

## STUDY OF THE POTENTIAL OF ZERO VALENT MAGNESIUM FOR ITS CAPACITY TO REDUCE TOXIC CR (VI)

Undegaonkar M. G.

Department of Chemistry, ASC College, Badnapur, Jalna (MS), India.

(E-mail: [undegaonkar@gmail.com](mailto:undegaonkar@gmail.com))

### ABSTRACT

Hexavalent chromium [Cr (VI)] is one of the most toxic and non-biodegradable pollutants. Reduction of Cr (VI) is achieved by applying zero valent magnesium ( $Mg^0$ ). The rate of reaction is directly proportional to  $Mg^0$  concentration whereas inversely proportional to Cr (VI) concentration. Presence of NaCl has a stimulatory effect on Cr (VI) reduction reaction. The reaction took place in acidic environment created by acetic acid. The demerit of this Cr (VI) remediation method is generation of magnesium acetate as a co-pollutant.

**KEY WORDS:** Hexavalent chromium [Cr(VI)], magnesium acetate, zero valent magnesium ( $Mg^0$ )

### INTRODUCTION

Hexavalent chromium is one of the most hazardous pollutants. Few of its adverse effects on health include mutations, irritation, corrosion of the skin and respiratory tract. It is also known to cause lung cancer (Bhinde *et al.*, 1986; Ganguli and Tripathi, 2002; Holmes *et al.*, 2008; Liu *et al.*, 2006). Chromium is widely used in many industrial processes, such as steel production, alloy preparation, wood preservation, tanneries, metal corrosion inhibition, paints pigments, electroplating etc (Abskharon *et al.*, 2009). Effluent of such industries is loaded with toxic hexavalent chromium. These effluents severely pollute the environment (Elsayed and Saba, 2009). Chromium also exists in non-toxic trivalent state which is necessary for fat and glucose metabolism and proper functioning of insulin (Thacker *et al.*, 2007). The reduction of Cr (VI) to Cr (III) is therefore an attractive and useful process for remediation of Cr (VI) contamination (Liu *et al.*, 2006). Based on this fact many chemical and biological methods of Cr (VI) reduction to Cr(III) have emerged. Few examples of well-studied chemical agents for Cr (VI) reduction are ferrous sulfide (Mullet *et al.*, 2004), siderite (Erdem *et al.*, 2004), magnetite (Peterson *et al.*, 1996) and copper in presence of superoxide (Abu-saba *et al.*, 2000). For electrochemical reduction zerovalent ferrous  $Fe^0$  electrode (Aguilar *et al.*, 2005), and solid electrodes [glassy carbon, gold, boron doped diamond] (Welch *et al.*, 2005) have been used. Apart from this photocatalytic reduction (Mohapatra *et al.*, 2004) and photochemical reduction (Mytych *et al.*, 2003) is also possible. Biological reduction methods have exploited microorganisms like *Bacillus* sp. and *Pseudomonas fluorescence* LB 300 (Wang *et al.*, 1995), Sulfate reducing bacteria (Cheung *et al.*, 2003), indigenous bacteria in the effluent (Dermou *et al.*, 2005) and *Rhizopus nigricans* (Bai *et al.*, 2003). Although numerous chemical methods are available for reduction of hexavalent chromium but these are expensive. There are very few reports for use of zerovalent metals for use of Cr (VI) reduction. Zerovalent ferrous has been used extensively (Marius Gheju, 2011). And much less work has been done on use of zerovalent magnesium (Jae Seon Park and Gyehyeon Lee, 2008) and zerovalent aluminium (Lin *et al.*, 2009). The biological methods demand for specially designed bioreactors and must be maintained at proper conditions. Thus these methods are costly and labor intensive. Evidently, there is need of an economic treatment method by which industries should able to meet the desired environmental standard for hexavalent chromium. The goal of this research work is to develop a chemical method that exploits zero valent magnesium for reduction of Cr (VI) to Cr (III).

### MATERIALS AND METHODS

$Mg^0$  granules (20 mesh),  $K_2PdCl_6$  [Hexachloropalladate (IV) dipotassium] were purchased from Sigma Aldrich Chemical Pvt. Ltd. (Mumbai, India). Acetone, glacial acetic acid, sulfuric acid, 1,5-Diphenyl carbazide and Potassium dichromate were purchased from Merck Ltd. (Mumbai, India). All chemicals were of high purity and analytical grade. No pretreatment was performed on any of the chemicals and were used as received.

#### **$Mg^0$ mediated reduction of Cr (VI):**

Stock solution of Cr (VI) (5000 ppm) prepared in distilled water using potassium dichromate. Appropriate volume from the stock solution diluted into distilled water to achieve desired final concentrations of Cr (VI). To this  $Mg^0$  granules were added. The reaction was initiated with addition of glacial acetic acid. The reaction mixture was kept homogeneous by constant stirring with magnetic stirrer. Aliquots from the reaction mixture withdrawn at suitable time intervals and residual concentration of Cr (VI) were estimated by Diphenyl carbazide method according to procedure outlined in standard methods of APHA (1995).

#### **Kinetics studies of Cr (VI) reduction:**

Kinetics studies for Cr (VI) reduction were carried out with respect to varying  $Mg^0$  concentration, varying Cr (VI) concentration, varying glacial acetic acid concentration and presence of NaCl at different concentration.

**Effect of varying  $Mg^0$  concentration:** For this  $Mg^0$  was added in concentrations (0.5 mg/ml, 1 mg/ml, 1.5 mg/ml and 2 mg/ml). Concentration of other components was kept fixed in each reaction viz. Cr (VI); 100 ppm and glacial acetic acid; 0.083 M. Final reaction volume was 100 ml.

**Effect of varying Cr (VI) concentration:** Concentration of Cr (VI) varied in range 200 ppm – 1000 ppm. Other reactants were added in fixed concentration ( $Mg^0$ ; 1.5 mg/ml and glacial acetic acid concentration; 0.083 M) and reaction volume was 100 ml.

**Effect of varying glacial acetic acid concentration:** These experiments were carried out by varying glacial acetic acid concentration (0.258 M and 0.43 M) at fixed  $Mg^0$  concentration (1.5 mg/ml) and Cr (VI) concentration (100 ppm) constant through each experiment. Reaction volume was fixed at 100 ml.

**Effect of addition of sodium chloride solution:** In these experiments varying sodium chloride concentration (5 ml of each 0.1 M and 1 M) was added to a reaction mixture composed of  $Mg^0$  (1.5 mg/ml), Cr (VI) (100 ppm) and glacial acetic acid (0.083 M).

## RESULTS

**Cr (VI) reduction reaction:** Visual evidence for the reduction of Cr (VI) was observed by the change in the color of reaction mixture from bright orange to orange yellow to green (at the end of reaction). The overall reaction can be represented as follows:  $1.5 Mg^0 + 3 CH_3COOH + Cr(VI) \longrightarrow Cr(III) + 1.5 Mg^{2+} + 3 CH_3COO^- + 1.5 H_2$

**Effect of varying  $Mg^0$  concentration:** With increase in the concentration of  $Mg^0$  from 0.5 mg/ml to 2 mg/ml the time required to reduce the Cr (VI) reduced (Fig. 1) and the reaction rate constant increased linearly (Table. 1). In the graphical representation R2 value of with all four  $Mg^0$  concentrations was above 0.71.

**Table-1:** Relation of initial  $Mg^0$  concentration with Cr (VI) reduction rate.

| $Mg^0$ Concentration (mg/mL) | Rate Constant ( $min^{-1}$ ) |
|------------------------------|------------------------------|
| 0.5                          | 0.0364                       |
| 1.0                          | 0.0416                       |
| 1.5                          | 0.0628                       |
| 2.0                          | 0.1142                       |

**Table-2:** Rate constant values at varying Cr (VI) concentration.

| Cr (VI) Concentration (ppm) | Rate Constant ( $min^{-1}$ ) |
|-----------------------------|------------------------------|
| 200                         | 0.0416                       |
| 400                         | 0.0380                       |
| 600                         | 0.0304                       |
| 800                         | 0.0296                       |
| 1000                        | 0.0244                       |

**Table-3:** Rate constant values at varying acetic acid concentration.

| $CH_3COOH$ Conc. (M) | Rate Constant ( $min^{-1}$ ) |
|----------------------|------------------------------|
| 0.083                | 0.0628                       |
| 0.258                | 0.2452                       |
| 0.430                | 0.3971                       |

**Table-4:** Rate constant values in presence of sodium chloride.

| NaCl Concentration (M) | Rate Constant ( $min^{-1}$ ) |
|------------------------|------------------------------|
| 0.0                    | 0.0628                       |
| 0.1                    | 0.0840                       |
| 1.0                    | 0.2344                       |

**Effect of varying Cr (VI) concentration:** From Fig.2 it is evident that, as Cr (VI) concentration was increased, the effective reaction time was reduced. Similarly the Cr (VI) reduction rate was reducing with every increase in initial Cr (VI) concentration. This shows that lower initial concentration of Cr (VI) is optimum for Cr (VI) reduction reaction.

**Effect of varying acetic acid concentration:** Increase in concentration of acetic acid (0.083 M, 0.258 M and 0.43 M) increased speed of Cr (VI) reduction (Fig. 3). The increasing acetic acid concentration also increased reaction rate constant (Table 1). The acidic environment was thus found to be promoting Cr (VI) reduction.

**Effect of sodium chloride on Cr (VI) reduction:** The effect of NaCl at two different concentrations (0.1M and 1.0M) on the reduction of Cr (VI) to Cr (III) was examined. Figure 4 shows effect of NaCl on reaction rate. Presence of NaCl was found to be stimulating Cr (VI) reduction. The rate constant of reaction in absence of NaCl was fairly low than in presence of NaCl. The higher concentration (1.0M) of NaCl resulted in almost three time higher reaction rate constant as compared to lower concentration (0.1M) of NaCl (Table 4).

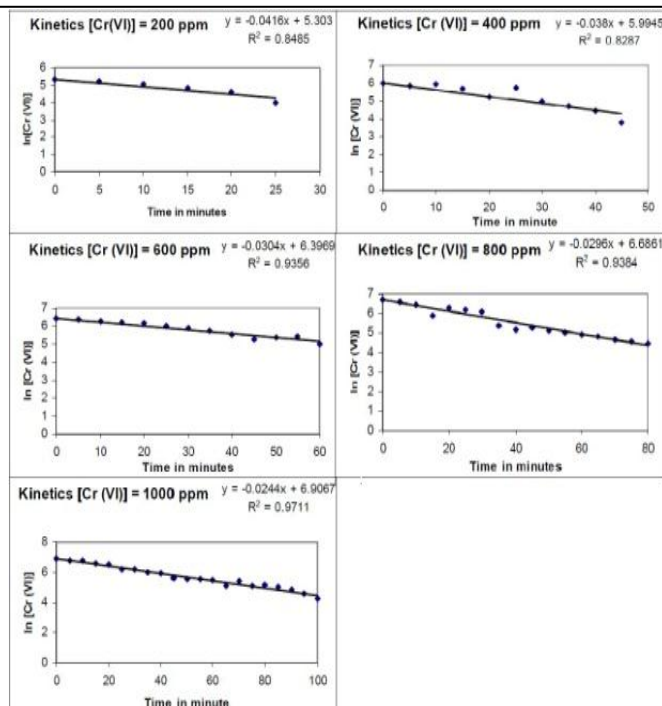


Figure 2: Effect of varying Cr (VI) concentration.

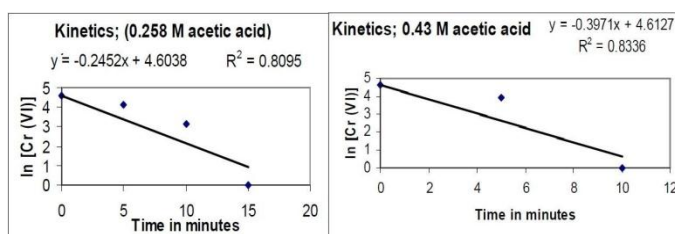


Figure 3: Effect of varying acetic acid concentration.

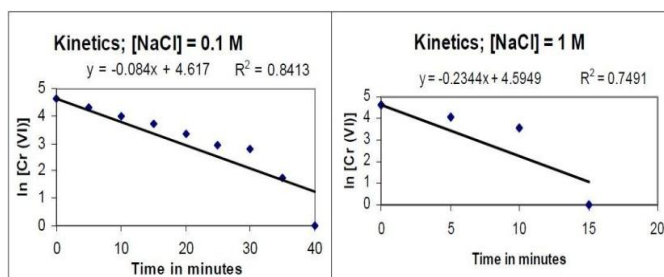


Figure 4: Effect of sodium chloride on Cr (VI) reduction.

## DISCUSSION

In the current research work potential of  $Mg^0$  for reduction of toxic Cr (VI) was analyzed. Also few process parameters were optimized. The basic reaction present work  $0.5mg/ml Mg^0$  was reacted with  $0.1mg/ml Cr (VI)$  and within 60 min almost 50% of the Cr (VI) was reduced. Whereas, Jae Seon Park *et al.* (2008), reported that in the reaction of  $0.00002 mg/ml Cr (VI)$  and  $0.5mg/ml Mg^0$  it took 20hr to reduce the Cr (VI) less than 50% of the initial concentration. As per present experimental observation  $Mg^0$  is less efficient in comparison to  $F^0$  since only  $0.4 mg/ml F^0$  was required to remove 100% Cr (VI) in 60min (Shao-feng Nio *et al.*, 2005). Another observation of this work was increasing initial concentration of Cr (VI) reduced the reaction rate and also reduced the rate constant. This observation is in accordance with Marius Gjeju (2011) who reported that most of the studies which investigated the effect of this parameter reported that an increase of Cr (VI) concentration has a detrimental effect on Cr (VI) reduction rate. Ozer *et al.* (1997), also found in their column studies carried out at an initial Cr (VI) concentration ranging from 250 to 750 mg/L that the

amount of treated solution decreased with the increase of Cr(VI) concentration. The reduction reaction required acidic environment which in the current work was created by addition of glacial acetic acid. And it was seen that increasing concentration of glacial acetic acid accelerated the Cr (VI) reduction speed and it also improved considerably the reaction rate constant. Jae Seon Park *et al.* (2008), also reported that the rate of Cr (VI) reduction increased with decreasing pH. Similar finding has been reported with  $\text{Fe}^0$  (Alidokht *et al.*, 2011; Chen *et al.*, 2007; Dutta *et al.*, 2010; Geng *et al.*, 2009; Qian *et al.*, 2008; Weng *et al.*, 2007; Wu *et al.*, 2009). This observation can be explained by the fact that oxidation reaction of zero-valent metals is proton consuming reaction (Jae Seon Park *et al.*, 2008). The  $\text{Mg}^0$  method proposed here is easier and cheaper as compared to  $\text{Al}^0$  based method of Lin *et al.* (2009). The  $\text{Al}^0$  method of Cr (VI) reduction uses Polyoxometalate (POM,  $\text{HNa}_2\text{PW}_{12}\text{O}_{40}$ ) as a catalyst which accelerates Cr (VI) reduction by Al. Though the reduction reaction is quicker, it needs to be carried out in presence of  $\text{N}_2$  or  $\text{O}_2$  and at pH 1 (Lin *et al.*, 2009).

## CONCLUSION

Zero valent magnesium was effective for Cr (VI) reduction. Rate of reduction of Cr (VI) is directly proportional to  $\text{Mg}^0$  and glacial acetic acid concentration. This method of Cr (VI) reduction can be carried out only in acidic medium. This chemical method is cheaper, less time consuming, mechanically easier and no sludge is generated. Generation of co pollutant Magnesium acetate [ $\text{Mg}(\text{CH}_3\text{COO})_2$ ] is demerit of this method.

## REFERENCES

- Abskharon R.N.N., Gad El-Rab S.M.F., Hassan S.H.A. and Shoreit A.A.M. (2009).** Reduction of toxic hexavalent chromium by *E. coli*. *Glob. J. Biotech. Biochem.* **4**(2):98-103.
- Abu Saba K.E., Sedlak D.L. and Flegal A.R. (2000).** Indirect reduction of hexavalent chromium by copper in the presence of superoxide. *Marine Chem.* **69**:33-41.
- Aguilar R., Martine S.A., Rodriguez M.G. and Soto G. (2005).** Process analysis for treatment of industrial plating wastewater: simulation and control approach. *Chem. Eng. J.* **105**:139-145.
- Alidokht L., Khataee A.R., Reyhanitabar A. and Oustan, S. (2011).** Reductive removal of Cr (VI) by starch-stabilized  $\text{Fe}^0$  nanoparticles in aqueous solution. *Desalination.* **270**:105-110.
- APHA. (1998).** Standard methods for examination of water and wastewater. 20th ed. American Public Health Association, Washington, DC. Pp 3.59-3.61.
- Bai R.S. and Abraham T.E. (2003).** Studies on chromium (VI) adsorption-desorption using immobilized fungal biomass. *Bioresour. Technol.* **87**:17-26.
- Bhinde J.V., Dhakephalkar P.K. and Paknikar K.M. (1996).** Microbiological process for the removal of Cr (VI) from chromate bearing cooling tower effluent. *Biotechn. Lett.* **18**:667-672.
- Chen S.S., Cheng C.Y., Li C.W., Chai P.H. and Chang Y.M. (2007).** Reduction of chromate from electroplating wastewater from pH 1 to 2 using fluidized zero valent iron process. *J. Haz. Mat.* **142**:362-367.
- Cheung K.H. and Gu J.D. (2003).** Reduction of chromate by an enrichment consortium and an isolate of marine sulfate reducing bacteria. *Chemosphere.* **52**:1523-1529.
- Dermou E., Velissariou A., Xenos D. and Vayenas D. V. (2005).** Biological chromium (VI) reduction using a trickling filter. *J. Haz. Matrl.* **126**:78-85.
- Dutta R., Mohammad S.S., Chakrabarti S., Chaudhuri B., Bhattacharjee S. and Dutta B.K. (2010).** Reduction of hexavalent chromium in aqueous medium with zerovalent iron. *Water Env. Res.* **82**:138-146.
- Elsayed E. M. and Saba A. E. (2009).** The electrochemical treatment of toxic hexavalent chromium from industrial effluents using rotating cylinder electrode cell. *Int. J. Electrochem. Sci.* **4**:627-639.
- Erdem M., Gijr F. and Tumen F. (2004).** Cr (VI) reduction in aqueous solutions by siderite. *J. Haz. Mat.* **113**:217-222.
- Ganguli A. and Tripathi A.K. (2002).** Bioremediation of toxic chromium from electroplating effluent by chromate reducing *Pseudomonas aeruginosa* A2hr in two bioreactors. *Appl. Microbiol. Biotechnol.* **58**:416-420.
- Geng B., Jin Z., Li T., and Qi X. (2009).** Kinetics of hexavalent chromium removal from water by chitosan- $\text{Fe}^0$  nanoparticles. *Chemosphere.* **75**:825-830.
- Holmes A.L., Wise S.S and Wise J.P. Sr. (2008).** Carcinogenicity of hexavalent chromium. *Indian. J. Med. Res.* **128**:353-372.
- Lin C.J., Wang S.L., Huang P.M., Tzou Y.M., Liu J.C., Chen C.C., Chen J.H. and Lin C. (2009).** Chromate reduction by zero-valent Al metal as catalyzed by polyoxometalate. *Water Res.* **43**(20):5015-5022.
- Liu G.Y., Xu W.H., Zeng M. G., Li X. and Gao H. (2006).** Cr (VI) reduction by *Bacillus* sp. isolated from chromium landfill. *Process Biochem.* **41**:1981-1986.
- Marius Gheju. (2011).** Hexavalent chromium reduction with zero-valent iron (ZVI) in aquatic systems. *Water Air Soil Pollut.* **222**:103-148.

- Mohapatra P., Samantaray S.K. and Parida K. (2004).** Photocatalytic reduction of hexavalent chromium in aqueous solution over sulfate modified titania. *J. Photochem. Photobiol. Chem.* **170**:189-194.
- Mullet M., Boursiquot S. and Ehrhardt J.J. (2004).** Removal of hexavalent chromium from solutions by mackinawite, tetragonal FeS. *Colloids Surfaces A.* **244**:77-85.
- Mytych P., Karocki A. and Stasicka Z. (2003).** Mechanism of photochemical reduction of Cr (VI) by alcohols and its environmental aspects. *J. Photochem. Photobiol. Chem.* **160**:163-170.
- Ozer A., Altundogan H.S., Erdem M. and Tumen F. (1997).** A study on the Cr(VI) removal from aqueous solutions by steel wool. *Env. Pollution.* **97**:107-112.
- Park Jae Seon and Lee Giehyeon. (2008).** Preliminary results of Cr (VI) reduction by zero valent magnesium (ZVM) powder. *Geochimica et Cosmochimica Acta.* **72**(12):723.
- Peterson M.L., Brown G.E. and Parks G.A. (1996).** Direct XAFS evidence for heterogeneous redox reaction at the aqueous chromium/magnetite interface. *Colloid. Surface. Phychem. Eng. Asp.* **107**:77-88.
- Qian H., Wu Y., Liu Y. and Xu X. (2008).** Kinetics of hexavalent chromium reduction by iron metal. *Front. Env. Sci. Eng. China.* **2**:51-56.
- Shao-feng Niu, Yong Liu, Xin-hua Xu. and Zhang-hua Lou. (2005).** Removal of hexavalent chromium from aqueous solution by iron nanoparticles. *J. Zhejiang Univ. Sci.* **6B**(10):1022-1027.
- Thacker U., Parikh R., Shouche Y. and Madamwar D. (2007).** Reduction of chromate by cell-free extract of *Brucella* sp. isolated from Cr(VI) contaminated sites. *Bioresource. Technol.* **98**:1541-1547.
- Wang Y. and Changsong X. (1995).** Factors affecting hexavalent chromium reduction in pure cultures of bacteria. *Water Resources.* **29**:2467-2474.
- Welch C.M., Nekrassova O. and Compton R.G. (2005).** Reduction of hexavalent chromium at solid electrodes in acidic media: reaction mechanism and analytical applications. *Talanta.* **65**:74-80.
- Weng C.H., Lin Y.T., Lin T.Y. and Kao C.M. (2007).** Enhancement of electrokinetic remediation of hyper Cr (VI) contaminated clay by zero-valent iron. *J. Haz. Mat.* **149**:292-302.
- Wu Y., Zhang J., Tong Y. and Xu X. (2009).** Chromium (VI) reduction in aqueous solutions by Fe<sub>3</sub>O<sub>4</sub>-stabilized Fe<sup>0</sup> nanoparticles. *J. Haz. Mat.* **172**:1640-1645.