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## SYNERGISTIC ELIMINATION OF Cr(VI) AND Ni(II) IONS WITH TRACE AMOUNTS OF TITANIA PHOTOCATALYST NANOPARTICLES

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### Abstract

The separate and simultaneous photocatalytic reduction of poisonous Cr(VI) and Ni(II) ions were examined with trace amounts of commercial titania nanoparticles (up to 50 mg/L). A direct irradiation photo-reactor, equipped with ultrasonic source was employed. The effects of four influencing parameters, catalyst dosage, pH, temperature and metal ions concentration ratio were investigated. The simultaneous operations, in the ternary Cr(VI)/Ni(II)/TiO<sub>2</sub> system, show a synergism in reduction efficiency compared to just individual ions treatments. The influence of the hole scavengers to intensify the process was appeared in the order of ethylene glycol > formic acid > citric acid. Under the best found conditions of [TiO<sub>2</sub>]=40 mg/L, pH=7.5, T=35° C, ratio of [Cr(VI)]<sub>0</sub>/[Ni(II)]<sub>0</sub>=0.5 and 100 mg/L ethylene glycol, 58.9% reduction in Cr(VI) and 66.0% in Ni(II) ions were achieved after 110 min irradiation. The perfect reaction kinetic was determined for individual ions. Accordingly, the energy consumption was evaluated. This parameter, together with the significant achieved efficiency, confirms the high performance of the used process in comparison with a similar simultaneous reduction work.

*Key words:* divalent nickel, energy consumption, hexavalent chromium, nano titania, simultaneous reduction

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### 1. Introduction

Heavy metals in aquatic systems pose a potential danger to the ecosystem at various scales due to their toxicity and non-destroyable nature. They have infinite lifetime and may accumulate to a toxic level in different places (Samarghandi et al., 2011). Mining and ore excavation can produce heavy metal pollution in both local and downstream waters as well as groundwater sources. Metal ions such as pb(II), Cr(VI), Ni(II) and Hg(II) are commonly occurring as toxic metals in natural ecosystems due to the effluent of refineries, electroplating, casting industries, storage batteries and nickel-plating plants (Xu et al., 2006; Yoon et al., 2009). In aquatic environments, two common pollutant metal ions are nickel and chromium which usually appear as Ni(II), Ni<sup>0</sup>, Cr(VI), and Cr(III) (Chen and Ray, 2001). Though the high reported toxicity for Cr(VI) and Ni(II); only slight toxicity has been reported for Cr(III) and Ni<sup>0</sup> (Siboni

et al., 2012). So, converting to less harmful species would be beneficial.

Different methods have been proposed for the treatment of aqueous solutions containing Ni(II) and Cr(VI); e.g. precipitation, ion exchange, electrolysis, adsorption, membrane separation and photocatalysis (Caliman et al., 2002; Lacour et al., 2001; Malkoc and Nuhoglu, 2006; WHO, 2006; Sadeghi et al., 2017; Wu and Peng, 2011). In the last important process, titanium dioxide has been mostly used, because of very efficient photocatalyst activity, non-toxicity nature, chemically stable and low cost (Bhatkhande et al., 2001). As documented in the literature, the main step in this process is the formation of electron–hole pairs ( $e_{CB}^- - h_{VB}^+$ ) on the catalyst surface upon irradiation with the proper photon energy to overcome the band gaps. Titanium dioxide semiconductor contains sufficient reducing power to cause chromium and nickel ions reduction. It is since band gap of TiO<sub>2</sub>

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is around 3.2 eV with energy of conduction band  $-0.3$  eV and valence band  $+2.9$  eV at pH 5.6 (Blake et al., 1991). Therefore, any metal ions having a reduction potential less negative than  $-0.3$  eV would be reduced by photo-generated electrons of  $\text{TiO}_2$ . The reduction of metal ions is normally occurred by capturing the photo-excited conduction band electrons, while water or other organics are oxidized by the valence band holes.

Photocatalytic reduction of metal ions such as Cr(VI) and Ni(II) has been investigated several times; however, just with individual metal ions and in cases in the presence of organic compounds (with the aim of their decomposition). All investigations have been with very high level titania concentrations, within 250-2000 mg/L (Dozzi et al., 2012; Kabra et al., 2008a; Schrank et al., 2002; Siboni et al., 2012; Testa et al., 2004). It is while; there is very limited information about simultaneous photocatalytic treatment of binary metal ions. In this regard, Aman et al. (2011) have investigated the simultaneous photoreductive removal of copper (II) and selenium (IV). Recently, Siboni et al. (2012) have reported the photocatalytic removal of Cr(VI) and Ni(II) by UV/ $\text{TiO}_2$  process, under limited conditions and with  $\text{TiO}_2$  nano particles as high as 1000 mg/L. A decrease in the removal efficiency of each ion has been reported in the presence of other ion.

In this research, the simultaneous photocatalytic reduction of chromium and nickel ions in aqueous media is investigated using trace amounts of titania nanoparticles (less than 50 mg/L). Low dosage catalyst loading is practically interested due to separation problems and regeneration. Under these conditions, the synergistic effect in treatment of the species is sought. The influence of temperature is also investigated; the case that has not been reported so far. Applying temperature, within the conventional range, can play an important role to alter the performance of this kind of processes. This parameter as well as solution pH and  $[\text{Cr(VI)}]/[\text{Ni(II)}]$  initial concentration ratio (an alternative in real industrial wastewaters) are examined. The reaction kinetic is studied to present a clear reduction progress for individual metals. Meantime, the effect of presence of a number of hole scavengers is studied. Finally, for practical applications, the process performance is evaluated in terms of reactions kinetic, energy consumption and process efficiency.

## 2. Material and methods

### 2.1. Reagents

All the used reagents and chemicals in this work were analytical grade and were used as received from the suppliers. Potassium dichromate, nickel nitrate hexa-aqua, 1,5-diphenylcarbohydrazide (DPC), acetone, 1-(2-Pyridylazo)-2-naphthol (PAN), ethanol and Triton X-100 (for analysis) were all Merck products. Sulfuric acid and sodium hydroxide (for pH adjustment) were also purchased

from Merck. Titanium dioxide nano particles (P-25 purity  $> 99.5\%$ ) was supplied by Plasma Chem with BET surface area of  $50 \text{ m}^2/\text{g}$  and the average particle diameter of 21 nm. All aqueous solutions were prepared using deionized water with conductivity less than  $0.08 \mu\text{S}/\text{cm}$ .

### 2.2. Photo-reactor and procedure

A 1.25 L cylindrical photo-reactor made of glossy stainless steel was used. The light source was a 250 W mercury lamp with the wavelength range of 280–400 nm and the maximum emission of 365 nm, located centrally in the reaction media with perfect light utilization. For the aim of well mixing of the reactor content and fine dispersion of the catalyst particles, an ultrasound source (28 kHz, 60 W) was located at the outside bottom of the reactor. The desired reaction temperature was adjusted and maintained constant via a stainless-steel water-flow jacket, connected to a thermostat bath.

To run each experiment, a solution (1 L) containing the desired concentrations of Cr(VI) and Ni(II) ions was prepared and after adjustment of pH (using sulfuric acid and sodium hydroxide dilute solutions) was transferred into the reactor and then temperature was set to the desired value. The corresponding amount of the catalyst particles was added and prior to light irradiation, the suspension was sonicated for 5 min and then maintained mixing for 30 min in dark to ensure adsorption/desorption equilibria of chromium and nickel onto  $\text{TiO}_2$  surface. Very low changes in the metals concentration were recorded at pH near neutral (7.5) in dark. All the experiments were performed while the content were continuously mixing with a simple mechanical impeller. Initial total concentration of metal ions in mixed solution was maintained at 10 mg/L, having Cr(VI) and Ni(II) with 1:1 concentration ratio (except where mentioned).

To follow the reaction progress 2 mL samples were withdrawn at different times for analysis. The nano particles were separated with vigorous centrifuging and then analyzed for their residual Cr(VI) and Ni(II) concentrations.

### 2.3. Analytical method

Changes in the concentration of of Cr(VI) and Ni(II) ions were observed from its absorbance band obtained by a UV-vis spectrophotometer (Jasco, model 760). The concentration of Cr(VI) ions was determined with colorimetry at  $\lambda_{\text{max}}=542$  nm relevant to the complex formed with DPC in acidic solution (pH 2.5) (Clesceri et al., 1998). Similarly, the amount of Ni(II) ions was determined by colorimetry at  $\lambda_{\text{max}}=568$  nm using PAN as the color agent. Accordingly, the best complex formation for Ni(II) conditions were provided with 2.5 mL of 1.0% Triton X-100 water solution, 2 mL of buffer solution (pH 8.5), 1.0 mL of 0.01% PAN solution in ethanol, together with 2 mL of collected sample, all added into a 10 mL standard flask and volume was made up to the marked level with

deionized water (Clesceri et al., 1998). A calibration based on Beer-Lambert law was utilized. The maximum wavelength and the molar absorption coefficient of both ions are not much dependent on the solution pH within the range of 4.5-8.5. Using this method, the reduction efficiency percentage (*RE*) at any time was obtained from (Eq. 1):

$$RE = \frac{[C]_0 - [C]_t}{[C]_0} \times 100 \quad (1)$$

where  $[C]_0$  and  $[C]_t$  are initial and the appropriate time ions concentration of either Cr(VI) or Ni(II) ions, respectively. It is noteworthy that during the process, the solution pH showed no sensible change.

### 3. Results and discussion

#### 3.1. Cr(VI)/TiO<sub>2</sub> system

In preliminary experiments, the photocatalytic reduction of Cr(VI) in the binary Cr(VI)/TiO<sub>2</sub> system was studied with 5 mg/L initial Cr(VI) concentration, TiO<sub>2</sub> loading of (8-50) mg/L, solution pH within 2.5-6.5 and temperature within the conventional range of 20 to 40 °C. As the photocatalyst loading increases to 33 mg/L, the reduction efficiency of Cr(VI) increases. When the catalyst amount was further increased, a negative effect was observed (Fig. 1a) which is assumed due to the blockage of light caused by excessive catalyst loading (Saien and Nejadi, 2007). At acidic pHs, dichromate (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>), hydrogen chromate (HCrO<sub>4</sub><sup>-</sup>), and the chromate (CrO<sub>4</sub><sup>2-</sup>) anion species are adsorbed onto the positively charged catalyst surface (Ku and Jung, 2001).

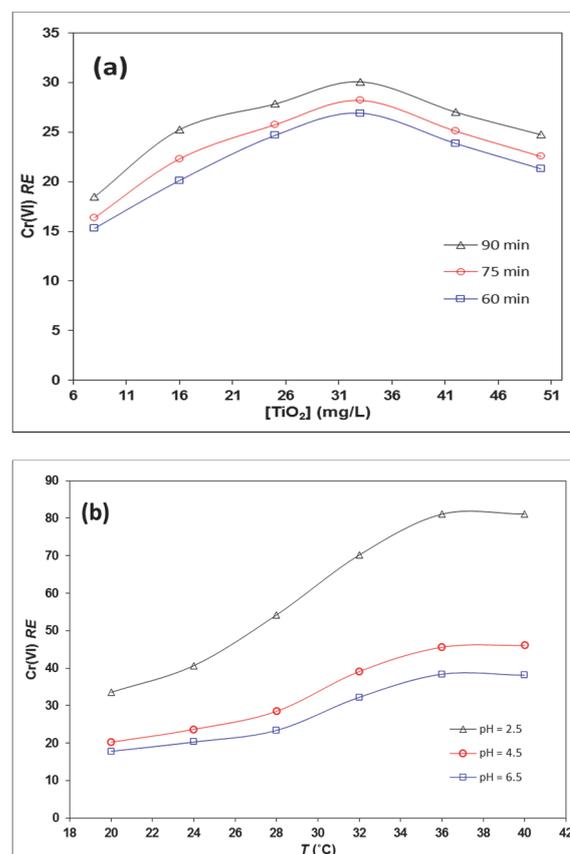
It has been pointed that the redox potential of Cr(VI)/Cr(III) pair decreases by 98 mV per pH unit (Gratzel, 1983). Therefore, the presence of acid sites on catalyst surface may favor Cr(VI) reduction. Results also show that Cr(VI) photocatalytic reduction proceeds with temperature from 20 to 36 °C and then remains almost constant, perhaps due to disfavorable effect of temperature on adsorption; however, an inverse variation was relevant with pH as presented in Fig. 1(b). Finally, it is observed that for this stage, under the found optimum conditions of [TiO<sub>2</sub>] = 33 mg/L, pH = 2.5 and *T* = 36 °C, 81.0% efficiency is achieved after 120 min.

#### 3.2. Ni(II)/TiO<sub>2</sub> system

For nickel in the binary Ni(II)/TiO<sub>2</sub> system, experiments were conducted with 5 mg/L initial Ni(II) ion concentration, TiO<sub>2</sub> loading of (8-50) mg/L, pH within 7.5-9.5 and temperature within (20-40) °C. Results show that reduction efficiency of Ni(II) increases with photocatalyst loading up to 42 mg/L (Fig 2a) and adding more nano particles does not improve the efficiency. Further, increasing pH from 7.5 to 8.5 and then to 9.5, results in 35, 76 and 86% Ni(II) reduction, respectively; at 36 °C and after 90

min treatment (Fig. 2b). As is well known, the surface of the catalyst is positively charged at pHs < pH<sub>ZPC</sub> and negatively charged at pHs > pH<sub>ZPC</sub>. So, TiO<sub>2</sub> surface faces more negative charges by increasing pH, leading to higher adsorption of Ni(II) ions and therefore higher *RE* achievement.

Results in Fig. 2b show that, increasing temperature from 20 to 36 and then to 40 °C at a fixed pH of 7.5 results about 16.3, 36.7 and 37.1% enhancements in *RE*, respectively. Results show that increasing temperature, over 34 °C, does not significantly improve the efficiency. Also increasing reaction time plays an important role in nickel treatment, similar to Cr(VI)/TiO<sub>2</sub> system. At the best-found conditions of [TiO<sub>2</sub>] = 42 mg/L, pH= 9.5, *T*= 34 °C and after 90 min, 85.0% efficiency was achieved for Ni(II) reduction. As can be resulted from Figs. 1a and 2a, irrespective of the applied pH (6.5 for chromium and 7.5 for nickel), photocatalytic reduction of Ni(II) is relatively faster compared with Cr(VI), under nearly similar conditions.



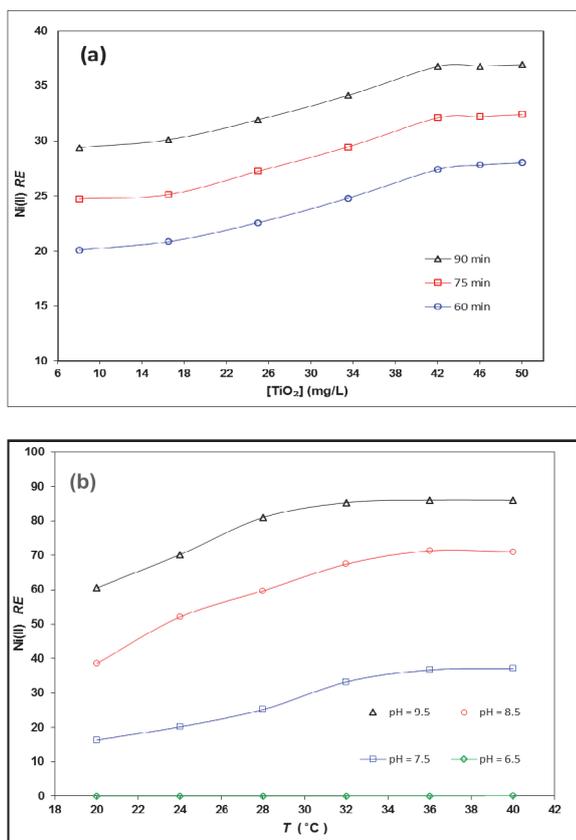
**Fig. 1.** (a) Effects of photocatalyst concentration and reaction time under conditions of; [Cr(VI)]<sub>0</sub> = 5 mg/L, pH = 6.5 and *T* = 36 °C, and (b) effect of temperature and solution pH under conditions of; [Cr(VI)]<sub>0</sub> = 5 mg/L, [TiO<sub>2</sub>] = 33 mg/L and *t* = 120 min; on Cr(VI) photocatalytic reduction

#### 3.3. Cr(VI)/Ni(II)/TiO<sub>2</sub> system

##### 3.3.1. General considerations

In this step, solutions containing mixture of 5 mg/L of each Cr(VI) and Ni(II) ions were used.

Experiments were conducted with 40 mg/L TiO<sub>2</sub> loading, at pH 7.5, 25 °C and during 110 min operations.



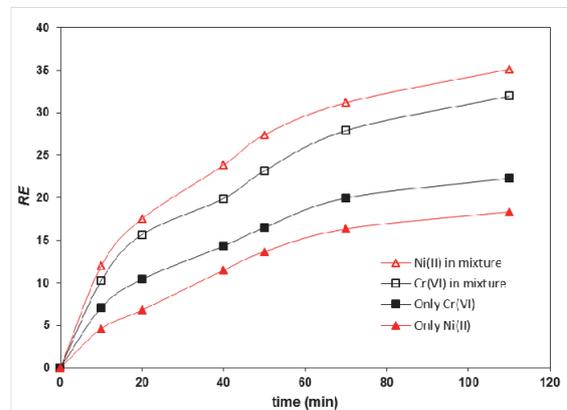
**Fig. 2.** (a): Effects of photocatalyst concentration and reaction time under conditions of; [Ni(II)]<sub>0</sub> = 5 mg/L, pH = 7.5 and T = 34 °C, and (b): Effect of temperature and solution pH under conditions of; [Ni(II)]<sub>0</sub> = 5 mg/L, [TiO<sub>2</sub>] = 42 mg/L and t = 90 min; on RE of Ni(II)

The TiO<sub>2</sub> dosage and reaction time were within the values used for individual ions. The pH of chromium-nickel plating industrial wastewaters are usually within 5.5-7 (Kabra et al., 2008 b; Mirbagheri et al., 2011), but due to results of Ni/TiO<sub>2</sub> system that showed no any reduction under low pHs; thereby, pH 7.5 (a moderate pH for both ions) was employed here for the mixture of ions. Interestingly, as presented in Fig. 3, a synergism in efficiency was appeared due to the simultaneous interaction of the present metal ions during reduction process and of course under the same specified conditions. Hence, this synergistic effect causes an enhancement of about 65% in the average RE after 110 min treatment.

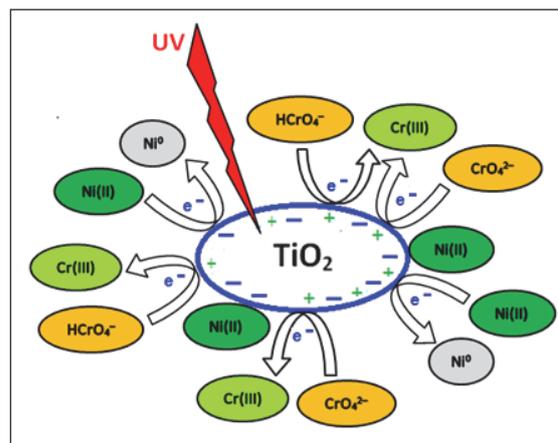
The presumed reasons for the increased photocatalytic process activity in the mixture can be due to the following items:

(i) The adsorption capacity on the surface of TiO<sub>2</sub> particles is highly affected by the coexisting ions. Nickel ions tend to be adsorbed because of attraction of opposite charges between nickel cations and the titania particles at neutral or near neutral solution pH (Kabra et al., 2008b). So, this adsorption leads the catalyst particles to find dominant positive charge and

in turn, favoring the chromium anion species (HCrO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>2-</sup>) to find more tendency for adsorption on the catalyst surface. Fig. 4 gives a schematic presentation of this enhanced simultaneous photocatalytic reduction. The “+” and “-” symbols on the TiO<sub>2</sub> surface represent surface charges of adsorbed nickel cations and vacant zones, respectively.



**Fig. 3.** Comparison between individual binary systems and in Cr(VI)/Ni(II)/TiO<sub>2</sub> ternary system; [Cr(VI)]<sub>0</sub> = [Ni(II)]<sub>0</sub> = 5 mg/L, [TiO<sub>2</sub>] = 40 mg/L, pH = 7.5 and T = 25 °C



**Fig. 4.** Schematic presentation of Cr(VI) adsorption, favored by Ni(II) adsorption onto TiO<sub>2</sub> photocatalyst surface

(ii) Electrons at the conduction band of TiO<sub>2</sub> can reduce Cr(VI) and Ni(II) to Cr(III) and Ni<sup>0</sup> respectively. But the holes are not involved in the reduction of these metal ions, and even produce •OH from water, which will possibly oxidize Cr(III) into Cr(VI) (Wu et al., 2013) and Ni<sup>0</sup> and Ni(II) into NiO (Suri et al., 1993) or even Ni(III); and then the formed Ni(III) ions can be converted again to Ni(II) ions by receiving the excited electrons (Devi et al., 2010), i.e. a sort of ions cycling.

At the same time, NO<sub>3</sub><sup>-</sup> counter-ions, initiated from nickel nitrate salt, enhance photocatalytic reduction of metal ions and this can be explained as a result of trapping the photogenerated valance band holes and hydroxyl radicals via following equations (Meichtry et al., 2014) (Eqs. 2-3):



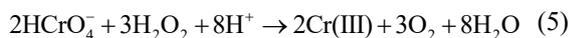
Thus, captured holes by nitrate ions and also through Ni ions cycling cause the photopromoted conduction band electrons become more readily available for reduction of metal ions, and thus inhibiting electron-hole recombination.

To ensure this matter, the presence of zero valent nickel as well as its oxide species of NiO (due to oxidation of metallic nickel), was detected by high-resolution XPS analysis of TiO<sub>2</sub> particles which were collected after the reaction (Fig. 5). The Ni 2p peaks and the satellites show the presence of these two species of nickel. The spectrum of Ni<sup>0</sup> fits by broad peaks at 853.6 and 870.9 eV (Grosvenor et al., 2006), and the NiO by Ni 2p peaks at 857.6 and 874.2 eV (Prieto et al., 2012), specified by arrows in Fig. 5.

Also, NO<sub>3</sub><sup>-</sup> ions in the solutions are capable in reducing Cr(VI) directly through nitrite reductant ions (NO<sub>2</sub><sup>-</sup>) produced from NO<sub>3</sub><sup>-</sup> photolysis (Hsu et al., 2007; Penpolcharoen et al., 2001) (Eq. 4):



and indirectly by generating H<sub>2</sub>O<sub>2</sub> molecules (Mack and Bolton, 1999), which leads to rapid reduction of Cr(VI) according to (Pettine et al., 2002) (Eq. 5):



The effects of operational parameters that facilitate simultaneous elimination of both Cr(VI) and Ni(II) ions in UV/TiO<sub>2</sub> process are discussed below.

### 3.3.2. Effect of pH

pH is one important parameter in the photocatalytic reduction. It has influence on target metal ion species type, catalyst surface charge and also

on the process mechanism. In this regard, a range of solution pH from 4.5 to 8.5 was investigated. As is observed in Fig. 6, the chromium reduction decreases with pH; while the nickel reduction increases with a higher trend of variation; hence, the average RE tends to increase with pH up to about 7.5 and then exhibits a reduction. So, the optimum appeared pH for this treatment was 7.5.

On decreasing and increasing pH below and above 7.5, average photocatalytic reduction decreases. The presumed reasons for this variation are: (i) as pH decreases, the repels between Ni(II) ions and catalyst surface are strengthened, because the pH of zero-point charge of TiO<sub>2</sub> (P-25) is 6.8 and the surface becomes positive charged (Ollis et al., 1991; Pujara et al., 2007). (ii) by increasing pH more than 7.5, the predominant species of chromium will be HCrO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>2-</sup> anions; thus, this time, repels between these ions and catalyst surface (higher negative surface charge as pH increases beyond 7.5) increases, coincident with less ions adsorption on the catalyst surface. (iii) The catalyst may, to some extent, become deactivated at high pH levels due to precipitates that block the active sites of the catalyst. In this regard, Cr(III) is likely to precipitate as Cr(OH)<sub>3</sub> (Matthews, 1987) and Ni(II) in the form of Ni(OH)<sub>2</sub>. At the same time, formation of NiO can also deactivate the catalyst surface (Lin and Rajeshwar, 1997).

The above discussion clears that the interaction of TiO<sub>2</sub> particles with electron donor and acceptor is favored for metal ions reduction at high pH levels (more than pH<sub>zpc</sub>), while low pHs (less than pH<sub>zpc</sub>) favor anionic electron donors and acceptors (Ollis et al., 1991; Pujara et al., 2007). In another word, at low and high pH levels only one of chromium or nickel ions adsorption is favored; however, at or close neutral pHs (7.5 here) both of the ions tend to significant adsorption and then reduce due to TiO<sub>2</sub> photocatalyst activity. Fig. 7 demonstrates the function of TiO<sub>2</sub> surface in contact with ions at different pH levels.

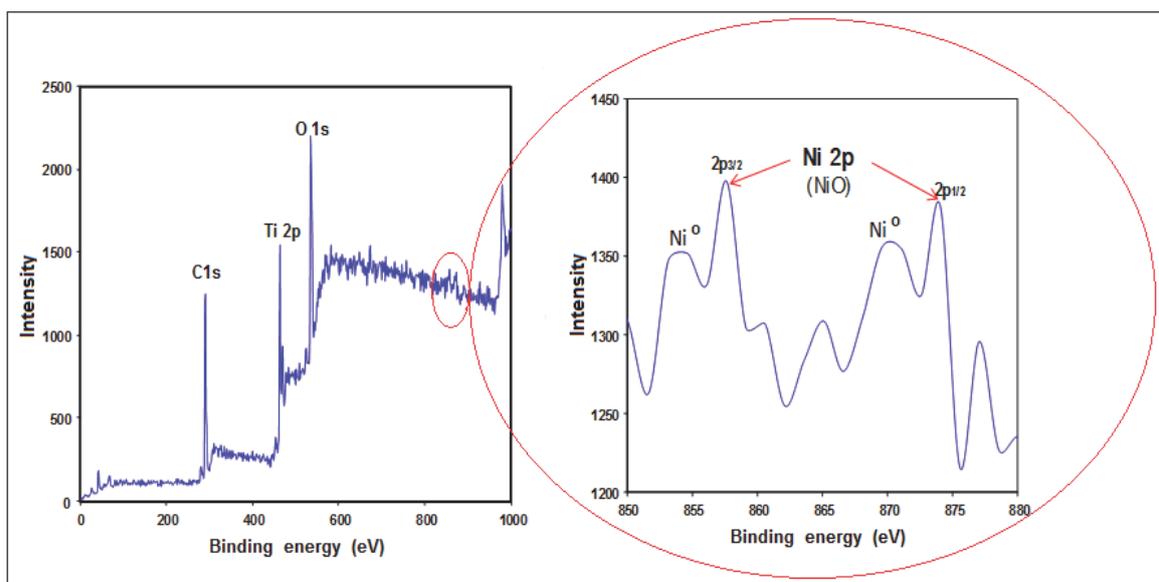
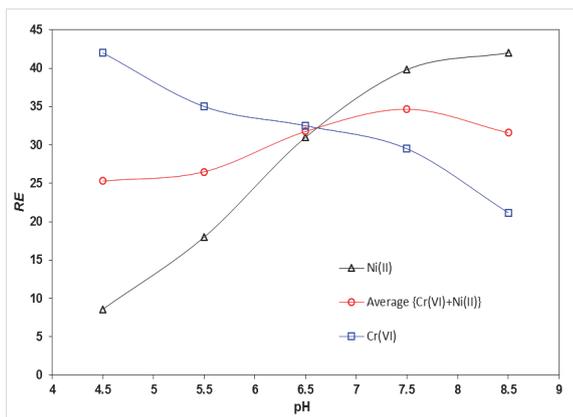
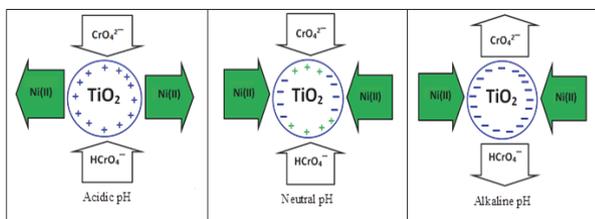


Fig. 5. XPS spectrum of Ni 2p peaks and satellites for TiO<sub>2</sub> particles after reduction process



**Fig. 6.** Effect of solution pH on individual Cr(VI), Ni(II) and their average RE in Cr(VI)/Ni(II)/TiO<sub>2</sub> ternary system; [Cr(VI)]<sub>0</sub> = [Ni(II)]<sub>0</sub> = 5 mg/L, [TiO<sub>2</sub>] = 40 mg/L, T = 25 °C and t = 110 min



**Fig. 7.** The function of TiO<sub>2</sub> particles in contact with Cr(VI) and Ni(II) ions at different pH levels

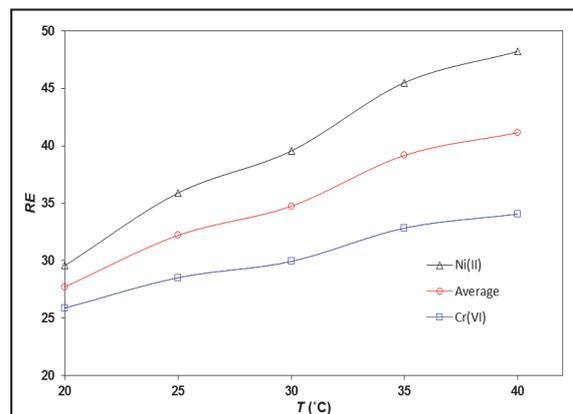
### 3.3.3. Effect of temperature

Increasing temperature from 20 to 40 °C, at near neutral pH of 7.5, leads efficiency to enhance 8.2 and 18.6% for Cr(VI) and Ni(II) ions, respectively; after 110 min. An increase in temperature will enhance mobilization of the reacting species and provide a higher reaction rate with respect to the reaction activation energy. Also, increasing temperature helps the reaction to compete more effectively with the electron-hole pair recombination (Saïen et al., 2010). Fig. 8 shows the variation of reduction efficiency with temperature. From this figure, temperature of 35 °C can be selected as a low enough temperature with significant enhancement in average reduction of ions (42.1%).

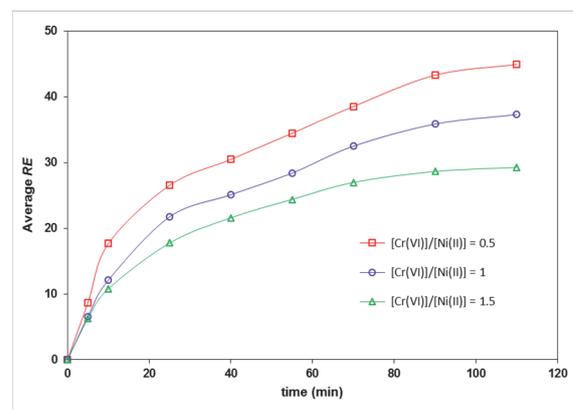
### 3.3.4. Effect of [Cr(VI)]/[Ni(II)] initial concentration

Fig. 9 shows the effect of different initial concentration ratio of Cr(VI) and Ni(II) on the average photocatalytic RE of Cr(VI) and Ni(II) with 40 mg/L catalyst dosage, pH 7.5 and temperature of 35 °C. Initial concentration of metal ions was maintained at 10 mg/L, having Cr(VI) to Ni(II) concentration ratios in 0.5 (3.33 and 6.67 mg/L), 1 (5 and 5 mg/L) and 1.5 (6 and 4 mg/L) in the experiments. With the concentration ratio of 0.5, the highest reduction efficiency is achieved due to higher NO<sub>3</sub><sup>-</sup> ions concentration that in turn provide more NO<sub>2</sub><sup>-</sup> ions, capable in reducing of Cr(VI) ions according to Eqs. (4) and (5). The mechanism of Cr(VI) reduction

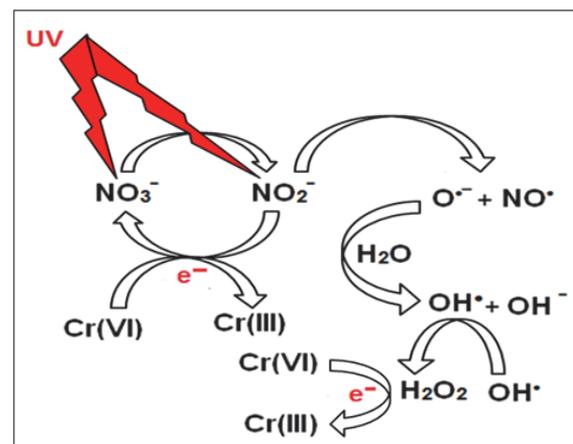
reaction, enhanced by NO<sub>2</sub><sup>-</sup> ions is summarized in Fig. 10.



**Fig. 8.** Variation of individual and average RE of Cr(VI) and Ni(II) ions with temperature; [Cr(VI)]<sub>0</sub> = [Ni(II)]<sub>0</sub> = 5 mg/L, [TiO<sub>2</sub>] = 40 mg/L, pH = 7.5 and t = 110 min



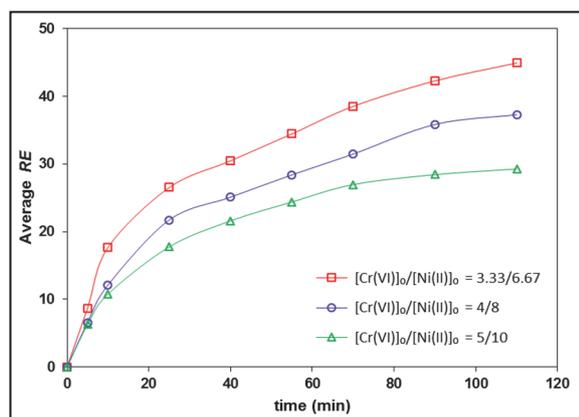
**Fig. 9.** Effect of initial concentration ratio on average RE; [TiO<sub>2</sub>] = 40 mg/L, pH = 7.5 and T = 35 °C



**Fig. 10.** Schematic presentation Cr(VI) reduction by photolysis of NO<sub>3</sub><sup>-</sup> ions

Another effect of NO<sub>3</sub><sup>-</sup> ions, supplemented with Ni(II) ions, can be delaying the conversion of Ni<sup>0</sup> to NiO by scavenging the holes and so preventing deactivation of the surface of TiO<sub>2</sub>, which was discussed in section 3.3.1.

At the preferred ratio of  $[\text{Cr(VI)}]_0/[\text{Ni(II)}]_0 = 0.5$ , we also studied the effect of varying the total ions concentration with binary concentrations of (3.33, 6.67), (4, 5) and (8, 10) mg/L for Cr(VI) and Ni(II) ions respectively, under the optimum mentioned conditions. It can be seen in Fig. 11 that average *RE* decreases as the total concentration increases. This is due to the fact that for a specific irradiation and catalyst dosage, an increased initial substrates concentration leads to a decrease in *RE* of ions.



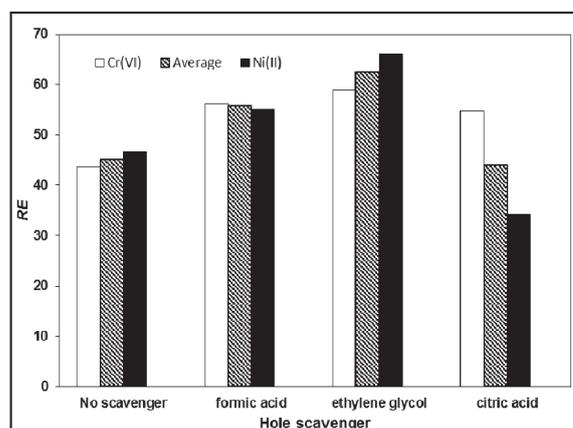
**Fig. 11.** Effect of initial Cr(VI) and Ni(II) concentrations on average *RE* of Cr(VI) and Ni(II) ions;  $[\text{TiO}_2] = 40$  mg/L,  $\text{pH} = 7.5$  and  $T = 35^\circ\text{C}$

### 3.3.5. Process intensification with hole scavengers

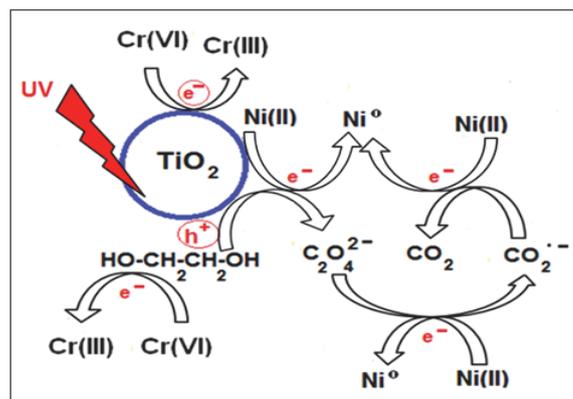
A hole scavenger is oxidized by the generated holes of photocatalyst particles. This helps directly to inhibit the  $e_{\text{CB}}^- - h_{\text{VB}}^+$  recombination and promotes photocatalytic reduction of metal ions. It has been demonstrated that oxidation of scavengers, produces strong reducing agents such as radical anions (Litter, 1999). In this study, three conventional hole scavengers, formic acid, citric acid and ethylene glycol were used. The amount of each added scavenger was 100 mg/L (consistent with the used average concentration in the previous works of Kabra et al., (2008a), and Nguyen et al., (2003)). The results presented in Fig. 12 show that the reduction of Cr(VI) and Ni(II) is strengthened (compared with no scavenger case) with ethylene glycol and formic acid; however, no pronounced change with citric acid. The anionic nickel-citrate complex which is formed with citric acid is repelled by the negatively charged  $\text{TiO}_2$  particles (Kabra et al., 2007). The average photoreduction enhancements with the scavengers are appeared in the order of: ethylene glycol > formic acid > citric acid with relevant 62.5, 55.7 and 44.1% *RE* and causing +38.6, +23.5 and -2.2% changes, respectively. By using only 40 mg/L photocatalyst about 45% average *RE* was achieved without scavenger and reached to 62.5% under the same conditions when ethylene glycol scavenger was used.

Enhanced photocatalytic reduction in the presence of ethylene glycol and formic acid can be attributed mostly to the fact that ethylene glycol is first oxidized to oxalate ion ( $\text{C}_2\text{O}_4^{2-}$ ) intermediate with

irradiated  $\text{TiO}_2$  in aqueous medium, and in turn, produces  $\text{CO}_2^-$  by further oxidation. This recent species which is also produced by formic acid, is able to reduce Cr(VI) and Ni(II) and is converted to  $\text{CO}_2$  itself. These reactions also inhibit the  $e_{\text{CB}}^- - h_{\text{VB}}^+$  recombination (Forouzan et al., 1996; Wang et al., 2004). A simplified reduction mechanism with ethylene glycol scavenger function is presented in Fig. 13.



**Fig. 12.** Effect of different hole scavengers (100 mg/L) on photoreduction of Cr(VI) and Ni(II) ions;  $[\text{TiO}_2] = 40$  mg/L,  $\text{pH} = 7.5$ ,  $T = 35^\circ\text{C}$ ,  $[\text{Cr(VI)}]_0/[\text{Ni(II)}]_0 = 0.5$  (3.33 and 6.67 mg/L) and  $t = 110$  min



**Fig. 13.** A simplified scheme of Cr(VI) and Ni(II) photoreduction mechanism in the presence of ethylene glycol

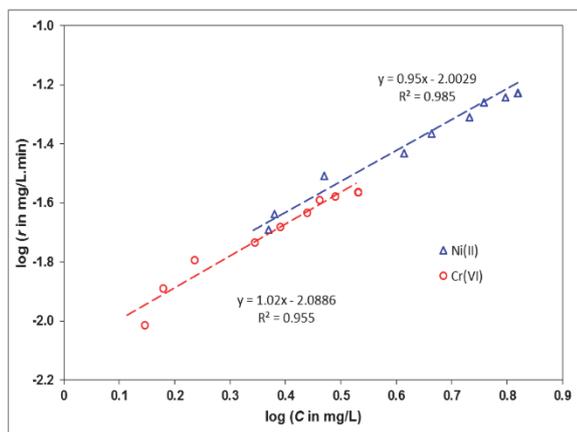
### 3.4. Kinetic studies

For practical applications, the kinetic model was investigated under the found optimum conditions for individual components in the mixture solution. The average *RE* reaches to 62.5% in mixed solution after 110 min; of which 58.9 and 66.0% efficiencies are relevant to chromium and nickel ions respectively.

Based on the well-known power law kinetic model (Kumar et al., 2007; Saien et al., 2003; Sharma et al., 2012) in the form (Eq. 6):

$$r = -\frac{d[C]}{dt} = k[C]^n \quad (6)$$

where  $r$ ,  $[C]$ ,  $k$  and  $n$  are the reaction rate, metal concentration, rate constant and order of the reaction respectively; to obtain kinetic parameters, the differential method of data analysis, based on the ions concentration variation versus time (9 data points) was employed. Fig. 14 presents the goodness of fitting with Eq. (6). The obtained kinetic parameters, in addition to the coefficient of determination ( $R^2$ ) for each metal ion are given in Table 1. The Cr(VI)/Ni(II)/TiO<sub>2</sub> process globally reveals a pseudo first order reaction for each component.



**Fig. 14.** Variation of the reduction rate of Cr(VI) and Ni(II) versus its concentration in mixed solution;  $[\text{Cr(VI)}]_0/[\text{Ni(II)}]_0 = 0.5$  with (3.33/6.67 mg/L),  $[\text{TiO}_2] = 40$  mg/L,  $\text{pH} = 7.5$ ,  $T = 35$  °C,  $[\text{ethylene glycol}] = 100$  mg/L

**Table 1.** Kinetic parameters of Cr(VI) and Ni(II) reduction in the mixed solution

| Component | $k$  | $n$  | $R^2$ |
|-----------|--|------|-------|
| Cr(VI)    | $8.15 \times 10^{-3} [(\text{mg/L})^{-0.02}] / \text{min}$ | 1.02 | 0.955 |
| Ni(II)    | $9.93 \times 10^{-3} [(\text{mg/L})^{0.05}] / \text{min}$  | 0.95 | 0.985 |

### 3.5. Energy consumption and process evaluation

There are several vital factors in selecting a waste treatment technology, including economics, regulations, effluent outlet quality, operation (maintenance, control, safety) and flexibility to change upsets. Although all these factors are important, process economic is often dominant (Khataee et al., 2012). Electrical energy consumption,  $E_{EC}$ , is the main parameter in the photochemical processes economic. Here,  $E_{EC}$  can be calculated according to the proposal of the photochemistry commission of the International Union of Pure and Applied Chemistry (IUPAC), for first order reactions as (Bolton et al., 2002; Khataee and Mirzajani, 2010) (Eq. 7):

$$E_{EC} = \frac{1000Pt}{60V \log \{ [C]_0 / [C]_t \}} \quad (7)$$

where  $P$  is the electric power (kW) of the photochemical system,  $V$  is the volume (L) of the solution in the reactor,  $[C]_0$  and  $[C]_t$  concentrations of pollutant (either chromium or nickel, here) before and after treatment respectively, and  $t$  is the reaction duration time (110 min here).

Accordingly, the electrical energy related to the reduction under conditions of 40 mg/L loading of TiO<sub>2</sub>, initial pH 7.5,  $T = 35$  °C and ratio of  $[\text{Cr(VI)}]_0/[\text{Ni(II)}]_0 = 0.5$  in mixed solution of 3.33 mg/L Cr(IV) and 6.67 mg/L Ni(II), in the presences of 100 mg/L ethylene glycol after 110 min are 560.43 and 517.14 kWh/m<sup>3</sup> for chromium and nickel, respectively. Considering the current electrical energy price in U.S. market as 0.068 US\$/kWh in 2013 (US Government Energy Information Administration, 2013), the electrical energy cost will be 38.1 and 35.2 US\$/m<sup>3</sup> respectively. The  $E_{EC}$  values in this work, related in individual system and in the mixed solution, under the found optimum conditions, in comparison with other reported processes (first order reactions and using nanoparticles for photocatalyst) are listed in Table 2. It has to be noted that in the simultaneous treatment either in the previous work (Siboni et al., 2012) or in this work, the power consumption was calculated for each ion in relation to its contribution in total  $RE$ .

Results show that energy consumption,  $E_{EC}$ , in this work is lower than those for individual metal process in the other work, each under their specified operating conditions. Also, results indicate that for mixtures, energy consumptions are close to corresponding values in the other work. In both works it is clear that using mixture of metals leads to a lower energy consumption. The energy consumption values can be regarded as a rough evaluation of the effectiveness of the processes and the experimental conditions examined in similar works.

A valid criterion in this regard can be proposed, as process efficiency ( $PE$ ), when  $RE$  is assigned to unit electrical energy consumption and unit photocatalyst concentration, given in the empirical equation of (Eq. 8):

$$PE = \frac{RE}{E_{EC} \times [\text{TiO}_2]} \quad (8)$$

where  $E_{EC}$  and  $[\text{TiO}_2]$  are the electrical energy consumption in kWh/m<sup>3</sup> and the catalyst loading in mg/L. Generally,  $PE$  reflects to the efficiency achievement with respect to the level of energy consumption as well as the amount of used catalyst. Accordingly, the effect of temperature and the reaction progress with time are contributed in the  $PE$  via  $E_{EC}$  parameter.

The  $PE$  value in the present work (under mentioned conditions) is significantly higher than relevant other reported processes (individual and mixture) (Table 2). This matter together with the significant achieved efficiency, confirm the high performance of the used process.

**Table 2.** Comparing the performance of different photoalytic Cr(VI) and Ni(II) reduction processes

| System and initial concentration (mg/L)  | [TiO <sub>2</sub> ] (mg/L) | pH  | T (°C) | UV dose (W/L) | time (min) | scavenger (mg/L)     | RE (%) | E <sub>EC</sub> (kWh/m <sup>3</sup> ) | PE (defined unit)      | Ref.                 |
|--|----------------------------|-----|--------|---------------|------------|----------------------|--------|---------------------------------------|------------------------|----------------------|
| Cr(VI)/TiO <sub>2</sub> , 5 (individual) | 1000                       | 7   | 25     | 125           | 120        | -                    | 58     | 663.71                                | 8.73×10 <sup>-5</sup>  | Siboni et al., 2012* |
| Ni(II)/TiO <sub>2</sub> , 5 (individual) | 1000                       | 7   | 25     | 125           | 120        | -                    | 50     | 830.50                                | 6.02×10 <sup>-5</sup>  | "                    |
| Cr(VI)/TiO <sub>2</sub> , 5 (mixture)    | 1000                       | 7   | 25     | 125           | 120        | -                    | 48     | 449.5                                 | 1.07×10 <sup>-4</sup>  | "                    |
| Ni(II)/TiO <sub>2</sub> , 5 (mixture)    | 1000                       | 7   | 25     | 125           | 120        | -                    | 46     | 457.35                                | 1.01×10 <sup>-4</sup>  | "                    |
| Cr(VI)/TiO <sub>2</sub> , 5 (individual) | 33                         | 2.5 | 36     | 250           | 120        | -                    | 81     | 608.7                                 | 4.01×10 <sup>-3</sup>  | This work            |
| Ni(II)/TiO <sub>2</sub> , 5 (individual) | 42                         | 9.5 | 34     | 250           | 90         | -                    | 85     | 455.2                                 | 4.44×10 <sup>-3</sup>  | "                    |
| Cr(VI)/TiO <sub>2</sub> , 3.33 (mixture) | 40                         | 7.5 | 35     | 250           | 110        | ethylene glycol, 100 | 58.9   | 560.43                                | 2.63 ×10 <sup>-3</sup> | "                    |
| Ni(II)/TiO <sub>2</sub> , 6.67 (mixture) | 40                         | 7.5 | 35     | 250           | 110        | "                    | 66     | 517.14                                | 3.19×10 <sup>-3</sup>  | "                    |

\*The reduction efficiencies in ref. (Siboni et al., 2012) are considered without a part of physically adsorbed Cr(VI) and Ni(II) ions on photocatalyst particles

#### 4. Conclusions

At least 65% enhancement in average RE was achieved due to synergistic effect, when aqueous mixed solutions of Cr(VI) and Ni(II) were treated with TiO<sub>2</sub> photocatalyst particles in a high-performance photo-reactor. The adsorption of nickel ions as well as the counter ion NO<sub>3</sub><sup>-</sup> function assist the chromium reduction and inhibit nickel oxidation under near neutral pH of 7.5. Also, photo-generated electron-hole pairs can be separated via Ni ions cycling, leading to the improvement of electron transfer efficiency.

The most important findings are: (i) Operating conditions of [TiO<sub>2</sub>] = 40 mg/L, pH 7.5 and temperature 35°C as well as using 100 mg/L ethylene glycol scavenger were found as optimum conditions; (ii) Increasing temperature from 20 to the optimum 35°C leads to an 42.1% enhancement in average RE. (iii) The activity of the used hole scavengers was appeared in the order of ethylene glycol > formic acid > citric acid. (iv) Applying the pertinent conditions, an average RE of 62.5% (chromium 58.9% and nickel 66.0%) were achieved; (v) Pseudo first order reactions for Cr(VI), Ni(II) photocatalytic reduction in the mixture are relevant; (vi) Electrical energy consumption analysis showed a relatively low required energy for the simultaneous treatment in comparison with a previous work; and (vii) Based on different criteria including economic parameters, the significant preference of the used process was demonstrated.

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