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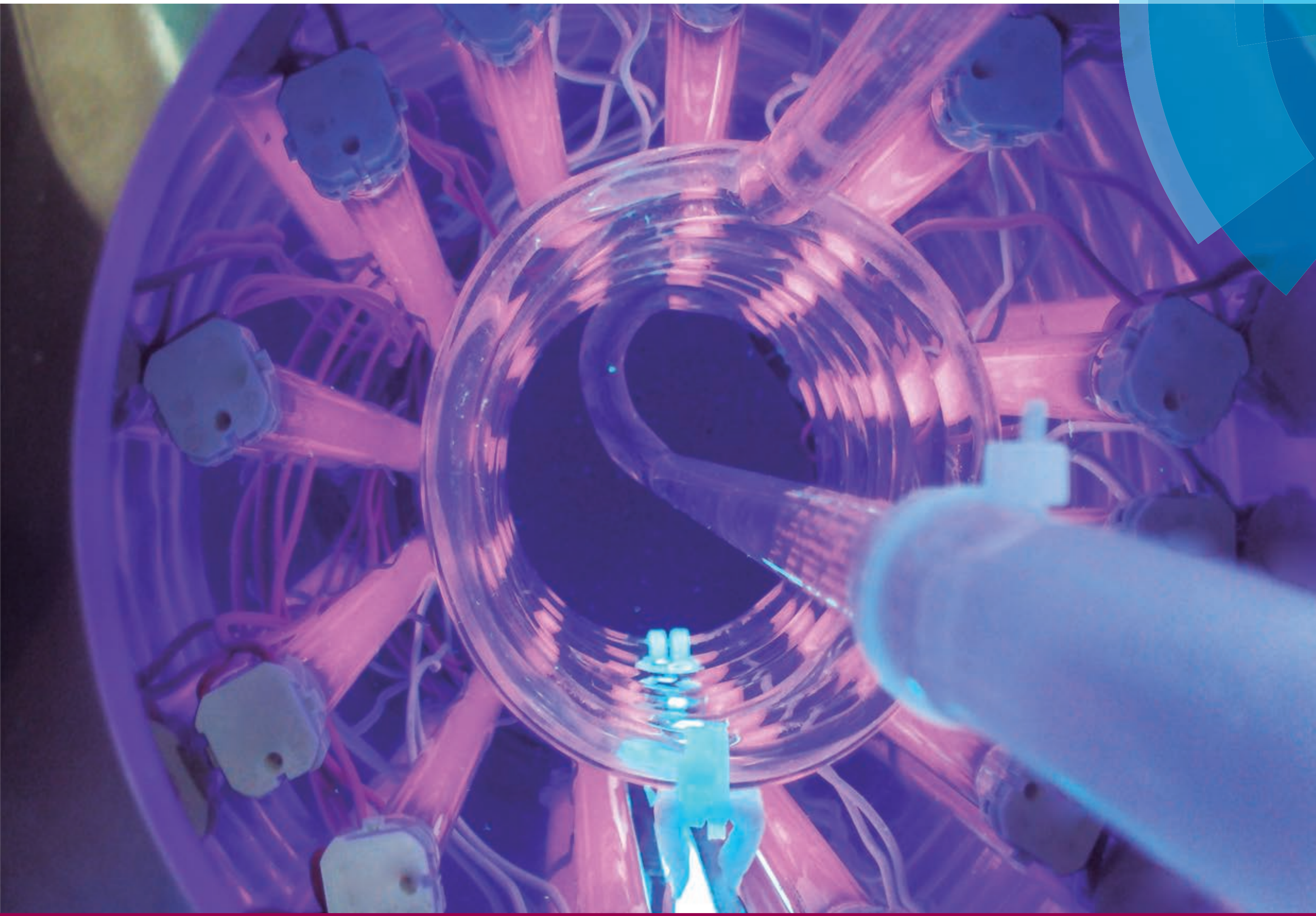

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Wastewater remediation using a spiral shaped reactor for photochemical reduction of hexavalent chromium

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The hexavalent chromium contained in wastewater of some industries is toxic to most microorganisms and potentially harmful to human health. The application of photochemical reduction of Cr(VI) in the treatment of wastewater from the electroplating industry was studied, and a continuous reactor in spiral shape made of borosilicate was designed and constructed (SSR). The statistical model of a circumscribed central composite design (CCCD) was used to investigate the influence of the amount of ethanol and the initial concentration of hexavalent chromium on total Cr(VI) reduction. A total Cr(VI) reduction of 46.0% was achieved under the optimal conditions established by the experimental design, using a synthetic Cr(VI) solution. In addition, the photochemical reduction of Cr(VI) follows pseudo first-order kinetics. The SSR exhibited similar behavior to that of the plug flow reactor (PFR), and presented higher photonic efficiency than the batch reactor. Finally, the designed reactor was effective when applied to real wastewater, showing a total Cr(VI) reduction of 51.8%, and its configuration is suitable for scale up.

1. Introduction

Heavy metals found in the environment originate mainly from the improper discharge of wastewater,[1] and leather tanners, paint and dye factories, producers of photographic material, electroplating companies, mines, and metallurgical and electronic plants are among the possible sources of chromium.[2–4] The electroplating industry is characterized by its excessive consumption of water and energy, and generation of large amounts of wastewater containing heavy metals such as copper, nickel, and chromium. Among these inorganic pollutants, hexavalent chromium is an important industrial metal that is considered a priority pollutant since it is toxic to most organisms.[5] This form of chromium is carcinogenic and mutagenic to animals and can cause irritation and corrosion to human skin.[6]

The methods generally employed for hexavalent chromium removal are chemical precipitation, adsorption, reverse osmosis, ion exchange, electrolysis, *etc.* However, most of these methods require either high amounts of energy or large quantities of chemicals.[3,4] The problems associated with conventional techniques have been the main reasons behind the attempts to develop alternative clean technologies for chromium remediation,[4] whereby photochemical reduction is one of these technologies.

Neat chromate(VI) is photochemically inactive, but its effective photoreduction is observed when irradiated in the presence of a sacrificial electron donor.[7–10] The photochemical reduction of Cr(VI) by alcohols in an acidic medium has been studied, and some pathways have been proposed. The most generally accepted mechanism (eqn (1)–(5)) consists of two-electron reduction of Cr(VI) giving rise to an aldehyde or ketone and a Cr(IV) species. The formation of the chromate(VI) ester is mostly assumed to be a necessary condition for redox or photoredox reactions.[7,8]

$$HCrO_4^- + ROH \leftrightarrow ROCrO_3^- + H_2O \tag{1}$$

$$ROCrO_3^- + h\nu \rightarrow Cr(IV) + \text{aldehyde/ketone} \tag{2}$$

$$Cr(IV) + Cr(VI) \rightarrow 2Cr(V) \tag{3}$$

$$3Cr(V) \rightarrow 2Cr(VI) + Cr(III) \tag{4}$$

and/or

$$Cr(V) + ROH \rightarrow Cr(III) + \text{aldehyde/ketone} \tag{5}$$

Literature review showed few studies on the photochemical reduction of Cr(VI) by alcohols,[8] phenol and its halogen derivatives,[9] and glycerol.[10] However, there were no systematic and comparative studies that analyze the effect of each parameter of the reaction, or the interaction between them, on photochemical reduction reactions of Cr(VI) with alcohols under

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UV and visible radiation. Furthermore, the application of sustainable treatments such as photochemistry with alcohols to remediate Cr(VI) present in wastewater discharges of electroplating industries has not been found in the literature. Therefore, we initiated a research line that aims to fill this gap.

In previous work, we studied Cr(VI) reduction by photochemistry with ethanol under UV and visible radiation; photocatalysis with TiO_2 in the presence of ethanol under UV radiation; and the application of these processes for the treatment of Cr(VI) containing wastewater from the electroplating industry. The experiments were carried out in a glass batch reactor irradiated with a mercury vapor lamp, with controlled temperature and agitation of the reaction medium. We concluded that the most suitable process for industrial application was photochemistry with ethanol under UV radiation, which presented 98.5% of total Cr(VI) reduction for real wastewater.[11] However, the design and construction of a large-scale reactor is essential to the industrial application of the photochemical process.

Thus, the main objective of this work was to design and build a semi-pilot scale reactor in order to enable the industrial application of photochemical reduction of hexavalent chromium in the treatment of wastewater from the electroplating industry. Initially, a spiral shaped reactor (SSR) was designed and built. Subsequently, the influences of the initial Cr(VI) concentration and ethanol amount were investigated using an experimental design, and the designed reactor was compared with the batch reactor used by Machado *et al.*[11] Finally, experiments were conducted using real wastewater from an electroplating plant.

2. Experimental section

2.1. Materials

Potassium dichromate (Fmaia) was used as it was received, and deionized and distilled water was used to prepare the solutions. Absolute ethyl alcohol (Nuclear) was used in the reactions of photochemical reduction of Cr(VI). Untreated wastewater containing Cr(VI) was collected directly from a storage tank in the electroplating plant. Information about the real wastewater is presented in Table 1.

2.2. Spiral shaped reactor (SSR)

A continuous reactor in spiral shape made of borosilicate (255 cm long and 1 cm diameter) was designed and built. The reactor was placed inside a stainless steel chamber (19.1 cm internal diameter and 42.4 cm height), containing 12 evenly distributed UV tubular fluorescent lamps (Xelux 8 Watt, 16 mm diameter). The radiation of the lamps was measured (2.5 mW cm^{-2}) at the beginning of each test using a radiometer (Cole–Parmer Instrument, Series 9811 Radiometer), and the total irradiated area was 801.1 cm^2. A centrifugal pump was used in order to circulate a Cr(VI) solution through the reactor and a storage tank, as shown in Fig. 1. The liquid samples were collected through a syringe-catheter system located in the storage tank. A flow rate of 100 L h^{-1} was measured using a rotameter and a reaction volume of approximately 2800 mL (spiral reactor, pipes and storage tank) was used.

Table 1 Information about the real wastewater

Information	Quantity
Hexavalent chromium	1100 mg L^{-1}
Color	Orange
pH at 25 °C	2.9
COD	<5 mg L^{-1}
Total aluminum	3.1 mg L^{-1}
Total copper	179 mg L^{-1}
Total nickel	36.1 mg L^{-1}

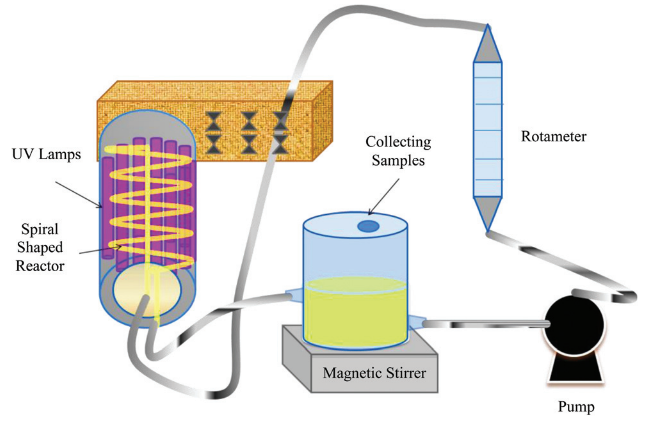

Fig. 1 Spiral shaped reactor apparatus.

The synthetic Cr(VI) solution was prepared from potassium dichromate ($K_2Cr_2O_7$) and was kept under vigorous magnetic stirring for approximately 1 hour. For the photochemical reduction reactions with ethanol, carried out in the SSR, an aqueous Cr(VI) solution of a known concentration (100 mg L^{-1}) was added to the storage tank and diluted with deionized and distilled water in order to obtain the desired initial Cr(VI) concentration (16, 20, 30, 40 and 44 mg L^{-1}). Then, a known volume of ethanol was added to the storage tank, and the solution's pH was adjusted. These reactions occurred in 1 hour and the progress of the photochemical reduction reaction of Cr(VI) was monitored by collecting samples at fixed intervals (0, 15, 30, 45 and 60 minutes). Subsequently, the samples were analyzed using a spectrophotometer (Varian Cary 100) by absorbance measurement at a wavelength of 348 nm.[3,5,12,13]

In the photochemical reduction reactions using real wastewater, the wastewater was added to the storage tank along with a known volume of ethanol. These reactions occurred in 6 hours and the samples were collected at fixed intervals. Subsequently, the samples were diluted and analyzed using a spectrophotometer.

All experiments were carried out maintaining the solution's initial pH and operating temperature constant at 2.0 and 30 °C, respectively. We decided to do so based on the literature[3,5,8] and our previous results.[11] An increase in the reaction rate was observed when the acidity increased. This was interpreted in terms of higher susceptibility of $HCrO_4^-$, in comparison with CrO_4^{2-}, to undergo reduction and chromate(VI) ester formation.[8] Moreover, Mytych *et al.*[8] reported that the reaction rate is insensitive to temperature within 283–303 K.

2.3. Methodology of the response surface

The statistical model of a circumscribed central composite design (CCCD) was employed for the optimization of photochemical reduction of Cr(VI) with ethanol in SSR. The design consists of three types of points: 2^k cube points (factorial design points), 2^k axial points, and N_0 center points. In the present case, three replications at the center point and two numbers of factors (k) were utilized leading to a total of 11 experimental runs. The distance of axial points from the center points (α) was fixed at 1.41, based on the number of factors chosen for the experiment. The variables (factors) used in the study were the initial Cr(VI) concentration (X_1) and the ethanol amount (X_2). The percentage of the total reduction (Y) of Cr(VI), as given by the following equation, was considered as the response.

$$Y = \left[\frac{C_0 - C_t}{C_0}\right] \times 100 \tag{6}$$

where C_0 is the initial Cr(VI) concentration and C_t is the concentration achieved after the photochemical treatment. The real values of the process variables (factors), their variation limits and number were selected based on the preliminary experiments. The coded values along with real values of the factors are shown in Table 2.

A regression model was proposed, and results were analyzed using Statistica software version 10. The model was statistically validated with the same software using the analysis of variance (ANOVA). The quality of the fit for the polynomial model was expressed by the coefficient of determination (R^2). Model terms were selected or rejected based on the probability value within a 95% confidence interval (or 5% significance level).

2.4. Calculation of the photonic efficiency (ξ)

The photonic efficiency, ξ, being defined as the ratio of the reaction rate and the incident photon flux[14–18] was calculated according to Bouzid *et al.*,[18] to compare the efficiency of spiral shaped and batch reactors.

Table 2 Real and coded levels of the independent variables

Factors	Real values of coded levels				
	$-\alpha$	-1	0	+1	$+\alpha$
Cr(VI) concentration (mg L^{-1})	16	20	30	40	44
Ethanol amount (%) ($V_{ethanol}/V_{total}$)	0.8	1.5	3.25	5.0	5.7

3. Results and discussion

3.1. Experiments of photochemical reduction of Cr(VI) with ethanol carried out in a SSR

The SSR flow was analyzed using a tracer injected by pulse. The results showed that the reactor presented similar behavior to that of a plug flow reactor (PFR).

Table 3 shows the experimental design used for the photochemical reduction reactions of Cr(VI) with ethanol under UV radiation. Some variables were unaltered in all these tests (flow of 100 L h^{-1}, UV 2.5 mW cm^{-2}, 30 °C and initial pH of 2.0). The response factor (Y) was defined as the percentage of total Cr(VI) reduction after 1 hour of reaction.

The polynomial (eqn (7)) obtained from the multivariable analysis, with a coefficient of determination (R^2) of 0.9641, indicated a good fit between the experimental data and the statistical model. In the polynomial equation, the values in parentheses represent the standard deviation for each coefficient, and x_1 and x_2 represent the coded values of the initial Cr(VI) concentration and ethanol amount, respectively.

$$Y(\%) = 24.7(\pm 0.8) - 4.7x_1(\pm 0.9) + 12.1x_2(\pm 0.9) \tag{7}$$

Additionally, these reactions proved to be dependent on the initial Cr(VI) concentration and the ethanol amount, with linear interactions. The linear coefficient of the effect of the initial Cr(VI) concentration was negative, indicating that the lower the initial Cr(VI) concentration, the higher the total Cr(VI) reduction, while the effect of the ethanol amount was positive, indicating that the higher the ethanol amount, the higher the total Cr(VI) reduction. As can be seen in Table 3, run 3 resulted in the greatest total Cr(VI) reduction at 46.0% with the initial Cr(VI) concentration at 20 mg L^{-1} and the ethanol amount at 5% (v/v). These conclusions are evident in Fig. 2, which depicts the response profiles for the experimental data obtained.

On comparing the results obtained using the SSR with the results obtained from the batch reactor studied in our previous work,[11] the same behavior as the parameters evaluated in the

Table 3 Circumscribed central composite design of experiments along with observed and predicted values of response

Run	Coded levels of variables		Actual levels of variables		Response (% total reduction)	
	x_1	x_2	X_1	X_2	$Y_{observed}$	$Y_{predicted}$
1	−1	−1	20	1.5	15.9	17.3
2	1	−1	40	1.5	9.3	7.9
3	−1	1	20	5.0	46.0	41.5
4	1	1	40	5.0	34.0	32.1
5	$-\alpha$	0	16	3.25	30.8	31.3
6	$+\alpha$	0	44	3.25	17.2	18.0
7	0	$-\alpha$	30	0.8	7.3	7.6
8	0	$+\alpha$	30	5.7	37.1	41.8
9	0	0	30	3.25	24.5	24.7
10	0	0	30	3.25	24.4	24.7
11	0	0	30	3.25	24.8	24.7

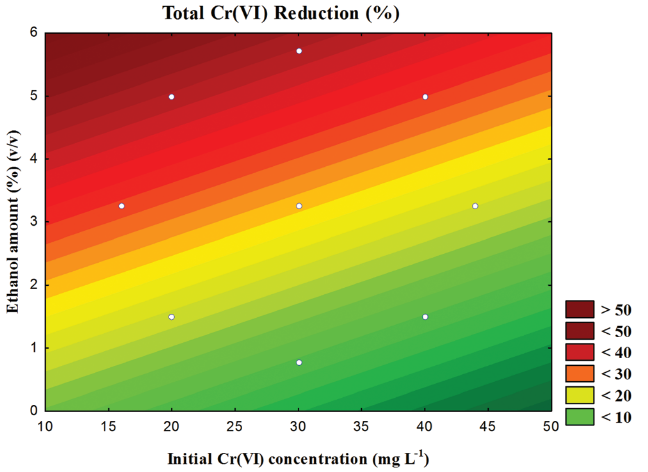

Fig. 2 Response profiles showing the percentage of Cr(VI) reduction.

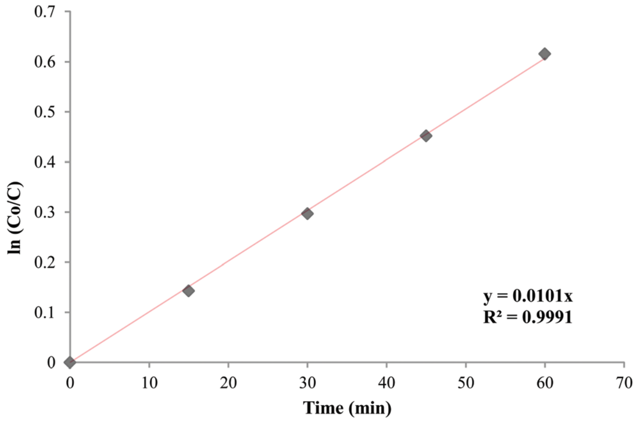

Fig. 3 Pseudo first-order kinetics to photochemical reduction of Cr(VI). ($C_{Cr(VI)}$ = 20 mg L^{-1}, $V_{ethanol}$ = 5.0% (v/v), pH = 2.0, T = 30 °C, and 2.5 mW cm^{-2}.)

Table 4 Specification about the reactors

Specifications	Batch reactor[a]	SSR
Total Cr(VI) reduction	96.1%	46.0%
Reaction volume	150 mL	2800 mL
Reaction time	1 h	1 h
Irradiation	5.8 mW cm^{-2}	2.5 mW cm^{-2}
Irradiated surface area	56.7 cm^2	801.1 cm^2
Photonic efficiency	1.43%	2.52%

[a] The reactor used by Machado *et al.*[11]

statistical model was observed. Table 4 presents information about the batch reactor and SSR.

Table 4 shows that the batch reactor presented higher total Cr(VI) reduction (96.1%) than the SSR (46.0%) under maximum yield conditions. However, the SSR is more efficient than the batch reactor, presenting a photonic efficiency of 2.52% compared to 1.43% for the batch reactor.

3.2. Kinetics of reduction reaction

Fig. 3 presents the reaction kinetics of photochemical reduction of Cr(VI), under maximum yield conditions established in the experimental design, considering that this reaction occurs by pseudo first-order kinetics.[8] In Fig. 3, a line passing through the origin with a correlation coefficient (R^2) of 0.9991, indicating that the photochemical reduction of Cr(VI) follows pseudo first-order kinetics, can be observed. Thus, the specific reaction rate, k, for these conditions is equal to 0.0101 min^{-1}.

3.3. Tests with real wastewater

Tests were performed using real wastewater from the electroplating industry in order to verify the industrial application of the SSR. Experiments were carried out with different ethanol amounts (20 and 40% (v/v)) and 6 hours of reaction. The results are shown in Table 5, along with the results obtained for the batch reactor. A total Cr(VI) reduction of 49.2% and 51.8% was observed for an ethanol amount of 20% and 40%, respectively. These values of total reduction were higher than those obtained under the maximum yield conditions established in the experimental design, containing a synthetic Cr(VI) solution (46.0%). Thus, the spiral shaped reactor, which was designed and built, was effective when applied to real wastewater, and its configuration is suitable for scale up.

4. Conclusion

The application of photochemical reduction of hexavalent chromium, using a spiral shaped reactor, in wastewater remediation was studied. The results obtained showed that

Table 5 Comparison of total Cr(VI) reduction

Reactions	Reactor	TR[b] synthetic	Experimental conditions	TR wastewater
Photochemistry, ethanol, UV	SSR	46.0%	$C_{Cr(VI)}$ = 1100 mg L^{-1}, pH = 2.2, ($V_{ethanol}$ = 20%), and 2.5 mW cm^{-2}, 6 hours of reaction	49.2%
Photochemistry, ethanol, UV	SSR	46.0%	$C_{Cr(VI)}$ = 1100 mg L^{-1}, pH = 2.2, ($V_{ethanol}$ = 40%), and 2.5 mW cm^{-2}, 6 hours of reaction	51.8%
Photochemistry, ethanol, UV	Batch[a]	96.1%	$C_{Cr(VI)}$ = 1100 mg L^{-1}, pH = 2.0, ($V_{ethanol}$ = 40%), and 5.8 mW cm^{-2}, 6 hours of reaction	98.5%

[a] Results presented by Machado *et al.*[11] [b] Maximum yield conditions established in the experimental designs.

total Cr(VI) reduction increases with an increase in ethanol amount and decreases with an increase in initial Cr(VI) concentration. The spiral shaped reactor (SSR), which was designed and constructed, presented higher photonic efficiency than the batch reactor. The Cr(VI) photochemical reduction follows pseudo first-order kinetics. Furthermore, the SSR is effective when applied to real wastewater, and its configuration is suitable for scale up.

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