Mechanism and kinetics of reduction of Cr(VI) by D-glucose in aqueous phase

Sutanu Maiti[a], Sudarsan Neogi[b] and Binay K. Dutta[a]*

[a]School of Environmental Science and Engineering, [b]Department of Chemical Engineering,
Indian Institute of Technology, Kharagpur-721 302, West Bengal, India

E-mail: bkdutta@iitkgp.ac.in

Among the various reducing agents used for remediation of Cr(VI) in contaminated soil, glucose is an attractive one since it has reasonable cost and does not have any adverse effect when an excess is used to satisfy the process needs. The objective of this work was to investigate the process of reduction and the kinetics and mechanism for Cr(VI) reduction by D-glucose in the aqueous phase. Experimental reduction rates were determined for different values of the process parameters such as the mole ratio of the reactants, pH, temperature as well as the initial Cr(VI) concentration. Nearly 60% reduction of Cr(VI) has been achieved after 1 h with stoichiometric amount of glucose in aqueous phase. Almost complete reduction could be achieved by using 50% excess glucose. The effective reduction of Cr(VI) by D-glucose suggests that this is a potentially useful technique for reduction of Cr(VI) for *ex situ* remediation of Cr(VI) contaminated soil.

Keywords: Kinetics, hexavalent chromium, reduction, D-glucose, diphenyl carbazide, *ex situ*, soil remediation.

Introduction

Chromium is widely used in a variety of industrial processes such as metal electroplating, leather tanning and manufacture of products for corrosion protection. Soil contamination because of illegal dumping of wastes from above industries has been a problem in many countries including India[1a,2].

This occurred frequently when there was no rules limiting disposal of hazardous wastes. Remediation of contaminated soil, especially with Cr(VI) contamination has been a big challenge. Many attempts have been reported on finding out an effective and suitable reducing agent for *in situ* remediation or by extracting it by soil washing followed by *ex situ* reduction in the aqueous phase. The reducing agents tried so far include sulfides[1b], nanoscale Zero-valent Iron (ZVI)[1c], hydrazine[1d], ascorbic acid[1e], sodium metabisulfite[1f], hydrogen sulfide etc.[1g]. It is desirable that the excess reducing agent does not create any contamination and on this ground glucose is a good candidate for this job. Studies of the reduction rate and development of rate equation are important for design of systems for *ex situ* reduction of aqueous Cr(VI) extract. Reduction of Cr(VI) with glucose in an aqueous extract and the effects of different parameters on the reduction rate have been reported here.

Materials and methods:

Cr(VI) stock solution was prepared by dissolving a weighed amount of dried $K_2Cr_2O_7$ in Milli-Q deionized water. Analytical reagent grade (Merck Life Science) D-glucose solution at requisite concentration was also prepared for the experiments. Experiments were started after mixing the Cr(VI) and glucose solutions at a predetermined ratio in a beaker kept homogeneous by a magnetic stirrer. The pH of the solution was adjusted by addition of a few drops of 0.01 (*M*) H_2SO_4 and 0.02 (*M*) NaOH as necessary. Samples were drawn from time to time, filtered through a PTFE syringe filter and centrifuged at 3000 rpm for about 5 min to remove the Cr(III) generated. The clear sample was analyzed for the remaining Cr(VI) by 1,5-diphenyl carbazide (DPC) spectrophotometric technique at 540 nm (US EPA method 7196A) to follow the course of the reaction. One ml of properly diluted sample was taken in a 15 ml falcon tube to which were added 9 ml of 0.02 (*M*) H_2SO_4 and 0.2 ml DPC reagent (250 mg in 50 ml acetone). Five minute reaction time for development of color was allowed followed by measurement of absorbance. Several sets of experiments were conducted to investigate the effects of various process parameters on the rate of Cr(VI) reduction. The initial concentrations of Cr(VI) were set at 6000,

5000, 4000 and 3000 mg/L. To study the effect of molar ratios of Cr(VI) to glucose, the molar ratios were set at 1:1, 1:1.5, 1:2.5. The pH values of solutions were varied at 2.24, 3.15, 4.39 and 4.45 and the temperature was fixed 25°C, 35°C and 45°C.

Results and discussion

Effect of initial Cr(VI) concentration on the reduction of Cr(VI):

Effect of initial Cr(VI) concentration on the reduction of Cr(VI) by glucose was investigated at various initial Cr(VI) concentrations ranging from 3000 to 7000 mg/L. As shown in Fig. 1, fractional concentration of Cr(VI) gradually decreases with increase of initial Cr(VI) concentration. At 60 min contact time, percentage reduction of Cr(VI) at 3000, 4000, 5000, 6000 and 7000 mg/L were achieved at 65.36%, 62.1%, 59.76%, 57.26% and 54.63% respectively. It was also observed that the time required for complete reduction of Cr(VI) increased with increase of initial Cr(VI) concentration. This observation compared well with that of the reduction of Cr(VI) by polystyrene tris(2-aminoethyl)amine[1h]. It was also observed that the time required for complete reduction of Cr(VI) increases with increase of initial Cr(VI) concentration. Further, the kinetics of Cr(VI) reduction as seen in Fig. 2, gives a linear relationship between Cr(VI) concentration and time. Thus, the reaction followed first order kinetics with respect to Cr(VI). Rate constants at different initial Cr(VI) concentrations are listed in Table 1. The rate constant decreases with increase of initial Cr(VI) concentration. These findings are supported by the literature reports of other workers[1i,j].
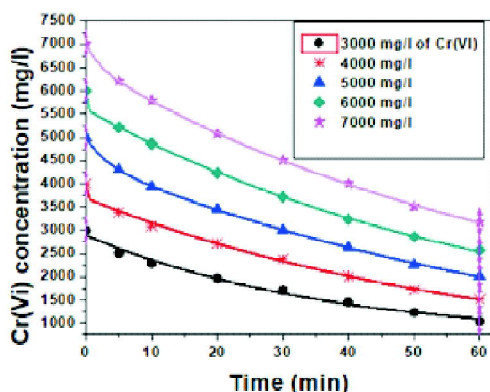

Fig. 1. Effect of initial Cr(VI) concentration on the reduction of Cr(VI) at temperature 25°C, pH 4.45, mole ratio 1:1.5 and stirring speed = 400 rpm.
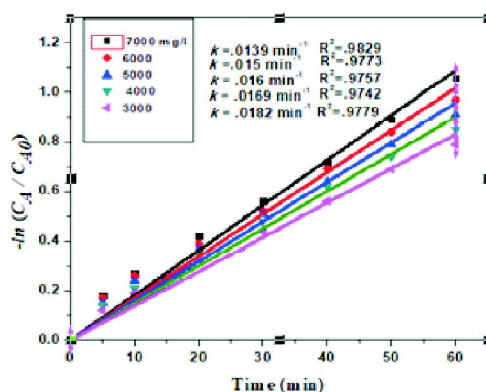

Fig. 2. Plot of $-\ln(C_A/C_{A_o})$ vs time at different initial Cr(VI) concentration at temperature 25°C, C_{A_o} = initial Cr(VI) concentration, C_A = Cr(VI) concentration after certain time, pH 4.45, mole ratio 1:1.5 and stirring speed = 400 rpm.

Table 1. Rate constant values and correlation coefficients at different initial Cr(VI) concentrations

Initial Cr(VI) concentration (mg/L)	Rate constant, k (min^{-1})	R^2
3000	0.0182	0.978
4000	0.0169	0.974
5000	0.016	0.976
6000	0.015	0.9773
7000	0.0139	0.983

Effect of mole ratio of Cr(VI) to glucose on the reduction of Cr(VI):

Effect of molar ratio of Cr(VI) to glucose on Cr(VI) reduction was examined by setting the molar ratio to 1:1, 1:1.5 and 1:2.5 (Fig. 3). Increased mole ratio predictably enhanced the rate and extent of reduction. The stoichiometric mole ratio of the reactants is 1:1.5 and this parameter as well as the pH of the reaction medium has significant influence of reduction of Cr(VI). Nearly 63.95% Cr(VI) was reduced when the molar ratio was set at 1:2.5 over a reaction time of 1 h, but only 54.17% was reduced when a molar ratio of 1:1 was used. Nearly 83.23% Cr(VI) was reduced at mole ratio set at 1:2.5 over a reaction time of 3 h. In this respect, the result of present study is in reasonable agreement with the Yameng *et al.*[1k]. Wang and Xu[1l] studied the Cr(VI) reduction in aqueous solution saturated with potassium bicarbonate where they have achieved complete reduction of Cr(VI) at molar ratio of
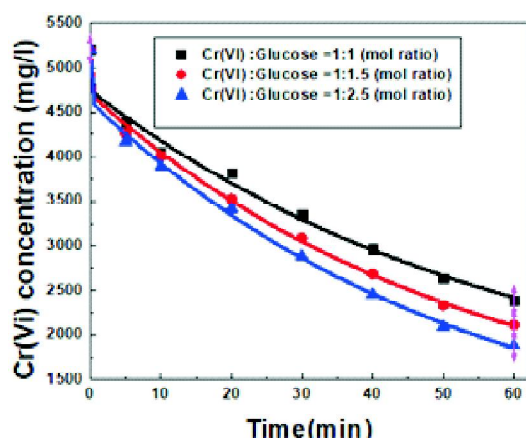
Fig. 3. Effect of molar ratios of Cr(VI) to glucose on the reduction of Cr(VI) at initial Cr(VI) concentration 5200 mg/L, pH 4.45, temperature 25°C and stirring speed = 400 rpm.

1:10; the reason may be the influence of pH has not been considered. Subsequently, kinetics of Cr(VI) reduction was studied under different molar ratios. As shown in Fig. 4, the Cr(VI) reduction reaction was found to be first order with respect to glucose and reduction rate is also much faster at a
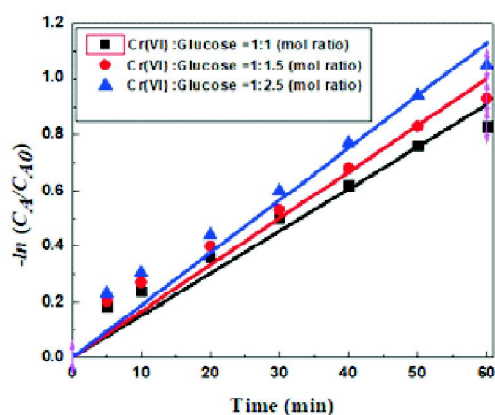

Fig. 4. Plot of $-\ln (C_A/C_{A_0})$ vs time at different molar ratios of Cr(VI) to glucose at pH 4.45 and temperature 25°C.

higher mole ratio of the reactants. The rate constant values under different molar ratios were obtained from the slopes of the linearized plots and are shown in Table 2. The apparent rate constant increases with increasing molar ratios. The solution pH also has considerable effect of the reduction rate. The lowest pH used is 2.2. A lesser pH would surely enhance the reaction but will not be practically relevant.

Table 2. Rate constant values and correlation coefficients at different molar ratios of Cr(VI) to glucose

Molar ratio	Rate constant, k (min^{-1})	R^2
1:1	0.0151	0.983
1:1.5	0.0167	0.984
1:2.5	0.0188	0.985

Effect of pH on the Cr(VI) reduction:

The effect of initial pH on the reduction of Cr(VI) using glucose was investigated by changing initial pH of glucose + Cr(VI) solution from 2.24 to 4.45 and keeping other experimental conditions constant. The results are shown in Fig. 5. As observed from Fig. 5, Cr(VI) reduction is pH dependent. Under acidic conditions, the reduction rate of Cr(VI) increasing with decreasing pH. Nearly 64.31% reduction was achieved at pH 2.24 that reduces to 59.34% at pH 4.45. A decrease in rate constant is also noticed from 0.01748 min^{-1} at pH 2.236 to 0.0156 min^{-1} at pH 4.45 (Table 3). It was also observed from Fig. 6 that the rate constant is linearly dependent on the pH. At the end of all experiments, the pH was measured and it was found that the value of pH slightly increased, which demonstrated that the reaction is consuming H$^+$. Therefore, the increase of H$^+$ concentration enhanced reduction of Cr(VI) to Cr(III). These observations are similar to the reported results in the literature[1m].
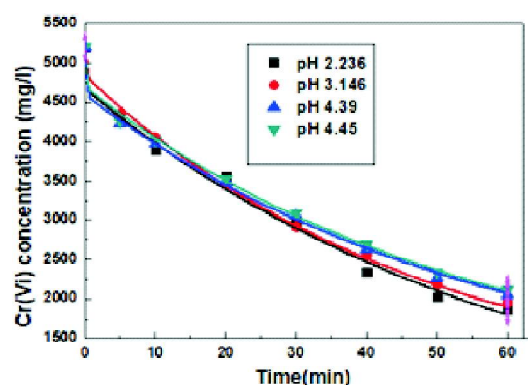

Fig. 5. Effect of pH on the reduction of Cr(VI) at temperature 25°C, Cr(VI) to glucose mole ratio 1:1.5 and initial Cr(VI) concentration 5200 mg/L, stirring speed = 400 rpm.

Table 3. Rate constant values and correlation coefficients at various pH

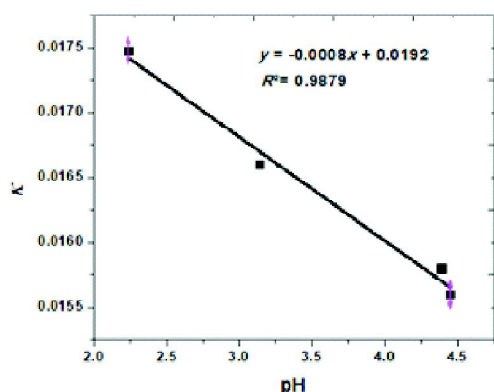| pH	Rate constant, k (min⁻¹)	R^2
2.236	0.0175	0.9832
3.146	0.0166	0.9902
4.39	0.0158	0.9886
4.45	0.0156	0.9865

Fig. 6. Dependence of the rate constant k on pH.

Effect of temperature on Cr(vi) reduction:

The effect of temperature on Cr(vi) reduction was studied in the range of 25–45°C. A plot of Cr(vi) concentration with respect to time (Fig. 7) shows that increase in temperature increases the rate of Cr(vi) as expected. It was also observed that increase in temperature increases the Cr(vi)
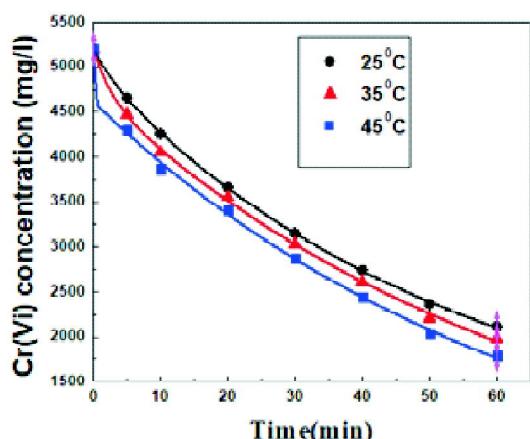

Fig. 7. Effect of temperature on the reduction of Cr(vi) under the following experimental conditions: Cr(vi) to glucose = 1: 1.5, pH = 4.45, stirring speed = 400 rpm.

reduction efficiencies. Nearly 65.63% Cr(vi) reduction has been achieved at temperature 45°C compared to 59.35% at temperature 25°C with stoichiometric addition of glucose. This observation is also similar to the Gheju *et al.*[1n] and Zi-Fang Chen *et al.*[10] where Cr(vi) reduction in aqueous solution by sugarcane molasses was studied.

Reaction rate expression for Cr(vi) reduction:

From the above results on time-concentration plots at different initial Cr(vi) concentrations and different stoichiometric ratios of Cr(vi) and glucose in solution, a second order rate expression for Cr(vi) reduction appears suitable.

We propose a rate equation in C_A and C_B as

$$- \frac{d[C_A]}{dt} = k_1 [C_A][C_B] \tag{1}$$

where C_A and C_B represent the concentrations of Cr(vi) and glucose in solution at any time, respectively. Time-Cr(vi) concentration data (Fig. 7) obtained at different temperatures was considered for the data fit in order to validate eq. (1). The data fit was found to be second order with correlation coefficients of 0.991, 0.989 and 0.993 at temperature 25, 35 and 45°C respectively as shown in Fig. 8.
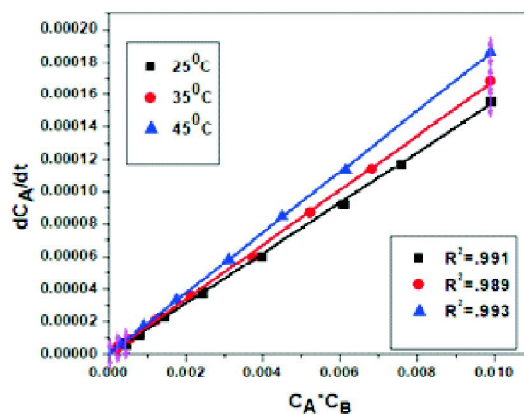

Fig. 8. Plot of the function dC_A/dt vs $C_A \times C_B$ at different temperatures.

Conclusions

In the present work, we tested the effectiveness of glucose as a reducing agent for the Cr(vi) reduction in wastewater and also studied the effects of initial Cr(vi) concentration, molar ratio of Cr(vi) to glucose, pH and temperature on the Cr(vi) reduction. The results showed that Cr(vi) was reduced by glucose effectively with increasing Cr(vi) to glu-

cose mole ratio. Nearly 63.95% and 59.35% of Cr(vi) was reduced in 60 min at 1:2.5 and 1:1.5 mole ratio at pH 4.45 at temperature 25°C. Effect of pH was not so much as compared to mole ratio. Almost 65.63% and 61.9% of Cr(vi) was reduced in 1 h at 1:1.5 mole ratio and at a temperature of 45°C and 35°C respectively which indicate some effect of temperature with Cr(vi) reduction. However, about 83% of Cr(vi) reduction was achieved in 3 h at 1:2.5 mole ratio and at a pH of 4.45. It is clear from the results that complete reduction is achievable within a reasonable time with some excess glucose even at a very mild pH of 4.45. For practical application in remediation of contaminated sites, the job may be done *in situ* by mixing the contaminated soil with glucose and allowing adequate time for reaction. Alternatively, it can be done (and is really dome in many cases) by extracting Cr(vi) with water, separating the leachate from the soil and treating the leachate with the reagent to decontaminate it before the wash water can be recycled and reused. The above results establish that it is possible to achieve complete reduction only with 50–100% excess glucose with is quite reasonable compared to much higher excess used for other reducing agents such as calcium polysulfide.

Acknowledgements

References

1. (a) D. Rai, L. E. Eary and J. M. Zachara, *Sci. Total Environ.*, 1989, **86**, 15; (b) M. S. Iorungwa, R. A. Wuana, S. G. Yiase, T. A. Tor-Anyiin and P. D. Iorungwa, *International Journal of Science and Research*, 2015, **4(2)**, 1142; (c) Pallavi Mitra, Debasish Sarkar, Sampa Chakrabarti and Binay K. Dutta, *Chemical Engineering Journal*, 2011, **171**, 54; (d) Tiangui Wang and Hongbin Xu, *J. Hazard. Mater.*, 2005, **B123**, 176; (e) Xiang-Rong Xu, Hua- Bin Li, Xiao-Yan Li and Ji-Dong Gu, *Chemosphere*, 2004, **57**, 609; (f) M.S. Iorungwa, R. A. Wuana, S. G. Yiase and T. A. Tor-Anyiin, *Journal of Environment and Earth Science,* 2014, **4(16)**, 61; (g) C. Kim, Q. Zhou and B. Deng, *Environ. Sci. Technol.*, 2001, **35**, 2219; (h) Lina Odeh, Iman Odeh, Mustafa Khamis, Mahmoud Khatib, Mohannad Qurie, Ziad Shakhsher and Mutaz Qutob, *American Journal of Analytical Chemistry*, 2015, **6**, 26; (i) Quanping Wu, Jun Zhao, Guohui Qin, Chengyang Wang, Xinli Tong and Song Xue, *Applied Catalysis B: Environmental,* 2013, **142-143**, 142; (j) R. Bayen, M. Islam, B. Saha and A. K. Das, *Carbohydr. Res.*, 2005, **340**, 2163; (k) Tiangui Wang and Hongbin Xu, *J. Hazard. Mater.*, 2005, **B123**, 176; (l) Yameng Ma, Fangfang Li, Yuling Jiang, Weihua Yang, Lv Lv, Haotian Xue and Yangyang Wang, *Bull. Environ. Contam. Toxicol.*, 2016, **97**, 392; (m) Baloyi Jeffrey, Seadira Tumelo, Mpfunzeni Raphulu and Aoyi Ochieng, "Simultaneous Photocatalytic Reduction of Cr(vi) and Oxidation of Citric Acid in Aqueous Solutions", Integrated Waste Management & Environmental Engineering (ICCIWEE'2014), April 15-16, 2014, Johannesburg; (n) M. Gheju and A. Iovi, *J. Hazard. Mater.,* 2006, **B135**, 66; (o) Zi-Fang Chen, Yong-Sheng Zhao, Jia-Wen Zhang and Jing Bai, *Water Air Soil Pollution*, 2015, **226**, 363.

2. Ministry of Env. Forests and Climate Change, Govt. of India, Inventory and mapping of Probably Contaminated Sites in India, Report prepared by COWI Denmark, 2015.