

Article

Role of Sulfate-Reducing Bacteria in the Removal of Hexavalent Chromium by Biosynthetic Iron Sulfides (FeS_{1+x})

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Abstract: The reduction of Cr(VI) by biosynthesis iron sulfides (FeS_{1+x}) under anoxic conditions has been studied extensively. However, the role of sulfate-reducing bacteria (SRB) when FeS_{1+x} containing SRB removes contaminants during in situ remediation still needs further study. The secondary kinetic constant of biosynthetic FeS_{1+x} with the presence of SRB (called BS-FeS_{1+x}) was 1.72 times that of FeS_{1+x} with the absence of SRB (called BNS-FeS_{1+x}) under FeS_{1+x}:Cr(VI) molar ratio = 10:1, indicating that SRB had a promoting effect on the removal of Cr(VI). Additionally, XPS showed that 5.7% of Cr(VI) remained in the solid phase in the BS-FeS_{1+x} system, indicating BS-FeS_{1+x} could not only remove Cr(VI) by reduction but also by adsorption. Meanwhile, the Cr(VI) removal efficiency of BS-FeS_{1+x} was 100% under anoxic conditions with FeS_{1+x}:Cr(VI) molar ratio = 1:1, which was higher than BNS-SRB (93.4%). SRB could enhance the Cr(VI) removal efficiency, which was possibly due to the constant release of S(-II) and the improvement of the stability and dispersion and the buffering effect. This discovery provided an inspiring idea of the application of biosynthetic iron sulfides to in situ remediation.

Keywords: iron sulfides; SRB bacteria; Cr(VI); stabilization; buffering capacity



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1. Introduction

The first form of iron sulfide formed by sulfate-reducing bacteria (SRB) under anoxic conditions is mackinawite (FeS) [1–5]. FeS is widely used in environmental remediation because of its unique physical and chemical properties, which can reduce and convert various pollutants under anoxic conditions, including halogenated solvents, high-valence inorganic pollutants and radioactive nuclear elements.

Due to biomaterials' advantages such as high reaction efficiency and environmental benignity, biomaterials are widely used in various catalysts for environmental remediation; for example, some research used microbial fuel cells to treat wastewater [6–10]. However, in previous studies, chemically synthesized materials were typically used, which could not be recycled in situ by newly grown microorganisms [11,12]. SRB like *Desulfovibrio vulgaris* could indirectly reduce Fe(III) by reducing sulfate to S^{2−} and binding to Fe²⁺, or by producing S^{2−} and then binding to each other [13,14]. Some SRB, such as *Shewanella oneidensis* MR-1, produce FeS by directly reducing sulfite and Fe(III) [13,15,16], and some SRB, such as *Desulfovibrio capillatus*, use iron citrate and Na₂S₂O₃ to produce FeS. Studies have shown that biosynthesis of FeS by SRB has two-and-a-half times the adsorption capacity of As(III) than chemical synthesis, owing to the higher porosity of biosynthesized FeS [17,18]. Huo et al. [19] found that the dechlorination rate of biosynthesis was 4.8 times that of chemical synthesis due to the smaller and better dispersed particle size of FeS synthesized by *Shewanella putrefaciens* strain CN32. Additionally, biosynthesized FeS contained more disulfide bonds (S-S) and structural Fe(II), which could significantly

improve pollutant removal capacity. At present, most research has only focused on the difference in properties between biosynthesis and chemical synthesis, but the role of SRB in biosynthesis was ignored. Moreover, Wu et al. [20] found that some natural substances could enhance FeS stability and provide buffering capacity. Hence, in the in situ remediation process, SRB will also attend to the removal reaction; therefore, through this study, we wanted to examine the role of SRB in the removal of hexavalent chromium by biosynthetic iron sulfides.

Among many heavy metal contaminants, hexavalent chromium (Cr(VI)) is considered a preferred study pollutant because it is widely present in natural water, with high fluidity and toxicity [21,22]. Chromium exists mainly in natural environmental media (water, soil and underground) in two chemical valence states: one is Cr(III), and the other is Cr(VI) [23,24]. Previous studies have investigated the removal of Cr(VI) by multiple materials (e.g., activated carbon and organic matter), but further treatment of adsorbed Cr(VI) or reduced Cr(III) ions is also required. FeS has a strong chromium removal effect, so it is widely used; meanwhile, biosynthesis is closer to nature and more environmentally friendly. Thus, it is very necessary to study the removal of Cr(VI) by biosynthetic FeS.

It is interesting to know how the SRB in iron sulfides affect the Cr(VI) removal efficiency. The purpose of this study is to use SRB existing in the natural environment for FeS_{1+x} synthesis and solve three main problems: 1. explore the characterization and analysis difference between biological FeS_{1+x} and traditional chemical synthesis of FeS_{1+x}; 2. investigate the role of SRB when biosynthetic FeS_{1+x} remove the Cr(VI); 3. study the mechanism of the SRB effect on pollutant removal, which could provide scientific guidance for subsequent in situ remediation of Cr(VI) contamination.

2. Materials and Methods

2.1. Chemicals

Pure (>99%) ferrous sulfate heptahydrate (FeSO₄·7H₂O), acetic acid, sodium acetate, HNO₃, acetic acid, ammonium acetate, zinc acetate, sulfuric acid (H₂SO₄), hydroxylamine hydrochloride, etc., were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Na₂S·9H₂O, K₂Cr₂O₇, o-phenanthroline reagent, HCl, NaOH, diphenylcarbohydramine, perferramine sulfate, and N-N-dimethyl-p-phenylenediamine were purchased from Aladdin Chemistry Co. Ltd., Shanghai, China. All water used in the experiment was deionized water.

2.2. Material Preparation

The preparation of chemical FeS nanoparticles followed a modified method from Liu et al. [25]; after weighing out 31.591 g of FeSO₄·7H₂O, it was dissolved in 250 mL of deionized water. Then, 27.273 g of sodium sulfide octahydrate was dissolved in 250 mL of deionized water; after, the ferrous sulfate solution was poured into a 1 L brown bottle. Next, the above solution was put in a magnetic stirrer for stirring at a speed of 1000 r/min, and the prepared sodium sulfide solution was added dropwise to the ferrous sulfate solution. Finally, the pellets, prepared as above, were dried, and centrifuged at 7000 rpm for 10 min; the supernatant was removed and new oxygen-free water was added. The samples were dried and centrifuged at 7000 rpm for 10 min to remove the supernatant. The obtained chemical FeS was stored in an anoxic environment prior to use.

The SRB (*Sulfovibrio vulgaris* ATCC 7757) Manassas, VA, US was purchased from the China Microbial Culture Center (CGMCC®), Beijing, China. A quantity of 0.3 mL of suitably functional liquid medium was aspirated with a sterile pipette and gently shaken to dissolve the lyophilized bacteria into suspension. The entire bacterial suspension was transplanted in the medium at 37 °C. Then, 1 mL of SRB in the logarithmic growth phase solution was injected into an anaerobic flask and was placed in a constant-temperature incubator at 37 °C for about 6 days.

The preparation of biosynthetic FeS was performed by dissolving 5 g of ferrous sulfate heptahydrate in anoxic water, slowly injecting the SRB into an anaerobic bottle, and then

placing it in a constant-temperature incubator at 100 rpm, 37 °C for about 6 days. The samples were dried and centrifuged at 10,000 rpm to discard the supernatant. The obtained biosynthesized FeS was stored in anoxic conditions at 0 °C.

2.3. Batch Experiments

The role of SRB in the in situ remediation was studied by a set of two control groups. The system that retained SRB without centrifugation or other steps after the synthesis of FeS was called BS-FeS_{1+x}. The next group was referred to as BNS-FeS_{1+x}, which was treated by multiple pre-processing steps to remove the SRB.

A quantity of 20 mL of 11.4 mM Cr(VI) solution was placed into a 200 mL anoxic bottle; the headspace was filled with high-purity nitrogen to ensure the anoxic environment of the bottle. The initial pH of the solution was adjusted to 5.0, 7.0 and 9.0 with 1 M HCl and 5 M NaOH solutions. Unless otherwise stated, there were no buffers added in the batch experiments to control the solution pH.

In order to explore the role of SRB, this study used 11.4 mM BS-FeS_{1+x} and BNS-FeS_{1+x} to remove Cr(VI). The addition of a buffer (HEPES) group was set as comparative experiments in both chemical synthesis and biosynthesis. Since SRB might have the capacity to remove Cr(VI) alone, we also removed Cr(VI) with SRB. Different concentrations of FeS_{1+x} solution (1.14, 5.7, and 11.4 mM) were added to an anoxic flask and placed on a magnetic stirrer at 200 rpm in order to study the efficiency of FeS_{1+x} in the repair of wastewater containing Cr(VI). Periodically, the aqueous suspensions (2 mL) were withdrawn from the bottles and filtered through 0.22 µm membranes (Navigator, China) to determine the concentration of Cr(VI).

2.4. The Cr(VI) Removal Kinetic Models and Adsorption Kinetic Models

Pseudo-first-order (Equation (1)) and second-order kinetic (Equation (2)) models were adopted to investigate the removal kinetics of Cr(VI) by FeS. The formulae were represented as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

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

where q_e is the removal capacity (mg/g); q_t represents the equilibrium removal quantity (mg/g); k_1 and k_2 represent the constant of pseudo-first-order kinetic (min^{-1}) and pseudo-second-order kinetic ($\text{g}/(\text{mg} \cdot \text{min})$); and t represents the reaction time (min).

General-order (GO) models—see Equation (3)—were used to fit the kinetic data [26–28]. The corresponding equations were summarized as follows:

$$q_t = q_e - \frac{q_e}{\left[k_N \cdot (q_e)^{n-1} \cdot t \cdot (n-1) + 1 \right]^{n-1}} \quad (3)$$

where t is the contact time (min), and q_t , q_e are the amounts of adsorbate adsorbed at time t . k_N is the general-order rate constant ($(\text{mg} \cdot \text{g}^{-1})^{n-1} \cdot \text{min}^{-1}$); n is the order of the general-order model (dimensionless).

2.5. Chemical Analysis and Instrumental Characterization

Periodically, samples were withdrawn to analyze the total S(-II) and Fe(II). The aqueous Cr(VI) and Fe(II) were filtered immediately and measured through a 0.22 µm membrane (Navigator, China) by a UV-vis spectrophotometer (SP-756P, Shanghai spectrum). Cr(VI), S(-II) and Fe(II) were measured at 540, 665 and 510 nm wavelength, respectively. Fe(II) was sampled and mixed with 1 mL of acetate buffer and 0.4 mL of 0.5% 1,10-phenanthroline, then quantified at 510 nm after 10 min [29,30]. Specifically, S(-II) was sampled and mixed with 1 mL of 0.2% 4-amino-dimethylaniline and 0.2 mL of 0.25 M ammonium ferric sulfate, then quantified at 665 nm after 10 min [29]. Cr(VI) concentration was determined using

5 g/L of 1,5-diphenylcarbazide at 510 nm [31]. The solid samples of each period were collected after centrifugation at 10,000 rpm for 5 min. Then, they were washed with deionized water and stored under anoxic conditions for further analysis. After the Cr(VI) removal experiment, the remaining solid was collected and saved in the same steps. The structure and distribution of FeS were analyzed using scanning electron microscopy (SEM) (Hitachi, S-4800). An X-ray powder diffractometer (XRD) (D/max-RB) was used to analyze the mineral composition of samples. X-ray photoelectron spectroscopy (XPS) (Thermo Kalpha, Waltham, MA, USA) was employed to investigate the surface composition of particles.

3. Results and Discussion

3.1. Characteristics of the Biosynthetic Iron Sulfides

The synthesized FeS_{1+x} showed different morphological characteristics as time increased (Figure 1) [32]. Within 2 days, biosynthesized FeS_{1+x} presented multiple prismatic clusters (Figure 1a). Probably, a small amount of vivianite was formed during the synthesis process [14]. Then, after the sixth day, it exhibited unique morphological features and rosette-like particle form (Figure 1b) because as the bacteria continued to metabolize and grow, the use of elemental P led to the collapse and dissolution of vivianite [33,34]. Previous research using TEM has shown that FeS_{1+x} produced by different SRB showed different growth states; for example, obvious iron flocs with unclear edges were formed in the *Shewanella oneidensis* MR-1 group on day three [20]. Thus, in further studies, we need more precise instruments to characterize this phenomenon. Studies have shown that during FeS biosynthesis, sulfur-mediated iron reduction depended on the release rate of biological S^{2-} [14]. It was quite different from the morphology of chemically synthesized FeS, which was usually in the form of irregularly shaped crystalline or lamellar nanoparticles or layered particles [14]. Biosynthetic FeS_{1+x} was not a single ferrous sulfide particle formed during the synthesis process but also a variety of pyrites minerals and elemental sulfur. It has been reported that both biological and chemical synthesis processes were very susceptible to the formation of vivianite due to free phosphate.

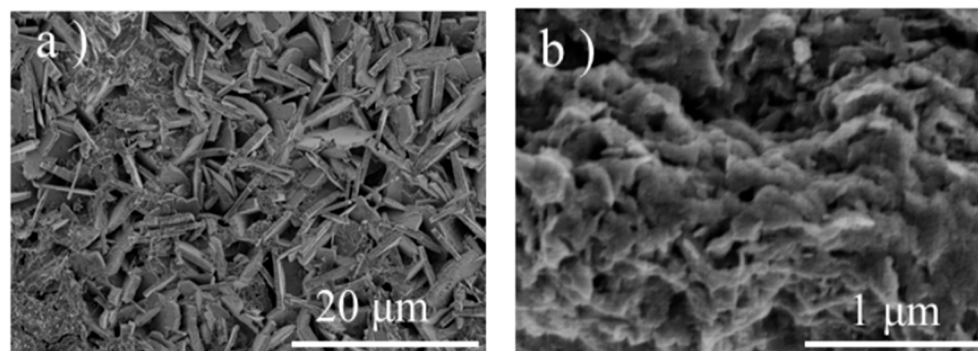


Figure 1. Scanning electron microscopy of biosynthetic FeS_{1+x} in (a) 2 days and (b) 6 days.

XRD presented the diffraction peaks of mackinawite (FeS) accompanied by a small quantity of peaks of vivianite, S_8 and Fe_3S_4 (Figure 2). The crystalline form of FeS was very poor [35] because of the dissimilatory bacterial reduction of sulfate. SRB used sulfate as external electron acceptors to obtain energy and nutrients by oxidizing low-molecular-weight organic compounds (e.g., lactic acid, lactic acid, acetate). Lactic acid was an electron donor, and acetic acid was released when lactic acid was incompletely oxidized. Water hydrogen sulfide (or disulfide) and water ferrous material could react and precipitate to amorphous iron sulfide [36]. The amount of vivianite formed was smaller, which could be ascribed to the competition of free S^{2-} and PO_4^{3-} . Meanwhile, Picard et al. [32] found that un-inactivated microorganisms would continuously produce S^{2-} , which is more conducive to the formation of FeS.

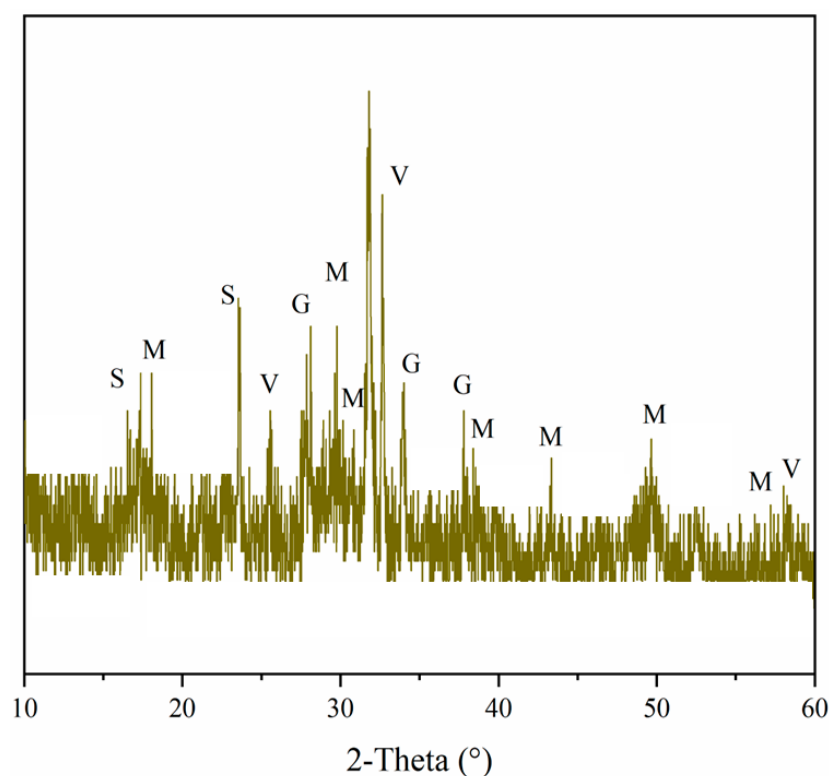


Figure 2. XRD diagram of biosynthetic FeS_{1+x} . S: Sulfur; M: FeS; G: Fe_3S_4 ; V: vivianite.

3.2. Cr(VI) Reduction under Anoxic Conditions

The Cr(VI) removal efficiency of BS- FeS_{1+x} reached 68.5% within 1 min; the removal amount per unit mass was $Q_m = 55.18 \text{ mg/g}$, and the equilibrium removal efficiency was 100% in 15 min (Figure 3). Meanwhile, Cr(VI) could be completely removed under the anoxic conditions, indicating that BS- FeS_{1+x} had a good removal performance on Cr(VI). It has been reported that FeS featured a rapid Cr(VI) removal rate before the first half an hour, followed by slower removal in the next several hours [37]. By comparing the R_2 of the fitted model with the theoretically calculated q_e and the actual q_e , the pseudo-first-level fitted R_2 of the BS- FeS_{1+x} was 0.972, and the theoretical removal equivalent q_e was 24.38 mg/g (Figure 3 and Table 1). It was found that the removal kinetics of BS- FeS_{1+x} on Cr(VI) were more fitted with the pseudo-secondary kinetic model, which was consistent with the kinetic results of removing Cr(VI) with FeS in other studies [34,38]. The pseudo-secondary kinetic constant k_2 of the BS- FeS_{1+x} was $2.59 \times 10^{-2} (\text{min}(\text{mg/g})^{-1})$ $R_2 = 0.998$, and the theoretical removal equivalent was 73.52 mg/g . Further evaluating the kinetic process, $t_{0.5}$ and $t_{0.95}$ were studied. The values were calculated from the best model (general-order model). These values correspond to the times (min) when 50% and 95% of saturation (q_e) are attained, respectively (Table 1). The $t_{0.5}$ and $t_{0.95}$ of BS- FeS_{1+x} and BNS- FeS_{1+x} were 0.43, 7.61 and 0.96, 18.29 min, respectively. This result also proved that BS- FeS_{1+x} had a good Cr(VI) adsorption capacity.

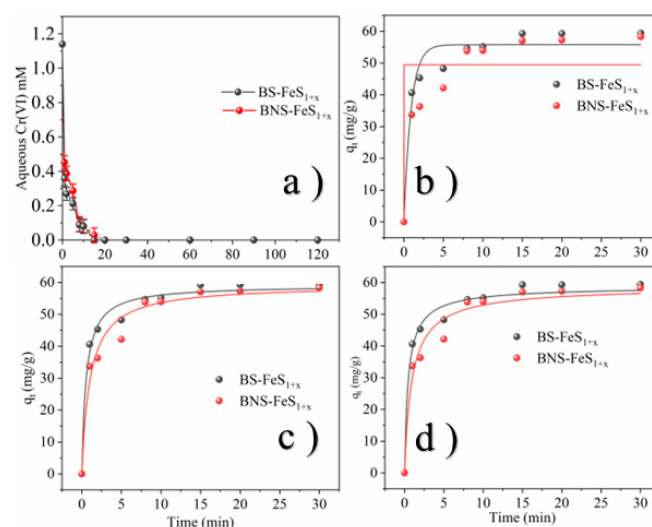


Figure 3. Kinetics of removal of Cr(VI) by biosynthesis of FeS_{1+x}. (a): the amount of Cr(VI) removed by BS-FeS_{1+x} and BNS-FeS_{1+x}; (b): pseudo-first-order kinetic; (c): pseudo-secondary kinetic model fitting of BS-FeS_{1+x} and BNS-FeS_{1+x} removal Cr(VI); (d): adsorption kinetic models of Cr(VI). Reaction conditions: FeS_{1+x} dosage concentration was 11.4 mM; Cr(VI) dosage concentration was 1.14 mM; initial pH was 5.0; reaction time was 2 h; and speed was 200 rpm. BS-FeS_{1+x}: biosynthesis of iron sulfides containing SRB. BNS-FeS_{1+x}: biosynthesis of iron sulfide dry particles without SRB. Data were plotted as means of duplicates, and the error bars indicate the standard deviation.

It still had 5.7% Cr(VI) in the solid phase of BS-FeS_{1+x} after anoxic 2 h, indicating that BS-FeS_{1+x} could not only remove Cr(VI) by reduction but also by adsorption (Figure 4 and Table 2). In addition, the larger the porosity of BS-FeS_{1+x}, the stronger the adsorption effect [39]. The higher porosity and the presence of SRB both contributed to the better Cr(VI) removal efficiency of BS-FeS_{1+x}. SRB could make FeS more uniformly dispersed on cells and secreted extracellular polymeric substances (EPS) as an intermediate, which might also improve the electron transport. EPS had a strong buffering capacity and contained more disulfide bonds (S-S) and structural Fe(II) due to the rich functional groups, which could improve the reducing effect of Cr(VI) [18,19].

The changes in Fe(II) and S(-II) were measured to determine the transfer of Fe(II) and S(-II) during the removal of Cr(VI) by BS-FeS_{1+x}. Fe(II) and S(-II) in BS-FeS_{1+x} would be rapidly oxidized according to the formula and the theoretical calculation. BS-FeS_{1+x} could theoretically reduce 1.05 mM of Cr(VI) at 10 min, while in this study, it removed 1.06 mM of Cr(VI), indicating that SRB might play an important role in removing Cr(VI). Additionally, it was found that the S(-II) concentration was 12.46 mM, which was greater than the theoretical value of 11.4 mM (Figure 5). It could be ascribed to the release of S during biosynthesis reaction [34].

Table 1. Kinetic constants for the removal and adsorption of Cr(VI) using biosynthesis of FeS_{1+x}.

	Pseudo-Frist-Order Kinetic			Pseudo-Secondary Kinetic			General-Order Models				Experiment Data
	k ₁ (min ^{−1})	q _e (mg/g)	R ²	k ₂ (min(mg/g) ^{−1})	q _e (mg/g)	R ²	k _n	n	t _{0.5}	t _{0.95}	q _e (mg/g)
BS-FeS _{1+x}	2.01 × 10 ^{−1}	24.38	0.972	2.59 × 10 ^{−2}	73.52	0.998	0.017	2.19	0.43	7.61	59.28
BNS-FeS _{1+x}	2.00 × 10 ^{−1}	31.31	0.976	1.50 × 10 ^{−2}	62.42	0.996	0.0099	2.15	0.96	18.29	57.83

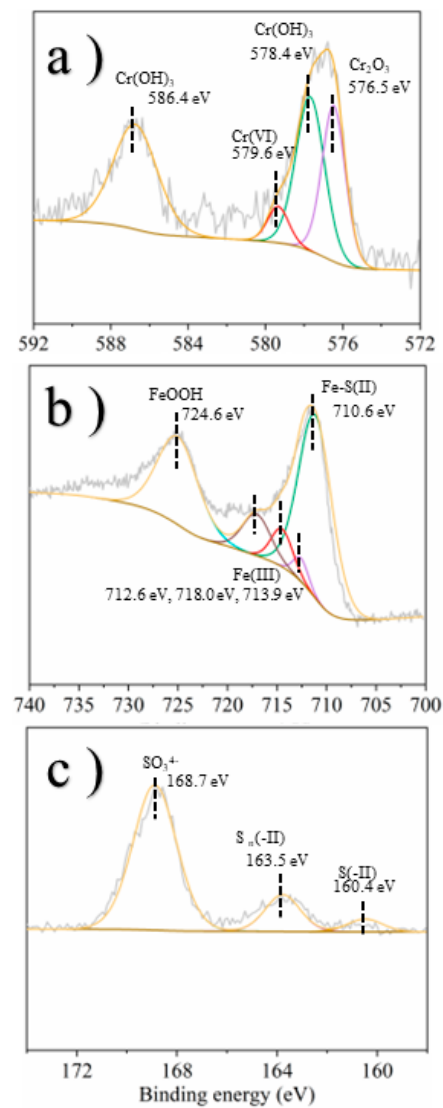


Figure 4. XPS spectra of (a): Cr 2p_{1/2}, (b): Fe 2p_{3/2}, and (c): S 2p_{3/2} after reaction in the presence of FeS. Solid samples were prepared under the following experimental conditions: FeS_{1+x} = 11.4 mM; initial Cr(VI) = 1.14 mM; stirring speed = 200 rpm. The C1s peak at 284.8 eV was chosen to calibrate all the peak positions.

Table 2. XPS analysis fit results of Cr(VI) 2p_{1/2}, S 2p_{3/2} and Fe 2p_{3/2} under anoxic conditions. BS-FeS_{1+x}: biosynthesis of iron sulfides containing SRB.

Type	Elements	B.E.(eV)	Species	Relative Fraction(%)
BS-FeS _{1+x}	Fe 2p _{3/2}	710.6 eV	Fe(II)-S	45.3
		712.6 eV, 718.0 eV, 713.9 eV	Fe(III)	19.5
		724.6 eV	FeOOH	35.2
	S 2p _{3/2}	163.5 eV	Sn(-II)	15.9
		160.4 eV	S(-II)	5.5
		168.7 eV	SO ₄ ²⁻	78.6
	Cr 2p _{1/2}	579.6 eV	Cr(VI)	5.7
		576.5 eV, 578.4 eV, 586.4 eV	Cr(III)	94.3

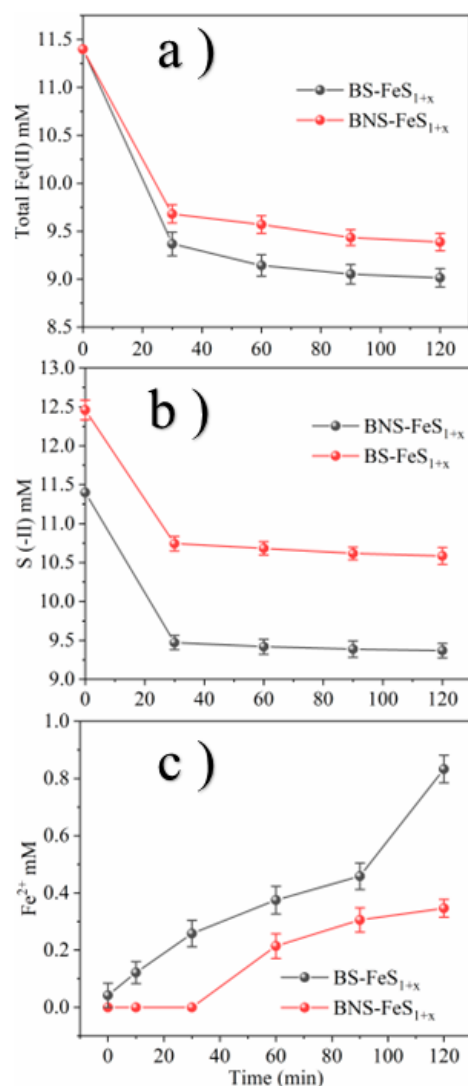


Figure 5. Changes in the concentration of Fe(II) and S(-II) when Cr(VI) is removed from the suspension of BS-FeS_{1+x} and BNS-FeS_{1+x}. (a): Fe(II) concentration change, (b): S(-II) concentration change, and (c): Fe²⁺ concentration change. Reaction conditions: FeS_{1+x} dosage concentration was 11.4 mM; Cr(VI) dosage concentration was 1.14 mM; initial pH was 5.0; reaction time was 2 h; and speed was 200 rpm. BS-FeS_{1+x}: biosynthesis of iron sulfides containing SRB. BNS-FeS_{1+x}: biosynthesis of iron sulfide dry particles without SRB. Data were plotted as means of duplicates, and the error bars indicate the standard deviation.

3.3. Role of *Srb* Bacteria in Cr(Vi) Removal

3.3.1. The Stabilization by SRB

In this study, in order to better understand the role of SRB during pollutant removal, BS-FeS_{1+x} and BNS-FeS_{1+x} were used to remove Cr(VI) in comparative experiments. Therefore, we hypothesized that SRB was one of the reasons for the better removal performance of BS-FeS_{1+x}. The difference in Cr(VI) removal efficiency between BS-FeS_{1+x} and BNS-FeS_{1+x} was examined to confirm the hypothesis. Cr(VI) could be quickly removed by both BS-FeS_{1+x} and BNS-FeS_{1+x} systems (Figure 3a). Therefore, the pseudo-secondary reaction kinetics were explored. The Cr(VI) removal rate of BNS-FeS_{1+x} was $1.50 \times 10^{-2} \text{ (min(mg/g)}^{-1})$, which was 0.58 times that of BS-FeS_{1+x} (Table 1). It could be seen that the solubility of BNS-FeS_{1+x} powder was limited, so the contact area with Cr(VI) was relatively limited. The FeS suspension could be evenly distributed in the solution, and the contact area with pollutants was greatly increased after the addition of the FeS suspension [40]. However, the role of SRB was still a point of controversy. Therefore,

the effect of chemically synthesized FeS suspension and dry particles was also tested. The pseudo-secondary kinetic constant of chemically synthesized FeS dry particles was 0.72 times that of suspension (Figure 6 and Table 3). The $t_{0.5}$ and $t_{0.95}$ of chemically synthesized FeS suspension and dry particles were 0.67, 24.77 and 1.94, 32.57 min, respectively (Table 3). Compared to BS-FeS_{1+x} and BNS-FeS_{1+x}, we found that the difference between BS-FeS_{1+x} and BNS-FeS_{1+x} was greater than that of chemically synthesized FeS, indicating that although the suspension could promote the dispersion and dissolution of FeS, SRB also played a significant role in promoting the removal of Cr(VI). EPS could reduce aggregation of FeS by increasing the negative surface charge and then reducing the propensity of nanoparticles to aggregate [41,42].

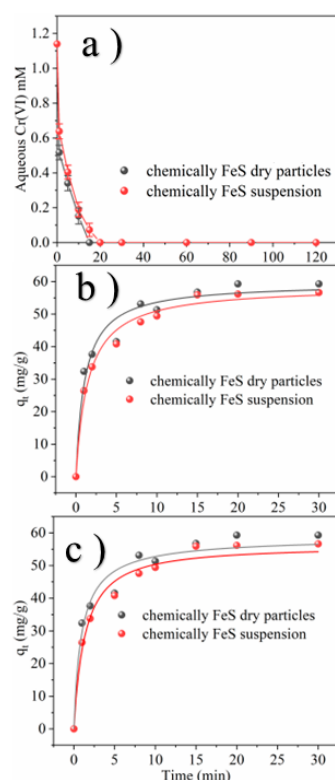


Figure 6. (a,b): Removal effect and reaction kinetics of Cr(VI) by suspension and dry particles of chemical synthesis FeS; (c): adsorption kinetic models of Cr(VI). Reaction conditions: FeS dosage concentration was 11.4 mM; Cr(VI) dosage concentration was 1.14 mM; initial pH was 5.0; reaction time was 2 h; and speed was 200 rpm. Data were plotted as means of duplicates, and the error bars indicate the standard deviation.

Table 3. Kinetic parameters of chemical synthesis FeS suspension and dry particles for Cr(VI) removal and adsorption.

Type	Pseudo-Secondary Kinetic			General-Order Models			
	k_2 (min(mg/g) ^{−1})	q_e (mg/g)	R^2	k_n	n	$t_{0.5}$	$t_{0.95}$
chemical synthesis FeS suspension	1.37×10^{-2}	61.31	0.995	0.0098	2.14	0.67	24.77
chemical synthesis FeS dry particles	1.00×10^{-2}	60.18	0.993	0.022	1.86	1.94	32.57

3.3.2. Enhancement Content of Reductive Species by SRB

It was found that Cr(VI) could also be removed in SRB systems without the presence of Fe(II) (Figure 7). The Cr(VI) removal efficiency of SRB alone reached 63.2% (0.72 mM) within 60 min, and the subsequent reaction reached equilibrium within 150 min (Figure 8), which might be caused by the fact that Cr(VI) could provide electrons to SRB to release a

small amount of S(-II). Therefore, the change in the S(-II) concentration during the reaction was measured. It showed that the peak content of S(-II) reached 3.53 mM at 1 min (Figure 7). It is worth noting that, theoretically, the S(-II) consumed should be not less than 1.43 mM at 60 min. However, the consumption of S(-II) at 60 min was 1.06 mM. It also showed that SRB could remove Cr(VI) by consuming S(-II). Additionally, substances such as EPS produced by SRB might also adsorb Cr(VI) and improve the removal effect of biosynthetic FeS.

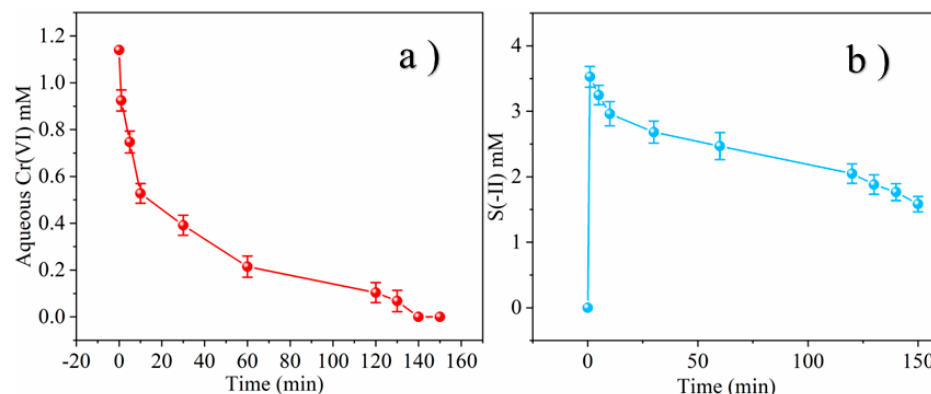


Figure 7. Removal of Cr(VI) by SRB bacteria alone. (a): Cr(VI) removal action, (b): change in concentration of S(-II) in solution. Reaction conditions: Fe(II) dosage concentration was 0 mM; Cr(VI) dosing concentration was 1.14 mM; the initial pH of the reaction was 5.0; the reaction time was 2 h; and the speed was 200 rpm. Data were plotted as means of duplicates, and the error bars indicate the standard deviation.

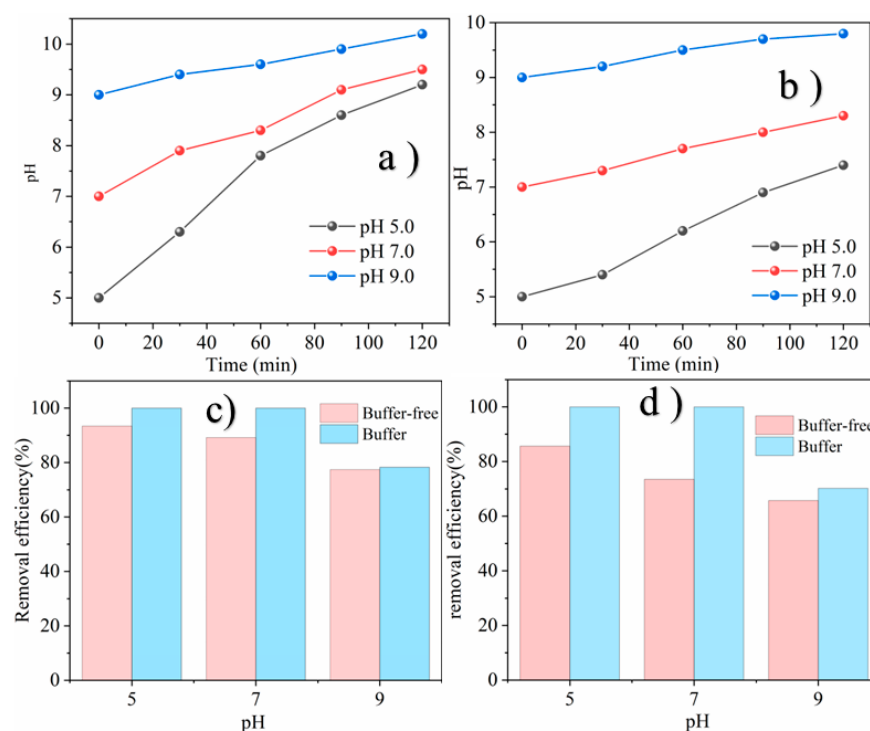


Figure 8. Chemically synthesized FeS and BS-FeS_{1+x} removed Cr(VI) with or without pH buffer. (a,b): pH change without buffer, (c,d): Cr(VI) removal comparison with or without buffer. Reaction conditions: FeS_{1+x} dosage concentration was 1.14 mM; Cr(VI) dosing concentration was 1.14 mM; reaction time was 2 h; and the speed was 200 rpm. BS-FeS_{1+x}: biosynthesis of iron sulfides containing SRB. Data were plotted as means of duplicates, and the error bars indicate the standard deviation.

The change in S(-II) in the BNS-FeS_{1+x} system did not share the same trend with the BS-FeS_{1+x} system (Figure 5). Generally, it could be concluded that SRB would directly remove part of Cr(VI) by producing S(-II). Meanwhile, it was found that Fe(II) in the BS-FeS_{1+x} remained at a higher value than BNS-FeS_{1+x} (Figure 5). This indicated that SRB could accept electrons and continuously release S(-II) during the reaction. It would have a promotion effect on the reduction of structural Fe(III), which accelerated the cycle of Fe(II)/Fe(III) in the system [43,44]; this would increase the Fe(II) in solution and could also promote the rapid dissolution of Fe(II) [43]. Thus, the presence of SRB was one of the reasons for the increase in the removal efficiency. This extraordinary activity of the BS-FeS_{1+x} was mainly attributed to its well-dispersed structure and higher content of reductive species, such as structural Fe(II) and disulfide [19].

To further explore the increased Cr(VI) removal efficiency of BS-FeS_{1+x}, the amount of dissolved Fe(II) during the reaction was also examined. In the BS-FeS_{1+x} system, the dissolved Fe(II) appeared before the reaction and always maintained a high value during the reaction. However, the dissolved Fe(II) in the dry particle system did not appear until 30 min. It could be seen that BS-FeS_{1+x} could not only continuously release S(-II) but also promote Fe(II) dissolution due to the presence of SRB, thereby improving the reduction ability of FeS to remove Cr(VI). EPS and other substances in SRB could promote dissolution or complexation with Fe during biosynthesis [43,45,46].

3.3.3. The Buffering Capacity of SRB

As mentioned above, the presence of SRB could not only promote the stabilization of FeS_{1+x} but also promote the production of reducing agents. In order to find out whether SRB had a buffering effect on the pH, the biosynthetic and chemically synthesized suspensions were used in the buffer and buffer-free systems.

In the chemical synthesis FeS system, the Cr(VI) removal efficiency without the presence of buffers at pH 5.0, 7.0 and 9.0 was 85.6%, 73.5% and 65.7%, respectively, while the Cr(VI) removal efficiency reached 100% when pH was 5.0 and 7.0 in the buffer system (Figure 8). Additionally, the Cr(VI) removal efficiency with the absence of buffers slowly decreased with the increase in pH. The BS-FeS_{1+x} systems shared the same trend with the chemical synthesis FeS system in the absence of buffers. In the no-buffer system, the Cr(VI) removal efficiency was 93.4%, 89.2% and 77.4% when pH was 5.0, 7.0 and 9.0, respectively; in the buffer system, the Cr(VI) removal efficiency was 100%, 100% and 78.3% at pH 5.0, 7.0 and 9.0, respectively (Figure 8). Moreover, it was found that when there was no buffer in the solution, the pH changed greatly in the chemical synthesis group. When the pH was 5.0, 7.0 and 9.0 in the chemical synthesis FeS system, the pH increased to 9.2, 9.5 and 10.2 after 2 h, respectively (Figure 8), while in the BS-FeS_{1+x} buffer-free system, the pH of the solution rose to 7.4, 8.3 and 9.8 after 2 h, respectively (Figure 8). Liu and Wang et al. found EPS has a strong buffering capacity [17,46]. Compared with the chemical synthesis group, it was found that the presence of SRB inhibited the change in pH, which would enhance the Cr(VI) removal efficiency. Research has shown that pH also had an influence on the morphology of the final product Cr(III). When the pH is within 6–8 at the end of the reaction, Cr(III) can completely break away from the solution phase in the form of precipitate [24,47]. Hence, when BS-FeS_{1+x} is used for in situ remediation, the presence of SRB can not only promote the reduction of Cr(VI), but also play a buffering role to make Cr(III) easier to precipitate, thereby removing the pollutants. However, the role of SRB in removing Cr(VI) should be further explored by analyzing the EPS extraction.

As mentioned above, we have summarized the role of SRB (Figure 9). SRB have three main points of promotion. First, SRB could release more S(-II), which not only reduced Cr(VI) directly but also might have reduced Fe(III) to Fe(II). Second, SRB could promote the dispersion and dissolution of FeS to make FeS more stable. Moreover, the buffering effect of SRB could reduce the change in pH, resulting in the high value of the removal efficiency. SRB itself had been less-studied for Cr(VI) removal. We compared the effects of FeS on Cr(VI) in other studies (Table 4). The maximum removal capacities of BS-FeS_{1+x} and

BNS-FeS_{1+x} were 73.52 mg/g and 62.42 mg/g, respectively, and both materials displayed a good removal capacity toward Cr(VI) compared to many other adsorbents. These experimental results demonstrated that both BS-FeS_{1+x} and BNS-FeS_{1+x} were excellent adsorbents for Cr(VI) uptake from aqueous solutions.

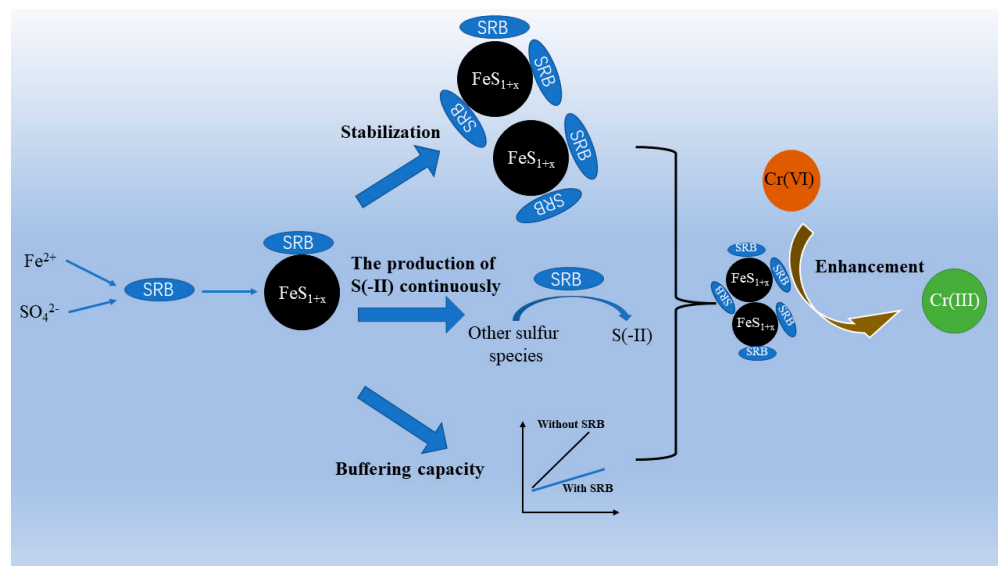


Figure 9. Conceptualized illustration of the mechanisms of the effect of SRB on the removal of Cr(VI) under anoxic conditions.

Table 4. Maximum adsorption capacities of some adsorbents for the removal of Cr(VI) ions.

Sample	pH	Reaction Time	Removal Capability (mg/g)	References
FeS ^a	5.5	72 h	38.6	[20]
FeS@FeO ^a	5.6	1 h	66.7	[20]
Fe/FeS ^a	5	48 h	69.7	[43]
BS-FeS _{1+x}	5	2 h	73.52	This study
BNS-FeS _{1+x}	5	2 h	62.42	This study

^a: Chemically synthesized FeS.

3.4. Effects of pH and FeS-to-Cr(III) Molar Ratios on Cr(VI) Reduction

It has been considered that the removal of heavy metals is influenced by initial pH [48,49]. Therefore, removal kinetic simulations were performed. The pseudo-secondary kinetic constants k_2 of BS-FeS_{1+x} at pH 5.0 was 1.7 and 3.0 times higher than those of pH 7.0 and 9.0, respectively, and they were the same as the adsorption kinetic models (Figure 10a,b and Table 5). It showed that pH had a great influence on Cr(VI) removal, and its reaction rate decreased with the increase in pH [37,50]. Other substances containing Fe²⁺ or S²⁻ respond similarly to pH during the removal of Cr(VI) [51,52]. The influence of pH could be explained by the following reasons: 1. The increase in pH leads to greater formation of iron (hydr)oxides on the FeS surface, resulting in fewer reactive points [53]. 2. OH⁻ increased in the solution with the pH, which intensifies the competition for FeS with the oxygenated anions of Cr(VI) [54,55]. 3. The main forms of Cr under acidic conditions are Cr₂O₇²⁻ and CrO₄²⁻. As the pH increases, there is only a stable form of Cr (CrO₄²⁻) and a less polymerized form of Cr oxide in the solution. HCrO₄⁻ is more easily adsorbed on the FeS surface under acidic conditions, resulting in a faster reaction rate [56]. Different molar ratios of Cr(VI) and FeS, such as 1:1, 1:5 and 1:10, were used to explore the effect of Cr(VI) and BS-FeS_{1+x} ratio on the removal of Cr(VI). The Cr(VI) removal efficiency of 1:1, 5:1 and 10:1 molar ratio was 93.4%, 100% and 100%, respectively (Figure 10c), and

the trend gradually expanded as the initial concentration increased. The $t_{0.5}$ and $t_{0.95}$ of BS-FeS_{1+x} at different pH and molar ratios illustrated that pH and molar ratio were the important factors in adsorption.

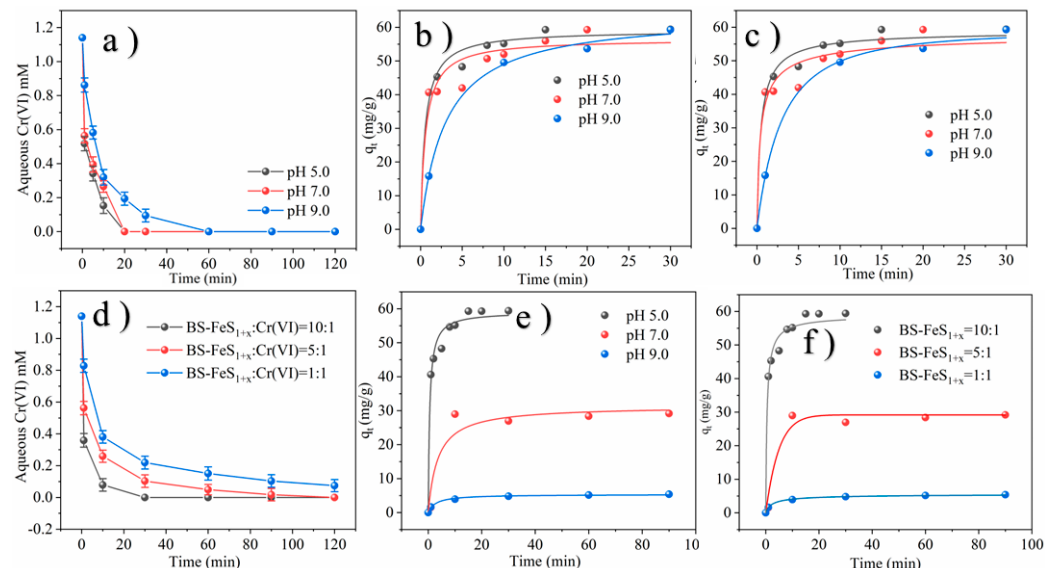


Figure 10. (a): Removal effect, (b): Pseudo-second-order kinetic fitting of Cr(VI) removal by BS-FeS_{1+x} under different pH conditions (5.0, 7.0 and 9.0), (c): Adsorption kinetic models of Cr(VI) under different pH, (d): Removal effect, (e): Pseudo-second-order kinetic fitting of Cr(VI) removal under different FeS_{1+x}:Cr(VI) molar ratios (10:1, 5:1 and 1:1), and (f): adsorption kinetic models of Cr(VI) under different molar ratios. Reaction conditions: FeS dosage concentration was 11.4 mM; Cr(VI) dosage concentration was 1.14 mM; initial pH was 5.0; reaction time was 2 h; and speed was 200 rpm. BS-FeS_{1+x}: biosynthesis of iron sulfides containing SRB. Data were plotted as means of duplicates, and the error bars indicate the standard deviation.

Table 5. Kinetic constants for the removal and adsorption of Cr(VI) using biosynthetic FeS_{1+x} under different pH (5.0, 7.0, 9.0) and FeS:Cr(VI) molar ratios (10:1, 5:1, 1:1).

pH	k_2 (min(mg/g) ^{−1})	q_e (mg/g)	R^2	k_n	n	$t_{0.5}$	$t_{0.95}$
5.0	2.59×10^{-2}	73.52	0.998	0.017	2.19	0.43	7.61
7.0	1.53×10^{-2}	60.86	0.996	0.0019	2.77	0.50	24.32
9.0	0.94×10^{-2}	62.22	0.992	0.031	1.57	2.59	42.34
FeS:Cr(VI)							
10:1	2.59×10^{-2}	73.52	0.998	0.017	2.19	0.43	7.61
5:1	0.45×10^{-2}	62.56	0.998	0.245	0.945	3.32	13.51
1:1	0.73×10^{-1}	50.45	0.997	0.018	2.78	3.59	234.15

4. Conclusions

Biosynthetic FeS_{1+x} showed different properties from chemical synthesis. During synthesis, it would produce other iron minerals (i.g. vivianite), and with the increase in time, the morphology of FeS_{1+x} also changed. BS-FeS_{1+x} showed good performance with respect to the Cr(VI) removal efficiency and rate. At the same time, the presence of SRB promoted the removal of Cr(VI). There were three main reasons for this phenomenon: 1. The presence of SRB could continuously generate S, which not only reduced Cr(VI) directly but also might make Fe(III) become Fe(II) again. 2. The presence of SRB could also play a role in stabilizing FeS_{1+x}. 3. Meanwhile, the buffering effect of SRB could reduce the change in pH, resulting in the high value of the removal efficiency. In summary, in actual in situ pollutant remediation the presence of SRB can enhance Cr(VI) removal efficiency.

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