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Solar photocatalytic degradation of azo-dyes by photo-Fenton process

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Abstract

A solar photocatalytic degradation of the azo-dye acid orange 24 was carried out by means of a photo-Fenton reaction promoted by solar energy. The dye degradation was monitored during the experimental runs through UV/Vis absorption as well as COD and TOC concentration determination and toxicity reduction. In most cases, a discoloration higher than 85% was reached using 50 kJ/l of accumulated energy. In the case of the best reaction conditions, a discoloration of up to 95% and a toxicity reduction from 37 to 5 TU were accomplished with 50 kJ/l. In the same experiment, the removal of COD up to 88% and TOC up to 85% was reached after 105 kJ/l. Results consigned in this work are comparable to others reported in literature for different dyes. The reduction on toxicity values obtained by this methodology was most relevant and present dye degradation by the solar photo-Fenton process as an interesting alternative for coupling with biological processes.

Keywords: Solar photocatalytic degradation; Photo-Fenton process; Advanced oxidation technologies; Azo-dye; Discoloration; Compound parabolic concentrators

1. Introduction

The textile industry is one of the most water-demanding sectors. Its consumption can reach from 25 to 250 m^3 of water per ton of product, depending on the processes, the final quality of the product, the type and form of the fibers and the machinery and the equipment employed [1]. In Mexico, the main water supply source for the textile industry is underground water (97%) and only 3% is obtained from surface water sources [2]. In the unitary operations involved in the textile industry, physical and chemical processes are used to obtain a useful final product, generating along the way many sub-products, which are discharged to wastewater in most of the cases [3]. Wastewater from dyeing process contains a wide variety of water-soluble chemical products, which are very difficult to remove by means of the usual wastewater treatment methods such as filtration, flocculation, sedimentation or adsorption. Most of the dyes used in the textile industry are highly stable, soluble in water, resistant to reactions with chemical agents and low biodegradable; additionally, the use of non-controlled oxidative reactions can generate highly toxic byproducts [4].

Over 100,000 different types of dyes are commercially available [5] and 700,000 tons are produced yearly all over the world. Nearly 50% of these dyes are azo-type dyes [6]. Azo-type dyes are widely used in the dyeing of several natural and synthetic materials. In particular, acid orange 24 (AO24) is one of the most problematic azo-type dyes since it is barely degraded by biological processes [7] and is commonly treated by means of non-controlled chemical oxidation using chlorine and hydrogen peroxide.

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Advanced oxidation processes (AOPs) have been previously described as a promising option to remove persistent pollutants from contaminated water when conventional water treatment processes are not efficient enough. AOPs are based on physicochemical processes that are able to produce deep changes in the chemical structure of the pollutants and are defined [8] as processes involving the in situ generation and use of highly oxidising agents, mainly hydroxyl radicals ($HO^{\bullet}$). The hydroxyl radical possesses inherent properties that enable it to attack organic pollutants in water to obtain a complete mineralization into CO_2, water and mineral acids such as sulfuric, hydrochloric and nitric acids [9–13].

One of the most used AOPs for acid wastewater treatment is the process reported by Fenton in 1894 [14]. Fenton's process uses H_2O_2 and ferrous salts to generate hydroxyl radicals. The main advantage of Fenton's method is the use of iron, which is an abundant and non-toxic element along with hydrogen peroxide which is easily handled and an environmentally friendly agent. Nevertheless, Fenton's reaction cannot completely mineralize organic pollutants since normally less than 50% of the organic carbon can be converted to CO_2 [15]. Furthermore, the biggest disadvantage of this methodology is the sludge generation due to iron and pollutant molecules flocculation. When the process uses ultraviolet (UV) radiation, visible light or a combination of both, the process is known as the photo-Fenton process. The photo-Fenton process has several advantages, mainly an increase of the degradation rate and no sludge generation [16–17]. In addition, hydroxyl radicals can be generated through the use of solar energy.

The photo-Fenton process starts with the combination of H_2O_2 with Fe^{2+} (Eq. (1)) or Fe^{3+} (Eq. (2)). The reactions involved are briefly described as:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{-} + HO^{\bullet} \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe{-}OOH^{2+} + H^{+} \qquad (2)$$

When irradiation is involved, the Fe^{3+} generated by Fenton's reaction (Eq. (1)) is continuously reduced to Fe^{2+}:

$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\bullet} \qquad (3)$$

The reaction process starts again (Eq. (1)) using photogenerated Fe^{2+} [18]. In particular for dye degradation, visible radiation can increase the reaction rate through the generation of free radicals by means of the Fe^{2+} regeneration as previously proposed [19] and showed in Eqs. (4) and (5).

$$Dye + h\nu \rightarrow Dye^{*} \qquad (4)$$

$$Dye^{*} + Fe^{3+} \rightarrow Dye^{+} + Fe^{2+} \qquad (5)$$

Several papers dealing with application of AOPs to dye degradation have been published recently [20–28]. The photo-Fenton process for wastewater treatment using artificial energy sources (UV lamps) has been found useful to dye degradation. Studies testing alternative energy sources suggest that photo-Fenton process could be an economic alternative when using solar light [20,21]. Despite the advantages of the use of solar energy, few papers dealing with the use of this energy source for the degradation of dyes have been reported. The aim of this work is to test the efficiency of the photo-Fenton process when the sun is used as the source of light, applied to the degradation of azo dyes.

2. Methodology

2.1. Reagents

The reagent water used for synthetic samples with acid orange 24 was obtained from a Nanopure (Barnstead) unit. The chemicals used in the experiments, $FeSO_4 \cdot 7H_2O$ (Baker), H_2O_2 (50%, stabilized) industrial grade and sodium hydroxide (Merck) were used as received. Catalase (Sigma, 2200 UA/mg) was used to quench the photo-Fenton reaction in samples before analysis. Acid orange 24 (AO24, see Fig. 1 for chemical structure), industrial grade, was supplied by Orion Co. (Cuernavaca, Morelos).

2.2. Photoreactor

Solar photocatalytic experiments were performed in a bench scale system consisting of eight compound parabolic concentrators (CPC) with a total collection surface of 0.8 m^2 (see Fig. 2). The CPC system was facing the sun on a platform slopped 19° (equal to local latitude). The photocatalytic reaction was carried out in eight pyrex glass tubes, each one having 100 cm in length and 2.54 cm of internal diameter, located in the focus of the CPC collector. The total volume of the system was 8 l.

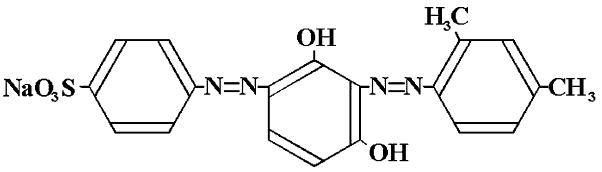

Fig. 1. Chemical structure of the acid orange 24 (AO24) dye.

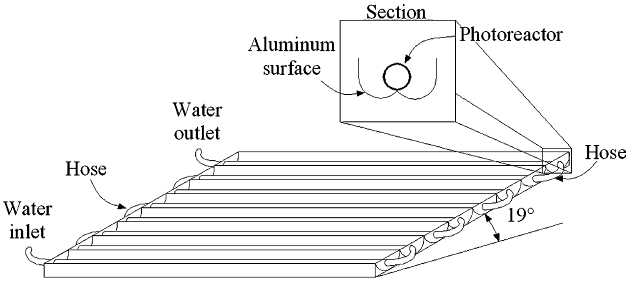

Fig. 2. Bench scale solar collector used for photocatalytic degradation experiments with AO24.

2.3. Irradiation experiments

Synthetic samples were prepared by dissolving 200 mg/l (4.46×10^{-4} M) of AO24 in reagent water. Six different Fe^{2+} and H_2O_2 ratio combinations were used for experimental runs. Additionally, an experiment using only H_2O_2 was carried out. The Fe^{2+} concentrations tested were of 7.16×10^{-5} M, 1.07 and 1.43×10^{-4} M while the H_2O_2 concentrations used were of 5.2 and 7.8×10^{-3} M. The initial pH in the synthetic samples was of ca. 5.5 and no further pH adjustment was performed during the experiments.

For each experiment, an initial sample (25 ml, $t = 0$) was taken immediately after obtaining the AO24–water mixture. The Fe^{2+} was then added to the system and the reaction mixture was homogenized for 10 min with the solar collector covered. After this time, the H_2O_2 was added and the cover was removed. Sampling was performed every 5 min. After 30 min of irradiation, more H_2O_2 (equal to the initial concentration) was added to the system.

2.4. Sample handling

The AO24 concentration was determined using a diode array HP-8452A UV/Vis at 430 nm. The total absorptive spectrum for each sample was also determined in the UV/Vis equipment by scanning from 190 to 820 nm. The total organic carbon (TOC) concentration was determined in a Shimatzu 5000-A unit. The chemical oxygen demand (COD) was also determined in some of the samples using the Standard Methods Procedure [29]. Toxicity tests were carried out using Microtox® (Microbics Co.) equipment.

2.5. Evaluation of solar radiation

All the experiments were performed under the same solar conditions between 12:00 and 14:00 h in November. The incident global radiation on the CPC collector was determined using a Li-Cor pyranometer (LI-200SA) in a wavelength range between 280 and 2800 nm. Since the photo-Fenton reaction allows the use of wavelengths from 300 to 650 nm for solar driven processes, the actual incoming irradiation was estimated using as reference an AM1.5 standard [30], from which a 0.35 factor was obtained for the radiation included in this wavelength range which was applied for estimating the accumulated energy. Radiation measurements were performed every 5 min in all the experiments using the Li-Cor pyranometer located in the same platform than the CPC system and tilted at the same angle to avoid tilt angle adjustments. Accumulated energy was computed using the relation previously reported by Goslich et al. [31]:

$$Q_n = Q_{n-1} + \Delta t G_n (A/V), \quad \Delta t = t_n - t_{n-1} \qquad (6)$$

where Q_n is the accumulated energy, Δt is the time between radiation measurements and G_n is the adjusted global radiation measured in the pyranometer in each experiment, A is the module area and V the total system volume.

3. Results

3.1. Color removal

Fig. 3 shows the color removal obtained using the different amounts of Fe^{2+} tested and maintaining the initial H_2O_2 concentration equal to 5.2×10^{-3} M. It can be seen that when no Fe^{2+} was used, color removal reached values around 4–7% using 50–150 kJ/l of accumulated energy, which means that a slight photolysis took place. The observed effect of the Fe^{2+} concentration was clear: the higher the Fe^{2+} concentration, the faster the color removal. As it can be observed from Fig. 3, using concentrations of $Fe^{2+} = 7.16 \times 10^{-5}$ M and concentrations of $H_2O_2 = 5.2 \times 10^{-3}$ M, color elimination was continued until it reached 75% using 100 kJ/l. The final value for color removal in this experimental run was 85% with 150 kJ/l. When the Fe^{2+} concentration was increased to 1.07×10^{-4} M using the same amount of H_2O_2, 90% of the color was removed using only 83 kJ/l of accumulated energy.

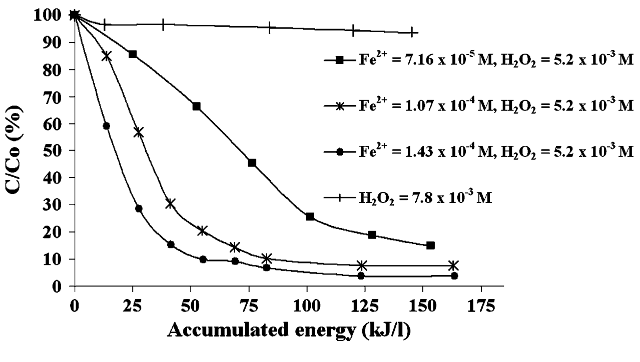

Fig. 3. Color removal at low hydrogen peroxide concentrations.

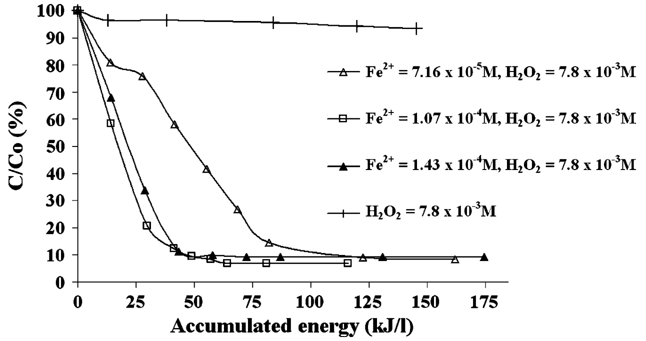

Fig. 4. Color removal at high hydrogen peroxide concentrations.

Fig. 4 shows the influence of the Fe^{2+} concentration on color removal with higher H_2O_2 amounts. As shown, further increases in the H_2O_2 concentration also produced important increases in the reaction rate. For instance, with $Fe^{2+} = 7.16 \times 10^{-5}$ M and $H_2O_2 = 7.8 \times 10^{-3}$ M, the color removal obtained was 85% using 80 kJ/l of accumulated energy, which means a higher color removal by using half of the energy needed with lower H_2O_2 concentrations (see Fig. 3). Combinations of high Fe^{2+} concentrations and low H_2O_2 values and vice versa generated similar removal rates; for example when using $Fe^{2+} = 1.43 \times 10^{-4}$ M and $H_2O_2 = 5.2 \times 10^{-3}$ M (molar ratio 1:0.32:11.66; AO24:Fe^{2+}:H_2O_2) the color removal reached was 70% using 25 kJ/l and the same result was obtained when the molar ratio changed to 1:0.24:17.49; AO24:Fe^{2+}:H_2O_2.

3.2. Colorant degradation

AO24 degradation was monitored in the experimental runs by means of UV/Vis scanning of the whole range of wavelengths available for a diode array. As it can be seen in Fig. 5, AO24 showed important radiation absorption around 430 nm. The intensity of the signal at 430 nm becomes smaller as the irradiation time increases until no signal is detected in the analyzed wavelength range. No additional UV/Vis signals were detected in the sample analysis, meaning that no radiation absorbing intermediates at this wavelength were generated. Nevertheless, a generation of intermediates was detected when the experiment was monitored through TOC and COD concentrations, as shown in Fig. 6. The results of a representative experimental run are shown, where the trends of the behavior of TOC, COD, color and toxicity concentrations were similar to the rest of the experiments.

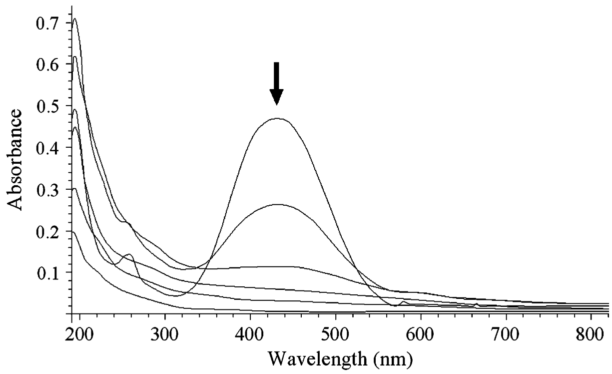

Fig. 5. UV/Vis light absorption decreasing for AO24 during degradation experiments.

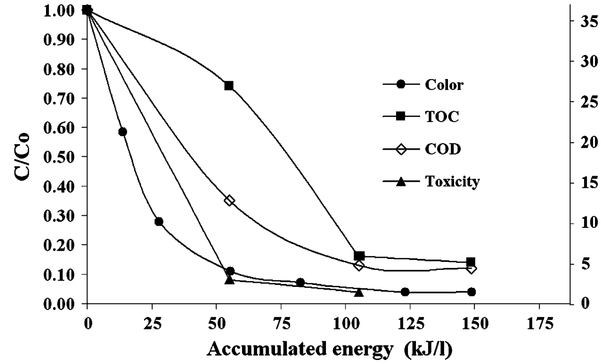

Fig. 6. Color removal, TOC, COD concentrations and toxicity value as a function of accumulated energy in AO24 degradation.

As it can be seen, the remaining TOC concentration is always higher than the color and COD concentrations. The explanation for this behavior is the generation of intermediates. Despite the fact that different trends were obtained at the beginning of the treatment, the final values for color removal, TOC and COD concentrations were fairly similar. After 150 kJ/l, color had decreased over 90%, whereas TOC and COD concentrations had, at the end of the experiment, decreased by 85%, both generating very similar final concentrations (see Fig. 6). This result can be explained by considering that in the earlier stages of the process, AO24 degradation generates an important quantity of partially oxidized intermediates, many of them unable to absorb visible light. As the process runs, intermediates generated earlier increase their oxidation stage up to almost complete mineralization at the end of the experiment.

Toxicity measurements carried out during the experiments determined that an important decrease in this parameter was reached around 50 kJ/l of total energy. This trend agreed with the one observed for colorant degradation, which shows a high value for the same accumulated energy. The continuation of the treatment for another 100 kJ/l did not show any important decreases in both, toxicity or colorant concentration. Motivated by the results discussed above and looking for a trend, since this relationship could be used to determine the stage of the degradation process, tests were made for a relation between color and toxicity. As shown in Fig. 6, once the color had been depleted and the toxicity reduced, the total organic carbon concentration remained high, showing that generated intermediates were still in the solution. More than another 50 kJ/l were necessary to remove most of this organic matter. Coupling photocatalysis with other treatment technologies, such as biological degradation, could be an interesting issue to develop in this area as it has been proposed earlier [32–34]. In this way, the relatively high operational costs of this kind of advanced oxidation process can be justified if the process enhances the biodegradability of the wastewater generating intermediates easily degradable in further biological treatments.

For comparative purposes, it is sometimes useful to explain the results in terms of irradiation time instead of accumulated energy. To achieve this it has to be assumed that the average solar radiation able to drive the photo-Fenton process ($\lambda = 300–650$ nm) on a perfect sunny day during 2 h around noon is ca. 280 W/m^2. Having this considered and while agreeing with Caceres et al. [35], we obtained that 9 kJ/l is equivalent to 4 min of irradiation time. Fig. 7 shows the same results presented in Fig. 6 but as a function of calculated irradiation time (T_{280W}).

Data from Fig. 7 can be compared with other results of dye degradation using photocatalysis. Zhao et al. [19] carried out the degradation of acridine orange using the photo-Fenton reaction. They obtained 25% of mineralization in 100 min of irradiation time with a 500 W halogen lamp using a hydrogen peroxide concentration 14 times higher than those used in this work. Mansilla et al. [36] used TiO_2 photocatalysis for orange II degradation. Their results were 90% of TOC removal in 250 min of irradiation time using a 125 W mercury lamp and O_2 (400 ml/min) as an oxidising agent. Tanaka et al. [37] performed orange G and acid orange 7 degradations by photocatalysis using TiO_2 as a catalyst without any oxidising agent. They obtained 90 and 95% of TOC decrease for each dye in 180 and 150 min of irradiation time, respectively. As far as we can see, solar driven photo-Fenton processes can compete with any of the discussed approaches in terms of dye mineralization or process time.

3.3. Reaction kinetics

Generally, the behavior of the degradation rate can be explained by a first order kinetic with respect to the substrate [11]. Considering this, the rate constant for colorant degradation can be expressed as:

$$\ln C/C_0 = -kQ_n \tag{7}$$

where C and C_0 are the dye concentrations corresponding to Q_n and Q_0, respectively, and k is the reaction rate constant. According to Eq. (7), if we tabulate the term in the left hand versus the term in the right hand of the equivalence, we will obtain a straight line with a slope equal to the reaction rate constant. Fig. 8 shows the correlation between $\ln C/C_0$ and $-kQ_n$, illustrating that a good correlation was obtained between experimental and mathematical results. From there, a k value equal to 3.66×10^{-2} 1/kJ was determined as the reaction rate constant. This result is interesting considering that by means of the rate constant value it is possible to compute the accumulated energy (or irradiation time) necessary to perform complete color degradation if we know the initial dye concentration in a specific water discharge. Knowing the energy requirements of a particular solar process is a very important topic that will allow calculating the collection area requirements or, in other words, the scaling-up factor of the process.

4. Conclusions

The photo-Fenton process using solar energy offers a very valuable alternative for the degradation and

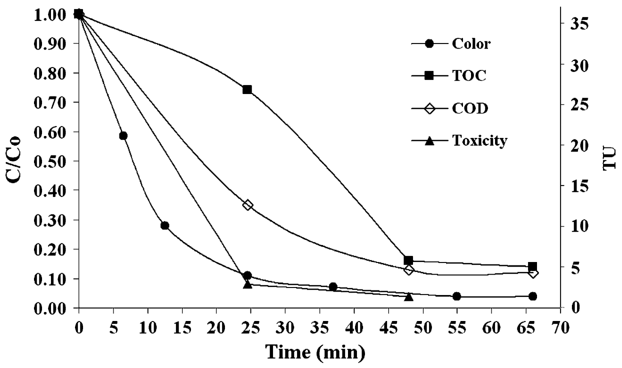

Fig. 7. Color removal, TOC, COD concentrations and toxicity value as a function of T_{280W} in AO24 degradation.

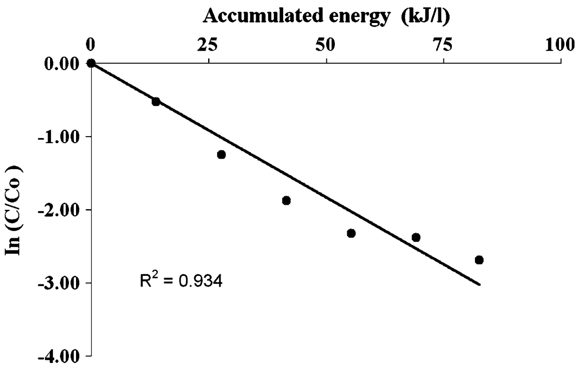

Fig. 8. Correlation between $\ln C/C_0$ and $-kQ$ for: experimental data (●) and calculated data (continuous line).

mineralization of the acid orange 24 dye dissolved in water. All the experiments presented in this work reached a color removal over 85% using 50 kJ/l of accumulated energy. Concentrations of $Fe^{2+} = 1.43 \times 10^{-4}$ M and $H_2O_2 = 5.2 \times 10^{-3}$ M were determined as optimal concentrations for the photocatalytic process since it was possible to reach a disappearance of colorant as high as 95%, an 88% reduction of COD and an 84% removal of TOC using 105 kJ/l (representing a little more than 65 min of irradiation time if $T_{280\mathrm{W}}$ is considered).

Results from this work are comparable with previous reports in literature for the degradation of some other colorants using homogeneous and heterogeneous photocatalysis. Nevertheless, the solar methodology discussed in this work presents the main advantage of avoiding the use of lamps by using an environmentally friendly, cheap and widely distributed energy source, i.e. the sun.

The toxicity tests performed during the experiments showed that it is possible to reduce toxicity values from 35 toxicity units (TU) to less than 5 TU using only approximately 50 kJ/l, which corresponds to a toxicity reduction over 85% after 25 min ($T_{280\mathrm{W}}$). This result together with the high TOC reduction in the same stage of the process lead us to propose the relevance of coupling the photo-Fenton process and biological treatment in order to complete the mineralization of dyes once the biodegradability has been enhanced by the advanced oxidation technology.

A mathematical approach to the reaction rate kinetic was used in order to get an approximation of the reaction rate constant. The used model agrees satisfactorily with experimental data and allows the determination of the rate constant of the process, which is a very important parameter for scaling-up.

Results strongly suggest that solar driven AOPs are very promising wastewater treatment technologies. In particular, solar photocatalysis is currently considered the most successful application of solar photons, mostly because it is non-selective and can be applied to complex mixtures of contaminants. These statements are confirmed by the first commercial project implemented in Spain, where residues from empty pesticide bottles are treated by photo-Fenton process, shows the success of the methodology [38].

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