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Article

Photodegradation of Soluble and Emulsive Cutting Fluids using TiO_2 as Catalyst

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Este artigo descreve os resultados da fotodegradação de três tipos de fluidos de corte solúveis e emulsionavéis em meio aquoso, usando TiO_2 como catalisador em suspensão e radiação UV. O TiO_2 mostrou ser um catalisador efetivo na degradação dos fluidos de corte investigados. A velocidade de degradação depende do pH e da natureza dos fluidos. O melhor desempenho do catalisador foi observado em pH = 8,0 para todos os fluidos, quando mais de 70% da carga orgânica foi decomposta.

This paper describes results of the photo-degradation of three types of soluble and emulsive cutting fluids in an aqueous medium, using TiO_2 as catalyst in suspension and UV radiation. The TiO_2 proved to be an effective catalyst for the degradation of the cutting fluids investigated. The degradation rate depends on pH and nature of the fluids. The best performance of catalyst was observed at pH 8.0 for all the fluids when most of 70% of the organic load was decomposed.

Keywords: photocatalysis, machining lubricants, aqueous effluents

Introduction

Cutting Fluids (CF) are extensively used in the metal working industry to cool and lubricate the tool–work piece interface. They are based on emulsive and water-soluble oils: synthetic; semi-synthetic; and biodegradable.[1] The resultant emulsions contain a mixture of free and emulsified oils, surfactants, and various additives like antifoaming agents, bactericides, rust inhibitors and dyes.[2] The use of CF produces a large amount of oily wastewater that requires treatment prior to discharge in water bodies or for its reuse, since the manufacturing industries are under increasing pressure from regulators agencies. This, coupled with an increase in waste disposal cost, has made the disposal of these fluids a significant issue. The aqueous phase, which still contains oil contaminants, is conditioned and sent to a sewage treatment plant.[3] Several methods for the separation of emulsified oils have been proposed,[4] but the three most common methods used for the treatment of waste CF are based on physical process of separation,[5] coagulation (physicochemical), centrifugation (mechanical)[6] and membrane techniques.[7-9] These methods are expensive and are inefficient for soluble organic compound. The complexity of this liquid waste, allied with the wide variety of lubricants available on the market, generates residues whose elimination requires advanced oxidation processes (AOP), which allow treating this residue in situ.

Heterogeneous photocatalysis has received a great deal of attention as an advanced oxidation process for degrading persistent organic compounds, reducing chemical oxygen demand (COD) and eliminating microorganisms in water bodies to allow for its reuse.[10-13] The advantage of this process is that it leads to the total mineralization of the organic contaminants, whether they are simple or complex molecules. To date, the most efficient procedure for the treatment of contaminated waters consists of UV light irradiation of suspensions of a semiconductor (TiO_2) in solutions containing the organic substrate to be degraded.

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Among AOP are distinguished those that use TiO_2 as catalyst because of its high photostability,[14] its good chemical stability within a wide range of pH values, and its low risk to human health and to the environment. However, TiO_2 has been used with good results in the treatment of waters with high organic vegetable or fossil fuel content, there does not exist much information in literature regarding the photodegradation of CF using TiO_2. Therefore, this study investigated the photocatalytic degradation of three types of soluble and emulsive cutting fluids in an aqueous medium, using TiO_2 in suspension as a function of pH.

Experimental

All the reagents used in this study were of analytical grade without previous purification. Commercial cutting fluids were used, and their compositions were analyzed by chromatography, using a HP 5890 gas chromatograph equipped with an HP-5 column (25 m × 0.22 mm i.d. × 0.33 µm film) coupled to a flame ionization detector. Also was used FTIR (BOMEN model MB102) and a mass spectrometer CGMS 5970, equipped with an HP-1 column (50 m × 0.22 mm i.d. × 0.33 µm film) were used determine the nature of the organic substrate.

The photodegradation study was carried out with 0.5 g L^{-1} of TiO_2 (Degussa P 25) suspended in solutions containing 120 mg L^{-1}, 60 mg L^{-1} and 50 mg L^{-1}, in organic carbon, of the cutting fluids, whose types were labeled A, B and C according to their nature. The photodegradation activity was investigated as a function of the pH of the solution and the photocatalytic experiments were conducted in a cylindrical reactor in which the sample was kept under agitation, saturated with oxygen at a temperature of 25 °C, and irradiated with light at predominant wavelength of 365 nm, produced by four 15 W light bulbs. At varied time intervals, aliquots (10 mL) were removed from the sample and filtered through 0.22 µm membranes (Millipore), then organic carbon content was measured using a TOC-V_{CPH} apparatus (Shimadzu).

Results and Discussion

In Table 1 summarises the nature of cutting fluids studied. Figure 1 shows the results of the photodegradation of the fluids as a function of irradiation time in pH 4.0. An activation time of approximately 1 hour, after that the degradation of all samples takes place. After 2 hours of irradiation, the activity to decompose fluid C was about three-fold greater than the activity to decompose the others, *i.e.*, during this time there was a decomposition of about 70% of the organic load of fluid C compared with only 25% of the load of the other solutions. After 2 hours the catalytic activity to decompose fluid C increased slightly, as indicated by the slope of the decomposition curve, while its decomposing performance remained constant for fluids A and B. At the end of 4 hours of irradiation, these fluids showed a degradation of 90% and 70%, respectively.

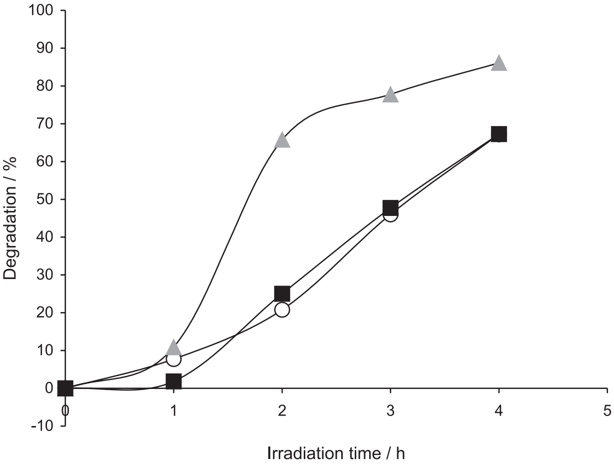

Figure 1. Photodegradation at pH 4.0 of fluids A(○), B (■) and C (▲), as a function of irradiation time.

Table 1. Composition of the cutting fluids studied

Oil	Nature and Solubility in water	Compounds found	Size of the chains (carbon atoms)
A		Esters with cyclic alkene	22 carbon atoms
	Vegetal	Aliphatic esters	20-26 carbon atoms
	Soluble	Silicones	non-determined structures
B		Glycol	3 carbon atoms
	Synthetic	Tertiary amines	8- carbon atoms
	Soluble	Phthalic acid esters	12-16 carbon atoms
		Silicones	non-determined structures
C		N-paraffins	10-21 carbon atoms
	Synthetic + Mineral	Fatty amide	16-23 carbon atoms
	Emulsive	Alcohol with conjugated double bonds	8 carbons atoms

As with the acid pH, the catalytic performance in pH 11 needs 1 hour to be activated. The activity to decompose fluid B increased exponentially, while there was a slight activity with the other fluids. At this pH, the degradation after 4 hours was about 70% for fluid B and less than 30% for the other fluids (Figure 2).

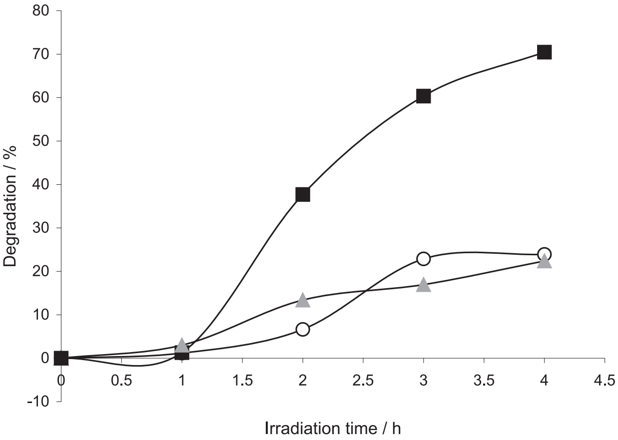

Figure 2. Photodegradation of fluids A (○), B (■) and C (▲), pH 11.0, as a function of irradiation time.

Figure 3 shows the results of the same study conducted in pH 8.0. In this condition the catalyst displayed its best performance with all the fluids investigated. All the degradation curves displayed a sigmoid profile. The activation stage for degradation of fluid C began in the first instant of irradiation and, after 1 hour, it was twice as high as the activity to degrade the other fluids. However, after 4 hours, fluids A and C had reached a degradation of about 90% and fluid B around 80%.

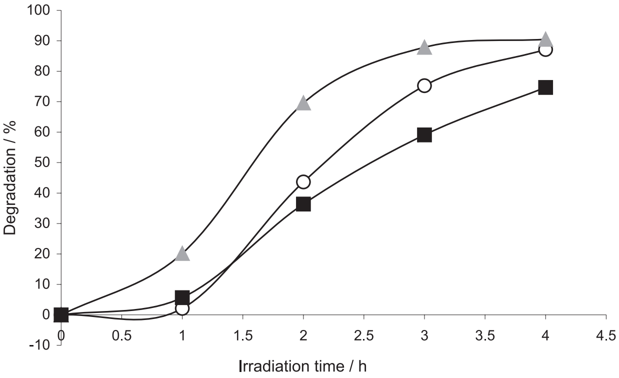

Figure 3. Photodegradation of fluids A (○), B (■) and C (▲), pH 8.0, as a function of irradiation time.

Figure 4 shows the photodegradation results of the fluids after 4 hours of irradiation as a function of pH. It can be seen that, for fluid B, there was no alteration in the catalytic performance at the different values of pH studied. However, for fluids A and B, this performance was variable according to the pH, with greater degradation occurring between pH 4.0 and 8.0 and much less in the alkaline medium. This may be related with the interactions between the surface of the catalyst and the lubricants' constituents.

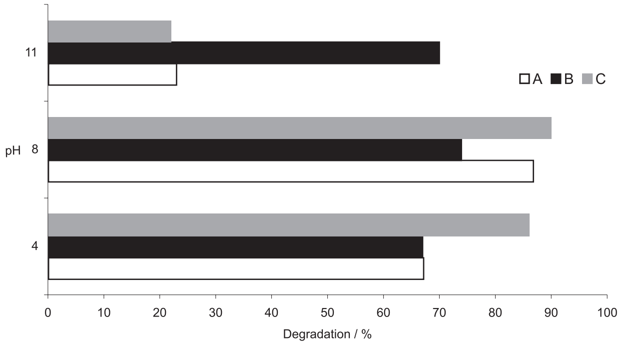

Figure 4. Photodegradation of cutting oils at different values of pH, after 4 hours of irradiation under UV light (λ=365nm).

One must take into account the dissociations the TiO_2 underwent as a function of the pH, represented by the equations below:

$$-TiOH_2^+ \leftrightarrow -TiOH + H^+ \qquad (1)$$

$$-TiOH \leftrightarrow -TiO^- + H^+ \qquad (2)$$

This material presented two values of pKa: 2.4 and 8.0.[14,15] The degree of dissociation as a function of pH is shown in Figure 5. In the pH 4.0 the surface of the catalyst is neutral, while at pH 8.0, 50% of the species appear in neutral form and 50% in negative form. At pH 11.0, there is a predominance of the negative form, which may lead to electrostatic repulsion among the constituents of the cutting fluid and the surface of the catalyst, since esthers and amides undergo alkaline hydrolysis and dissociation,

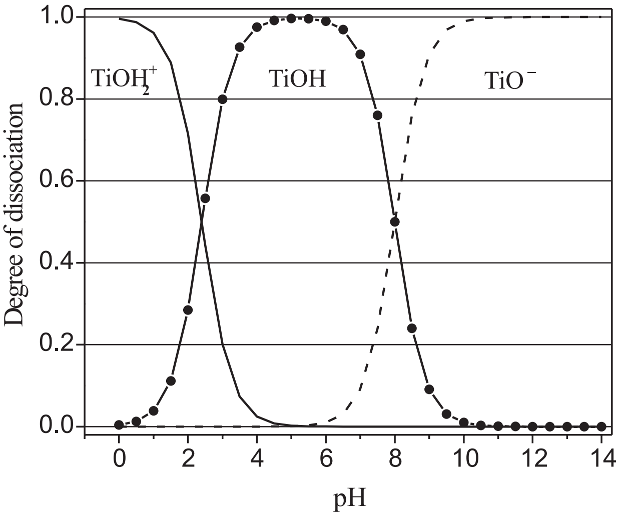

Figure 5. Degree of dissociation of the TiO_2 surface as a function of the pH of the medium, highlighting the predominant bands of each of its forms.

remaining in the negatively charged form. Their acid hydrolysis is possible; however, in this case, there are molecules of carboxylic acids and alcohols as products of transformation, which appear in neutral or negative form and do not undergo the effect of repulsion in relation to the catalyst material, favoring adsorption and subsequent degradation. In the case of the amides, one possible product is the corresponding tertiary amine, which appeared positively charged both at pH 4.0 and pH 8.0, although no repulsion phenomena were observed. At pH 11.0 some deprotonation of these amines is likely to occur; however, since the surface is neutral, the interaction between the organic species and the catalytic surface is weak, leading to a similar degradation as at pH 4.0.

Conclusions

Photocatalysis using TiO_2 as a catalyst proved to be effective for the degradation of the cutting fluids investigated. The degradation rate was found to be related to the nature of the fluids and to that of the groups at the surface of the TiO_2, according to the pH. The best catalytic activity was attained at pH 8.0 for all the fluids. The proposed method could be used in the treatment of polluted waters by industrial effluents coming from organic sources. Studies of methodologies for immobilization of TiO_2 on solid supports and of process application using the visible light are being developed. Thus, it would be possible to eliminate the filtration step and reduce costs.

Acknowledgments

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