การรีดิวซ์โครเมียม (VI) ในน้ำผ่านปฏิกิริยาเร่งด้วยแสงโดยใช้ซิลเวอร์โด๊ปซิงค์ออกไซด์ภายใต้แสงยูวี

Photocatalytic reduction of Cr(VI) in aqueous solution by silver doped zinc oxide under ultraviolet light irradiation

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Received: January, 2014; Accepted: May, 2014

บทคัดย่อ

งานวิจัยนี้ได้ศึกษาการรีดิวซ์โครเมียมวาเลนท์ซีหกในสารละลายน้ำด้วยซิลเวอร์โด๊ปซิงค์ออกไซด์ภายใต้สภาวะแสงยูวี โดยซิลเวอร์โด๊ปซิงค์ออกไซด์สังเคราะห์ด้วยวิธีโฟโตดิโพซิชันโดยปรับเปลี่ยนอัตราส่วนโดยโมลของซิลเวอร์ที่โด๊ป บนซิงออกไซด์ ได้ศึกษาปัจจัยที่มีผลต่อประสิทธิภาพการรีดิวซ์โครเมียมวาเลนท์ซีหก ได้แก่ ค่าความเป็นกรด ด่าง อัตราส่วนโดยโมลของซิลเวอร์ที่โด๊ปบนซิงค์ออกไซด์ ความเข้มข้นเริ่มต้นของสารละลายโครเมียมวาเลนท์ซีหก ($K_2Cr_2O_7$) รวมถึงชนิดและปริมาณของสารเอื้อให้เกิดปฏิกิริยา ณ สภาวะแวดล้อม ผลการทดลองพบว่า ที่สภาวะความเป็นกรด pH 3 ความเข้มข้นเริ่มต้นของสารละลาย $K_2Cr_2O_7$ 300 ppm การโด๊ปซิลเวอร์บนซิงค์ออกไซด์ ที่อัตราส่วนโดยโมล 1.5 : 1 และการเติมไฮโดรเจนเปอร์ออกไซด์ 1%V ให้ประสิทธิภาพการรีดิวซ์สูงสุดถึง 96% เทียบกับซิงค์ออกไซด์ที่ไม่ได้โด๊ปซิลเวอร์ซึ่งให้ประสิทธิภาพการรีดิวซ์ 69% การศึกษาจลนพลศาสตร์ พบว่าการรีดิวซ์โครเมียมวาเลนท์ซีหกด้วยซิงค์ออกไซด์และซิลเวอร์โด๊ปซิงค์ออกไซด์ เป็นไปตามความสัมพันธ์ของปฏิกิริยาอันดับหนึ่ง อย่างไรก็ตาม การโด๊ปซิลเวอร์และการเติมไฮโดรเจนเปอร์ออกไซด์จะเพิ่มอัตราการรีดิวซ์เริ่มต้นแต่มีผลเล็กน้อยต่ออัตราการรีดิวซ์รวม

คำสำคัญ : ปฏิกิริยารีดักชันชนิดเร่งด้วยแสง; โครเมียมวาเลนท์ซีหก; ซิลเวอร์โด๊ปซิงค์ออกไซด์; จลนพลศาสตร์

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Abstract

Photocatalytic removal of Cr(VI) from aqueous solution using synthesized Ag doped ZnO(Ag/ZnO) under ultraviolet (UV) light irradiation was studied in this works. Firstly, Ag/ZnO at various mole ratio of Ag was synthesized by the photodeposition method. Then removal efficiency of Cr(VI) by the photocatalysts was investigated with variation of the solution pH, Ag/ZnO dosage, initial Cr(VI) concentration ($K_2Cr_2O_7$) and types and loading of sacrificial reagents at ambient temperature. Maximum removal of Cr(VI) was observed at pH 3, 300 ppm initial concentration of $K_2Cr_2O_7$, 1.5:1 mole ratio Ag dope ZnO and addition of H_2O_2 1%V as sacrificial reagent can reach up to 96% in comparison to the undoped ZnO (69%). Based on the kinetic study, it was found that photocatalytic reduction of both ZnO and Ag/ZnO is followed the first-order kinetic reaction. However, doping of Ag as well as H_2O_2addition can enhance initial rate but less effect in overall rate regarded to none-added system.

Keywords : Photocatalytic reduction; Chromium (VI); Silver doped Zinc oxide; Kinetics

Introduction

The presence of toxic heavy metals in aquatic bodies has been known to be one of the causes of pollution problems. Most of metals are mainly problematic because of less biodegradationbutaccumulation in living tissues of aquatic animals and plants. So, it is then being biodegradation but accumulation concentrated throughout the food chain. Some heavy metals are essential micronutrients for plants and animals at low doses, but in higher doses they candetrimentally affect the health of most living organisms (Shrivastava et al, 2003.,Yemane et al, 2008., Pécou et al, 2006). Removal of heavy metals from wastewaters is generally performed by accompanying various chemical and physical processes such as hydroxide precipitation, ion exchange, adsorption and membrane processes (Young et al, 2001). The chemical precipitation seems to be the most popular process forheavy metalremoval from wastewaters. However, the process based on non-destructive techniques can only remove and transfer the toxic substance. Thus, a new type of chemical pollutants may be raised and further removal process has to be required (Arslan et al, 2000.,Chaudhri et al, 2000).

Chromium (Cr) compounds are widely used in many industries. Large amounts of chromium are released into environment from dyeing and printing in textile industries, chemical manufacture, leather tannery, metal plating, and processing industrial wastewater (Lozano et al, 1992.,Suksaby et al, 2007). Chromium generally presents in water with two stable oxidation states including hexavalent Cr(VI) and trivalent Cr(III) species. Cr(VI) species are known as toxic and carcinogenic agents leading tovarious health problems whereas Cr(III) is 500 times less toxic than the hexavalent ones and can be readily precipitated out of solution in the form of $Cr(OH)_3$ (Eary et al, 1988.; Yurik et al, 1999.; Barrera-Díaza et al, 2012). Several methods have been actively applied to remove heavy metal ions including chemical precipitation, ion exchange, adsorption, membrane filtration, electrochemical treatment technologies and liquid extraction (Nameni et al, 2008.,Fu et al, 2011., Gherbi et al, 2011). These methods are non-economical but however, ineffective at low concentrations. Thus, development of more effective and durable systems becomes necessary (Gherbi et al, 2011). It is known that the most common process for Cr(VI) removal is through reduction to Cr(III), followed by Cr(III) precipitation under the basic conditions (Fang et al, 2007). However, the chromium hydroxide sludge is considered to be a hazardous waste and the quantities may be substantial and are generally difficult to be clear up (Young et al, 2001).

An environmental friendly treatment process, photocatalysis has become to be quite interesting in the elimination of the toxic metal and organic compounds. The photocatalytic techniques have been mentioned to be one of the most interesting process for wastewater treatment because of its advantages over other traditional techniques such as convenient set-up, quick and low concentration oxidation and none of high toxic products are observed after photocatalytic process has reached (Arsana et al, 2012). The reduction of Cr(VI) to Cr(III) by photocatalytic approach has been reported. Photocatalytic reduction of Cr(VI) to Cr(III) of many semiconductor catalysts such as ZnO (Shao et al, 2009., Chakrabarti et al, 2009), ZnS (Karunakaranet al, 2009), TiO_2 (Yingzhao, et al, 2011., Wang et al, 2010., Yang et al, 2006), WO3 (Yang et al, 2010) and CdS (Wang et al, 1992) had studied.

ZnO had considered as a promising photocatalyst due to its high photocatalytic activity, photo-stability, wide-band gap, less toxic and inexpensive. ZnO can be excited at room temperature under low excitation energy and the surface of ZnO support strong chemisorptions of oxygen and are sensitive to ultraviolet (UV) radiation (Assadi et al, 2012). However, the problem of this approach is the electron-hole pair recombination of the photocatalyst leading to ineffective catalytic activity. Doping of metal ions, metal oxides or sensitized polymers as co-catalyst can improvethe activity of photocatalyst by prevention of electron-hole pair recombination. Addition of sacrificial reagent or metal ions in the test solution can also enhance the efficiency of photocatalytic activity. The photoreduction of Cr(VI) to Cr(III) can be achieved via a photocatalytic process with a simplified mechanism as follows:

$$\mathrm{ZnO} + hv \longrightarrow \mathrm{ZnO}\ (h^{+}_{VB} + e^{-}_{CB}) \qquad (1)$$

$$\mathrm{Cr_2O_7^{2-}} + 14\mathrm{H^+} + 6e^{-}_{CB} \longrightarrow 2\mathrm{Cr^{3+}} + 7\mathrm{H_2O} \qquad (2)$$

$$2\mathrm{H_2O} + 4h^{+}_{VB} \longrightarrow \mathrm{O_2} + 4\mathrm{H^+} \qquad (3)$$

$$\mathrm{H_2O} + h^{+}_{VB} \longrightarrow \mathrm{OH^{\bullet}} + \mathrm{H^+} \qquad (4)$$

$$e^{-}_{CB} + \mathrm{O_2} \longrightarrow \mathrm{O_2^{\bullet -}} \qquad (5)$$

$$\mathrm{H_2O} + \mathrm{O_2^{\bullet -}} \longrightarrow \mathrm{HOO^{\bullet}} + \mathrm{OH^-} \qquad (6)$$

$$2\mathrm{HOO^{\bullet}} + \mathrm{H_2O} + e^{-}_{CB} \longrightarrow \mathrm{H_2O_2} + \mathrm{OH^-} \qquad (7)$$

$$\mathrm{H_2O_2} + \mathrm{O_2^{\bullet -}} \longrightarrow \mathrm{OH^{\bullet}} + \mathrm{OH^-} + \mathrm{O_2} \qquad (8)$$

$$\mathrm{H_2O_2} + e^{-}_{CB} \longrightarrow \mathrm{OH^{\bullet}} + \mathrm{OH^-} \qquad (9)$$

$$\mathrm{Cr(VI)} + \mathrm{H_2O_2} + \mathrm{H^+} \longrightarrow \mathrm{Cr(III)} + \mathrm{H_2O} + \mathrm{O_2} \qquad (10)$$

The electron in Valence Band (VB) is excited to Conduction Band (CB) by UV light absorption with equal or higher energy than energy band gap of ZnO leading to simultaneous generation of a hole (h^+) in VB forming of electron-hole pair separation (eq.1). Cr(VI) in aqueous acidic solution is adsorbed on ZnO surface and gain excited electron in CB of ZnO via photoreduction reaction (eq.2). Water molecules can act as electron donor to fulfill the positive hole via oxidation reduction (eq.3 and 4). H_2O_2 can be produced from eq.5-7 and also act as electron donor for the positive hole (eq.8 and 9). In addition, the forming H_2O_2 can also involve in reduction reaction of Cr(VI) as shown in eq.10. The fast recombination of electron-hole pair can reduce the photocatalytic activity of ZnO, so lengthening of excited electron in CB of ZnO will enhance the activity. Thus, in this work, photocatalytic reduction of Chromium (VI) in aqueous solution by silver doped zinc oxide as photocatalyst was investigated. The $K_2Cr_2O_7$ was used as a Chromium (VI) sample. Effect of mole ratio of the silver doping, pH, initial concentration of $K_2Cr_2O_7$ as well as sacrificial reagent on the photoreduction rate was also investigated.

Experimental

Photosynthesis of Ag-ZnO

The photocatalysts; Ag-ZnO was synthesized by photodeposition method. 2 g of ZnO was dissolved in 50 mL deionized water. The solution was adjusted to pH 3 by HCl solution. The amount of $AgNO_3$ (QRëCCo, Ltd) with 0.5, 1, 1.5, 2 and 2.5 mole ratio versus ZnO was required to add into slurry. The slurry was stirred well under UV irradiation for 3 hrs and then dried in the air oven at 100°C for 12 hrs. The dried solid was grounded in an agate mortar then calcined at 600°C for 6 hrs in a furnace.

Photocatalytic reduction of Cr(VI)

Photocatalytic activity of Ag doped and undoped ZnO were performed by the batch technique. The parameters affect to the photocatalytic efficiency of Ag doped and undoped ZnO were studied including initial concentration of Cr(VI), amount of photocatalyst and pH of solution. An experimental setup was shown in Figure 1.

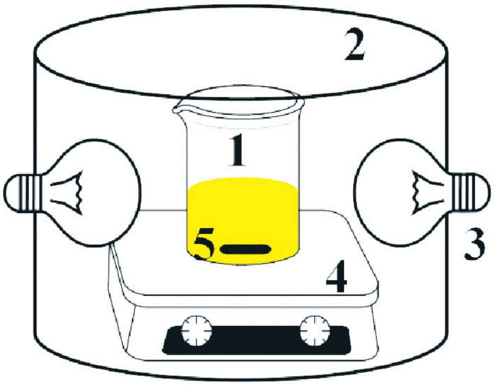

Figure 1. Schematic representation of the experimental set-up; 1) Beaker glass reactor, 2) Reaction box with tinfoil pasted on inside wall, 3) UV lamp; 4) Magnetic stirrer, and 5) Magnetic bar.

The experimental set-up for photocatalytic reduction of Cr(VI) by Ag doped and undoped ZnO in this works schematically shown in Figure 1. Each photocatalysis experiment was performed in a 500 mL beaker. During the experiment, the test solution in the beaker was constantly stirred and illuminated by four surrounding household fluorescence lamps (18 W) or visible-light lamps with a wavelength of 400-500 nm (18 W). One gram of photocatalyst was added into 50 mL of 100 ppm Cr(VI) ($K_2Cr_2O_7$, QRëCCo, Ltd) solution sample. Each experiment was run within 1 hour. All experiments were carried out at ambient temperature. The radiation density flux on all the surface area was assumed to be constant for each run. Concentration of the residual Cr(VI) in the solution at various reaction times was analyzed using a 1.5-Diphenylcarbarzide (QRëCCo, Ltd) colorimetric method (T80+ model UV-Vis spectrophotometer, PG Instrument Ltd)

The photocatalytic reduction efficiency of Ag doped and undoped ZnO is calculated based on equation (11):

$$\%\ \text{efficiency} = \frac{C_0 - C_t}{C_t} \times 100 \qquad (11)$$

Where C_0 and C_t are initial and variable concentrations of Cr(VI), respectively.

Kinetics of the photocatalytic reduction of Cr(VI) by the photocatalyst was analyzed in terms of pseudo first- and second-order kinetic models. A plot of $\ln (C_e/C_t)$ versus times used to describe the pseudo first-order kinetic model as the following equations (12):

$$\text{In}\ (C_e - C_t) = \text{In}C_e - k_1 t \qquad (12)$$

When k_1 is pseudo first-order rate constant obtained from slope of the straight line.

Results and discussion

Photocatalytic reduction of Cr(VI) by ZnO and Ag/ZnO

The basis of photocatalytic activity of ZnO and Ag doped ZnO are illustrated in Figure 2A and 2B, respectively. The photocatalytic process of Ag doped ZnO is similar to the undoped ones but different in step 2. In this step, Ag nanoparticles doped on the ZnO surface act as a sink for electron and improve of the electron-hole pair separation generated in Eq. 1. Photogenerated electron can be easily trapped by Cr(VI) as shown in step 2. The enhancement of photocatalytic activity based on Ag doping ZnO is due to the electron transfer rate of photogenerated electron to Ag surface is higher than those of the electron-hole pair recombination rate.

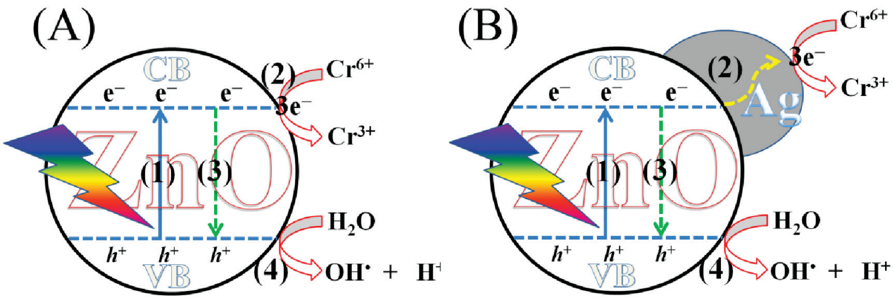

Figure 2. The basis of photocatalytic activity of ZnO and Ag doped ZnO.

Effect of pH

The percentage of Cr(VI) photoreduction by ZnO and 1:1 Ag:ZnO in Ag/ZnO particles in a function of pH for a 100 ppm solution of Cr(VI) containing 1g of the photocatalysts is shown Figure 3. As can be seen, the percentage of Cr(VI) reduction increase when pH is going from 1 to 3 then decreased dramatically up on increasing pH afterward. The similar result can be found both in undoped and metal doped systems. The reduction of Cr(VI) in acidic conditions occurs via eq.2. The maximum photoreduction activity of ZnO and Ag/ZnO has reached up to 66% and 82%, respectively at pH 3. The results in this work is in agreement to the previous work which the maximum photocatalytic reduction of Cr(VI) by ZnO was also found at pH 3 (Assadi et al, 2012). However, it is evidenced

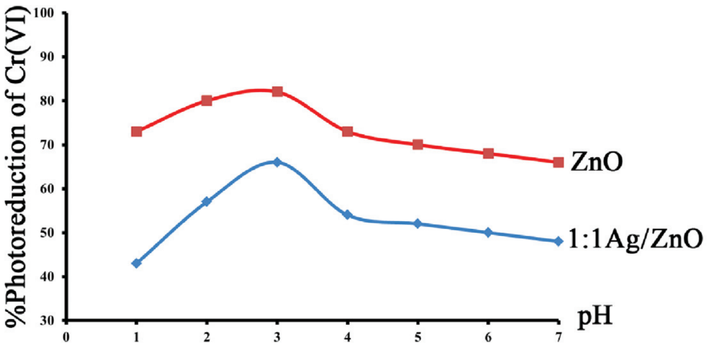

Figure 3. Percentage of Photoreduction of Cr(VI) in function of pH. Initial Cr(VI) concentration 100 ppm, solution volume 50 cm^3, ZnO and 1:1 Ag:ZnO loading 1g, irradiation time 60 min, ambient temperature.

that ZnO can reduce Cr(VI) in pH range between 5 and 9 (Young et al, 2001). Thus, a suitable pH for the maximum photocatalytic reduction of Cr(VI) using ZnO and Ag/ZnO is pH 3. It can be noted that ZnO and Ag/ZnO maybe used in photoreduction of Cr(VI) contaminated aqueous solutions in a wider range of pH because pH values of soil and groundwater are generally between 5 and 9 (Xu et al, 2004). The photoreduction of Cr(VI) in basic condition is occurred via equation (13):

$$Cr_2O_7^{2-} + 14H_2O + 3e^-_{CB} \longrightarrow Cr(OH)_3 + 5OH^- \qquad (13)$$

The photocatalytic reduction of Cr(VI) by ZnO and Ag/ZnO as a function of pH can be ascribed in terms of chromic species. The neutral chromic acid molecule, H_2CrO_4, is the dominant species for pH less than 2, while the concentrations of negatively-charged $HCrO_4^-$,$Cr_2O_4^{2-}$ and $Cr_2O_7^{2-}$ species were dominant for pH greater than 2 (Young et al, 2001). At low pH 1 and 2, the neutral H_2CrO_4 species is assumed to exhibit a lower affinity for the positively-charged ZnO surface. For solution pH greater than 3, the negatively-charged species of Cr(VI) is assumed to increase gradually and therefore stronger interacs between these species and positively-charged ZnO is a result of higher photocatalytic reduction activity. Conversely, at high pH, ZnO possess negatively charged surface, so the negatively-charged species would be repelled and lack an electrostatic affinity leading to reduction of the extent of adsorption of Cr(VI) and its photoreduction.

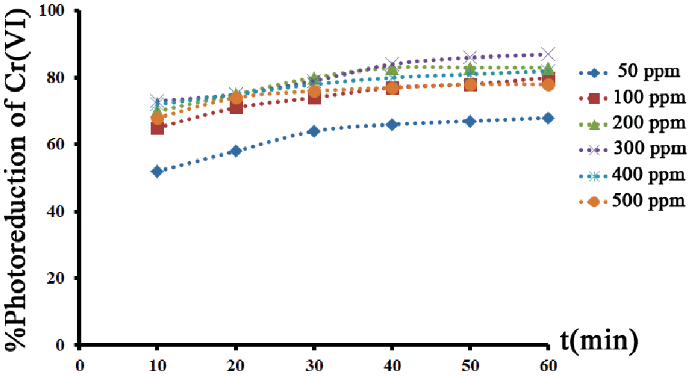

Figure 4. Percentage of Photoreduction of Cr(VI) in function of initial concentration of Cr(VI); 1:1 Ag:ZnO in Ag/ZnO loading 1g, solution volume 50 cm^3 at pH 3, irradiation time 60 min, ambient temperature.

Effect of initial concentration

Based on the maximum photoreduction was found at pH 3, the effect of initial concentration of Cr(VI) on photoreduction by Ag/ZnO was carried out at this pH condition. The effect of initial concentration of Cr(VI) on photoreduction was studied in the range of 50-500 ppm using 1:1 Ag:ZnO dose at 1g in 50 cm^3 solution. Figure 4. shows the variation of reduction percentage of Cr(VI) in function of irradiation time for various Cr(VI) concentration. It is indicated that upon increasing Cr(VI) concentration in the investigated range, the photoreduction of Cr(VI) was increased to the maximum at 300 ppm and decreased afterward. The percentage of photoreduction of Cr(VI) increased from 68 % to 87 % from concentration 50 ppm to 300 ppm Cr(VI). In fact, in a solution with constant amount of the catalyst, the active sites of catalyst are adsorbed completely by a limit of substrate concentration.

Effect of mole ratio of Ag doping

The effect of mole ratio of Ag doping on ZnO was investigated. Ag:ZnO was synthesized by photodeposition method. Mole ratio of Ag was varied from 0.5 to 2.5 with constant ZnO (regarded to 1 mol). The condition was performed at 300 ppm Cr(VI), Ag:ZnO dose 1g, solution volume 50 cm^3 at pH 3, irradiation time 60 min, ambient temperature. Figure 5. shows the variation of reduction percentage of Cr(VI) in function of irradiation time for various mole ratio of Ag doping. As a result, photoreduction of Cr(VI) is increased from 0.5 up to 1.5 mole ratio of Ag doping. Maximum percentage of photoreduction up to 89% was found at 1.5:1 Ag:ZnO . The higher mole ratio

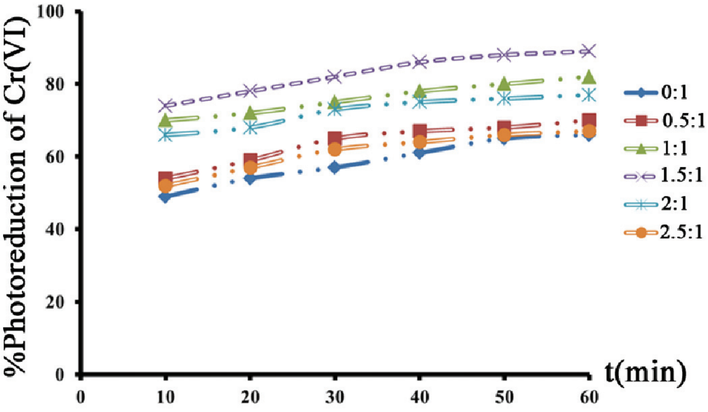

Figure 5. Percentage of Photoreduction of Cr(VI) in function of Ag mole ratio doping on ZnO; Ag/ZnO loading 1g, solution volume 50 cm^3 at pH 3, irradiation time 60 min, ambient temperature.

of Ag doping reduces the activity of ZnO. This is due to the excess coverage of Ag which limits the reach of incident light on catalyst surface and reduce the photogeneratedelectron-hole pair (Arsana et al, 2012; Carpet al, 2004) then leading to lowering of photoreduction of Cr(VI).

Effect of sacrificial reagent

Additions of some oxidant species, namely sacrificial reagent can accelerate the overall photoreduction by either fulfill the positively charged hole of VB or reduction of photogenerated electron to form reactive intermediate species. In this section, the effect of sacrificial reagentto the photoreduction of Cr(VI) by ZnO and Ag/ZnO was investigated. Three reagents including H_2O_2, CH_3OH and C_2H_5OH were used for the test compare to non-added system. The test was performed at 300 ppm Cr(VI), ZnO loading 1g, solution volume 50 cm^3 at pH 3, irradiation time 60 min, ambient temperature. 1 %V of sacrificial reagents added (Figure 6A.), Similarly, the observation of this effect was also performed for the most effective Ag:ZnO (1:1). The plot is represented in Figure 7A.

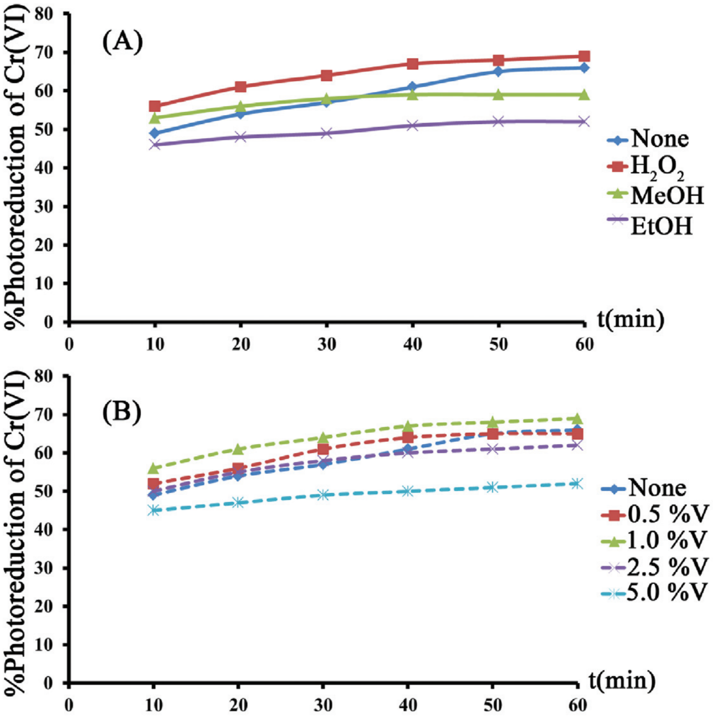

Figure 6. Percentage of Photoreduction of Cr(VI) in function of sacrificial reagents; ZnO loading 1g, solution volume 50 cm^3 at pH 3, irradiation time 60 min, ambient temperature. (A) 1%V of sacrificial reagents added, (B) variation of H_2O_2 added.

For undoped system, As a result, H_2O_2 system possesses the highest photoreduction of Cr(VI) reached to 69 % followed by 66 % methanol, non-added 60 % and ethanol 52 %, respectively. In the case of 1:1 Ag:ZnO, H_2O_2 system also accelerates photoreduction of Cr(VI) as high as 95% follow by methanol 90 % and ethanol 81 %, respectively. Ethanol system also shows the lowest efficiency of Cr(VI) photoreduction even for non-added system (89 %). Similar result was also found (Young et al, 2001). Addition of H_2O_2 in Ag/ZnO system can enhance the photoreduction efficiency based on the reaction in eq. 10 for $Cr_2O_7^{2-}$ species. Enhancement of H_2O_2 system is also due to the reduction efficiency of Cr(VI) as $HCrO_{4-}$ species as in equation (14):

$$2HCrO^{-} + 3H_2O_2 + 8H^{+} \longrightarrow 2Cr_3^{+} + 3O_2 + 8H_2O \qquad (14)$$

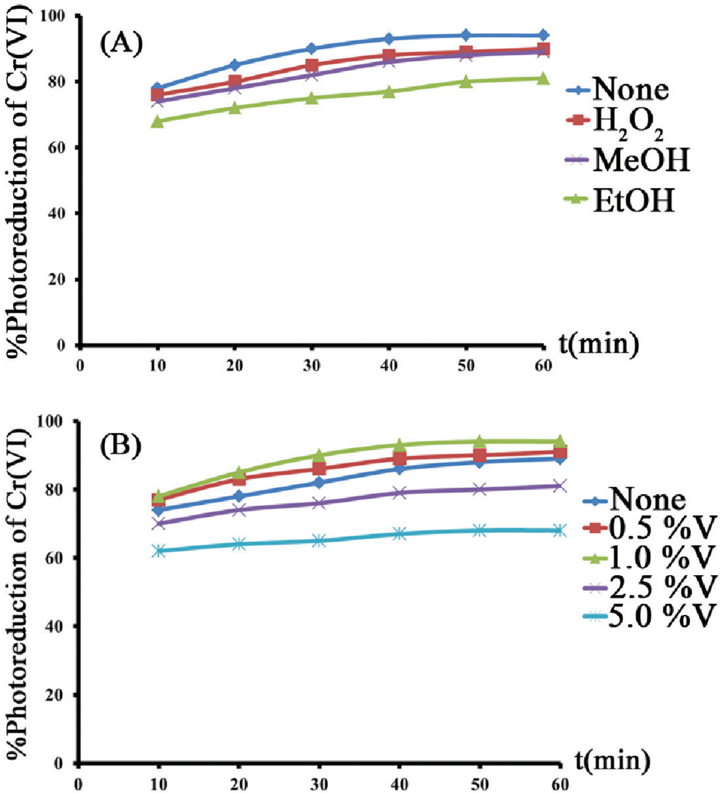

Figure 7. Percentage of Photoreduction of Cr(VI) in function of sacrificial reagents; 1:1 Ag:ZnO loading 1g, solution volume 50 cm^3 at pH 3, irradiation time 60 min, ambient temperature. (A) 1%V of sacrificial reagents added, (B) variation of H_2O_2 added.

For alcohol additive systems, both CH_3OH and C_2H_5OH act as electron donor for fulfillment of photogenerated positively-charged hole(h^+) where CH_3OH is more reactive than C_2H_5OH. This can be noted that H_2O_2 is suitable for being use as sacrificial reagent for photoreduction of Cr(VI) system based on their reactive, inexpensive and toxic by-product.

Time-concentration profiles for the reduction with various H_2O_2 dosages are shown in Figure 6B. and 7B., for undoped and 1:1 Ag:ZnO, respectively. Based on the result, both systems show the similar trend but different in quantity of photoreduction and H_2O_2 loading. At higher concentration up to 2.5 and 5 %V reduces the reduction efficiency of both systems which maximum efficiency was found at 1%V of H_2O_2. It is possibly that high loading of H_2O_2 can raise pH of the solution to be more basic due to decomposition of H_2O_2. When exposed to sunlight or metallic impurities, hydrogen peroxide rapidly decomposes to oxygen gas as in equation (15):

$$H_2O_2 \longrightarrow H_2O + O_2 \qquad (15)$$

The rapidly produced O_2 can involve in the catalytic reaction by reacting with e^-_{CB} forming superoxide radical ($O_2^{\bullet -}$) via eq. 5. Subsequently, formation of peroxyl radical ($^{\bullet}OOH$) and OH^- in eq.6 and H_2O_2 and OH^- in eq.7. H_2O_2 is consequently reactive to form OH^- via eq.8 and 9. It is to be noted that life cycle of H_2O_2 is involved either positive or negative way to the photocatalytic reaction of Cr(VI) by semiconductor. Excessive H_2O_2 may lead to negative effect to the efficiency of photocatalytic system.

Kinetic study of photocatalytic reduction of Cr(VI) by ZnO and Ag/ZnO

Kinetics of the photocatalytic reduction of Cr(VI) by ZnO and Ag/ZnO was observed. Concentration of Cr(VI) in the test solution at available time were determined from the standard concentration curve. Figure 8 and 9 represent a plot of ln (C_0/C_t) versus time based on eq.2 to follow the first-order kinetic reaction for the variation of sacrificial reagents (A) and loading of H_2O_2 dose (B), respectively for undoped and 1:1 Ag:ZnO systems. The relationship between ln (C_0/C_t) and reaction time for all systems was linear with R^2 more than 0.9000. Thus it can be concluded that the photocatalytic reduction of Cr(VI) by both undoped and Ag doped ZnO is occurred following the first-order kinetic reaction either with or without sacrificial reagents. It has also been reported that Cr(VI) photoreduction using TiO_2 follows first order kinetics (Khalil et al, 1998., Ku et al, 1999., Das et al, 2006). The data calculated for first-order rate constant, *k* at various sacrificial reagents and loading of H_2O_2 dose are shown in Table 1.

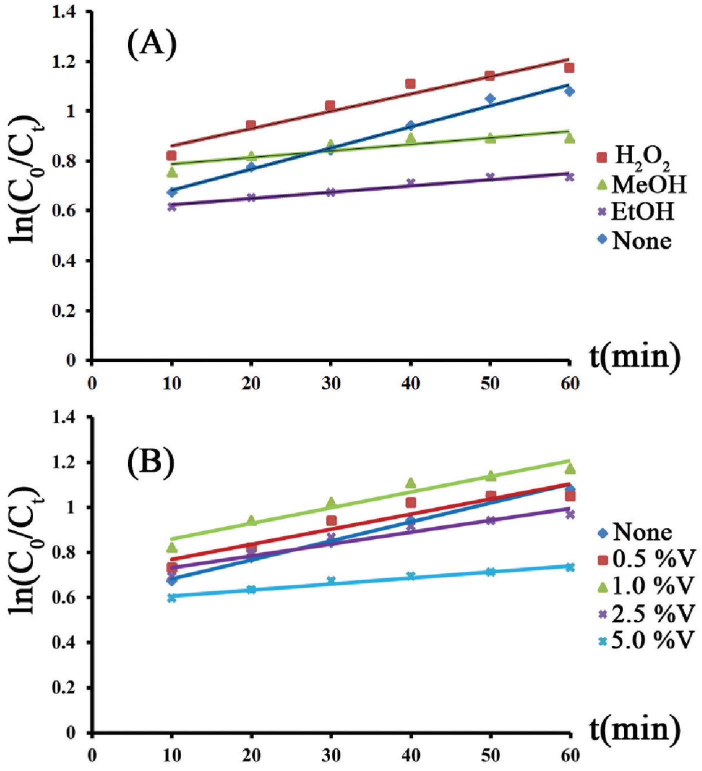

Figure 8. Dependence of $\ln(C_0/C_t)$ on time for photoreduction of Cr(VI); ZnO loading 1g, solution volume 50 cm^3 at pH 3, irradiation time 60 min, ambient temperature. (A) 1%V of sacrificial reagents added, (B) variation of H_2O_2 added.

The first-order rate constants for the various sacrificial reagents are in increasing in this order: None (19.76/23.28 min^{-1}) < EtOH (26.46/28.87 min^{-1}) < MeOH (32.56/33.45 min^{-1}) < H_2O_2 (39.34/41.13 min^{-1}) for undoped system and 1:1 Ag:ZnO systems, respectively. The highest rate constant of both undoped and 1:1 Ag:ZnO system is found at 1% V loading up to 39.34 and 41.13 min^{-1}, respectively. The overall rate decreases dramatically to 26.58/27.42 and 21.93/15.56 min^{-1}. It is to be noted that overall rates of the entire reaction time for ZnO and 1:1 Ag:ZnO are not much different. So, addition of effective sacrificial reagent and doping Ag with suitable loading on ZnO affect the initial rate of photocatalytic reduction of Cr(VI) but notdiffer much in overall reaction rate.

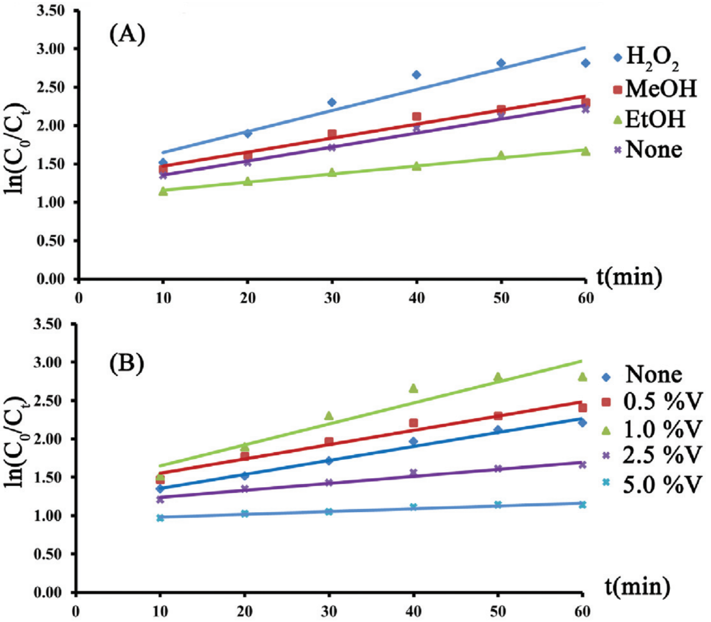

Figure 9. Dependence of $\ln(C_0/C_t)$ on time for photoreduction of Cr(VI); 1:1 Ag:ZnO loading 1g, solution volume 50 cm^3 at pH 3, irradiation time 60 min, ambient temperature. (A) 1%V of sacrificial reagents added, (B) variation of H_2O_2 added.

Table 1 Rate constant value for photoreduction of Cr(VI) over ZnO and 1:1 AgZnO

Condition	1:1 Ag/ZnO		ZnO	
Sacrificial effect	R^2	k (min^{-1})	R^2	k (min^{-1})
None	0.9887	23.28	0.9429	19.76
C_2H_5OH 1%V	0.9537	28.87	0.9464	26.46
CH_3OH 1%V	0.9838	33.45	0.9788	32.56
H_2O_2 1 %V	0.9214	41.13	0.9856	39.34
H_2O_2 loading effect				
None	0.9887	23.28	0.9429	19.76
0.5 %V	0.9214	39.33	0.9856	37.57
1.0 %V	0.9611	41.13	0.9231	39.34
2.5 %V	0.9667	27.42	0.9002	26.58
5.0 %V	0.9479	15.56	0.9743	21.93

Conclusion

Photocatalytic removal of Cr(VI) from aqueous solution using synthesized Ag doped ZnO compare with undoped ones under ultraviolet (UV) light irradiation was studied. Effect of initial concentration of Cr(VI), solution pH, mole ratio of Ag doping, types and quantitative loading of sacrificial reagent were taken into account. Maximum removal of Cr(VI) was observed at pH 3, 300 ppm initial concentration of Cr(VI) with H_2O_2 1%V at ambient condition. The removal efficiency of Cr(VI) was continuously enhanced with increasing of Ag:ZnO ratio, but gradually decreased above 1.5:1 Ag:ZnO mole ratio because of the increased blockage of the incident UV light source. The kinetics of both undoped and Ag doped ZnO either with or without sacrificial reagent followed the first-order reaction. Doping of Ag and H_2O_2 addition can enhance the photocatalytic activity to remove Cr(VI) via photocatalytic reduction up to 95 % which is higher than the undoped one (69 %). Addition of sacrificial reagents enhances the initial rate but a bit effect to the overall rate constant for the entire reaction time.

Acknowledgement

This work was financially supported by The Faculty of Engineering, Khonkaen campus to SK and SW through the undergraduate project development fund. Institute of Research and Development, RMUTI was also acknowledged for the partial support.

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