

THE ENHANCEMENT OF BENZOQUINONE ON CR (VI) REDUCTION BY EXCESS SLUDGE

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Abstract: The excess sludge is rich in reducing substances, which can convert highly toxic hexavalent chromium (Cr(VI)) into less toxic trivalent chromium (Cr(III)). However, the process often suffers from low electron transfer efficiency. This study investigated the effect of the electron shuttle benzoquinone on the reduction of Cr(VI) by excess sludge. The results showed that, in a system containing 2 g/L of excess sludge and 5 mg/L of Cr(VI), after 30 minutes of reaction, the Cr(VI) removal efficiency increased from 43.2% to 76% as the benzoquinone concentration rose from 0 to 6 μM . However, when the benzoquinone concentration further increased to 10 μM , the removal efficiency decreased to 59.8%. Without benzoquinone, the Cr(VI) removal efficiencies within 30 minutes were 95.8%, 82.8%, 43.2%, 35.7%, and 23.6%, when the pH values were 3, 5, 7, 9, and 11, respectively. After adding benzoquinone, these values changed to 95.5% and 84.8% at pH 3 and 5, and increased to 76%, 54.2%, and 33.4% at pH 7, 9, and 11, respectively. These results indicate that benzoquinone can promote the reduction of Cr(VI) by excess sludge under neutral and alkaline conditions, while under acidic conditions or in the presence of bicarbonate, it has little effect on Cr(VI) reduction.

Keywords: Cr(VI) reduction; Excess sludge; Electron shuttle; Benzoquinone

1 INTRODUCTION

Chromium in nature mainly exists in two valence states: hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)). Among them, Cr(VI) exhibits strong mobility and high toxicity, whereas Cr(III) is almost non-toxic and readily precipitates [1]. Cr(VI) is widely present in industrial wastewater from electroplating, metallurgy, leather processing, and other industries, and its direct discharge can cause severe environmental harm [2]. Reducing Cr(VI) to Cr(III) is one of the important approaches for mitigating Cr(VI) pollution [3].

It is estimated that the amount of excess sludge generated by municipal wastewater treatment plants in China will reach 100 million tons by 2025 [4]. Excess sludge is rich in organic matter, ferrous iron, and microorganisms [5]. These components can serve as electron donors to reduce Cr(VI) to Cr(III) [6]. The use of excess sludge for Cr(VI) reduction not only enables detoxification of Cr(VI), but also promotes the resource utilization of excess sludge. However, the complex composition of excess sludge imposes inherent limitations, including low electron utilization efficiency and inadequate Cr(VI) reduction performance. Benzoquinone, as an electron shuttle, can reversibly cycle between its oxidized form (BQ) and reduced form (H_2Q), enabling rapid electron transfer [7]. BQ may enhance the efficiency of electron transfer from excess sludge to Cr(VI), thereby improving the reduction efficiency of Cr(VI). Due to its operational simplicity, environmental friendliness, and low cost, benzoquinone has become an indispensable auxiliary agent in heavy metal remediation technologies [8].

The objective of this study is to investigate the role of benzoquinone in the reduction of Cr(VI) by excess sludge. Batch experiments were conducted to examine the effects of Cr(VI) concentration, benzoquinone concentration, pH, reaction time, and bicarbonate ions (HCO_3^-) on the reduction of Cr(VI) by sludge. The findings of this study may provide data and practical support for the application of excess sludge in Cr(VI) reduction.

2 MATERIALS AND METHODS

2.1 Experimental Materials

Potassium dichromate, sodium sulfate, benzoquinone, diphenylcarbazide, concentrated sulfuric acid, phosphoric acid, hydrochloric acid, sodium hydroxide, and sodium bicarbonate were all of analytical grade. The activated sludge used in the experiments was collected from the emergency treatment facility of the Huangjiahua Wastewater Treatment Plant and appeared dark gray in color.

2.2 Experimental Methods

2.2.1 Batch reduction experiments

All reactions were conducted in 150 mL conical flasks with a working volume of 100 mL. The sludge dosage was fixed at 2 g/L, and the initial Cr(VI) concentrations were set at 2, 3, 4, 5, and 6 mg/L. The pH of the system was adjusted to 7 using sodium hydroxide or sulfuric acid. The reaction mixtures were stirred at 300 rpm using a magnetic stirrer. At 0, 5,

15, 30, 60, and 120 min, 2 mL samples were collected for the determination of Cr(VI).

2.2.2 Single-factor experiments

To investigate the effect of benzoquinone on Cr(VI) reduction by excess sludge, the Cr(VI) concentration was fixed at 5 mg/L, while the benzoquinone concentration ranged from 2 to 10 μM . With the benzoquinone concentration fixed at 6 $\mu\text{mol/L}$, the system pH was adjusted to 3, 5, 9, and 11 to examine the influence of pH on Cr(VI) reduction. In addition, the HCO_3^- concentration was set at 1, 3, and 5 mM to evaluate the effect of bicarbonate concentration on the reduction of Cr(VI) by excess sludge in the presence of benzoquinone.

2.3 Analytical Methods

The concentration of Cr(VI) was determined using the diphenylcarbazide spectrophotometric method, with a detection limit of 0.004 mg/L. A pseudo-first-order kinetic model $\frac{C_t}{C_0} = \exp^{-kt}$ was applied to fit the variation of Cr(VI) concentration over time, where C_0 and C_t represent the concentrations of Cr(VI) at the initial time and at time t , respectively, and k is the reaction rate constant.

3 RESULTS AND DISCUSSION

3.1 Reduction of Cr(VI) by Excess Sludge under Different Initial Cr(VI) Concentrations

The experimental results are shown in Figure 1. As the initial Cr(VI) concentration increased, the removal efficiency of Cr(VI) decreased. For example, at a reaction time of 60 min, when the initial Cr(VI) concentration increased from 2 to 6 mg/L, the removal efficiency gradually declined from 91.7% to 64.6%.

The fitting results are presented in Table 1. With increasing initial Cr(VI) concentration, the reaction rate constant decreased from 0.034 to 0.018 min^{-1} . This can be attributed to the limited availability of electrons provided by the excess sludge, resulting in a finite capacity for Cr(VI) reduction [9].

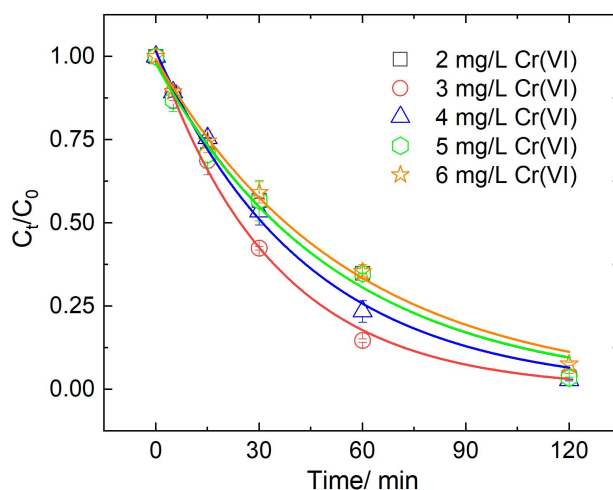


Figure 1 Effect of Cr(VI) Concentration on Cr(VI) Reduction

Table 1 Pseudo-First-Order Kinetic Parameters of Cr(VI) Reduction under the Condition Of Different Cr(VI) Concentrations

Cr(VI) concentration (mg/L)	Reaction rate constant, k (min^{-1})	R^2
2	0.034±0.002	0.996
3	0.029±0.001	0.997
4	0.023±0.002	0.994
5	0.019±0.002	0.988
6	0.018±0.001	0.996

3.2 Effect of Benzoquinone Concentration on Cr(VI) Reduction

To investigate the effect of benzoquinone concentration on Cr(VI) reduction, the Cr(VI) concentration was fixed at 5 mg/L, the sludge dosage at 2 g/L, and the pH at 7, while varying the benzoquinone concentration. The experimental results are shown in Figure 2.

As the benzoquinone concentration increased, its promoting effect on Cr(VI) reduction by excess sludge first increased and then decreased. For example, at 30 min, as the benzoquinone concentration increased from 0 to 6 μM , the removal efficiency of Cr(VI) rose from 43.2% to 76%. However, when the benzoquinone concentration further increased to 10 μM , the removal efficiency decreased to 59.8%. The fitting results are presented in Table 2. When the benzoquinone

concentration was below 10 μM , the optimal promoting effect was observed at 6 μM .

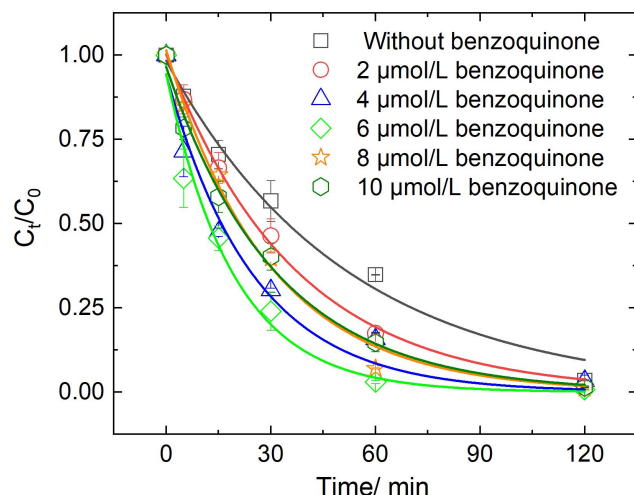


Figure 2 Effect of Benzoquinone Concentration on Cr(VI) Reduction by Excess Sludge

Table 2 Pseudo-First-Order Kinetic Parameters of Cr(VI) Reduction by Excess Sludge under the Condition of Different Benzoquinone Concentrations

Benzoquinone concentration (μM)	Reaction rate constant, k (min^{-1})	R^2
0	0.019 ± 0.002	0.989
2	0.027 ± 0.001	0.998
4	0.04 ± 0.005	0.978
6	0.052 ± 0.007	0.981
8	0.034 ± 0.003	0.992
10	0.032 ± 0.002	0.994

Benzoquinone can act as an electron shuttle, undergoing cyclic transformation between BQ and H_2Q . BQ can accept electrons from organic matter, Fe(II), and other electron donors in excess sludge, thereby being reduced to H_2Q . Subsequently, H_2Q transfers these electrons to Cr(VI) and is oxidized back to BQ, enabling it to repeatedly accept electrons from the sludge [7]. Within an appropriate concentration range, an increase in benzoquinone concentration enhances the number of transferable electrons, thereby progressively improving the reduction of Cr(VI) by excess sludge. However, the electron supply provided by excess sludge is limited [9], further increases in benzoquinone concentration do not result in additional electron transfer. Moreover, at excessively high concentrations, benzoquinone tends to form dimers [10], which adversely affect its electron transfer capability and consequently weaken its promoting effect on Cr(VI) reduction by excess sludge.

3.3 Effect of pH on Cr(VI) Reduction by Excess Sludge in the Presence of Benzoquinone

As shown in Figure 3, the reduction rate of Cr(VI) by excess sludge decreased with increasing pH. For example, at a reaction time of 30 min, in the system without benzoquinone, as the pH increased from 3 to 5, the removal efficiency of Cr(VI) decreased from 95.8% to 82.8%. After the addition of benzoquinone, the removal efficiencies of Cr(VI) were 95.5% and 84.8%, respectively (Figure 3a). As shown in Figure 3b, benzoquinone promoted the reduction of Cr(VI) by excess sludge under neutral and alkaline conditions. For instance, at a reaction time of 30 min, in the system without benzoquinone, as the pH increased from 7 to 9 and 11, the removal efficiency of Cr(VI) gradually decreased from 43.2% to 35.7% and 23.6%, respectively. After the addition of benzoquinone, the removal efficiency of Cr(VI) increased to 76%, 54.2%, and 33.4%, respectively.

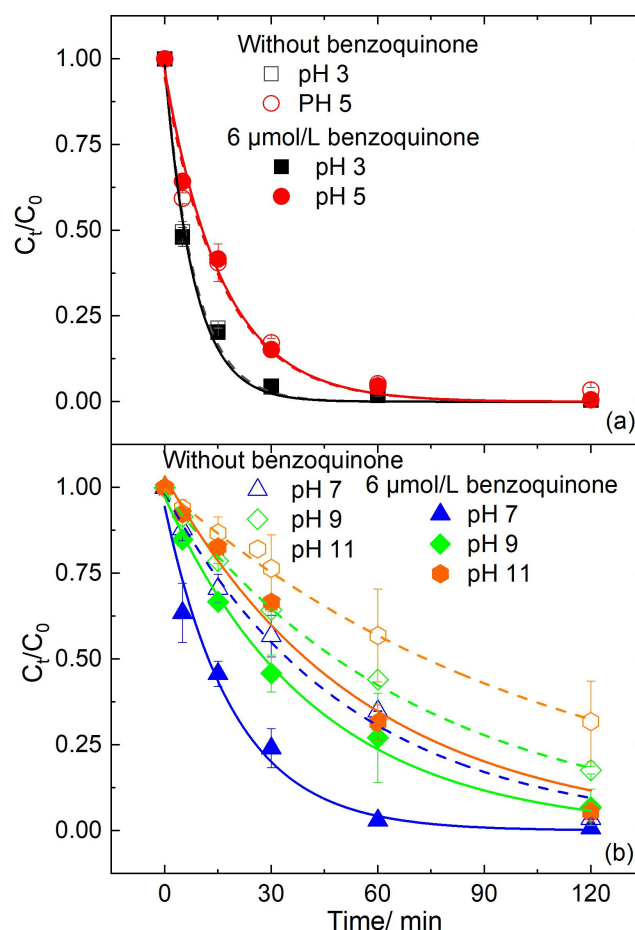


Figure 3 Effect of Benzoquinone on Cr(VI) Reduction by Excess Sludge under the Condition of (a) Acidic and Near-Neutral pH and (b) Alkaline pH

The fitting results are shown in Table 3. In the system without benzoquinone, as the pH increased from 3 to 5, 7, 9, and 11, the reaction rate constant decreased sequentially from 0.118 to 0.062, 0.019, 0.014, and 0.009 min^{-1} . In contrast, after the addition of benzoquinone, the reaction rate constants were 0.124, 0.062, 0.052, 0.024, and 0.018 min^{-1} , respectively.

Table 3 Pseudo-First-Order Kinetic Parameters of the Effect of Benzoquinone on Cr(VI) Reduction by Excess Sludge under the Condition of Different pH

pH	Benzoquinone (μM)	Reaction rate constant, k (min^{-1})	R^2
3	0	0.118±0.011	0.993
	6	0.124±0.012	0.992
5	0	0.062±0.009	0.976
	6	0.062±0.006	0.991
7	0	0.019±0.002	0.989
	6	0.052±0.007	0.981
9	0	0.014±0.001	0.999
	6	0.024±0.001	0.998
11	0	0.009±0.001	0.999
	6	0.018±0.002	0.982

The speciation of Cr(VI) is influenced by pH. When the pH is below 6, Cr(VI) predominantly exists as HCrO_4^- ; when the pH is above 7, it mainly exists as CrO_4^{2-} [1]. At pH values between 3 and 5, Cr(VI) is present in the form of HCrO_4^- . Excess sludge is typically negatively charged, and compared with CrO_4^{2-} , HCrO_4^- is more readily adsorbed by the sludge, which facilitates the reduction of Cr(VI). When the system pH ranges from 7 to 11, Cr(VI) mainly exists as CrO_4^{2-} , which is unfavorable for its contact with excess sludge and thus inhibits its reduction.

Under acidic conditions, excess sludge itself reduces Cr(VI) at a relatively fast rate; therefore, benzoquinone has a limited effect on the reduction process. In contrast, under neutral and alkaline conditions, reduced benzoquinone mainly exists in the forms of HQ^- and Q^{2-} [7, 10], which donate electrons and are oxidized to BQ, thereby accelerating electron transfer. Since the intrinsic reduction rate of Cr(VI) by excess sludge is relatively slow under these conditions, benzoquinone can significantly enhance the reduction of Cr(VI). As the pH increases, the reduction rate of Cr(VI) by excess sludge gradually decreases. Overall, benzoquinone has little effect under acidic conditions but markedly promotes Cr(VI) reduction under near-neutral and alkaline pH conditions.

3.4 Effect of Benzoquinone on Cr(VI) Reduction under Different HCO_3^- Concentrations

As shown in Figures 4 and 2, the inhibitory effect on Cr(VI) removal becomes more pronounced with increasing HCO_3^- concentration. The fitting results are presented in Table 4. In the absence of benzoquinone, as the HCO_3^- concentration increased from 1 to 5 mM, the reaction rate constant gradually decreased. After the addition of 6 $\mu\text{mol/L}$ benzoquinone, the reaction rate constants were nearly the same as those at the corresponding HCO_3^- concentrations without benzoquinone, indicating that benzoquinone has little effect on the reduction of Cr(VI) by excess sludge.

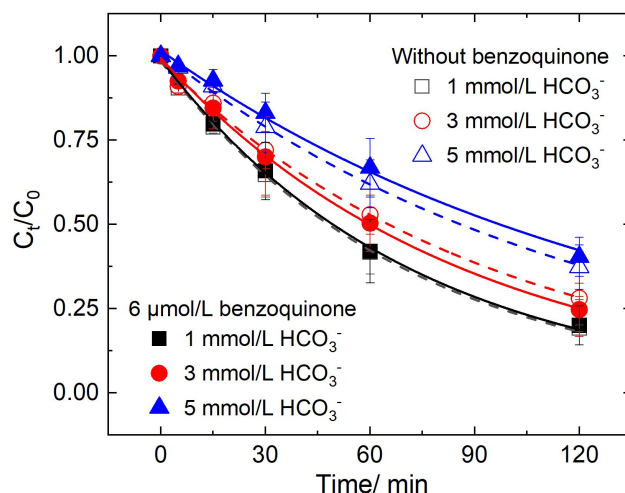


Figure 4 Effect of Benzoquinone on Cr(VI) Reduction by Excess Sludge under the Condition of Different HCO_3^- Concentrations

Table 4 Pseudo-First-Order Kinetic Parameters of the Effect of Benzoquinone on Cr(VI) Reduction by Excess Sludge under the Condition of Different HCO_3^- Concentrations

HCO_3^- (mM)	Benzoquinone (μM)	Reaction rate constant, k (min^{-1})	R^2
1	0	0.014 ± 0.001	0.999
	6	0.014 ± 0.001	0.999
3	0	0.01 ± 0.001	0.997
	6	0.011 ± 0.001	0.999
5	0	0.008 ± 0.001	0.998
	6	0.007 ± 0.001	0.995

On the one hand, HCO_3^- may compete with H^+ in the system, thereby altering the speciation of Cr(VI) and converting part of HCrO_4^- into CrO_4^{2-} [11], which is unfavorable for the contact and reaction between Cr(VI) and excess sludge, thus inhibiting the reduction of Cr(VI) by the sludge. On the other hand, HCO_3^- may react with dissolved or complexed Fe(II) in the excess sludge to form precipitates such as FeCO_3 , $\text{Fe}(\text{HCO}_3)^-$, and $\text{Fe}(\text{OH})_2$ [12], thereby decreasing the reductive activity of Fe(II) and suppressing Cr(VI) reduction. The concentration of benzoquinone is at the $\mu\text{mol/L}$ level, whereas that of HCO_3^- is at the mmol/L level, meaning that the concentration of benzoquinone is approximately three orders of magnitude lower than that of HCO_3^- . Therefore, the inhibitory effect of HCO_3^- on Cr(VI) reduction by excess sludge is stronger than the promoting effect of benzoquinone. Overall, HCO_3^- inhibits the reduction of Cr(VI) by excess sludge. In the presence of 1–5 mM HCO_3^- , the addition of 6 μM benzoquinone has little effect on the reduction of Cr(VI) by excess sludge.

4 CONCLUSIONS

- (1) As the Cr(VI) concentration increased from 2 mg/L to 6 mg/L, the removal efficiency of Cr(VI) after 30 min gradually decreased from 91.7% to 64.6%. This indicates that the ability of excess sludge to remove Cr(VI) weakens with increasing Cr(VI) concentration.
- (2) The addition of benzoquinone promotes the reduction of Cr(VI) by excess sludge. Moreover, with increasing benzoquinone concentration, the promoting effect first increases and then decreases.
- (3) As the pH increases, the reduction rate of Cr(VI) by excess sludge decreases. Under acidic conditions, benzoquinone has little effect on Cr(VI) reduction. Under neutral and alkaline conditions, benzoquinone enhances the reduction of Cr(VI) by excess sludge. For example, at a reaction time of 30 min, in the system without benzoquinone, as the pH increased from 7 to 9 and 11, the removal efficiency of Cr(VI) decreased from 43.2% to 35.7% and 23.6%, respectively; in the presence of benzoquinone, the removal efficiencies increased to 76%, 54.2%, and 33.4%, respectively.
- (4) The addition of HCO_3^- inhibits the removal of Cr(VI) in the system, and the inhibitory effect becomes more pronounced with increasing HCO_3^- concentration. The addition of benzoquinone has little effect on the reduction of Cr(VI) by excess sludge in systems with high HCO_3^- concentrations.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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