

# On the removal of hexavalent chromium from wastewater: a comparative study between photocatalytic and chemical reduction processes

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**Abstract:** - Common sources of chromium in wastewater are electroplating and leather industries. Hexavalent chromium is more toxic and carcinogenic compared to its trivalent counterpart. Conversion of Cr (VI) to Cr (III) in an aqueous medium both by chemical reduction using zerovalent iron and by photocatalytic reduction using UV radiation and ZnO semiconductor has been investigated using potassium dichromate as the model compound. Both the processes are effective to reduce Cr (VI) efficiently up to about 90% in 90 minutes. The process parameters were pH (varied from 1 to 6) and iron loading (0.5 to 1.0g/100mL) for chemical reduction, and ZnO loading (0 to 3g/L) and intensity of UV radiation (0 to 120W medium pressure Hg vapour lamp) for the photochemical process. Initial concentration of substrate solution was varied (40 to 125mg/L approx) in both cases. Kinetics of the chemical method was found to follow pseudo first order rate equation whereas the initial rate of the photochemical method was found to be independent of the concentration of potassium dichromate. Rate of reduction in chemical method increased with increase in loading of iron dust and with decrease in pH. Initial rate of photocatalytic reduction increased with increase in catalyst loading and intensity of UV radiation. A possible mechanism and the corresponding kinetic model have been proposed for the photo reduction and tested by experimental results.

**Keywords:** Hexavalent chromium, reduction, zerovalent iron, photocatalysis, rate.

## 1. Introduction

Metals found in industrial wastewater are toxic in some of their valance states. Among the two stable forms of Chromium available in the aquatic systems, Cr (VI) and Cr (III), trivalent chromium is less dangerous. Hexavalent chromium is a priority metal pollutant introduced into natural water from many industrial processes including leather tanning, textile, electroplating, metal cleaning, wood preservation and alloy preparation. Hexavalent chromium compounds are highly toxic when ingested or inhaled. Carcinogenesis caused by hexavalent chromium may result from the formation of mutagenic oxidative DNA lesions following intracellular reduction to the trivalent form. Consequently any hexavalent chromium present in wastewater should be reduced to Cr (III) before

discharge into the sewer. The treatment procedure of Cr(VI)-bearing wastewater often comprise reduction of Cr(VI) and any of the after treatments such as coagulation-precipitation [1], active carbon adsorption [2], ion-exchange or membrane separation [3]. Cr(VI) can be reduced by zero valent iron [3, 4], ferrous sulphate [5] and photocatalytic reduction using various semiconductors such as ZnO, TiO<sub>2</sub>, WO<sub>3</sub> etc under artificial or solar visible/ UV radiation [5, 6, 7, 8]. Chemical reduction by FeSO<sub>4</sub>, SO<sub>2</sub> or NaHSO<sub>3</sub> before hydroxide precipitation is a very effective technique but the chromium hydroxide sludge is substantial in amount and difficult to dispose of [9]. Moreover these methods are highly sensitive to pH and controlled by the cost of chemicals. Active carbon adsorption and ion exchange are only suitable in the laboratory scale and at a low concentration (less than 100ppm) of chromium ion [3].

Cost and efficiency of regeneration are not always agreeable. An electrochemical technique such as electro dialysis is also expensive due to costly membranes.

Photocatalytic method is based on the reactive properties of electron-hole pairs generated in the semiconductor particles under illumination by UV/visible light having energy greater than the band-gap energy of the semiconductor. This clean method is widely used for treatment of the drinking water and industrial wastewater by oxidizing organic pollutants. The reducing capacity of the semiconductor photocatalysis which uses the generated electron on the semiconductor surface is, however, less explored. Some reports are available for the reduction of heavy metals from wastewater [8, 9]. Utilization of solar energy can make the process economically more attractive. In case of mixed effluent, the organic pollutants present are simultaneously oxidized; this is an important advantage of this process over the others. But photocatalytic process requires one "hole scavenger" (or sacrificial electron donor) to make the photogenerated electron available for reduction. Moreover a source of UV radiation and the semiconductor photocatalyst increase the cost of the process.

With regard to the cost consideration, metallic iron has received a great attention as a reducing agent for Cr(VI). El-Shazly et al [3] used scrap iron bearings in a fixed bed to reduce Cr (VI) in an acidified solution of potassium dichromate. Salem et al [10] attempted to remove Cr (VI) from aqueous solution of potassium dichromate in presence of quaternary ammonium salts in a batch process, with an iron cylinder of 1.4cm diameter and 7cm height immersed in the solution. The process was found to be diffusion-controlled. Kinetics of the reduction of nitrate, nitrite and Cr (VI) has been studied by Alowitz et al.[11]. Under appropriate conditions, a complete removal of Cr (VI) has been reported. The rate is rapid at low pH and is proportional to  $Fe^0$  loading [11]. When steel wool was used in a semi batch process, the reduction was facilitated by increasing concentration of acids and the precipitation was economized using  $CaCO_3$  [4]. In all cases, it was observed that the reduction is highly sensitive to pH. Though iron can very effectively reduce Cr (VI), chromate is a well-known passivator of iron. Corrosion inhibition and passive oxide effects on the kinetics of reduction has been studied by Mellitas et al [12]. They carried out batch and continuous experiments in the concentration-range of 100 to 10000  $\mu g/L$ . Electrochemical measurements were made to determine the free corrosion potential and corrosion rate.

## 2. Problem Formulation

In the present study, we started with the same potassium dichromate solution and reduced it using both zero valent iron and photo reduction with ZnO/ UV. A comparative study was made with respect to the rate of reduction and influence of the process parameters on the reduction process. Process variables in case of photoreduction were loading of ZnO photocatalyst and intensity of UV radiation whereas the same in case of chemical reduction were loading of iron particles and pH. It was observed that photocatalytic process was not pH-sensitive whereas chemical process was highly dependent on pH. Furthermore, too much lowering of pH in case of photocatalysis would cause undesirable ZnO catalyst corrosion. Initial concentration of potassium dichromate solution was varied in both the processes.

### 2.1 Materials and methods

#### 2.1.1 Materials

AR grade potassium dichromate, GR grade zinc oxide and electrolytic grade iron dust were from LOBA Chemie, India. Methanol (GR) was from SD Chemicals, India. Freshly prepared double distilled water was used to prepare solutions. LR grade hydrochloric acid and sodium hydroxide from SD Chemicals were used for maintaining pH.

ZnO had mean particle size of 146.7 nm (*Zeta Plus, Brookhaven Instrument Corporation*) and a BET surface area of 3.23  $m^2/g$ . Illuminance of the UV lamp at different electrical powers for the photoreactor have been measured using Metravi 1330 series digital lux meter.

#### 2.1.2 Methods

The residual concentration of potassium dichromate has been determined using a UV-vis spectrophotometer Shimadzu UV-160A at 349nm in a 1cm quartz cell [13] against standard linear calibration curve. Experiments were repeated thrice and the standard deviation was within  $\pm 3\%$

#### 2.1.3 Experimental set up and procedure

For the chemical reduction process, 50mL of potassium dichromate solution of a particular concentration are taken in 120mL corning glass bottles. After adjusting the pH of the solution, weighed amount of iron powder were added to it. The bottles were shaken in a constant temperature shaker bath (at  $25 \pm 1^\circ C$ ), withdrawn at particular time intervals and analyzed for the residual Cr (VI). Separate sets were used for different time intervals to minimize interference due to withdrawal of samples. A stainless steel reactor of 0.15m diameter and 0.25m height fitted with a stainless steel cooling coil was used for photo reduction. A 125W medium pressure Hg vapour lamp has been inserted in a quartz sleeve at the center of the reactor as source of UV radiation. The reactor was provided with an insulating jacket. Temperature of the reactor was kept constant at  $25 \pm 1^\circ C$

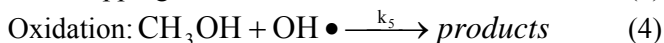
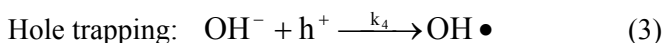
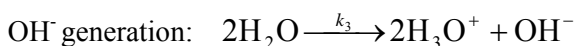
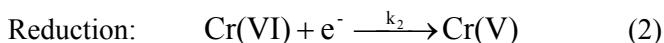
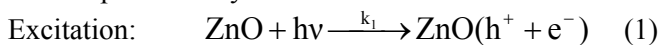
by circulating cooling water. The reaction mixture was kept under suspension using a magnetic stirrer. The suspension volume was 2000mL including the volume of methanol added for hole scavenging. Aliquots of about 15mL were withdrawn, filtered and analyzed after every 15 minutes. Experiments conducted in dark showed no significant adsorption of Cr(VI) on ZnO. Blank experiments were conducted without ZnO where it was observed that the photolysis was also negligible. It may thus be concluded that the reduction in the concentration of dichromate was mainly because of photo catalysis.

### 3. Problem Solution

#### 3.1 Mechanism and kinetics

It has been established that reduction of Cr (VI) in photocatalytic process proceeds via single-electron-steps [14]. Therefore the formation of unstable Cr (V) species may be considered as the key-step towards formation of Cr (III) that is reduction of Cr (VI).

The following steps can be envisaged for the reduction of hexavalent chromium in aqueous medium in presence of ZnO photo catalyst and UV radiation:

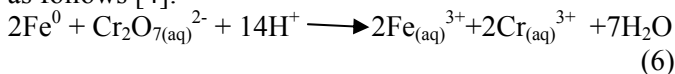


Experimental results show that the initial rates are nearly independent to the initial concentration of dichromate solution (Figure 1). Assuming a pseudo steady state for the formation of holes (h<sup>+</sup>) and electron (e<sup>-</sup>), the initial rate of photoreduction follows the kinetic equation as below:

Initial rate of reduction =  $2k_1[I_{UV}] [ZnO]$  (5)

That is, the initial rate follows zero order kinetics with respect to substrate (potassium dichromate). The explanation may be as follows: at the beginning, the concentration of dichromate is high and the electrons available from the excitation of the semiconductor are all used by the abundantly available dichromate ion in the vicinity, resulting in a zero order reaction with respect to the substrate. Thus the rate at this stage depends only upon the loading of ZnO and intensity of UV radiation.

On the other hand, overall rate of reduction in the chemical reduction followed pseudo first order kinetic model (rate constant k<sub>1</sub> min<sup>-1</sup>). The overall reaction is as follows [4]:



#### 3.2. Influence of process parameters

As described before, it was envisaged that loading of iron dust and pH would have influence on the extent and rate of chemical reduction process whereas the photocatalytic process would be affected by loading of photocatalyst and intensity of UV radiation.

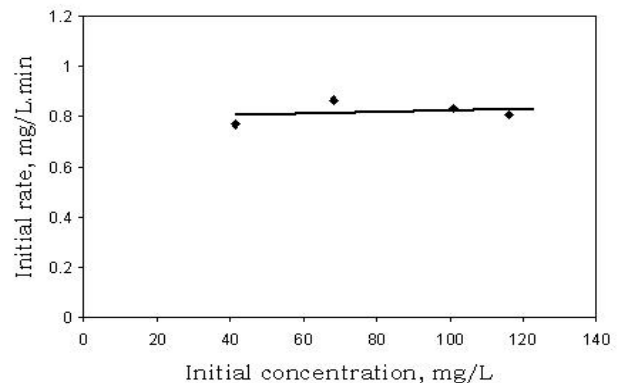


Figure 1: Initial concentration vs initial rate for photocatalytic reduction of Cr(VI)

Initial concentration is expected to affect rate of reaction in both the cases.

For chemical reduction using iron dust, time - concentration data have been collected varying different process parameters such as iron particle loading, initial concentration of dichromate solution and pH of the reaction medium. In all cases, the kinetic data could be interpreted fairly well with the pseudo first order model (Table 1). It was observed that the reduction was highly sensitive to the pH of the medium which was supported by the available reports [5,9]. Experiments were conducted using three values of pH; 1.5, 2.5 and 3.5

Table 1: Rate constants for chemical reduction of Cr(VI)

| Parameter  | Value | k <sub>1</sub> , min <sup>-1</sup> | R <sup>2</sup> |
|--|-------|------------------------------------|----------------|
| pH (temp 25°C, iron 1g/50mL, Initial conc. 50mg/L)             | 1.5   | 0.0355                             | 0.9630         |
|  | 2.5   | 0.0298                             | 0.9211         |
|  | 3.5   | 0.0282                             | 0.9460         |
| Initial concentration, mg/L (pH 3.5, iron 1g / 50mL) temp 25°C | 50    | 0.0282                             | 0.9460         |
|  | 75    | 0.0225                             | 0.9826         |
|  | 100   | 0.020                              | 0.9662         |
| Iron loading, g/ 50mL (pH 3.5, temp 25°C Initial conc. 50mg/L) | 0.50  | 0.0078                             | 0.9456         |
|  | 0.75  | 0.0155                             | 0.9632         |
|  | 1.00  | 0.0282                             | 0.9460         |

Figure 2 shows the time-concentration profile for the reduction of Cr (VI) at different pH ranges. The inset shows data fitting for determination of rate constant.

Reduction at the neutral pH was almost negligible and was not included in Figure 2. Decrease in pH, however, increased the extent of reduction, though at the same time, it should be kept in mind that decrease in pH means increase in the acid-load of the downstream water, which should be neutralized before discharge to the surface water bodies. The stoichiometry of Equation

6 shows that the reduction efficiency is highly dependent on acid concentration. At lower initial pH of the dichromate solution, more iron is solubilized and it may also be possible that Fe (II) ions form in the first step of oxidation of zerovalent iron and then Fe (II) carry on the reduction of Cr(VI) [9].

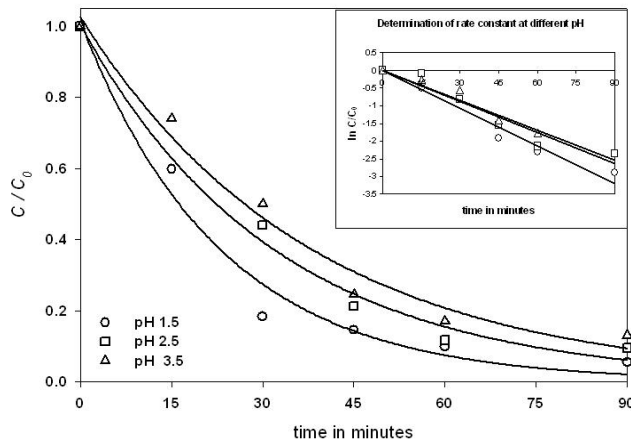


Figure 2: Time -concentration profiles for the reduction of hexavalent chromium by zero valent iron at various pH  
[Iron loading 1.0g, Initial concentration 50mg/L, solution volume 50mL, temperature 25°C]

Loading of iron dust were increased from 0.5 to 1.0g per 50mL. Extent of reduction expectedly increased with the increase in iron loading. Time – concentration profile of reduction of Cr (VI) at different iron loading is shown in Figure 3 and the corresponding pseudo first order rate constants are indicated in Table 1.

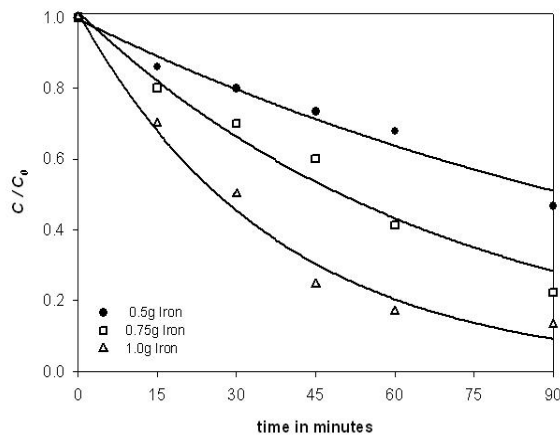


Figure 3: Time-concentration profiles of reduction of hexavalent chromium with zerovalent iron at various iron loading.  
[Initial concentration 50mg/L, pH 3.5, solution volume 50ml, temperature 25°C]

For photocatalytic process, initial rate of degradation increased with the increase in ZnO loading from 0 to 3g/L of suspension volume (Figure 4 inset). Increase in the amount of ZnO means increase in the active sites for catalysis and hence the increase. Time-concentration profile at various ZnO loading has been shown in Figure 4. Figure 4 inset also validates the proposition of Equation 5. Value of  $k_1$  determined from Figure 4 was  $3.6572 \times 10^{-4} (\text{mg/L} \cdot \text{min of potassium dichromate}) / (\text{g/L ZnO loaded}) \cdot (\text{lux of UV radiation})$  considering 125W (388 lux) UV lamp in a 2L reactant volume.

The electrical power of the UV lamp could be varied from 0 to 125W range. Corresponding illuminances have been measured in lux. It was observed that there was no reduction at all in absence of UV radiation.

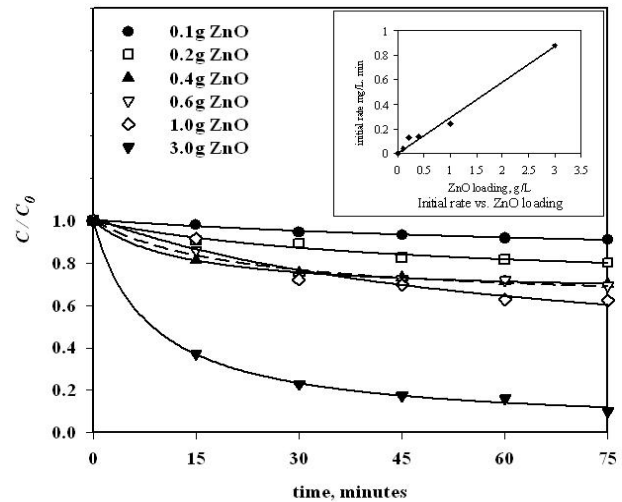


Figure 4: Time-concentration profile for photoreduction of hexavalent chromium at various ZnO loading  
[Dichromate solution conc. 50mg/L, UV radiation 388 lux, concentration of methanol 1.25 mol/L, pH 5.5, temperature 25°C]

As the electrical power as well as the illuminance was increased, initial rate of reduction increased (Equation 5). With the increase in the amount of radiation, the number of quanta which excites the semiconductor sites increases; this explains the direct relationship between the two.

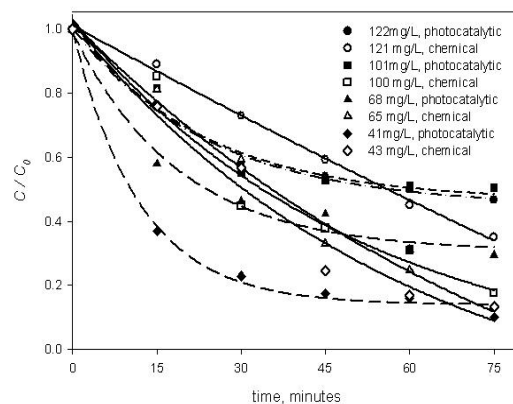
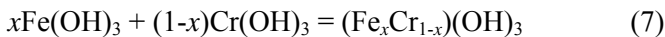


Figure 5: Comparison between time-concentration data of the two reduction processes at various initial concentrations  
[photocatalytic process: ZnO loading 0.6g/L, methanol 0.625mol/L, UV radiation 388 lux, pH 5.5  
chemical process: iron dust loading 1g/ 50mL, pH 3.5, temperature 25°C]

Increase in initial concentration of potassium dichromate keeping the pH and iron loading unaltered decreased the extent and overall rate of reaction in case of chemical reduction (Figure 5) whereas for photocatalysis, initial rate of reduction was independent of the initial solution concentration, as described before. The difference in mechanism has been manifested in the nature of the two curves. For the chemical process, this decrease in the overall rate of reduction may be explained with the passivating effect of Cr (VI) over iron. A solid solution

of mixed oxides may form on the surface of iron [12] as follows:



where  $x$  can range from 0 to 1.

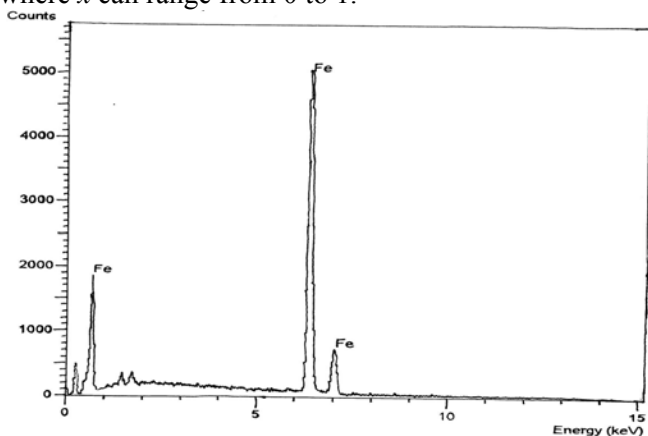


Figure 6A: EDS image of iron dust before reaction with dichromate

According to the available literature [12], this can be attributed to the effect of potential on the rate of electrochemical reaction by a corrosion inhibitor like dichromate.

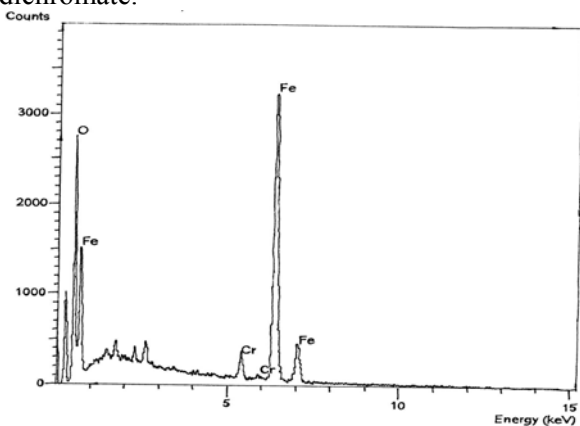


Figure 6B: EDS image of iron dust after reaction with dichromate

EDS analysis also supports the proposition. High oxygen content in the spent iron may be due to the deposition of oxides of iron and chromium on the surface of iron particle (Figure 6 B). It may be worth mentioning here that the initial rate for the chemical reduction increased with increase in the initial concentration of dichromate. At the beginning, the rate of reaction increases depending upon the increased availability of chromium ion near iron particles with increasing concentration, but as the time of contact increases the passivating effect comes into consideration and the rate decreases; hence the decrease in overall rate. For the photocatalytic process, methanol was added as hole scavenger. It was observed that the initial rate was very small when no methanol was added. But after 0.625 mol methanol was added per liter of solution, initial rate was enhanced more than 100% of its value without alcohol. After that, even if we increased the concentration of methanol, there was no further enhancement of the initial rate (Figure 7).

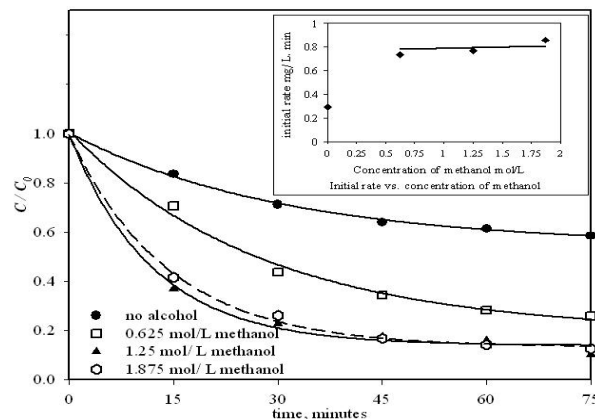


Figure 7: Time-concentration profile at different concentrations of methanol [Dichromate solution concentration 50mg/L, UV radiation intensity 388 lux pH 4.5, ZnO loading 3g/L, temperature 25°C]

This may be due to the fact that at the particular experimental condition, all the holes generated must have scavenged by the minimum volume of methanol added.

### 3.3. Characterization of the iron particles before and after reaction with potassium dichromate solution

SEM (LEO S-440) image (1250 times magnified, Figure 8A) shows that before being exposed to dichromate solution the iron particles are of about 120 micron size on an average. The shape of the particles can be approximated as spheres. A critical examination reveals the regular nature of the contour and compact surface of it. Energy Dispersive Spectrometry (EDS, Oxford Link Isis) associated with SEM shows that the electrolytic grade iron dust contains only pure iron (Figure 6 A). After reacting with potassium dichromate solution at pH 3.5, no considerable change has been observed in the size of the iron particle (Figure 8B). Surface morphology of the particle was observed to have changed into a loose and brittle one compared to its compact and rigid structure before reaction.

From the darker part of the SEM image of a single iron particle in the back scatter mode (Figure 9), it can be concluded that chromium occupies a portion of a single iron particle. EDS output with peaks of chromium (Figure 6B) also supports the observation. EDS output of ZnO particles after a photocatalytic reduction reaction indicated no peak of chromium.

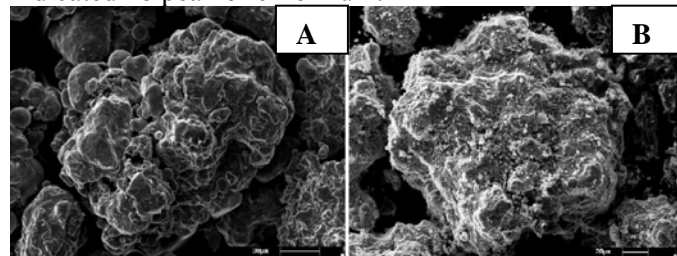


Figure 8 A and B: SEM images of unreacted and reacted iron particle

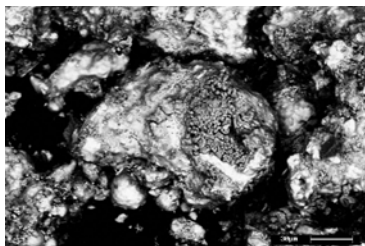


Figure 9: Back scattered SEM images of reacted iron particle

It may be recalled here that no adsorption was observed on ZnO surface in the dark reaction. Therefore it may be concluded that the reduction reaction possibly occurred in solution instead of the catalyst surface.

#### 4. Conclusion

Hexavalent chromium has been reduced both by zero valent iron and by ZnO-UV photocatalysis and the results were compared. About 90% reduction of the original Cr (VI) present could be achieved by both the processes within 90 minutes. Initial rate of reduction increased with increase in catalyst loading in case of photocatalytic reduction whereas the reduction increased with increase in the iron dust loading in the chemical process. Chemical reduction was highly sensitive towards pH. Increase in the intensity of UV radiation expectedly enhanced the initial rate of photo reduction. In case of chemical reduction reaction kinetics followed pseudo first order equation with respect to Cr(VI) concentration and the lumped rate parameter increased with decreasing initial concentration. Initial rate of reduction was independent of initial concentration of dichromate for the photocatalytic reduction.

Chemical method imparted a huge dissolved solid load and high acidity which should be neutralized before discharge to surface water to precipitate out the Cr(III) obtained by reduction. Photocatalytic method has been carried out in a higher pH range, so its neutralization will be easier; but it imparts suspended solid load due to the presence of insoluble ZnO and an added cost for the UV radiation unless solar radiation is used.

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