

Photocatalytic Reduction of Hexavalent Chromium in Wastewater Using ZnO - a Comparison between UV and Sunlight

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Abstract—Hexavalent chromium is more toxic and carcinogenic compared to the trivalent one. Both (+3) and (+6) states of chromium are stable under most natural water environments but trivalent chromium can be eliminated easily by precipitation. Reduction of Cr(VI) is therefore important for removal of the same from wastewater. Photocatalytic reduction method is based on the reactive properties of an electron-hole pair generated in the semiconductor when irradiated by UV/vis light having energy greater than the band-gap energy of the semiconductor. In the present research a comparative study has been performed using ZnO semiconductor for the reduction of hexavalent chromium in wastewater under UV and solar energy separately. Effects of different process parameters were studied and a kinetic model was proposed. Use of sunlight as a renewable energy for the treatment of wastewater containing hexavalent chromium is indeed an eco-friendly approach.

Keywords: Hexavalent chromium; Reduction; Photocatalysis; ZnO; Sunlight; UV; Comparison.

1. INTRODUCTION

Chromium is used in a number of industrial applications, including tanning, industrial water cooling, electroplating, petroleum refining and paper pulp production. Hexavalent chromium [Cr(VI) or Cr⁶⁺] is a danger to human health. In the environment, Cr(VI) is highly mobile and therefore, Cr(VI) can move throughout aquifers to contaminate groundwater and other sources of drinking water. Cr(III) is relatively immobile, insoluble in aqueous systems, less toxic and even essential in human and animal nutrition [1-3]. There are several conventional techniques like chemical reduction-precipitation to treat chromium containing wastewater. Most of them demand large quantities of chemicals and energy. Besides, some of them generate huge quantity of sludge that is difficult to dispose of. Hence employing a renewable source of energy, at least partially, for an environmental remediation process

would make the same more attractive. In the present study, simulated wastewater containing hexavalent chromium as potassium dichromate (K₂Cr₂O₇) has been treated with Zinc Oxide (ZnO) semiconductor photocatalyst separately under UV and solar radiation to reduce Cr⁺⁶ to Cr⁺³. Methanol (CH₃OH) has been used as the hole scavenger. Average intensity of the sunlight was about 75 klux (30.15 mW/cm²). UV light was provided by three number of 4W black lamps (0.90mW/cm²) inserted in quartz sleeves immersed in the reaction mixture within the reactor. Process parameters were initial concentration of substrate, loading of photocatalyst, pH, concentration of the hole-scavenger (Methanol) and intensity of UV radiation (in case of UV assisted photoreduction). It was observed that under otherwise identical conditions, after 120 minutes, 36.36% Cr⁺⁶ was removed by sunlight whereas by UV light 46.60% Cr⁺⁶ was removed from 50 mg/L of dichromate solution. The kinetics of the photocatalytic degradation process has also been investigated. Use of sunlight made the process energy- efficient.

2. MATERIALS AND METHODS

2.1 Materials and instruments

Potassium dichromate (GR grade) was received from LOBA Chemie, India. Methanol (GR) was from SD Chemicals, India. Zinc oxide powder was purchased from SRL, India. 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 m²/g. Freshly prepared double distilled water was used to prepare solutions. Intensity of solar radiation was measured using *MetraVi 1330* digital lux meter. Illuminance of the UV lamp (with maximum total intensity of 0.8-0.9 mW/cm²) was measured using UV meter (model no. *OPTEL, LB 01*). pH of a solution was measured with a digital pH meter (*Eutech Instruments Waterproof pH Tester 20*). The

concentration of potassium dichromate in solution was determined at $\lambda_{\max} = 349 \text{ nm}$ using a 1 cm quartz cell in a UV-vis spectrophotometer (Shimadzu UV-160A).

2.2 Experimental set up and procedure

UV photoreduction experiments were carried out in a cylindrical stainless steel reactor, 0.12m in diameter and 0.25m in height, fitted with a cooling water jacket. Three UV lamps (4W each) with maximum total intensity of $0.8\text{-}0.9 \text{ mW/cm}^2$ were inserted in quartz sleeves around the center of the reactor (Figure 1a). Solar experiments were carried out in a SS -box type reactor with a quartz glass cover and having a cooling water circulation system (Figure 1b).

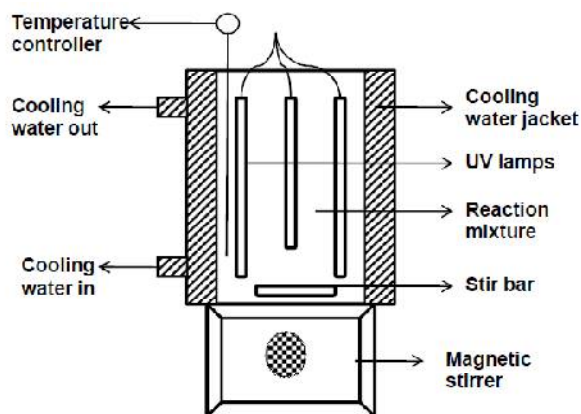


Figure 1a: Experimental set up for UV photocatalysis

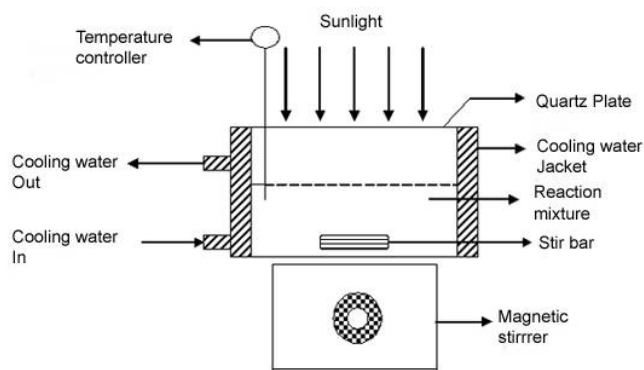


Figure 1b: Experimental set up for solar photocatalysis

The capacity of the reactor was about 550 mL. The reactor temperature was maintained constant at $30 \pm 1^\circ\text{C}$ by cooling water circulation. Potassium dichromate solution, weighed quantity of ZnO and methanol (25ml.) were taken together in the reactor. A homogeneous suspension was maintained using a magnetic stirrer. The total suspension volume was 500ml. Aliquots of sample were withdrawn at 10minutes interval, filtered with Whatman 42 filter paper and the filtrate was analyzed spectrophotometrically for the residual potassium dichromate content. Photocatalysis was carried out in the absence of UV/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.

3. RESULTS AND DISCUSSIONS

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. Blank experiments carried out without any photo-catalyst added did not indicate any photolysis or photochemical change in the substrate. Thus the observed reduction of chromate was due to photocatalytic effect of ZnO and the sacrificial electron donor only. A considerable amount of methanol was found to be adsorbed on the surface of the photocatalyst.

3.1 Influence of process parameters on the photocatalytic reduction

In both processes the major parameters that influence the rate and conversion of Cr(VI) to Cr(III) are the initial concentration of the substrate, loading of the semiconductor catalyst, pH, concentration of hole scavenger (methanol) and intensity of the UV radiation (in case of UV assisted photocatalysis).

3.1.1 Initial concentration of substrate

The profiles of the dimensionless concentration, C/C_0 against time with various initial concentrations is shown in Figure 2. Here C_0 is the initial concentration and C is the concentration at any time t of $\text{K}_2\text{Cr}_2\text{O}_7$ with time of irradiation. The extent of photo-reduction decreases with increasing initial concentration of the substrate. Since the absorbance of the solution increases with increase in $\text{K}_2\text{Cr}_2\text{O}_7$ concentration, it becomes increasingly difficult for the UV/solar radiation to reach the surface of the photo-catalyst; hence the photo-reduction decreases. Similar phenomena were reported by Ku and Jung [4] and Chakrabarti *et al.* [5]. However, the initial rates were found to be nearly independent to the initial concentration of dichromate solution used in the experimental range (Figure 3). This may be due to the fact that within this concentration range of Cr(VI), the photogenerated electrons are sufficient for reduction. As a result, the initial reaction order with respect to the substrate becomes virtually zero.

3.1.2 ZnO loading

Both the extent and initial rate of reduction were found to increase with the increase in ZnO loading from 0 to 0.4g in 500ml when UV/sunlight was used for

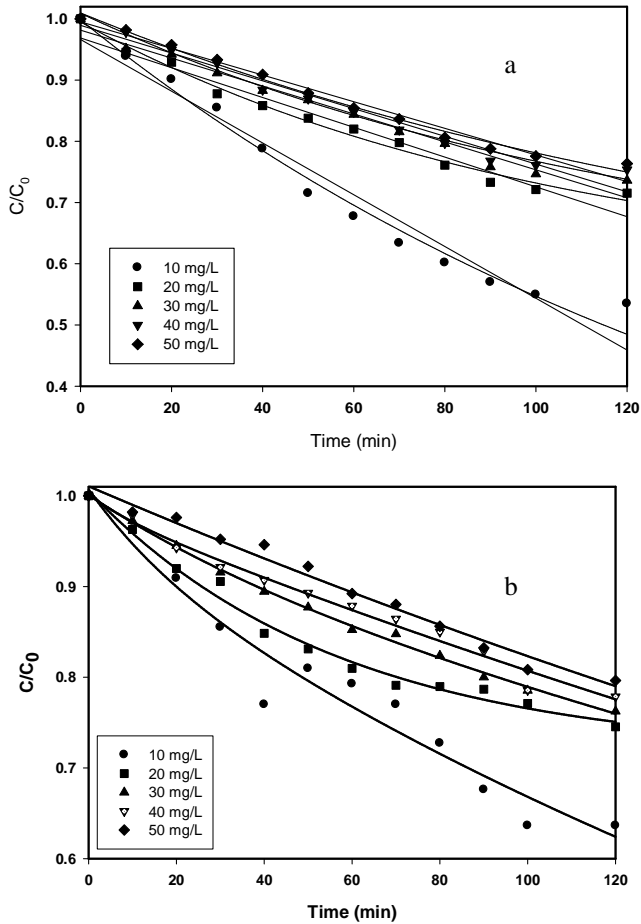


Figure 2: Dimensionless time-concentration plots for different initial concentrations of dichromate solution with respect to a) UV intensity (0.80-0.90 mW/cm²) and b) solar intensity (30.15 mW/cm²) [ZnO loading 0.4 gm/L, concentration of methanol 1.25 mol/L, solution volume 500mL, temperature 30°C, pH 5.5]

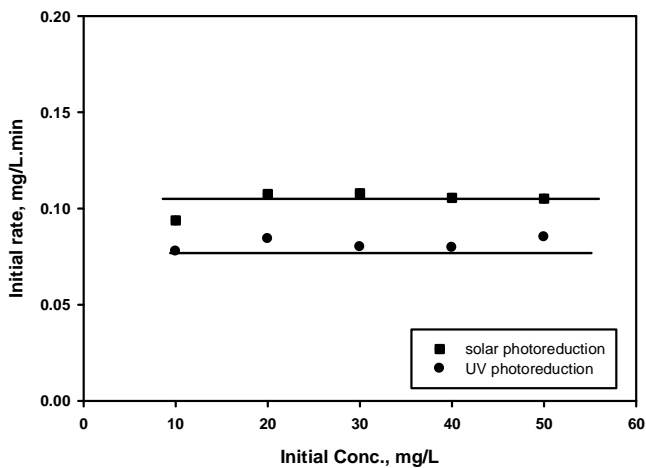


Figure 3: Initial substrate concentration vs. initial rate of photoreduction with respect to UV intensity (0.80-0.90 mW/cm²) and solar intensity (30.15 mW/cm²) [ZnO loading 0.4 gm/L,

concentration of methanol 1.25 mol/L, solution volume 500mL, temperature 30°C, pH 5.5]

activation. Increase in the amount of ZnO means increase in the active sites for catalysis. After that critical value, with increase in the photo catalyst loading up to 0.4g, the initial rate decreased since the suspension becomes too turbid to allow UV/solar radiation through it (Figure 4). So in both cases, the initial rate should be proportional to the loading of zinc oxide photo catalyst only. From fitting initial rate against ZnO loading, a straight line ($R^2 = 0.987$) passing through origin leading to a value of $0.277 \text{ (mg. L}^{-1}\text{). min}^{-1}\text{.(g ZnO)}^{-1}$ of k_1^0 was obtained for UV photo reduction and in case of solar photo reduction the value of k_1^0 was $0.555 \text{ (mg. L}^{-1}\text{). min}^{-1}\text{.(g ZnO)}^{-1}$ ($R^2=0.978$). (plot not shown here)

The rate equation thus becomes:

$$\text{Initial rate: } -dC / dt(t = 0) = k_1^0 [ZnO] \text{ (Eq.1)}$$

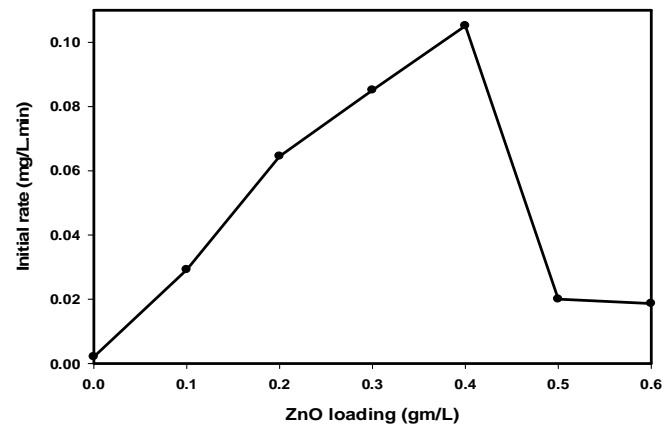
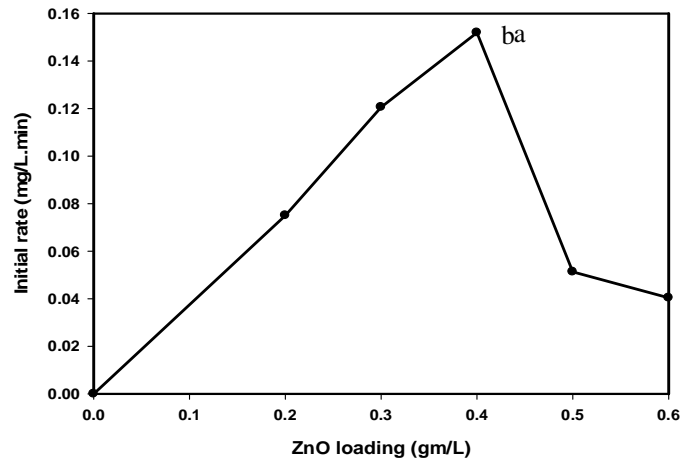


Figure 4: ZnO-loading vs. initial rate of photoreduction with respect to a) UV intensity (0.80-0.90 mW/cm²) and b) solar intensity (30.15 mW/cm²) [Initial concentration of substrate: 50mg/L, methanol concentration 1.25 mol/L, solution volume 500mL, temperature 30°C, pH 5.5]

3.1.3 pH

The pH of the solution was an important parameter in photocatalytic processes. Time concentration plots at various pHs of the medium has been shown in Figure 5.

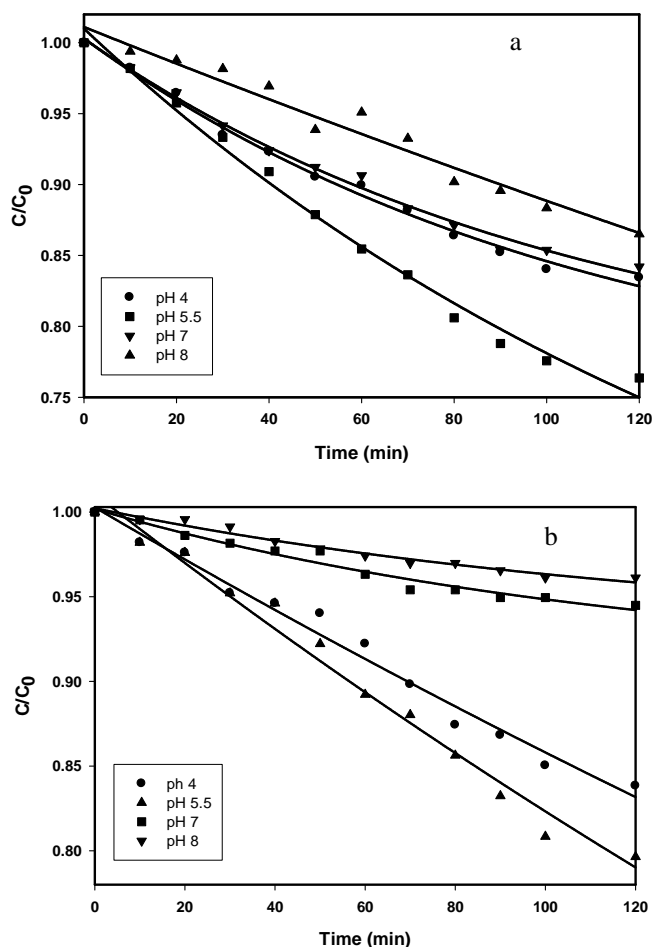


Figure 5: Dimensionless time–concentration plots for different pH with respect to a) UV intensity (0.80-0.90 mW/cm²) and b) solar intensity (30.15 mW/cm²) [Initial concentration of substrate 50mg/L, ZnO loading 0.4gm/L, solution volume 500mL, temperature 30°C, methanol concentration 1.25mol/L]

It appeared that the conversion was maximum at a pH 5.5 but decreased rapidly with increasing pH. The catalyst dissolves at a low pH; a high pH was detrimental to both the catalyst and the oxidizing species. This observation has been supported by other researchers also [5, 6]. Wang *et al.* [7] reported low conversion of Cr(VI) as well as “photocorrosion” of ZnO at neutral to basic pH.

3.1.4 Intensity of UV radiation

Intensity of UV radiation was varied from 0.35 to 0.90 mW/cm² by varying the number of lamps and the corresponding illuminance was measured by UV meter. No

reduction of the dichromate in the absence of UV radiation was observed.

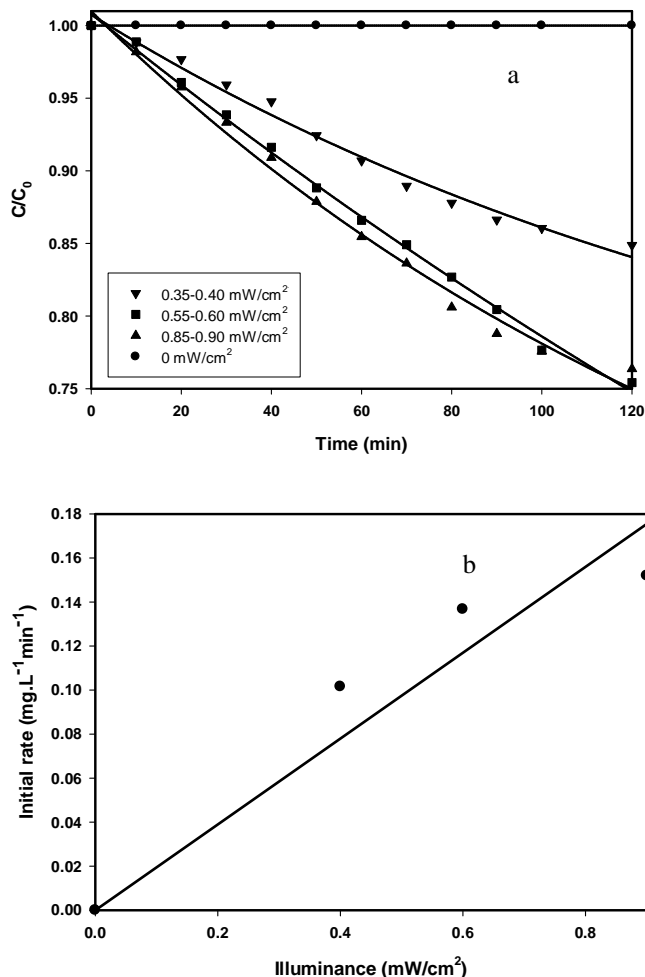


Figure 6. a): Dimensionless time–concentration plots for different intensities of UV radiation b) Intensities of UV radiation vs. initial rate of photoreduction [Initial concentration of substrate 50mg/L, ZnO loading 0.4gm/L, solution volume 500mL, temperature 30°C, methanol concentration 1.25mol/L, pH 5.5]

An increasing UV intensity enhanced both the initial rate and the extent of degradation (Figure 6a&b). However intensity of sunlight remained constant within the experiment period.

3.1.5 Initial concentration of methanol

It was observed that the initial rate was very low without methanol; the extent of photo-reduction reaction becomes slow in the absence of a sacrificial electron donor. However, the concentration of this sacrificial donor did not appear to affect the initial rate substantially after a certain critical value presumably because of an excess methanol present in the solution.

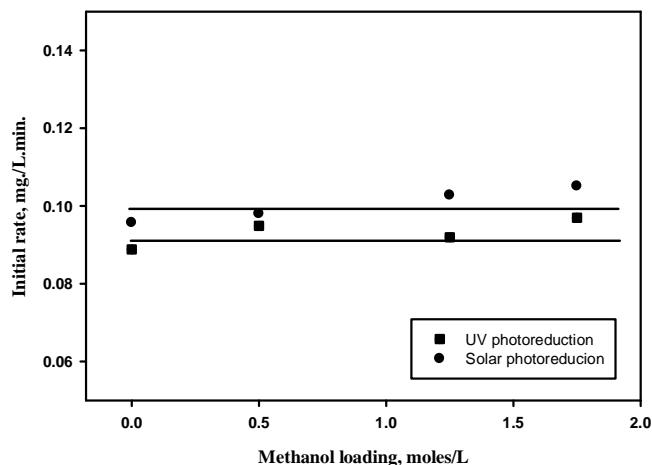


Figure 7: Methanol loading vs. initial rate of photoreduction with respect to UV intensity (0.80-0.90 mW/cm²) and solar intensity (30.15 mW/cm²) [Initial concentration of substrate 50mg/L, ZnO loading 0.4gm/L, solution volume 500mL, temperature 30°C, pH 5.5]

The initial rate was observed to increase as methanol loading was increased up to 1.25 mol/L, but after that the initial rate did not change considerably with further addition of methanol (Figure 7). Therefore 1.25 moles/L methanol was chosen for most of the experiments.

4. CONCLUSION

ZnO as the semiconductor photocatalyst can effectively reduce hexavalent chromium in aqueous solutions to the trivalent state under UV/solar radiation in presence of methanol, a sacrificial electron donor. 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 loading in suspension and on the UV dosage (in case of UV assisted photoreduction). The extent of degradation as well as its initial rate increased with the loading of the photocatalyst and intensity of UV radiation.

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