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Study on the Arsenate Removal from Raw As(V)-Rich Wastewater Using Zero-Valent Iron

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Abstract: Due to the large volumes of solid waste produced by the traditional arsenic-rich lime iron salt precipitation method treatment produced during wet-smelting by precious metal workshops, raw As(V)-rich wastewater from a domestic metallurgical enterprise was chosen as the research object. Zero-valent iron (ZVI) was used to remove arsenate (As(V)) from raw wastewater. Factors affecting the adsorption of As(V), such as the ZVI size and adsorption time, were investigated. The As(V) removal percentage was >98.2% when using 40, 100, 250, or 300 mesh ZVI in a 2.8 mg·L⁻¹ As(V) solution at pH 7, with an iron mass–wastewater ratio of 5 g/100 mL, and 12 h reaction time. The As(V) removal percentage was >86.5% when using 40 mesh ZVI after 50 min of reaction. A comprehensive evaluation was performed on the effects of factors such as cost and water head loss. Here, 40 mesh ZVI was used for column-based separation, in which the mass of solid waste was very small. Column experiments indicated that the adsorbent more efficiently eliminated arsenate in comparison to the earlier reported adsorbents. High bed volumes (BV) of 3200 BV, 6300 BV, and 8400 BV up to a breakthrough concentration of 100 µg·L⁻¹ were achieved for arsenate removal in the presence of 2.8 mg·L⁻¹ of arsenic. The empty bed contact times (EBCTs) were 2.6 min, 5.1 min, and 9.8 min, respectively. Furthermore, the concentrations of other pollutants such as Cu²⁺, Zn²⁺, F⁻, Cd²⁺, Cr⁶⁺, Pb²⁺, and F⁻ met the national discharge standard. The elimination of As(V) and other heavy metals from solutions employing ZVI is efficient, cheap, and produces no secondary environmental pollution, making it an ideal candidate for heavy metal removal from wastewater.

Keywords: zero valent iron (ZVI); arsenate (As(V)); adsorption; column experiments; empty bed contact time (EBCT)



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1. Introduction

As one of the most toxic chemical elements, arsenic is regarded by the World Health Organization as a first priority issue among toxic substances. Chronic exposure to arsenic contaminated drinking water is a major cause of arsenic poisoning, especially in developing countries. Arsenicosis and visible skin lesions have been diagnosed in thousands of people in West Bengal, Bangladesh, and China [1,2]. Arsenic-containing wastewater is mainly produced during non-ferrous metal smelting. Common treatment methods include precipitation, coagulation, ion exchange, adsorption, extraction, membrane separation, biotechnology, and photocatalytic oxidation [3–5]. Lime iron salt coagulation has become the most common method for treating raw acidic arsenic-containing wastewater because of

its low cost, simple and stable operation, and high arsenic removal efficiency (>98%) [6]. It operates by adding (or using existing) Fe^{3+} (Fe^{2+}) ions and adjusting the wastewater to the appropriate pH by using lime to form a hydroxide colloid that adsorbs and reacts with arsenic in wastewater to form insoluble salt precipitates; however, the large amount of solid waste generated by this method and the stacking of arsenic-containing solid wastes require special sites and produce secondary pollution due to arsenic leaching. These factors pose great risks to groundwater and the surrounding environment [7]; therefore, the treatment of arsenic-containing wastewater urgently requires an efficient and cheap method that produces only small amounts of solid waste [8].

Iron is a benign metal from an environmental perspective and is found to be widely available (availability wise, it is second in the Earth's crust). Its electrode potential E^0 (Fe^{2+}/Fe) is -0.14 V, allowing for it to strongly reduce a variety of other metal ions [7]. Moreover, it has the advantages of wide sources, a low price, easy availability, and good operability. In recent years, the removal of heavy metals from wastewater by zero-valent iron (ZVI) has been investigated [9,10]. Nano zero-valent iron (nZVI) has found interest in the treatment of arsenic-containing water because of its small scale, large surface effects, and strong adsorption capacity [11,12]; however, iron nanoparticles are very fine and easily deactivated and condensed in water, which makes them difficult to recycle and reuse. Solid–liquid separation is often required after treatment. Although the loading of nano-zero-valent iron has been shown to improve these shortcomings, it has not been applied in actual wastewater treatment projects due to its high cost [13].

Millimeter industrial ZVI powder has a good balance between its particle size, costs, and performance [14]. This paper intends to research the basic parameters of iron powder particle size, reaction time, and empty bed contact time to provide a high-efficiency, low-cost, arsenic-containing wastewater treatment process for treating actual high-arsenic wastewater by using millimeter industrial ZVI as the adsorbent. The goal of this work was to apply ZVI to remove arsenic from raw industrial wastewater. The effects of several parameters on As(V) elimination were investigated, including ZVI sizes, contact time, concentration of DO, and fixed bed column study.

2. Experiment

2.1. Materials and Reagents

All of the analytical grade chemical reagents used in this study were purchased from Sinopharm chemical reagent Co., Ltd. (Sinopharm chemical reagent Co., Ltd., Shanghai, China). All of the solutions were produced by utilizing deionized (DI) water.

The experimental water sample was taken from a non-ferrous metal smelting wastewater equalization tank. The displacement was about $200 \text{ m}^3 \cdot \text{d}^{-1}$. The composition of the wastewater can be found in Table 1. The water sample was adjusted to $\text{pH } 7 \pm 0.2$ before the experiment.

Table 1. Wastewater parameters.

Parameter	Total Copper (mg/L)	Total Arsenic (mg/L)	Total Lead (mg/L)	Total Zinc (mg/L)	Total Cadmium (mg/L)	Total Chromium (mg/L)	F^- (mg/L)	pH
Wastewater	5.89	2.81	0.875	4.74	0.82	1.83	4.85	4–6

The reagents used in this study, such as sodium hydroxide, hydrochloric acid, citric acid, and sodium citrate, were purchased from Sinopharm Chemical Reagent Co., Ltd., all of which were above analytical purity. The water used in the experiment was deionized water, and no arsenic was detected by the potassium borohydride reduction hydrogenation-atomic fluorescence method. The diameter of the water-based fiber filter membrane was $0.45 \mu\text{m}$ (Shanghai Xinya Purification Device Factory, Shanghai, China), and the size of the medical disposable plastic syringe was 5 mL. The particle sizes of the iron powders were 40, 100, 250, and 300 mesh. Carbonyl iron powder (100 mesh) was purchased from

Shenzhen Chuanghui Magnetic Material Factory (Shenzhen, China), whose composition is shown in Table 2.

Table 2. Key characteristics of the zero-valent iron.

Fe	C	Mn	Si	S
>98	0.24	0.30	0.11	0.02

Note: Particle size is 40–300 mesh; 100 mesh bulk density is $2.6 \text{ g}\cdot\text{cm}^{-3}$.

2.2. Experimental Equipment and Analytical Instruments and Methods

Around 5 mL of suspension was taken at specified intervals of time for both the batch and column experiments, filtered via a membrane filter of $0.45 \mu\text{m}$, and acidified prior to further analysis.

The main experimental instruments included a universal PF6-3 non-dispersive atomic fluorescence photometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China; the detection limit of the instrument was $0.1 \mu\text{g/L}$), peristaltic pump BT00-300T (Baoding Lange peristaltic pump, Baoding, China), HJ-3 temperature-controlled magnetic stirrer, and PHS-3C precision pH meter (Shanghai INESA Scientific Instrument Co., Ltd., Shanghai, China).

To determine the pentavalent arsenic, a certain amount of sample was added to 5% hydrochloric acid. Then, 1 mL of thiourea + ascorbic acid (both mass concentration is 5%; thiourea + ascorbic acid solution was the volume of the prepared test sample 10%) were added. After standing for 3 h, 5% hydrochloric acid was used as the carrier liquid, and 0.1 M KBH_4 was used as the reducing agent. Potassium borohydride reduction hydrogenation atomic fluorescence spectrometry was used for the determination of As(V).

The determination of Cu^{2+} , Zn^{2+} , Pb^{2+} , and Cd^{2+} in water was performed by atomic absorption spectrophotometry, and F^- was determined using the ion-selective electrode method.

All of the above experiments were repeated three times. The error did not exceed 5% each time.

The initial concentration is given by C_0 and C_t represents the As(V) at a time t (in $\text{mg}\cdot\text{L}^{-1}$). The percentage of removed Sb(V) (R%) is calculated making use of the below-mentioned expression:

$$R (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

2.3. Models

An external diffusion rate control model was applied to compute the As(V) adsorption kinetics in this study according to the following equation [15]:

$$\alpha = \frac{W_t}{W_e} = \frac{6}{R} \sqrt{\frac{D'_i t}{\pi}} \quad (2)$$

where W_t and W_e are the adsorption capacity and equilibrium adsorption capacity at time t (min), respectively ($\text{mg}\cdot\text{g}^{-1}$); D'_i is the effective diffusion coefficient; R is the average particle radius of the adsorbent (mm); t is the adsorption time (min); and π is the natural constant.

2.4. Experimental Methods

2.4.1. Influence of the Iron Powder Particle Sizes

First, 100 mL glass bottles were divided into five groups: Water (100 mL) was pipetted from each glass bottle, and the As(V) in the raw water was about $2.8 \text{ mg}\cdot\text{L}^{-1}$.

Three pieces of iron powder and carbonyl iron powder with diameters of 40, 100, 250, and 300 mesh were weighed. Each piece was 5 g (the solid–liquid ratio was $5 \text{ g}/100 \text{ mL}$) and was poured into the corresponding numbered glass bottles containing 100 mL of $2.8 \text{ mg}\cdot\text{L}^{-1}$ arsenic simulated solution. The glass bottles labeled 0–1, 0–2, and 0–3 did not contain added iron powder. Each glass bottle was sealed. The control group did not contain the iron powder.

The glass bottles were put inside a room-temperature gas bath thermostatic oscillator and then oscillated at 150 rpm for 12 h. Subsequently, a 0.45 μm membrane filter was used to filter the aqueous sample from the bottles.

2.4.2. Effect of the Contact Time

The arsenic solutions were treated with iron powder with different particle sizes, and then samples were taken at different times to detect the concentration of arsenic ions to select the optimal hydraulic retention time.

Three dried 2000 mL plastic bottles were used to conduct a group of parallel experiments, numbered 1, 2, and 3. Then, 1000 mL of $2.8 \text{ mg}\cdot\text{L}^{-1}$ As(V) solution was transferred into each plastic bottle. Three samples of iron powder (40 mesh), each weighing 50 g, were poured into the corresponding plastic bottle. The plastic bottles were placed in a gas bath constant-temperature oscillator at a speed of $150 \text{ r}\cdot\text{min}^{-1}$ at room temperature. Samples were taken at 0, 5, 10, 20, 30, 40, 50, 60, 90, 120, 180, 240, and 360 min, respectively, and were then filtered.

2.4.3. Effect of the Concentration of DO

In order to understand the impact of dissolved oxygen (DO) in the arsenic bearing solution containing iron powder of 40 mesh ($\sim 75 \mu\text{m}$), oxygen gas having high purity ($\text{O}_2 > 99.9\%$) was passed through for >30 min. On the other hand, nitrogen gas with a high purity ($\text{N}_2 > 99.9\%$) was introduced into an arsenic containing solution for >30 min for eliminating DO in order to simulate the anoxic state. Nano-zero valent iron was added in this case.

2.4.4. Fixed Bed Column Study

First, 40 mesh iron powder was filled in a glass column with an inner diameter of 10 mm and a column height of 400 mm (both ends of the column were filled with about 1 cm of glass wool to prevent adsorbent loss). The water sample was taken from a non-ferrous metal smelting wastewater conditioning tank and used as the inlet water for the column experiment. The designed empty bed contact times (EBCTs) were 2.6, 5.1, and 9.8 min, and the adsorption influent flowed upward. The penetration point of the arsenic adsorption penetration curve was determined as the point where the arsenic concentration in the effluent reached $100 \mu\text{g}\cdot\text{L}^{-1}$. The arsenic concentration in the effluent was followed with regular sampling.

3. Results and Discussion

3.1. Effects of the Sizes and Types of ZVI

The arsenic removal by different types of iron powders is shown in Figure 1, which shows that the treatment effect of ZVI with different particle sizes all exceeded 98%. A higher arsenic removal rate was obtained when using smaller powders. The removal rate of arsenic was 99.97% for 300 mesh and 98.17% for 40 mesh. The specific surface area of the adsorbent is an important parameter influencing the removal of As(V) by ZVI when the adsorbent mass is constant. Generally, the As(V) removal rate was found to increase through the enhancement of the surface area of iron, for example by a decrease in particle size. For example, Gillham and O'Hannesin first reported that a larger ZVI surface area could lead to greater rates of organic pollutant degradation [16].

Considering that a smaller particle size of the adsorbent meant a larger head loss during dynamic adsorption, 40 mesh iron powder was selected to reduce the energy consumption of the treatment process.

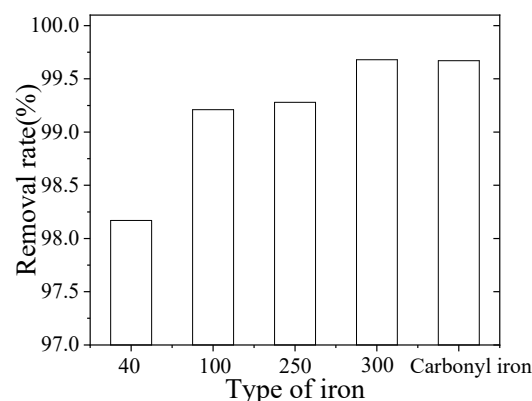


Figure 1. Effect of particle size of the industrial iron powder on As(V) removal.

3.2. Effect of Contact Time

The results in Figure 2 show the time dependent nature of As(V) removal. With increased contact time, there was continuous increase of the arsenic removal rate. From 0–50 min, the rate of arsenic removal increased rapidly, reaching 86.5% within 50 min, while the rate of removal of arsenic ions became flat after 50 min; therefore, the contact reaction time was set as 50 min. The previous research found that the kinetics of As(V)/Sb(V) adsorption by nanoscale zero-valent iron that was supported onto activated carbon (NZVI/AC) included two steps: a fast initial sorption followed by a much slower sorption process. The adsorption of As(V)/Sb(V) on the NZVI particles loaded in macropores or macro channels of the carbon could be fast, whereas the diffusion into mesopores or micropores could be remarkably slow as the macropores and channels were largely blocked by the iron in/on the AC [17,18]. However, the voids in the millimeter-scale ZVI particles in this study were too small for the As(V) to enter the interior of the ZVI particles. Therefore, its adsorption kinetic equilibrium time was only 50 min rather than 72 h [18].

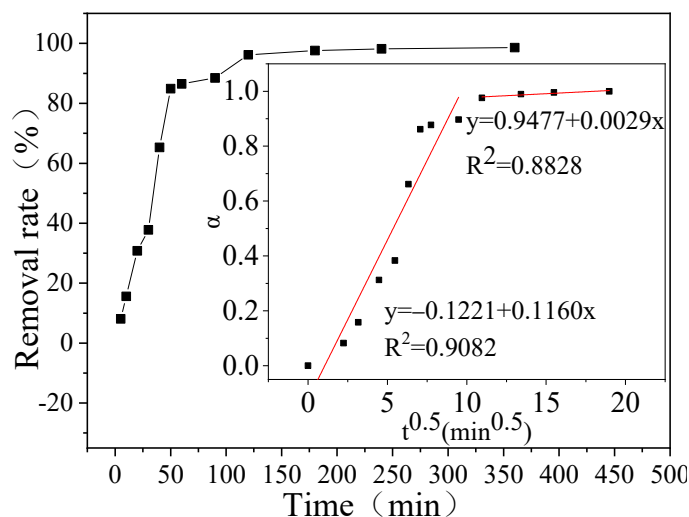


Figure 2. Effect of the reaction time on As(V) removal. Right inset shows modeling of the kinetics of arsenic adsorption onto ZVI by the Boyd model.

The Boyd model is an external diffusion rate control model. If the straight line passes through the origin, the adsorption and removal of pollutants is controlled by intraparticle diffusion [15]. Otherwise, the liquid collecting membrane is controlled by diffusion. This can be seen from the inset of Figure 2. The straight line does not pass the origin, indicating that the adsorption of arsenic by micron-scale ZVI is controlled by the liquid film diffusion.

The Boyd model of arsenic adsorption onto NZVI/AC also shows two distinct linear stages. The first straight portion was probably attributed to adsorption onto the NZVI in the macropores, while the second linear portion was likely due to diffusion into the meso- or micropores. The adsorption of arsenic on the NZVI particles loaded in macropores or macrochannels of the carbon could be fast, whereas diffusion into the mesopores or micropores could be remarkably slow, as the macropores and channels were largely blocked by the iron particles. When zero-valent iron is brought into contact with water, green rust is formed, as indicated by the SEM/EDX analysis [19,20]. Hence, in addition to the pore diffusion process, the adsorption of arsenic onto NZVI/AC also involved diffusion in the corrosion layers [21,22].

Coexisting ions such as Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , and $\text{Cr}_2\text{O}_7^{2-}$ reduce the removal rate of As(V), which compete with As(V) for active adsorption sites, resulting in a lower kinetic correlation coefficient, which is lower than the high correlation coefficients for simulated water samples in the literature [17]. This experiment has more reference significance for the raw industrial sewage project.

3.3. Effect of the Concentration of DO

As is evident from Figure 3, when the level of DO was low like in an anoxic condition ($\text{DO} < 0.5 \text{ mg}\cdot\text{L}^{-1}$) or had a low concentration of DO ($\sim 7 \text{ mg}\cdot\text{L}^{-1}$), the arsenic removal rate was not affected significantly, with slight decrease of percentage removal of arsenic from 94.92% to 93.16%. However, in the solution with a high DO level ($> 14 \text{ mg}\cdot\text{L}^{-1}$), there was a significant decrease for the arsenic removal rate from $\sim 93\%$ to 63.37%, signifying the negative impact of DO on the arsenic removal by ZVI. The level of DO in raw water is usually low during industrial operation, and thus will have insignificant effect on the removal rate of arsenic by ZVI, suggesting the possibility of efficient removal of arsenic from water by ZVI.

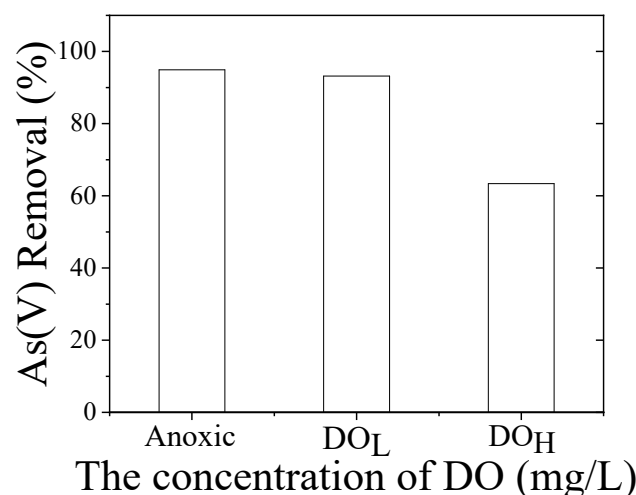


Figure 3. The effect of DO concentration on ZVI mediated the removal of arsenic at pH7, 25 ± 1 °C. Initial arsenic concentration was $2.81 \text{ mg}\cdot\text{L}^{-1}$; anoxic: $\text{DO} < 0.5 \text{ mg}\cdot\text{L}^{-1}$, $\text{DO}_L = 7.0 \text{ mg}\cdot\text{L}^{-1}$, $\text{DO}_H = 14 \text{ mg}\cdot\text{L}^{-1}$.

As per the earlier experimental results, the effect of DO on the reaction system containing zero-valent iron can be two pronged. The arsenic removal rate can be speed up in the presence of a moderate level of DO due to the corrosion of iron. On the other hand, the presence of a high DO level speeds up the formation of iron oxides on the surface of ZVI, thus passivating the ZVI surface and hindering the progress of the reaction between ZVI and arsenic [2,18,19].

3.4. Fixed Bed Column Study

Figure 4 shows the efflux curves of As(V) when EBCT was 2.6, 5.1, and 9.8 min. The influent concentration of As(V) was $2.8 \text{ mg}\cdot\text{L}^{-1}$ and the pH was 7.0. As can be seen from Figure 4, EBCT greatly influenced the outflow curve. When EBCT was 2.6 min, the concentration of As(V) was always lower than $100 \text{ }\mu\text{g}\cdot\text{L}^{-1}$, even though the outflow volume reached 3200 BV. When the EBCT was 5.1 min and the effluent volume was 6300 BV, As(V) reached a penetration point concentration of $100 \text{ }\mu\text{g}\cdot\text{L}^{-1}$, and the As(V) concentration remained at <50 between 0 BV and 3200 BV and rose slowly. When it reached 4400 BV, the effluent concentration reached $50 \text{ }\mu\text{g}\cdot\text{L}^{-1}$. When EBCT was 9.8 min and the effluent volume was 8400 BV, As(V) reached the penetration point concentration of $100 \text{ }\mu\text{g}\cdot\text{L}^{-1}$, and As(V) could be detected after 3500 BV. When it reached 6000 BV, the effluent concentration reached $50 \text{ }\mu\text{g}\cdot\text{L}^{-1}$. The adsorbent had a significant effect on the removal of As(V) when the contact time (min) was 2.6 min. When removing water and wastewater pollutants through an adsorption method, EBCT is generally 10–50 min [16]. The adsorption penetration point ($100 \text{ }\mu\text{g}\cdot\text{L}^{-1}$) still exceeded 8400 BV at a high influent As(V) concentration ($2.8 \text{ mg}\cdot\text{L}^{-1}$) and a relatively short EBCT (9.8 min), indicating that iron powder is an excellent adsorbent for practical arsenic removal.

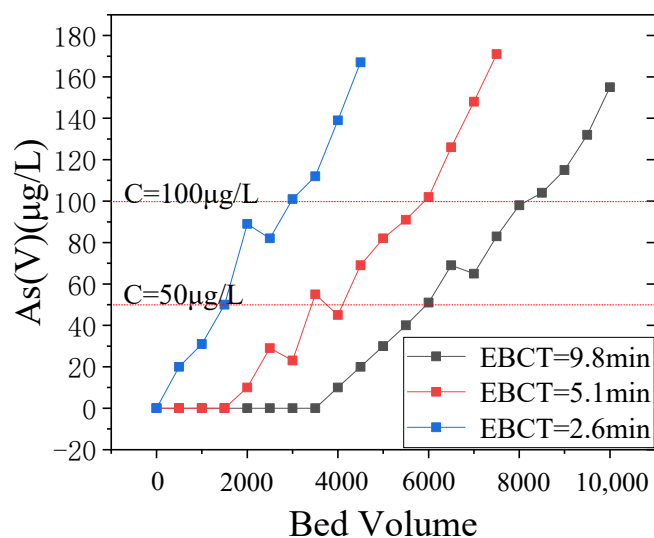


Figure 4. Effect of EBCT on As(V) removal.

As can be seen in Figure 4, upon increasing EBCT, the number of beds that could operate before iron powder adsorption penetration increased. This was mainly because upon increasing EBCT, the As(V) in the solution had more time to diffuse to the surface of the iron powder, where it is adsorbed. The contact time between arsenic and iron powder directly affected the adsorption and removal processes; thus, the iron powder column experiment may more accurately represent the actual fixed bed operation than traditional adsorption equilibrium experiments. In actual operation, adsorption may not reach equilibrium due to the influence of contact time.

3.5. Removal of Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , $\text{Cr}_2\text{O}_7^{2-}$, and F^- by a Fixed Bed Column

Arsenic-containing wastewater also contains Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , $\text{Cr}_2\text{O}_7^{2-}$, and F^- . When EBCT was 2.6 min and the effluent volume was 8400 BV, As(V) reached the penetration point concentration of $100 \text{ }\mu\text{g}\cdot\text{L}^{-1}$. At this time, the concentrations of Cu, Zn, F[−], Cd, Cr, and Pb in the wastewater were 455, 481, 889, 2.5, 14, and 49 $\text{ }\mu\text{g}\cdot\text{L}^{-1}$, respectively (Figure 5). This indicates that after the arsenic-containing wastewater was dynamically adsorbed using industrial-derived iron powder, all hazardous substances were treated in accordance with the standard and could be directly discharged or reused after further treatment.

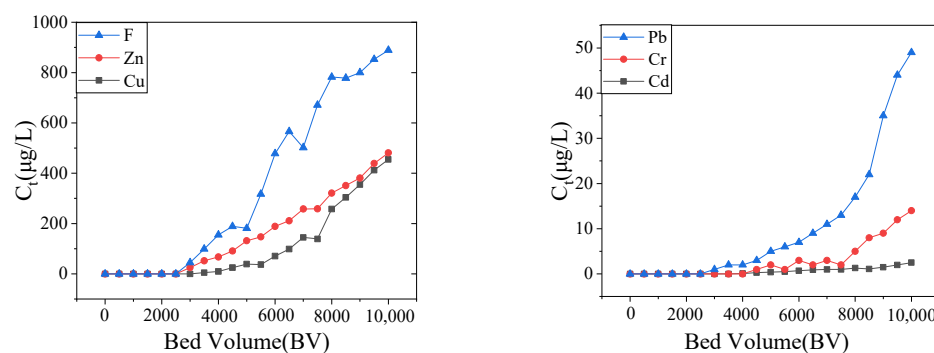


Figure 5. Effect of EBCT on the removal of Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Cr^{6+} , and F^- .

In the column operation, the possible mechanisms responsible for the remediation of metal ions include adsorption in the surface, ion exchange, oxidation, reduction, and precipitation (Figure 6) [18].

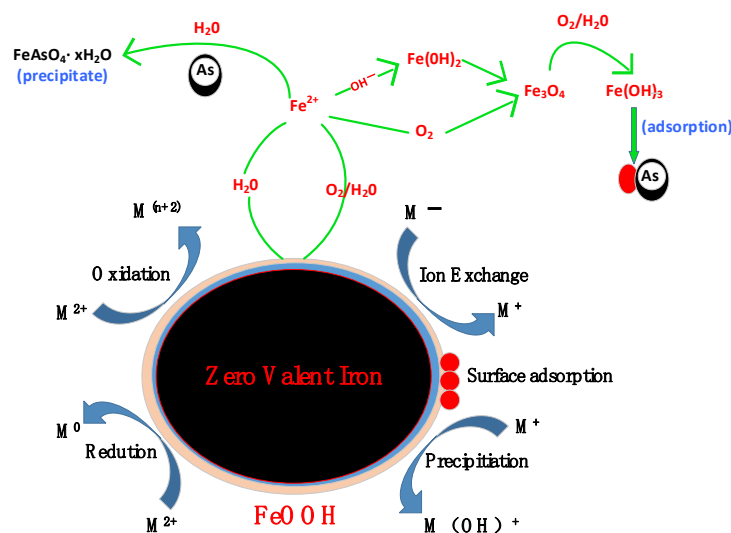


Figure 6. Schematic illustration of the mechanisms in the adsorption of As(V) and metal ions.

F^- is a stable form of fluorine, and its outer electron configuration is $2\text{S}^22\text{P}^5$, which is easy to bond with elements with empty orbitals through coordination bonds in solution. The surface of iron oxide has surface hydroxyl groups, and the surface hydroxyl groups can perform surface ligand exchange with F^- ; iron at the edge of the iron (hydro)oxide structure can be coordinated with F^- . In addition, the positive charge on the surface of iron (hydrogen) oxide can also have electrostatic adsorption with F^- . The above forces are the essential reasons for the adsorption of F^- by iron (hydroxide) oxides [19,20].

3.6. Mechanism for Arsenic Removal from Water by ZVI

Carbon is present as an impurity in the industrial grade zero-valent iron. The involvement of carbon, with a large portion as graphite, as a non-iron component of cast iron has been indicated in the process of iron corrosion and/or removal of the contaminant [18]. The corrosion mechanism of Fe^0 in the aqueous solution is reported to be mainly electrochemical [19,20]. A galvanic couple may be formed between Fe^0 and carbon impurities in ZVI, which probably behave as additional cathodes with the corresponding galvanic corrosion reaction leading to the generation and release of reactive Fe(II) and nascent hydrogen [21]. Literature reports have indicated that the sorbed amount of chlorinated compounds onto the reactive sites has positive impact on the reduction rates, and hence attainment of steady-state removal of pollutant in flow-through systems like packed beds

or permeable reactive barriers could be delayed by the nonreactive sorption by surface carbon [22,23].

The removal of arsenic from the aqueous solution via zero-valent iron is governed primarily by the adsorption, precipitation, and production of As(V)-Fe minerals. In the initial stage of the present study, the rate of As(V) removal was fast, which implied adsorption to be the principal mechanism in the first stages of reaction. As(V) adsorption could also take place via complexation or electrostatic reaction [24,25].

Over the course of the reaction, As(V) removal was found to be maximum at pH 4, which also exhibited a unique behavior during the reaction. Larger particles were produced via the clumping together of ZVI; the heavy metals co-precipitated in the solution due to the role played by some Fe oxides converted by corroded ZVI as a flocculent. Moreover, due to generation of Fe^{2+} , the electron transit from the core of Fe^0 is accelerated, leading to an enhanced reduction of antimony [26,27].

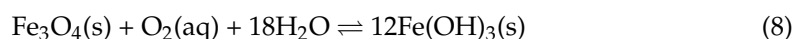
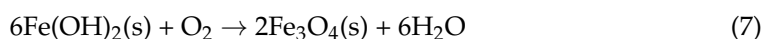
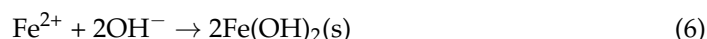
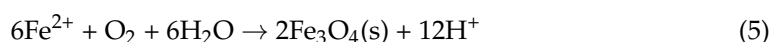
The current investigation showed a significant role of loaded iron in the removal of As(V). The corrosion of nano-iron will take place in the presence of water and soluble trace oxygen within it [1,2,17,23,28,29]. As per Bruce et al., prior to the formation of iron (hydrated) oxides, intermediate species such as iron (hydrate) oxides are formed by nano-iron, which was corroborated by EXAFS investigation [24,25,30,31]. The final product may contain maghemite ($-\text{Fe}_2\text{O}_3$), magnetite (Fe_3O_4), lepidocrocite ($-\text{FeOOH}$), and other minerals [19,26,27,32]. Finally, a large number of hydrated oxides having large As(V) adsorption capacity are formed on the iron surface as a consequence of series of multi-phase complex reactions, as mentioned above (see Figure 6).

The following reactions describe the above mentioned processes [28,33,34]:

Oxidation of Fe^0 takes place to Fe^{2+} via reaction with dissolved oxygen or water:



Further transformation of Fe^{2+} into iron (hydrated) oxides takes place by the solution pH and the oxidation–reduction potential and additional elements [35,36]:



The presence of large active sites ($-\text{OH}$) on the surface of hydrated iron oxide resulted in a high adsorption capacity for As(V) [37,38]. The bidentate binuclear chelate was probably responsible for the adsorption of As(V) on the surface of hydrated iron oxide [29,30,39,40]. Multiple literature reports have indicated this type of complex is formed on the surface of hydrated iron oxide in neutral to weakly alkaline media [41,42]. As per Bakshi et al., two mechanisms are responsible for the removal of As(V) from water via ZVI: (a) Co-precipitation of As(III) and Fe^{3+} as $\text{Fe}(\text{As})\text{OOH}$ onto the surface of the biochar due to simultaneous reduction of As(V) to As(III) and oxidation of Fe^0 to Fe^{3+} , and (b) adsorption of As(III) on preexisting FeOOH mineral surfaces [31,43,44].

Involvement of multiple processes makes the removal of arsenic by ZVI rather complex mechanistically [19,45,46]. Adsorption, reduction, surface precipitation, and co-precipitation with various iron corrosion products such as ferrous/ferric (hydr)oxides are believed to be involved in the removal of arsenic by ZVI [19,32,47–50].

4. Conclusions

The 40 mesh ZVI is an ideal adsorbent for As(V) removal from raw industrial wastewater. Static adsorption experiments showed that ZVI could treat high-arsenic wastewater

with a concentration of $2.8 \text{ mg}\cdot\text{L}^{-1}$, and the removal rate exceeded 86.5% when the reaction time was 50 min and the solid–liquid ratio was 5 g/100 mL. The low level concentration of DO significantly affected the decrease of percentage removal of arsenic. However, the high DO level ($>14 \text{ mg}\cdot\text{L}^{-1}$) significantly decreased the arsenic removal rate from ~93% to 63.37% by ZVI. Arsenic removal from the wastewater using ZVI is governed primarily by the adsorption, precipitation, and production of As(V)-Fe minerals. Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , $\text{Cr}_2\text{O}_7^{2-}$, and F^- in wastewater were effectively removed at the same time. The adsorption penetration point ($100 \text{ }\mu\text{g}\cdot\text{L}^{-1}$) still exceeded 8400 BV at a high influent As(V) concentration ($2.8 \text{ mg}\cdot\text{L}^{-1}$) and a relatively short EBCT (9.8 min), indicating that iron powder is an excellent adsorbent for practical arsenic removal. Considering the filler, procedure, energy loss, and solid waste disposal, the dynamic adsorption process in this paper has application prospects for arsenic removal from nonferrous metal smelting wastewater. As an efficient adsorbent to separate heavy metal ions from the environment, ZVI is an environmentally benign, cheap material that has attracted significant attention as a promising reactant for the removal of various environmental contaminants from wastewater due to its high reductive capacity.

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