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Remediation of Cr(VI) in solution using vitamin C*

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Abstract: The effectiveness of vitamin C in treating Cr(VI)-contaminated water is being evaluated. Cr(VI) is an identified pollutant of some soils and groundwater. Vitamin C, an important biological reductant in humans and animals, can be used to transform Cr(VI) to essentially nontoxic Cr(III). The removal efficiency was 89% when the mass concentration of vitamin C was 80 mg/L in 60 min, and nearly 100% Cr(VI) was removed when the mass concentration was 100 mg/L. Our data demonstrated that the removal efficiency was affected by vitamin C concentration, the reaction temperature and the dissolved oxygen concentration. The reaction mechanism of Cr(VI) by vitamin C was presented. Our study opens the way to use vitamin C to remediate Cr(VI)-contaminated soils and groundwater.

Key words: Hexalent chromium, Vitamin C, Reduction
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INTRODUCTION

Chromium is a commonly identified soils and groundwater contaminant. Cr(VI) is toxic, carcinogenic, and has great subsurface mobility. In contrast, Cr(III) is relatively non-toxic and immobile. Much research focused on the remediation of Cr(VI) such as adsorption by zeolites (Bowman, 2003) or silicas (Hideaki *et al.*, 2002), chemical reduction by ferrous iron (Buerge and Hug, 1999; Fendorf and Li, 1996) or zero-valent iron (Powell and Puls, 1997; Alowitz and Scherer, 2002), bioremediation by strains of bacteria (Chen and Hao, 1998) etc.

Vitamin C, an important biological reductant ubiquitous in humans and animals, is non-toxic, of which the reaction products (such as dehydroascorbic acid) can be degraded by microorganism in groundwater or soil and utilized in the combined remediation (chemical & biological) of groundwater or soil contaminated by heavy metals or halogenated organics. Certainly, vitamin C may be more expensive than other reductants such as Fe, FeS, but the dosage will be much less because vitamin C is dissolvable. Furthermore, those reductants will cause second pollution in the remediation but vitamin C not.

The present study is aimed at quantifying the effects of vitamin C concentration, or the reaction temperature and the dissolved oxygen concerntration on the rate of Cr(VI) reduction. The reaction mechanism of Cr(VI) by vitamin C is described. This report on the reduction of Cr(VI) by vitamin C offers opportunities for technological applications of vitamin C.

MATERIALS AND METHODS

Materials

All chemical reagents, such as potassium dichromate, sulfuric acid (98%) and diphenylcarbazide were analytical reagent grade. Vitamin C was purchased from Guanghua Chemical Mill of Shantou and freshly dissolved before use. Deionized water was used for preparing all solutions.

Batch experiments

The batch experiments for the reduction of

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Cr(VI) were performed in the same three-necked flask to which 500 ml CrO_4^{2-} aqueous solution was introduced. Then vitamin C solution was added. The reaction solutions was stirred under nitrogen flow and periodically sampled by glass syringe for analysis. Cr(VI) was determined spectrophotometrically with diphenylcarbazide at 540 nm.

The effects of various parameters on the Cr(VI) reduction were researched. The reaction temperature investigated was 10 to 35 °C, and the vitamin C concentration was 40 to 120 mg/L. When determining the effect of oxygen concentration, the deionized water was purged beforehand using nitrogen to drive the dissolved oxygen. Then nitrogen flow or oxygen flow of 0.3 L/min to 1.2 L/min was purged into the flask during the experiment. The pH value was initially 5.5 (the pH value of deionized water) and not controlled during the experiment.

RESULTS AND DISCUSSION

Effects of the reaction temperatures

To assess the effect of varying temperature, batch experiments were conducted at five temperatures: 10 °C, 15 °C, 25 °C, 30 °C and 35 °C. The results showed high Cr(VI) removal efficiency, 95% at temperature 35 °C and 85% at temperature 10 °C in one hour, respectively (Fig.1). The Cr(VI) removal efficiency increased with the increase of reaction temperatures. It is believed that high temperature can provide energy to accelerate the dehydrogenation of vitamin C, which accelerates the reaction rate. The disappearance of Cr(VI) in the initial five minutes satisfies pseudo-first-order kinetics, the k_{obs} values calculated by Eq.(1) are listed in Table 1.

$$\frac{dC_{Cr(VI)}}{dt} = -k_{obs}C_{Cr(VI)} \quad (1)$$

Assuming that k has Arrhenius behaviour, the activation energy, E_a, can be calculated from the relation below:

$$\ln k = A - \frac{E_a}{RT} \quad (2)$$

where E_a is the activation energy (kJ/mol), A the pre-exponential factor, k the observed pseudo-first-order reaction rate constant (min^{-1}), R the universal gas constant (8.314 J/(mol·K)), and T is the reaction temperature (K).

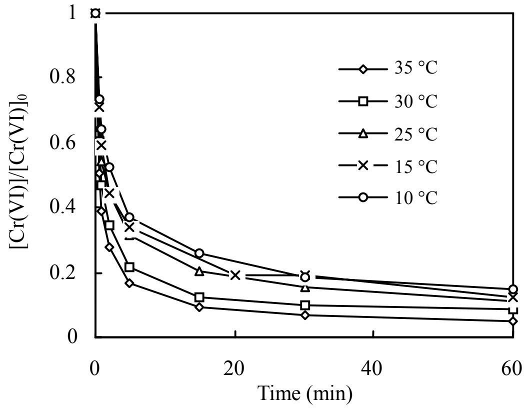

Fig.1 Effects of reaction temperatures on the Cr(VI) removal efficiency
$C_{vitamin\ C}$=80 mg/L, $C_{Cr(VI),ini}$=20 mg/L

Table 1 k_{obs} values for the reaction of Cr(VI) by vitamin C

T (°C)	10	15	25	30	35
k_{obs} (min^{-1})	0.179	0.193	0.196	0.267	0.307

As seen in Table 1, an increase in the reaction temperature can enhance the reaction rate significantly. The k values calculated at various temperatures were correlated by Eq.(3) and shown in Fig.2.

$$\ln k = 4.5199 - 1781/T \quad (3)$$

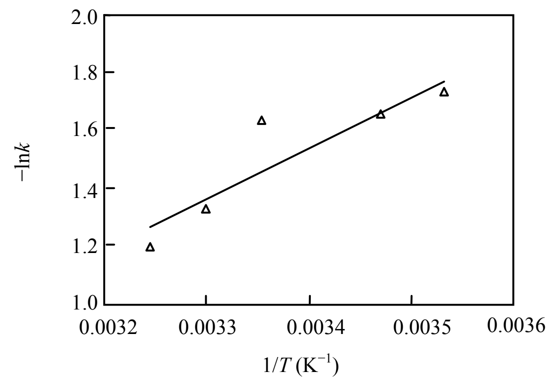

Fig.2 Correlation for reaction rate constant k

Effects of the initial vitamin C concentrations

Five initial vitamin C concentrations were employed in this study. Fig.3 shows that the increase of vitamin C concentration greatly enhanced the removal efficiency of Cr(VI). Nearly 100% Cr(VI) was removed when the mass concentration was 100 mg/L, but only 49% was removed when the mass concentration was 40 mg/L. The results indicated that the stoichiometry of Cr(VI) to vitamin C is 2:3.

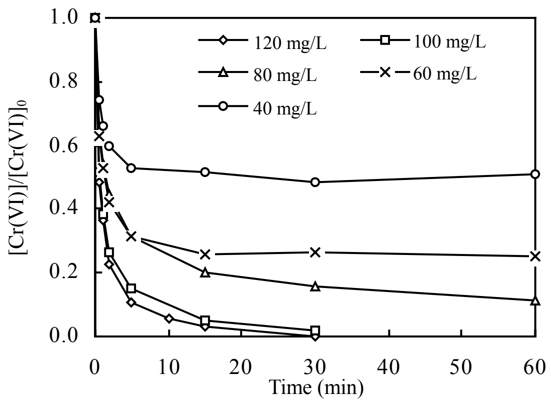

Fig.3 Effects of initial vitamin C concentrations on the Cr(VI) removal efficiency
$C_{Cr(VI),ini}$=20 mg/L, T=25 °C

Effects of oxygen concentrations

As shown in Fig.4, the removal efficiency was 94% on condition of nitrogen flow in one hour and 85% when oxygen flow was 1.2 L/min. The comparison suggested that oxygen slightly affected the reduction of Cr(VI), and that remediation of Cr(VI) by vitamin C could reach high efficiency in the exposure condition. Because the oxygen flow of 0.3 L/min is high enough to make the dissolved oxygen in the solution maximum, there are no discernible differences between the oxygen flow from 0.3 L/min to 1.2 L/min.

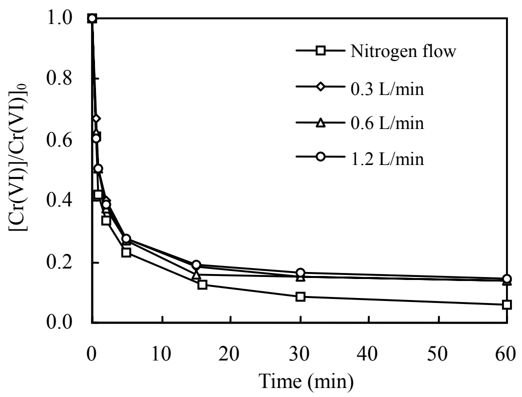

Fig.4 Effects of oxygen concentrations on the Cr(VI) removal efficiency
$C_{vitamin\ C}$=80 mg/L, $C_{Cr(VI),ini}$=20 mg/L, T=25 °C

Mechanism of reduction of Cr(VI) by vitamin C

In the redox reaction, Cr(VI) is reduced to Cr(III) and vitamin C is dehydrogenated to dehydroascorbic acid. The stoichiometry is 2:3. The whole reaction can be described by the following equation:

$$Cr_2O_7^{2-}+3C_6H_8O_6+8H^+\rightarrow 2Cr^{3+}+3C_6H_6O_6+7H_2O \quad (4)$$

CONCLUSION

The research demonstrated that the removal efficiency was apparently affected by the concentration of vitamin C and the reaction temperature but only slightly affected by oxygen concentration. The disappearance of Cr(VI) in the initial five minutes satisfies pseudo-first-order kinetics. During the reaction vitamin C is oxidated to dehydroascorbic acid. The stoichiometry of Cr(VI) to vitamin C is 2:3. The results denoted that vitamin C can removed Cr(VI) effectively in the exposure condition and normal temperature. The reaction products, dehydroascorbic acid, can be degraded by microorganism in groundwater or soil. Therefore, vitamin C is a good choice for the remediation of groundwater or soil contaminated by heavy metals.

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