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Optimization by factorial design of copper (II) and toxicity removal using a photocatalytic process with TiO_2 as semiconductor

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ABSTRACT

The photochemical process of Cu (II) reduction by heterogeneous photocatalysis using titanium dioxide (TiO_2) Degussa P-25 and a 254 nm UV-C lamp was studied. The aim of this work was to determine the efficiency of the photocatalytic process to remove 100 ppm of copper (II) ion concentration from a water solution.

A statistics-based experimental design with response surface methodology (RSM) was employed to investigate the effect of operating conditions on photocatalytic reduction. The experimental results were evaluated using multivariate analysis with the program MODDE 7.0. The parameters studied were catalyst mass, pH, and reaction time. After optimizing the variables, degradation kinetics were performed to corroborate the model. The regression analysis with R^2 value of 0.98 shows a close fit between the experimental results and the model predictions. The value obtained for the reaction rate constant was 0.0246 min^{-1}. Three-dimensional response surface plots were used to visualize parameter interactions. The optimum pH (4.3) and titanium dioxide mass (0.5 g) achieved the highest efficiency, reaching 80% of copper (II) ion reduction. Two different bioassays, using *Daphnia magna* and *Pseudomonas aeruginosa*, were performed to determine acute toxicity reduction after the treatment. The results obtained show that the bio-toxicity reduction reached 80%.

1. Introduction

Metal and non-metal contamination is one of the most important environmental problems [1,2]. Human activities annually increase in several billion tons the amount of metal in the terrestrial medium, and the total annual metal toxicity exceeds the total annual toxicity generated by the radioactive and organic wastewater. Effluents generated by industrial processes (including hydrometallurgical, superficial washing, and rinsing operations), metallic surface treatment, and in photography contribute polluting metallic agents to the environment, increasing metal accumulation in effluents with significant economic losses in raw materials [3,4].

Rock formation and volcanic activity produce the basal presence in natural waters with concentrations between 1.0 and 20 μg/L in superficial freshwaters and 0.15 μg/L in marine waters. Human activities increase their presence through emissions from mining and other activities where the copper ion is emitted [5–7]. In oxygenated atmospheres, copper is found in oxidation state (2+), which is predominant in superficial natural waters. In its oxidation state (2+), in addition to the free ion (Cu^{2+}), copper forms a complex with inorganic ligands such as H_2O, OH–, $CO_3{}^{2-}$, Cl^{1-} and $SO_4{}^2$; it is also found as a complex with organic ligands with phenolic and carboxylic groups [8–10].

Copper's oxidation state (1+) has a reduced presence in aquatic atmosphere. The free ion in oxidation state (1+) is unstable in solutions and tends to be disproportional with respect to copper (2+). Additionally, it remains elementary unless stabilized by a ligand agent. Copper (1+) is stable in forms such as cyanide, sulphide and fluoride. Copper is an essential micronutrient for the vertebrates and invertebrates, although it can be toxic for aquatic biota at relatively low concentrations [11–14]. The biodisponsibility of copper for the aquatic organisms depends on the total concentration and speciation, where its toxicity is mainly associated with the ionic form (Cu^{2+}). Several studies suggest the existence of a direct relation between copper toxicity and certain environmental variables [15–18]. Copper toxicity has been observed to increase when water hardness and dissolved oxygen diminish, decreasing in the presence of chelating agents, humic acids, amino acids and solids in suspension. Previous research found that toxicity in fish also varies inversely with respect to salinity, alkalinity, pH and size; other studies performed with several animal species indicate that copper toxicity also diminishes when total organic carbon and interaction with other metals in the water increase. Therefore, copper ions generally considered to be non-toxic can be toxic, interfering

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Table 1
Experimental matrix of variables and corresponding experimental and predicted response to optimize copper (II) removal.

Experimental	TiO_2 (g)	pH	Time (min)	Cu (II) removed (%) observed	Cu (II) removed (%) predicted
1	0.75(0)	2(−1)	15(−1)	67.90	64.4
2	1(1)	2(−1)	15(−1)	65.30	66.70
3	0.5(−1)	3.5(0)	15(−1)	74.28	78.20
4	0.75(0)	3.5(0)	15(−1)	78.01	76.95
5	1(1)	3.5(0)	15(−1)	75.91	76.22
6	0.5(−1)	5(1)	15(−1)	71.80	77.41
7	0.75(0)	5(1)	15(−1)	72.10	73.09
8	1(1)	5(1)	15(−1)	71.40	69.29
9	0.75(0)	2(−1)	67.5(0)	61.10	64.75
10	1(1)	2(−1)	67.5(0)	67.20	67.30
11	0.5(−1)	3,5(0)	67.5(0)	77.18	77.80
12	0.75(0)	3.5(0)	67.5(0)	76.71	76.78
13	1(1)	3.5(0)	67.5(0)	74.95	76.26
14	0.5(−1)	5(1)	67.5(0)	68.20	76.47
15	0.75(0)	5(1)	67.5(0)	71.40	72.36
16	1(1)	5(1)	67.5(0)	68.80	68.77
17	0.75(0)	2(−1)	120(1)	65.80	65.04
18	1(1)	2(−1)	120(1)	66.60	67.80
19	0.5(−1)	3.5(0)	120(1)	73.68	77.34
20	0.75(0)	3.5(0)	120(1)	79.62	76.51
21	1(1)	3.5(0)	120(1)	74.42	76.20
22	0.5(−1)	5(1)	120(1)	69.10	75.40
23	0.75(0)	5(1)	120(1)	66.70	71.50
24	1(1)	5(1)	120(1)	70.50	68.14
25	0.75(0)	3.5(0)	67.5(0)	77.31	76.78
26	0.75(0)	3.5(0)	67.5(0)	77.90	76.78
27	0.75(0)	3.5(0)	67.5(0)	78.17	76.78

with oxygen transport and metabolism, causing hypoxia with the corresponding alteration of the ATP route synthesis, inducing the death of aquatic vertebrates and invertebrates [19–24].

Metals are not biodegradable, remaining in ecosystems for a long time. As a result, many technologies such as precipitation, electrolysis, chemical oxidation, adsorption, chelation, or biological processes have been studied, although they are expensive [25–29]. Photocatalysis is a promising technology that can be applied to efficiently remove metal ions by reduction [30,31]. The fact that the TiO_2 Degussa P-25 has a band gap potential between −0.3 and +2.9 eV with respect to the normal hydrogen electrode (ENH) has determined the rank for anode and cathode reactions that are thermodynamically possible for TiO_2 [32].

The authors [33–35] indicated two mechanisms that could be occurring in the metallic ions removed by photocatalysis: (1) direct reduction by photogenerated electrons and (2) indirect reduction by intermediaries generated by oxidized organic compounds or oxidative processes produced by others metal involved in the process. Direct reduction is the simple route where metallic species, such as the copper ion, act as electron acceptor replacing oxygen. On the other hand, in the absence of organic compounds and electron acceptors, the copper can act as an electron trap being reduced to non-hazardous states by photocatalytic reduction [36–38]. Since the experimental design has been less studied to evaluate the optimization process, principally the capacity of titanium dioxide for reducing the metal ions [39], this study used response surface methodology to optimise the most influential parameters with respect to copper (II) ion reduction.

2. Experimental

2.1. Experimental design

A multivariate experimental design was implemented and analyzed with the program MODDE 7.0. The experimental variables studied were catalyst (TiO_2) concentration (g/L), reaction time (min) and pH, obtaining a quadratic matrix of 27 experiments. The rank of values associated with the variables: catalyst TiO_2 was between 0.5 and 1.0 g/L, reaction time (min) ranged between 15 and 120, and pH ranged between 2 and 5. Each experiment was performed with 100 mL of 100 mg L^{-1} of copper II solution.

Table 1 presents the experimental matrix generated by the program with the coded values (minimum (−1), maximum (1) and the central point (0)) and uncoded variables, relating them to each other.

Prior to photocatalytic treatment, the pH was adjusted with a bifunction Sen Tix WTW Inolab pH. Lamp radiation was measured with a radiometer PMA 2200 with a detector PMA 2120 UV.

2.2. Heterogeneous photocatalytic process

The heterogeneous photocatalytic process was carried out in a spherical reactor with TiO_2 Degussa P-25 in suspension and the

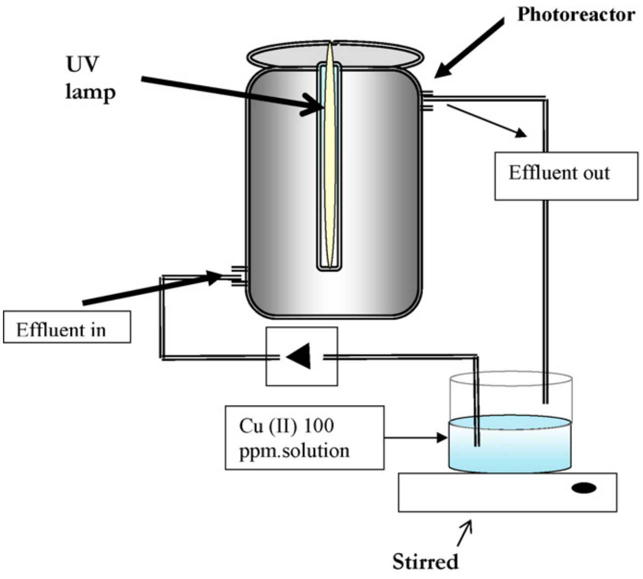

Fig. 1. Photoreactor used in the photocatalytics process.

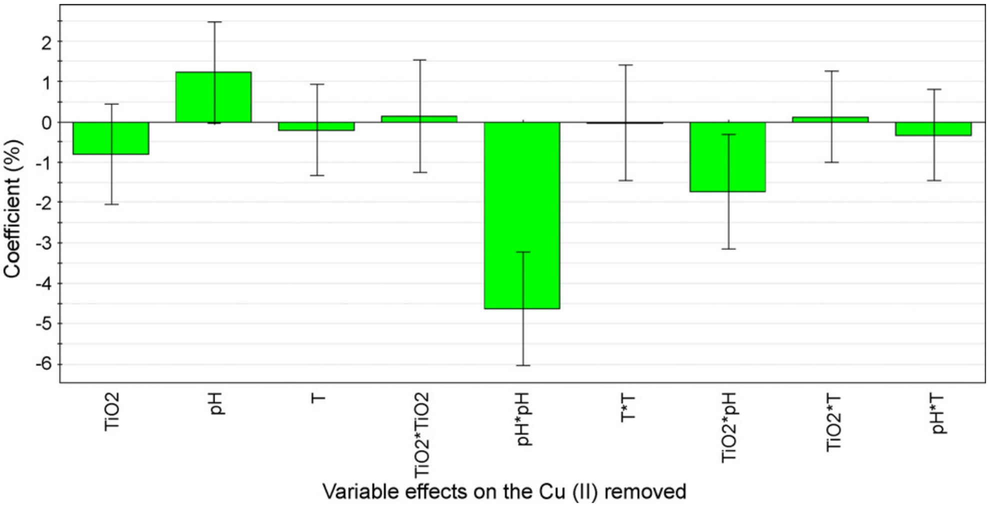

Fig. 2. Analysis the parameters influence over copper (II) ions reduction with 95% of confidence.

solution was irradiated with a UV-C lamp Philip (254 nm, 120 W). The lamp was suspended vertically inside the quartz glass cylinder in the middle of the reactor as shown in Fig. 1. The reactor containing 100 mL sample of the solution was constantly stirred using a magnetic stirrer. Prior to each experiment, the lamp was stabilized for 2 min.

The remaining copper (II) in solution was quantified with an atomic absorption flame spectrophotometer model GBC 902, the carrier gas was air–acetylene and the radiation source was a copper hollow cathode lamp with 324.7 nm and 4 mA current.

2.3. Toxicity assays

2.3.1. Toxicity assays for Daphnia magna

Acute toxicity was determined by exposing *Daphnia magna* nematodes before and after photocatalytic treatment. To assess the LC_{50} values, five dilutions were performed for every sample step and the respective control. For all dilutions, 20 nematodes were placed in four replicates with 10 mL of solution and five specimens. The test was maintained for 24 and 48 h at a temperature of 20 °C, assessing the individual mortality (%) in each dilution. The mortality was analyzed using the Probit statistical method and the LC_{50} values were calculated with the program TOSTAD.

2.3.2. Toxicity assays for Pseudomona aeruginosa

The bacterial *Pseudomona aeruginosa* was used to obtain a different response at the residual copper toxicity with the species located in a main level in the trophical chain. This species was chosen because it is a highly abundant environmental bacterium and it also has different genes that favour compound degradation in environment.

The McFarland method was used to determine bacterial concentration. This method compares bacterial biomass with a well-known turbidity tube (McFarland tube). The bacterial broth was prepared with 5 mL of tripticase agar and the bacterial inocula, diluting with distilled water until obtaining Mc Farland turbidity. Then, the inoculums were incubated during 24 h. Subsequently, 100 μL of inocula were added into different tubes containing five copper (II) dilutions, 2.5, 5.0, 10, 15 and 20 ppm, with the respective control. Each inoculum was seeded in duplicate and incubated at 37 °C during 5 days. The increasing biomass was controlled every 24 h.

2.4. Multivariate analysis

The mathematical multivariate analysis method is a powerful tool to optimize processes, simultaneously determining variables as others are modified. With this method, the reaction's operational variables can be simultaneously changed in order to identify the weight of each one and the relation between variables, indicating synergies and antagonisms between them. When the working range chosen for the operational variables is appropriate, the system can be optimized to find the suitable working region.

Most research in photocatalysis consists in monovariate analysis, even when this procedure leads to error when interactions between the variables occur. Thus, an experimental design that simultaneously studies different variables, such as multivariate analysis is necessary to obtain an empirical mathematical equation for factors as well as a response map that considers parameter influence in the process. Indeed, multivariate analysis can be used to draw a map of estimative response to determine the optimal response zone, thus obtaining more reduction at less cost in shorter time.

Multivariate analysis provides a polynomial equation describing the relation between experimental variables and the final response is expressed as percentage. This methodology was used to study the capacity of TiO_2 in copper (II) reduction depending on reaction time and pH. The experimental matrix for the three variables is a quadratic model with 27 experiments. The general polynomial response (Eq. (1)), a quadratic polynomial model, represents the associated response function, where b_0 is the average value of the experimental response, b_1 is the main effect of the coded variable X_1, b_2 is the second effect and b_3 is the third effect, b_{11}, b_{22} and b_{33} are the quadratic effects of coded X_1, X_2 and X_3 respectively, and b_{12}, b_{13} and b_{23} are the interaction effects between the respective coded variables.

$$\begin{aligned} Y_1 = {} & b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_{12} + b_{22}X_{22} + b_{33}X_{32} \\ & + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \end{aligned} \tag{1}$$

When working with two values for each variable (maximum and minimum) and n factors, the minimum number of tests will be equal to $2n$. This number of experiments can vary if intermediate levels are also identified in order to obtain a greater proximity to each variable's effect.

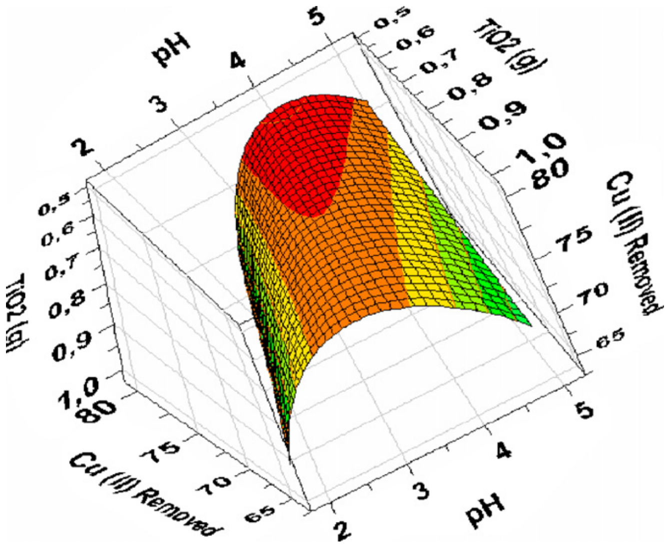

Fig. 3. Contour plots to the experimental design for the copper (II) removal.

Experimental optimization is used when the variables' effects depend on each other (interactive effect). Thus, the model draws the contour points (lines or curves), generating the response surfaces and predicting response values in the region of interest.

3. Results and discussion

3.1. Photocatalysis process optimization

The results of the quadratic model for the percentage of copper (II) removed are shown in Table 1. The optimum values for the selected variables were obtained by solving the regression equation and by analyzing the response surface contour plots. Fig. 2 shows the influence of each variable on the response and the correlation coefficient values for the statistics with 95% confidence. These values are close to 1, which means that the regression model provides an excellent description of the relationship between the independent variables and the response, where R^2 represents the fraction of the variation of the response explained by the model and Q^2 is the fraction of the variation of the response that can be predicted by the model. Fig. 3 shows the response surface of the quadratic matrix of 27 experiments, where the maximum response zone for copper (II) reduction is observed at pH between 3.5 and 4.5 and catalyst between 0.5 and 0.75 g. The optimal conditions for the copper (II) ions reduction (80%) was observed at pH 4.3 with an irradiation time of 67.5 min for 0.5 g of TiO$_2$.

Other studies [40–42] have found that an inorganic compound reduction is greater under acidic conditions, specifically at pH values near or below the catalyst's iso-electric point. In this case, TiO$_2$ has an anphoterical character with an iso-electric point at pH 6.8 [43,44], explaining copper reduction efficiency at low pH.

Developing the modelling equation where the importance of the parameters in the mathematical solution is given by the experimental design with respect to the weight of each variable. Thus, an empirical relationship between the response and the variables is expressed by the polynomial equation (Eq. (1)).

$$\begin{aligned} Y\ (\%) = {} & 76.98(\pm 1.0) + 1.23X_1(\pm 0.59) \\ & -0.8X_2(\pm 0.59) - 0.20X_3(\pm 0.54) - 4.64(\pm\, 0.66)X_1^2 \\ & + 0.15(\pm 0.66)X_2^2 - 0.029(\pm 0.68)X_3^2 - 1.73(\pm 0.67)X_1X_2 \\ & + 0.12(\pm 0.53)X_2X_3 - 0.33(\pm 0.53)X_1X_3 \qquad (1) \end{aligned}$$

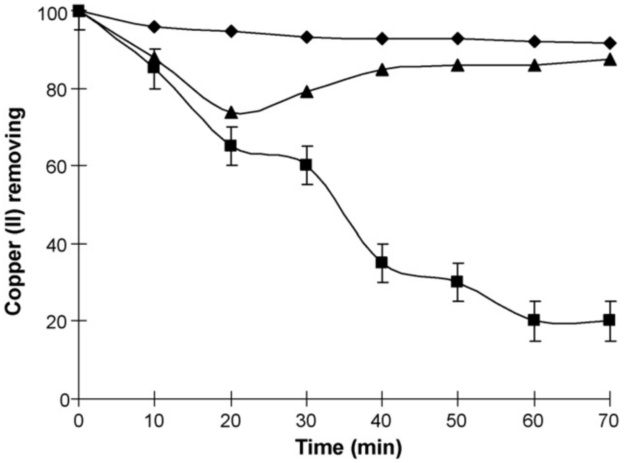

Fig. 4. Copper (II) removal kinetics using optimized AOP treatment TiO$_2$ 0.5 g/L and pH 4.3: (■) TiO$_2$/UV, (▲) TiO$_{2,}$ (♦) UV.

where Y (%): Cu (II) reduction in percentage, X_1: pH, X_2: TiO$_2$ in grams, X_3: reaction time in minutes.

Due to statistical analysis where the time results as an independent variable, it is left out of the following equation:

$$\begin{aligned} Y\ (\%) = {} & 76.98(\pm 1.0) + 1.23X_1(\pm 0.59) - 0.8X_2(\pm 0.59) \\ & - 4.64(\pm 0.66)X_1^2 - 1.73(\pm 0.67)X_1X_2 \qquad (2) \end{aligned}$$

The coefficients indicate the importance of the factor in the equation, observing that the pH is the most influential variable with dependency on the TiO$_2$ variable. The coefficient of the quadratic effect of pH ($P < <0.001$) and TiO$_2$ concentration ($P = 0.019$) were significant; the other factors were not significant with high P values.

To validate the experimental model, the following hypotheses were analyzed:

(D). ependency between the variables does not exist.

H_1. Dependency between the variables exists.

The Student test was applied using the quadratic differences between the results and their average, giving a probability of 0.05% for H_0 and a probability of 95% for H_1, corroborating hypothesis one: dependency between the variables exists.

To corroborate the statistical model, copper reduction kinetics was performed using the model's optimal point. Fig. 4 shows the photocatalysis's real effect on the process. As can be observed, the effect produced by TiO$_2$ absorption is 15% reduction, where absorption on the catalyst surface is important for the photocatalysis process [45,46]. On the other hand, the photolysis effect alone reached only a 25% reduction, demonstrating that the effect adsorption-photolysis achieves a higher reduction percentage, removing 80% copper (II). Concordant results were obtained when the model equation was solved for 95% confidence.

A clear tendency of the photocatalysis effect on the copper (II) reduction is observed, reaching a maximum between the 60 and 70 min. According to the studies, this tendency can be associated with the effect produced by the particles adsorbed on the catalyst's surface, increasing the photocatalytic activity of TiO$_2$ due to decreased efficiency of the recombination process [47,48], enhancing the possibility of electron reaction with copper (II). As observed in the first 20 min, the copper concentration slowly decreases, possibly due to copper (II) particles that are adhering to the catalyst surface, diminishing their surface area. Subsequently, the light incidence on the catalytic surface initiates the photocatalytic process, where time is the variable that controls the

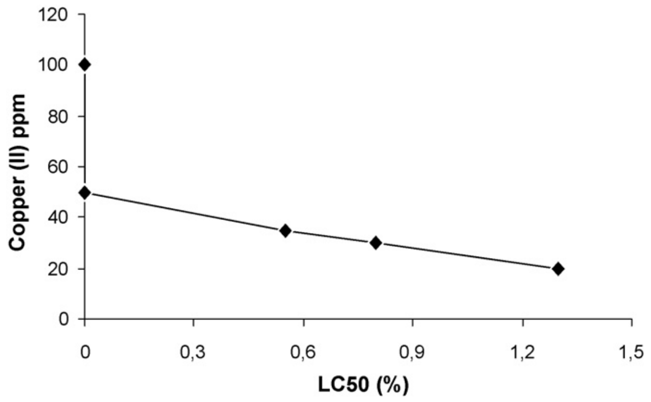

Fig. 5. *Daphnia magna* mortality with the copper (II) removed.

copper adsorption–desorption balance on the catalyst. This also explained the kinetics performance during the first 20 min prior to a greater copper (II) reduction, which remains constant after 60 min of reaction. When comparing the photocatalytic treatment with UV radiation only, it is observed that in this condition the curve remains constant over time without removing the initial copper (II) concentration, clearly indicating that the process is carried out by photocatalysis.

Other studies [49–51] on the importance of the Co-reductive effect of the metallic ions, when acting jointly in a photoreductive process, have demonstrated the efficiency of copper (II) reduction in the presence of chromium (VI) or organic compounds, describing the method as highly efficient. Such studies differ with the results obtained in this work: around 83% reduction was achieved in the presence of high copper (II) concentration (100 ppm) alone.

3.2. Toxicity test for Daphnia magna

The copper (II) remaining in the solution after photocatalytic treatment was found to be toxic for microorganisms. To obtain values of LC_{50}, the dilutions of 1, 2, 3, 4 and 5% and 0.2, 0.4, 0.6, 0.8 and 1% were prepared. At the highest concentrations, the LC_{50} values could not be determined since total mortality of the exposed individuals occurred in each dilution.

Fig. 5 shows the effect on *Daphnia magna*, where differences in mortality can be observed between the untreated copper (II) solution (100 ppm) and the optimal point where 20 ppm of copper (II) remained in solution, clearly observing a toxicity reduction between the initial and final copper concentrations. Nevertheless, although the copper (II) reduction was high, the amount remaining in solution continues to be toxic for *Daphnia magna*. As a result, the nematodes have a low tolerance capacity when compared for the ranking employed: studies indicate LC_{50} values for *Daphnia magna* of 0.12 ppm at 24 h and 0.1 ppm after 48 h exposure [52,53].

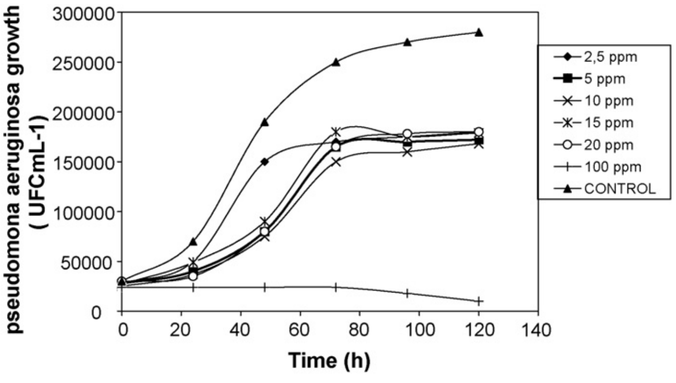

Fig. 6. *Pseudomona aeruginosa* at different copper (II) concentrations.

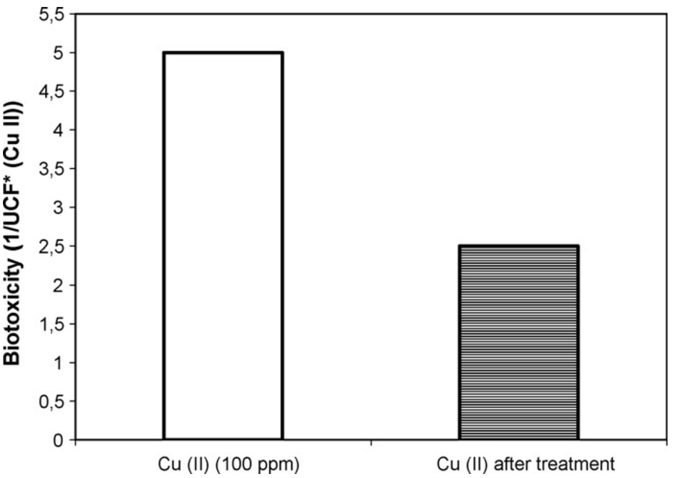

Fig. 7. Bio-toxicity as a function of copper (II) ions remaining in solution.

3.3. Toxicity test for Pseudomona aeruginosa

Fig. 6 shows the effect of the addition of different copper concentrations (II) on the growth of the environmental bacterium *Pseudomona aeruginosa*, where growth is observed to be not affected by the ranking of concentrations between 2.5 and 20 ppm. These concentrations are observed to have no inhibition effect on bacterial growth. Indeed, these concentrations favour growth, even when there is a difference in the growth's rate between the 24 and 72 h of exposure, where the velocity of bacterial growth is higher when the copper (II) concentration is 2.5 ppm. Nevertheless, it can be observed that for the initial concentration of 100 ppm, bacterial growth is completely inhibited.

Fig. 7 shows the efficiency of photocatalytic systems to improve treated water quality by reducing the bio-toxicity generating positive results for this trophic chain link since the bacterial presence is extremely important because it maintains the biological balance in the environment.

4. Conclusions

The experimental design used is a good mathematical tool to optimize the experimental results, verifying the validity and rapidly obtaining the optimal values for the variables. The present study has demonstrated the applicability of this experimental design to determine the pH and titanium dioxide dose in order to optimise the photocatalysis's efficiency when reducing high concentrations of copper (II) ions. The evaluation of the toxicity effect on *Pseudomona aeruginosa* shows complete detoxification, although a lower toxicity reduction was observed in the case of *Daphnia magna*.

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