

Photoreduction of Potassium Dichromate in Aqueous Solution using Cobalt doped ZnO Nanoparticles

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Abstract

Co-doped ZnO nanoparticles with different Cobalt contents were prepared by direct precipitation method. The materials were characterized by XRD, SEM and TEM techniques. The XRD results indicated that the particle size of pure ZnO and Co-doped ZnO is about 30-45nm. The toxic Cr(VI) in industrial wastewaters can be removed by a reduction from Cr(VI) to Cr(III). The reduction of Cr(VI) to Cr(III) can be achieved by a photocatalytic process. The effect of Co loading on the photocatalytic activity of Co-doped ZnO in the reduction of Cr(VI) was studied and the results are compared with the pure ZnO. The results showed that the rate of photoreduction of Cr(VI) over Co-doped ZnO is much higher as compared to that of pure ZnO. The photocatalytic reaction were carried out under UV radiation towards the reduction of Cr(VI) by varying different parameters such as irradiation time, pH of the solution, catalyst amount and substrate concentration.

Key words: Photocatalytic Reduction, Co-doped ZnO, Nano Particles, Cr(VI) Elimination, Environmental Pollution

Highlights

- Preparation of Co-doped ZnO nanoparticles with different Cobalt contents by direct precipitation method
- Investigation of the effect of Co loading on the photocatalytic activity of Co-doped ZnO in the reduction of Cr(VI)
- Study of different factors that affect the photocatalytic reduction of Cr(VI) to Cr(III) in aqueous solutions.

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Introduction

Chromium is one of the most toxic pollutants with great variety of industrial wastes. Chromates are frequent contaminants in wastewaters arising from industrial processes such as electroplating, leather tanning or paint making (1, 2). Cr(VI) is toxic to most organisms, carcinogenic in animals, and causes irritation and corrosion of the skin in humans. It is highly soluble in water and forms of mono- and divalent oxyanions, chromate ($\text{HCrO}_4^-/\text{CrO}_4^{2-}$) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) respectively, depending on its concentration and pH. Because it is only weakly adsorbed onto inorganic surface, Cr(VI) is mobile in nature. On the other hand, Cr(III) is readily precipitated or adsorbed on a variety of inorganic and organic substrate at neutral or alkaline pH. Cr(VI) has a toxicity one hundred times higher than that of Cr(III) (3). The geochemistry and toxicity of chromium in the natural environment is controlled by its valence state.

The methods employed for the removal of hexavalent chromium are chemical precipitation, reverse osmosis, ion exchange, foam flotation, electrolysis, photocatalytic reduction, adsorption, etc. However, most of these methods require either high energy or large quantities of chemicals whereas the photocatalytic process is found to be superior to all (4, 5). Semiconductor photocatalysis has been intensively investigated for its application to environmental pollutants degradation. It has been found that a variety of organic and inorganic pollutants can be oxidized or reduced by photogenerated holes and electrons over semiconductors (6).

TiO_2 is universally considered as the most photoactive catalyst, ZnO is a suitable alternative to TiO_2 in the degradation of several organic contaminants in both acidic and basic medium has stimulated many researchers to further explore the properties of this oxide in many photocatalytic reactions. However, ZnO has some drawbacks including the fast recombination rate of photogenerated electron-hole pair and a low quantum yield in the photocatalytic reactions in aqueous solutions, which obstruct commercialization of the photocatalytic degradation process. Therefore, various methods have been developed to reduce the e^-/h^+ recombination rate of ZnO in the photocatalytic processes. One of interesting approaches is to dope the transitions, alkaline and rare earth metal atoms on the surface of the semiconductors, which have been shown to reduce band gap energy and improve charge separation between photogenerated electron and holes (7). Recently, photoreduction of hexavalent chromium in aqueous medium with using of ZnO (8) and ZnO nanorods immobilized on kaolin clay (9) in the presence of organic compounds or hydrogen peroxide were investigated. On the other hand, Doping of ZnO with cobalt (Co) has been reported (10, 11) to cause hyperchromic shift in the optical absorption of ZnO, which is attributable to the shrinkage of the band gap. These changes in ZnO caused by Co ion were assumed to play an important role in the photocatalysis. In addition enhancement in the optical absorption owing to increase in surface defects by doping with Co, urge us to further investigate

undoped and doped ZnO nanoparticles and its photocatalytic activities.

The aim of the present work is to investigate the potential of Co-ZnO and ZnO nano particles as a photocatalyst under UV-vis radiation for studying different factors that affect the photocatalytic reduction of Cr(VI) to Cr(III) in aqueous solutions.

Experimental

Materials: Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cobalt nitrate hexahydrate, ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Sodium carbonate anhydrous (Na_2CO_3) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) were purchased from Merck (Analytical grade). All the chemicals were used without further purification.

Preparation of photocatalysts: Co-doped ZnO nano particles were prepared by direct precipitation method using zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) as the precursors of zinc and cobalt, respectively. In a typical synthesis ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and Na_2CO_3 were dissolved separately in double distilled water to obtain solutions with 1.5 and 2.25 mol/L concentration, respectively. Zinc nitrate solution was slowly added into vigorously stirred Na_2CO_3 solution. Cobalt nitrate in the required stoichiometry was slowly added into the above solution and a violet precipitate was obtained. The precipitate was filtered, repeatedly rinsed with distilled water and then washed twice with ethanol. The resultant solid product was dried at 80 °C for 4 h and calcined at 500 °C for 2 h. ZnO nano particles were also prepared by the same procedure without the addition of cobalt

nitrate solution. The doping concentrations of cobalt are expressed in wt%.

Photocatalytic reactor set up and photoreduction procedure: The photocatalytic activity was tested on the photoreduction of potassium dichromate. The photoreduction intermediates were not determined. The light was provided by a 400W high pressure Hg lamp without covering which was placed vertically in the reactor. The temperature of photoreduction system was adjusted by a water bath in which heating or cooling water recirculated through the jacket of the beaker. The pH was adjusted by using sulfuric acid (Merck) and sodium hydroxide (Merck). Prior to illumination, the reaction suspension was stirred continuously in dark for 30 min to ensure adsorption/desorption equilibrium. After irradiation, the suspension was filtered and was analyzed Cr(VI) quantitatively by measuring the absorbance at 350 nm by means of a RAYLEIGH (UV-1800) ultraviolet-visible (UV-vis) scanning spectrometer.

Characterization of photocatalysts: X-ray diffraction (XRD) patterns were recorded by a D8 Bruker Advanced, X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The patterns were collected in the range $2\theta = 10\text{--}80^\circ$ and continuous scan mode. Scanning electron microscopy (SEM) images were obtained on Philips XL30 equipped with an energy dispersive X-ray spectroscopy. Transmission electron microscope (TEM) images were obtained on a Philips CM10 transmission electron microscopy with an accelerating voltage of 100kV.

Results and Discussion

X-ray diffraction (XRD) studies: Fig. 1 shows the powder X-ray diffraction patterns of ZnO and Co-doped ZnO with 6% cobalt contents. All the materials showed a hexagonal wurtzite crystal structure. Average crystal size of ZnO and Co-doped ZnO calculated using Debye–Scherrer formula is 30–45 nm. The XRD patterns show that Co doping of ZnO nano particles does not change its wurtzite structure, but compared to

undoped ZnO, peak intensities of Co doped ZnO are decreased. The incorporation of Co into ZnO lattice is evidenced by the shrinkage or the expansion of the lattice parameters of ZnO in response to the transition metal dopant up to 6% Co after which both a and c parameter show increase. This varies, due to the fact that the ionic radius of Zn^{2+} (0.60 \AA) is a little bigger than that of Co^{2+} (0.58 \AA) in their tetrahedral coordination (12).

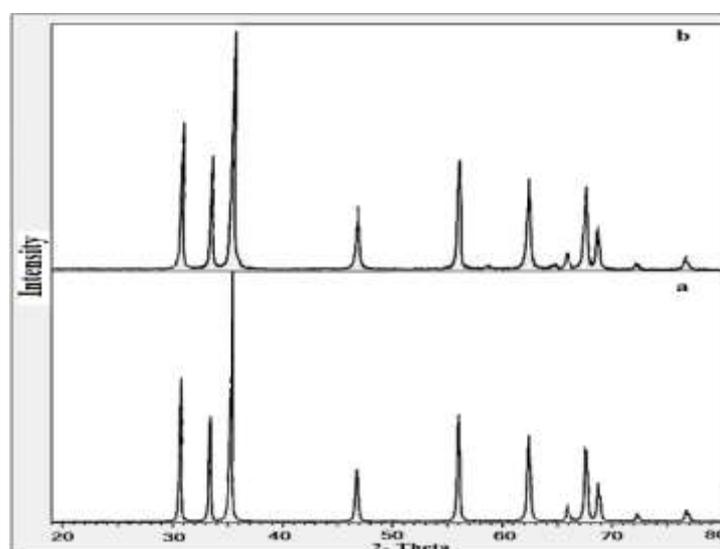


Fig. 1- XRD patterns of (a) Pure ZnO, (b) 6 wt% Co-doped ZnO

SEM and TEM micrographs: SEM micrographs of ZnO, 6wt% Co-ZnO nano particles are shown in fig. 2. It is observed that nano ZnO are in elliptical shapes. The morphology and particle size of them cannot be resolved using this technique. The EDX data of ZnO and 6 wt% Co-doped ZnO is shown in fig. 3. There are ZnO and Co peaks in the EDX pattern of Co-ZnO that this observation gave convincing evidence for the presence of cobalt on the surface of ZnO. The EDX analysis confirmed the percentages of Co in the respective samples to be close to the nominal values used for the preparation. Fig. 4.

illustrates transmission electron micrographs of ZnO and 6 wt% Co-doped ZnO. TEM is a useful technique for the analysis of the size and shape of ultrafine particles. Fig. 4(a) shows the nanocrystallites of pure ZnO with average size of ~40–50 nm, in agreement with XRD data. Fig. 4(b) exhibits 6 wt% Co doped ZnO nanocrystalline with average size of ~30–40 nm. In fact, it is demonstrated that Co dopant could inhibit the decrease of ZnO particle size. Therefore, this result may be attributed to the presence of dopant component in the ZnO framework.

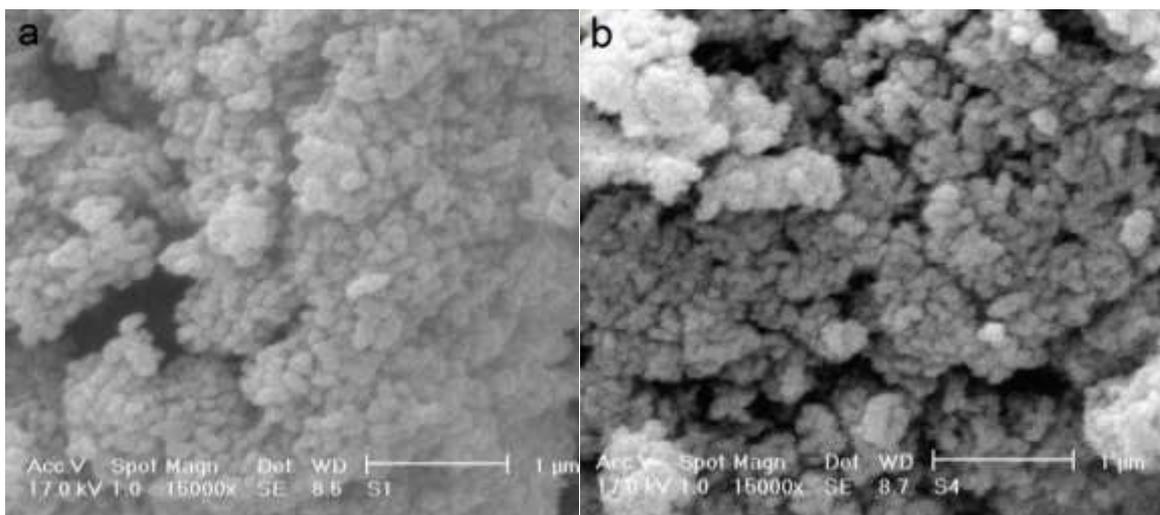


Fig. 2- (a) SEM image of ZnO, (b) SEM image of 6 wt% Co-doped ZnO

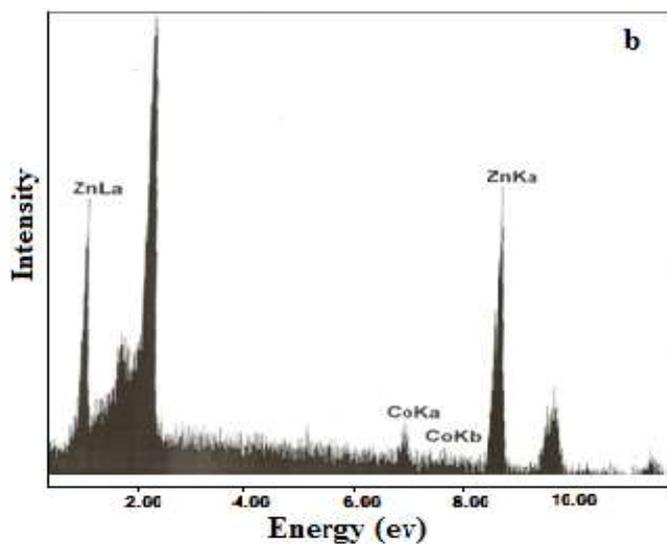


Fig. 3- EDX data of pure ZnO (a), 6 wt% Co-doped ZnO (b)

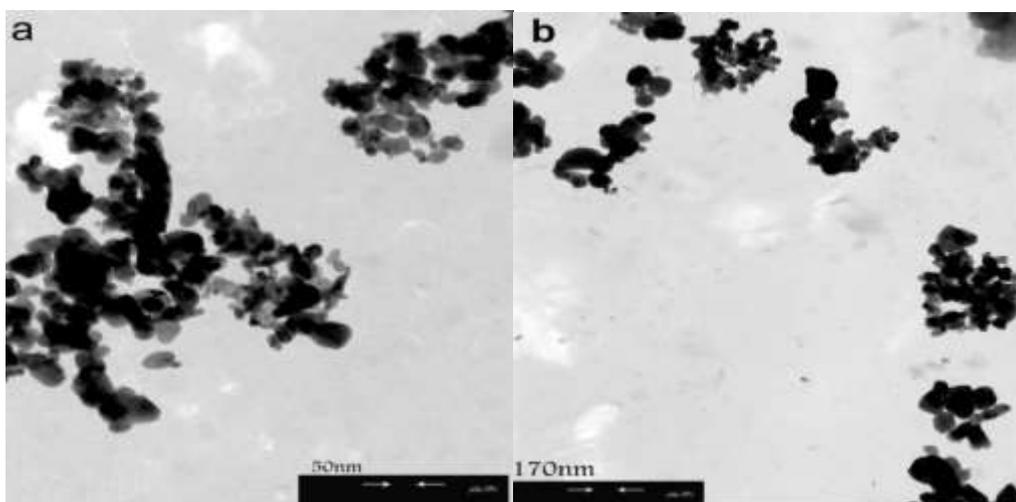


Fig. 4- TEM image of (a) 6% wt Co-ZnO (b) ZnO

Evaluation of the photocatalytic activities of ZnO and Co-ZnO nano particles in reduction of Cr(VI): The photocatalytic activity for photoreduction of Cr(VI) was studied using undoped and Co doped ZnO under UV and visible light irradiation. There was no considerable reaction rate when the irradiation was carried out in absence of photocatalysts. The experiment results showed that no concentration of chromium ions was absorbed on the surface of pure ZnO and Co doped ZnO in dark for 30min, too. The photocatalytic activity of pure ZnO and Co doped ZnO are shown in Fig. 5. The photocatalytic activity of ZnO (undoped) for Cr(VI) reduction was found to be lower than the Co doped ZnO. It could be seen that the photocatalytic activity of ZnO nanoparticles could be greatly improved after the doping appropriate content of Co. The optimum dopant (Co) concentration was found to be 6%. If the

dopant concentration was larger than its optimized value, the activity of ZnO nanoparticles began to decrease. This may be attributed to the structural changes of ZnO owing to Co^{2+} doping. However, we assume that at high dopant concentration, Co^{2+} may react more readily with oxygen to form CoO_x instead of taking interstitial or substitutional site in ZnO crystal. It is reported that the photocatalytic activity is dependent on crystallinity rather than the surface area or particle size (13). Interestingly, higher photocatalytic activity was observed for 6%wt concentration of cobalt in Co doped ZnO sample. The band gap of Co doped ZnO shows a decrease with increasing Co concentration up to 6% (14). It causes producing electron-hole pair in Co-ZnO which occurs quicker than pure ZnO. On the other hand, Co doped ZnO has native n-type donor defects (15). This property helps Cr reduction, too.

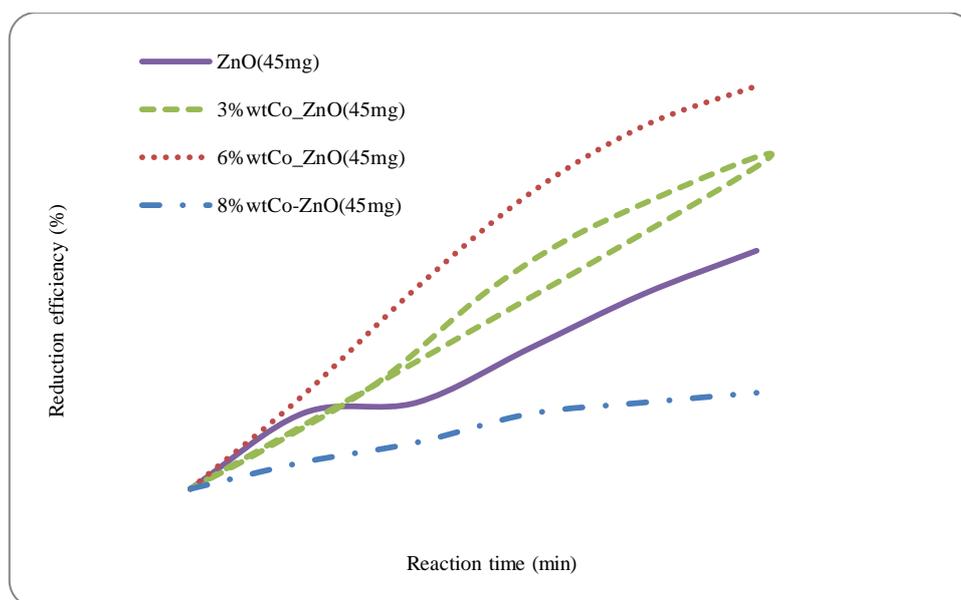


Fig. 5- The variation of the percentage of the amount of Cr(VI) photoreduced with illumination time at initial $[\text{Cr(VI)}]$ of 20mg/L using photocatalysts at acidic pH

Effect of pH: pH value is an important parameter affecting chemical and biological reactions in wastewaters (16). Thus, changes in pH could affect the removal of Cr(VI) in the rice straw solution. The results of Cr(VI) removal in the pH-effect experiment are presented in Table. 1. As seen in this table, a proper pH value for Cr(VI) removal was acidic pH. Many previous studies showed that the solution pH of wastewaters containing chromium was generally very acidic and the complete removal of Cr(VI) was observed only at highly acidic pH such as 2 (17-18). Our study also finds the same results. Only 32% and 10% of Cr(VI) were removed from the solution in the pH neutral and pH basic by ZnO at time of 75 min, respectively. The reason for this phenomenon is that the amount of $\text{Cr}_2\text{O}_7^{2-}$ absorbed on the photocatalyst surface decreases with the increase of initial pH. On the other hand, according to the reaction, $14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$, the photocatalytic reduction of $\text{Cr}_2\text{O}_7^{2-}$ should be in acidic solution (19). From above results, solution pH is of great importance for Cr(VI) removal by photocatalytic reduction.

Table 1- Effect of initial pH on the photocatalytic reduction of Cr(VI) by ZnO and 6%wt Co-ZnO (20 mg/L of Cr(VI) concentration, 45 mg of photocatalysts amount)

pH	acidic	neutral	basic
ZnO	53.29%	32.28%	9.94%
o-ZnO6%	90.15%	11.11%	4.08%

Effect of amount of ZnO and 6%wt Co doped ZnO: Fig. 6 shows the effect of the amount of ZnO and 6 wt% Co doped ZnO on the photocatalytic reduction of $\text{Cr}_2\text{O}_7^{2-}$. The results showed that the optimum photocatalyst weight for ZnO and Co-ZnO was found to be 75 mg and 45 mg, respectively, where a maximum light absorption by photocatalysts were attained. It shows that the optimum photocatalyst weight for Co-ZnO is lower than ZnO. When a lower mass of photocatalysts were used, less active sites for reduction of Cr(VI) are available. At the higher mass of the optimum photocatalysts, the actual photon absorption by ZnO and Co-ZnO would be less due to scattering of some incident light.

Effect of initial Cr(VI) concentration: The effect of initial Cr(VI) concentration on Cr(VI) removal was investigated over a range of 20-40 mg/L. As shown in Fig. 7, the Cr(VI) removal rate increased as Cr(VI) concentration decreased. For an initial concentration of 20mg/L of pollutant, it was observed that 90% and 53% of Cr(VI) was removed from the solution for effect of Co-ZnO and ZnO at 75 min, respectively, whereas the 67% and 24% removal of 40mg/L of Cr(VI) occurred by Co doped ZnO and ZnO in the same, respectively. The drop, due to the restriction of adsorption sites, presents on the surface of photocatalysts. At the lower initial concentration, sufficient adsorption sites are available for the sorption of Cr(VI). However, the numbers of Cr(VI) are relatively higher as compared to availability of adsorption sites at higher Cr(VI) concentration (16).

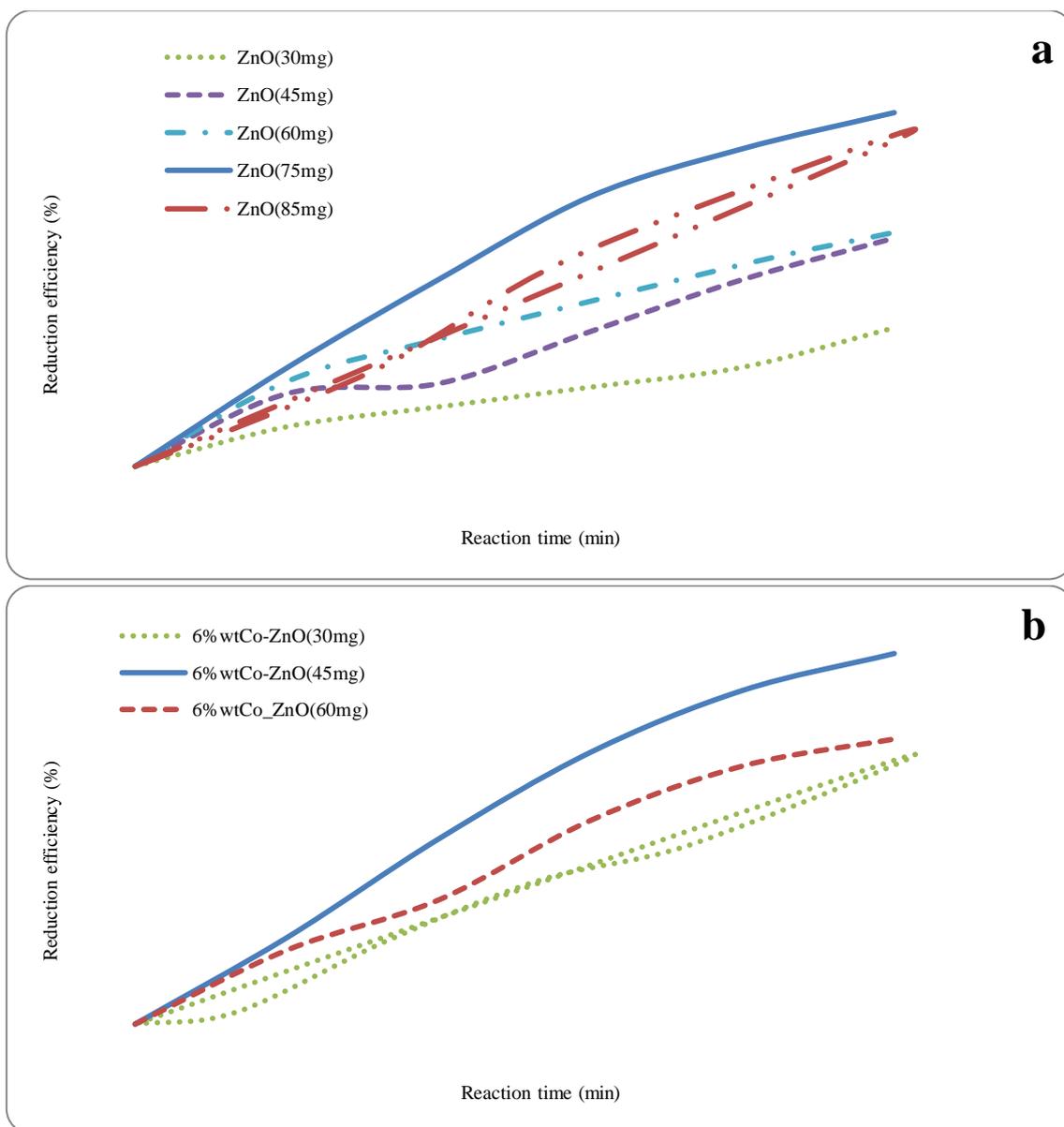


Fig. 6- The variation of the percent the amount of Cr(VI) photoreduced with illumination time at initial [Cr(VI)] of 20mg/L at acidic pH using different amounts of photocatalysts (a) ZnO (b) Co-ZnO6%

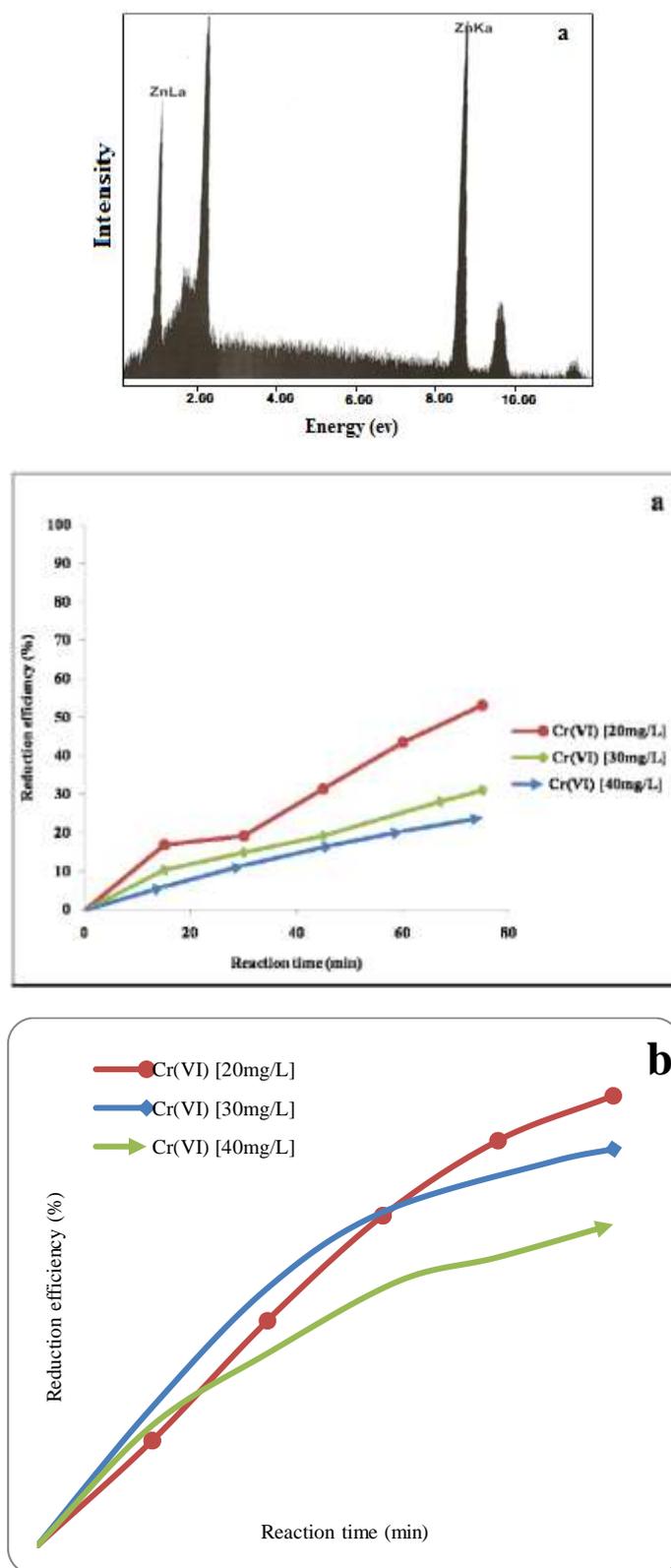


Fig. 7. Effect of initial Cr(VI) concentration on Cr(VI) removal by ZnO (45mg) (a) and 6 wt% Co doped ZnO (45mg) (b) at acidic pH

Conclusions

In the present work, an enhancement of the photocatalytic activity of ZnO catalyst, by doping with cobalt, has been confirmed in the reaction of Cr(VI) photoreduction. It was found that with a suitable amount (6 wt%) of the Co dopant effectively increases the photocatalytic activity of the ZnO. The Co²⁺ doped on the ZnO surface behave as a site where electrons accumulate. The optimal initial pH was acidic media and Cr(VI) removal rate increased with decreased Cr(VI) concentration and with increased time.

Therefore, Co doped ZnO with 6wt% may be a suitable photocatalyst which could convert Cr(VI) to the less toxic.

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References

- (1) Parida, K. M., Dash, S. S., Das, D. P. Physico-chemical characterization and photocatalytic activity of zinc oxide prepared by various methods. *Colloid and Interface Science* **2006**, 298, pp 787-793
- (2) Shao, D., Wang, X., Fan, Q. Photocatalytic reduction of Cr(VI) to Cr(III) in solution containing ZnO or ZSM-5 zeolite using oxalate as model organic compound in environment. *Microporous and Mesoporous Materials* **2009**, 117, pp 243-248
- (3) Yoon, J., Shim E., Bae, S., Joo, H. Application of immobilized nanotubular TiO₂ electrode for photocatalytic hydrogen evolution: Reduction of hexavalent chromium (Cr(VI)) in water. *Hazardous Materials* **2009**, 161, pp 1069-1074
- (4) Khalil, L. B., Mourad, W. E., Rophael, M. W. Photocatalytic reduction of environmental pollutant Cr (VI) over some semiconductors under UV/visible light illumination. *Applied Catalysis* **1998**, 17, pp 267-273
- (5) Mohapatra, P., Samantaray, S. K., Parida, K. Photocatalytic reduction of hexavalent chromium in aqueous solution over sulphate modified titania. *Photochemistry and Photobiology* **2005**, 170, pp 189-194
- (6) Wang, L., Wang, N., Zhu, L., Yu, H., Tang, H. Photocatalytic reduction of Cr(VI) over different TiO₂ photocatalysts and the effects of dissolved organic species. *Hazardous Materials* **2008**, 152, pp 93-99
- (7) Anandan, S., Vinu, A.; Mori, T., Gokulakrishnan, N., Srinivasu, P., Murugesan, V., Ariga, K. Photocatalytic degradation of 2, 4,6-trichlorophenol using lanthanum doped ZnO in aqueous suspension. *Catalysis Communications* **2007**, 8, pp 1377-1382
- (8) Assadi, A., Dehghani, M. H., Rastkari, N., Nasseri, S., Mahvi, A. H. Photocatalytic Reduction Of Hexavalent Chromium In Aqueous Solutions With Zinc Oxide Nanoparticles And Hydrogen Peroxide. *Environment Protection Engineering* **2012**, 38, pp 6-16
- (9) Shirzad-Siboni, M., Farrokhi, M., Darvishi, R., Soltani, Ch., Khataee, A., Tajassosi, S. Photocatalytic Reduction of Hexavalent Chromium over ZnO Nanorods Immobilized on Kaolin. *Engineering Chemical Research* **2014**, 53, pp 1079-1087
- (10) Colis, S., Bieber, H., Begin-Colin, S., Schmerber, G., Leuvrey, C., Dinia, A.

- Magnetic properties of Co-doped ZnO diluted magnetic semiconductors prepared by low-temperature mechanosynthesis, *Chemical Physical Letter* **2006**, 422, pp 529–533
- (11) Gandhi, V., Ganesan, R., Syedahamed, H. H. A., Thaiyan, M. Effect of Cobalt Doping on Structural, Optical, and Magnetic Properties of ZnO Nanoparticles Synthesized by Coprecipitation Method. *Journal of Physical Chemistry C* **2014**, 118, pp 9715–9725
- (12) Liu, X., Shi, E., Chen, Z., Zhang, H., Song, L., Wang, H., Yao, S. Structural, optical and magnetic properties of Co-doped ZnO films. *Journal of Crystal Growth* **2006**, 296, pp 135–140
- (13) Kanade, K. G., kale, B. B., baeg, J. O., Lee, S. M.; Lee, C. W., Moon, S. J., Chang, H. Self-assembled aligned Cu doped ZnO nanoparticles for photocatalytic hydrogen production under visible light irradiation Material. *Chemistry and Physics* **2007**, 102, pp 98-104
- (14) Venkataprasad Bhat, S.; Deepak, F.L. Tuning the bandgap of ZnO by substitution with Mn^{2+} , Co^{2+} and Ni^{2+} . *Solid State Communications* **2005**, 135, pp 345-347
- (15) Pemmaraju, C. D., Archer, T.; Hanafin, R., Sanvito, S. Investigation of n-type donor defects in Co-doped ZnO. *Journal of Magnetism and Magnetic Materials* **2007**, 316, pp 185-187
- (16) Gao, H., Liu, Y., Zeng, G., Xu, W., Li, T., Xia, W. Characterization of Cr(VI) removal from aqueous solutions by a surplus agricultural waste. *Rice straw Journal of Hazardous Materials* **2008**, 150, pp 446-452
- (17) Bai, R. S., Abraham, T. E. Studies on chromium(VI) adsorption–desorption using immobilized fungal biomass. *Bioresource Technology* **2003**, 87, pp 17-26
- (18) Baral, A., Engelken, R. D. Chromium-based regulations and greening in metal finishing industries in the USA. *Environmental Science Policy* **2002**, 5, pp 121-133
- (19) Shifu, C., gengyu, C. Study on the photocatalytic reduction of dichromate and photocatalytic oxidation of dichlorvos. *Chemosphere* 2005, 60, pp 1308-1315.

