ISSN : 0974 - 7451 Volume 7 Issue 8

Trade Science Inc.

Environmental Science
An Indian Journal

Current Research Paper

ESAIJ, 7(8), 2012 [288-295]

Zinc oxide nanoparticles for the photocatalytic reduction of hexavalent chromium in wastewater under sunlight

Prantik Banerjee*, Pallavi Mitra, Sampa Chakrabarti, Sekhar Bhattacharjee
Department of Chemical Engineering, University of Calcutta, 92, Acharya P. C. Road, Kolkata, 700 009, (INDIA)
E-mail: prantik.banerjee85@gmail.com; sampac@vsnl.net; sampac.2008@gmail.com;
pallavim8@gmail.com; sekharbhatta@gmail.com

Received: 3rd June, 2012 ; Accepted: 13th August, 2012

ABSTRACT

Common sources of chromium in wastewater are leather industries, electroplating, electronic, and timber. Hexavalent chromium is more toxic and carcinogenic than trivalent chromium. Photocatalytic reduction of Cr (VI) to Cr (III) in an aqueous medium under tropical sunlight and nanosized ZnO semiconductor catalyst has been investigated using potassium dichromate as the model compound. Methanol was added as a hole- scavenger for enhancement of the photo-reduction. Effects of the process parameters such as nano-ZnO loading (0 to 0.6g/L), initial concentration of substrate solution (10 to 50mg/L), pH (4-9) and methanol-dosing (0 – 1.75mol/L) have been investigated. The initial rate of the photochemical method was found to be independent of the concentration of potassium dichromate as well as concentration of methanol above an optimum value. A probable mechanism for the entire reaction and the corresponding kinetic model have been proposed for the photo reduction and proved by experimental results. Another rate equation based on the LHHW model compares well with the mechanistic rate equation.

KEYWORDS

Hexavalent chromium;
Photocatalytic reduction;
Zinc oxide nanoparticles;
Sunlight;
Initial rate;
Kinetic model.

INTRODUCTION

Chromium occurs in two common oxidation states - Cr (III) and Cr (VI). Hexavalent Chromium is toxic and carcinogenic. But Cr (III) is less toxic and can be readily precipitated or sorbed on a variety of inorganic and organic substances at alkaline or neutral pH[1,2]. Industrial sources such as leather tanning industries, chrome plating, electronic, metallurgical, and timber release Cr (VI) in effluent streams and therefore must be treated before it is discharged to surface water. The treatment procedure of Cr (VI)-bearing wastewater often comprises of reduction of Cr (VI) and post-treatment such as coagulation-precipitation, active carbon adsorption or membrane based processes and technologies[3-5].

Reduction of chromium occurs in an acidic medium in presence of an electron donor (e.g., Fe^{++}, Fe^0) a reducing anion (e.g., S^{2-}, SO_3^{2-}) or an oxidizable organic (e.g., an alcohol)[6-8]. An alternative clean route is photocatalytic reduction in presence of a semiconductor material such as ZnO, TiO_2, CdS or WO_3 under visible/ UV radiation[2,3,9,10]. The photocatalytic method is based on the reactive properties of an electron-hole pair generated in the semiconductor when irradiated by UV/visible light having energy greater than the band-gap energy of the semiconductor. Application of the photocatalytic technique for remediation of inorganic and organic pollutants in wastewater has been reviewed by Kabra et al.[11]. This method is widely used for treatment of the drinking water and industrial wastewater by oxidizing refractory organic contaminants. The capacity of a semiconductor photocatalyst such as ZnO to reduce any reducible pollutant which uses the generated electron on the semiconductor surface is, however, less explored. Photoreduction of a metal ion is accelerated if it is accompanied by simultaneous oxidation of an organic molecule that plays the role of a ligand or a 'sacrificial electron donor'. During the photo-reduction process, concurrent generation of one or more of the species $O_2^{\cdot}$, $HO_2^{\cdot}$, $OH^{\cdot}$, H_2O_2 and HO_2^- is reported. This occurs because of the fact that the medium (water) acts as the electron donor simultaneously with the sacrificial organic species acting as the hole scavenger. Only a few investigations on photo-reduction of Cr(VI) have been reported in the recent years. Ku and Jung[12] studied photoreduction of Cr (VI) in an irradiated suspension of TiO_2 (up to 12 g/L). Khalil et al.[13] studied the same using an irradiated suspension of ZnO, WO_3 and two varieties of TiO_2. The pH and initial concentration of Cr (VI) were reported to have affecting the photocatalytic process. Using a sacrificial organic species as a hole scavenger to enhance photoreduction of Cr (VI) has been reported in several recent publications. Schrank et al.[9] used Luranzol S Kong dye in presence of TiO_2 photocatalyst at pH values ranging from 2.5 and 7.0. Mytych et al.[8] studied photoreduction of Cr (VI) with simultaneous degradation of organic compounds such as phenols, chloro- and bromo-phenols, aliphatic alcohols and oxalate ligands. Carbon tetrachloride in presence of a non-ionic surfactant used as hole absorbers from suspended TiO_2 irradiated with visible light was reported by Cho et al.[14].

From the very onset of human civilization, man has utilized solar energy to meet various requirements, most important disinfection of water, or environmental remediation, a topic over which there has much hue and cry these days. The fact that fast depleting reserves of fossil fuel vis-a-vis deteriorating environment has further encouraged studies on more efficient usage of solar energy. Using advanced oxidation techniques by photocatalysts, solid, liquid and even gaseous wastes can be treated with the help of solar energy. India, being a tropical country, the daily average solar energy incident over India varies from 4 to 7 kWh/m^2 with about 2300 - 3200 sunshine hours per year, depending upon location (http://en.wikipedia.org/wiki/Earth%27s_energy_budget.html[15]. It is thus especially desirable that environmental remediation problems in countries like India may be addressed economically with the help of solar energy rather than employing a relatively costly power generated from fossil fuel.

Very few reports are available on the photocatalytic reduction of hexavalent chromium using solar radiation. Das et al.[16] studied the photocatalytic reduction of hexavalent chromium under solar irradiation using titania-pillared zirconium phosphate and titanium phosphate prepared by them as semiconductor catalyst. The reduction was favoured in acidic pH and the rate decreased with increase in initial concentration. The rate of reduction was pseudo-first order. Mahapatra et al.[17] prepared, characterized and studied the activity of the sulphate modified TiO_2 photocatalyst under solar radiation for reducing hexavalent chromium to the trivalent one. The photoreduction was enhanced by the presence of complexing agent like EDTA. Surface of the ZnO semiconductor was sensitized using humic acid by Selli et al[18] for enhancement of the reduction of hexavalent chromium under solar radiation. In a recent article, Kabra et al.[19] reported solar photoreduction of hexavalent chromium using TiO_2 catalyst and citric acid as electron donor. They found that the reduction was highly sensitive to pH and 100% reduction could be achieved within 1.5h in the strong acidic pH of 2. A few researchers have reported comparatively better photocatalytic activity of ZnO compared to TiO_2[20,21]. The undoped ZnO has the same band-gap energy of 3.2eV as that of TiO_2. From the comparative absorption spectra of ZnO and TiO_2, it may be observed from the absorption spectrum of ZnO consists of a single and broad intense absorption from 470 nm to lower wave lengths, whereas TiO_2 shows intense absorption from 420nm until band gap characteristic absorption maximum at 400 nm. The absorbance of ZnO is more than TiO_2 right from 470 to 350nm, the region where the light absorption due to band gap excitation occurs in both the materials[21]. That means ZnO absorbs large fraction of solar spectrum and more light quanta than TiO_2.

Use of nano-sized semiconductor particles is a very recent trend and the available reports are not many. In one of our previous works[22], we had studied the photocatalytic efficiency of nanoparticles generated employing different solvents, which was observed to be different due to different morphology of synthesized ZnO crystallites. We had also observed that nanoparticles have almost double reduction efficiency compared to that of commercially available microparticles of ZnO. Yang and Chan[23] studied photocatalytic reduction of hexavalent chromium in aqueous solution using dye-sensitized nanoscale ZnO under visible light. *Alizarin Red S* dye was used for sensitizing nano-ZnO prepared from $ZnSO_4$ and NH_4HCO_3. The light source was 4nos. 18W household fluorescent lamp and also solar radiation. They achieved reduction efficiencies of 75% with lamp and 90% with solar radiation after 17h with 20mg/L initial condition of hexavalent chromium. Yoon et al.[24] reduced hexavalent chromium in water using nanotubular TiO_2 electrode under UV radiation of a 1000W Xenon lamp. At pH 3, they achieved a reduction efficiency of 98% with a Cr(VI) solution of 1mg/L in 120 minutes. Yang et al.[25] used WO_3 doped TiO_2 nanotube array in presence of citric acid as sacrificial electron donor for photo reduction of hexavalent chromium. The radiations used were both in the UV and visible regions with Hg and Xe lamps respectively. Idris et al.[26] used magnetically separable photocatalyst beads made of γ-iron oxide nanoparticle and sodium alginate polymer to reduce hexavalent chromium photocatalytically. They obtained complete reduction of 50mg/L solution of dichromate within 50 minutes under solar irradiation. Ku et al.[27] studied the photocatalytic reduction of Cr(VI) in aqueous solution using ZnO/TiO_2 photocatalysts coupled with various ZnO dosages under 365 nm UV light illumination. They observed that ZnO/TiO_2 containing 2.0 mol% ZnO exhibited the lowest photoluminescence emission intensity and the maximum photocatalytic reduction of Cr(VI) in aqueous solutions due to the enhancement of charge separation by interparticle electron transfer.

In the present work, nanosized ZnO has been used as a semiconductor catalyst to reduce hexavalent chromium present in potassium dichromate under solar irradiation. The sacrificial electron donor was methanol and the justification of its use was explained in our previous work[28]. In the east coast of India in September – October, the average intensity of the sunlight was about 60 - 70 klux. The influence of process parameters such as ZnO loading, pH, quantity of methanol added and initial concentration of the substrate was studied. A possible mechanism with a rate equation has been modeled and tested with experimental data.

EXPERIMENTAL DETAILS

Materials

Potassium dichromate (GR grade) was received from LOBA Chemie, India. Methanol (GR) was procured from SD Chemicals, India. Zinc oxide nanopowder (< 100nm size, No. 544906) was purchased from Sigma-Aldrich and freshly prepared double distilled water was used to prepare solutions.

Characterization of semiconductor nanoparticles

The particle size was analyzed using a *Malvern DLS nanosizer* instrument. The mean particle size of the ZnO catalyst was 50 – 80 nm (Figure not shown) and the surface area was 15 - 25m^2/g. Crystal structure and purity of zinc oxide nanoparticles (Figure not shown) have been studied using *PANalytical PW 3040/ 60* XRD instrument. The cell volume was found to be 29.02644±0.117286 $Å^3$. The diffractometer system was X Pert PRO with 2θ from 5 to 80°. Particle sizes of the nanoparticles have been calculated using Scherrer equation[29].

$$t = 0.9\lambda/(B\cos\theta) \qquad (1)$$

where t is the grain thickness, λ is the wavelength of the radiations, B is FWHM value of the peaks and θ is the diffraction angle and the value of t was found to be 26nm. Size and surface morphology was also analyzed using AFM (*VEECO digital multimode nanoscope IIIa*) on glass slide (Figure not shown).

Intensity of solar radiation was measured using *Metravi 1330* digital lux meter. pH of the solution was measured by Eutech Waterproof pH Testr 20.

Analytical methods: The concentration of hexavalent chromium was determined spectrophotometrically at $\lambda_{max} = 349nm$ using a 1 cm quartz cell in a UV-vis spectrophotometer (*Shimadzu UV-160A*)[30].

Experimental set up and procedure

Solar experiments were carried out in a SS – box type reactor with a quartz glass cover and having a cooling water circulation system around it. The volume of the reactor was about 550 mL. It was mounted on a magnetic stirrer for mixing (Figure 1). Potassium dichromate solution, weighed quantity of ZnO and methanol were taken together. This reaction mixture was maintained as a suspension with the help of a magnetic stirrer. After ensuring the adsorption equilibrium, if any, in the dark, the reactor was exposed to the sunlight for 2h. Aliquots of about 25mL were withdrawn at particular time intervals, filtered using Whatman Nucleopore Polycarbonate membrane (No. 111103, porosity 0.05μm) filter and the filtrate was analyzed spectrophotometrically for the residual potassium dichromate content.

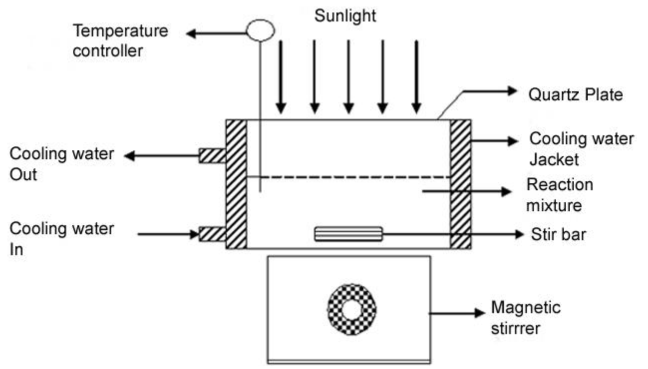

Figure 1 : Experimental set-up for photoreduction of hexavalent chromium under sunlight

RESULTS AND DISCUSSIONS

Blank experiments carried out without any photocatalyst added did not indicate any photolysis or photochemical change in the substrate. Thus the observed reduction of dichromate was due to photocatalytic effect of ZnO and the sacrificial electron donor only.

Adsorption experiments

Adsorption of dichromate on the ZnO particles was found to be negligible. EDS analysis of the spent catalyst from the adsorption experiment showed no Cr(VI) adsorbed on it. In spite of the dispute on the amount of adsorption, there is a general agreement in the literature[9,13] that ZnO adsorbs very little Cr(VI) at neutral or basic pH (the point of zero charge of the material occurs at a pH of 9.2) and our experiment was done at a close to neutral pH (pH = 5)[31].

We have filtered potassium dichromate solution without catalyst to study whether there is any adsorption/ reduction of Cr(VI) occurred by the membrane itself and we observed no adsorption / reduction of Cr(VI) during filtration through polycarbonate membrane. When adsorption experiment was conducted separately with a high concentration of alcohol (Figure 2), substantial adsorption of methanol was noted on the zinc oxide nanoparticle. The residual concentration of methanol was measured spectrophotometrically at $\lambda_{max} = 280nm$.

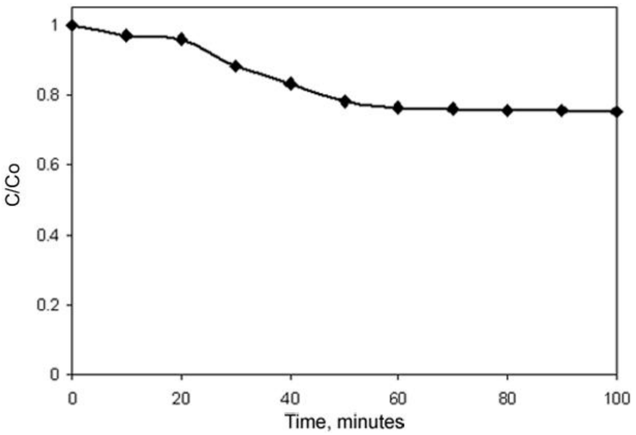

Figure 2 : Time concentration data for adsorption of methanol on nano-ZnO photocatalyst [Initial concentration of methanol: 20 mol/L, temperature 25°C, pH 5, nano-ZnO loading 0.5g in 150mL solution]

Influence of process parameters

We have varied the nano-ZnO loading from 0 to 0.6g/L and initial concentration of Cr (VI) from 10 to 50mg/L. It was observed that the initial rate increased with ZnO-loading up to 0.3g/L. After that the rate remained unchanged with ZnO–loading of 0.4g/L and thereafter, with further increase in loading, it decreased. Increase in the amount of ZnO means increase in the active sites for catalysis. Hence the increase in rate constant and percent degraded. But after a certain critical value, the suspended catalyst blocked the entry of sunlight and hence the decrease in the initial rate of reduction of Cr(VI). We have plotted ZnO loading up to 0.4 g/L against initial rate to get a straight line (Figure 3a). Under the otherwise same experimental conditions, initial rate of reduction with nanosized ZnO is about 2.8 times of that with microsized ZnO catalyst.

The range of initial concentration of the substrate we worked was from 10mg/L to 50mg/L. We observed that the percent reduced decreased with increase in the initial concentration which was reported before by Ku and Jung[12], Chakrabarti et al.[28], Iwata et al.[32], and Chakrabarti and Dutta[33]. However, the initial rate is more or less independent of initial substrate concentration (Figure 3b).

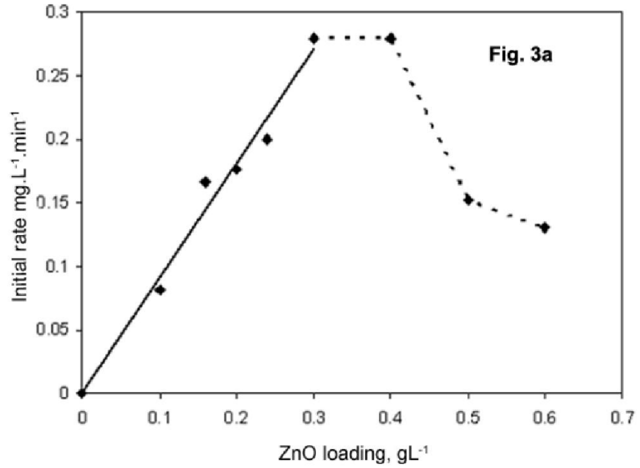

Figure 3a : ZnO-loading vs initial rate of photoreduction [Initial concentration of substrate: 50mg/L, methanol concentration 1.25 mol/L, solution volume 500mL, temperature 25°C, pH 5, solar light 70klux]

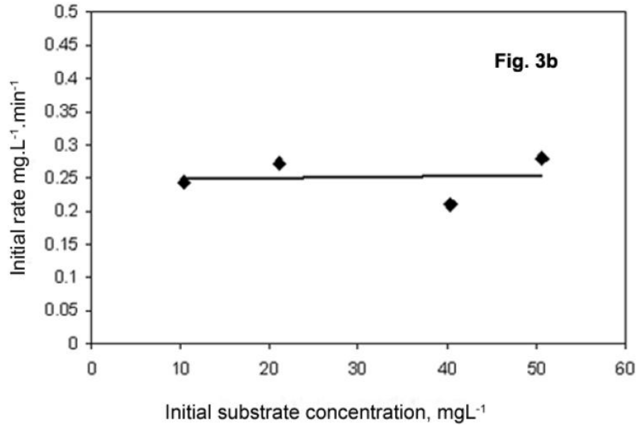

Figure 3b : Initial substrate concentration vs initial rate of photoreduction [ZnO-loading 0.4g/L, methanol concentration 1.25mol/L, temperature 25°C, pH 5, solar light 70klux]

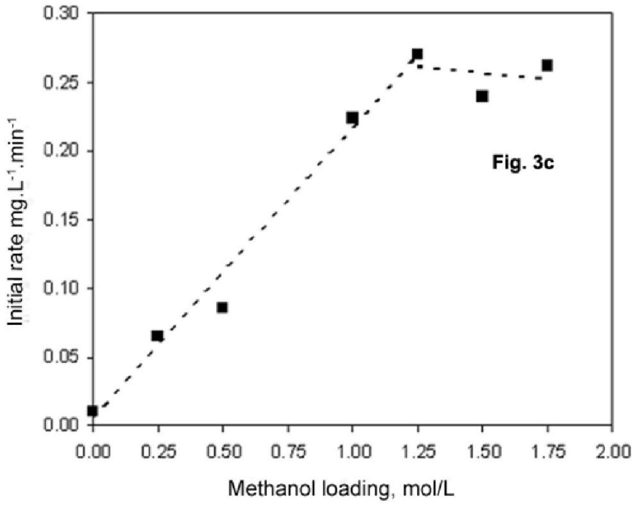

Figure 3c : Concentration of methanol vs initial rate of photoreduction [Initial concentration of substrate 50mg/L, nanoZnO loading 0.2g, solution volume mL, temperature 25°C, pH 5, solar light 70klux]

The photoreduction experiment has been conducted in different pH to study its effect on the photoreduction. The pHs selected were 4, 5, 7 and 9. It was observed that the initial rate was maximum at pH 4 and remains nearly the same at pH 5. However the initial rates were lower in neutral (pH 7) and alkaline (pH 9) medium. We have conducted the baseline experiments at pH 5.

We have used methanol as hole-scavenger and increased the quantity of methanol added from 0 to 1.75mol/L in a set of experiments. We observed an enhancement in the initial rate up to 1.25mol/L, after that the initial rate did not change considerably with addition of more methanol (Figure 3c). Therefore we fixed our experiments with 1.25mol/L methanol.

Photo-reduction – steps, mechanism and rate equation

The following reaction pathway is proposed for the reduction process where the first step is the generation of hole-electron pair after the surface of ZnO nanoparticles was irradiated with sunlight.

Photo-excitation: $$\mathrm{ZnO} + h\nu \xrightarrow{k_1} \mathrm{ZnO}(h^+ + e^-) \qquad (2)$$

The hole is responsible for oxidation and the electron is responsible for reduction. As reduction is the desired route here, we have used methanol as hole-scavenger. There was no change in the initial rate of reduction of Cr(VI) by addition of methanol beyond 1.25mol/L. This means that all the holes generated at that particular ZnO loading and light-intensity, have been scavenged by the amount of methanol added. Since the quantity of methanol is in large excess, we can safely assume that the recombination of hole-electron pair is negligible.

Turchi and Ollis[34] suggested four modes of photocatalytic reactions, where one of the described reaction occurring between two free species in the fluid phase forming H_2O_2. In one of the studies, Khalil et al[13] has suggested that since there was no appreciable adsorption of Cr(VI) on ZnO surface, and it is also possible that homogeneous reduction of Cr (VI) in solution occurs by photogenerated H_2O_2[13]. Dissolved oxygen acts as the electron scavenger and generates H_2O_2.

Generation of H_2O_2:

$$\frac{1}{2}O_2 + H^+ + ZnO(e^-) \xrightarrow{k_2} \frac{1}{2}H_2O_2 \qquad (3)$$

A parallel reduction reaction may have occurred through adsorbed methanol (since we observed adsorption of methanol and not the substrate on the surface) which gives rise to methoxy radicals upon hole scavenging.

Hole scavenging by methanol:

$$CH_3OH + \quad ZnO(h^+) \xrightarrow{k_4} CH_3O^\bullet \qquad (4)$$

The reduction of Cr (VI) to Cr (III) may proceed either with hydrogen peroxide (vide Eq. 3 above) and/or with the methoxy radicals (vide Eq. 4 above) generated in situ. The reduction reactions are given below (Eqns (5) and (6)). Equations 5 and 6 are based on two observations: (i) quite a considerable amount of methanol adsorbed on nano-zinc oxide. (ii) a typical FTIR spectra (Jasco FTIR-670 Plus) of a reaction mixture showed peaks at 1009 cm^{-1} (69% transmission) and 835 cm^{-1} (55% transmission). These peaks are characteristic of an aldehyde which is formaldehyde in this case. Khalil et al.[13] suggested homogeneous reduction of hexavalent chromium by photogenerated H_2O_2 responsible for supply of electron to the hexavalent chromium in solution

Reduction of Cr(VI):

$$Cr(VI) + \frac{1}{2}H_2O_2 + H^+ \xrightarrow{k_3} Cr(III) + H_2O + O_2 \qquad (5)$$

$$Cr(VI) + CH_3O^\bullet \xrightarrow{k_5} Cr(III) + products \qquad (6)$$

A mechanistic rate expression for photo-reduction can be developed on the basis of the above reaction steps. Generation and consumption of H_2O_2 and methoxy radicals are assumed to occur at pseudo-steady state[28].

$$\frac{d}{dt}[H_2O_2] = k_2[O_2]^{1/2}[H^+][e^-] - k_3[Cr(VI)][H_2O_2]^{1/2}[H^+] \; = \; 0 \; (7)$$

$$\frac{d}{dt}[CH_3O^\bullet] = k_4[CH_3OH][h^+] - k_5[Cr(VI)][CH_3O^\bullet] \; = \; 0 \; (8)$$

The initial rate of reduction [from Eq. (4) and Eq (5)] is,

$$-\frac{d[Cr(VI)]}{dt} = k_3[Cr(VI)[H_2O_2]^{1/2}[H^+] + k_5[Cr(VI)][CH_3O^\bullet] \; (9)$$

Combining Eqs (6), (7) and (8),

$$\textbf{Initial rate} = k_2[O_2]^{1/2}[H^+][e^-] \; + \; k_4[CH_3OH][h^+] \; (10)$$

Again, the pseudo-steady state assumption applied to the generation of holes and the electrons leading to

$$\frac{d}{dt}[h^+] = k_1[ZnO][h\nu] - k_4[CH_3OH][h^+] \; = \; 0 \qquad (11)$$

and

$$\frac{d}{dt}[e^-] = k_1[ZnO][h\nu] - \; k_2[O_2]^{1/2}[H^+][e^-] \; = \; 0 \qquad (12)$$

Combining Eqs (10), (11) and (12), the final form of the rate equation becomes:

Initial rate of reduction,

$$r_i = 2\,k_1[ZnO][h\nu] = k\,[ZnO] \qquad (13)$$

The initial rate is thus directly proportional to the catalyst loading as the intensity of solar radiation remains constant. This corroborates to our experimental observation indicated in Figure 3a.

At constant loading of ZnO,

$$\textbf{the initial rate } r_i = k'' \qquad (14)$$

Eq..(14) means the initial rate is independent of initial substrate concentration and methanol concentration. The proposition is supported by the experimental data described in Figures 3b and 3c. A recent article by Wang et al.[35] reports that the rate of reduction is independent of the substrate concentration; this supports our Eq. (13) as deduced from the present model.

Several researchers proposed the LHHW rate equation to determine the rate constant for photocatalytic reduction of hexavalent chromium[9,12]. But there are reports which suggest that photocatalytic processes do not always obey LH equation[36,37]. Although we did not observe any appreciable adsorption of Cr(VI) on the ZnO photocatalyst surface, but adsorption of methanol could lead to a LHHW-type pathway of the reduction reaction through the formation of the methoxy radicals [Eq. (4)]. To test this possibility we selected the following form of the LHHW equation for the initial rate:

$$\textbf{Initial Rate, } r_i' \; = \frac{k' C_A}{1 + K C_A} \qquad (15)$$

We could regress the data very nicely (R^2=0.99). Moreover we observed that since KC_A>>1 at the experimental range, the LH equation reduced to the form where initial rate was independent of the initial concentration of the substrate. Following the equation [Eq. (15)] suggested by Minero and Vione[36] for a well-stirred open system where the substrate is very poorly adsorbed on the photocatalyst, it was observed that the initial rate is directly proportional to the catalyst loading only. This, once again revalidates our proposed Eq. (13).

The value of the zero order rate constant from the LHHW model is 0.29 mg L^{-1} min^{-1}. Using ZnO loading as 0.3g/L, the value of rate constant from our proposed model [k'' in Eq. (14)] comes to be 0.28 mg. L^{-1}.min^{-1} which are in good agreement. Figure 4 shows a parity diagram showing the experimental and predicted values of the initial rates at different loading of ZnO photocatalyst.

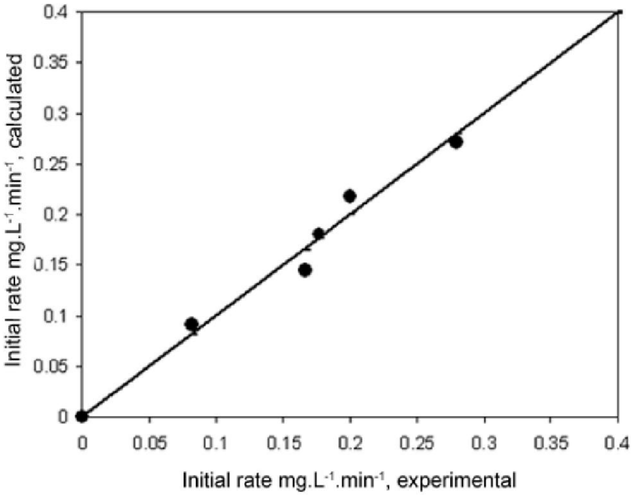

Figure 4 : Parity diagram showing experimental and predicted initial rates

From Eq. (13), the rate constant k_1 for photo-excitation reaction can be determined with known loading of ZnO. The average value comes to be 0.013 (mg. L^{-1}.min^{-1}). (g ZnO.L^{-1})$^{-1}$. klx^{-1}.

CONCLUSION

Hexavalent chromium in aqueous solutions can be effectively reduced to the trivalent state using nano sized ZnO as the semi-conductor photo-catalyst under solar radiation in presence of methanol as a sacrificial electron donor. Under constant intensity of solar radiation, the extent of degradation as well as its initial rate could be increased by increasing the loading of the photocatalyst. About 43 % reduction of the substrate could be achieved over a reaction time of 120 minutes using only 0.5g nano ZnO per litre of substrate solution. The initial reaction rate was practically independent of the concentration of the substrate as well as of the sacrificial electron donor but showed a linear dependence on the catalyst in suspension. A kinetic model has been suggested based on a possible sequence of reactions. We also observed that the model fitted in the initial rate which was calculated from the experimental data.

ACKNOWLEDGEMENTS

A research grant no. Conv./ 002/ NanoRAC (2008) dated 12.12.08 from the Centre for Research in Nanoscience and Nanotechnology, University of Calcutta. Prof. Basab Chaudhuri, Registrar, University of Calcutta. Prof. Binay K. Dutta, Chairman, West Bengal Pollution Control Board.

REFERENCES

[1] L.A.G.Rodenas, A.D.Weisz, G.E.Magaz, M.A.Blesa; J.of Colloid Interf.Sci., **230**, 181 **(2000)**.

[2] B.Sun, E.P.Reddy, P.G.Smirniotis; Environ.Sci. Technol., **39**, 6251 **(2005)**.

[3] X.Wang, S.O.Pehkonen, A.K.Ray; Ind.Eng.Chem. Res., **43**, 1665 **(2004)**.

[4] A.R.Bowers, C.P.Huang; Prog.Wat.Technol., **12**, 629 **(1980)**.

[5] P.S.Kulkarni, V.Kalyani, V.V.Mahajani; Ind.Eng. Chem.Res., **46**, 8176 **(2007)**.

[6] S.-S.Chen, C.-Y.Cheng, C.-W.Li, P.-H.Chai, Y.-M.Chang; J.Hazard.Mater., **142**, 362 **(2007)**.

[7] R.Dutta, S.S.Mohammad, S.Chakrabarti., B.Chaudhuri, S.Bhattacharjee, B.K.Dutta; Wat.Environ.Res., **82**, 138 **(2010)**.

[8] P.Mytych, A.Larocki, Z.Stasicka; J.Photochem. Photobiol.A: Chem., **160**, 163 **(2003)**.

[9] S.G.Schrank, H.J.José, R.F.P.M.Moreira; J.Photochem.Photobiol.A: Chem., **147**, 71 **(2002)**.

[10] J.Domènech, J.Muňoz; Electrochim.Acta, **32**, 1383 **(1987)**.

[11] K.Kabra, R.Chaudhary, R.Sawhney; Ind.Eng. Chem.Res., **43**, 7683 **(2004)**.

[12] Y.Ku, I.Jung; Wat.Res., **35**, 135 **(2001)**.
[13] L.B.Khalil, W.E.Mourad, M.W.Rophael; Appl. Catal.B, Environ., **17**, 267 **(1998)**.
[14] Y.Cho, H.Kyung, W.Choi; Appl.Catal.B, Environ., **52**, 23 **(2004)**.
[15] http//en.wikipidia.org/wiki/Earth's_energy_budget; Accessed on July 26, 2009, **(2009)**.
[16] D.P.Das, K.Parida, B.R.Deb; J.Mol.Catal.A: Chem., **245**, 217 **(2006)**.
[17] P.Mohapatra, S.K.Samantaray, K.Parida; J.Photochem.Photobiol.A: Chem., **170**, 189 **(2005)**.
[18] E.Selli, A.De Giorgi, G.Bidoglio; Environ.Sci. Technol., **30**, 598 **(1996)**.
[19] K.Kabra, R.Chaudhary, R.L.Sawhney; Int.J. Sustain.Energy, **26**, 195 **(2007)**.
[20] C.Lizama, J.Freer, J.Baeza, H.D.Mansilla; Catal. Today, **76**, 235 **(2002)**.
[21] S.Sakthivel, B.Neppolian, M.V.Shankar, B.Arabindoo, M.Palanichamy, V.Murugesan; Sol. Energ.Mat.Sol.Cells, **77**, 65 **(2003)**.
[22] P.Banerjee, S.Chakrabarti, S.Maitra, B.K.Dutta; Ultrason.Sonochem., **19**, 85 **(2012)**.
[23] G.C.C.Yang, S.W.Chan; J.Nanoparticle.Res., **11**, 221 **(2009)**.
[24] J.Yoon, E.Shim, S.Bae, H.Joo; J.Hazard Mater., **161**, 1069 **(2009)**.
[25] L.Yang, Y.Xiao, S.Liu, Y.Li, Q.Cai, S.Luo; Appl. Catal.B: Environ., **94**, 142 **(2010)**.
[26] A.Idris, N.Hassan, N.Suriani, M.Ismail, E.Misran, N.M.Yusof, A.-F.Ngomsik, A.Bee; Wat.Res., **44**, 1683 **(2010)**.
[27] Y.Ku, Y.-H.Huang, Y.-C.Chou; J.Mol.Catal.A: Chem., **342-343**, 18 **(2011)**.
[28] S.Chakrabarti, B.Chaudhuri, S.Bhattacharjee, A.K.Ray, B.K.Dutta; Chem.Eng.J., **153**, 86 **(2009)**.
[29] A.L.Patterson; Phys.Rev., **56**, 978 **(1939)**.
[30] S.Goeringer, C.R.Chenthamarakshan, K.Rajeswar; Electrochem.Commun., **3**, 290 **(2001)**.
[31] M.Kosmulski; Adv.Colloid Interfac., **152**, 14 **(2009)**.
[32] T.Iwata, M.Ishikawa, R.Ichino, M.Okido; Surf.Coatings Technol., **169/170**, 703 **(2003)**.
[33] S.Chakrabarti, B.K.Dutta; J.Hazard.Mater., **B112**, 269 **(2004)**.
[34] C.S.Turchi, D.F.Ollis; J.Catal., **122**, 178 **(1990)**.
[35] X.Wang, K.Maeda, A.Thomas, K.Takanabe, G.Xin, J.M.Carlsson, K.Domen, M.Antonietti; Nat.Mater., **8**, 76 **(2009)**.
[36] C.Minero, D.Vione; Appl.Catal.B: Environ., **67**, 257 **(2006)**.
[37] D.Vione, C.Minero, V.Maurinoa, M.E.Carlottib, T.Picatonottoa, W.Pelizzetti; Appl.Catal.B: Environ., **58**, 79 **(2005)**.