Environment Conservation Journal 8 (3) 1-4, 2007 (ISSN 0972-3099)

Reduction of chromium (VI) by the application of a strong reducing reagent

Jatin Srivastava*, Harish Chandra**, Ajay Singh***, Nishant Rai** and Sachin Chauhan**

* Department of Environmental Sciences, Institute of Biological science and Biotechnology, Chatrapati Sahu Ji Maharaj University, Kanpur

**Department of Microbiology, Gayatri College of Biomedical Sciences, G.M.S. Road, Near Ballupur Chowk, Dehradun

***Department of Chemistry, Gayatri College of Biomedical Sciences, G.M.S. Road, Near Ballupur Chowk, Dehradun

Abstract

Photochemical reduction of Cr (VI) into Cr (III) has been reported earlier in the presence of glycerol (Yurkow *et al.*, 2002). The introduction of EDTA salt in the reagent that is prepared to have an incomplete reaction enhances the rate of reduction as it enhances the ionic strength considerably. The acid and a carbon source was provided through the reaction of glycerol and concentrated Sulphuric acid. The reagent thus formulated is efficient enough to reduce the hexavalent chromium as evident by its appearance in the solution.

Keywords: Glycerol containing solution, Ionic strength, Rate of reduction, reducing reagent.

Introduction

The reduction of metals from higher reactive state to the lower at lower pH value in any liquid media is a common chemical phenomenon. The fate of chromium in the environment is strongly dependent on its valence state (Jeremy F. et al., 2000). The industries such as electroplating, tanneries, and electronic equipments washing contain several heavy metals such as chromium, iron, nickel, silver etc in their effluents. However, chromium levels in air, water, and food are generally very low. The major human exposure is occupational (Chou 1989). Hexavalent chromium is reactive enough and a potent carcinogen (Gibb *et al.*) also exhibits high mobility in soil and groundwater as it forms CrO_{4}^{2} the mobile anion. The carcinogenicity is generally attributed to the Cr (VI), due to being readily taken up by the cells. Trivalent chromium on the other hand is less toxic and essential in human and animal nutrition with almost no mobility in the soil and waters owing to almost insoluble. In North India tanneries are the main source of hexavalent chromium apart from the mining of chromite (FeCr,O₄) ore that eventually introduce the metal into the ground water. It has been however, made mandatory for all tanners to reduce the level of such pollutants and to install the treatment plant to treat the wastewater prior to the discharge of the effluent. Chemically reduction of heavy metals is being given priority just to speed-up the process of pollution mitigation. Important reductants in natural systems are organic compounds and divalent iron. (Barlet et. al, 1988, Fendorf 1995, and Richard et al., 1991). Iron divalent has been reported to be as good as any other reductant capable enough to reduce chromium hexavalent (Ignaz et al., 1998). Very recently the use of polyols have been introduced for the photochemical reduction of Chromium (VI) to Chromium (III) (Yurkow et al., 2002).

The chrome-reducing reagent is based on the same experiment (Yurkow *et al.*, 2002) with having a little chemical changes and the comprehensive understanding about the reactions. The reagent thus prepared is capable enough to reduce the chromium metal even in little amount.

Copyright by ASEA All rights of reproduction in any form reserved

(1)

Srivastava et al.

Material and Method

Potassium dichromate was used to prepare the 1mg/liter solution at low pH. Cr (VI) and Cr (IV) forms can be generated in a test tube at different pH conditions viz., 7.3 to 7.5 and pH 6.8 respectively. The colours of the solutions were yellow initially before the mixing of the reagent. The colour profile was the basic parameters to know the reduction processes as was suggested by Yurkow *et al.*, 2002 that visible colour change from yellow to green following the chromium reduction.

Reagent was prepared by mixing two different chemical solutions i.e., organic part made of Glycerol in methanol with a little supplement of EDTA (di-sodium salt) to elevate the mobility of metal ions in the solution (Chen & Curtright 2001), and the inorganic part i.e., a strong acid especially we used Sulphuric acid but other such as hydrochloric and acetic acid may also be used as has already been tried. 10 ml of each solution of metal was taken into the 15 ml vials and were than mixed with the reagent 100 to 500 μ l in the triplicates. The time of the change of color of solution was recorded . Increasing the pH value by the addition of sodium hydroxide precipitated the reduced metal out.

Results

Primary alcohol groups can chemically reduce chromium in reactions containing strong acids to produce trivalent chromium (Headlam and Lay, 2001). Acrolein produced in the reaction of sulfuric acid and glycerol with a supplement of EDTA and methanol found to be having strong reducing property. At low pH polyols can reduce the metals like chromium. EDTA that helps to bind metals in the solution (surrounding groups) also accelerated the speed of reaction. As in experiment three different solutions were prepared viz., glycerol with sulfuric acid, glycerol in methanol with sulfuric acid and glycerol in methanol with sulfuric acid. The time of the reduction processes varies greatly in accord with their chemical composition.

Sol. A < Sol. B < Sol. C

Sol. C i.e., having EDTA supplemented acrolein shows comparatively faster reduction and only with in a little amount used.

Discussion

Glycerol when reacts with sulphuric acid in concentrated forms Acrolein which, is in the solution due to the dehydration of Glycerol. Glycerol has two primary alcoholic groups that after the removal of two water molecules produce acrolein (1.1) an alkenic aldehyde, which is inflammable, volatile organic compound have a very pungent smell. In the reagent solution plenty of sulphuric acid is present thus there appears

saturation where the production of acrolein stops and the solution starts to act as a strong reductant.

The reagent, which is made with the mixing of three different chemicals viz., Glycerol, EDTA and acid. The acrolein formed in due reactions is stable for several months and act as a confirm electron donor which enable the reduction processes. The basic requirement is acidity of solution where the acidity should remain near pH 2.0.

(2) Environment Conservation Journal Now the reagent is mixed with the solution of potassium dichromate the reaction between chromate ions and the mixture of acrolein, glycerol and sulphuric acid where the sulphuric acid accounts more than others. Thus an oxidation process starts with the reduction of chromium in the solution. (1.2, 1.3, 1.4) EDTA increases the mobility of active chromate ions.

Reactions

1.1- CH2OH – CHOH – CH ₂ OH Glycerol			Conc. H ₂ SO ₄	$CH_2 = CH - CHO + 2H_2O$ Acrolein	
				↓ Functional Aldehyde	
1.2- K2Cr2O7	+	H ₂ SO ₄	Redox react.	$K_2SO_4 + Cr_2 (SO_4)_3 + 2H2O$	

1.3- [Glycerol + Sulphuric acid - Acrolein] + [EDTA] - Strong Reductant - {A}

[Sulphuric acid + Potassium di Chromate] - Strong oxidizing agent - {B}

1.4-
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O$$

Mixed reaction of {A} & {B}

A visible color change from yellow to green is observed following chromium reduction. And it has been suggested by Yurkow *et al.*, 2002 that the conversion of hexavalent chromium Cr (VI) to Cr (III) was determined by measuring the increase in absorbance at 590 nm.

Summary

Concentrated Suphuric acid when reacts with glycerol produces Acrolein and plenty of sulphuric acid stops the reaction in a known quantity and volume. This stopped reaction further gets started when aqueous solution of potassium di chromate is introduced. Two reactions simultaneously occurs in the solution as the reagent it self is a strong reductant and the potassium di chromate solution and sulphuric acid acts as a strong oxidizing agent. Thus both the reactions ultimately results in the reduction of the chromium VI and render a green colour to the solution a characteristic feature of III valent Chromium.

References

Yurkow, E. J., Hong, J., Min, S. and Wang Su*; 2002. Photochemical reduction of hexavalent chromium in glycerol-containing solutions. *Environmental pollution*, 117:1-3

Chen, H. and Cutright, T., 2001. EDTA and HEDTA effects on Cd, Cr, and Ni uptake by Helianthus annuus. *Chemosphere*, 45:21-28.

Chou, I. N., 1989. Distinct cytoskeleton injuries induced by As, Cd, Co, Cr, and Ni compounds. *Biomed. Environ. Sci.*, 2:358-365.

Frank C. Lu, 1996. Basic Toxicology. Third Edition, published at Taylor and Francis publishers USA.

(3) Environment Conservation Journal

Srivastava et al.

- Gibbs, H. J., Lees, P. S., Pinsky, P. F., Rooney, B. C., 2000. Lung Cancer among workers in chromium chemical production. *Am. J. Ind. Med.*, 38 (2): 115–126.
- Headlam, H.A. and Lay, P.A., 2001. EPR spectroscopic studies of the reduction of chromium (VI) by methanol in the presence of peptides Formation of long lived chromium (V) peptide complexes. *Inorg. Chem.*, 40 (1):78 – 86.
- Ignaz J. Buerge and Stephan J. Hug; 1998. Influence of Organic Ligands on Chromiumn (VI) Reduction by Iron (II). *Environ. Sci. Technol.*, 32:2092–2099.
- Jeremy F., Joshua C., David F., Ken K., Bruce B. and Maxim B. Non-Metabolic reduction of Cr(VI) by bacterial surfaces under nutrient absent conditions. *Journal of conference abstracts*, 5(2): 396.
- Calder, L.M., 1988. In *Chromium in the Natural and Human Environments;* Nriagu, I.O., Nieboer, E. Eds.; Wiley: New York, pp 215–229.
- Bartlett, R. J. and James, B. R., 1988. In *Chromium in the Natural and Human Environments;* Nriagu, I.O., Nieboer, E. Eds.; Wiley: New York, pp 267–304.
- Palmer, C.D.; Wittbrodt, P.R., 1991. Processes affecting the remediation of chromium contaminated sites. Enviorn. Health Perspectives 92: 25-40.

(4) Environment Conservation Journal