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Decontamination of soil washing wastewater using solar driven advanced oxidation processes

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ABSTRACT

Decontamination of soil washing wastewater was performed using two different solar driven advanced oxidation processes (AOPs): the photo-Fenton reaction and the cobalt/peroxymonosulfate/ultraviolet (Co/PMS/UV) process. Complete sodium dodecyl sulphate (SDS), the surfactant agent used to enhance soil washing process, degradation was achieved when the Co/PMS/UV process was used. In the case of photo-Fenton reaction, almost complete SDS degradation was achieved after the use of almost four times the actual energy amount required by the Co/PMS/UV process. Initial reaction rate in the first 15 min (IR_{15}) was determined for each process in order to compare them. Highest IR_{15} value was determined for the Co/PMS/UV process (0.011 mmol/min) followed by the photo-Fenton reaction (0.0072 mmol/min) and the dark Co/PMS and Fenton processes ($IR_{15} = 0.002$ mmol/min in both cases). Organic matter depletion in the wastewater, as the sum of surfactant and total petroleum hydrocarbons present (measured as chemical oxygen demand, COD), was also determined for both solar driven processes. It was found that, for the case of COD, the highest removal (69%) was achieved when photo-Fenton reaction was used whereas Co/PMS/UV process yielded a slightly lower removal (51%). In both cases, organic matter removal achieved was over 50%, which can be considered proper for the coupling of the tested AOPs with conventional wastewater treatment processes such as biodegradation.

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1. Introduction

Oil exploration and production zones are very frequently contaminated with petroleum hydrocarbons or its derivatives. In Mexico, the most important exploration and production zones are located South-east of the country. Soil contamination, as result of the improper disposal practices or accidental spillage of hydrocarbons to the environment, has been widely documented as a serious environmental issue mainly because of the possibility of these pollutants to leach to underground water affecting water quality of this very important supply source [1–3]. Restoration of soil contaminated with hydrocarbons at the sites has become a very interesting scientific challenge, mainly because of the actual complexity of the matrix. There are several remediation techniques that have proven to be excellent options for remediation purposes. One of them is surfactant enhanced soil washing. Surfactant–oil–water systems have been studied recently due to their enhanced oil recovery potential [4]. Surfactants increase the aqueous solubility of non-aqueous phase liquids (NAPLs) by reducing their surface/interfacial

tension at air–water and water–oil interfaces [5], but also promoting micelization of oil droplets and avoiding its consequent mobilization.

With the growing interest of surfactants' application in environmental remediation, several authors [6–8] have studied the removal of single and double components of petroleum hydrocarbons through soil washing using aqueous surfactant solutions and concluded that this approach is a promising remediation technique [9,10]. Many papers related to the surfactant enhanced soil washing deals with aspects such as the selection of ideal surfactant and doses, soil washing mechanisms and modeling of the process [11,12], the use of different driving forces for surfactant enhanced soil washing, i.e. air sparging and flotation [13,14] and other engineering aspects [15].

Our research group has been studying for years this remediation technique at laboratory, pilot plant and full-scale levels, for decontamination of soil containing diesel, gasolines, crude oil and other petroleum fractions [9,10,16,17]. We have found that sodium dodecyl sulphate (SDS), a common representative of synthetic surfactant with a simple hydrocarbon chain widely used in commercial detergent formulations and nowadays for environmental remediation [18–21], possesses greater petroleum hydrocarbon removal than other surfactants employed [5,20,22].

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Soil washing technology consists of the use of solvents, usually in the presence of surfactants, to increase the solubility of petroleum hydrocarbons. Washing fluid is then injected into the soil where it extracts adsorbed contaminants. Subsequently, the surfactant solution carrying the extracted contaminants is recovered and submitted to a treatment process. The solution containing both surfactant and contaminants desorbed from the soil could be passed through different physical–chemical and/or biological processes with the goal of recycling the water. These processes frequently consist of coagulation–flocculation–sedimentation steps coupled with an activated sludge system. Other ways to separate spend surfactants from water is the use of tangential-flow membranes, i.e. ultra-filtration [23] or interchange columns [24].

Biodegradation is the most frequent technology used for the removal of surfactants and other pollutants from soil washing wastewater as widely reported in the literature [25,26]. Nevertheless, the problem of the removal of pollutants in washing water becomes more complicate since it concerns the biodegradation of both the surfactant and extracted contaminants obtained from the soil. In this case, the presence of pollutants with high toxicity and persistence may inhibit the applicability of biological treatment [27]. To date, only few studies dealing with the treatment of surfactants and chemicals present in effluents from soil washing processes have been reported and even fewer studies have dealt with the complete detoxification of the complex mixtures generated during these processes.

Advanced oxidation processes are being used as alternative processes for water treatment applications with pesticides, dyes and surfactants [28–31]. They are based on the generation of strong oxidizing species capable of reacting non-selectively with any organic compound. This oxidizing species can be generated by both non-photochemical and photochemical technologies.

The Fenton method is a common oxidation process that includes the formation of hydroxyl radicals (2.8 V of oxidation potential) by the combination of ferrous salt and hydrogen peroxide. The addition of radiation, like UV and visible light, accelerates the generation of this radicals and it is known as photo-Fenton process. The use of other transition metals with the combination of oxidants had being studied. The cobalt/peroxymonosulfate (Co/PMS) system was tested for the degradation of several organic pollutants [29,30,32,33]. The combination of UV light (using lamps or solar radiation) to promote the formation of radical species in this system was recently explored [30,34,35].

In a recent work, we reported the application of photoassisted Fenton-like processes for surfactant degradation [41]. Few studies dealing with Fenton and photo-Fenton process for the pretreatment of wastewater from soil washing process had been reported [36,37] and, to our knowledge, no reports dealing with the treatment of soil washing wastewater containing both surfactants and petroleum hydrocarbons using solar driven cobalt/PMS/UV process have been published. The aims of this study is to determine the applicability of Fenton and solar driven Fenton-like processes as alternative technologies for the treatment of surfactant and hydrocarbons mixture contained in the soil washing wastewater.

2. Experimental

2.1. Reagents

Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was purchased from Baker and cobalt acetate (CoAcO_2) from Aldrich. The oxidants employed were hydrogen peroxide (Aldrich, 50% stabilized) and sodium peroxymonosulfate (PMS), active component of OXONE[®] manufactured by DuPont, was obtained from Aldrich. All reagents were ACS reagent grade and were used as received.

2.2. Contaminated soil

Soil contaminated with oil was excavated from a production zone at Tabasco Mexico. Torres et al. [42] have made an extensive characterization of this soil, including the average TPH content (150–670 mg/kg) and the TPH value for every particle size (from meshes 4–100), Cd, Cu, Cr, Ni, V and Zn contents, electrical conductivity (126 mS/cm), pH (about 5.7) an density (2.5 g/cm³), among others.

2.3. Wastewater generation

In a previous work [42] it was determined that sodium dodecyl sulphate, SDS, at a dose of 1.0% removes more than 35% of the initial TPH concentration in soil. In this work, the same surfactant and dose was employed. SDS is an anionic surfactant with a molecular weight about 288 g/gmol and a critical micellar concentration (CMC) of 400 mg/L.

Approximately 20 L of wastewater were produced in a 1 L beaker equipped with 4 baffles (T/10 wide, where *T* is the tank diameter). The tank was filled with 800 mL of surfactant solution and 25 g of the contaminated soil. The soil/surfactant solution was agitated at different speeds for 2.5 h. At the end of the washing procedure, the soil and surfactant solution were separated by decanting the fluid. Wastewater containing surfactant, desorbed hydrocarbon and other soil constituents were stored at 4 °C until its use in the advanced oxidation process (AOPs) experiments.

2.4. Analytical methods

The amount of the anionic surfactant in each sample was determined using a spectrophotometer UV–vis Hewlett Packard 8452 A by using the methylene blue active substances (MBAS) analysis, according to the standard methods for the examination of water and wastewater [38]. Chemical oxygen demand (COD) was analyzed at the beginning and end of the experimental runs as an index of the presence of organic matter (surfactant, petroleum hydrocarbons and others) in the soil washing wastewater using the volumetric titration method [38] because we have found that this procedure provides more accurate results and minimize H_2O_2 or PMS interference. In order to assure the lack interference of the oxidant agent in the sample during COD determination, blank samples including a oxidant agent concentration equal to the initial one in the reaction mixtures were analyzed.

2.5. Soil washing wastewater treatment

2.5.1. Experiments in the dark

In a precedent work [41] we have studied the actual oxidation of the surfactant used for soil washing (SDS) and found the best conditions applicable to its oxidation. In this work we used those previously identified conditions for SDS oxidation to real wastewater. Two transition metal concentration (cobalt or Fe^{2+} , 0 and 10 mM) and two oxidant agent initial concentration (H_2O_2 or PMS, 0 and 32 mM) were tested for the experimental runs. Table 1 shows the actual results of initial characterization of the soil washing wastewater, before any dilution, used for the experiments.

Experimental procedure for the experiments in the dark was carried out in a 2 L Erlenmeyer flask covered with foil aluminum to avoid irradiation of the solution. The quantity necessary to reach the initial concentration of transition metal (Fe^{2+} or cobalt) was added in 2 L of the wastewater. After adding the transition metal, a sample of 100 mL, corresponding to the initial time ($t = 0$), was obtained, quenched and immediately analyzed. Then the appropriate volume of the oxidant (H_2O_2 or PMS) to reach the desired concentration was

Table 1
Initial characterization of the soil washing wastewater, before any dilution

Parameter	Units	Value
pH	Unitless	5.21
Conductivity	$\mu\text{S}/\text{cm}$	1,353
COD	mg/L	20,153
BOD	mg/L	8,410
Total solids	mg/L	14,919
Hardness, as CaCO_3	mg/L	337
MBAS	mg/L	3,638
Oil and grease	mg/L	94.5
Al	mg/L	429
Cr	mg/L	1.25
Fe	mg/L	290
Pb	mg/L	1.11

added to the mixture. The solution remained in constant agitation during the experiment. Sampling and preservation, with NaOH 12N for Fenton reaction and methanol (pesticide grade) for Co/PMS process, as previously reported [32,35], was performed after 5, 10, 15, 30, 45 and 60 min of reaction and immediately analyzed for MBAS determination. All the experimental runs were performed by triplicate in order to determine average and standard deviation values for each run.

2.5.2. Experiments in the presence of radiation

For experiments using radiation, a bench-scale study was carried out using a tubular pyrex glass reactor located in the focus of a compound parabolic concentrator (CPC) detailed elsewhere [28,39,41]. The system is bended 19° (local latitude) and has a total collection surface of 0.1 m^2 . Experimental conditions for solar driven process were the same as the experiments performed in the dark. The reaction solution was put in circulation in the reactor for 5 min to achieve homogeneous conditions. A sample of 100 mL, corresponding to zero time (initial conditions), was taken and preserved appropriately for each process. Afterwards, the oxidant was added to reach the desired initial concentration and samples were taken after 5, 10, 15, 30, 45 and 60 min of reaction. As in the case of experiments in the dark, every experimental run was performed by triplicate in order to obtain average and standard deviation values.

Global radiation from 280 to 2800 nm was measured at each sampling with a Li-Cor pyranometer (LI-200SA) placed at the same slope to avoid angle adjustments. 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, from which a 0.35 factor was obtained for the radiation included in this wavelength range as proposed by Chacon et al. [28]. In the case of Co/PMS experiments, able to use the UV part of the solar spectrum [35], global solar UV radiation was obtained using a total UV radiometer (Eppley, TUVR) which is able to measure in a wavelength range between 295 and 385 nm. Accumulated energy, defined as the total amount of radiative energy reaching the reactor since the beginning of the experiment up to a given time by unit volume, was determined using the relation previously reported by Goslich et al. [40]:

$$Q_n = Q_{n-1} + \Delta t G_n \left(\frac{A}{V} \right), \quad \Delta t = t_n - t_{n-1} \quad (1)$$

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

3. Results and discussion

3.1. Processes in dark conditions

Results obtained for the experiments performed under absence of radiation are shown in Fig. 1. As seen, insignificant surfactant degradation was achieved when soil washing wastewater was put in contact with H_2O_2 or PMS in the dark during 60 min. The effect of Fenton reagents in the degradation of the surfactant is evident. For the conditions employed (10 mM Fe^{2+} ; 60 mM H_2O_2), 48% of SDS degradation was achieved in 60 min of reaction time. It is worth to note here that SDS degradation obtained in real soil washing wastewater is lower than those we found when working synthetic SDS samples. For the latter, 63% of SDS removal efficiency was determined for the same reaction time [41]. This behavior can be rationalized by considering the actual complex composition of real soil washing wastewater compared with synthetic SDS samples only by considering total petroleum hydrocarbon (TPH's) concentration in the real sample (6.8 mg/L) [42].

Other works [36] had reported surfactant removal over 95% for wastewater containing an anionic surfactant with an initial concentration of 10 mg/L using 0.33 mM FeSO_4 and 1.76 mM H_2O_2 and an initial pH around 3. Marked differences between these results reported by Lin et al. [36], and those showed in this work are probably due to the initial SDS concentration. In this work, SDS initial concentration was over 3600 mg/L, as obtained from soil washing process, over three orders of magnitude higher than those reported by Lin et al. [36].

Fig. 1 also shows the result of the experiment performed in dark conditions with the Co/PMS process. Final degradation of the ionic surfactant under tested conditions (10 mM cobalt; 30 mM PMS) was 52%. By comparing this result with Fenton reaction (10 mM Fe^{2+} ; 60 mM H_2O_2) only a slightly difference, 4% of SDS removal is observed.

In order to compare all the experimental results reported, initial reaction in the first 15 min (IR_{15}) values for the dark Fenton and Co/PMS processes are depicted in Table 2. From Table 2, it is interesting to note that treating soil washing wastewater with PMS alone in the dark results in the lowest IR_{15} value, 1×10^{-4} mmol/min. Application of H_2O_2 under dark conditions improved the initial rate almost twice. The use of transition metal as catalyst improved the initial rate up to one order of magnitude in both cases.

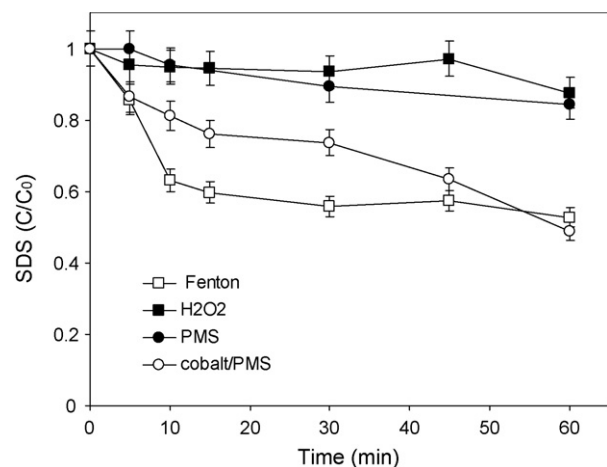


Fig. 1. Degradation of SDS (initial concentration 3638 mg/L) using different conditions of the Fenton reagents under dark conditions.

Table 2IR₁₅ values for different photoassisted and non-photoassisted Fenton and Co/PMS tests

Reaction conditions (dark experiments)	IR ₁₅ × 10 ⁻⁴ (mmol/min)	Reaction conditions (irradiated experiments)	IR ₁₅ × 10 ⁻⁴ (mmol/min)
[PMS] = 32 mM	1	[PMS] = 4 mM	20
[H ₂ O ₂] = 60 mM	1.9	[H ₂ O ₂] = 60 mM	10
[cobalt] = 10 mM; [PMS] = 32 mM	20	[cobalt] = 10 mM; [PMS] = 32 mM	110
[Fe] = 10 mM; [H ₂ O ₂] = 60 mM	20	[Fe] = 10 mM; [H ₂ O ₂] = 60 mM	72

3.2. Solar-driven processes

Fig. 2 shows the results of application of solar radiation to Fenton reaction and Co/PMS process. The figure depicts the behavior of SDS concentration using the same conditions used for dark experiments.

No effect of solar radiation alone (photolysis) was observed for any of the experiments. Application of the oxidant agents, hydrogen peroxide and PMS in the presence of solar radiation showed a slight improvement in SDS degradation. H₂O₂ degraded 28% of the initial SDS using around 18 kJ/L of accumulated energy whereas PMS achieved 52% of SDS degradation for the same Q_n value. When transition metal catalyst is used, very interesting results were observed for both processes. In the case of photo-Fenton reaction, almost complete SDS degradation was reached with 12 kJ/L of accumulated energy. On the other hand, cobalt/peroximonosulfate produced complete SDS degradation in about 2.7 kJ/L. These results agree with those obtained for synthetic SDS samples reported previously [41]. In that work we found the same trend, except for Co/PMS/UV test where a Q_n value close to 5 kJ/L was determined. This small difference is most probably due to experimental variation than to real experimental kinetic reasons.

For comparative purposes, IR₁₅ values for irradiated experiments are also depicted in Table 2. In this case, H₂O₂ showed the lower initial rate value (1 × 10⁻³ mmol/min), over five times higher than the value determined for process under dark conditions (1.9 × 10⁻⁴ mmol/min). PMS is highly activated by radiation as can be seen from the IR₁₅ value determined under irradiation

Table 3

Organic matter depletion, measured as COD, determined under photoassisted conditions for the tested oxidation processes

Oxidation process	Initial COD (mg/L)	Final COD (mg/L)	Removal (%)
[cobalt] = 10 mM; [PMS] = 32 mM	20,080	10,233	51
[Fe ²⁺] = 10 mM; [H ₂ O ₂] = 60 mM	20,020	6,075	69

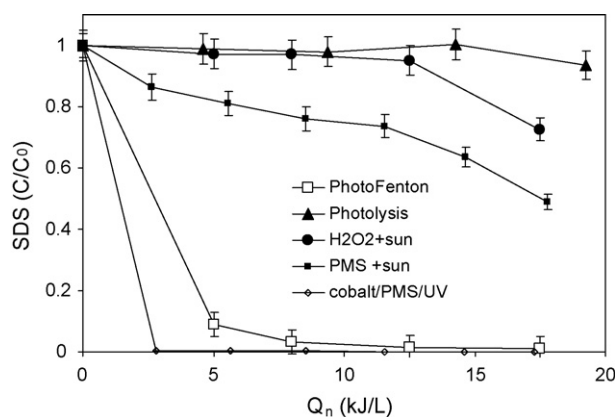


Fig. 2. SDS degradation (initial concentration 3638 mg/L) using Fenton reaction (10 mM FeSO₄; 60 mM H₂O₂) and Co/PMS/UV (10 mM Co; 32 mM PMS) under solar radiation as function of accumulated energy Q_n (kJ/L). SDS degradation achieved using H₂O₂ and PMS alone under solar radiation is also shown.

(2 × 10⁻³ mmol/min); 20 times higher than the value for dark conditions and twice the value for H₂O₂. Comparable results observed in experiments performed in the dark for Fenton and Co/PMS were not longer observed when solar radiation was used. Photo-Fenton reaction resulted in an IR₁₅ value of 7.2 × 10⁻³ mmol/min whereas the rate of Co/PMS/UV process reached 1.1 × 10⁻² mmol/min. Despite this improvement of the initial reaction rate, the actual values obtained are far from these reported previously for synthetic SDS solutions [41]. Again, we believe that this difference is due to the high organic load in real soil washing wastewater. In order to test this hypothesis, we determined chemical oxygen demand at the beginning and end experimental runs in the presence of radiation. The results are shown in Table 3.

As shown, the behavior of the organic matter present in the wastewater is quite different from that presented by SDS. It is clear that, if SDS is completely oxidized in the very early stages of the processes, organic matter present after 1 h of irradiation (Q_n = 20 kJ/L) must be associated with total petroleum hydrocarbons (TPHs) and other organics present in the effluent. Despite the potential complexity of the chemicals included in the waste water, results from Table 3 show that the tested processes are capable to remove at least half of its initial concentration. It is interesting to note that photo-Fenton reaction achieved the highest COD removal, 69%, compared with Co/PMS/UV despite the fact that the latter exhibited the fastest SDS degradation. We believe that sulfate radicals generation in the Co/PMS/UV process occurs fast and propagation reaction produced by these radicals (recognized as highly oxidizing species) could degrade SDS as fast as experimentally observed. Nevertheless, as irradiation proceeds, the capability of Fenton reagents to use UV and part of the visible radiation starts to make the difference. As stated earlier, in the best case solar UV radiation can reach 9% (we have determined an average of 5%) whereas the UV + visible wavelength range used by photo-Fenton reagents have been proposed as far as 35% [28]. Considering the difference in the radiation field available to promote the different processes, without considering other parameters (i.e. catalysts' quantum yields), the experimental results became reasonable.

Despite the fact that both tested processes are not able to completely remove all amount of COD from the effluent, actual COD reduction for experimental runs is anyway interesting, considering the potential coupling of AOP's with other non-conventional wastewater treatment processes. In particular, coupling photoassisted-AOP's with biological processes is currently considered an interesting emerging technology [43–46]. Considering different biodegradability tests using the Zahn–Wellens procedures, solutions become biocompatible by elimination of 45% of the initial organic matter [47]. We have achieved the removal of over 50% of initial COD load, which is a direct measurement of the organic matter in the wastewater [48], in the lower case so we could speculate that the final effluent is biocompatible or at least much more biocompatible than the initial wastewater.

4. Conclusions

Real soil washing wastewater was tested for its oxidation treatment using two different advanced oxidation processes in the

presence and absence of radiation. Results from experimental runs showed that surfactant present in the effluents (sodium dodecyl sulphate, SDS) is easily removed by the photoassisted procedures requiring low accumulated energy to complete the degradation process.

Comparison between photoassisted and non-photoassisted procedures showed an important difference caused by the use of solar radiation to drive the oxidation process. In the same way, the effect of the transition metal catalyst (cobalt and iron) was demonstrated have an important role in the processes, improving the reaction rate in both cases compared with the experiments performed using the oxidant agent (hydrogen peroxide or PMS) alone.

In order to test the efficiency of the proposed methods to carry out the removal of other organic component presents in the soil washing wastewater (i.e. total petroleum hydrocarbons), the chemical oxygen demand was determined at the start and end of the photoassisted procedures. It was found that both technologies tested were able to reduce the total organic matter content in the effluent achieving a COD removal as high as 69%, in the case of photo-Fenton and 51% for cobalt/PMS/UV. Despite complete oxidation of organic matter was not possible after almost 20 kJ/L of accumulated energy (around 1 h of solar irradiation), the produced effluent can be considered as more biocompatible and the possibility of coupling the photoassisted processes with biological treatment becomes an important approach for effluent treatment.

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