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ORIGINAL ARTICLE

Combined photocatalytic and Fenton oxidation for oily wastewater treatment

Yasmina Mokhbi[1] · Mourad Korichi[1] · Zineb Akchiche[1]

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Abstract

Our studies focused on assessing the effectiveness of the heterogeneous photocatalysis method (TiO_2/UV) and examining the feasibility of photocatalysis coupling with hydrogen peroxide in the treatment of oily industrial wastewater. Our oily water sample was taken from the de-oiling Haoud Berkaoui station entering, which is located 770 km in southern of Algiers); the AOPs investigated are TiO_2/UV (photocatalysis) and $TiO_2/UV/Fe^{2+}/H_2O_2$ (photocatalysis–Fenton's reagent). This method is used as an alternative or in addition to the conventional treatment techniques (coagulation–flocculation–decantation and filtration…etc). In this work, first we copulated between the two photocatalytic methods (TiO_2/UV) and the Fenton's reagent (H_2O_2/Fe^{+2}) and then we studied the effect of various experimental factors on the treatment process: pH, initial concentration for each of the TiO_2, H_2O_2, Fe^{2+}, and oil pollutants and finally temperature. The study showed a marked improvement in efficiency on the treated water quality in terms of color, turbidity, and COD under optimized conditions (oil concentration, quantity of catalysts, temperature, Fenton's reagent concentration, and the pH of the solution).

Keywords UV irradiation · Fenton's reagent · Pollutant · Photocatalysis · TiO_2 · COD · Advanced oxidation process

List of symbols

UV	Ultraviolet
TiO_2	Titanium dioxide
COD	Chemical oxygen demand
AOPs	Advanced oxidation process
Re%	Oil removal rate
pH_{PZC}	pH at the surface of a solid at zero charging

Introduction

Recently, the search for alternative methods for the treatment of oily wastewater has led to discover new technologies. Among these technologies, the so-called advanced oxidation processes (AOPs) are booming. This technology is based on the production of non-selective reactive oxidative species that will enable the oxidation of a large number of organic pollutants (Glaze et al. 1987; Bauer and Fallmann 1997). The oxidant most commonly used is the hydroxyl radical due to its high reactivity ($E° = 2.73$ V). Figure 1 shows details of all the processes, in which the AOPs are divided into two major methods: homogenous and heterogeneous, containing several techniques:

1. Chemical oxidation processes (H_2O_2/Fe^{2+} and H_2O_2/O_3) (Klavarioti et al. 2009);
2. Photocatalytic processes (H_2O_2/UV, O_3/UV) (Fe^{2+}/H_2O_2/UV and TiO_2/UV);
3. Sonochemical oxidation processes;
4. Electrochemical oxidation processes (Klavarioti et al. 2009).

Among these techniques, heterogeneous photocatalysis, particularly titanium dioxide, proved to be an effective mean for the removal of pollutants present in water. This technique relies on the excitement of a semiconductor (TiO_2) by a UV light source in the aqueous phase.

Photocatalytic applications for water pollution have already reached the stage of industrial pilot. These studies have shown the efficiency of the process on families of very different organic compounds such as dyes (Guillard et al. 2003), pesticides (Hermann et al. 2000), and saturated or unsaturated hydrocarbons (Herrmann et al.1999) and phenols (Sun et al. 2009). Also recently, Wang et al. (2009)

✉ Yasmina Mokhbi
mokhbi26@gmail.com

[1] Fac. des Sciences Appliquées, Lab. Dynamique, Interactions et Réactivité des Systèmes, Univ. Ouargla, BP 511, Ouargla, Algeria

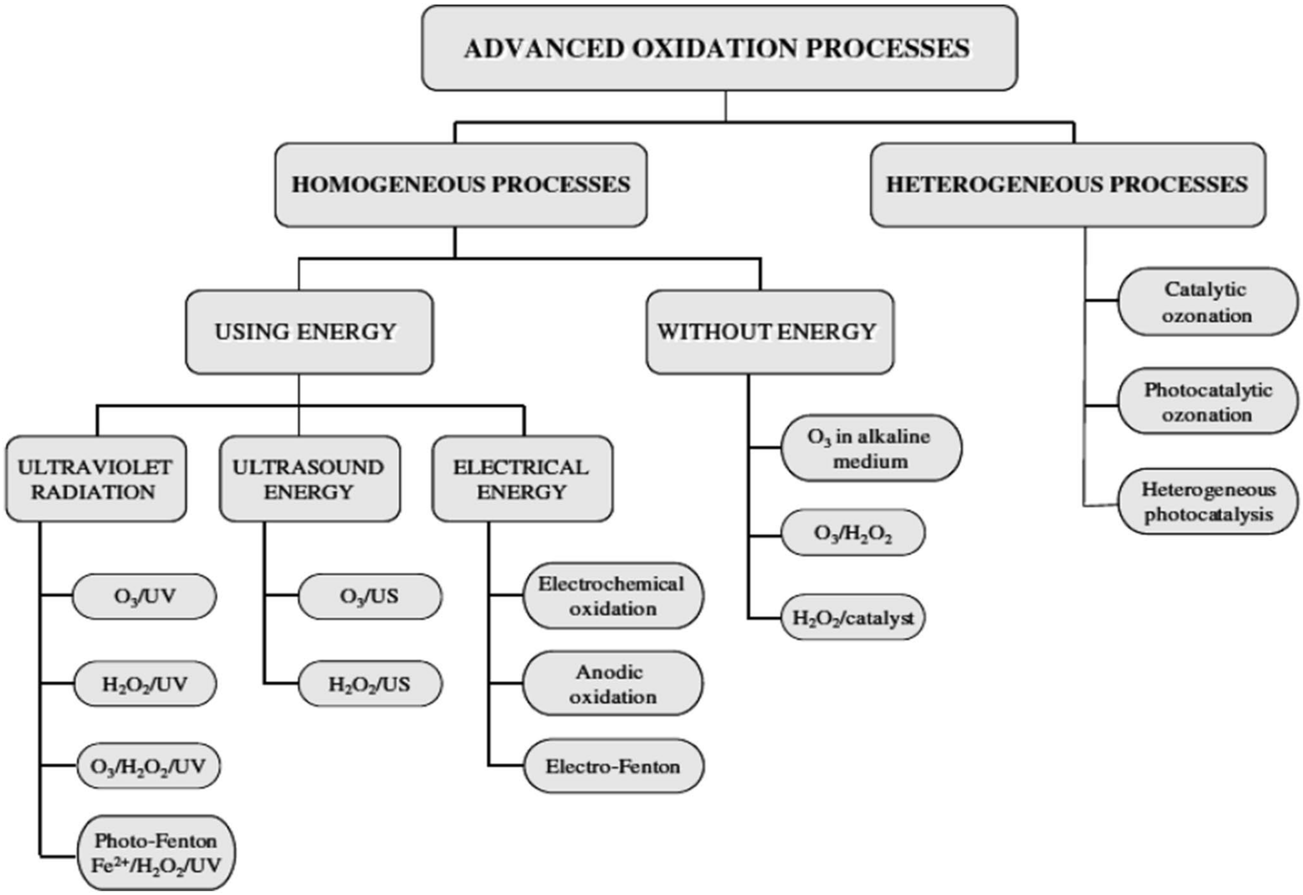

Fig. 1 Classification of advanced oxidation processes

obtained a degradation of 4-chlorophenol by photocatalysis with a nano-titanium dioxide catalyst. In the aqueous solution, photocatalytic degradations of more than 360 organic compounds have been studied (Huchon 2006). Today TiO_2 is the most used semiconductor in photocatalysis.

In the other hand, Fenton's reagent method also has a very positive influence on treatment process especially for non-degradable organic pollutants.

Fenton's reagent also removes or degrades a wide variety of contaminants in aqueous solution either alone such as

- Textile industries (Arslan and Teksoy 2007; Liu et al. 2007), pharmaceutical (as a pre-treatment) (San Sebastián Martínez et al. 2003), dyeing (Gulkaya et al. 2006), dyes (Wang 2008), olive oil mills (Rivas et al. 2001; Beltrán-Heredia et al. 2001), oil (Gao et al. 2004), and cosmetics (Bautista et al. 2007);
- Reduction of polynuclear aromatic hydrocarbons (Beltrán et al. 1998) and treatment of brines (Rivas et al. 2003);
- The degradation of phenol and biphenols (Carriazo et al. 2005; Ioan et al. 2007);
- Oxidation of plastic additives industry wastewater, rubber (Flotron 2004);

Or in combination with other processes such as

- Coagulation/Fenton's reagent: for the treatment of effluent from the herbicide production industry (Martins et al. 2005) and for the treatment of landfill leachates (Martins et al. 2005; Rivas et al. 2004);
- Treatment of wastewater containing pesticides for biological treatment combined with coagulation (Chen et al. 2007).

However, the utilization of the AOPs requires certain range for what is known as COD (chemical oxygen demand) (Umar et al. 2010). It means that only wastes with relatively small COD contents (≤ 5 g l^{-1}) can be suitably treated by means of these processes, and if COD value was out of range, then other methods would be much more suitable for the treatment process as shown in (Fig. 2). Due to the large costly reactants that are required for the process in case of

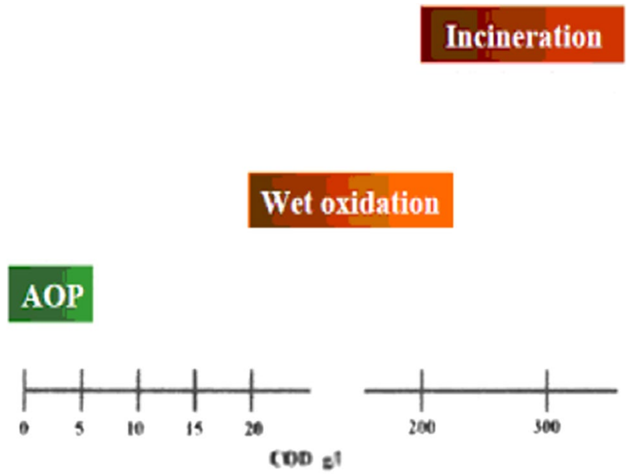

Fig. 2 Different technologies for the treatment of wastewater according to the chemical oxygen demand COD

high COD value, it would be more appropriate to use wet oxidation or incineration methods (Andreozzi et al. 1999).

Various experiments have shown that the value of COD in oily wastewater does not exceed 5 g per 1 liter, so the advanced oxidation process is best option to treat this kind of water.

The maximum allowed COD value for the national discharge standard is (100 mg l^{-1}) which is difficult to achieve with the conventional physical–chemical treatment methods. Therefore, it often becomes a difficult problem for oil field that produces oily water.

Objective

The objective of this work is to study the effectiveness of photocatalysis with Fenton's reagent for treating oily wastewater and the efficacy of some experimental factors such as pH and temperature, initial concentrations of TiO_2, Fe^{2+} and H_2O_2 on the oily wastewater treatment process.

The term photocatalysis was introduced in the 1930s. It is still a subject to a lot of researches. Photocatalysis is a special case of heterogeneous catalysis triggered by the irradiation of semiconductor materials with photons of energy adapted to the solid, and photocatalysts generate the formation of reagents, capable of decomposing by oxidation–reduction of organic or inorganic substances (Matthews et al. 1991).

The idea of photocatalysis method is centered about the excitation of a semiconductor (usually, titanium dioxide, TiO_2) by light (UV or visible). Under the action of photons, the semiconductor (or catalyst) produces highly oxidizing free radicals allowing the destruction of compounds adsorbed on its surface (Mukherji et al. 2011; Fujishima and Honda 1970).

The semiconductor TiO_2 converts photon energy into chemical energy by oxidation–reduction reaction. This causes the activation sites of TiO_2 and molecular degradation of the compounds present (Herrmann et al. 1999). The degradation process then consists in a succession of radical oxidations initiated by strong oxidants such as $OH^{\cdot}$.

The $OH^{\cdot}$ is directly generated by the photolysis of water molecules adsorbed on the active sites of TiO_2 (Fenton 1894).

Organic pollutants adsorbed on the catalyst are then degraded by successive radical reactions in non-toxic mineral species. The degradation capacity of the semiconductor is related to several parameters:

- the nature and intensity of light irradiation source or incident number photons for TiO_2 activation of and the nature of the reaction medium is the amount of TiO_2 (or active sites) for the production of hydroxyl (Kozlova et al. 2004) inside the water.
- Nature and concentrations of pollutants.

The following diagram (Fig. 3) summarizes all the physical and chemical processes that create the photocatalytic phenomenon.

The Fenton's reagent also is one the important AOPs methods which has been efficiently used as a chemical process for wastewater treatment and pre-treatment (Fenton 1894). The Fenton's system consists of ferrous salts combined with hydrogen peroxide under acidic conditions.

This reaction allows the generation of hydroxyl radicals as shown in the following reaction

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \quad (1)$$

Fe^{3+} produced can react with H_2O_2 and hydroperoxyl radical in the so-called Fenton-like reaction, which leads to regenerating Fe^{2+} (reactions 2, 3). Fe^{2+} regeneration is also possible by reacting with organic radical intermediates (reaction 4) given by Perez et al. (2002) as follows:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+} \quad (2)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + H^{+} + O_2 \quad (3)$$

$$Fe^{3+} + R^{\cdot} \rightarrow Fe^{2+} + R^{+} \quad (4)$$

Materials and methods

Wastewater characterization

To study the effect of degradation on the efficiency of processes used on the oily waters, we took our sample from

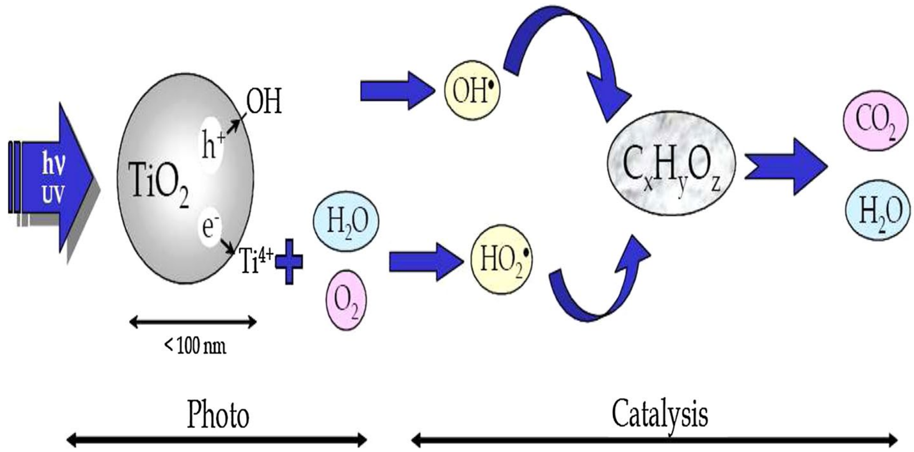

Fig. 3 Physical and chemical processes of the photocatalytic phenomenon

Haoud Berkaoui inlet station. The main properties of the oily wastewater are COD of 1298 mg/l, turbidity of 120 NTU, pH 6.3, and suspended solids of 435 mg/l.

Samples are taken under strict aseptic conditions to avoid accidental contamination during handling. Sampling was carried out as follows:

The samples are taken using a sampling rod rinsed with the water to be taken.

Glass bottles and jerry cans designed for water sampling are pre-washed, rinsed thoroughly to remove any traces of detergent.

Preservation

- Completely filled vials are tightly closed and then covered with aluminum foil to provide double protection against possible contamination.
- The filled vials are kept in a refrigerator at low temperature (5–10 °C).

This water will then be tested by the advanced oxidation method proposed for the degradation of oil and organic material in water and analyzed by spectroscopic method to determine the chemical oxygen demand (COD) in the water.

Experimental materials

The basic catalyst that we used while combining Fenton's reagent with heterogeneous photocatalytic handling is the titanium dioxide.

Powder of TiO_2, of crystalline structure anatase > 99%, has size between 5 and 10 nm, with a specific surface SBET of approximately 320 $m^2 g^{-1}$.

Fe^{2+} in Fenton's reagent (Fe^{2+}/H_2O_2) is prepared by making a solution from Fe^{2+} salt. H_2O_2 was obtained in liquid (30% of H_2O_2) from a commercial supplier. Sulfuric acid is used for adjusting the pH of the oily wastewater samples during treatment. Properties of chemicals used in this work are presented in Table 1.

Methodology

All photochemical experiments were carried out in a batch-mode laboratory-scale unit using a 500-ml beaker. First, the pH value of the oily wastewater samples was adjusted at the desired values with sulfuric acid or sodium hydroxide before being tested with the oxidation, and then, ferrous ions solution and hydrogen peroxide were added to produce hydroxyl radicals. Therefore, the combination was agitated by magnetic stirring and exposed to UV radiation (254 nm wavelength), as demonstrated in Fig. 4. Samples were taken every 30 min in the discontinuous experiments for COD measurements.

Irradiation system

The primary radiation range of the UV lamp used in this work is 365 nm, which corresponds to energy of about 3.4 eV. This energy is greater than the width of the forbidden band of TiO_2

Table 1 Properties of chemicals used in the study

Compound	Molecular weight	Formula	Manufacturer	Purity
Iron chloride tetrahydrate	198.8	$FeCl_2–4H_2O$	Sigma-Aldrich	98.0%
Hydrogen peroxide	134.01	H_2O_2	Sigma-Aldrich	30 wt%
Sulfuric acid	98.08	H_2SO_4	Sigma-Aldrich	97.0%
Sodium hydroxide	39.997	NaOH	Sigma-Aldrich	73%

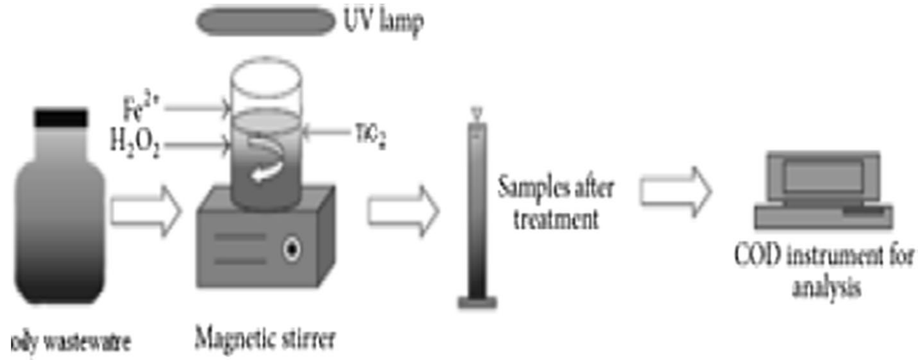

Fig. 4 Schematic diagram of a laboratory-scale (photocatalysis–Fenton's reagent) test

(3.2 eV). So it will activate the material by generation of electrons and holes.

Analytical determinations

The oil concentration is one of the important parameters of oily wastewater treatment. This concentration of oil is reported in the form of mg/l. There are several methods to detect the presence of oil in the waste water and also to measure the amount of this oil such as COD measurement, measurement of turbidity, and total organic carbon (TOC) measurement (Portela et al. 2001; Rachu 2005).

The appropriate method is determined based on several parameters: the range of the existing quantity of oil, the response time of the measurement, the desired accuracy and the cost. However, for the specific application of measuring the pollution rate of oily wastewater, the choices are limited.

COD is used as a measure of pollutants. It is normally measured in industrial wastewater treatment plants and gives an indication of the effectiveness of the treatment process. It is generally expressed in terms of COD removal, measured as a percentage of the purified organic material during processing.

The COD measurements were done with the use of HACH analyzer (model HACH DR-2400). Turbidity was measured using a HACH 2100 N IS Turbidity meter (ISO method 7027). The pH of the wastewater was adjusted using a digital pH-meter (model PHM62 Radiometer). The oil removal rate (Re%) is expressed by equation (Portela et al. 2001; Wanichkul et al. 2000):

$$Re\% = \frac{y_0 - y}{y_0} \times 100,$$

where y_0 and y are the COD of the emulsion of the initial state and the final state, respectively.

Results and discussion

The studied experiments presented the results of the influence of experimental factors on coupling system (photocatalysis–Fenton's reagent) of oil degradation. The results were as follows:

TiO_2 concentration

The results show positive influence of TiO_2 concentration increase on the degradation rate, due to the increase in the number of oil molecules that were absorbed by the TiO_2. The optimum TiO_2 dosage in combined system (photocatalysis–Fenton's reagent) achieved was 0.8 g/l. TiO_2 dosage greater than the maximum value (0.8–1 g/l) has a negative effect on this process since the excess TiO_2 particles increase the turbidity of the solution that will decrease the penetration of light into the solution, resulting in a reduction in production of hydroxyl radicals ($OH^{\cdot}$) at the TiO_2 surface available to degrade the organic compounds in the oily water. These explanations were also mentioned by several studies (Fujishima and Honda 1970; Saien and Nejati 2007; Lee et al. 2003; Bauer et al. 1999).

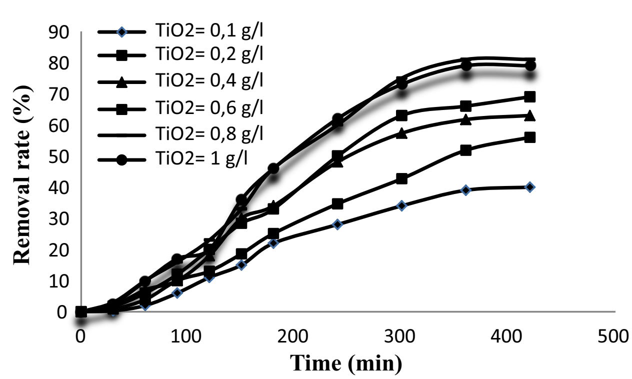

Fig. 5 Influence of TiO_2 concentration on the (photocatalysis–Fenton's reagent) system (working conditions: pH 6.3; H_2O_2 = 400 mg/l; Fe^{2+} = 40 mg/l)

The relation between the oil removal rate (Re%) and TiO_2 concentration is shown in Fig. 5.

Fenton's reagent concentration

H_2O_2 concentration

Figure 6 shows the impact of the increase in H_2O_2 on degradation rate of the pollutant with the use of TiO_2. The oil removal rate (Re%) goes up with the increase in H_2O_2 concentration, However, the excess amount of hydrogen peroxide can cause the auto-decomposition of H_2O_2 into oxygen and water, decreasing the hydroxyl radicals production level. Therefore, decreasing the concentration of hydroxyl radicals and reagents reduces efficiency (Mukherji et al. 2011; Moraes et al. 2004; Tony et al. 2009). Based on that, the optimum H_2O_2 concentration in combined system (photocatalysis–Fenton's reagent) is between 400 and 600 mg/L.

Iron concentration

Similar to the previous experimental factors (TiO_2, Fe^{2+}), the oil removal rate (Re%) increases with increasing iron concentration in the solution. The optimal concentration of iron observed was between 40 to 60 mg/l and going beyond that value adversely affects the process as shown in Fig. 7. This could be explained by:

- The addition of ferrous ions increases the turbidity of the wastewater during phototreatment, which prevents the absorption of the UV light necessary for the photo-Fenton process.
- The excess of ferrous ions may react with a compound that produces an OH˙ radical that inhibits the reaction rate (Neyens et al. 2003).

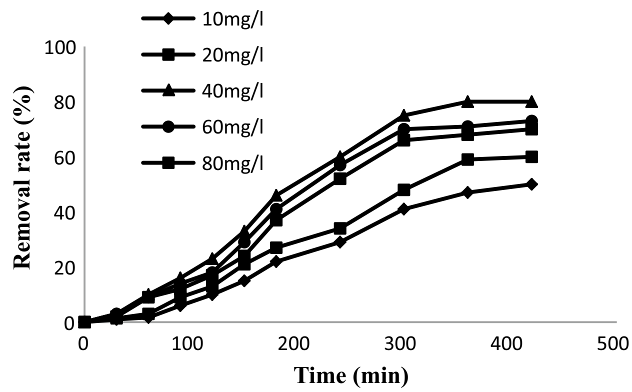

Fig. 7 Influence of Fe^{2+} concentration on the (photocatalysis–Fenton's reagent) system (working conditions: pH 6.3; TiO_2 = 0.8 g/l; H_2O_2 = 400 mg/l)

pH

The pH value is an important parameter for AOPs process especially for photocatalytic and Fenton's reagent catalysts degradation of charged organic pollutants, because the pH value of solution will change the existed configuration of degraded species and surface charges of catalysts.

To investigate the influence of the initial pH on oil photodegradation, oily water solutions are prepared and the initial pH are adjusted either with an H_2SO_4 solution or with a NaOH solution according to the desired pH. These mixtures are irradiated under the same experimental conditions as without pH adjustment. The results obtained are given in Fig. 8.

The shape of the curves is identical according to the pH. From Fig. 8, it can be stated that the performance of the photocatalytic degradation of the pollutant is strongly related to the initial pH of the sample to be irradiated. The

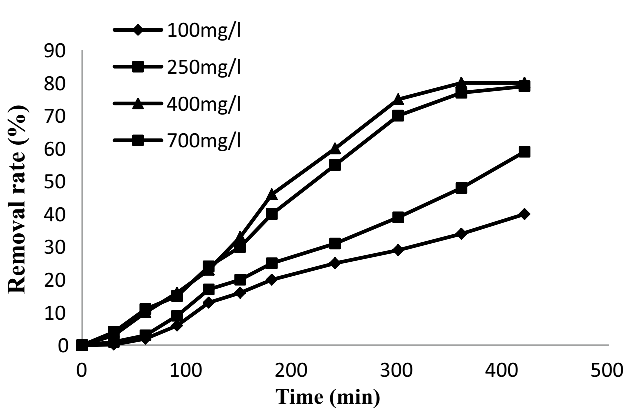

Fig. 6 Influence of H_2O_2 concentration on the (photocatalysis–Fenton's reagent) system (working conditions: pH 6.3; TiO_2 = 0.8 g/l; Fe^{2+} = 40 mg/l)

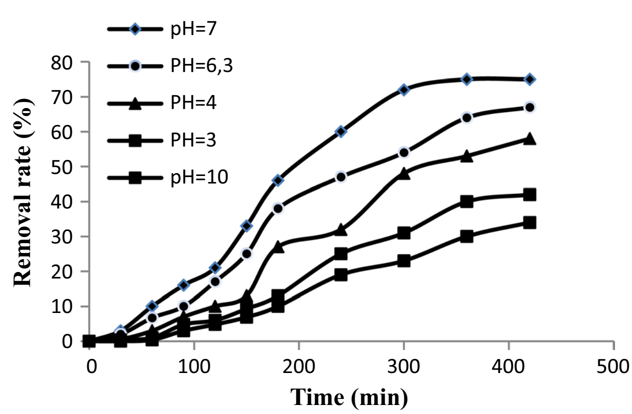

Fig. 8 Influence of pH on the (photocatalysis–Fenton's reagent) system (working conditions TiO_2 = 0.8 g/l; H_2O_2 = 400 mg/; Fe^{2+} = 40 mg/l)

best oil degradation efficiencies were obtained at the initial pH values between 6 and 7. On the other hand, very acidic or very basic solutions delay the photocatalytic process of the pollutant. This could be due to the fact that the oil is a nonionic compound and that the better efficiency would be obtained at the PZC pH of the catalysts which, moreover, is close enough to the natural pH (6.8) (Mustafa 2014) of the irradiated oil solution.

Initial concentration of the pollutant (oil)

From a real sample of oily water, synthetic samples were prepared to vary the initial concentration, actual sample mixture diluted with distilled water.

The first sample was diluted for 50% and COD value found was 700 mg/l; the second sample was diluted for 25% and COD value found was 300 mg/l. The two samples were compared with the original sample (100% concentration)

We performed the test with $H_2O_2 = 400$ mg/l, $Fe^{+2} = 40$ mg/l, $TiO_2 = 0.8$ g/l, and pH (6.3) in different sample concentrations 300, 700, and 1298 mg-COD/l, under the following conditions: stirring and artificial UV. The results of the evolution of the COD are given in Fig. 9:

This experiment has proven that the degradation rate is increased after diluting the initial emulsion concentration, and it also shows that the oil removal rates (Re%) are 79, 88, and 98% for the COD of 1298, 700, and 300 mg/l, respectively. This could be attributed to the decrease in turbidity of the oily wastewater. The emulsion turbidity for an initial COD of 1298 mg/l was 120 NTU. However, it gave only 25 NTU when the initial COD was 300 mg/l.

Decreasing turbidity clearly helps in the penetration of the UV light, what leads to the oil removal rate improvement. This result is consistent with the findings reported by Najjar et al. (2001).

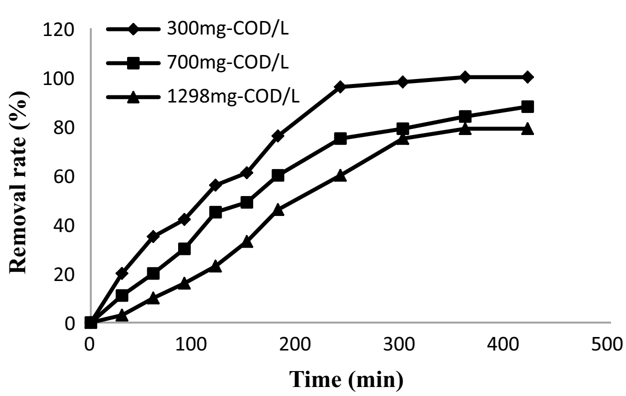

Fig. 9 Influence of initial pollutant concentration on oil degradation by (photocatalysis–Fenton's reagent) system at working conditions: $H_2O_2 = 400$ mg/l, $Fe^{+2} = 40$ mg/l, pH = 6.3 and $TiO_2 = 0.8$ g/l

Temperature

In general, it is agreed that the increase in temperature increases the number of collisions between molecules and therefore results in an improvement in oxidation rate (Wu et al. 2010; Guedes et al. 2003).

Figure 10 gives the influence of changing temperature on the treatment efficiency. The higher degradation of oily wastewater Re% (up to 85%) was observed in 50 °C.

However, this value cannot be considered as an optimal temperature according to some literature reports (Guedes et al. 2003; Kavitha and Palanivelu 2005; Lucas and Peres 2009). Those experiments have reported the optimal temperature from 30 to 50 °C. Therefore, going over that range had some opposite effects on the degradation rate due to self-accelerating decomposition of hydrogen peroxide when the temperature approaches 60 °C causing decrease in the production rate of OH˙ which can disturb the treatment process.

Conclusion

In this work, we studied the efficiency of combining two treatment methods (photocatalysis–Fenton's reagent) with an ultraviolet light source for oily wastewater treatment. This technique is based on the generation of hydroxyl radicals and represents a very promising alternative as oily organic pollutants are toxic substances on which conventional treatment processes sometimes have no effect.

We were able to reach the optimal experimental conditions to remove pollutants by investigating the influence of different experimental factors on the oil removal, including pH, initial concentration for each of the TiO_2, H_2O_2,

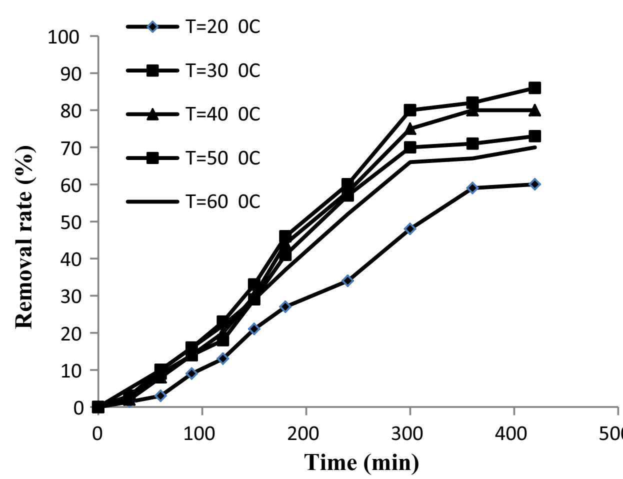

Fig. 10 Influence of temperature on oil degradation by (photocatalysis–Fenton's reagent) system at working conditions: $H_2O_2 = 400$ mg/L, $Fe^{+2} = 40$ mg/L, pH = 6.3 and $TiO_2 = 0.8$ g/L

Fe^{2+}, oil pollutants, and temperature. The results were as follows:

- The optimal amount of catalyst (TiO_2) is generally a function of the surface and the irradiated volume of the reactor. Photocatalysis is more of a surface phenomenon than a mass quantity of catalyst to be irradiated. The realization of a reactor to treat large volumes of water would therefore increase the amount exposed to the light of this reactor. The best elimination rate obtained for a TiO_2 concentration equals to 0.8 g/l corresponding to a removal rate of 80% of the COD.
- As for Fenton's reagent, the optimal dose of Fe^{+2} and H_2O_2 is approximately 40 mg/l and 400 mg/l, respectively. The increase above these concentrations has a negative effect on the degradation process which means a decrease in the efficiency of COD removal.
- The initial oil concentration of the oily water solution has shown a good influence in the process for low values, and it turns out that exceeding 25% of oily water concentration negatively affects the process; the best removal of COD recorded was 98%.
- The optimum temperature is found for (photocatalysis–Fenton's reagent) degradation of oily wastewater. The highest degradation reached (83%) was at 45 °C and over than this degree, the results were unsatisfactory, because hydrogen peroxide undergoes self-accelerating decomposition at higher temperature.
- Regarding pH value, best recorded results (80%) were between 6 and 7, and also the results showed that the very acidic ($pH = 2$) or very basic solution ($pH = 10$) has a negative effect on the degradation process.

The overall results of this study (heterogeneous photocatalysis treatment coupled with Fenton's reagent) summarize that the application of the photocatalytic process is a feasible method for treating oily wastewater, which allows a significant reduction in COD.

Nowadays, the study demonstrates an economical and effective strategy for removing both a large portion of oily organic pollutants and oils that generally coexist in industrial wastewater as an alternative to several successive treatment processes.

One of the disadvantages of this system is the use of artificial light which can increase the processing cost because of the average life of the lamp and the consumption of electrical energy. In this context, the use of sunlight would significantly reduce the cost of treatment, thus providing an important step toward industrial applications. Generally speaking, this process can be qualified as a cleanup process and it is a part of a sustainable development perspective and its operation is based on renewable energy.

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