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Degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) using cobalt-peroxymonosulfate in Fenton-like process

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Abstract

2,4-Dichlorophenoxyacetic acid (2,4-D) was degraded using both Fenton reagent and cobalt-peroxymonosulfate (Co/PMS) advanced oxidation processes (AOPs) in the dark and under solar radiation as source of light in photo-assisted AOPs. Four different concentrations of the transition metal (cobalt or Fe(II)) were tested maintaining constant the initial oxidant agent (PMS or hydrogen peroxide) concentration. The effect of temperature was investigated in the dark for both processes and the activation energy was determined for each process. For the processes performed in the dark, the maximum degradation for 2,4-D (86%) was achieved using Co/PMS (0.25 mmol L^{-1} of cobalt) in 48 min, while the dark Fenton achieved a maximum degradation of 2,4-D (17%) using 0.1 mmol L^{-1} of Fe(II). Complete 2,4-D degradation was achieved when the samples were irradiated by the sun using the same conditions described for 5 min of reaction time. In the case of solar-driven Co/PMS, complete 2,4-D degradation was achieved after 40 min using 0.004 mmol L^{-1} of cobalt. Pseudo first order reaction rate constants determined in the dark for Fe/H_2O_2 and Co/PMS processes indicated that Co/PMS is able to perform the degradation of the pesticide at the same reaction rate as Fenton reagent, despite the fact that cobalt concentration is 100 times lower than Fe(II) concentration. Solar light increased the kinetic constant in the Co/PMS complex by 33 times compared with that obtained under dark conditions. Attempt to follow 2,4-D degradation using the photo-Fenton process was not possible since complete degradation occurred after the first 5 min of irradiation using [Fe] = 0.1 mmol L^{-1}.

Keywords: 2,4-D; Co/PMS; AOPs; Advanced oxidation processes; Chemical; Degradation; Fenton reagent; Oxidation; Oxone; Peroxymonosulfate; Photocatalytic; Photocatalysis; Solar energy; Treatment; Water

1. Introduction

In recent years, the increase in production and use of pesticides for agriculture has resulted in the presence of a variety of persistent contaminants in the environment, including in surface water and groundwater [1]. Pesticide-related concerns in Mexico include water pollution due to runoff of the cultivated land, poor handling of pesticides in agricultural activities, little or no environmental monitoring, lack of safety measures and emergency plans, and disposal of pesticide containers without prior cleaning. Specifically, 2,4-D was selected in this study because it is an authorized pesticide and one of the most widely used in Mexico [1]. The United States Environmental Protection Agency (EPA) classifies 2,4-D as a compound that can potentially cause nervous system damage for short-term exposure at levels above the maximum concentration level (MCL) and kidneys and liver problems at long-term [2]. Recent studies suggested that 2,4-D is detectable during the application and after a long period of use in surface water and groundwater [3].

Several conventional processes, including adsorption and biological treatment, are commonly applied for the removal of 2,4-D in contaminated water [1,4,30]. Some alternative processes have also been explored in the destruction of 2,4-D, other pesticides, and a variety of other organic contaminants [3]. Among emerging treatment approaches, advanced oxidation processes (AOPs) are considered among the most effective and are currently gaining significant importance in water treatment applications [5]. These processes involve the generation of very reactive oxidizing species (i.e., free radicals) with sufficient oxidizing power to complete degrade toxic organic compounds

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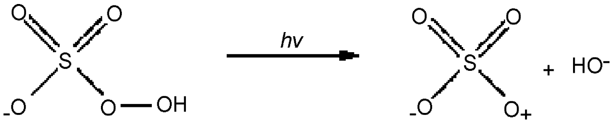
in water. Radicals generated by AOPs are usually very efficient on chemical attack and degradation of environmental organic pollutants [6]. Consequently, AOPs are of high interest to the scientific and industrial communities involved in water treatment and have been successfully applied to the detoxification of water polluted with a wide variety of chemicals such as pesticides, phenols, hydrocarbons, surfactants, and dyes [5,7–12]. One of the established AOPs is the Fenton reagent (Fe^{2+}/H_2O_2), which is used in field-scale applications. However, more recent studies have extended the combination of other transition metals and oxidants and presented promising results [5,10]. One of these systems that has shown very interesting reactivity is the cobalt/peroxymonosulfate (Co/PMS), which has demonstrated promising results for the oxidation of some specific organic pollutants such as 2,4-dichlorophenol, atrazine and naphthalene [5,10,28,29]. The system includes the generation of sulfate radicals through the decomposition of peroxymonosulfate by cobalt, according to the following reaction [5]:

$$Co^{2+} + HSO_5^{-} \rightarrow Co^{3+} + SO_4^{\bullet -} + HO^{-} \qquad (1)$$

When Fenton process uses ultraviolet (UV) radiation, visible light or a combination of both, the resulting process (known as photo-Fenton) has several advantages, including the increase of degradation rate and the flexibility of using alternative energy sources (i.e., solar radiation) for driving the process [13–16]. Similarly, synergistic effects in the degradation rate of Fenton-like processes, such as Co/PMS combined with UV radiation, have been recently explored [10]. It has been reported that the use of UV-C light (i.e., in the germicidal range) promotes the generation of radical species through the photolysis of the oxidants according to the following reaction [10,17,18]:



(2)

Nevertheless, only little has been reported on the actual mechanism of how the light enhances the reaction rate in this process when both the catalyst and the oxidant are present. The Co/PMS/UV process has shown an increase in the degradation rate for tested pollutants [10] when compared with the dark Co/PMS system. To our knowledge, no studies on the use of solar radiation as the source of light in the Co/PMS/UV processes have been reported. The aims of this work are to test the potential of the Co/PMS and solar-driven Co/PMS/UV processes to degrade 2,4-dichlorophenoxyacetic acid (2,4-D), an important environmental organic pollutant, and compare them with the Fenton and photo-Fenton processes using the sun as the source of energy.

2. Experimental

2.1. Reagents

2,4-D (2,4-dichlorophenoxyacetic acid) primary standard, purity higher than 95%, was obtained from Chem Service. For the degradation experiments, 2,4-D was used as its commercial formulation (Hierbamine®, Syngenta) with a concentration of the active ingredient (a.i. = 59 ± 1%). The concentration of 2,4-D in Hierbamine® was determined using the 2,4-D primary standard. Stock solution (1 mg/mL) of the pesticide was prepared directly in water. In the degradation experiments, appropriate amount of 2,4-D stock solution was used for spiking the water sample to obtain the desired initial concentration (100 mg/L). The initial pH in the synthetic samples was of ca. 5 and no further pH adjustment was performed nor for Co/PMS neither Fe/H_2O_2 experiments. Cobalt acetate $Co(AcO_2)_2$ (Aldrich), sodium peroxymonosulfate (PMS from OXONE®, Aldrich; it should be noted that OXONE® is a product manufactured by DuPont), hydrogen peroxide (Aldrich, 50% stabilized) and $FeSO_4{\cdot}7H_2O$ (Baker) were ACS reagent grade and were used as received. Excess methanol (Burdick & Jackson, pesticide grade) was used to quench Co/PMS reactions as proposed by Anipsitakis et al. [28]. Catalase (Sigma, 2200 UA/mg) was used to quench the Fenton and photo-Fenton reaction in samples before analysis as previously reported [12].

2.2. Apparatus and analytical methods

The analysis of 2,4-D was carried out without any extraction procedure by HPLC–UV/vis using a Hewlett-Packard 1050 liquid chromatograph equipped with a UV diode array detector. The analysis was performed at isocratic regime using a Hypersil-GreenEnv, 5 μm × 250 mm × 4.6 mm column (Thermo Hypersil-Keystone). The mobile phase was 75% (v/v) of 2% acetic acid and 25% (v/v) acetonitrile. The flow rate was 1 mL/min and the UV–vis detector wavelength was set at 280 nm.

2.3. Pesticide degradation experiments

2.3.1. Systems in the absence of solar light

Dark Co/PMS and Fe/H_2O_2 degradation experiments were carried out in 1.8 mL screw cap glass vials with 1 mL 2,4-D solution (50 mg/L). For dark Co/PMS experiments, four cobalt concentrations (0.00, 0.004, 0.040 and 0.250 $\mathrm{mmol\,L^{-1}}$) were tested at the same initial PMS molar concentration (1 $\mathrm{mmol\,L^{-1}}$). Dark Fenton experiments were carried out using four Fe(II) concentrations (0.000, 0.004, 0.040 and 0.100 $\mathrm{mmol\,L^{-1}}$). The initial concentration of hydrogen peroxide was kept at the same value for all experiments (1 $\mathrm{mmol\,L^{-1}}$). The procedure for the degradation experiments was the following: Once the pesticide solution was added in the 1.8 mL vial, the appropriate volume of transition metal stock solution (cobalt or Fe(II)) was added to achieve the desired initial concentration. The solution was shaken using a vortex mixer. Then the oxidant solution (H_2O_2 or PMS) was added to the 2,4-D-transition metal mixture until the desired concentration was achieved and a sample was analyzed considering this as the initiation point (t_0) of the dark reaction. The reaction mixture was kept in the dark for the entire duration of each experimental run. A sample of 25 μL was obtained every 12 min and analyzed for pesticide concentration in the HPLC system. The reaction was followed until HPLC analysis showed no significant further variation on the pesticide concentration.

2.3.2. *Experiments under controlled temperature*

These experiments were carried out to determine the effect of the temperature on the degradation process. In order to do this, the lowest concentration of transition metal and oxidant able to achieve the minimum pesticide degradation in the non-irradiated experiments, in each case, was chosen (0.004 mmol L^{-1} of cobalt, 1 mmol L^{-1} of PMS, 0.100 mmol L^{-1} of Fe(II), 1 mmol L^{-1} of H_2O_2). The degradation tests were performed in the dark at 20, 30 and 40 ± 1 °C in a controlled temperature bath Lauda RM 20 (Brinkmann Instruments). Each solution was placed in an Erlenmeyer flask (total reaction mixture 50 mL) covered with aluminum foil to avoid interaction by incident light, submerged in the water bath and maintained under constant mechanical agitation. In this case, the reagents were added in the same sequence as detailed in Section 2.3.1. After the addition of the oxidant, the reaction mixture was sampled at 5, 10, 15, 30, 45 and 60 min of reaction and analyzed for 2,4-D concentration in the HPLC system.

2.3.3. *Systems in the presence of solar light*

Experiments for solar-driven AOPs were performed in a bench scale system consisting of one compound parabolic concentrator (CPC) with a total collection surface of 0.1 m^2 widely described elsewhere [12,19]. The CPC system was facing the sun on a platform sloped 19° (equal to local latitude). The AOPs reactions were carried out in a Pyrex glass tube 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 1.5 L.

Synthetic samples were prepared by adding 2,4-D and the transition metal (Fe(II) or cobalt) in 1.5 L of water to reach final concentrations equal to those (0.25 mmol L^{-1} for cobalt and 0.1 mmol L^{-1} for Fe(II)) that had demonstrated the highest 2,4-D degradation (i.e., as percent removal) as determined during the experiments performed in the dark. Once the transition metal was added to each experiment, an initial sample (5 mL, $t = 0$) was taken and analyzed immediately. While the solar collector was covered, the reaction solution was mixed for 5 min to achieve a homogeneous solution. After this time, the oxidant (either H_2O_2 or PMS) was added and the cover of the collector was removed. Sampling was performed after 5, 10, 15, 30, 45 and 60 min of irradiation. No further addition of transition metal or oxidant agent was carried out in all the experimental runs.

All experiments involving the presence of solar radiation were performed under the same solar conditions between 12:00 and 14:00 local time in April 2006. The incident global radiation on the solar collector was determined every 2 min using a Li-Cor pyranometer (LI-200SA) able to measure solar radiation in a wavelength range between 280 and 2800 nm and located at the same angle as the solar collector to avoid tilt angle adjustments. For determining reaction kinetic parameters, a simple first order kinetic model was used to fit the results for both dark and solar-based AOPs.

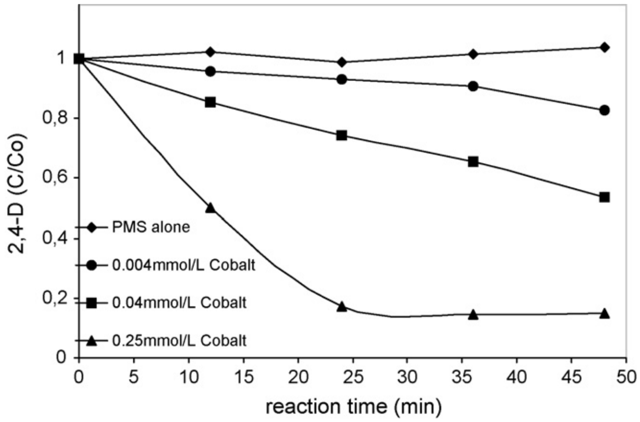


Fig. 1. Degradation of 2,4-D using the Co/PMS system in the dark. The initial PMS concentration in all the experiments was 1 mmol L^{-1}.

3. Results and discussion

3.1. *Co/PMS system in the dark*

Fig. 1 depicts the results of 2,4-D degradation in experiments using the Co/PMS in the dark. As it can be seen, cobalt concentration showed an important effect on the reaction rate and the extent of the overall 2,4-D degradation at the end of the reaction run. When no cobalt was added to the reaction mixture, no pesticide degradation was observed. As the transition metal concentration was increased from 0 to 0.004 mmol L^{-1}, an important effect was observed in the reaction rate. Whereas no degradation was observed in experiments without cobalt, 18% of 2,4-D degradation was achieved as cobalt concentration was increased to 0.004 mmol L^{-1} in 48 min. In general, an increase in cobalt concentration resulted in an increase in the removal efficiency of 2,4-D. The latter was increase from 47% to 86% in 48 min when the molar concentration of cobalt increased from 0.04 to 0.25 mmol L^{-1}, respectively.

The kinetic constants obtained considering first order reaction kinetics are presented in Table 1. It is important to mention that the first order kinetic model proposed fits relatively well ($R^2 \geq 0.97$) the experimental results. An increase in cobalt concentration caused a gradual increase in both the degradation efficiency and the rate constants. For example, at initial cobalt concentrations of 0.004, 0.04, and 0.25 mmol L^{-1}, the ratios of the rate constants were 1, 3.5, and 4.6, respectively.

Results from experiments using the Co/PMS system in the dark under controlled temperature are presented in Table 2. As shown, temperature has a noticeable effect on the process. An increase of temperature caused an improvement in the kinetic

Table 1
Kinetic constant (k) values for the Co/PMS and Fenton processes in the dark

[Cobalt] (mmol L^{-1})	k (min^{-1})	[Fe^{2+}] (mmol L^{-1})	k (min^{-1})
0.004	0.0036	0.004	–
0.04	0.0129	0.04	–
0.25	0.06	0.1	0.0038

The concentration of the oxidant in both cases was 1 mmol L^{-1}.

Table 2
Kinetic constant values for three different temperatures used for dark Co/PMS

Temperature (°C)	Reaction time (min)	k (min^{-1})
20	48	0.0036
30	48	0.0045
40	48	0.0089

Experimental conditions tested were [Cobalt] = 0.004 mmol L^{-1} and [PMS] = 1 mmol L^{-1}.

constants. It is worthy to mention that studying the role of temperature in this range is important since measurements of water temperature in the solar photoreactor indicated an increase in solution temperature to values as high as 40 °C. From the kinetic results at different temperatures, an activation energy value of 34.3 kJ/mol was determined for the process using the Arrhenius equation.

The initial reaction rates for the first 15 min (IR_{15}) were also calculated. The initial reaction rates were 0.0009, 0.0038 and 0.0039 mmol/min for 20, 30 and 40 °C, respectively. These values are comparable to those previously reported by Anipsitakis and Dionysiou [5]. They determined an initial reaction rate of Co/PMS of 0.0052 mmol/min for 2,4-dichlorophenol (2,4-DCP) for reaction mixture at pH 2 and 0.0269 mmol/min for a pH value of 3.0 using [PMS] = 1.227 mmol L^{-1} and [Cobalt] = 0.028 mmol L^{-1}.

3.2. *Solar Co/PMS process*

Fig. 2 shows 2,4-D degradation using Co/PMS in the presence of solar radiation. In order to obtain a better comparative analysis, pesticide degradation is shown as function of reaction time. Nevertheless, results from average solar radiation for each experiment (in W/m^2) are also depicted in Fig. 2 in order to show that the solar radiation conditions during experiments were comparable.

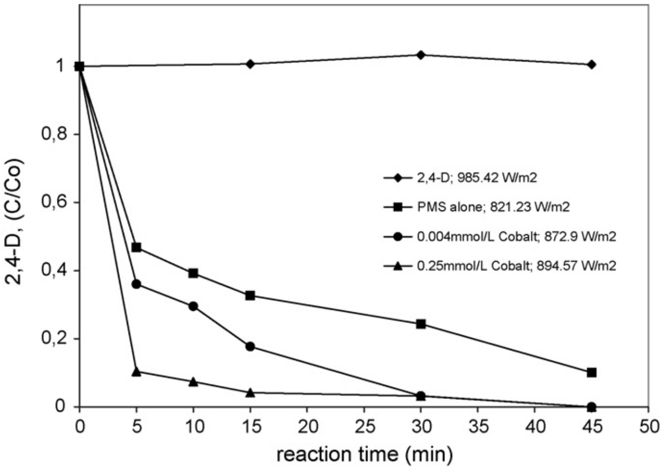


Fig. 2. 2,4-D degradation in the presence of solar radiation under different cobalt initial concentrations. The initial concentration of PMS for the experiments with cobalt is 1 mmol L^{-1}. The average global radiation (in W/m^2) measured during each experimental run is also shown in the legend.

It is interesting to note that no 2,4-D degradation was observed in experiments using only solar radiation. When merely 1 mmol L^{-1} of PMS was added into the contaminated solution, 90% of the initial 2,4-D concentration was degraded in 45 min of irradiation. These results agree with previous reports [10] for the decomposition of PMS by UV radiation. When adding 0.004 mmol L^{-1} of cobalt under the same PMS concentration, complete 2,4-D degradation was observed for the same irradiation time. The catalytic effect caused by the transition metal is obvious. When cobalt concentration was increased to 0.25 mmol L^{-1}, a degradation of 90% was achieved after the first 5 min of reaction.

Table 3 shows kinetic constants values obtained for the results presented in Fig. 2. The results show that the solar-driven Co/PMS process (Co/PMS/solar) is several times faster than the dark Co/PMS process. At the same reaction conditions, solar aided experiments showed significantly higher k values. For example, the dark Co/PMS process (with [Cobalt] = 0.004 mmol L^{-1} and [PMS] = 1 mmol L^{-1}) has a value of $k = 0.0129$ min^{-1}. When solar radiation is used, at the same reaction conditions, the value is $k = 0.128$ min^{-1}, one order of magnitude higher.

The values of k shown in Table 3 allowed us to differentiate between the temperature effect on the process in the presence of solar light. As mentioned above, in the solar-driven processes, the solution temperature was increased up to 40 °C at the end of each experimental run. The results discussed in Tables 2 and 3 clearly show that the presence of solar radiation caused a significant increase in the reaction rate constant, much higher than that obtained due to increase in temperature. Whereas the increase in temperature to 40 °C (i.e., in the absence of solar light) resulted in a k value of 0.0089 min^{-1} (2.3 times faster than that obtained in the dark Co/PMS system at 20 °C), the presence of solar radiation (including UV-A and IR radiation) increased the k value to 0.128 min^{-1} (approximately 35 times the value obtained in the dark Co/PMS system at 20 °C). The improvement in the reaction rate for the Co/PMS/solar process compared to the PMS/solar process is very interesting. Anipsitakis and Dionysiou [10] reported no significant differences when testing the effect of an inorganic salt of cobalt in the Co/PMS/UV reagent under UV-C radiation (germicidal, $\lambda = 253.7$ nm) for 2,4-DCP degradation. They found that, after 120 min of reaction, the extent of 2,4-DCP degradation achieved with the Co/PMS/UV was identical to that obtained with the PMS/UV reagent. In a more recent work, they identified the influence of the cobalt counterion in the pathway degradation of 2,4-DCP with the Co/PMS system and also in the degradation kinetics observed for 2,4-DCP degradation using this process [28,29]. In the present

Table 3
Values of kinetic constant for the Co/PMS/solar process

Reagent concentration	k (min^{-1})
1 mmol L^{-1} PMS	0.0393
0.004 mmol L^{-1} cobalt	0.1286
0.25 mmol L^{-1} cobalt	0.2283

PMS concentration was 1 mmol L^{-1} in all cases.

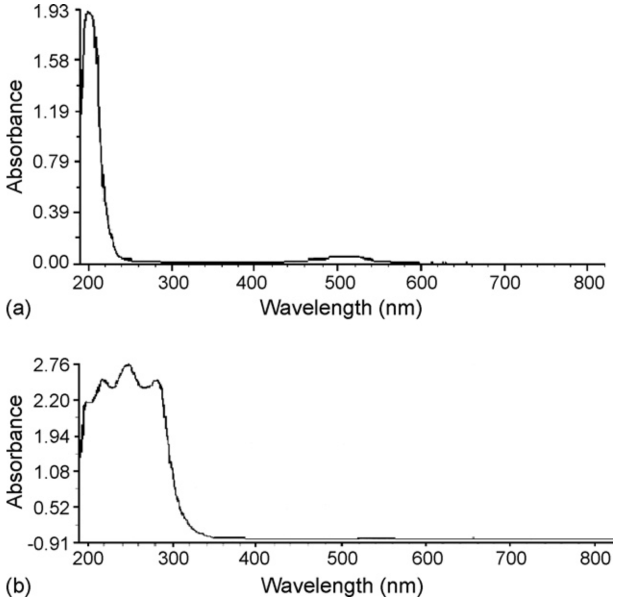


Fig. 3. UV–vis absorption bands in the wavelength range from 190 to 800 nm for (a) cobalt acetate in deionized water (0.004 mmol L^{-1}) and (b) potassium peroxymonosulfate (PMS, 1 mmol L^{-1}) in deionized water.

work, the use of an organic salt of cobalt in the oxidation process showed an important advantage on the degradation of 2,4-D, mainly for solar aided experiments. Nevertheless, systematic studies dealing with the possible role of the cobalt salt counterion during the solar driven process are still in progress. To try to find out the possible interaction between solar radiation and the reaction mixture in Co/PMS/solar process, the absorbance spectra in the range of 190–800 nm of all species at the initial concentrations used in this work in deionized water were measured with UV–vis spectrophotometer and are depicted in Figs. 3a and b and 4.

It can be observed, from Fig. 3a and b, that no radiation absorption was determined neither for cobalt acetate or PMS in the region of solar UV radiation (300–400 nm). Nevertheless, when both reagents are put together in the same vessel, the absorption bands of the PMS showed a shift to lower frequencies after the first minutes of reaction as depicted in Fig. 4. This figure shows changes in PMS absorbance bands in the range from 190 to 400 nm for different reaction times after adding cobalt. Reagent concentrations were equivalent to those used for 2,4-D degradation experiments (0.25 mmol L^{-1} of cobalt and 1 mmol L^{-1} of PMS). The absorption spectra were determined every 30 s during 5 min. As showed, in the earliest seconds no significant changes in the absorptions bands were determined. After 2.5 min, an important shifting of the band at ca. 210 nm was detected and an increase in the absorption band near 350 nm (from almost 0 at t_0 to near 0.25 absorbance units, AU, at time 2.5 min).

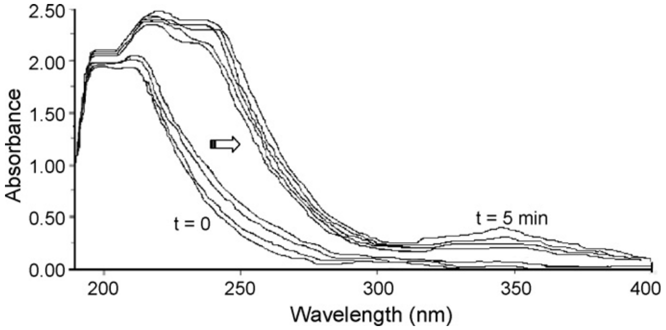


Fig. 4. Change in the PMS absorption bands in the wavelength range (190–400 nm) after different reaction times with the addition of cobalt to the reaction mixture.

As the reaction proceeded, this absorption band increased achieving an absorbance value of 0.5 AU. These results are interesting and may provide insights on the role of solar radiation in driving this process. No radiation absorption occurred initially in the wavelength range for solar radiation when the Co/PMS reagents were analyzed separately. Once the transition metal and the oxidant agent were mixed together, interaction between both of them could produce a transition state adduct able to absorb in the UV region of the solar spectrum. Both conditions, the capability to absorb in the solar UV region as well as the sensitivity showed by the reaction mixture to the increase of temperature could be the reason of the increase in the reaction rate observed for solar driven Co/PMS/UV process.

3.3. *Dark Fenton process*

Results from 2,4-D degradation using dark Fenton reagent are depicted in Table 4. As it can be seen, except for the highest Fe(II) concentration, no pesticide degradation was observed for all the ferrous sulfate concentrations tested. Kinetic constant *k* values obtained from fitting the data in Table 4 to the first order kinetic model proposed are shown in Table 1.

From these results, it is clear that Fenton reagent is not able to perform the same pesticide degradation under similar reaction conditions to those tested for dark Co/PMS reagent. Comparison of results from both processes, showed that pesticide degradation determined at the highest Fenton reagent conditions ([Fe] = 0.1 mmol L^{-1}; [H_2O_2] = 1 mmol L^{-1}) were similar to the 2,4-D degradation achieved when soft Co/PMS dark conditions ([Cobalt] = 0.004 mmol L^{-1}; [PMS] = 1 mmol L^{-1}) were tested (17% final 2,4-D degradation in both cases).

The effect of temperature was also investigated for the Fenton reagent and the results are presented in Table 5. As observed for the dark Co/PMS process, a rise in temperature caused an increase in the final 2,4-D degradation. For the case of Fenton process, the effect of temperature was actually more pronounced than that observed for Co/PMS. Whereas

Table 4
2,4-D degradation using dark Fenton reagent

Reagent concentration	Reaction time (min)	Final 2,4-D degradation (%)
1 mmol L^{-1} H_2O_2	48	–
0.004 mmol L^{-1} $FeSO_4$	48	–
0.04 mmol L^{-1} $FeSO_4$	48	–
0.1 mmol L^{-1} $FeSO_4$	48	17

Oxidant agent (H_2O_2) concentration in all cases was 1 mmol L^{-1}.

Table 5
Effect of temperature on final 2,4-D degradation and k values for dark Fenton process

Temperature (°C)	Reaction time (min)	Final 2,4-D degradation (%)	k (min^{-1})
20	48	17.36	0.0038
30	48	59.76	0.0111
40	45	95.04	0.0604

Experimental conditions were [Fe] = 0.1 mmol L^{-1} and [H_2O_2] = 1 mmol L^{-1}.

Table 6
2,4-D degradation under irradiated conditions for photo-Fenton process

Reaction conditions	Reaction time (min)	Final 2,4-D degradation (%)
0.01 mmol L^{-1} $FeSO_4$	60	4
0.05 mmol L^{-1} $FeSO_4$	60	14
0.1 mmol L^{-1} $FeSO_4$	5	100

Oxidant concentration was 1 mmol L^{-1}.

for Co/PMS an increase of 20 °C (from 20 to 40 °C) generated the increase from 17% to 42% in pesticide degradation (see Table 2); with Fenton reagent the same increase in temperature enhanced the final pesticide degradation from 17% to 95%. A similar trend was observed for the kinetic data obtained (see also Table 5). When the temperature was increased from 20 to 40 °C, the k value increased from 0.0038 to 0.06 min^{-1}, over one order of magnitude. These results agreed with results reported in previous studies [22,23]. In particular, Sagawe et al. [24] demonstrated the possibility of a combined photochemically- and thermally-enhanced photoreactive Fenton system utilizing solar infrared as energy source. These investigators reported that in the case of photochemically and thermally enhanced Fe/H_2O_2 systems, the removal rate of target compounds (i.e., 4-chlorophenol) could be increased by over two orders of magnitude compared with the dark Fenton systems.

Using kinetic data from Table 5, the value of the activation energy calculated for the Fenton reagent was 105.15 kJ/mol. Comparing this result with that reported by Barb et al. [20] for 2,4-D degradation using Fe(II)/H_2O_2 reagent (39.5 kJ/mol), activation energy obtained is around three times higher. Rationalization of this result can be done considering the experimental conditions tested. In this work, no pH adjusting was performed during experimental runs neither for Co/PMS or Fenton reagent in order to have a better comparative basis between both systems. It is well known that Fenton reagent performance in water detoxification is improved at low pH values [21,26,27]. Activation energy for Fenton process at almost neutral pH value (ca. 6.5) was determined, whereas Barb et al. and Lee et al. [20,25] determined this value using a pH range between 1 and 3.3. Assuming that they have tested 2,4-D degradation using Fenton reagent under optimal conditions, reported activation energy for Fe/H_2O_2 is comparable to the one determined for Co/PMS process (34.3 kJ/mol).

3.4. Photo-Fenton process

Due to the lack of 2,4-D degradation using low Fe(II) concentrations under dark Fenton process, the transition metal concentration was increased in order to achieve best pesticide degradation results. Table 6 shows the results obtained by increasing Fe(II) concentration for solar driven photo-Fenton process.

Using 0.01 mmol L^{-1} of Fe(II), only a 4% of 2,4-D degradation was achieved. Increasing the transition metal concentration by five times resulted in an increase of the final pesticide degradation by approximately 14% in both cases after 60 min of irradiation. Using a molar concentration of iron of 0.1 mmol L^{-1}, 100% of 2,4-D degradation was achieved in only 5 min of irradiation. Meanwhile, at non-irradiated conditions, only 17% of degradation was obtained with 0.1 mmol L^{-1} of Fe(II) at 60 min of reaction. Rossetti et al. [31] reported a degradation of 29.3% of formic acid with the Fenton reagent (1 mmol L^{-1} Fe^{3+} and 6.93 mmol L^{-1} H_2O_2) in the absence of solar light and 80.7% when radiation from the sun was applied. An enhancement of 51.4% in the degradation of formic acid during 1 h of reaction employing solar radiation with a plane collector was obtained. In our case, an improvement of 83% was achieved in the presence of solar radiation under the conditions mentioned before. These results are comparable and showed evidence of the improvement in the degradation of organic pollutants with solar radiation using the Fenton reaction like in previous studies [12,13,15,32]. Attempts to fit the results from Table 6 to the first order kinetics failed because the collected data did not show a linear behavior or were not enough to complete the reaction kinetics.

The high effect of temperature on the Fenton process depicted in Section 3.3 was differentiated from the effect of solar radiation on the process. Fig. 5 shows a comparison between 2,4-D degradation using Fenton reagent conditions at different reaction temperatures and pesticide degradation under the same conditions (0.1 mmol L^{-1} of Fe(II); 1 mmol L^{-1} H_2O_2) but involving solar radiation. From Fig. 5, it is easy to note that the use of solar radiation to promote Fenton process implies considerable

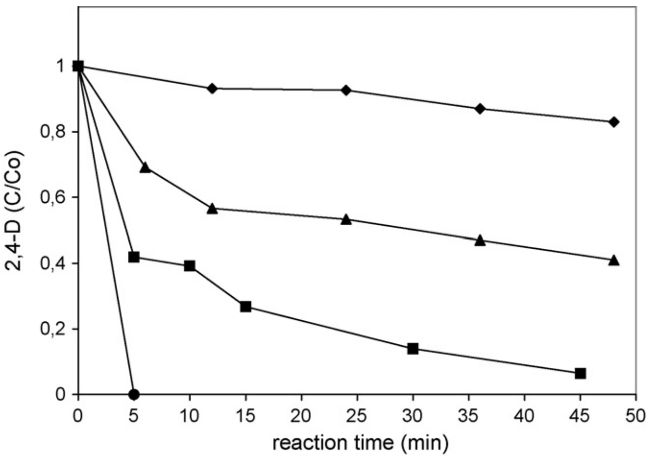


Fig. 5. Comparison of the temperature and solar radiation effect for photo-Fenton process. Experimental conditions were [Fe(II)] = 1 mmol L^{-1} and 20 °C (diamonds), 30 °C (triangles), 40 °C (squares) and using solar radiation (circles) ([Fe(II)], 0.1 mmol L^{-1}; average radiation, 1000 W/m^2).

increase of reaction rate. Even if the kinetic constants were not determined for each experiment using first order kinetics, calculation of initial reaction rate for the first 5 min (IR_5) provides interesting results. IR_5 values at 20, 30, and 40 °C were 0.0028, 0.0124, and 0.0234 mmol/min, respectively. For example, an increase in reaction temperature of 20 °C (from 20 to 40 °C) caused an enhancement of the initial reaction rate by almost one order of magnitude. When solar radiation was utilized, the IR_5 reached 0.04 mmol/min, almost twice the value observed in the dark at 40 °C.

4. Conclusions

The degradation of 2,4-D was performed using sulfate radicals generated by the conjunction of peroxymonosulfate with an organic salt of cobalt (Co/PMS) and hydroxyl radicals generated by the Fenton reagent in experiments performed in the dark or in the presence of solar light. The results showed that the use of solar light is very beneficial to the degradation efficiency of these processes.

Experimental results revealed a significant enhancement in the degradation efficiency of the Co/PMS/UV and Fe/H_2O_2/UV process when using solar radiation. This effect demonstrated to be independent from the increase of temperature caused by IR radiation absorption in the solar photoreactor.

Kinetic data obtained from the experiments showed that the application of solar radiation as driving force for both processes increased the reaction rate constant approximately by one order of magnitude when compared to the dark processes. Comparison between the two processes studied using kinetic data demonstrated that the Co/PMS reagent exhibited 2,4-D degradation efficiency as high as the photo-Fenton process and that the former reagent is capable of performing the process efficiently without pH adjustments and solar radiation highly improved the reaction rate. In this study, the applicability of solar radiation to drive sulfate radical-based AOPs was demonstrated for the first time. The results revealed that by using solar light as energy source for the photo-process, a significant enhancement in the reaction rate constant was achieved for the degradation of 2,4-D pesticide, a widely distributed, highly toxic and environmentally important pollutant in aquatic systems.

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