reduction by zero-valent iron

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ABSTRACT

Zero-valent iron (ZVI) is an inexpensive agent that can remove many common environmental contaminants. The effects of dissolved oxygen (DO), pH, initial selenite concentration (Se(IV)), ZVI dosage and particle size as well as reaction temperature on Se(IV) removal by ZVI were systematically investigated in this study. Se(IV) removal by ZVI was more favored under oxic conditions with higher reaction rate than under anoxic conditions, ascribing to the promoted ZVI corrosion rate in the presence of DO. Moreover, Se(IV) removal by ZVI was enhanced with increasing ZVI dosage and reaction temperature but decreased with increasing pH and ZVI particle size. The removal rate of Se(IV) by ZVI experienced an increase and then a decrease with initial Se(IV) concentration ranging from 9.9 to 78.6 mg L^{-1}. To further describe the reaction rate, a pseudo-first-order kinetics was employed, and the calculated activation energy, by fitting the rate constants at different temperatures, was determined to be 32.86 kJ mol^{-1}. When fixing other conditions, good linear correlation could be observed between pseudo-first-order reaction rate constants (k_{obs}) and ZVI dosage. Compared with other methods for Se(IV) removal reported in literatures, reduction by ZVI was considered a promising technique, which could rapidly and effectively eliminate Se(IV) from waters.

Keywords: Selenite; Zero-valent iron; Kinetics; Activation energy; Reduction

1. Introduction

Selenium is an essential trace element yet it is of potential toxicity at elevated concentration [1]. The environmental concern regarding selenium has been attributed to its potential to cause either toxicity or deficiency in humans, animals, and some plants within a very narrow concentration range [2]. Selenium poisoning of water systems may occur during crude oil processing in refinery operations, discharging agricultural drainage waters from seleniferous farm lands to wetlands [3] and treating mining wastewater that contains elevated levels of selenium [4]. Drinking water limits for Se vary from 10 μg L^{-1}, as recommended by the World Health Organization and adopted by Australia, Japan, and Canada, to

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50 $\mu g\,L^{-1}$ as mandated by the US EPA. According to the Japanese Environmental Quality Standards for water pollution amended in 1993, the maximum concentration of selenium permissible in industrial wastewater is 0.1 $mg\,L^{-1}$ [5]. Se exists in water in four oxidation states (−II, 0, IV, and VI). The oxidized forms of Se, Se(VI), and Se(IV), are highly soluble, thus bioavailable and potentially toxic while its reduced forms, Se(0) and Se(−II), are insoluble and correspondingly much less bioavailable [6]. According to the US EPA report (FRL-5649-7), the acute toxicity of Se(IV) is almost 10 times greater than that of Se(VI) and both species exist simultaneously in aerobic surface water in comparable concentrations [1]. Therefore, there is an urgent need to develop efficient, feasible and environmentally friendly methods to remove Se(IV) and Se(VI), particularly Se(IV), from water. In view of the insolubility character of elemental Se (Se (0)) (3×10^{-9} $mol\,L^{-1}$) [7] combined its less toxicity, reduction of Se(IV) to Se(0) is considered a feasible technique for removing Se(IV) from wastewater.

Various technologies, including bacterial reduction, membrane filtration, catalytic reduction, ion exchange, chemical reduction, and reverse osmosis, had been employed for Se(IV) removal from water [8–11]. However, these treatment technologies are not cost-effective for practical application [12]. In recent years, the use of zero-valent iron (ZVI) for removing toxic chemicals from water has received immense attention [13,14]. ZVI, cheap and easy to produce, is considered a versatile and environmentally benign agent for removing contaminants by adsorption, reduction or oxidation. ZVI was originally applied in remediation of ground water containing halogenated organic compounds and nitrate [15,16]. Recent researches have shown that many inorganic contaminants, including chromate, uranyl, copper, cadmium, aluminum, zinc, nickel and metalloids such as selenocyanate [4], can be effectively removed by ZVI. However, little work has been performed on the use of ZVI for removing Se(IV). Considering the redox potentials of Fe^{2+}/Fe^{0} and Se(IV)/Se(0) couples, as shown in Eqs. (1) and (2), reducing Se(IV) by ZVI is theoretically feasible.

$$Fe^{2+} + 2e^{-} \rightarrow Fe^{0} \qquad E^{0} = -0.440\,V \tag{1}$$

$$H_2SeO_3 + 4H^{+} + 2e^{-} \rightarrow Se + 3H_2O \quad E^{0} = +0.74\,V \tag{2}$$

Therefore, the objective of this work was to study the feasibility of Se(IV) removal by ZVI. In order to optimize the operating conditions, the kinetics for Se (IV) removal by ZVI relevant to dissolved oxygen (DO), pH, initial Se(IV) concentration, ZVI dosage and particle size as well as reaction temperature were investigated in this study.

2. Materials and methods

2.1. Materials

Chemicals, including Na_2SeO_3, CH_3COONa, CH_3COOH, MES, and TRIS were used as received in this study. All solutions were prepared in ultrapure water (18 MΩ cm) generated from a Milli-Q water system. The ZVI powders, with d_{50} of 7.4 μm, 32.0 μm, and 56.3 μm, were purchased from Beijing Dk Nano technology Co., LTD and used in this study without further treatment.

2.2. Batch reduction tests and chemical analysis

Batch tests were carried out in 500-mL glass bottles, and the solutions were open to the air or purged with nitrogen gas during continuous mixing with a magnetic stirring bar. For the anoxic systems, the solution was purged with nitrogen gas for 30 min to remove oxygen before the addition of ZVI, and the solution was continuously purged with nitrogen gas during the reaction. The solution pH was maintained constant (±0.1 pH unit) by adding different buffer solutions (0.1 M CH_3COONa –CH_3COOH, 0.1 M MES and 0.2 M TRIS were employed for the experiments conducted at pH 4.0–5.0, pH 6.0, and pH 7.0, respectively.). The tests were initiated by adding predetermined dosage of ZVI. At fixed time intervals, aliquots of 5 mL sample were withdrawn from the center of the reactor by a Teflon tube connected to a plastic syringe and immediately filtered with a 0.22-μm-pore diameter membrane. After that the filtrates were acidified with one drop of 65% HNO_3 and then analyzed for residual Se(IV) concentration with Perkin Elmer Optima 5,300 DV ICP-OES. Fe(II) concentration in the filtrate was determined by the modified ferrozine method using a TU-1901 UV/visible spectrophotometer at a wavelength of 562 nm. The oxidation reduction potential (ORP) during reaction was monitored with an ORP sensor connected to a pHS-3C pH meter. All experiments were run in triplicates for a given condition, and all points in the figures are averaged and error bars represent the standard deviation.

3. Results

3.1. Effect of DO on Se(IV) removal at various pH levels

The effect of DO on Se(IV) removal by ZVI was evaluated over the pH range of 4.0–7.0 by comparing the experimental results obtained open to air with those under anoxic condition, as shown in Fig. 1. Since ZVI was applied in large excess, Se(IV) removal using ZVI could be described by a generalized pseudo-first-order kinetic model, where the rate was proportional to the Se(IV) concentration with an expression shown as Eq. 3 and the corresponding half-lives ($t_{1/2}$) could be calculated by Eq. (4).

$$r = \frac{-\mathrm{d}[\mathrm{Se(IV)}]}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{Se(IV)}] \tag{3}$$

$$t_{1/2} = \frac{\ln 2}{k_{\mathrm{obs}}} \tag{4}$$

where [Se(IV)] is Se(IV) concentration (mg L^{-1}) at time t (min), k_{obs} is the observed pseudo-first-order reaction rate constant and $t_{1/2}$ stands for the half-lives of Se(IV) removal.

The removal of Se(IV) by ZVI at pH 4.0–7.0 could be well simulated with pseudo-first-order kinetic model under either oxic or anoxic conditions, with R^2 values ranging from 0.969 to 0.996. The values of regression coefficient R^2, observed pseudo-first-order reaction rate constant k_{obs}, and half-lives ($t_{1/2}$) are summarized in Table 1. The observed rate constants decreased from 0.467 to 0.037 min^{-1} and from 0.215 to 0.021 min^{-1}, respectively, under oxic conditions and anoxic conditions as pH increased from 4.0 to 7.0. Obviously, Se(IV) removal by ZVI was strongly dependent on pH and more favored at lower pH. Moreover, the reaction was evidently inhibited at all pH investigated when DO was excluded by purging nitrogen, which was well consistent with the results reported by Yoon et al. [17,18] that the reaction rates of Se(VI) or Cr(VI) with ZVI were smaller under anoxic conditions compared with their counterparts under oxic conditions.

In the present study, aqueous Fe(II) production under both oxic and anoxic conditions were monitored during reaction, and the results are illustrated in Fig. 1. As expected, much more Fe(II) release under oxic conditions than under anoxic conditions could be observed in the time scale investigated. This indicated a more rapid ZVI corrosion rate in the presence of DO. Meng et al. [4] also reported that the corrosion rate of ZVI in the presence of oxygen was much higher than that of anaerobic corrosion. Thus, it was safe to conclude that Se(IV) removal was coupled with ZVI corrosion and higher Se(IV) removal rate could be obtained accompanied with faster ZVI corrosion induced by lower pH and the presence of DO.

3.2. Effect of Se(IV) concentration

The effect of initial Se(IV) concentration varying from 9.9 to 78.6 mg L^{-1} on kinetics of Se(IV) removal by ZVI at pH 6.0 are presented in Fig. 2(a). A rapid decrease in Se(IV) concentration was observed at the initial stage, followed by a mitigatory exponential decline with prolonging reaction time. Over 96% of Se (IV) removal could be achieved within 45 min, independent of initial Se(IV) concentration. With initial Se (IV) concentration increasing from 9.9 to 19.7 mg L^{-1}, k_{obs} increased from 0.137 to 0.207 min^{-1}, but it dropped to 0.081–0.088 min^{-1} as the initial Se(IV) concentration was increased to 39.6–78.6 mg L^{-1}. Correspondingly, the half-lives of Se(IV) varied from 3.3 to 8.6 min over the initial Se(IV) concentration range of 9.9–78.6 mg L^{-1}. Therefore, Se(IV) removal by

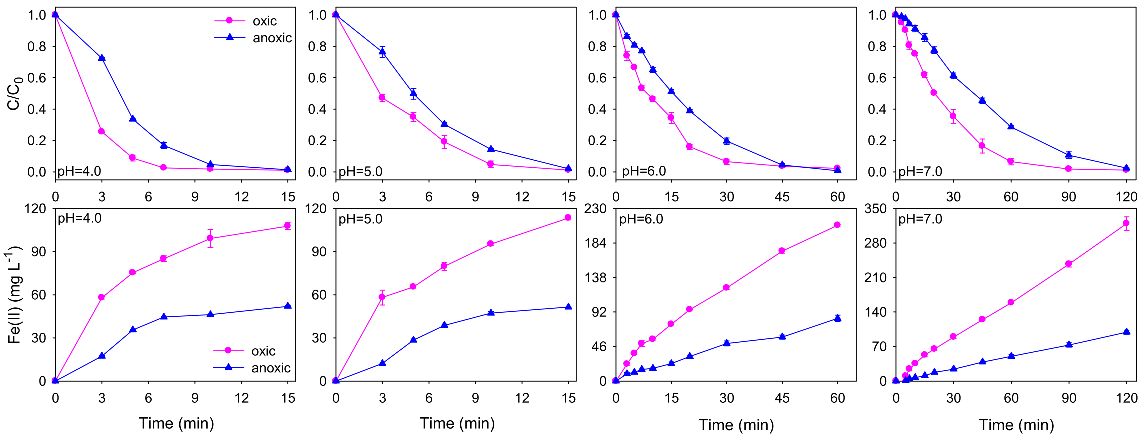

Fig. 1. Influence of DO on Se(IV) removal and Fe(II) release in the process of Se(IV) removal by ZVI at various pH levels. Reaction conditions: 1.0 g L^{-1} Fe^0, 39.6 mg L^{-1} Se(IV), 0.01 M NaCl, T = 298 K.

Table 1
Pseudo-first-order rate constants and half lives of Se(IV) removal by ZVI under different conditions

[ZVI] (g L^{-1})	[Se(IV)] (mg L^{-1})	pH (±0.1)	Size of ZVI d_{50} (μm)	DO	T (K)	k_{obs} (min^{-1})	$t_{1/2}$ (min)	R^2
1.0	39.6	4.0	7.4	O_2[a]	298	0.467	1.5	0.999
1.0	39.6	5.0	7.4	O_2	298	0.239	2.9	0.994
1.0	39.6	6.0	7.4	O_2	298	0.081	8.6	0.995
1.0	39.6	7.0	7.4	O_2	298	0.037	18.5	0.996
1.0	39.6	4.0	7.4	N_2[b]	298	0.215	3.2	0.969
1.0	39.6	5.0	7.4	N_2	298	0.161	4.3	0.977
1.0	39.6	6.0	7.4	N_2	298	0.051	13.6	0.994
1.0	39.6	7.0	7.4	N_2	298	0.021	33.8	0.993
1.0	9.9	6.0	7.4	O_2	298	0.137	5.1	0.990
1.0	19.7	6.0	7.4	O_2	298	0.207	3.3	0.993
1.0	78.6	6.0	7.4	O_2	298	0.088	7.9	0.988
0.1	39.6	6.0	7.4	O_2	298	0.011	63.0	0.980
0.5	39.6	6.0	7.4	O_2	298	0.038	18.5	0.980
1.0	39.6	6.0	7.4	O_2	298	0.081	8.6	0.990
1.0	39.6	6.0	32.0	O_2	298	0.039	18.0	0.990
1.0	39.6	6.0	7.4	O_2	278	0.027	25.9	0.995
1.0	39.6	6.0	7.4	O_2	288	0.040	17.5	0.993
1.0	39.6	6.0	7.4	O_2	308	0.094	7.4	0.996

[a] Open to the air.
[b] Purged with nitrogen.

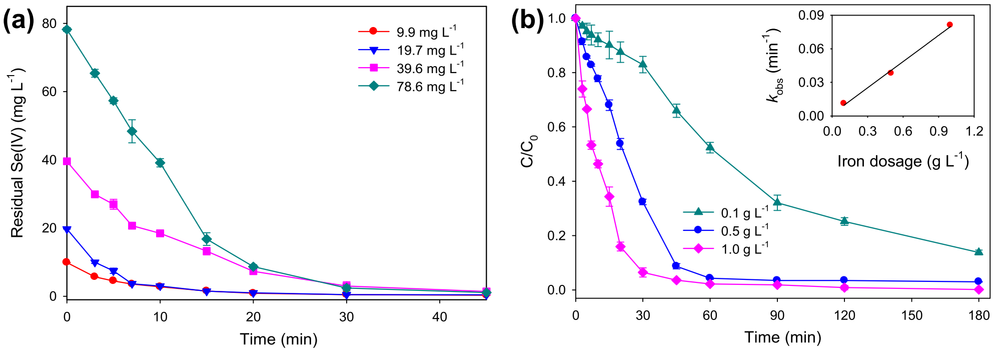

Fig. 2. Effect of (a) initial Se(IV) concentration and (b) ZVI dosage on kinetics of Se(IV) removal by ZVI. The inset shows the correlation of k_{obs} with iron dosage. Reaction conditions: (a) 1.0 g L^{-1} Fe^0, pH = 6.0, 0.01 M NaCl, T = 298 K; (b) 39.6 mg L^{-1} Se(IV), pH = 6.0, 0.01 M NaCl, T = 298 K.

ZVI could yield considerable high efficiency and would not be subjected to the limitation of Se(IV) concentration relevant to the environment.

3.3. Effect of ZVI dosage

The influence of ZVI dosages (0.1, 0.5, and 1.0 g L^{-1}) on Se(IV) removal rate was investigated with initial Se (IV) concentration of 39.6 mg L^{-1} at pH 6.0, as shown in Fig. 2(b). About 96 and 98% of Se(IV) could be removed within 60 min when ZVI were dosed at 0.5 g L^{-1} and 1.0 g L^{-1}, respectively, whereas only ~86% of Se(IV) could be removed within 180 min when ZVI dosage was 0.1 g L^{-1}. Since the reaction occurred on the metal iron surface, it was universally acknowledged that the available metal surface area played a crucial role in the kinetics of Se(IV) removal by ZVI. Increasing the applied ZVI dosage, more available active sites will be supplied for Se(IV) rapid adsorption and reduction, resulting in higher removal rate. Moreover, good linearly correlation relationship could be plotted between the applied ZVI dosage and its corresponding k_{obs}, as demonstrated in the inset of Fig. 2(b).

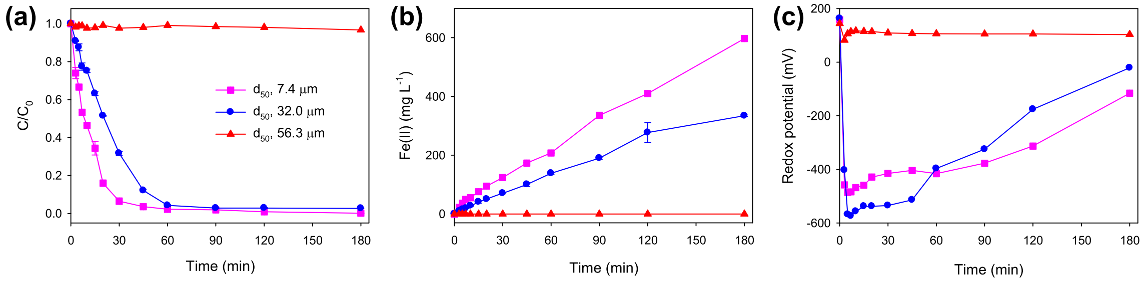

Fig. 3. Influence of ZVI particle size on (a) Se(IV) removal, (b) Fe(II) release, and (c) redox potential in the process of Se (IV) removal by ZVI. Reaction conditions: 1.0 g L^{-1} Fe^0, 39.6 mg L^{-1} Se(IV), pH = 6.0, 0.01 M NaCl, T = 298 K.

3.4. Effect of ZVI particle size

Particle size is an important factor determining the reactivity of ZVI. Therefore, Se(IV) removal by ZVI of different particle sizes (d$_{50}$ of 7.4, 32.0, and 56.3 μm) were compared, as shown in Fig. 3(a). Obviously, the removal rate of Se(IV) declined significantly with increasing d$_{50}$ of ZVI. Over 96% of Se(IV) could be removed in 60 min when d$_{50}$ of ZVI was 7.4 or 32.0 μm, while negligible Se(IV) removal was observed in 180 min when d$_{50}$ of ZVI was 56.3 μm. Although high efficiency could be obtained for both ZVI d$_{50}$ of 7.4 and 32.0 μm, the difference in removal rate constants was obvious. The k_{obs} for ZVI with d$_{50}$ of 7.4 μm was fitted 2 times larger than that for ZVI with d$_{50}$ of 32.0 μm, indicating that relative smaller particle size of ZVI was more suitable for Se(IV) removal, with its larger specific surface area.

ZVI with smaller particle size not only resulted in a larger Se(IV) removal rate but also a more rapid Fe (II) generation rate, as shown in Fig. 3(b). Moreover, the ORP of the systems, in which ZVI with d$_{50}$ of 7.4 or 32.0 μm was applied, experienced a sharp decrease and then a slow rebound, as illustrated in Fig. 3(c). However, negligible Fe(II) release was observed for ZVI with d$_{50}$ of 56.3 μm and the variation of ORP was insignificant, consistent with the phenomenon that almost no Se(IV) removal was observed for ZVI with d$_{50}$ of 56.3 μm. Therefore, the particle size of ZVI is considered a critical factor that could affect the reaction rate of Se(IV) with ZVI.

3.5. Effect of reaction temperature

The reaction temperature is generally believed a key role in a chemical reaction. To investigate the influence of reaction temperature, some tests were carried out at different temperatures ranging from 278 to 208 K. As illustrated in Fig. 4(a), the removal efficiency of Se(IV) by ZVI was not heavily dependent on reaction temperature, and nearly, 100% Se(IV) could be removed within 90 min at all temperatures observed. However, Se(IV) removal rate by ZVI was gradually promoted in accordance with the elevated temperature. Based on the obtained reaction rate constants at different temperatures, the activation energy of the removal process of Se(IV) by ZVI can be obtained according to the Arrhenius equation:

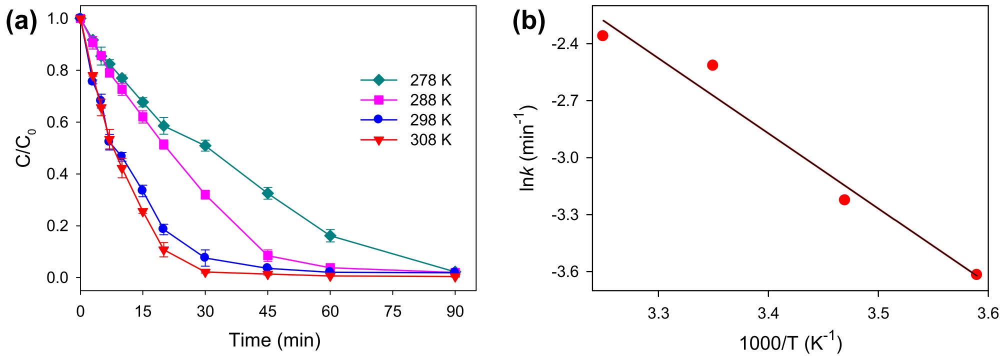

Fig. 4. (a) Effect of temperature on Se(IV) removal by ZVI; (b) Arrhenius plot for Se(IV) removal by ZVI. Reaction conditions: 1.0 g L^{-1} Fe^0, 39.6 mg L^{-1} Se(IV), pH = 6.0, 0.01 M NaCl.

Table 2
Comparison of selenite removal by adsorption and abiotic reduction

Technologies	Adsorbent or reductant	Major reaction conditions	Se(IV) uptake cap. (mg g^{-1})	Ref.
Adsorption	Fe-Mn hydrous oxide	$[\mathrm{Se(IV)}]_0 = 0$–500 mg L^{-1}, $[\mathrm{Adsorbent}]_0 = 2$ g L^{-1}, pH = 6–8, $T = 22$℃, reaction time = 24 h	18.45–26.71	[24]
	γ-Al_2O_3	$[\mathrm{Se(IV)}]_0 = 79$ mg L^{-1}, $[\mathrm{Adsorbent}]_0 = 10$ g L^{-1}, pH = 6, reaction time = 24 h	~7.9	[25]
	Iron-coated GAC	$[\mathrm{Se(IV)}]_0 = 2$ mg L^{-1}, $[\mathrm{Adsorbent}]_0 = 0.3$–2.8 g L^{-1}, pH = 5±0.3, $T = 25$℃, reaction time = 48 h	~2.5	[26]
	Al oxide coated sand	$[\mathrm{Se(IV)}]_0 = 0$–158 mg L^{-1}, $[\mathrm{Adsorbent}]_0 = 100$ g L^{-1}, pH = 4.8–8.5, reaction time = 3 h	0.76–1.08	[27]
	Am-Fe$(OH)_3$	$[\mathrm{Se(IV)}]_0 = 79$ mg L^{-1}, $[\mathrm{Adsorbent}]_0 = 4$ g L^{-1}, pH = 4.0–8.5, $T = 25$℃, reaction time = 24 h	~19.5	[28]
	Natural hematite	$[\mathrm{Se(IV)}]_0 = 0.28$–39.0 mg L^{-1}, pH = 4.0, $[\mathrm{Adsorbent}]_0 = 5$ g L^{-1}, reaction time = 50 h, room temperature	0.39	[8]
	Natural goethite	$[\mathrm{Se(IV)}]_0 = 0.28$–39.0 mg L^{-1}, pH = 4.0, $[\mathrm{Adsorbent}]_0 = 5$ g L^{-1}, reaction time = 50 h, room temperature	0.523	[8]
	Al(III)/SiO_2 binary oxide	$[\mathrm{Se(IV)}]_0 = 0$–236 mg L^{-1}, pH = 5.0, $T = 25$℃, reaction time = 24 h	32.7	[29]
	Fe(III)/SiO_2 binary oxide	$[\mathrm{Se(IV)}]_0 = 0$–236 mg L^{-1}, pH = 5.0, $T = 25$℃, reaction time = 24 h	20.4	[28]
	Hematite	$[\mathrm{Se(IV)}]_0 = 31.5$ mg L^{-1}, pH = 3.5,$[\mathrm{Adsorbent}]_0 = 16$ g L^{-1}, $T = 25$℃, reaction time = 24 h	4.11	[30]
	Microwave-assisted Fe_3O_4	$[\mathrm{Se(IV)}]_0 = 0.25$–10 mg L^{-1}, pH = 4, $[\mathrm{Adsorbent}]_0 = 2.5$ g L^{-1},reaction time = 1 h, room temperature	2.38	
	Non microwave-assisted Fe_3O_4	$[\mathrm{Se(IV)}]_0 = 0.25$–10 mg L^{-1}, pH = 4, $[\mathrm{Adsorbent}]_0 = 2.5$ g L^{-1},reaction time = 1 h, room temperature	1.923	[12]
	Tropical soil	$[\mathrm{Se(IV)}]_0 = 0$–60 mg L^{-1}, pH = 4.7, The soil-to- solution ratio = 1:20, reaction time = 24 h, room temperature	0.145	[31]
	Calcined Mg-Al-Zr	$[\mathrm{Se(IV)}]_0 = 20$ mg L^{-1}, pH = 4, $[\mathrm{Adsorbent}]_0 = 0.5$ g L^{-1}, $T = 30$℃, reaction time = 2 h	29	[32]
	Fe(III)/Cr(III) hydroxide sludge	$[\mathrm{Se(IV)}]_0 = 20$–50 mg L^{-1}, pH = 6.5, $[\mathrm{Adsorbent}]_0 = 10$ g L^{-1}, $T = 32$℃, reaction time = 30 min	15.6	[33]
	Manganese nodule leached residues	$[\mathrm{Se(IV)}]_0 = 60$ mg L^{-1}, pH = 5, $[\mathrm{Adsorbent}]_0 = 2.0$ g L^{-1}, $T = 30$℃, reaction time = 3 h	54.6	[34]
	Nano-Jacobsite	$[\mathrm{Se(IV)}]_0 = 0.25$–10 mg L^{-1}, pH = 4, $[\mathrm{Adsorbent}]_0 = 2.5$ g L^{-1}, reaction time = 15 min, room temperature	6.57	[35]
	Mg–Fe–CO_3 layered double Hydroxide (LDH)	$[\mathrm{Se(IV)}]_0 = 50$ mg L^{-1}, pH = 6, $[\mathrm{Adsorbent}]_0 = 1.0$ g L^{-1}, $T = 30$℃, reaction time = 4 h	40	[36]
	Kemiron	$[\mathrm{Se(IV)}]_0 = 5$–15 mg L^{-1}, pH = 7, $[\mathrm{Adsorbent}]_0 = 0.1$ g L^{-1}, $T = 30$℃, reaction time = 48 h	52	[37]

(*Continued*)

Table 2 (*Continued*)

Technologies	Adsorbent or reductant	Major reaction conditions	Se(IV) uptake cap. (mg g^{-1})	Ref.
Abiotic reduction	Fe(II) adsorbed on freshly precipitated iron oxides	$[Se(IV)]_0 = 10.0$ mg L^{-1}, $[Fe(II)]_0 = 106.2$ mg L^{-1}, pH = 4.2–5.6, $T = 22 \pm 2$℃, reaction time = 11 days	0.086	[38]
	Pyrite	$[Se(IV)]_0 = 3.55 \times 10^{-3}$ mg L^{-1}, $[pyrite]_0 = 4.5$ g L^{-1}, pH = 5.0, $T = 26$℃, reaction time = 640 h	2.32×10^{-3}	[39]
	Mackinawite (FeS)	$[Se(IV)]_0 = 5.0$–198.03 mg L^{-1}, $[FeS]_0 = 0.5$ g L^{-1}, pH = 7.0–10.0, reaction time = 30–480 min	62.1–174.2	[23]
	Pyrite−greigite	$[Se(IV)]_0 = 31.58$ mg L^{-1}, $[FeS_2/Fe(II)\ Fe(III)_2S_4]_0 = 4.28$ g L^{-1}, pH = 6.2, reaction time = 30 min	6.64	[40]
	Siderite	$[Se(IV)]_0 = 58.43$ mg L^{-1}, $[FeCO_3]_0 = 75$ g L^{-1}, pH = 7.3, reaction time = 24 h	0.73	[41]
	Zero-valent iron	$[Se(IV)]_0 = 9.9$–78.6 mg L^{-1}, $[Fe^0]_0 = 1.0$ g L^{-1}, pH = 6.0, $T = 25$℃, reaction time = 1 h	9.9–78.6	This study

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (5)$$

The plot of ln$k$ vs. $1/T$ is shown in Fig. 4(b). Obviously, a good linear correlation was observed between $\ln k$ and $1/T$, and the activation energy E_a was determined to be 32.86 kJ mol^{-1}. This value was very close to activation energy (E_a) of the dechlorination by Pb/Fe (37.86 kJ mol^{-1}) [19]. Considering the well-acknowledged fact that the activation energy for ordinary thermodynamically favored reactions is usually between 60 and 250 kJ/mol [20], the small value of activation energy for Se(IV) removal by ZVI indicated easy occurrence of the reaction and its less temperature dependency for the application in real practice.

4. Discussion

A variety of treatment technologies, including adsorption, biological reduction, abiotic reduction, membrane filtration and anion exchange, had been explored for selenite removal in the literature. Biological reduction of selenite had been investigated with various microbes such as Thauera selenatis, Enterobacter taylorae, Rhizobium sp., Azospira oryzae, Bacillus sp. and Desulfovibrio desulfuricans subsp. Aestuarii [21]. Most of the aforementioned microbes are facultative anaerobes that consume electron donors like molasses, acetate, ethanol, and methanol in addition to hydrogen gas [21]. Microbial treatment, reducing Se (IV)–Se(0), is sometimes attractive due to its small amount of sludge formation after the treatment. However, this process suffered from a very low reaction rate reported by some researchers [11,22]. In addition, its sensitivity to oxygen and nitrate and high carbon source requirements restricted its application in practice. Among these methods, adsorption and abiotic reduction were believed to be more efficient than other methods. Thus, the major reaction conditions adopted in the studies investigating Se(IV) removal by adsorption and abiotic reduction and the corresponding Se(IV) uptake capacity were summarized in Table 2. Fe-, Mn-, or Al-oxyhydroxides have been extensively studied because adsorption of aqueous Se (IV) onto such mineral surfaces plays an important role in determining the mobility and bioavailability of selenium. However, the adsorption capacities of those adsorbents are very low, and selenium removal by iron oxyhydroxides will probably produce unstable residuals in landfills under anoxic condition. Due to the reduction of ferric to ferrous iron, Se species may be released again to the environment [23]. Thus, reduction of selenite to less toxic and soluble elemental selenium would be a viable and cost-effective approach for abatement of excess selenium in contaminated water. Many abiotic reduction methods employing Fe(II)-containing minerals have been employed for Se(IV) removal, as listed in Table 2. Among the abiotic reductants investigated in the literature, amorphous mackinawite (FeS) was the most efficient and its uptake capacity for Se(IV) varied from 62.1 to 174.2 mg g^{-1}. Although the Se(IV) uptake capacity by ZVI presented in this study was smaller than that of FeS reported in reference [23], ZVI was not necessarily less effective for Se(IV) removal than FeS because a larger solid/liquid ratio was employed in our study. Anyway, Table 2 revealed that Se(IV) removal by ZVI is much more effective than other reductants except mackinawite. Therefore, it was believed that Se(IV) removal by ZVI is a promising method.

5. Conclusions

Se(IV) removal by ZVI was found to follow pseudo-first-order kinetics in this study. Decreasing pH, open to air, decreasing ZVI particle size and increasing temperature could enhanced Se(IV) removal. Corrosion of ZVI was believed a crucial process for Se(IV) removal and aqueous Fe(II) release rate were in accordance with the trend of Se(IV) removal rate. The reaction activation energy was determined to be 32.86 kJ mol^{-1}. Compared to other methods for Se(IV) removal reported in the literature, reduction by ZVI is rapid and effective and thus is a promising method. However, further study is needed to gain insight into in-depth mechanism and optimize operation conditions in the near future in order to apply ZVI in real practice for treatment of Se(IV)-containing waters.

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