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Utilization of solar energy for photoreduction of industrial wastewater containing hexavalent chromium with zinc oxide semiconductor catalyst

Pallavi Mitra*, Prantik Banerjee, Sampa Chakrabarti, Sekhar Bhattacharjee

Department of Chemical Engineering, University of Calcutta, 92, Acharya P.C. Road, Kolkata 700 009, India
Tel. +91 033 2350 8386; Fax: +91 033 2351 9755; email: pallavim8@gmail.com

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ABSTRACT

Scarcities of water and energy are going to be critical in the near future. A possible remedy is to reuse industrial wastewater after suitable treatment using a renewable energy. In this work, wastewater containing hexavalent chromium is treated with Zinc oxide (ZnO) semiconductor photocatalyst in the presence of sunlight to reduce the more toxic hexavalent metal to its less toxic trivalent counterpart. Thirty five percent reduction was obtained after 2 h with 10 mg/L substrate, 0.4 g/L photocatalyst, and 75kLux solar radiation at 31°C temperature. Process parameters are initial concentration of substrate, loading of photocatalyst, pH and concentration of the electron donor. Initial rate of reduction varied only with ZnO-loading and hence it was zero order with respect to both the substrate and electron donor. An alternative rate equation based on the modified Langmuir Hinshelwood Hougen Watson (LHHW) model compares well with the mechanistic rate equation.

Keywords: Hexavalent chromium; Solar energy; Photoreduction; ZnO-semiconductor

1. Introduction

Among the total world population of 6,700 million, approximately 600 million people are suffering from chronic water scarcity and nearly one billion people do not get safe drinking water [1]. The most rational and reasonable remedies for this water crisis are to minimize wastage of water as well as to recycle and to reuse industrial wastewater. Treatment of industrial wastewater will demand a huge amount of energy in the coming years. Energy crisis, in turn, will worsen the problem of water crisis and vice versa since water and energy are very closely related. Energy required to produce such a large quantity of treated water will not be easily available from the conventional sources. So a serious participation of a non-conventional and renewable source of energy for the treatment of water and wastewater is required [1]. Solar energy is the most competent candidate as a source of renewable energy [1–3]. India is a tropical country and the daily average solar energy incident over India varies from 4 to 7 kWh/m^2 with about 2,300–3,200 sunshine hours per year, depending upon location [4,5].

Hexavalent chromium is used in a variety of industries including leather-chrome tanning, preservation of wood, production of stainless steel and textile dyes. Hence, hexavalent chromium comes into wastewater from such industries. Chromium is a priority

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*Corresponding author.

metal pollutant [6] and a potential carcinogen [7] that exists in two major oxidation states—trivalent [Cr (III)] and hexavalent [Cr(VI)] in aquatic environments. Cr(VI) occurs as the highly soluble oxyanions like $HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$. The chemical and toxicological behaviors of chromium depend on its oxidation state. Hexavalent chromium [8–11] is toxic to most living organisms and is a known carcinogen responsible for cancer in lungs, ulcers (i.e. chrome ulcers) and perforations of nasal septum and renal failure. Trivalent chromium is considered an essential nutrient for the human body and the toxicity of the trivalent chromium is 500–1,000 times less to a living cell than hexavalent chromium [12]. Trivalent chromium is less soluble in aqueous medium, so can easily be precipitated in an alkaline medium. However Cr(VI) species may be removed by adsorbents like surfactant modified montmorillonite clays [13], though the regeneration of spent adsorbent may cause a secondary pollution. Thus wastewater and industrial effluents containing chromium in the hexavalent state must be treated for reducing it to the trivalent state before discharging into surface water.

The conventional treatment of wastewater containing Cr(VI) often comprise reduction by zerovalent iron [14,15], coagulation or precipitation [16], active carbon adsorption [17], ion exchange or membrane separation [15]. Chemical reduction by $FeSO_4$, SO_2 or $NaHSO_3$ prior to precipitation by hydroxide is a very effective technique but the chromium hydroxide sludge is substantial in amount and is difficult to dispose of [18].

To get rid of the mentioned problems of removing chromium from wastewater, recently, semiconductor photocatalysis has been employed for reduction of hexavalent chromium to the trivalent one using various catalysts such as ZnO, TiO_2, WO_3 etc. under visible/ultraviolet radiation [19–22]. Details of the semiconductor photocatalysis has been discussed by several researchers [23–25]. This method has been originally used for the treatment of the drinking water and industrial wastewater by oxidizing the organic pollutants with the hydroxyl radical generated out of the hole and water [25–27]. Bahnemann [24] reviewed water treatment processes that used solar energy for excitation of semiconductors. Various solar reactors for the photocatalytic water treatment are described in this review and their overall performances have been compared.

Nevertheless, use of the photogenerated electron for reduction is comparatively less explored. A few reports are available on the photoreduction of Cr(VI) with artificial light source [19,20,28–31], whereas the reports on the solar photoreduction are even less. In most cases, the photocatalyst was TiO_2 [19,20,32]. Das et al. [33] studied the photocatalytic reduction of hexavalent chromium under solar irradiation using titania-pillared zirconium phosphate and titanium phosphate that was synthesized by them as the semiconductor catalyst. It was observed that the reduction was favored in acidic pH and the rate (pseudofirst-order) decreased with increase in initial concentration. Mahapatra et al. [34] prepared, characterized and studied the activity of the sulfate modified TiO_2 photocatalyst for reducing hexavalent chromium to the trivalent one under solar radiation. The presence of complexing agent like EDTA enhanced the extent of photoreduction. In a recent article, Kabra et al. [35] 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 1.5 h in the strong acidic pH of 2.

Undoped ZnO is almost similar to that of TiO_2 in terms of the same band gap energy (3.2 eV). But a few researchers have reported comparatively better photocatalytic activity of ZnO compared with TiO_2 [36–39] especially under solar light. Chakrabarti and Dutta [40] reported photo reduction of hexavalent chromium using ZnO but under artificial UV radiation. In another recent work, Liu et al. [41] synthesized ZnO sheets via microwave-assisted reaction of ZnO precursor in aqueous solution using a CEM microwave system and showed that ZnO sheets synthesized in 5 min time scale exhibited a optimal photocatalytic performance in the reduction of Cr(VI) with removal efficiency of 81%. Surface of the ZnO semiconductor was sensitized using humic acid by Selli et al. [42] for enhancement of the reduction of hexavalent chromium under solar radiation. However, ZnO shows a tendency of photocorrosion with the illumination of UV light [43,44]. Banerjee et al. [45] studied the kinetics of the photocatalytic reduction of hexavalent chromium using nanosized ZnO under solar radiations.

In this study we have treated simulated wastewater containing hexavalent chromium, as present in potassium dichromate ($K_2Cr_2O_7$) using laboratory-grade zinc oxide (ZnO) semiconductor catalyst under sunlight for reducing the hexavalent chromium to the trivalent variety. Methanol (CH_3OH) has been used as the hole scavenger. As a sacrificial electron donor, methanol readily consumes the hole and/or the OH· radical generated so that the holes and electrons cannot recombine and the electrons become available for the reduction of Cr(VI). It has a higher reduction capacity and is cheaper compared with other reagents reported in the literature (e.g., formic acid, humic acids, etc.). In the east coast of India in

September—October, the average intensity of the sunlight was about 75 klux (301.5 W/m^2). The influences of various process parameters such as the initial concentration of the substrate, loading of ZnO, the concentration of the sacrificial electron donor (here methanol) and the pH on the rate of photoreduction has been examined and the results obtained are discussed. The kinetics of the photocatalytic degradation process has also been investigated. The experimental data have successfully been fitted to a kinetic model previously proposed by Chakrabarti et al. [46] and to Langmuir Hinshelwood Hougen Watson (LHHW) equation.

2. Materials and methods

2.1. Materials

Potassium dichromate and ZnO (GR grade) were received from LOBA Chemie Pvt. Ltd., Bombay, India. Methanol (GR) was from SD Chemicals, India. Freshly prepared double-distilled water was used to prepare solutions. The mean particle size of the ZnO catalyst was 146.7 nm (*Zeta Plus, Brookhaven Instrument Corporation*), and the BET surface area was 3.23 m^2/g. The true density of the solid is 5,600 kg/m^3 whereas the bulk density is 880 kg/m^3. Illuminance of the UV lamp at different electrical power supply was measured using *Metravi 1330* digital lux meter. The data in the photometric unit (klux) however has been alternatively reported in the radiometric unit (W/m^2) using empirical conversion factors provided by Thimijan and Heins [47].

Analytical methods: The concentration of potassium dichromate in solution was determined at $\lambda_{max} = 349$ nm [48] using a 1 cm quartz cell in a UV–vis spectrophotometer (Shimadzu UV-160A).

2.2. Experimental set-up and procedure

Solar experiments were carried out in a box type photoreactor provided with a quartz glass cover and a cooling water circulation system (Fig. 1). The capacity of the reactor was about 550 mL.

The reactor temperature was maintained constant at 30 ± 1°C by cooling water circulation. Potassium dichromate solution, weighed quantity of ZnO, and methanol (25 ml) were taken together in the reactor. A homogeneous suspension was maintained using a magnetic stirrer. The total suspension volume was 500 ml. Aliquots of sample were withdrawn at 10 min interval, filtered with Whatman 42 filter paper and the filtrate was analyzed spectrophotometrically for the residual Cr(VI) content. The concentration of Cr(VI) in solution was determined at $\lambda_{max} = 349$ nm using a 1 cm quartz cell in a UV–vis spectrophotometer (Shimadzu UV-160A). Photocatalysis was carried out in the absence of solar light (dark reaction). A set of experiments to study the adsorption of Cr(VI) and of methanol on the ZnO particles were performed separately. pH of the starting solution was 5.5, and the experiments were conducted in that pH range. Blank experiments carried out without any photocatalyst did not indicate any photolysis or photochemical change in the substrate.

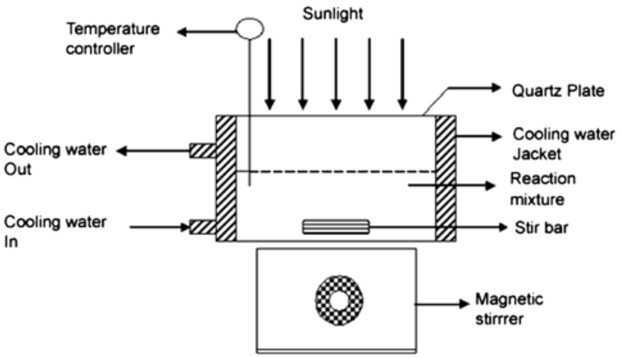

Fig. 1. Experimental set-up for photoreduction of hexavalent chromium under sunlight.

3. Results and discussion

3.1. Adsorption experiment in the dark

Adsorption of dichromate on the ZnO particles was found to be negligible. EDS image of the spent ZnO (not shown) also indicates no chromium on ZnO surface. Wang et al. [16] also reported low but non-zero adsorption of chromium at nearly the same pH. A considerable amount (0.009 mol/g) of methanol was found to be adsorbed on the surface of the photocatalyst. Since adsorption is a pre-requisite of photocatalysis, adsorption of methanol affects the mechanism of reduction to a great extent.

3.2. Influence of process parameters on the photocatalytic reduction

The major process parameters influencing the rate of reduction of Cr(VI) to Cr(III) are initial substrate concentration, loading of the semiconductor catalyst, pH and concentration of the sacrificial electron donor (here methanol).

The change in the dimensionless concentration, C/C_0 where C_0 is the initial concentration of $K_2Cr_2O_7$,

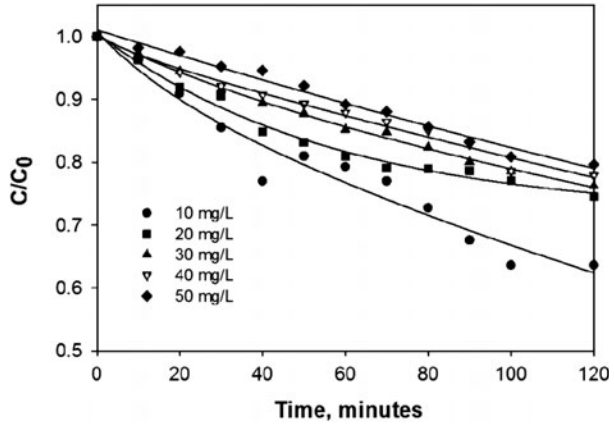

Fig. 2. Dimensionless time–concentration plots for different initial concentrations of dichromate solution [ZnO loading: 0.4 g/L, concentration of methanol 1.25 mol/L, solution volume 500 mL, temperature 30°C, pH 5.5, solar intensity 301.5 W/m^2 (75 klux)].

with time of irradiation, at various values of C_0, is shown in Fig. 2.

The extent of photo-reduction decreases with increasing initial concentration of the substrate from 10 to 50 mg/L. We observed that the percent reduced decreased with increase in the initial concentration which was reported before by several authors [20,40,46]. However, the initial rate of reduction in the present work is observed to be nearly independent of initial substrate concentration (Fig. 3).

This is because of more abundant presence of dichromate ions at the beginning that readily consumes the electrons available from the excitation of the semiconductor.

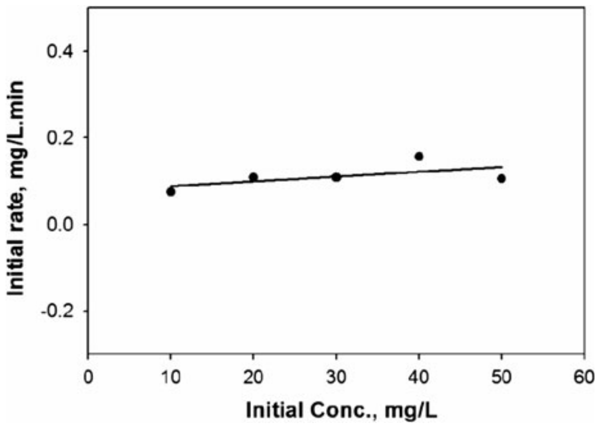

Fig. 3. Initial substrate concentration vs. initial rate of photoreduction [ZnO-loading 0.4 g/L, methanol concentration 1.25 mol/L, solution volume 500 mL, temperature 30°C, pH 5.5, solar intensity 301.5 W/m^2 (~75 klux)].

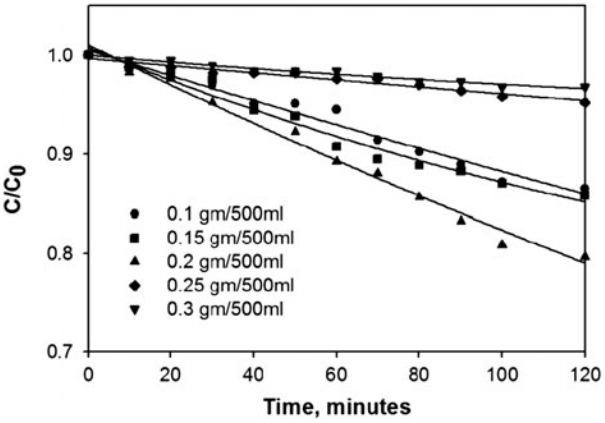

Fig. 4. Dimensionless time–concentration plots for different loadings of ZnO catalyst [initial concentration of substrate 50 mg/L, concentration of methanol 1.25 mol/L, solution volume 500 mL, temperature 30°C, pH 5.5, solar intensity 301.5 W/m^2 (~75 klux)].

Loading of the photocatalyst (ZnO) was varied from 0 to 0.6 g/L (Fig. 4). As the ZnO-loading was increased from 0 to 0.4 g/L in a set of experiment with 50 mg/L Cr(VI), 1.25 mol/L methanol at a pH of 5.5 and temperature of 31°C, both the extent and initial rate of degradation were found to increase up to a particular loading.

After that critical value of the photocatalyst loading of 0.4 gm/L in this particular experimental condition, the initial rate decreased since the suspension became too turbid to allow solar radiation through it. Fig. 5 shows the variation of initial rates with at different ZnO loadings up to the critical one. The ini-

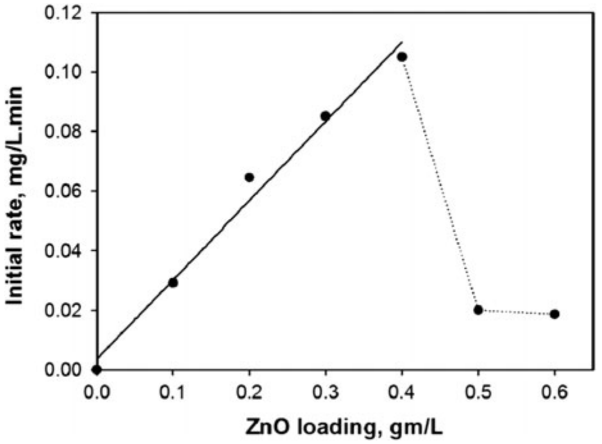

Fig. 5. ZnO-loading vs initial rate of photoreduction [initial concentration of substrate: 50 mg/L, methanol concentration 1.25 mol/L, solution volume 500 mL, temperature 30°C, pH 5.5, solar intensity 301.5 W/m^2 (~75 klux)].

tial rate decreases as the loading is increased from 0.4 gm/L.

Time–concentration profiles of Cr(VI) reduction with different dosing of methanol are shown in Fig. 6. It was observed that the initial rate was very low without methanol; the extent of photoreduction reaction became slow due to recombination of hole and electron in absence of a sacrificial electron donor. The quantities of methanol added were increased from 0 to 2 mol/L in a set of experiment. The initial rate was observed to increase as methanol-dosing was increased up to 1.25 mol/L, but after that the initial rate did not change considerably with further addition of methanol (Fig. 7).

The concentration of this sacrificial electron donor does not affect the initial rate substantially after a certain critical value because of an excess methanol present in the solution that may be sufficient to scavenge all the photo-generated holes at those particular experimental conditions. Therefore we have chosen the methanol loading for our baseline experiment as 1.25 mol/L. Another important parameter in photocatalytic processes is the pH of the solution. The range of pH for the photocatalytic reduction of Cr(VI) using ZnO is rather limited. The catalyst, being amphoteric in nature, dissolves at both high and low pH. A high pH is also detrimental for the oxidizing species (i.e., •OH or H_2O_2 generated in course of irradiation of the catalyst). This observation has been supported by other researchers also [30,46]. Wang et al. [16] reported low conversion of Cr(VI) as well as "photocorrosion" of ZnO at neutral to basic pH. It may be mentioned that TiO_2 is more resistant to lower solution pH and Cr(VI) reduction has been reported at a pH as low as 2 [27,49]. We varied the pH from 4 to 8 and it was observed that reduction rate was maximum at 5.5. The rate decreased thereafter (Fig. 8).

So we conducted the baseline experiments at a constant pH of 5.5 which is slightly below the neutral pH. Time–concentration plots at various pHs and variation of initial rate with pH of the solution has been shown in Figs. 8 and 9, respectively. It is evident from Fig. 10 that maximum photocatalytic reduction occurs near pH 5–5.5. It was so since ZnO is amphoteric in nature; it is reactive in both strong acidic and strong alkaline media and not capable of acting as a catalyst.

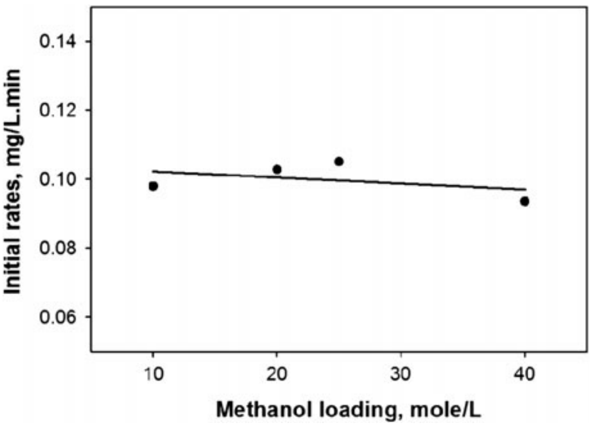

Fig. 7. Methanol loading vs. initial rate of photoreduction. [Initial concentration of substrate 50 mg/L, ZnO loading 0.4 g/L, solution volume 500 mL, temperature 30°C, pH 5.5, solar intensity 301.5 W/m^2 (~75 klux)].

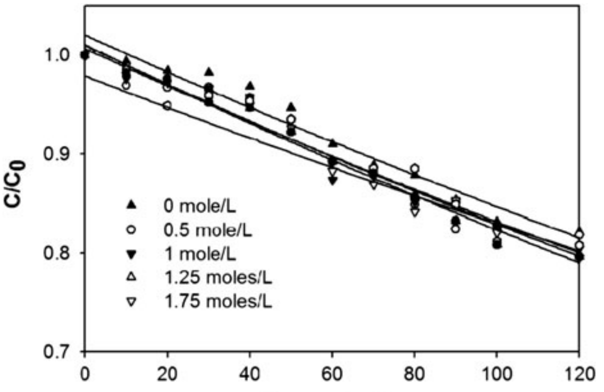

Fig. 6. Dimensionless time–concentration plots for different concentrations of methanol. [Initial concentration of substrate 50 mg/L, ZnO loading 0.4 g/L, solution volume 500 mL, temperature 30°C, pH 5.5, solar intensity 301.5 W/m^2 (~75 klux)].

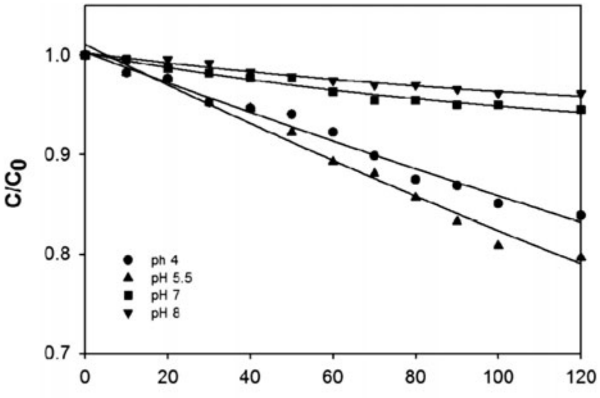

Fig. 8. Dimensionless time–concentration plots for different pH. [Initial concentration of substrate 50 mg/L, ZnO loading 0.4 g/L, solution volume 500 mL, temperature 30°C, methanol concentration 1.25 mol/L, solar intensity 301.5 W/m^2 (~75 klux)].

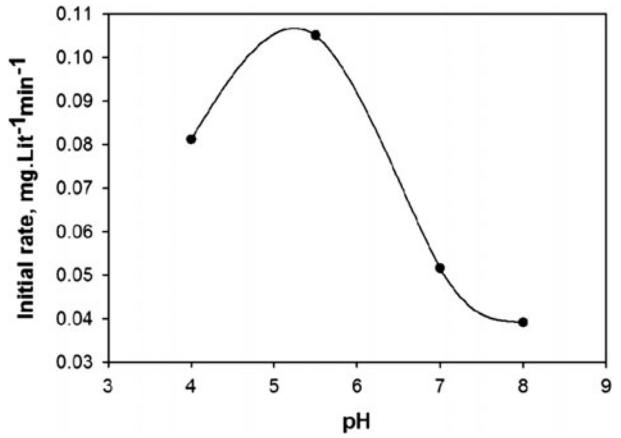

Fig. 9. pH vs. initial rate of photoreduction. [Initial concentration of substrate 50 mg/L, ZnO loading 0.4 g/L, solution volume 500 mL, temperature 30°C, methanol concentration 1.25 mol/L, solar intensity 301.5 W/m^2 (~75 klux)].

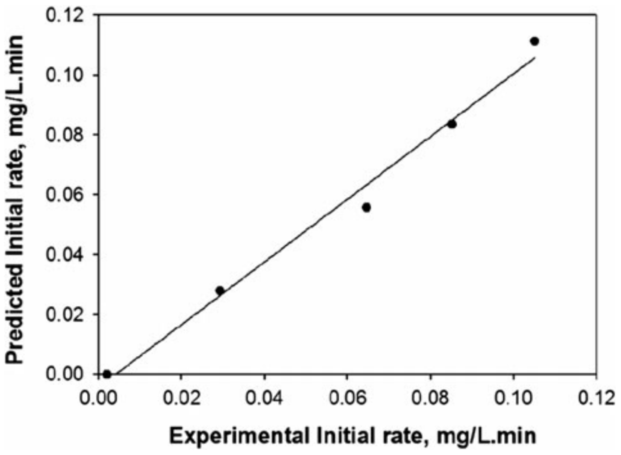

Fig. 10. Parity diagram showing the experimental and predicted values of the initial rates at different loading of ZnO photocatalyst. [ZnO loading: 0.4 g/L, solar intensity 301.5 W/m^2 (~75 klux), pH: 4.5, temperature: 30°C].

Change in temperature did not affect the rate of photocatalytic reduction of Cr(VI). This has already been established by several researchers including Bhatkhande et al. [27] and Domėnech and Muňoz [21].

3.3. A mechanistic rate equation for the photoreduction

The proposed reaction pathway for the reduction of chromium in aqueous medium in the presence of ZnO photocatalyst has been discussed in detail in previous work of the same research group, Chakrabarti et al. [46]. Khalil et al. [28] suggested homogeneous reduction of hexavalent chromium by photogenerated H_2O_2 responsible for the supply of electron to the hexavalent chromium in solution. In spite of the powerful oxidizing ability of hydrogen peroxide, it acts as a reductant ($E_0 = +0.68\,V$) when reacting with stronger oxidizing agents such as chlorine ($E_0 = 1.77\,V$), potassium permanganate ($E_0 = 1.52\,V$), and potassium dichromate ($E_0 = 1.33\,V$). Moreover, the adsorbed methanol generates methoxy radical while scavenging the photo-generated holes on the surface. This methoxy radical can also act as a reducing agent. Both the routes of reduction have been considered in our proposed model.

The first step of a photocatalytic reaction is excitation of semiconductor:

$$\mathrm{ZnO} + hv \xrightarrow{k_1} \mathrm{ZnO}\ (h^+ + e^-) \tag{1}$$

$$\text{Reduction of } \mathrm{Cr(VI)} : \mathrm{Cr(VI)} + \mathrm{H_2O_2} + \mathrm{H^+} \xrightarrow{k_2} \mathrm{Cr(III)} + \mathrm{H_2O} + \mathrm{O_2} \tag{2}$$

$$\mathrm{Cr(VI)} + \mathrm{CH_3O^{\cdot}} \xrightarrow{k_3} \mathrm{Cr(III)} + \text{products} \tag{3}$$

Under the constant intensity of solar irradiation during the experiments with varying ZnO-loading, the initial rate depends only on the loading of ZnO, hence $k = 2k_1[hv]$

The final form of the rate equation for the of Cr (VI) was obtained as below

$$r_i = 2k_i[\mathrm{ZnO}][hv] = k[\mathrm{ZnO}] \tag{4}$$

where k_1 is the rate constant for the following photo-excitation reaction.

The above rate equation Eq. (4) indicates a zero-order reduction reaction with respect to the substrate as well as to that of methanol over the range of parameter values used in this study. Wang et al. [50] reported that the rate of reduction is independent of the substrate concentration; this supports our Eq. (3). This is also in conformity with our findings presented in Figs. 3 and 7.

The linear plot of the initial rates versus. ZnO-loadings obtained from the experimental data is given in Fig. 5. This proves the validity of Equation 3 modeled. The value of the rate constant k' for photo-excitation reaction was obtained from Fig. 5 as 0.00036 $(\mathrm{mg\,L^{-1}\,min^{-1}})$. $(\mathrm{g\,ZnO\,L^{-1}})^{-1}$ $(\mathrm{W/m^2})^{-1}$ that is 0.002 $(\mathrm{mg\,L^{-1}\,min^{-1}})$. $(\mathrm{g\,ZnO\,L^{-1}})^{-1}\,\mathrm{klx^{-1}}$ [46]. Fig. 10 shows a parity diagram showing the good agreement ($R^2 = 0.9875$) between the predicted and experimental values of the initial rates at different loading of ZnO photocatalyst.

3.4. Rate equation obtained from the LHHW model

Ku and Jung [20], in their work on photoreduction of Cr(VI) using TiO_2, suggested a Langmuir–Hinshelwood type rate equation which was approximated by a pseudo-first-order equation at low Cr(VI) concentration. They observed the rate constant to be linear in the UV intensity similar to our observation. Schrank et al. [19] also suggested a Langmuir–Hinshelwood rate equation in their work on photo-reduction of Cr (VI) using the same catalyst. Therefore, we have examined whether our experimental data comply with the same equation. Adsorption is a pre-requisite of the LHHW mechanism, But as mentioned before, we did not observe any appreciable adsorption of Cr(VI) on the ZnO catalyst. Instead, a considerable amount of methanol was adsorbed. So, adsorption of methanol could lead to a LHHW-type pathway of the reduction reaction through the formation of the methoxy radicals [51]. To test this possibility we selected the following form of the LHHW equation for the initial rate:

$$r_i' = \frac{kC_A}{1 + KC_A} \tag{5}$$

The corresponding linearized form of the equation is:

$$\frac{C_A}{r_i'} = \frac{1}{k} + \frac{K}{k} C_A \tag{6}$$

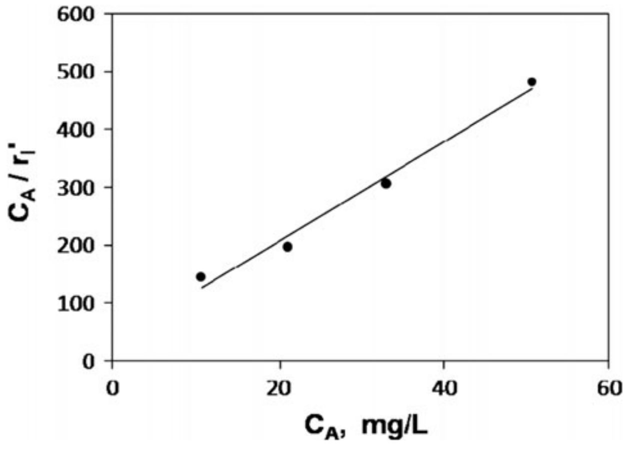

Fig. 11. LHHW fitting of the photocatalytic reduction of potassium dichromate with ZnO [ZnO loading: 0.4 g/L, solar intensity 301.5 W/m^2 (~75 klux), pH: 4.5, temperature: 30°C].

The fitting of data with the above equation ($R^2 = 0.98$) has been shown in Fig. 11. The values of k and K obtained from the slope and intercept are 8.622 min^{-1} and 33.29 (mg/L)$^{-1}$, respectively.

At the concentrations (C_A in mg/L) of Cr(VI) used in this work, $KC_A >> 1$ and hence Eq. (5) reduces to initial rate,

$$r_i' = \frac{k}{K} = k_0 \tag{7}$$

It implies that the initial reaction rate is zero order with respect to the concentration of the substrate and concentration of methanol added. It means that the data fitted well to LHHW model and at a special condition, this LHHW equation reduced to zero order with respect to the concentration of the substrate and concentration of methanol added as given by us based on the proposed mechanism and experimental data (Figs. 3 and 7). The value of the initial rate from the LHHW model [k_0 in Eq. (7)] is 0.115 mg L^{-1} min^{-1}. Using ZnO loading as 0.4 g/L, the value of initial rate from our proposed model [r_i in Eq. (3)] comes to be 0.111 mg L^{-1} min^{-1} which are in good agreement.

4. Conclusion

From the above experiments and observations, it may be concluded that ZnO semiconductor can be effectively utilized to reduce hexavalent chromium to its trivalent state in presence of sunlight and methanol as sacrificial electron donor. Blank experiments carried out without any photo-catalyst added did not indicate any photolysis or photochemical change in the substrate. The extent of degradation as well as its initial rate increased with increase in the loading of the photocatalyst. Though the extent of photoreduction was found to decrease with increasing initial concentration of Cr(VI), the initial rates were found to be nearly independent to the initial concentration of dichromate solution and to the concentration of methanol. Both the extent of degradation and initial rate was found to be maximum at pH 5.5. The model obtained in our previous work [47] fits in the initial rate calculated from the experimental data. The values of the rate constants have been determined. The experimental and predicted initial rates were in good agreement. An alternative rate equation based on the LHHW model led to the same zero-order form as the proposed rate equation. The initial rates derived by the two models are comparable with that obtained from the experimental data.

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References

[1] J. Blanco, S. Malato, P. Fernández-Ibáñez, D. Alarcón, W. Gernjak, M.I. Maldonado, Review of feasible solar energy applications to water processes, Renew. Sust. Energ. Rev. 13 (2009) 1437–1445.

[2] C. Agrafiotis, M. Roeb, A.G. Konstandopoulos, L. Nalbandian, V.T. Zaspalis, C. Sattler, P. Stobbe, A.M. Steele, Solar water splitting for hydrogen production with monolithic reactors, Sol. Energy 79 (2005) 409–421.

[3] R. Swenson, The production peaks in petroleum and natural gas: information, misinformation, awareness, and implications, in: Proceedings of the ISES 2005 Solar World Congress, 2005.

[4] http://en.wikipidia.org/wiki/Earth's_energy_budget.

[5] http://www.solarindia.online.com/solar-india.html.

[6] U.S. Environmental Protection Agency, Fed. Registr. 52 (1987) 12866.

[7] S. Venitt, L.S. Levy, Mutagenicity of chromates in bacteria and its relevance to chromate carcinogenesis, Nature 250 (1974) 493–495.

[8] M.Z. Hauschild, Putrescine (1,4-diaminobutate) as an indicator of pollution induced stress in higher plants; barley and robe stressed with Cr(III) or Cr(VI), Ecotoxicol. Environ. Saf. 26 (1993) 225–247.

[9] S.E. Fendorf, Surface reactions of chromium in soil and waters, Geoderma 67 (1995) 55–71.

[10] L. Travieso, R.O. Canizarez, R. Borja, F. Benitez, A.R. Dominguez, Heavy metal removal by microalgae, Bull. Environ. Contam. Toxicol. 62 (1999) 144–151.

[11] P. Cheryl, M.B. Susan, Reflections of hexavalent chromium: health hazards of an industrial heavy weight, Environ. Health Perspsct. 108 (2000) 48–58.

[12] M. Costa, Potential hazards of hexavalent chromate in our drinking water, Toxicol. Appl. Pharmacol. 188 (2003) 1–5.

[13] N. Mahadevaiah, B. Venkataramani, B.S. Jai Prakash, Interaction of chromate on surfactant modified montmorillonite: breakthrough curve study in fixed bed columns, Ind. Eng. Chem. Res. 47 (2008) 1755–1759.

[14] A. Özer, H.G. Altundoğan, M. Erdem, F. Tümen, A study of the Cr(VI) removal from aqueous solutions by steel wool, Environ. Pollut. 97 (1997) 107–112.

[15] A.H. EI-Shazly, A.A. Mubarak, A.H. Konsowa, Hexavalent Chromium reduction using a fixed bed of scrap bearing iron spheres, Desalination 185 (2005) 307–316.

[16] X. Wang, S.O. Pehkonen, A.K. Ray, Removal of aqueous Cr (VI) by a combination of photocatalytic reduction and coprecipitation, Ind. Eng. Chem. Res. 43 (2004) 1665–1672.

[17] A.R. Bowers, C.P. Huang, Activated carbon process for treatment of automotive application for chromium wastewaters containing hexavalent chromium, Prog. Water Technol. 12 (1980) 629–634.

[18] L.E. Eary, D. Rai, Chromate removal from aqueous wastes by reduction with ferrous ion, Environ. Sci. Technol. 22 (1988) 972–977.

[19] S.G. Schrank, H.J. Jose, R.F.P.M. Moreira, Simultaneous photocatalytic Cr(VI) reduction and dye oxidation in a TiO_2 slurry reactor, J. Photochem. Photobiol. A: Chem. 147 (2002) 71–76.

[20] Y. Ku, I. Jung, Photocatalytic reduction of Cr(VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide, Water Res. 35(1) (2001) 135–142.

[21] J. Domènech, J. Muñoz, Photocatalytical reduction of Cr(VI) over ZnO power, Electrochem. Acta. 43 (2004) 1383–1386.

[22] J.K. Yanga, S.M. Leeb, M. Farrokhic, O. Giahid, M. Shirzad Sibonic, Photocatalytic removal of Cr(VI) with illuminated TiO_2, Desalin. Water Treat. 46 (2012) 375–380.

[23] K.W. Boer, Survey of Semiconductor Physics, Van Nostrand Reinhold, New York, 1990, p. 249.

[24] D. Bahnemann, Photocatalytic water treatment: solar energy applications, Sol. Energy 77 (2004) 445–459.

[25] M. Romero, J. Blanco, B. Sànchez, A. Vidal, S. Malato, A.I. Cardona, E. Garcia, Solar photocatalytic degradation of water and air pollutants: challenges and perspectives, Sol. Energy 66 (1999) 169–182.

[26] C.S. Turchi, D.F. Ollis, Photocatalytic degradation of organic water contaminants: mechanism involving hydroxyl radical attack, J. Catal. 122 (1990) 178–192.

[27] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, Photocatalytic degradation for environmental application—a review, J. Chem. Technol. Biotechnol. 77 (2001) 102–116.

[28] L.B. Khalil, W.E. Mourad, M.W. Rophael, Photocatalytic reduction of environmental pollutant Cr(VI) over some semiconductors under UV/visible light illumination, Appl. Catal. B: Environ. 17 (1998) 267–273.

[29] P. Mytych, P. Cielsa, Z. Stasicka, Photoredox processes in the Cr(VI)–Cr(III)-oxalate system and their environmental relevance, Appl. Catal. B: Environ. 59 (2005) 161–176.

[30] P. Mytych, A. Larocki, Z. Stasicka, Mechanism of photochemical reduction of chromium(VI) by alcohols and its environmental aspects, J. Photochem. Photobiol. A: Chem. 160 (2003) 163–170.

[31] P. Mytych, Z. Stasicke, Photochemical reduction of chromium (VI) by phenol and its halogen derivatives, Appl. Catal. B: Environ. 52 (2004) 167–172.

[32] Y. Cho, H. Kyung, W. Choi, Visible light activity of TiO_2 for the photoreduction of CCl_4 and Cr(VI) in the presence of nonionic surfactants (Brij), Appl. Catal. B: Environ. 52 (2004) 23–28.

[33] D.P. Das, K. Parida, B.R. Deb, Photocatalytic reduction of hexavalent chromium in aqueous solution over titania pillared zirconium phosphate and titanium phosphate under solar radiation, J. Mol. Catal. A: Chem. 245 (2006) 217–224.

[34] P. Mohapatra, S.K. Samantaray, K. Parida, Photocatalytic reduction of hexavalent chromium in aqueous solution over sulphate modified titania, J. Photochem. Photobiol. A: Chem. 170 (2005) 189–194.

[35] K. Kabra, R. Chaudhary, R.L. Sawhney, Photocatalytic reduction of Cr(VI) in aqueous titania suspensions exposed to concentrated solar radiation, Int. J. Sustain. Energy 26 (2007) 195–207.

[36] C.A.K. Gouvea, F. Wypych, S.G. Moraes, N. Duran, N. Nagata, P. Peralta-Zamora, Semiconductor assisted photocatalytic degradation of reactive dye in aqueous solution, Chemosphere 40 (2000) 433–440.

[37] C. Lizama, J. Freer, J. Baeza, H. D. Mansilla, Optimized photodegradation of reactive blue 19 on TiO_2 and ZnO suspensions, Catal. Today 76 (2002) 235–246.

[38] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO_2, Sol. Energy Mat. Sol. Cells. 77 (2003) 65–82.

[39] D. Sil, S. Chakrabarti, Photocatalytic degradation of PVC–ZnO composite film under tropical sunlight and artificial UV radiation: A comparative study, Sol. Energy 84 (2010) 476–485.

[40] S. Chakrabarti, B.K. Dutta, Photocatalytic degradation of textile dyes in aqueous solutions using ZnO as semiconductor catalyst, J. Hazard. Mater. B112 (2004) 269–278.

[41] X. Liu, T. Lv, L. Pan, Z. Sun, C.Q. Sun, Microwave-assisted synthesis of ZnO for photocatalytic reduction of Cr(VI) in aqueous solution, Desalin. Water Treat. 42 (2012) 216–221.

[42] E. Selli, A. De Giorgi, G. Bidoglio, Humic acid-sensitized photoreduction of Cr(VI) on ZnO Particles, Environ. Sci. Technol. 30 (1996) 598–604.

[43] A.V. Dijken, A.H. Janssen, M.H.P. Smitsmans, D. Vanmaekelbergh, A. Meijerink, Size-selective photoetching of nanocrystalline semiconductor particles, Chem. Mater. 10 (1998) 3513–3522.

[44] B. Neppolian, S. Sakthivel, B. Arabindoo, M. Palanichamy, V. Murugesan, Degradation of textile dye by solar light using TiO_2 and ZnO photocatalysts, J. Environ. Sci. Health 34 (1999) 1829–1838.

[45] P. Banerjee, P. Mitra, S. Chakrabarti, S. Bhattacharjee, Zinc oxide nanoparticles for the photocatalytic reduction of hexavalent chromium in wastewater under sunlight, Environ. Sci. Ind. J. 7 (2012) 288–295.

[46] S. Chakrabarti, B. Chaudhuri, S. Bhattacharjee, A.K. Ray, B.K. Dutta, Photoreduction of hexavalent chromium in aqueous solution in the presence of zinc oxide as semiconductor catalyst, Chem. Eng. J. 153 (2009) 86–93.

[47] R.W. Thimijan, R.D. Heins, Photometric, radiometric and quantum light units of measure: a review of procedures for interconversion, Hortscience 18(8) (1983) 18–822.

[48] T. Iwata, M. Ishikawa, R. Ichino, M. Okido, Photocatalytic reduction of Cr(VI) on TiO_2 film formed by anodizing, Surf. Coating Technol. 169 (2003) 703–706.

[49] J.A. Navio, J.J. Testa, P. Djedjeian, J.R. Padron, D. Rodriguez, M.I. Litter, Iron-doped titania powder prepared by a sol-gel method. Part II: photocatalytic properties, Appl. Catal. A: Gen. 178 (1999) 191–203.

[50] S.L. Wang, C.C. Chen, Y.M. Tzou, C.L. Hsu, J.H. Chen, C.F. Lin, A mechanism study of light-induced Cr(VI) reduction in an acidic solution, J. Hazard. Mater. 164 (2009) 223–228.

[51] F. Jiang, Z. Zheng, Z. Xu, S. Zheng, Z. Guo, L. Chen, Aqueous Cr(VI) photo-reduction catalyzed by TiO_2 and sulfated TiO_2, J. Hazard. Mater. B134 (2006) 94–103.