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PHOTOCATALYTIC REDUCTION OF HEXAVALENT CHROMIUM IN AQUEOUS SOLUTIONS WITH ZINC OXIDE NANOPARTICLES AND HYDROGEN PEROXIDE

Photocatalytic reduction of Cr(VI) to Cr(III) in aqueous solutions under UV irradiation and ZnO semiconductor catalyst was investigated using potassium dichromate as a model compound. The effects of pH, catalyst dose (0.05–0.15 g/dm^3), Cr(VI) initial concentration (0.1–15 mg/dm^3) and hydrogen peroxide concentration on photocatalytic reduction of Cr(VI) were investigated. The reduction rate of chromium was more favorable in acidic solution. Hydrogen peroxide was added as a reduction reagent for enhancement of the photoreduction. The process of photoreduction of Cr(VI) approximately followed first-order kinetics. Drinking water samples and wastewater were collected and photocatalytically treated for reduction of Cr(VI).

1. INTRODUCTION

Chromium (Cr) compounds are used in industries for chromium plating, wood preservation, textile dyeing and pigmentation, pulp and paper manufacturing, and tanning. The wastewater resulting from these industrial processes contains high contents of Cr, which contaminates the natural environment affecting human health [1]. Chromium occurs in several oxidation states, trivalent (Cr^{3+} and $CrOH^{2+}$) and hexavalent ($HCrO_4^-$ and $Cr_2O_7^{2-}$). Cr(VI) is toxic for humans, animals, plants and microorganisms

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and is associated with the development of various chronic health disorders including organ damage, dermatitis and respiratory impairment [2]. Cr(III) is known to be less toxic than Cr(VI) or nontoxic and an essential nutrient for human and animals, but long-term exposure to a high concentration of Cr(III) may cause poisoning symptoms such as allergic skin reactions [3–5]. Therefore, discharge of Cr(VI) to surface water is regulated to <0.05 mg/dm^3, according to the US EPA, whereas total chromium (containing Cr(III), Cr(VI), and other forms of chromium) is regulated to be discharged at <2 mg/dm^3 [5, 6]. Many methods that have been actively investigated to remove heavy metal ions are chemical precipitation, ion exchange, adsorption, membrane filtration, electrochemical treatment technologies and liquid extraction [7–9]. These methods are non-economical and often ineffective at low concentrations. Thus, it is clear that the prospect of developing more efficient and durable systems become necessary [9].

As a friendly environmental treatment process, photocatalysis has proved to be quite interesting in the elimination of chromate, which can comply with the World Health Organization guidelines: to decrease the maximum concentration at less than 5 mg/dm^3 [8, 9]. Cr(VI) is reduced by photolysis or photoelectrochemically to less hazardous oxidation states namely trivalent state. Cr(III) is readily precipitated in neutral or alkaline solutions as $Cr(OH)_3$ or adsorbed by various substrates [10]. Many semiconductor catalysts, such as ZnO [3, 11, 12], ZnS [13], TiO_2 [14–16], WO_3 [17], and CdS [18] have been studied to investigate the photocatalytic reduction of Cr(VI) to Cr(III). Among the photocatalysts, WO_3 is less available; cadmium itself is a toxic heavy metal and CdS is prone to easy deactivation and photocorrosion [12]. ZnO can be excited at room temperature under low excitation energy. The surfaces of ZnO support strong chemisorptions of oxygen and are sensitive to ultraviolet (UV) radiation. The most important specification of ZnO is non-toxicity, which provides attractive applications to photocatalytic reaction [11].

The photoreduction of Cr(VI) to Cr(III) can be achieved via a photocatalytic process with a simplified mechanism as follows:

$$\mathrm{ZnO} + h\nu \rightarrow \mathrm{ZnO}\,(\mathrm{h}^+ + \mathrm{e}^-) \tag{1}$$

$$\mathrm{Cr_2O_7^{2-}} + 14\mathrm{H}^+ + 6\mathrm{e}^- \rightarrow 2\mathrm{Cr}^{3+} + 7\mathrm{H_2O} \tag{2}$$

$$2\mathrm{H_2O} + 4\mathrm{h}^+ \rightarrow \mathrm{O_2} + 4\mathrm{H}^+ \tag{3}$$

$$\mathrm{H_2O} + \mathrm{h}^+ \rightarrow {}^{\bullet}\mathrm{OH} + \mathrm{H}^+ \tag{4}$$

$$\mathrm{Cr(VI)} + \mathrm{H_2O_2} + \mathrm{H}^+ \rightarrow \mathrm{Cr(III)} + \mathrm{H_2O} + \mathrm{O_2} \tag{5}$$

UV light illumination on ZnO produces hole–electron pairs (reaction (1)) at the surface of the photocatalyst. After the hole–electron pairs being separated, the electrons can reduce Cr(VI) to Cr(III) (reaction (2)), and the holes may lead to generation of O_2 in the absence of any organics (reaction (3)). In the photocatalytic reaction process, reduction reagents are important to eliminate the oxidative pollutants (such as

Cr(VI)). The reduction reaction of Cr(VI) with hydrogen peroxide leads to Cr(III) (reaction (5)); therefore, H_2O_2 is responsible for supplying of electron to the hexavalent chromium in solution [12, 19].

Photoreduction of hexavalent chromium in aqueous medium using ZnO as semiconductor catalyst in the presence of a 125 W medium pressure Hg lamp as a source of UV radiation has been carried out in the present study. Hydrogen peroxide has been used as the reduction reagent. H_2O_2 is both not toxic and effective and it converts to O_2 and H_2O in the reaction with Cr(VI).

The purposes of this study were: (1) Investigating the effect of ZnO dose on the photocatalytic reduction of Cr(VI) to Cr(III); (2) Studying the effect of hydrogen peroxide (as reduction reagent) on the photocatalytic reduction of Cr(VI) and (3) Studying the effect of initial concentrations of substrate and pH on Cr(VI) photocatalytic reduction.

2. EXPERIMENTAL

Apparatus. A Perkin-Elmer Lambda 25 UV/VIS Spectrometer (Perkin-Elmer, Norwalk, CT) with 1 cm cell was used. The concentration of potassium dichromate in solution was determined by the diphenylcarbazide photometric method at 540 nm [20].

Materials. Potassium dichromate and hydrogen peroxide (GR grade) were obtained from Anateb Chemie, Iran, zinc oxide (GR) from Nanoespadena, Iran. H_2O_2 2% solution was prepared by dilution of 30% hydrogen peroxide in distilled water immediately before use. The characteristics of ZnO nanoparticles are given in Table 1. Freshly prepared double distilled water was used to prepare solutions. The pH value of the suspension was adjusted by adding 0.1 and 0.01 M HCl and NaOH.

Table 1

The characteristics of ZnO nanoparticles

Chemical formula	ZnO
Purity	99.8%
Particle size	6–12 nm
BET	40–150 m^2/g
Shape	aggregates with rod-like shapes
Color	yellowish-white
Particle shape	spherical
Surface density	105 kg/m^2
Crystals structure	hexagonal
Other elements	Ca, Al, Fe
Template phase	ZnO

2.3. EXPERIMENTAL SET-UP AND PROCEDURE

Photoreduction experiments were carried out in a cylindrical glass reactor, 0.12 m in diameter and 0.3 m high, fitted in a cooling bath. A 125 W medium pressure Hg vapor lamp (Table 2) was inserted in a quartz sleeve at the center of the reactor as the source of UV radiation. Initial concentration of substrate solution and pH were varied from 0.10 to 15 mg/dm^3 and 5–9, respectively.

Table 2

The characteristics of UV lamp

Parameter	Value
Irradiation intensity	1020 μW/cm^2
Lifetime	10 000 h
Current	3.25 A
Voltage	130+15 V
Arc length	31 mm
Diameter	10 mm
Length	65
Lamp type	125 W (MPUV)

The reactor temperature was maintained constant at 20 ± 1 °C by circulating chilled water. The total suspension volume was 1000 cm^3. Prior to irradiation, the suspension was magnetically stirred for 20 min in dark to ensure adsorption–desorption equilibrium. Liquid samples were withdrawn at various time intervals, centrifuged at 5000 rpm for 30 min to remove ZnO nanoparticles and analyzed to monitor the progress of the reaction. The removal percent of Cr(VI) was calculated from the difference between the initial and final concentrations (C_0 and C_{final}, respectively):

$$\text{Removal [\%]} = \frac{C_0 - C_{\text{final}}}{C_0} \times 100 \tag{6}$$

3. RESULT AND DISCUSSION

3.1. EFFECT OF pH

The percentage of Cr(VI) adsorbed onto ZnO particles in a function of pH for a 0.5 mg/dm^3 solution of Cr(V1) containing 0.5 mg/dm^3 of ZnO is shown Fig. 1, curve a. The amount of chromate adsorbed on ZnO particles was negligible and being practically zero at pH > 8. As can be seen, the percentage of Cr(VI) adsorbed decreased upon increasing pH.

The effect of pH on the adsorption rate of Cr(VI) on ZnO particles may be clarified through the distribution of Cr(VI) species in aqueous solution in function of pH based on the following reactions:

$$H_2CrO_4 \rightleftarrows H^+ + HCrO_4^- \tag{7}$$

$$HCrO_4^- \rightleftarrows H^+ + CrO_4^{2-} \tag{8}$$

$$2\,HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + 2H_2O \tag{9}$$

H_2CrO_4 is the major species for pH < 2, while $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$ form in significant concentration at pH > 2 [4, 19]. Since the ZnO surface carries more negative charges in alkaline solutions, neutral H2CrO4 species and negatively-charged $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$ species electrostatically would be repelled from these negatively charged surface groups of ZnO, and thus decreases the extent of adsorption of Cr(VI) at higher pH values [19, 21].

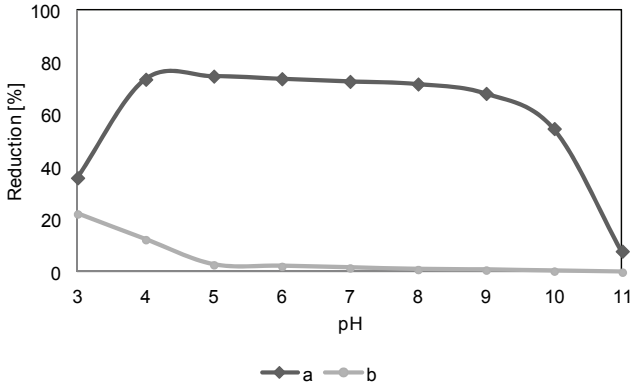

Fig. 1. Percentage of Cr(VI) adsorbed (curve b) and photoreduced (curve a) in function of pH. Initial Cr(VI) concentration – 0.5 mg/dm^3, solution volume – 1000 cm^3, ZnO loading – 0.05 g/dm^3, irradiation time – 15 min, temperature – 20 °C

pH effect on the photocatalytic reduction of Cr (VI) is different from the results of adsorption studies [19]. The pH of the hexavalent chromium solution has a strong effect on the photocatalytic processes [22]. The reduction of Cr(VI) in acidic and basic conditions probably occurs via the following reactions [19,23]:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \tag{10}$$

$$Cr_2O_7^{2-} + 14H_2O + 3e^- \rightleftarrows Cr(OH)_3 + 5OH^- \tag{11}$$

However, photocatalytic reduction of Cr(VI) to Cr(III) consumes protons in acidic solution and produces hydroxyls in alkaline solution [11]. Therefore the percentage of

reduction of Cr(VI) to Cr(III) decreases upon increasing pH. Results of the experiments are shown in Fig. 1, curve b. As can be seen, for pH higher than 8, the percentage of Cr(VI) photoreduced decreases upon increasing pH and the conversion is maximum (about 70%) at pH range of 4–5. A suitable pH range for the photocatalytic reduction of Cr(VI) using ZnO is between 4 and 8 and because pH values of soil and groundwater were generally between 5 and 9 [2], therefore ZnO may be used in photoreduction of Cr(VI) contaminated aqueous solutions in a wider range of pH. The catalyst dissolves in acidic [11, 24] and basic [24] solutions and high pH is detrimental to the reduction reagents (i.e., H_2O_2 as supply of electrons discussed later). Other researchers have also supported our results [11, 12].

Several investigations on photoreduction of Cr(VI) indicated that the apparent global rate of photocatalytic reduction appears to follow the Langmuir–Hinshelwood kinetics. It has been found that the process follows first-order kinetics [3, 19, 25]:

$$\ln \frac{C_0}{C} = k_{\text{red}} t \tag{12}$$

where k_{red} is the photocatalytic reduction rate constant, C is the Cr(VI) concentration after t, and t is the illumination time. The k_{red} of Cr(VI) reduction by UV/ZnO process for aqueous solutions of various pH are listed in Table 3, indicating that the reduction rates increased upon decreasing pH.

Table 3

First order reduction rate constants of Cr(VI) in UV/ZnO process at various pH

pH	k_{red} [min^{-1}]	r^2
5	0.02475	0.9955
7	0.02244	0.9930
9	0.01954	0.9117

3.2. EFFECT OF CATALYST DOSE AND HYDROGEN PEROXIDE CONCENTRATION (REDUCTION REAGENT)

The effect of catalyst dose on the initial rate of photoreduction was studied in the range of the catalyst concentrations of 0.05–0.15 g/dm^3. Figure 2 shows the variation of reduction percentage of Cr(VI) in function of irradiation time for various ZnO loadings which indicates that upon increase in the catalyst dose in the investigated range, both the extent and rate of degradation were increased. The percentage of photoreduction of Cr(VI) increased from 78.3% to 97%. In fact, in a solution with constant amount of substrate increasing in the catalyst does, the active sites increases and en-

hances the interception of UV radiation by the particles which in turn increases the adsorption of Cr(VI) and ultimately increases the rate of photoreduction. Similar results have been previously reported by Chakraberti et al. [12] and Prakasini et al. [26].

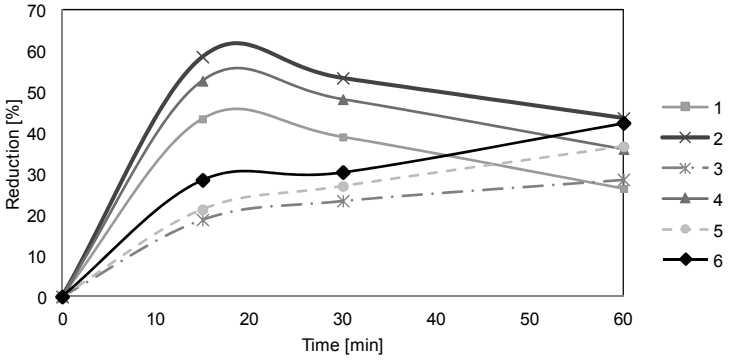

Fig. 2. Dependences of removal percentage on time for various loadings of ZnO catalyst and hydrogen peroxide: 1 – 0.5 mol/dm^3 H_2O_2, 2 – 1.0 mol/dm^3 H_2O_2, 3 – 1.5 mol/dm^3 H_2O_2, 4 – 0.05 g/dm^3 ZnO, 5 – 0.10 g/dm^3 ZnO, 5 – 0.15 g/dm^3 ZnO. Initial concentration of Cr(VI) – 5 mg/dm^3, temperature – 20 °C, pH – 5, UV radiation – 1020 μW/cm^2, solution volume – 1000 cm^3

According to Shao et al. [11], when reduction reagent is absent in the solution, H_2O could work as electron donor in the photocatalytic reduction of Cr(VI) to Cr(III), and H_2O_2 can be detected in solution. In order to reduce Cr(VI) to Cr(III) completely, a large dosage of reduction reagent (herein, i.e., H_2O_2) has to be used. H_2O_2 is easily available, and the problem of possible accumulation of intermediate products is low. Other reagents used are oxalate [11], methanol [12], citric acid [17], ethanol [19], formic acid [27], and humic acids [28]. In this study, H_2O_2 was used since it is cheaper than other reduction reagents reported in the literature, has a high capacity as an electron supplier for the hexavalent chromium in solution, and eventually it converts to O_2 and H_2O. An experimental scheme of possible reactions for the photocatalytical reduction of Cr(VI) using ZnO as a photocatalyst may be summarized as follows. Under UV/visible illumination, the first way is photo-generation of a hole–electron pair in the ZnO conduction band [3, 28].

$$\mathrm{ZnO} + h\nu \rightarrow \mathrm{ZnO}(\mathrm{h}^+ + \mathrm{e}^-) \tag{13}$$

Electrons are responsible for reduction of Cr(VI) and water is oxidized to oxygen by reaction with holes:

$$\mathrm{H_2O} + 2\mathrm{h}^+ \rightarrow \frac{1}{2}\mathrm{O_2} + 2\mathrm{H}^+ \tag{14}$$

In addition to these reactions, oxygen in solution acts as the hole scavenger and generates H_2O_2 which reduces Cr(VI) according to [12]:

$$O_2 + H^+ + ZnO(e^-) \rightarrow 2H_2O_2 \quad (15)$$

$$2HCrO_4^- + 3H_2O_2 + 8H^+ \rightleftarrows 2Cr^{3+} + 3O_2 + 8H_2O \quad (16)$$

The quantity of produced H_2O_2 is low and by adding external H_2O_2 to the solution Cr(VI) will be reduced and thereby enhances the photoreduction efficiency. Despite high oxidation ability of H_2O_2, it acts as a reluctant (E_0 = 0.68 V) when reacting with stronger oxidizing agents such as potassium dichromate (E_0 = 1.33 V) [4].

Time–concentration profiles for the reduction with various H_2O_2 dosages are shown in Fig. 2. It was observed that the initial rate was low without H_2O_2; the extent of photoreduction reaction becomes slow in the absence of a reduction reagent. However, H_2O_2 can reduce Cr(VI) under UV illumination, and thereby decreases the concentration of Cr(VI) in solution

$$2H_2O_2 = 2H_2O + O_2 \qquad \Delta H = -99 \text{ kJ/mol} \quad (17)$$

Chakrabarti et al [12] studied photoreduction of Cr(VI) in an irradiated suspension of ZnO and they obtained similar results. Khalil et al [4] studied the same using an irradiated suspension of ZnO, WO_3 and two types of TiO_2. In another study [11] ZnO was used as photocatalyst and oxalate as a reduction reagent which reduced Cr(VI) under UV illumination. Our results are supported with those reported above.

3.3. PHOTOCATALYTIC REDUCTION OF Cr(VI) AT VARIOUS INITIAL CONCENTRATIONS

Photocatalytic reduction of Cr(VI) at 20 ± 1 °C at its various initial concentrations is shown in Fig. 3. The initial concentration of Cr(VI) was in the range of 0.1–0.15 mg/dm^3.

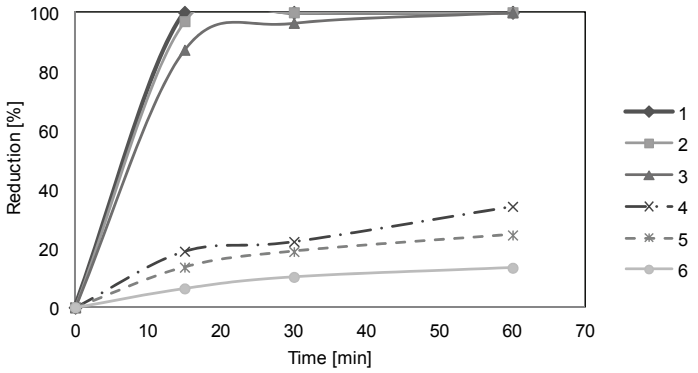

Fig. 3. Dependences of removal percentage on time for various initial concentrations of dichromate solution: 1– 0.10 mg/dm^3 Cr(VI), 2 – 0.25 mg/dm^3 Cr(VI), 3 – 0.50 mg/dm^3 Cr(VI), 4 – 5 mg/dm^3 Cr(VI), 5 – 10 mg/dm^3 Cr(VI), 6 – 15 mg/dm^3 Cr(VI), ZnO loading – 0.1 g/dm^3, temperature – 20 °C, pH – 7, UV radiation – 1020 μW/cm^2

As can be seen, ZnO has a very high capacity in the removal of Cr(VI) from solution under UV irradiation. Almost all Cr(VI) was reduced for initial concentration of 0.1–0.5 mg/dm^3 but it gradually decreases upon increasing the initial concentration of Cr(VI) up to 15 mg/dm^3. When the initial concentration of Cr(VI) increased from 0.5 to 5 mg/dm^3, the photoreduction percentage decreased from 100% to 35.2% after an hour irradiation time. This is due to fact that with increasing initial concentration of Cr(VI), a large amount of UV radiations is absorbed by substrate before it reaches the surface of the ZnO particles and then the reduction decreased [12]. By observing the color change of the ZnO particles, the white-colored particles became yellow after adsorption of Cr(VI), and then gradually turned into green during the photocatalytic reduction of Cr(VI) to Cr(III). Therefore, for high initial Cr(V1) concentrations of Cr(VI) a yellow deposit on ZnO particles is observed, which corresponds to the adsorption of anionic Cr(V1) species [21].

3.4. KINETIC STUDIES

The variation of initial chromium concentration in the range of 0.1–15 mg/dm^3 on photoreduction process was studied under constant condition of pH and catalyst dose. It has been found that the photoreduction follows the first order kinetics, which is in agreement with the reported order on ZnO [3]. Some authors [3, 19, 26] also reported that Cr(VI) photoreduction using TiO_2 follows first order kinetics. Figure 4 shows a linear relationship between Cr(VI) concentration and illumination time that was observed in experimental conditions.

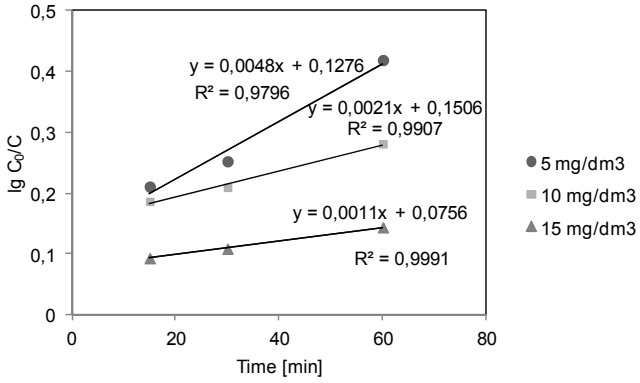

Fig. 4. Dependence of lg(C_0/C) on time for photoreduction of Cr(VI); catalyst dose – 0.1 g/dm^3, pH – 7

The data calculated for first-order rate constant k at various Cr(VI) concentrations are given in Table 4. The constant rate was found to decrease upon increasing initial Cr(VI) concentration.

Table 4

Rate constant value for photoreduction of Cr(VI) over ZnO

Time [min]	C = 5 mg/dm^3 (K_{red} = 0.0098 dm^3/min)		C = 10 mg/dm^3 (K_{red} = 0.00802 dm^3/min)		C = 5 mg/dm^3 (K_{red} = 0.00221 dm^3/min)	
	lg(C_0/C)	K [dm^3/min]	lg(C_0/C)	K [dm^3/min]	lg(C_0/C)	K [dm^3/min]
15	0.092	0.01405	0.081	0.01242	0.04	0.00621
30	0.110	0.00841	0.091	0.00698	0.047	0.00362
60	0.182	0.00698	0.122	0.00468	0.062	0.00240

3.5. APPLICATION FOR A REAL SAMPLE

Drinking water samples were collected at the point of use from Birjand city in Iran due to its high Cr(VI) concentrations. The initial concentration of Cr(VI) in the samples was 0.077 mg/dm^3. The physicochemical data for the samples is presented in Table 5.

Table 5

Characterization of the water sample at pH 8.64

Parameter	Concentration [mg/dm^3]
SO_4^{2-}	375
NO_3^-	17
Cl^-	244
Mg^{2+}	76.6
Na^+	220
Cr(VI)	0.077
Ca^{2+}	40
TDS	834
Conductivity	1467 µs/cm
Alkalinity	60 mg $CaCO_3$/dm^3

The wastewater used in this study was collected from the effluent of a metal plating plant. The wastewater was characterized for pH, conductivity, and Cr(VI) and the data are presented in Table 6.

Table 6

Characteristics of wastewater

Parameter	Value
Cr(VI)	61.4 mg/dm^3
Conductivity	200 mS/cm
pH	4.0

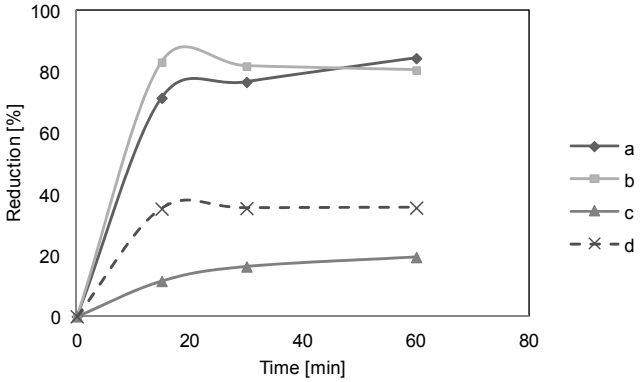

Fig. 5. Effect of photocatalytic process for removal of Cr(VI) on real samples; ZnO concentration – 0.15g/dm^3, H_2O_2 concentration 1.5 mol/dm^3: a) UV/ZnO water sample, b) UV/ZnO/H_2O_2 water sample, c) UV/ZnO wastewater sample, d) UV/ZnO/H_2O_2 wastewater sample

In order to remove Cr(VI) from real samples, they were treated in optimum conditions of photocatalytic process; results are shown in Fig. 5. As can be seen, photocatalytical reduction processes of UV/ZnO and UV/ZnO/H_2O_2 decreased the percentage of Cr(VI) to 83.1% and 73.5% after 15 min irradiation, respectively. Also, the residual concentrations of Cr(VI) after treatment by these processes reached less than maximum acceptable concentration (MAC) in drinking water (MAC = 0.5 mg/dm^3) according to USEPA [6]. However, when the same doses of ZnO and hydrogen peroxide were used for the treatment of wastewater sample and since the initial concentration of Cr(VI) was high, the removal efficiency was lower than that in the water sample. Thus for increasing reduction of Cr(VI), important factors such as ZnO loading, H_2O_2 concentration and irradiation time should be increased.

4. CONCLUSIONS

Hexavalent chromium in aqueous solutions can be effectively reduced to the trivalent state using ZnO as the semiconductor photocatalyst under UV irradiation, in the presence of H_2O_2 as a reduction reagent. The extent of degradation as well as its initial rate increased with the loading of the photocatalyst and concentration of H_2O_2. H_2O_2 was used as a supply of electron for photocatalytic reduction of Cr(VI) in solution. The pH effect on the reduction of Cr(VI) by UV/ZnO process was found to be different from the adsorption of Cr(VI) by ZnO particles indicating that the surface reduction step was rate determining. The results showed that Cr(VI) reduction by UV/ZnO photocatalytic process is more effective for the pH in range of 4.8–8.0 and the conversion is maximum (ca. 70%) at pH range of 4–5. The residual concentration of Cr(VI)

in water sample was lower than MAC indicator in drinking water after photocatalytic treatment.

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