

Optimization of Cr(VI) Photocatalytic Reduction by UV/TiO₂: Influence of Inorganic and Organic Species and Kinetic Study

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Background & Aims of the Study: Chromium is widely detected in surface waters and underground waters, which usually appear as Cr(VI), and Cr(III), at sites associated with industrial activities. Cr(VI), in effluent streams with a high level of mobility and notorious mutagenic and carcinogenic toxicity; thus Cr(III) does not have much mobility in soil. So, converting it into less harmful species could be beneficial.

Materials & Methods: Cr(VI) photocatalytic reduction in aqueous media was analyzed using desperately low dosages of nanoparticles of commercial titania. A directly imposed irradiation photoreactor equipped with a supersonic source was applied. The optimization of the reduction process was done using the central composite design (CCD) experimental. The residual concentration of Cr(VI) ion was determined by colorimetrically method. In addition, the impact of other factors, including water matrix and hole scavengers, also reduction kinetics were studied.

Results: A quadratic equation for reduction efficiency was proposed, and the adequacy of it was evaluated by a variety of statistical methods. A maximum of 80.6% reduction in aqueous samples containing an initial concentration of Cr(VI) within the investigated optimum operating condition (TiO₂ dose of 33 mg/L; pH of 2.5, T=35 °C and t=120 min) was obtained. Results indicate that UV irradiation alone is an acceptable method for Cr(VI) reduction maybe due to H₂O₂ photolytic generation. The results show Cr(VI) photoreduction was greatly enhanced by about 88.2% when NO₃⁻ was used in comparison with SO₄²⁻ anion. The photoreduction enhancements with the scavengers are appeared in the following order ethylene glycol > formic acid > citric acid with relevant. Maximum reduction of 96.5% for Cr(VI) was obtained in the presence of ethylene glycol hole scavenger. The results indicated that the process rate can be presented with a pseudo-first-order kinetic model.

Conclusion: The results showed, the CCD design was approximately adequate in Cr(VI) reduction, so it can be a suitable option for water quality improvement. The addition of inorganic or organic species can act as scavenging hydroxyl radicals- which are photo-generated- and valanceband holes that are on the photocatalysts of the semiconductor, and consistently, enhance the photocatalytic reduction of Cr(VI) ion.

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Background

Heavy metal ions are commonly occurring as toxic metals in natural ecosystems due to the effluent of electroplating, electronic, tanning

industries and etc. (1,2). These ions are assimilated, stored, and concentrated by organisms that are exposed to them (3,4). In aquatic environments, one common pollutant metal ion is chromium that usually appears as Cr(VI) and Cr(III) (5). Though Cr(VI) has high

toxicity; only a slight toxicity have been reported for Cr(III), and it is easily precipitated at neutral and alkaline pH (6). So, the reduction of Cr(VI) to Cr(III), which is less harmful would be beneficial.

Precipitation, ion exchange, adsorption, electrolysis, membrane processes and photocatalysis are common methods have been proposed for the treatment of Cr(VI) ion in wastewater (7-11). In the photocatalysis process, mostly titanium dioxide is used, because it's really active photocatalytically, and it's inexpensive, as well (12). Formation of electron-hole pairs ($e_{cb}^- - h_{vb}^+$) on the catalyst surface when a photon with enough energy is used to overcome the band gaps of titania is the main step in this process. On the catalyst surface when is used a photon with enough energy is used to overcome the band gaps of titania is the main step in this process. It is clear that the band gap of TiO_2 is around 3.2 eV with the conduction band -0.3 eV and the valence band of $+2.9$ eV at pH 5.6 (13). Cr(VI) ion which has a reduction potential less negative than -0.3 eV would be reduced by generated electrons of TiO_2 ; while water and organic pollutants are oxidized by the holes either directly or indirectly.

Photocatalytic reduction of Cr(VI) ion has been investigated several times; The existing researches in the literature, on the reduction of chromium, are about the application of OFAT in very high concentrations of TiO_2 (on the level 103 mg/L or above) (14,15). In the this research, photo-reduction was conducted using small amounts of TiO_2 particles, and to better evaluate the Cr(VI) reduction efficiency, the RSM methodology based on CCD was used. Low dosage catalyst loading practically resolves separation and regeneration problems. TiO_2 initial dosage and three important operational variables including pH, temperature and time were contemplated to study the effect of these on the reduction efficiency (RE) of chromium and to evaluate the optimum conditions. In order to realize the impact of

other factors such as inorganic anions and hole scavengers, a number of experiments were designed and performed on the Cr(VI) reduction efficiency. Finally, to put this into practice, the process performance is evaluated from the aspect of reactions kinetics, process efficiency and energy consumption.

Aims of this study:

The aims in this research were to demonstrate the successful application of CCD using a very low dosage of TiO_2 in a sono-photo reactor as a suitable reactor; and the impact of inorganic and organic species on the photocatalytic reduction efficiency.

Materials & Methods

Chemicals

All the used chemicals used in this research were of analytical grade (purity $>99.5\%$). TiO_2 (P-25, purity $>99.5\%$, 75% anatase, 25% rutile) was obtained from Plasma Chem. with $50\text{ m}^2/\text{g}$ and 21 nm specific surface area and mean particle size, respectively. The other chemicals including potassium dichromate, 1,5-diphenylcarbohydrazide (DPC), hydrochloric acid, sodium nitrate, sodium sulfate, sodium hydroxide, ethylene glycol, formic acid and citric acid were purchased from Merck Company. Deionized water (conductivity less than $0.08\ \mu\text{S}/\text{cm}$) was utilized for the solutions.

Procedure and analytical method

Photocatalytic experiments were conducted in a cylindrical sono-photo reactor made of glossy stainless steel with dimensions in 90 mm diameter and 200 mm in height (16). The light source was A 250 W mercury bulb with a maximum emission wavelength of 365 nm which was centrally-located; and it irradiated the solution around, directly. An ultrasound source with the following features was placed at the outside bottom of the reactor for both fine mixing and the catalyst particle dispersion during each experiment (28 kHz, 60 W). A water-flow jacket was used to keep the temperature constant during the reaction.

The Cr(VI) solution was prepared with 5.0 mg/L of potassium dichromate in deionized water, after adjusting the pH with either dilute hydrochloric acid or sodium hydroxide. One liter of the solution was added to the reactor and then predetermined amounts of the TiO₂ particles were added also, mixing and temperature adjustment were completed, and the UV bulb was switched 2 milliliter samples were withdrawn periodically from the solution. The aqueous samples were centrifuged to separate the nano particles. The Cr(VI) ions residual concentration was determined colorimetrically with 1,5-diphenylcarbohydrazide at $\lambda_{\max}=542$ nm (17). By utilizing this methodology, the percentage of reduction efficiency (RE) was calculated with the following equation at any moment:

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

[Cr(VI)]₀ and [Cr(VI)]_t in this equation represent the initial and time concentrations of Cr(VI), respectively.

Besides the variables applied in the RSM and optimization, the impact of other variables, like water matrix and hole scavengers, on Cr(VI) reduction were accounted for. To measure the impact of water matrix, the sample solutions containing determined amounts of dissolved salts such as NaNO₃ and Na₂SO₄ were used. Also, the batch tests were initiated by adding three hole scavengers to test the impact of them on the reduction efficiency. Furthermore, to investigate the reduction kinetics of Cr(VI), a power law kinetic model was applied, in optimum conditions. Also, the consumption of

electrical energy as a practical and economic parameter was evaluated.

Experimental design and statistical analysis

In the current study, the central component design (CCD), which is the most conventional type of response surface methodology (RSM), was employed to optimization of photocatalytic Cr(VI) reduction process. The required number of experiments (N) is obtained using $N = 2^k + 2k + C_0$ where “k” is the parameters number and C₀ is the replicate number of the central point, respectively (18). The variable parameters were the solution pH, TiO₂ dosage, time and temperature. The aggregate number of required experimental runs was 30. The quadratic equation determines the best mathematical relationship between variable parameters and the adsorption process efficiency:

$$y_{Pred} = \beta_0 + \sum_i^k \beta_i x_i + \sum_i^k \beta_{ii} x_i^2 + \sum_i^{k-1} \sum_{j=i+1}^k \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

where y stands for the forecasted response, β_0 the constant, β_i the linear, β_{ii} the quadratic and β_{ij} the interaction coefficients and “xi, xj” are the impactful process variables, m is the number of variables and ε is the residual error. Design Expert 8.0 software was applied to design the experiments and graphical investigation of the obtained data. The dependability of the defined model was explained via analysis of variance (ANOVA) and R² coefficient. The experimental ranges of the coefficients concerning Cr(VI) reduction are summarized in Table 1.

Table 1) Ranges and levels of the experimental variables

Variables	Levels and ranges				
	- α	(-1)	(0)	(+1)	+ α
Solution pH, x_{pH}	1.8	2.5	4.0	5.5	6.1
[TiO ₂] dosage (mg/L),	1.0	8.0	25.0	42.0	49.0
Temperature (°C), x_T	16.7	20.0	28.0	36.0	39.3
Reaction time (min), x_t	47.6	60.0	90.0	120.0	132.4

Results

The Mathematical Modeling

The outcomes of using CCD model to Cr(VI) ion reduction show that RE ranges from 8.9 to 82.2% in various conditions. In order to obtain the right data, the numbers were fitted experimentally to come up with the best removal efficiency equation. A quadratic equation was developed (Eq.3) which correlates with reduction efficiency as an initial pH function, TiO₂ dosage, temperature and time

$$RE = 28.36 - 12.06x_{pH} + 4.34x_{TiO_2} + 10.96x_T + 7.63x_i - 4.45x_{pH}x_T - 3.61x_{pH}x_i + 3.61x_i x_T + 4.68x_{pH}^2 - 4.61x_{TiO_2}^2 + 3.07x_T^2 + 2.07x_i^2$$

(3)

The analysis of variance (ANOVA) was performed for the quadratic developed model.

Table 2) Analysis of variance (ANOVA) for Cr(VI) reduction^a

Source of variations	Sum of squares	Degrees of freedom	Mean square	F-Value	Prob>F
Regression	8116.0	11	737.8	219.1	<0.0001
Residual	60.6	18	3.4		
Lack of Fit	52.1	13	4.0	2.3	<0.1773
Pure Error	8.5	5	1.7		
Cor Total	8176.6	29			

$$^a R^2 = 0.993, \text{adj-}R^2 = 0.988, \text{pred-}R^2 = 0.976$$

An adequacy check of the obtained applied model is essential in the experimental analysis. A suitable model can ensure an excellent estimation of real conditions. In Figure 1, the predicted values for Cr(VI) reduction of the model have been plotted versus the experimentally determined data. The R² determined coefficient was calculated as 0.992 for Cr(VI) reduction, indicating a good agreement between the predicted data and the experimental data.

Results in Table 2 demonstrate that the model of regression was determined to be (0.993), which demonstrates that 99.3% of the variables affects the determination of the reduction efficiency of Cr(VI). The amount of the Adj-R² (0.988) is also very adjacent to the corresponding R² value. Moreover, the value of pred-R² which is 0.9758 seems to demonstrate good agreement with that of Adj-R². The amount of prob>F which is less than 0.0001 and the 219.07 F-value imply that this equation is satisfactory. The latter criterion is obtained from mean square model divided by the residual mean square (18).

Also, the F-value which is lack-of-fit (an experiment to compare the variance which is lack-of-fit with the pure error variance) and is 2.35, implies that the lack-of-fit value is not significantly related to the pure error.

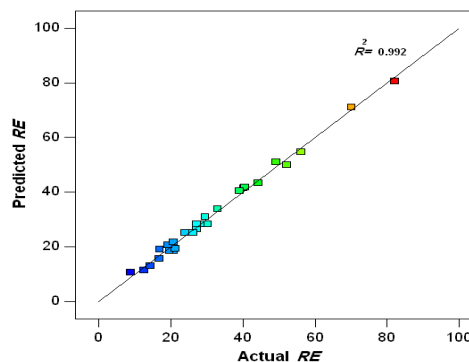


Figure 1) The plot of predicted versus actual Cr(VI) reduction percentage

Discussion

Evaluating Results and Chemical Aspects

The photocatalytic Cr(VI) reduction in the Cr(VI)/TiO₂ system was studied with 5 mg/L initial Cr(VI) concentration, TiO₂ loading of (8-50) mg/L, solution pH between 2.5 and 6.5 and temperature within the conventional range of 20 to 40 °C. As the photocatalyst loading increases to 33 mg/L, the efficiency of Cr(VI) reduction increases. When the catalyst amount was further increased, a negative effect was observed due to the blockage of light caused by excessive catalyst loading (19). At acidic pHs, dichromate (Cr₂O₇²⁻), hydrogen chromate (HCrO₄⁻), and the chromate (CrO₄²⁻) anion species are adsorbed onto the positively charged catalyst surface (20). It has been pointed that the redox potential of Cr(VI)/Cr(III) pair decreases by 98 mV per pH unit (21). Therefore, the presence of acid sites on catalyst surface may favor Cr(VI) reduction. Results also show that Cr(VI) photocatalytic reduction rises with any temperature increase, from 20 to 36 °C and then remains almost constant, perhaps due to disfavorable effect of temperature on adsorption; however, a contradicting variation was relevant with pH. Furthermore results show that RE increases as the reaction time increases; however, the variation is more respondent at low pHs and high temperatures, exhibiting a more pleasant reaction. After screening the factors and their interactions, a maximum of 81.5% Cr(VI) reduction is predictable with titania dosage of about 33 mg/L, and other conditions including pH=2.5, T=35 °C and t=120 min. The confirmatory experiment run an efficiency of 80.6% of Cr(VI) under these conditions (Figure 2). This closeness confirms the validity of the model reliability. It was also identified that the Cr(VI) photocatalytic reduction obeys the first order kinetic model. The rate constant of Cr(VI) photocatalytic reduction at the mentioned conditions was $1.37 \times 10^{-2} \text{ min}^{-1}$.

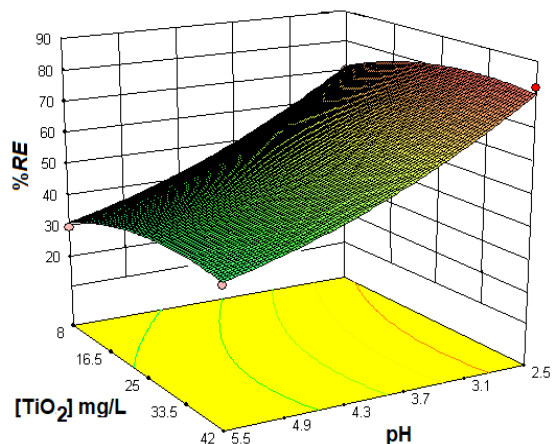
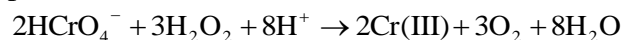


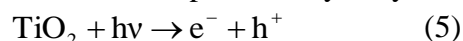
Figure 2) The response surface plots for Cr(VI) reduction under best conditions: [TiO₂]=33 mg/L, pH=2.5, T=35 °C and t=120 min

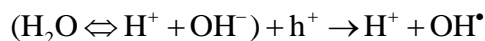
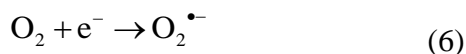
To investigate the contributing branches in the reduction; experiments were performed under optimum conditions either in the presence (photocatalysis) or in the absence (photolysis) of titania. The trend of Cr(VI) concentration variations during the processes time is depicted in Figure 3. As shown in the inset figure, obtained REs at two typical moments, for both the cases. The RE exceeds 60% and 80% for the photocatalysis, and 41% and 62% for the photolysis, after 60 and 120 min, respectively. These indicate that photocatalysis operates more significantly and effectively than the photolysis alone; however, UV irradiation alone is an acceptable method. It can be said that the cavitation process occurs in the solution and during aqueous sonolysis, reactive radicals such as hydroxyl radicals, are generated and joined together to form H₂O₂ (22) which contributes in the reduction of Cr(VI) (Eq. 4) in the photolysis process (23).



(4)

The higher possibility of H₂O₂ photocatalytic production in an acidic condition (following equations) (24,25) can also be a reason for higher efficiencies in photocatalytic systems.





(7)

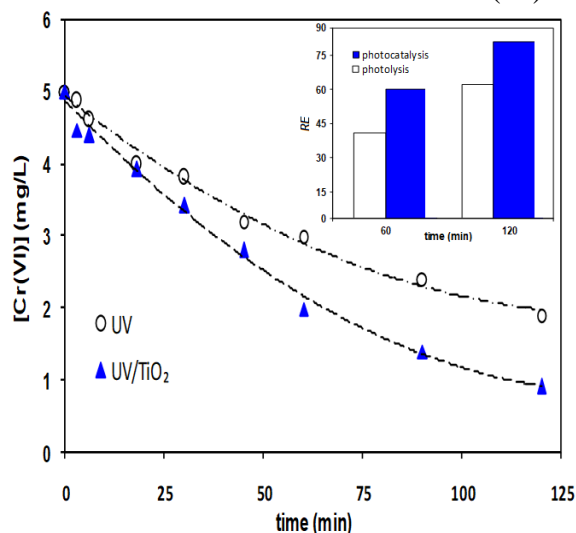
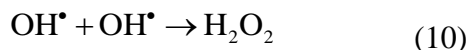
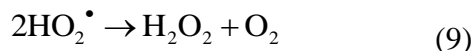
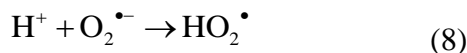
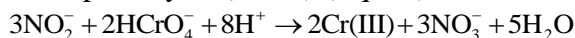


Figure 3) The variation of Cr(VI) concentration versus time; the inset figure presents a comparison of RE values after two different times for the photolysis and photocatalysis processes; pH=2.5, [TiO₂]=33 mg/L and T=35 °C

Effects of inorganic anions

NO₃⁻, Cl⁻ and SO₄²⁻ are inorganic anions that are usually present in chromium containing wastewaters. Inorganic anions can play the role of scavenging photo-generated hydroxyl radicals and holes- that are valance-band- on the semiconductor photocatalysts and consistently, enhance the metal ions photocatalytic reduction (26). To do so, the effect of NO₃⁻ and SO₄²⁻ anions on Cr(VI) reduction was studied with 50 mg/L nitrate or sulfate ion, which originated from NaNO₃ or Na₂SO₄ salt, being present in the solution; and the outcomes were illustrated in Figure 4. The addition of NO₃⁻ and SO₄²⁻ anions increased Cr(VI) photoreduction. The holes may be captured by sulfate or nitrate ions that cause the conduction-band electrons which are photo-

promoted to become more available for Cr(VI) reduction, and inhibit the electron-hole recombination. The results show that Cr(VI) photoreduction was greatly enhanced (by about 88.2%) when NO₃⁻ was used. This can be explained that the NO₃⁻ ions in the solutions are capable in reducing Cr(VI) directly through nitrite reductant ions (NO₂⁻) produced from NO₃⁻ photolysis (27,28) (Eq. 11):



(11)

and indirectly by generating H₂O₂ molecules (29), which leads to rapid reduction of Cr(VI) according to (Eq. 4) (23).

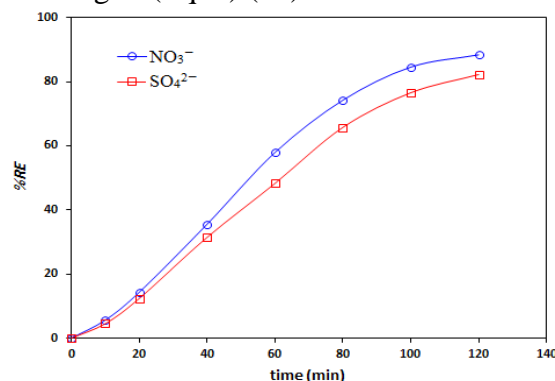


Figure 4) Effect of water matrix on Cr(VI) photocatalytic reduction; pH=2.5, [TiO₂]=33 mg/L, [NO₃⁻]=[SO₄²⁻]=50 mg/L and T=35 °C

Effect of Hole Scavengers

In this study, to promote photocatalytic reduction of Cr(VI) ion, three conventional hole scavengers including formic acid, citric acid and ethylene glycol of 100 mg/L were used. Hole scavengers can be used to inhibit the recombination. In Figure 5 shows that the reduction of Cr(VI) ion is strengthened (compared with no scavenger case) with ethylene glycol and formic acid; however, there was no pronounced change with citric acid. The photoreduction enhancements with the scavengers appeared to be in the following order: ethylene glycol>formic acid>citric acid with relevant. Enhancement of the photocatalytic reduction, with ethylene glycol

and formic acid presence, can be attributed mostly to the fact that ethylene glycol is first oxidized to oxalate ion ($C_2O_4^{2-}$) intermediate with irradiated TiO_2 in aqueous medium, and in turn, produces CO_2 by further oxidation. This recent species which is also produced by formic acid, has the ability to reduce $Cr(VI)$ and is converted to CO_2 itself. These reactions also inhibit the recombination (30,31). A simplified reduction mechanism with ethylene glycol scavenger function in Figure 6 is presented. In this research, by using 33 mg/L photocatalyst and in the presence of 50 mg/L nitrate anion about 88.2% RE was achieved without scavenger after 120 min and reached to 96.5% under the same conditions when ethylene glycol scavenger was used.

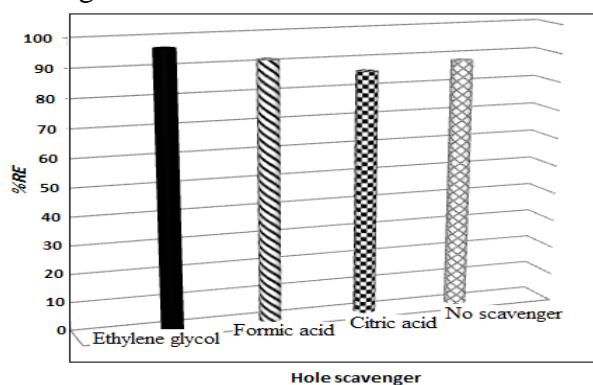


Figure 5) Effect of different hole scavengers (100 mg/L) on photoreduction of $Cr(VI)$ ion; $[TiO_2]=33$ mg/L, $pH=2.5$, $T=35^\circ C$, $[NO_3^-]=50$ mg/L and $t=120$ min

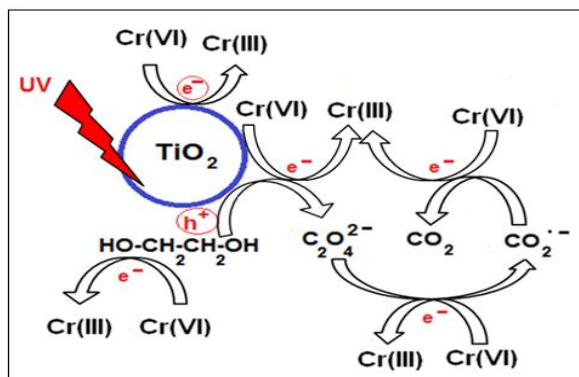


Figure 6) A simplified scheme of $Cr(VI)$ photocatalytic reduction mechanism in the presence of ethylene glycol

Kinetic Study

For practical applications, the kinetic model was investigated under the found optimum conditions. The RE reaches to 96.5% in solution after 120 min.

For this purpose, a power law kinetic model (32) in the form (Eq. 12):

$$r = -\frac{d[Cr(VI)]}{dt} = k[Cr(VI)]^n \quad (12)$$

where r , $[Cr(VI)]$, and k are the reaction rate, chromium concentration and rate constant, respectively and n is order reaction; to obtain kinetic parameters, the differential method of data analysis, based on the ions concentration variation versus time with 8 data points, was employed. Figure 7 presents the goodness of fitting with Eq. (12). The obtained kinetic parameters, in addition determination (R^2) coefficient for $Cr(VI)$ ion is presented in Table 3. The $Cr(VI)/UV/TiO_2$ process globally reveals a pseudo first order reaction.

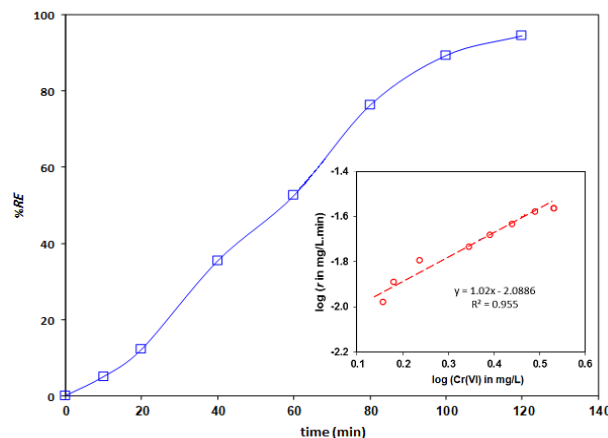


Figure 7) $Cr(VI)$ reduction efficiency versus time under conditions of $pH=2.5$, $[TiO_2]=33$ mg/L, $[NO_3^-]=50$ mg/L, $[Ethylene\ glycol]=100$ mg/L, $T=35^\circ C$ and $t=120$ min. Inset figure is the kinetic plot of the reactions under the same conditions

Table 3) Kinetic parameters of Cr(VI) reduction; pH=2.5, [TiO₂]=33 mg/L, [NO₃⁻]=50 mg/L, [Ethylene glycol]=100 mg/L, T=35 °C and t=120 min

Process	Order	Rate constant	R ²
Cr(VI)/UV/TiO ₂	0.95	2.04×10 ⁻² (mg/L) ^{0.05} /min	0.930

Energy Consumption Evaluation

There are several vital factors in selecting a waste treatment technology, such as, effluent outlet quality, operation conditions, economics and etc., which all are important, this is while the economics is often dominant (33). Electrical energy consumption, EE, is the main parameter in the photochemical processes economic that can be obtained (in kWh/m³) for first order reactions which proposed by IUPAC, as (34) Eq: 13 (33). Eq. 13:

$$E_E = \frac{1000Pt}{60V \log\left\{\frac{[\text{Cr(VI)}]_e}{[\text{Cr(VI)}]_i}\right\}} \quad (13)$$

where P is the electric power (kW) of the photochemical system, V is the volume (L) of

Table 4) Comparing the performance of different photocatalytic Cr(VI) reduction processes

[Cr(VI)] _i (mg/L)	[TiO ₂] (mg/L)	pH	T (°C)	UV dose (W/L)	time (min)	sacrificial reagent	RE (%)	E _E kWh/m ³	PE	Ref.
10	1000	2	25	7	300	-	70	66.9	1.05×10 ⁻³	(20)
150	2000	2.5	22	3000	60	formic acid	95	2305.9	2.06×10 ⁻⁵	(36)
150	2500	2.5	25	1000	180	-	80	4292.1	7.46×10 ⁻⁶	(37)
150	1000	3	25	1200	120	EDTA	90	2400.0	3.74×10 ⁻⁵	(38)
5	33	2.5	35	250	120	-	81	608.7	4.01×10 ⁻³	This work
5	33	2.5	35	250	120	Ethylene glycol	96.5	343.8	8.50×10 ⁻³	This work

Assessment of Process Performance

A valid criterion in this regard can be proposed, as process efficiency (PE), when RE is determined to unit EE and unit photocatalyst amount (32), presented in the practical equation of (Eq. 14):

$$PE = \frac{RE}{E_E \times [\text{TiO}_2]} \quad (14)$$

where E_E and [TiO₂] are consumption the electrical energy in kWh/m³ and the catalyst

the solution in the reactor, and t is the reaction time (min).

Accordingly, the electrical energy related to the reduction under conditions of 33 mg/L loading of TiO₂, initial pH 2.5, T=35 °C and in the presences of 50 and 100 mg/L nitrate anion and ethylene glycol, respectively after 120 min are 343.8 kWh/m³ for chromium. Considering the current electrical energy price in U.S. market as 0.06 US\$/kWh in 2017 (35), the electrical energy cost will be 20.6 US\$/m³ respectively. The EE values in this work in comparison with other reported processes (first order reactions and using nanoparticles for photocatalyst) are listed in Table 4.

loading in mg/L. Generally, PE reflects to the efficiency achievement with respect to the level of consumption energy as well as the used catalyst amount. Accordingly, the effect of temperature and the reaction progress with time are contributed in the PE via EE parameter. The PE value in the present work (under mentioned conditions) is significantly higher than relevant other reported processes (Table 4). This matter together with the significant achieved efficiency, confirm the high performance of the used process.

Conclusion

Potocatalytic reduction of Cr(VI) to Cr(III) in the presence of titanium dioxide nanoparticles was studied with solution pH, dose of TiO₂, temperature and reaction time factors. The most important results: (i) Application of a central composite experimental design helped in finding a maximum of about 81% reduction in solutions containing 5 mg/L of Cr(VI), under operating conditions of pH of 2.5; titania dose of only 33 mg/L and temperature of 35 °C during about 120 min of treatment process; (ii) The results show Cr(VI) photoreduction were greatly enhanced when NO₃⁻ was used in comparison with the addition of SO₄²⁻ anions; (iii) The activity of the used hole scavengers were appeared in the order of ethylene glycol>formic acid>citric acid; (iv) Appling the pertinent conditions, RE of 96.5% were achieved; (v) Pseudo first order reactions for Cr(VI) photocatalytic reduction is relevant; (vi) Electrical energy consumption analysis showed a relatively low required energy for the this study in comparison with a previous work; and (vii) Based on different criteria including economic parameters, the significant preference of the used process was demonstrated.

Footnotes

Acknowledgement:

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Conflict of Interest:

The Authors have no conflict of interest. Furthermore, authors declare that a part of the results in this study has been presented at the International Conference Engineering and applied sciences which were held in Dubai at 2016.

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