Cr(VI) removal from aqueous solution by dried activated sludge biomass

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ABSTRACT

Batch experiments were conducted to remove Cr(VI) from aqueous solution using activated sludge biomass. The effects of acid pretreatment of the biomass, initial pH, biomass and Cr(VI) concentrations on Cr(VI) removal efficiency were investigated. Proton consumption during the removal process and the reducing capacity of sludge biomass were studied. The results show that acid pretreatment could significantly improve Cr(VI) removal efficiency and increase Cr(VI) reducing capacity by 20.4%. Cr(VI) removal was remarkably pH-dependent; lower pH (pH = 1, 2) facilitated Cr(VI) reduction while higher pH (pH = 3, 4) favored sorption of the converted Cr(III). Lower Cr(VI) concentration as well as higher biomass concentration could accelerate Cr(VI) removal. Cr(VI) reduction was not the only reason for proton consumption in the removal process. Pseudo-second-order adsorption kinetic model could successfully simulate Cr(VI) removal except under higher pH conditions (pH = 3, 4).

1. Introduction

Chromium is a common contaminant which mainly exists in two stable states, Cr(III) and Cr(VI), in aquatic environment. Cr(VI) is of particular concern due to its high toxicity to human, animals, and plants. And the presence of Cr(VI) in wastewater in high concentration could significantly inhibit biomass growth during biological treatment processes [1]. Reduction of Cr(VI) to less mobile and toxic Cr(III) by a variety of inorganic and organic reductants has been recognized as an important remediation strategy for Cr contaminant control [2].

Conventional technologies for Cr(VI) removal from aqueous solution include chemical reduction/precipitation, ion exchange, membrane separation, and adsorption [3]. An increasing attention has been paid recently to the use of eco-friendly and low-cost biomaterials for Cr removal from wastewater, such as bacteria, fungi, algae, industrial and agricultural wastes [4–7].

Waste activated sludge, mainly consisting of polysaccharides, proteins and lipids, has been proved to be an effective biosorbent which could bind metal ions by various functional groups, such as carboxyl, carboxylic acid and amine groups [8–10]. Selvaraj et al. [11] evaluated the effectiveness of distillery sludge as biosorbent to remove Cr(VI) from aqueous solution and then used adsorption-based models to describe the process. Liu et al. [12] proved with X-ray absorption near-edge spectroscopic analysis that, Cr(VI) ions could be reduced to Cr(III) ions by wine processing waste sludge. More recent investigations have recommended the biomaterials of seaweed [13], fungi [14] and agricultural wastes [15] as organic reductants rather than adsorbents for Cr(VI) removal from wastewater. It is obvious that reduction of Cr(VI) is of great importance in Cr(VI) contaminant control. However, more attention has been paid to the adsorption behavior of Cr(VI) by sludge biomass while the reducing potential of sludge biomass as one kind of organic reductant for Cr(VI) has seldom been discussed.

The removal of Cr(VI) by various biomaterials is influenced by many factors including Cr(VI) concentration, biomass properties, pH, etc. [16–19]. Among these, pH is one of the most important environmental factors, which affects not only biomass surface chemistry but also metal speciation [20]. Higher removal efficiency of Cr(III) was found at pH 7–8 while lower pH favored removal of Cr(VI) [21,22]. In addition, the properties of biomass also played an important role in Cr(VI) removal [23]. Although waste activated sludge may have a potential of high reducing capacity due to its high amount of organic substances, low removal ratio (less than 40%) of Cr(VI) was attained while wine processing waste sludge was used [12]. The possible reason is that protons in the solution were considerably consumed by the sludge and then Cr(VI) reduction was impeded. Acid pretreatment could effectively improve Cr(VI) removal when sediment [24], brown seaweed [25], palm flower [21], and green alga [26] were adopted as biosorbents, by replacing the natural mix of ionic species bound on the biomass surface with protons to increase the positive charges which would facilitate the sorption of Cr anions. The effect of acid pretreatment on Cr(VI) removal by sludge biomass has not been investigated yet.

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Table 1
Experimental parameters for the Cr(VI) removal processes.

Test	Sludge biomass sample	Biomass concentration (g/L)	Initial Cr(VI) concentration (mg/L)	Initial pH value	Time
Acid pretreatment	Raw and protonated	10	0 (control test), 100	2	24 h
Initial Cr(VI) concentration	Protonated	10	50, 100, 150, 200	2	Until equilibrium
Biomass concentration	Protonated	5, 10, 15, 20	100	2	Until equilibrium
Initial pH value	Protonated	10	100	1, 2, 3, 4	Until equilibrium
Reducing capacity	Protonated	0.171, 0.332, 0.491	300	1	10 days
	Raw	0.190, 0.377, 0.498	300	1	10 days

In this study, activated sludge was used for Cr(VI) removal and acid pretreatment of sludge biomass was adopted to improve its removal efficiency. To elucidate the possible mechanisms involved in Cr(VI) removal, reducing capacity of sludge biomass, proton consumption during the removal process and the factors affecting Cr(VI) removal were investigated. Kinetic models based on reduction and adsorption were applied to describe the process. The objective of this study was to indicate whether protonated sludge biomass could be a potential alternative to existing reducing agents and adsorbents for Cr(VI) removal from aquatic environment.

2. Materials and methods

2.1. Preparation of sludge biomass

The activated sludge was obtained from the aeration tank of a municipal wastewater treatment plant in Shanghai, China. The plant treats 75000 m^3/d of wastewater (93% from domestic and 7% from industrial origins) using anaerobic-anoxic-oxic process. The sludge was dried at 60 °C to constant weight after precipitation and centrifugation. The dried sludge was ground, sieved and the particles obtained with diameter of less than 0.45 mm were stored in a desiccator as raw sludge biomass for the following experiments. The elemental analysis (Vario EL III, Elementar, German) showed that the raw sludge biomass contained 29.5% of carbon, 4.9% of hydrogen, 58.1% of oxygen, 5.7% of nitrogen and 1.8% of sulfur (by dry weight, the same below).

The protonated sludge biomass was prepared by adding 5 g of the raw sludge biomass into 250 mL of HCl solution (0.1 mol/L) and then stirring the mixture at 200 rpm for 8 h at 25 ± 0.1 °C [26]. Thereafter, the acid-treated biomass was washed with deionized water several times until the pH did not change, and then the sludge was dried, ground, sieved, as the raw sludge biomass was done.

The metal compositions of the raw and protonated sludge biomass were determined by an inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ICP-optima 2001DV, Perkin-Elmer, USA) after acid digestion with aqua regia.

2.2. Preparation of Cr(VI) solution

The stock solution of 1000 mg/L Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ (analytical reagent grade) in deionized water. All working concentrations were obtained by diluting the stock solution with deionized water, and pH was adjusted to the desired values with 1 mol/L HCl or 1 mol/L NaOH solution.

2.3. Cr(VI) removal experiments

Batch experiments were performed in 250-mL conical flasks by mixing desired amount of the sludge biomass with 100-mL solution of known Cr(VI) concentration. The effects of acid pretreatment of biomass, initial Cr(VI) and biomass concentrations, initial pH values as well as contact time on Cr(VI) removal were studied, as illus-

trated in Table 1. To explore the reducing capacity of the sludge biomass, a small amount of the biomass was used to contact with 300 mg/L Cr(VI) at initial pH 1.0 until Cr(VI) concentration remained unchanged. In these biomass-limited experiments, Cr(VI) could still exist in the solution after the biomass was completely oxidized by Cr(VI). Except for the experiments conducted to evaluate the effect of acid pretreatment on Cr(VI) removal efficiency and reducing capacity of the sludge biomass, all the biomass used in this study was protonated. In all the experiments, the flasks were agitated on a shaker at 200 rpm at room temperature (25 ± 0.1 °C). Control tests (without addition of Cr(VI)) were conducted for comparison. The solution was intermittently sampled (1.5 mL from each flask) and centrifuged at 4000 rpm for 15 min, and the supernatant was used for the determination of Cr(VI) and total Cr. All the experiments were conducted in duplicate to confirm the results and the data were the mean values of the replicate determinations (with relative standard deviation less than 5%).

2.4. Chromium analysis

The concentrations of total Cr in the liquid samples were determined by an ICP-AES (ICP-optima 2001DV, Perkin-Elmer, USA). The concentrations of Cr(VI) were analyzed by measuring the absorbance of the purple complex of Cr(VI) with 1,5-diphenylcarbohydrazide at 540 nm by a 732 UV spectrophotometer (Precision & Scientific Instrument Co., Shanghai, China) [27]. The concentrations of Cr(III) were then obtained from the difference between total Cr and Cr(VI) concentrations.

3. Results

3.1. Effect of acid pretreatment on Cr(VI) removal

As illustrated in Fig. 1a, the suspension pH of the raw biomass increased from 2.0 to 6.0 in 24 h during the Cr(VI) removal process, namely 99.99% of hydrogen ions in the solution were consumed by 1 g of sludge biomass. This weakened the redox reaction and induced a considerable decrease of Cr(VI) removal (Fig. 1b). Similar result was found in the study of Liu et al. using wine processing waste sludge [12]. And they proposed that the increase of pH was attributed to the dissolution of basic materials of sludge biomass.

Sludge biomass is a typical organic complex mainly presenting a negative surface charge which could easily bind with positive cations. And Cr(VI) ions mostly exists as the following oxyanions: $Cr_2O_7^{2-}$ in strongly acidic medium (pH < 1), $HCrO_4^-$ in acidic environment (pH 2–6), and CrO_4^{2-} in neutral and alkaline conditions (pH > 6) [2]. Therefore, the raw biomass was not much favorable for Cr(VI) sorption. After acid pretreatment, however, the functional groups of the biomass were protonated and positively charged, thus becoming available for Cr(VI) anion sorption. Fig. 1b proves that only 65.0% of Cr(VI) removal ratio was attained by the raw sludge
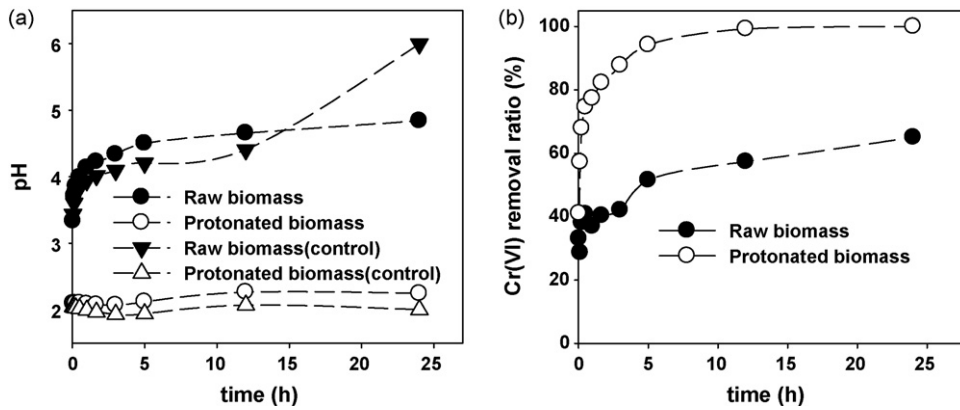
Fig. 1. Effect of acid pretreatment on (a) the suspension pH and (b) Cr(VI) removal efficiency (Cr(VI) = 100 mg/L, initial pH = 2, sludge biomass = 10 g/L).

Table 2
Metal concentrations in the raw and protonated sludge biomass.

Metal	Ca	Mg	Al	Fe	Cr (total)
Raw sludge biomass (mg/g)	9.33	3.07	4.25	6.20	0.02
Protonated sludge biomass (mg/g)	0.28	1.09	3.46	6.22	0.02

biomass while the protonated sludge biomass removed almost 100% of Cr(VI) from the solution within 12 h.

The pH value changed little (1.9–2.3) in the tests with protonated biomass. Marked differences in the content of Ca (reduced by 97.0% after acid pretreatment) and Mg (reduced by 64.5% after acid pretreatment) were observed between the raw and protonated sludge biomass, while only negligible effects on Fe and Cr removal (Table 2) were obtained. These results confirmed that

Ca and Mg ions contributed a lot in hydrogen ions consumption. Acid pretreatment of sludge biomass could successfully remove most of hydrogen ions consuming substances and supply comparatively steady acid environment which will facilitate Cr(VI) removal.

3.2. Effect of initial pH on Cr(VI) reduction and total Cr removal

The effect of initial pH on Cr(VI) removal by the protonated sludge biomass was shown in Fig. 2. Cr(VI) could be completely removed from the aqueous solution, even at pH 4, as long as sufficient contact time was given. The contact time required for complete removal of Cr(VI) was 3 h, 24 h, 240 h and 360 h at initial pH 1, 2, 3, and 4 respectively, and the corresponding final pH was 1.0, 2.1, 4.5 and 5.1 (data not shown).
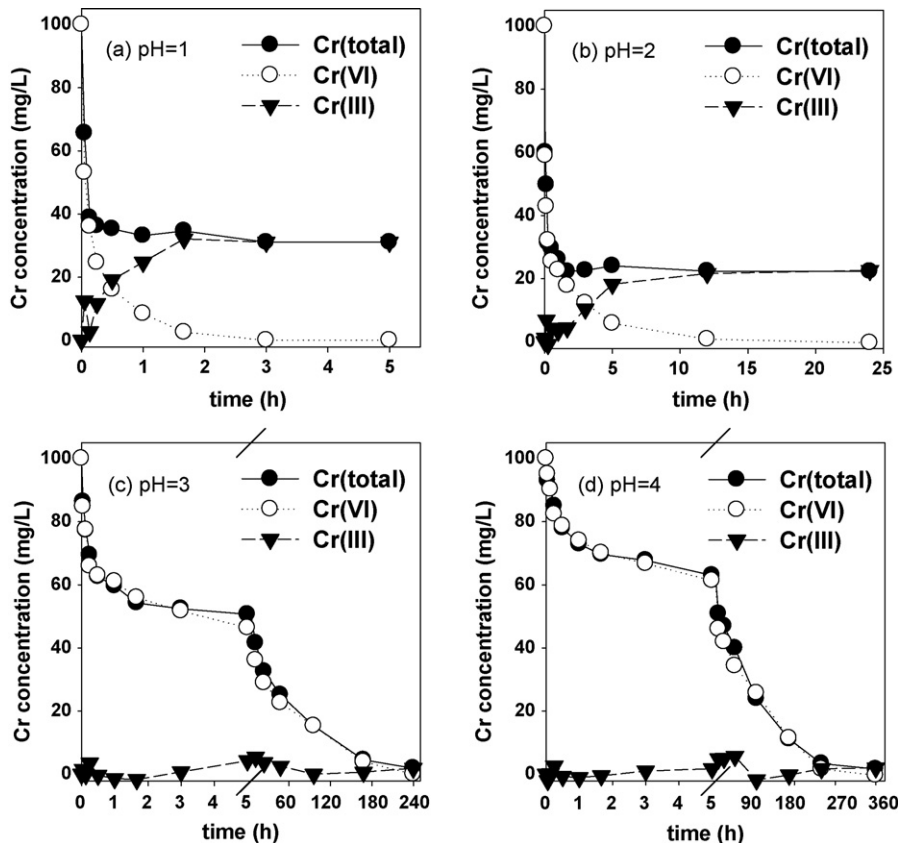

Fig. 2. Effect of initial pH on Cr removal (protonated sludge biomass = 10 g/L, Cr(VI) = 100 mg/L).
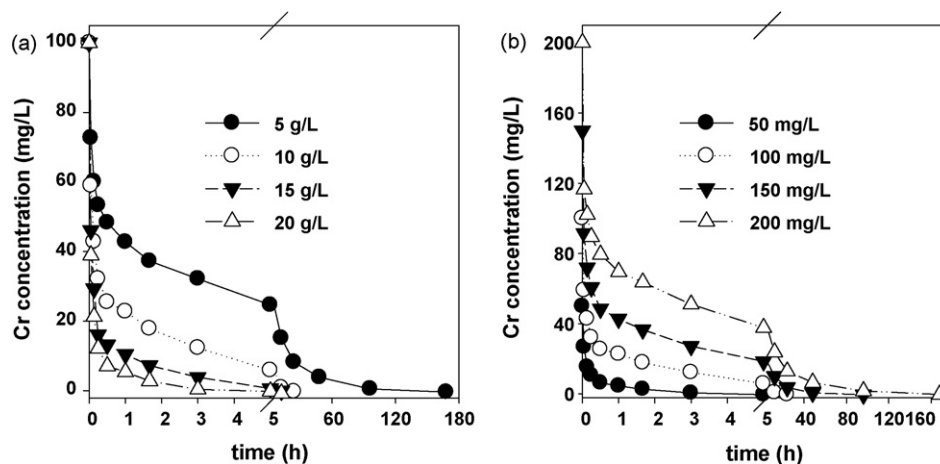
Fig. 3. Effects of (a) initial protonated sludge biomass concentration (initial pH = 2, Cr(VI) = 100 mg/L) and (b) Cr(VI) concentration (initial pH = 2, protonated sludge biomass = 10 g/L) on Cr(VI) removal.

Table 3
Cr(VI) removal under biomass-limiting condition.

Biomass-limited experiments	Protonated sludge biomass			Raw sludge biomass		
Biomass concentration (g/L)	0.171	0.332	0.491	0.190	0.377	0.498
Final Cr(VI) concentration (mg/L)	258	224	200	261	231	212
Cr(VI) reduced/biomass (mg/g)	246	229	203	204	184	176
Average Cr(VI) reducing capacity (mg/g)		226			188	

The Cr(VI) concentration decreased rapidly and Cr(III), which initially did not exist, appeared in the aqueous phase and its concentration increased proportionally to the Cr(VI) depletion at initial pH 1 and 2. These results indicated that Cr(VI) was reduced to Cr(III) when contacting with the biomass and some of the converted Cr(III) released into the aqueous phase. The removal procedure was supposed to involve sorption and reduction which may go through certain stages: (i) sorption of Cr(VI) onto the biomass surface, (ii) reduction of Cr(VI) to Cr(III) by surface functional groups, (iii) release of the converted Cr(III) from, or sorption to various functional groups of the biomass depending on environmental factors, especially pH value. Cr(VI) usually exists in anionic form while Cr(III) preferably exists in cationic form. The biomass surface was positively charged at low pH which facilitated the sorption of anions while hampered the sorption of cations. This resulted in higher removal of Cr(VI) and lower sorption efficiency of the converted Cr(III) in acidic environment. The total Cr removal ratio was 68.9% and 77.7% respectively at pH 1 and 2.

Cr(VI) reduction rate was relatively slow at pH 3 and 4 compared with that at pH 1 and 2, and longer contact time was required for complete removal of Cr(VI). Not only Cr(VI) but also total Cr achieved high removal ratio, i.e., 98.1% for initial pH 3 and 98.4% for initial pH 4. The Cr(III) concentrations in the solution were always at a low level (never more than 6 mg/L), different from the increasing trend at lower pH (pH = 1, 2), indicating that the formation of Cr(III) may be a limit step under higher pH conditions (pH = 3, 4) due to limited H$^+$ available for Cr(VI) reduction. According to the aqueous equilibrium calculation for Cr(III) solubility using Visual MINTEQ, almost 100% of Cr(III) could be dissolved at pH < 4, while only 2.5 mg/L of Cr(III) is dissolved at pH 5.1, and 50.2 mg/L of Cr(III) is soluble at pH 4.5. It could be suggested that besides reduction and adsorption, precipitation of the converted Cr(III) also played an important role in Cr removal under higher pH conditions.

3.3. Effects of biomass and Cr(VI) concentrations on Cr(VI) removal

The effect of sludge biomass concentration on Cr(VI) removal at initial pH 2.0 was shown in Fig. 3a. In all of the batch tests with 5, 10, 15 and 20 g/L of biomass, Cr(VI) could be completely removed from the solution, and the equilibrium time was 168 h, 24 h, 12 h, and 5 h respectively. A rapid removal of Cr(VI) took place in the first 30 min, then the rate slowed down. The equilibrium time was also dependent on initial Cr(VI) concentration. The respective equilibrium time with initial Cr(VI) concentrations of 50, 100, 150 and 200 mg/L was 5 h, 12 h, 96 h and 168 h (Fig. 3b). Lower Cr(VI) concentration as well as higher biomass concentration could enhance the removal ratio and shorten the equilibrium time for Cr(VI) removal.

3.4. Cr(VI) reducing capacity of sludge biomass

Biomass-limited experiments were conducted to evaluate the Cr(VI) reducing capacity of the raw and protonated sludge biomass. Table 3 shows that 1 g of the protonated sludge biomass could reduce 226 mg of Cr(VI) at pH 1, while 1 g of the raw biomass could only reduce 188 mg of Cr(VI). It indicated that acid pretreatment could improve the reducing capacity of the biomass by 20.4%. Compared with the common chemical reductant FeSO$_4$·7H$_2$O which could reduce 62.4 mg of Cr(VI) per gram theoretically, the Cr(VI) reducing capacity of protonated sludge biomass is 3.6 times higher. Therefore, sludge biomass might be a potential substitute for chemical reductants.

4. Discussion

4.1. Proton consumption during the Cr(VI) removal

To gain an insight into the role of H$^+$ during the Cr(VI) removal, equilibrium batch experiments were conducted with different
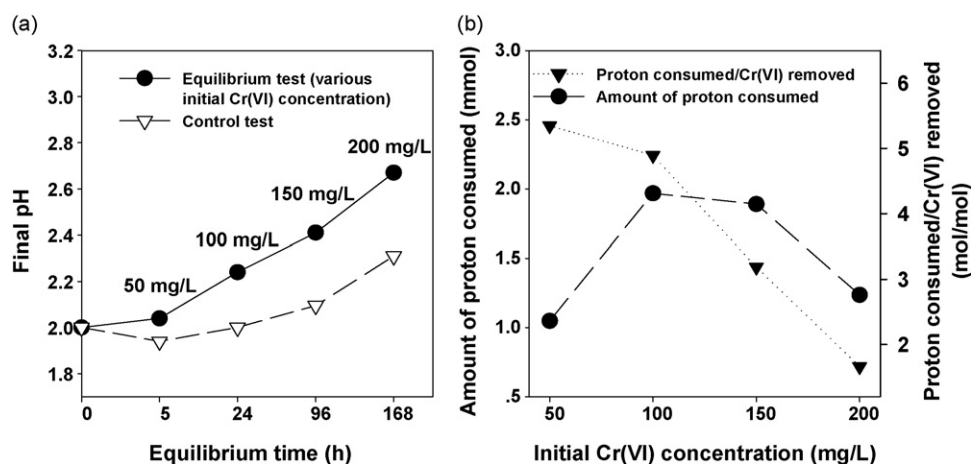
Fig. 4. Final pH (a) and proton consumption (b) during Cr(VI) removal with various initial Cr(VI) concentrations (sludge biomass = 10 g/L, initial pH 2).

Cr(VI) concentrations at uniform initial solution pH (pH = 2). The equilibrium time for completely removed Cr(VI) from aqueous solution of various initial Cr(VI) concentrations of 50, 100, 150, 200 mg/L, was 5, 12, 96, 168 h, respectively. The ratio of proton consumed (mol) to Cr(VI) removed (mol) was calculated by subtracting the final proton concentration of each trial from that of the control test and then divided by the amount of Cr(VI) reduced. Fig. 4a shows that the final pH increased with the increasing amount of Cr(VI) reduced. Compared with the pH values of the control test, it is obvious that hydrogen ions had participated in the Cr(VI) removal process.

Reduction of Cr(VI) was supposed to be the main cause for proton consumption in the solution [13]. However, the proton consumption ratio decreased remarkably with the increasing amount of Cr(VI) (Fig. 4b). This implies that Cr(VI) reduction was not the only reason for pH fluctuations. The reactions which hydrogen ions

participated in were complex. Biosorption of the converted Cr(III) through ion exchange was supposed to be the main reason for the increased acidity [12]. Meanwhile, hydrolysis of the converted Cr(III) may also contribute to the pH decline. As pH increased, sorption and hydrolysis of the converted Cr(III) were more favorable, which may explain the decrease of proton consumption ratio.

In this study, $HCrO_4^-$ was the predominant Cr(VI) species according to the pH conditions [28,29]. The theoretical proton consumption amount for reducing 1 mol $HCrO_4^-$ is 7 mol (Eq. (1)), obviously higher than the maximum proton consumption ratio 2.46 mol/mol in this study, 1.17 mol/mol in Park's literature [13], and 4.45 mol/mol in Gao's study [30]:

$$HCrO_4^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \quad E^0 = +1.35\,V \qquad (1)$$
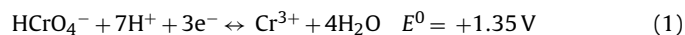
It could be deduced that the changes in H^+ resulted from other reactions besides Cr(VI) reduction were also very

Table 4
Regression parameters of the kinetic models for Cr(VI) removal.

Item	Value	Pseudo-first-order			Pseudo-second-order		
		R^2	SE	k	R^2	SE	k
Reduction kinetics							
Initial Cr(VI) concentration	50	0.9493	0.3145	1.1195	0.8620	0.2539	0.5409
	100	0.9684	0.2490	0.3326	0.8991	0.1399	0.1008
	150	0.9465	0.3709	0.0991	0.8716	0.1984	0.0328
	200	0.9105	0.408	0.0429	0.9294	0.0485	0.0058
Initial biomass concentration	5	0.9523	0.3319	0.0488	0.8560	0.225	0.0181
	10	0.9684	0.2490	0.3326	0.8991	0.1399	0.1008
	5	0.9429	0.3484	0.7514	0.7924	0.2791	0.2895
	20	0.9506	0.3839	1.4354	0.7997	0.5656	0.9628
Initial pH	1	0.9799	0.1749	1.7492	0.8948	0.0521	0.2175
	2	0.9684	0.2490	0.3326	0.8991	0.1399	0.1008
	3	0.9383	0.2194	0.0162	0.8781	0.0241	0.0012
	4	0.9479	0.2597	0.0143	0.6970	0.0904	0.0018
Adsorption kinetics							
Initial Cr(VI) concentration	50	0.9493	0.3145	1.1195	0.9996	0.0049	2.7027
	100	0.9684	0.2490	0.3326	0.9989	0.0140	0.4587
	150	0.9465	0.3709	0.0991	0.9997	0.0190	0.1628
	200	0.9105	0.4080	0.0429	0.9996	0.0291	0.0700
Initial biomass concentration	5	0.9523	0.3319	0.0488	0.9993	0.0399	0.0503
	10	0.9684	0.2490	0.3326	0.9989	0.0140	0.4587
	15	0.9429	0.3484	0.7514	0.9995	0.0064	1.9546
	20	0.9506	0.3839	1.4354	0.9999	0.0029	4.7619
Initial pH	1	0.9799	0.1749	1.7492	0.9990	0.0022	1.2346
	2	0.9684	0.2490	0.3326	0.9989	0.0140	0.4587
	3	0.9383	0.2194	0.0162	0.9931	0.4686	0.0289
	4	0.9479	0.2597	0.0143	0.9851	1.0052	0.0131

important, and could not be neglected even under low pH conditions.

4.2. Kinetic study of Cr(VI) removal

Adsorption-based kinetic models were widely used to describe Cr(VI) removal process with various biosorbents [31–33]. From the above analysis, both adsorption and reduction may be involved in Cr(VI) removal by sludge biomass, hence classical kinetic models based on reduction and adsorption were applied to fit the experimental data respectively (Eqs. (2)–(5)).

Pseudo-first-order reduction:

$$\frac{dC}{dt} = -k_1 C, \quad \ln C = \ln C_0 - k_1 t \tag{2}$$

Pseudo-second-order reduction:

$$\frac{dC}{dt} = -k_2 C^2, \quad \frac{1}{C} = k_2 t + \frac{1}{C_0} \tag{3}$$

Pseudo-first-order adsorption:

$$\frac{dq}{dt} = k_3(q_e - q), \quad \ln(q_e - q) = \ln q_e - k_3 t \tag{4}$$

Pseudo-second-order adsorption:

$$\frac{dq}{dt} = k_4(q_e - q)^2, \quad \frac{1}{q_e - q} = \frac{1}{q_e} + k_4 t \tag{5}$$

where C_0 and C are the concentrations of Cr(VI) in the solution (mg/L) at time 0 and t respectively; q and q_e are the adsorption amount of Cr(VI) per gram of sorbent at time t and at equilibrium (mg/g); and k_1, k_2, k_3, k_4 are the apparent rate constants.

The rate constants k_1, k_2, k_3, k_4 were estimated by a linear regression using Sigmaplot 9.0 software and the results are listed in Table 4.

Table 4 indicates that the kinetic models based on reduction reaction, either pseudo-first-order or pseudo-second-order, could not describe the experimental data well, while the pseudo-second-order adsorption model fitted quite well with the batch tests data ($R^2 > 0.998$ and SE < 0.04) for different initial Cr(VI) or biomass concentrations. Although the correlation coefficients R^2 were high ($R^2 > 0.985$) at pH 3 and 4, the pseudo-second-order model was not suitable for simulating the Cr(VI) removal due to their high SE (SE > 0.45), indicating possible differences in the Cr(VI) removal mechanisms at two different pH conditions (pH = 1, 2 and pH = 3, 4). The sorption and reduction of Cr(VI) under lower pH conditions (pH = 1, 2) were more quick than that at higher pH conditions (pH = 3, 4), during which, sorption/desorption and precipitation of the converted Cr(III) may be involved.

5. Conclusions

The sludge biomass could successfully remove both Cr(VI) and the converted Cr(III) from aqueous solution. The mechanisms of Cr(VI) removal involved sorption and reduction of Cr(VI). Acid pretreatment of sludge biomass could successfully remove most of hydrogen ions consuming substances and supply comparatively stable acid environment which facilitated Cr(VI) removal. The Cr(VI) reducing capacity of the raw sludge biomass was about three times higher than that of $FeSO_4 \cdot 7H_2O$. Acid pretreatment of the biomass could further improve the Cr(VI) removal efficiency by 20.4%. Cr(VI) could be completely removed from the aqueous solution, even at pH 4, as long as sufficient contact time was given. Low Cr(VI) concentration, high biomass concentration, as well as low pH could enhance the removal rate and shorten the equilibrium time. Hydrogen ions participated in the reduction of Cr(VI), however, it

was not the only reason for pH fluctuation during the process. Sorption as well as hydrolysis of the converted Cr(III) may also play an important role in pH fluctuation. Kinetic models based on reduction reaction could not describe the experimental data well, while the pseudo-second-order adsorption model fitted quite well with the data except under higher pH conditions (pH = 3, 4). Activated sludge biomass has proved to be a promising biosorbent, as well as an organic reductant, for Cr(VI) removal from aqueous environment.

Acknowledgements

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