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REMOVAL OF CHEMICAL OXYGEN DEMAND FROM TANNERY WASTEWATER BY FENTON'S REAGENT

ELIMINATION DE LA DEMANDE CHIMIQUE EN OXYGÈNE DES EAUX USÉES DE LA TANNERIE PAR LE PROCEDE FENTON

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ABSTRACT

The characterization of the tannery wastewater by analysis of a certain number of physico-chemical parameters has shown an important organic pollutant load, particularly expressed by chemical and biological oxygen demand (5280 mg/L for COD and 1300 mg/L for BOD).

The aim of this work is to remove of COD from tannery wastewater by using one of the most efficient advanced wastewater treatment, the Fenton reaction.

The parameters influencing the COD removal, namely hydrogen peroxide concentration, ferrous ions concentration and pH have been studied.

The effectiveness of this process, defined as a reduction of COD was 87% using a concentration of $2x10^{-3}$ mol/L of Fe^{+2} and 10^{-2} mol/L of H_2O_2. The optimal pH is 3.5.

So, it has been proved that the Fenton process can be a feasible technique for the treatment of tannery wastewater as a preliminary stage preceding its further biological treatment.

Key words: Advanced oxidation process, Chemical demand oxygen, Fenton process, Tannery wastewater

RESUME

La caractérisation des eaux usées de la tannerie par analyse d'un certain nombre de paramètres physico-chimiques a montré une charge polluante organique importante, exprimée notamment par la demande chimique en oxygène et la demande biologique en oxygène (5280 mg / L pour la DCO et 1300 mg / L pour la DBO).

L'objectif de cette étude est l'élimination de la DCO des eaux usées de la tannerie en utilisant la technique d'oxydation avancée « réaction de Fenton ».

Les paramètres influençant l'élimination de la DCO, à savoir la concentration en peroxyde d'hydrogène, la concentration en ions ferreux et le pH du milieu ont été étudiés.

Le taux de réduction de la teneur de la DCO est de 87% dans des conditions expérimentales bien déterminées : concentration de Fe^{+2} = $2x10^{-3}$ mol / L, H_2O_2 :10^{-2} mol / L et un milieu acide (pH = 3,5).

Ainsi, il a été prouvé que le processus de Fenton peut être une technique réalisable pour le traitement des eaux usées de la tannerie en tant qu'étape préliminaire pour un éventuel traitement biologique.

Mots clés: Processus d'oxydation avancée, demande chimique de l'oxygène, procédé de Fenton, eaux usées de la tannerie

INTRODUCTION

The industrial world is increasingly facing the problem of the control of toxic substances emissions in the environment, particularly in the form of liquid effluent (Forstner and Wittmann, 1983). The complexity and difficulty of the problem arising from the diversity of emission sources, the quantitative importance of these rejections and their varied composition (Crine, 1993).

The tannery is one of the oldest and most polluting industries. It transforms animal hides into leather after preliminary treatment depilation - liming to remove the epidermis, followed by a process called tanning.

The leather industry is characterized by high water consumption, a significant waste in volume and carrying very high polluting loads. These effluents contain protein colloids, fats and tannins, debris of flesh and hair, dyes and others which are responsible for high levels of COD and BOD, and toxic elements such as sulfide and chromium. The uncontrolled release of tannery effluents to natural water bodies increases health risks for human beings and environmental pollution. They may stop assimilative phenomena due to heavy load of various organic, on the one hand, and the presence of large amounts of toxic elements on the other hand. This results in bacterial anaerobioses reactions which give these waters and the receiving environment unpleasant odors that impede all aquatic life.

To remove part of the organic load, biological processes are usually used, because they are more economic than chemical processes. In some cases, however, due to the high organic load, toxicity or presence of biorecalcitrant compounds, biological processes cannot be used, since no chemical oxygen demand (COD) removal is achieved biologically. For these wastewaters, the biochemical oxygen demand (BOD) is orders of magnitude lower than the COD. Thus a biological treatment is not feasible. In these cases, chemical pre-treatment can adequately reduce the COD prior to biological treatment (Martinez et al., 2003).

Among chemical processes, the advanced oxidation process has been used to reduce the organic load or toxicity of different waters and wastewaters (Alaton et al., 2002; Guzzella et al., 2002; Pérez et al., 2002).

One of the simplest and cheapest of this process, is Fenton‘s reaction, which consists in the non-selective and highly efficient oxidation of organic compounds by means of hydroxyl radicals (Perkowski et al., 1998; Park et al., 1999; Kusic et al., 2007; Modirshahla et al., 2007).

Fenton's reaction is based on the catalyzed decomposition of hydrogen peroxide by iron (II) to produce very reactive hydroxyl radicals:

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

The hydroxyl radicals which are second only to fluorine among common oxydants, could react rapidly and non-selectively with nearly all organic pollutants (Scott and Ollis, 1995; Miller et al., 1996; Safarzadeh-Amiri et al., 1997).

The objective of this work is to investigate the applicability of Fenton's reagent in the removal of COD from tannery wastewater and study the effect of some parameters (H_2O_2 concentration, Fe^{+2} concentration, pH and reaction time) on the degradation process.

THE STUDIED TANNERY DATA

The studied tannery consumes more than 40 000 m^3 of water / year, for a production of 2,000 leather per day (Datasheet TAMEG 2012**)**. Given the immensity of the industrial area and massive and relentless establishment of companies, a reliable census of the volume of water discharged is not always obvious, it should be noted that theoretically estimated volume is 168 m^3/day. The table 1 reports the volumes of the discharged water assigned to different parts of the tannery. This rejection is complex: organic materials, considerable rates of suspended solids and certain toxic compounds such as chromium.

Table 1 : Theoretical estimation of liquid discharges in the studied tannery

Workshop	Effluent volume (m^3)	Effluent quantity (%)
River	108	64.3
Tanning	48	28.6
Retanning	12	7.14
Total	168	100

EXPREIMENTAL SECTION

Sampling Method of Wastewater

The main collector tannery output is selected as the sampling point. It is the meeting place of all rejects including river, tanning and retanning workshops. Sampling was performed manually using a bucket with a depth of meshing of about 1.5 m. The sample is stored in containers in a dark and cool place at 4°C to avoid chemical modification.

Analytical Methodologies

Given the pollution load of tannery wastewater, all parameters that may be altered were analyzed in the laboratory in the shortest possible time in accordance with the conservation rules and standardized analytical methods (Rodier 1996). The pH was measured using a pH meter (HANNA pH 209), the turbidity by a turbidity meter (HANNA HI 88 713-ISO Turbidimeter), conductivity by a conductivity meter (ISO 7027 Method HACH), chromium has followed by atomic absorption (AA spectrometer SOLAAR ThermoElemental), chloride by the Mohr method (Rodier 1996), the analysis of BOD for 5 days and COD were measured according to the experimental protocols of the French standard for the first parameter and the ISO 6060-1989 standard for the second.

Fenton´s experimental procedure

The following parameters of Fenton's reaction were examined and optimized: H_2O_2 concentration, Fe^{2+} concentration, pH and reaction time.

The Fenton's oxidation experiments were carried out in 250mL beakers with a solution volume of 150 mL of tannery wastewater. The pH of wastewater was adjusted to 3.5 by means of sulfuric acid solution, before chemical oxidation process. Fenton's reaction is only effective in the acidic pH range (Barbusiński 2005). The various amounts of hydrogen peroxide solutions and $FeSO_4.7H_2O$ (in a solid state) were added with continuous magnetical stirring during the reaction period. Samples were withdrawn at 5, 10, 30, 60, 75 and 90 min.

Before analysis of COD, the solutions were neutralized with 10% NaOH to pH of about 11 to stop the oxidation reaction. After, samples were decanted and filtred to remove the formed ferric hydroxide.

The efficiency of wastewater treatment is measured by the value of the CODof the crude and treated water, expressed as a percentage T(%)according to the following equation (equation 2):

$$TX(\%) = \frac{(C_i X - C_f X)}{C_i X} x100 \qquad (2)$$

C_i and C_f are the initial and final concentration of COD before and after treatment.

RESULTS AND DISCUSSION

Characterization of the tannery wastewater

Wastewater, whether domestic, industrial or urban, contains various pollutants due to their physical and chemical nature. The growing interest in water quality has led to define these waters for a number of specific parameters in order to assess their potential action on the receiving aquatic medium and environment.

These parameters include concentrations. Other more significant parameters such as BOD and COD are essential to assess the degree of pollution of effluent. The physico-chemical analysis of tannery wastewater, given in Table 2, indicates that the Algerian standards defining the values limits of industrial liquid wastes (JORA N°26 of 23/04/2006), particularly for tanning industry, are often exceeded for many parameters (Official Journal of the Algerian Democratic and Popular Republic, 2006); for example the turbidity of the effluent is 732 NTU, the concentration of chromium is about 236.62 mg/L, values of COD and BOD_5 are given respectively as 1300 and 5280 mg/L.

In view of all the results, we can say that the tannery wastewater are mineral and organic nature; thereby, the biodegradation of these materials causes energy consumption of dissolved oxygen where possible eutrophication of the receiving environment with a deterioration of the fauna and flora and formation of harmful resistant species.

Table 2 : Physico-chemical characterization of tannery waste water

Analyzed parameters	Values	Algerian standard industrial effluents of tanning
Temperature (°C)	25	30
Color	Bleu	/
pH	6.41	6.5-8.5
Conductivity (ms/cm)	4,83	-
Turbidity (NTU)	732	-
Chlorides (mg/L)	1775	1200
COD (mg/L)	5280	850
BOD_5 (mg/L)	1300	350
Chromium (mg/L)	236.62	3

Fenton process

Effect of the hydrogen peroxide concentration

The H_2O_2 concentration played a crucial role in the efficiency of the degradation process.In order to investigate the influence of the hydrogen peroxide concentration on the Fenton process, the concentration of ferrous sulfate was kept constant $2x10^{-3}$ mol/L, while the amount of hydrogen peroxide was variable (10^{-3}, $5x10^{-3}$ and 10^{-2} mol/L).

Fig. 1 shows the result of COD removal depending on the hydrogen peroxide concentration.

A low concentration of H_2O_2 (10^{-3} mol/L) is insufficient to ensure the complete oxidation of organic matter. When the concentration of H_2O_2 is increased to $5x10^{-3}$ mol/L, the degradation rate reached 79 % in 1 hour.

The presence of high amount of H_2O_2 (10^{-2} mol/L) determines the mineralization up to 87% during the first 60 minutes, and then the mineralization degree does not grow any more in significant extent. This increase removal of COD is due to the oxidation power of Fenton process which was improved with increasing OH° radical amount obtained from the decomposition of increasing H_2O_2 (Hassan and Hameed, 2001).

According to Dhahir et al. (2014), with further increasing of hydrogen peroxide concentration, degradation efficiency is decreasing due to the scavenging nature of hydrogen peroxide towards OH° radical when it is present in higher concentration.

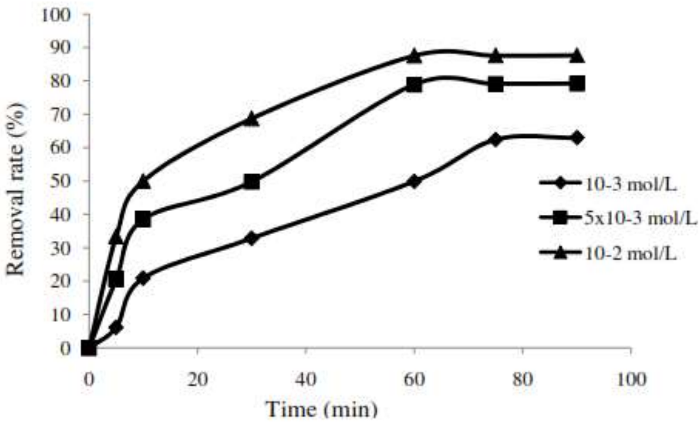

Figure 1: Effect of the hydrogen peroxide added on the COD reduction in tannery wastewater

Effect of the iron ion concentration

The influence of iron ion concentration on the removal of COD was studied at a constant hydrogen peroxide concentration (10^{-2} mol/L) and a variable amount of $FeSO_4$ (10^{-4}, $2x10^{-4}$, 10^{-3} and $2x10^{-3}$ mol/L).

As shown in Fig. 2, at the very low concentration values of Fe^{+2} (10^{-4}mol/L), the Fenton system is working, although the removal of COD is weak (51%). An increase of the Fe^{+2} ions concentration to $2x10^{-3}$ mol/L gives a spectacular removal of COD rate, since a reaction time of 60 minutes arises a87%

conversion degree.Hence, it can be said that higher ferrous doses lead to the generation of more OH° radicals. It also shows that higher ferrous doses not only make the redox reaction complete but also cause coagulation resulting in improved removal (Dhahir et al.2014).

In all cases, it is preferable to limit the concentration iron because of possible hydroxide precipitation of the formed iron and the oxidation of iron (II) by hydroxyl radicals (equation 3).

$$Fe^{+2} + OH° \longrightarrow Fe^{+3} + OH^{-} \quad (3)$$

Thus, iron was used at an initial concentration of 10^{-2}mol/L in the soot experiments.

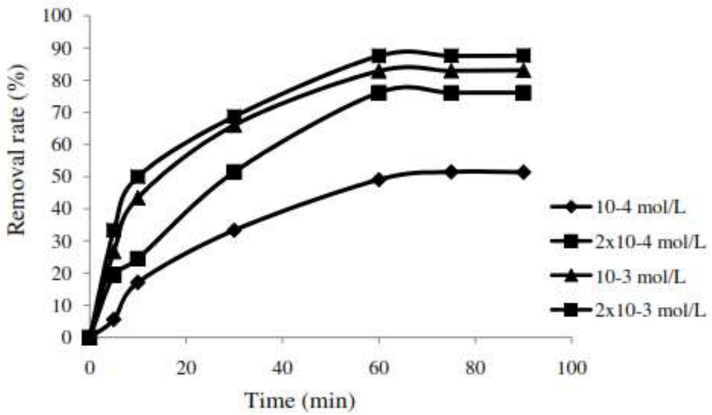

Figure 2: Effect of the $FeSO_4.7H_2O$ concentration on the COD reduction in tannery wastewater

Effect of pH

The effect of pH upon the efficiency of the Fenton process was carried out. Indeed, this parameter affects the iron ion solubility and the generation of OH°. The following pH values were investigated: 2, 2.5, 3, 3.5 and 4 in reaction system containing 10^{-2}mol/L of H_2O_2 and $2x10^{-3}$ mol/L of Fe^{+2}. Fig. 3 shows the result of COD removal.

As shown in figure 3, the efficiency of the removal of COD from tannery wastewater had a maximum at pH = 3.5. The decrease in pH of medium from 4 to 2 has decreased the COD elimination rate. At pH= 2, the removal of COD was reduced by more than half compared to pH equal to 3.5.

At higher pH non-reactive iron forms appear in wastewater: oxohydroxides or hydroxides precipitates and acts as radical scavengers. In this situation, the amount of iron available for radical generation is significantly lower than for the same dose, but in a lower pH. In addition the redox potential of OH° decreases with increasing pH (Bapu Ponnusami and Muthukumar 2014).

On the other hand, lowering the pH below 3, results in the appearance of numerous iron aquacomplexes and hydration H_2O_2 to $[H_3O_2]^+$, which is more stable and therefore less reactive with Fe^{+2} (Bogacki et al., 2015).

The studied wastewater has pH value close to neutral and the treatment process requires the pH adjustments.

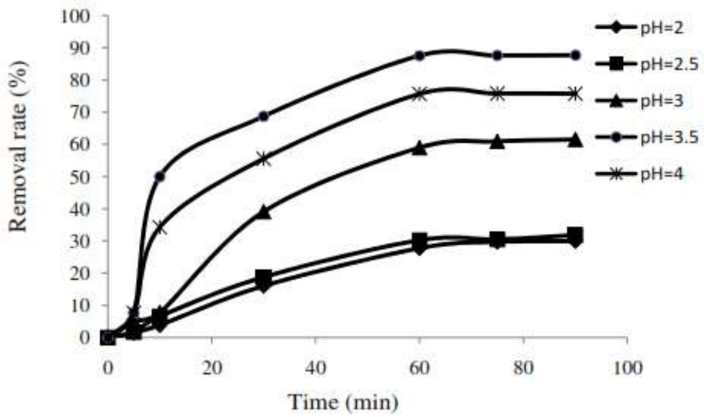

Figure 3: Effect of pH on COD reduction in tannery wastewater

CONCLUSION

This study presents results of the efficiency of the Fenton's reagent treatment of tannery wastewater.

The physico-chemical characterization of this liquid effluent showed a high pollutants load expressed especially by COD and BOD.

Laboratory study showed the importance of the concentration of reagents: H_2O_2 and Fe^{+2}, pH of medium and the reaction time on the reduction of COD.

The results of the treatment gave high efficiency of the Fenton process for removal of COD (87% during 60 minutes) under the following conditions: $2x10^{-3}$ mol/L of Fe^{+2}, 10^{-2} mol/L of H_2O_2 and acid pH (3.5).

Overall, the results of this work are a further evidence for the treatment of this type of wastewaters.

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