

Radiation-induced reduction of chromium(VI) in aqueous solution by γ -irradiation in a laboratory-scale

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Abstract: Radiation-induced reduction of chromium(VI)(Cr(VI)) by γ -irradiation was studied with an initial concentration of 42 mg/L in aqueous solutions. Several factors which might affect the reduction of Cr(VI) to Cr(III) were examined. pH of aqueous solution affects the reduction efficiency significantly. Acidic condition of aqueous solution accelerates the process. At pH 2, a reduction of 86.2% was achieved with the absorbed dose of 15 kGy, while, with the same dose, at pH 5 and 7, the reduction of Cr(VI) were only 36.3% and 22.2%, respectively. Ethanol (0.1% in V:V) and sodium carbonate (1 mmol/L) were added into the solution respectively as relatively non-toxic hydroxyl radical scavengers. Reduction rate increased greatly in the presence of ethanol at each pH. Reduction efficiency of Cr(VI) was enhanced in neutral condition with the addition of sodium carbonate, however, no enhancement was found in acidic condition. The reduction of Cr(VI) was restrained when the solution was saturated with oxygen; however, the restraint was not significant.

Keywords: γ -irradiation; radiation-induced reduction of Cr(VI); hydroxyl radical scavengers; kinetics

Introduction

Chromium compounds are extensively used in electroplating, leather-tanning and other industries. In China, chromium is incorporated into the environment, mainly into soils and streams of water, as a result of unregulated application and inappropriate waste-disposal practices (Chuan and Liu, 1996). For example, the concentration of total chromium in the main stream of Yangtze River was 16.7%–33.3% higher than the concentration limit in Chinese criterion of surface water at the end of 20 century (Liu, 2002). Cr(VI) is classified as a primary pollutants by both USEPA (QuiIntana *et al.*, 2001) and State EPA of China (1996) because of its mobility in soil and groundwater and its reported toxicological effects on organisms. In China, waste containing Cr(VI) has been categorized into the Contents of Hazardous Waste (No. HW21) (Liang, 2003).

Many methods were applied to remove Cr(VI) from aqueous solutions. The principle for most of them is the reduction of Cr(VI) to less toxic Cr(III) by subsequent sedimentation as Cr(OH)₃ in neutral or weak alkaline conditions (Pettine *et al.*, 1998a). Conventional methods for the reduction of Cr(VI) to Cr(III) are those such as electrolysis (Meng and Hu, 2000), photochemical reduction (Yurkow and Pikaev, 2002), chemical reduction (Pettine *et al.*, 1998), and biological reduction etc. (Liu *et al.*, 2004). These methods either consume large quantities of chemical reagent or have low reduction efficiency, which restrains their wide applications. Radiation-induced reduction is an effective method to remove certain heavy metals. This has been demonstrated for cadmium, lead and mercury in aqueous media

(Al-Sheikhly *et al.*, 1995; Kartasheva *et al.*, 1997). But for the case of Cr(VI) by γ -irradiation, very few researches have been made up to now, as well as very limited literature was found on the kinetics study (Yurik and Pikaev, 1999). In this study, several factors which might affect the reduction of Cr(VI) to Cr(III) were investigated. The explanations on the effect of Cr(VI) reduction were presented from the view of kinetics study.

1 Materials and methods

1.1 Sample preparation

Aqueous solution with Cr(VI) concentration of 42 mg/L was prepared by adding analytical-grade potassium dichromate to twice distilled water. HCl and NaOH were added to the solution to investigate the effect of pH on the reduction of Cr(VI). Ethanol (0.1% in V:V) and sodium carbonate (1.0 mmol/L) were used as relatively non-toxic hydroxyl radical scavengers. In order to determine the effect of dissolved oxygen (DO), nitrogen or oxygen in high purity was bubbled into samples respectively for 2 min to ensure that the solutions were saturated with them. The samples were then placed into the radiation field immediately. Samples bubbled without nitrogen or oxygen were irradiated as control.

1.2 Irradiation process

γ -ray was obtained from ⁶⁰Co source (1.85×10^{16} Bq), which is located in Institute of Atomic Energy, Jiangsu Academy of Agriculture Sciences, China. Samples (25 ml each) were placed in 50 ml airtight glass vessels, which were placed in radiation field to a specific distance from the source according to the doses expected. Irradiation process was lasted about 5 h. The doses that samples absorbed were determined

with silver dichromate dosimeter.

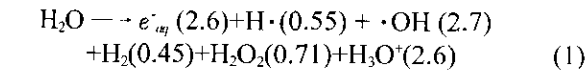
1.3 Analysis

Cr(VI) was determined colorimetrically at 540 nm using diphenyl carbazide reagent in acid solution with spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd., 722)(Xi *et al.*, 1995). pH value and DO were measured by pH monitor (Shanghai Kangyi Instrument Co., Ltd., PHS-2C) and DO meter (Yellow Spring Instrument Co. Inc, 52CE Type), respectively(SEPA of China, 2002).

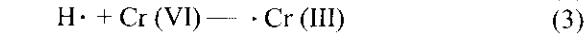
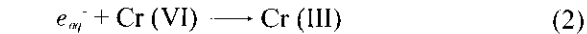
2 Results and discussion

2.1 Radiation-induced reduction of Cr(VI)

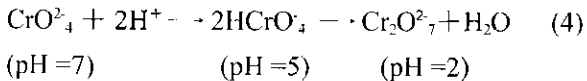
During irradiation, radiolysis of water took place within 10^{-7} s, producing three reactive species, such as hydrogen atoms, $H\cdot$, solvated electrons, e_{aq}^- , and hydroxyl radicals, $\cdot OH$, as well as less reactive species H_2O_2 , H_3O^+ and H_2 , which can be seen in Eq.(1)(The numbers in the brackets present the amount of the produced radicals/100 eV energy)(Cooper *et al.*, 1992).



The mechanism of radiation-induced reduction of Cr(VI) to Cr(III) has been outlined previously(Al-Sheikhly and McLaughlin, 1991). Both e_{aq}^- and $H\cdot$, the most reducing among these species, reduce Cr (VI) in aqueous solution to Cr (III), with rate constants of 2.1×10^{10} L/(mol \cdot s) and 2.0×10^{10} L/(mol \cdot s)(pH=7), respectively(Eq.(2) and (3))(Buxton *et al.*, 1987).



pH is a very important factor that affects the reduction of Cr (VI)(Fig.1). Reduction efficiency of Cr(VI) was enhanced in acidic condition. At pH 2, a reduction of 86.2% was achieved with an absorbed dose of 15 kGy; while, with the same dose, at pH 5 and 7, the reduction of Cr (VI) were only 36.3% and 22.2%, respectively. This can be explained by the fact that Cr (VI) exists mainly in different species at pH 7, 5 and 2 (Eq.(4)) (Quintana *et al.*, 2001; Zhang *et al.*, 2000).



The species has higher redox potential levels in lower pH conditions(e. g. $Cr_2O_7^{2-}/Cr^{3+}=0.98$, $HCrO_4^-/Cr(OH)_3 = 0.65$, $CrO_4^{2-}/Cr(OH)_3 = 0.56$) (Zhang *et al.*, 2000), so it is easier to be reduced in acidic conditions.

Under different conditions, the amount of Cr(VI) reduced from per unit absorbed dose, i.e. specific reduction efficiency, is different. Generally, *G* value can be used to express this parameter (Eq.(5))(Junko, 1997).

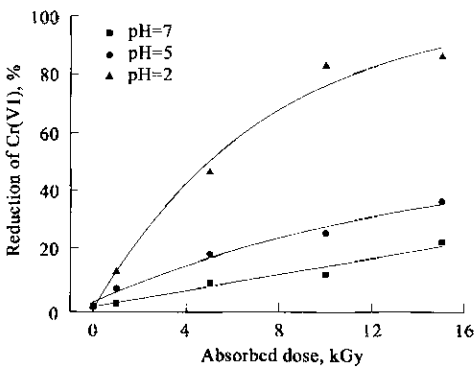


Fig.1 pH effect on the reduction of Cr(VI)

$$G = \frac{(\Delta R) (N_A)}{(D) (6.24 \times 10^{19})}$$

(5)

where ΔR is the amount of reduced Cr(VI), mol/L; N_A is the Avogadro constant, 6.02×10^{23} molecules/mol; *D* is the absorbed dose, 10^{-2} kGy; 6.24×10^{19} are the conversion constant from kGy to 100 eV/L, 100 eV/(L \cdot kGy); *G* is the specific reduction efficiency, molecules/100 eV.

According to Eq. (5), *G* values of Cr (VI) in different conditions were obtained, as shown in Table 1.

Table 1 *G* values of Cr(VI) under different conditions (molecules/100 eV)

Conditions	1 kGy	5 kGy	10 kGy	15 kGy
pH=7	0.18	0.08	0.09	0.11
pH=5	0.48	0.28	0.20	0.19
pH=2	0.92	0.72	0.65	0.45
pH=7, with 0.1% ethanol	1.15	1.06	-	0.51
pH=5, with 0.1% ethanol	1.76	1.30	0.76	0.51
pH=2, with 0.1% ethanol	3.75	1.56	0.78	0.52
pH=7, with 1 mmol/L Na ₂ CO ₃	0.52	0.27	0.19	0.13
pH=5, with 1 mmol/L Na ₂ CO ₃	0.83	0.39	0.22	0.22
pH=2, with 1 mmol/L Na ₂ CO ₃	0.78	0.67	0.63	0.47

G values increased with the enhancement of acidity. This is consistent with what the data in Fig.1. While in a given pH condition, almost all the reduction efficiency decreased with the increase of absorbed dose, which was also reported by other researchers (Chaychian *et al.*, 1998). This may be due to scavenging of e_{aq}^- by accumulating H_3O^+ at high doses, which counteracted the contribution of reaction in Eq.(2).

2.2 Kinetics study

By plotting the natural logarithm of Cr (VI) concentration as a function of absorbed doses, a linear relationship can be derived(not shown). This indicates that the reaction of Cr (VI) reduction is first-order one with respect to absorbed dose and can be described by Eq.(6) (Nickelsen *et al.*, 1994).

$$R_D = R_0 e^{-kD}$$

(6)

Where R_D is the residual concentration of Cr (VI) at any dose, mol/L; D is the absorbed dose, kGy; R_0 is the initial concentration of Cr (VI), mol/L; k is the kinetics constant, 1/kGy.

Using Eq. (6), $D_{0.9}$, the required dose to reduce 90% of initial concentration (i.e. where $R_D=0.1R_0$) is obtained(Eq.(7)).

$$D_{0.9} = \ln 0.1 / -k$$

(7)

$D_{0.9}$ and kinetics coefficient of the reduction of Cr(VI) to Cr (III) by γ -irradiation are listed in Table 2. At pH 7, $D_{0.9}$ is 149.1 kGy; while, at pH 5 and 7, $D_{0.9}$ decreases to 72.9 kGy and 15.9 kGy, respectively. On the other hand, k increases with the dropping of pH value. As a result, it is easier for Cr(VI) to be reduced at lower pH condition.

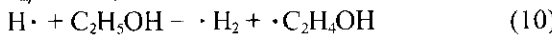
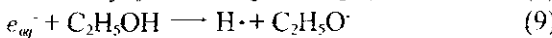
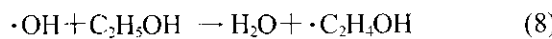
Table 2 $D_{0.9}$ and kinetics coefficient of the reduction of Cr(VI)			
	Equation	R^2	$D_{0.9}$, kGy
pH=7	$y=42.09e^{-0.01544x}$	0.9587	149.1
pH=5	$y=41.60e^{-0.03154x}$	0.9764	72.9
pH=2	$y=42.53e^{-0.14499x}$	0.9877	15.9
pH=5, bubbled with O ₂	$y=40.78e^{-0.02515x}$	0.9352	91.6
pH=5, bubbled with N ₂	$y=39.65e^{-0.03792x}$	0.9478	60.7
pH=7, with 0.1% ethanol	$y=42.93e^{-0.22513x}$	0.9963	10.2
pH=5, with 0.1% ethanol	$y=42.92e^{-0.33298x}$	0.9960	6.9
pH=2, with 0.1% ethanol	$y=42.12e^{-0.68309x}$	0.9986	3.4
pH=7, with 1 mmol/L Na ₂ CO ₃	$y=40.27e^{-0.011773x}$	0.8783	129.9
pH=5, with 1 mmol/L Na ₂ CO ₃	$y=39.93e^{-0.0336x}$	0.9330	68.5
pH=2, with 1 mmol/L Na ₂ CO ₃	$y=43.03e^{-0.14325x}$	0.9862	16.1

2.3 Hydroxyl radical scavengers

It is known that lots of hydroxyl radicals can be yielded for the radiolysis of water (Eq. (1)). The occurrence of this oxidizing species makes resultant Cr(III) reoxidized to Cr(VI). Therefore, to achieve maximum reduction efficiency, hydroxyl radicals should be scavenged from the system. In this study, ethanol and sodium carbonate were used for this purpose.

2.3.1 Ethanol

Ethanol reacts rapidly with $\cdot OH$, and to a lesser extent with e_{aq}^- and $H\cdot$ in aqueous solution with rate constants of 1.9×10^9 L/(mol \cdot s), 1.0×10^6 L/(mol \cdot s) and 1.7×10^7 L/(mol \cdot s), respectively, by the following (Buxton *et al.*, 1987; Johnston, 1989):



On the other hand, with the scavenging of $\cdot OH$, Eq. (1) was made to the right direction, which weakened the reaction of $\cdot OH$ with e_{aq}^- and $H\cdot$ and resulted in the increasing of e_{aq}^- and $H\cdot$. Consequently, Eq.(2) and (3) was enhanced. The enhancement of Cr (VI) reduction efficiency by ethanol is shown in

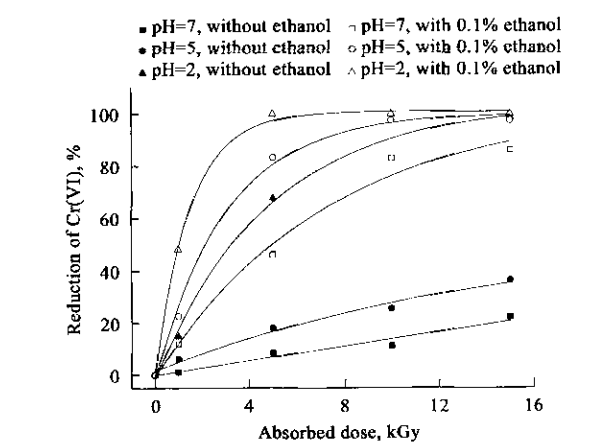


Fig.2 Ethanol effect on the reduction of Cr(VI)

Fig. 2.

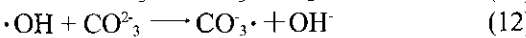
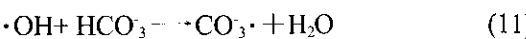
In the presence of ethanol (0.1%), reduction increased at each pH value, especially at pH 2, high reduction (99.9%) was achieved at low absorbed dose (5 kGy). The reaction was also first-order one in the presence of ethanol. Kinetics coefficient and $D_{0.9}$ are listed in Table 2. Kinetics constant (k value) of the reduction reaction increased remarkably in the presence of ethanol. Especially at pH 7, k increased by greater than 14 times. While $D_{0.9}$ decreased from 149.1, 72.9 and 15.9 kGy (pH=7, 5 and 2) to 10.2, 6.9 and 3.4 kGy, respectively. All of these suggest it is easier for chromium(VI) to be reduced in the presence of ethanol.

In order to clarify whether ethanol itself reacts with Cr(VI) under the experimental conditions, samples (with Cr(VI) concentration of 42.8 mg/L and without irradiation treatment) were added with ethanol, and then stirred for 10 min. Five hours later, Cr(VI) was analyzed (Table 3). There was almost no difference of Cr(VI) concentration after adding ethanol. Therefore, such conclusion could be made that the enhancement of ethanol to the removal of Cr(VI) was mainly due to its scavenging of $\cdot OH$, not reacting with Cr(VI).

Table 3 Cr(VI) concentration after adding ethanol			
Treatment	Cr(VI) concentration, mg/L		
	pH=2	pH=5	pH=7
with 0.1% ethanol(V:V)	42.6	42.8	42.8
with 1% ethanol(V:V)	42.8	42.9	42.7

2.3.2 Sodium carbonate

Hydrolyzation occurred shortly after the addition of sodium carbonate into aqueous solution, producing hydrolyzates of HCO_3^- and CO_3^{2-} ($pK_a=6.35$ and 10.25 , respectively). Both HCO_3^- and CO_3^{2-} react with $\cdot OH$ (rate constants are 8.5×10^6 L/(mol \cdot s) and 3.9×10^8 L/(mol \cdot s), respectively), by the following(Buxton *et al.*, 1987):



HCO_3^- and CO_3^{2-} also react with e_{aq}^- with rate constants of $6.0 \times 10^5 \text{ L}/(\text{mol}\cdot\text{s})$ and $3.9 \times 10^5 \text{ L}/(\text{mol}\cdot\text{s})$ (Buxton *et al.*, 1988), respectively. It is easily known that CO_3^{2-} is a better $\cdot\text{OH}$ scavenger than HCO_3^- by comparing those rate constants.

In the present work, a certain amount of sodium carbonate was added into the samples (to obtain the concentration of 1.0 mmol/L) just before γ -irradiation. Fig.3 compares the reduction efficiency of Cr (VI) by γ -irradiation in the presence and absence of sodium carbonate. The reduction of Cr(VI) was still first-order reaction in the presence of sodium carbonate. Kinetics coefficient and $D_{0.9}$ are listed in Table 2. In neutral condition (pH=7), reduction efficiency of chromium (VI) was enhanced with the addition of sodium carbonate ($D_{0.9}$ decreased from 149.1 to 129.9 kGy), but not as significant as the addition of ethanol. While at pH 2, no enhancement was seen (the two curves were almost superposed at pH 2 in Fig.3). This can be explained by the ionization equation of carbonic acid in aqueous solution(Eq.(13))(Zhou, 2003).

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.7 \times 10^{-11} \tag{13}$$

The concentration of HCO_3^- and CO_3^{2-} can be calculated according to Eq.(13). With the addition of 1 mmol/L sodium carbonate, the concentration of CO_3^{2-} is around $4.7 \times 10^{-4} \text{ mmol/L}$ at pH 7. Therefore, $\cdot\text{OH}$ can be scavenged to some extent (Zhou *et al.*, 2003). While when at pH 2, there is almost no CO_3^{2-} in the solution, which only results in the negligible enhancement.

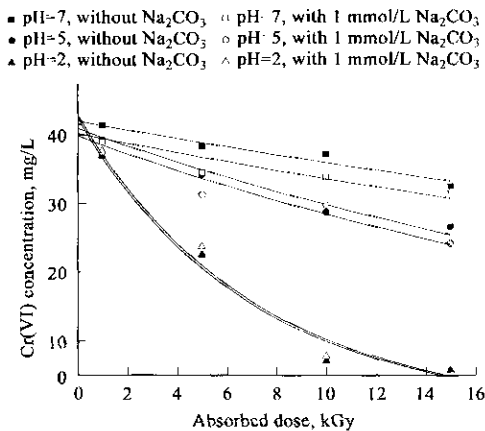


Fig. 3 Na_2CO_3 effect on the reduction of Cr(VI)

2.3.3 Effect of dissolved oxygen

In the presence of DO in solution, there is a competition of O_2 with Cr (VI) for e_{aq}^- and $\text{H}\cdot$, as follows(with rate constants of $1.9 \times 10^{10} \text{ L}/(\text{mol}\cdot\text{s})$ and $2.1 \times 10^{10} \text{ L}/(\text{mol}\cdot\text{s})$, respectively) (Buxton *et al.*, 1987).



In our study, solutions were saturated with N_2 and O_2 in high purity to obtain different DO concentrations. Samples without bubbling N_2 or O_2 were set as control (DO=7.8 mg/L). Residual Cr (VI) concentration of samples after irradiation is shown in Fig.4. Kinetics coefficient and $D_{0.9}$ are listed in Table 2.

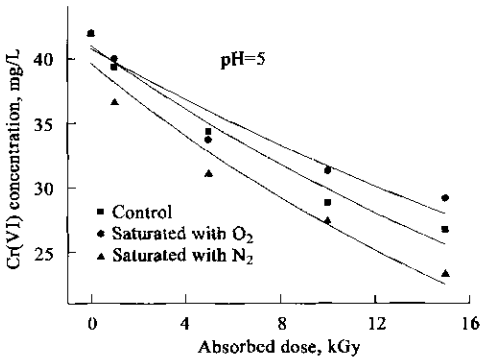


Fig.4 Dissolved oxygen effect on the reduction of Cr(VI)

Reduction efficiency of Cr (VI) was somewhat enhanced ($D_{0.9}$ decreased from 72.9 kGy to 60.7 kGy) when the solution was saturated with nitrogen (DO = 1.8 mg/L). While bubbled with oxygen, the solution was supersaturated with oxygen(DO=18.7 mg/L). As a result, the reduction of Cr(VI) was restrained. The restraint, however, was not significant($D_{0.9}$ increased only from 72.9 kGy to 91.6 kGy). This can be explained by the fact that DO was being exhausted in airtight vessels with the rising of absorbed dose. According to other researchers (Chaychian *et al.*, 1998), only about 0.8 and 0.4 kGy are needed to fully overcome the competition of O_2 with Cr (VI) for e_{aq}^- and $\text{H}\cdot$ when DO is 18.7 and 7.8 mg/L, respectively. Therefore, with aqueous solutions of Cr (VI)(42 mg/L) which requires 72.9 kGy for reducing 90% of the metal at pH 5, the initial concentration of DO is not a significant factor.

3 Conclusions

γ -Irradiation is an efficient method to reduce Cr(VI) to Cr(III). The reaction of Cr(VI) reduction is first-order one and solution pH is found to be a crucial factor controlling the efficiency of Cr(VI) reduction. An enhanced Cr(VI) reduction can be achieved under acidic reaction conditions.

Ethanol and sodium carbonate with appropriate concentration can be used as the hydroxyl radical scavengers. Reduction was accelerated remarkably in the presence of ethanol at each pH. This reduction reaction was enhanced to some extent in neutral condition with the addition of sodium carbonate, however, no enhancement was observed in acidic condition.

Dissolved oxygen in aqueous solution restrains the reduction efficiency of Cr(VI), while the restraint

is not significant.

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