Environment Protection Engineering

Vol. 37 2011 No. 3

JEREMI NAUMCZYK*, MAŁGORZATA KUCHARSKA*

TANNERY WASTEWATER TREATMENT BY ANODIC ELECTROOXIDATION COUPLED WITH ELECTRO-FENTON PROCESS

Investigations were performed on tannery wastewater, previously coagulated with $FeCl_3$. An electrolyzer was equipped with two graphite cathodes and $Ti/SnO_2/PdO_2/RuO_2$ anode, divided by the diaphragm made of asbestos fibre. The current density was: cathodic 2.0 A/dm^2 and anodic 2.1 A/dm^2. After 55 min of the process the catholyte was transferred into the anodic space and the process was continued. After 55 min of electro-Fenton process, the COD was reduced by 52.0% (current efficiency of COD removal was 10.6%). Electrooxidation continued by the anodic process resulted in elimination of ammonia in 55 min and a total reduction of COD by 72.9%. The coupled process d could be considered a simulation of the combined process under flow conditions. The effect of this process was compared to that of a two-steps process: Fenton process followed by indirect anodic oxidation.

1. INTRODUCTION

Tannery wastewater treatment represents a difficult technological problem. After conventional treatment, including sedimentation and biological process, effluents usually do not meet the requirements for COD, total solids and ammonia. Recently, a more effective and non-selective processes – advanced oxidation processes (AOPs) and electrooxidation have been extensively investigated.

Tannery wastewater treatment by anodic electrooxidation has been reported in few papers [1–5]. Results of present studies show that chlorine generated on the anode removes ammonia and reduces the COD value by 77.6% [1]. $Ti/SnO_2/PdO_2/RuO_2$ (SPR) anode is reported the most effective one [1]. Fenton process resulted in a reduction of COD by 63.7% [6].

---

*Faculty of Environmental Engineering, Department of Informatics and Environment Quality Research, Warsaw University of Technology, ul. Nowowiejska 20, 00-653 Warsaw, Poland. Corresponding author: J. Naumczyk, e-mail: jeremi.naumczyk@is.pw.edu.pl

Fenton oxidation is particularly attractive due to its simplicity and high efficiency in removal of organics [7–10]. In the Fenton process, hydroxyl radical, a very strong oxidant, is generated according to the equation:

$$Fe^{2+} + H_2O_2 + H^+ \longrightarrow Fe^{3+} + HO^\bullet + H_2O \qquad (1)$$

Additionally, a modified Fenton reaction has been reported as effective for treatment of wastewater polluted with pharmaceuticals [11].

In the last decade, application of the electrochemical method for Fenton process, named electro-Fenton (EF), has been reported. EF process can be conducted in several ways. In the former one, ferrous ion and oxygen are externally applied, but H_2O_2 is generated on the cathode, according to the reaction:

$$O_2 + 2H^+ + 2e^- \longleftrightarrow H_2O_2 \qquad (2)$$

Several cathodes such as mercury pool [12], graphite [13, 14], vitreous carbon [12], carbon-poly(tetrafluoroethylene) O_2 fed [14–17] can be applied. Those cathode materials allow one to conduct reaction (2) due to a high overvoltage of the hydrogen reduction. At the cathode, reduction of Fe^{3+} to Fe^{2+} is also possible.

In an another way, H_2O_2 is externally applied, while a sacrificial iron anode is used to generate ferrous ions [18–20], or H_2O_2 is externally applied and Fe^{2+} ions are electrogenerated via reduction of Fe^{3+} ions or $Fe(OH)_3$ sludge [16]. Both Fe^{2+} and H_2O_2 may also be electrogenerated at a sacrificial anode and cathode via two electroreduction of sparged oxygen [21].

In the case when H_2O_2 is generated, the cathode electrolyzer can be divided with a diaphragm into the catholyte and anolyte spaces. The advantage of an electrolyzer without a diaphragm is its lower current resistance, which results in lower energy consumption. However, in such a case, possibility of undesired decomposition of H_2O_2 exists according to the reaction (2) [17]. Various materials are used as diaphragms – sintered glass discs, synthetic fibres and cation exchange membranes [14].

As anodes, titanium plates were used mostly covered with precious metal oxides – DSA®. The way of preparing of the cathode material is very important. Results obtained by Da Pozzo et al. [14] show that a gas diffusion (carbon–PTFE) cathode is much more suitable than a graphite cathode. Additionally, Fort et al. [22] proved that the addition of azobenzene in gas diffusion cathode improved its efficiency, due to the reduction of the voltage of reaction (2).

EF process was applied to many types of wastewaters – landfill leachate [18, 20, 23], urban wastewater [13], wastewater after regeneration of ion exchangers [24]. This process was also widely used for oxidation of same organics – formaldehyde [25], aniline [21], dyes [16], atrazine [12], non-ionic surfactants [26], phenols [27], chlorophenols [28] and many others.

However, the EF process was applied to tannery wastewater only in one study [19]. Iron cathode and anode sized 6×7.5×2 mm^3 were used, placed at the distance of

6 cm, in a reactor with 45 cm^3 wastewater sample. At pH 3.0 and 7.2, after addition of 1670 mg/dm^3 of H_2O_2, the drop in COD after 10 min was 72% and 58%, respectively (initial value 2810 mg/dm^3). When EF process was conducted with the use of the carbon cathode and DSA type anode and after external addition of H_2O_2, the results seem to be more promising.

A high content of chlorides and ammonia is characteristic of tannery wastewater, thus the generation of chlorine at the anode should result in a significant removal of ammonia and COD. The aim of the studies presented in this paper was the evaluation of the effectiveness of the combined EF process with anodic electrooxidation by means of the anodic generated chlorine.

2. MATERIALS AND METHODS

Experiments were performed in an electrolyzer divided into anodic and cathodic parts by the asbestos fibre diaphragm. Dimensions of both parts were the same – 138×120×30 mm^3 and the volumes of catholyte and anolyte were 320 cm^3 each. As a cathode, two graphite plates were used, previously anodically activated with the current density of 3.0–3.3 A/dm^2 for 4 min, followed by the cathodic reduction to the potential of 1.5 V against a silver chloride electrode. The activation was conducted according to the Do and Yeh procedure [2]. $Ti/SnO_2/PdO_2/RuO_2$ (SPR) anode was used, with dimensions 10×10 cm^2. At the beginning of the process, both catholyte and anolyte spaces were filled with tannery wastewater (previously coagulated). Characteristics of those wastewaters was as follows: pH – 3, conductivity – 14566 μS/cm, COD 708 mg/dm^3, $N–NH_4$ – 404 mg/dm^3, Cl^- – 4930 mg/dm^3. Wastewaters were initially saturated with oxygen and then constantly aerated.

During the experiments, the catholyte was transferred into the anodic space at specific time intervals (50, 55 and 60 min), the catholyte space was filled with a new sample of wastewater and the process was continued by indirect anodic oxidation. This treatment was a simulation of the continuous (flow) process.

During the experiment, the cathodic current density was 2.0 A/dm^2, anodic current density 2.1 A/dm^2. The concentration of ferrous ions (added as $FeSO_4$) was 1500 mg/dm^3, the latter value turned to be the best in a classic Fenton process [6].

The effectiveness of the EF process was monitored by the determination, after specific intervals, the following parameters: temperature, $N-NH_4$ content and COD. pH was monitored constantly and (if necessary) adjusted with 1 M H_2SO_4 to 3.0–4.5. In the anolyte, temperature, chlorides, free and total chlorine, $N-NH_4$ and COD were determined. pH was monitored constantly and adjusted to the value of 4.0–4.5 with 1 M NaOH. Additionally, the voltage was measured. The catholyte current efficiency of H_2O_2 synthesis was determined in the following way: 10% solution of KJ was placed in the catholyte space of the electrolyzer and the process was conducted for

15 min. Iodine volatilized from the catholyte space was absorbed in 0.5 M $Na_2S_2O_3$. The current efficiency was calculated based on the total produced iodine.

Results of other investigations of those wastewaters (Fenton process, Fenton process followed by anodic electrooxidation and anodic electrooxidation) [6] show that the SPR anode is the most suitable and the optimum current density is 2.0 A/dm^2.

3. RESULTS AND CONCLUSIONS

Figure 1 shows time dependences of the COD values during all investigated processes. For the Fenton process, the H_2O_2/Fe^{2+} doses were 4000/1500 mg/dm^3 and pH was 3.5. These parameters were assumed as the optimum ones [1].

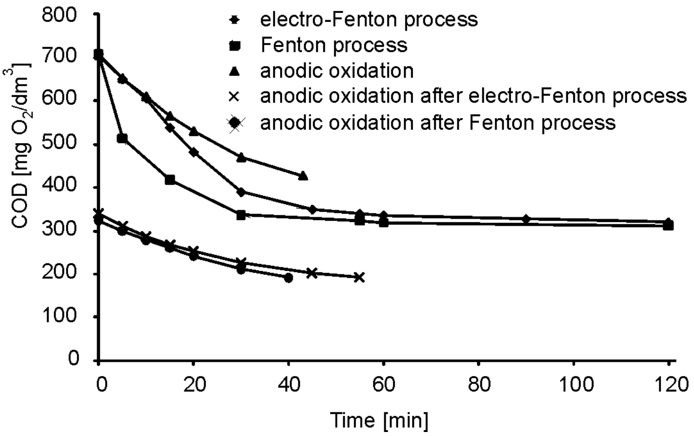

Fig. 1. COD during all investigated processes

During first 30 min of the EF process, an efficient reduction of COD was observed (44.9%). From 55 to 120 min the COD decrease was insignificant – from 52.0% to 54.8%, respectively. During the first 5 min the rate of the process was increasing.

In the case of a classic Fenton process, at the beginning COD decreased rapidly and then the process slowed down. Starting from 45 min, the both processes were similarly effective, the Fenton process being a little more efficient. After 55 min of the EF process, the COD decreased to 340 mg/dm^3 O_2 (52.0%). The rate of both, EF and classic Fenton processes, depended on the concentration of hydrogen peroxide. That is why only in case of the EF process, the rate of COD removal increased in the first 5 min – at the beginning the concentration of H_2O_2 was very low (in the classic Fenton process, the total dose of H_2O_2 was added at the beginning). Due to this, at the beginning the rate of the Fenton process was much higher than the rate of EF process. Insignificantly higher final effectiveness of the classic Fenton process could be explained by the higher pH in the EF process.

The increase in concentration of H_2O_2 in the EF process (Fig. 2) was rapid at the first 30 min (to 240 mg/dm^3), then it slowed down (327 mg/dm^3 after 120 min), despite the H_2O_2 consumption in EF process continuously decreasing. This could be explained by polarization of the electrode (evidenced by the increase in voltage in spite of increasing temperature), reaction between H_2O_2 and hydroxyl radicals

$$H_2O_2 + 2OH^{\bullet} \longrightarrow 2H_2O + O_2 \qquad (3)$$

and degradation of H_2O_2 caused by temperature increase and air flow. Also another cathodic reactions can take place.

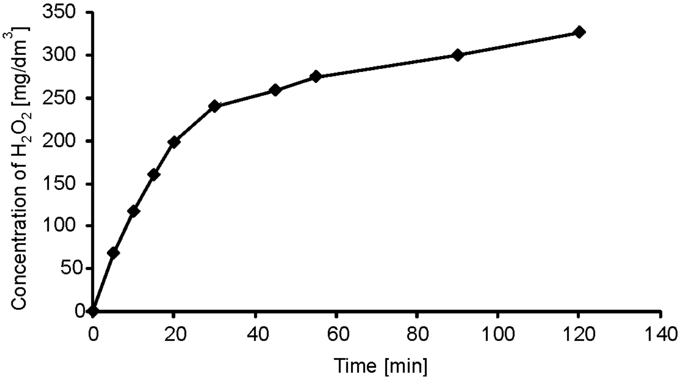

Fig. 2. H_2O_2 concentration during the electro-Fenton process

During the process, no permanent changes in the characteristics (activity) of the cathode were observed – the results were reproducible. A cathodic reaction of H_2O_2 synthesis describes Eq. (2). A summary of indirect cathodic oxidation of pollutants could be described as follows:

$$2H_2O + O_2 + 4e^{-} \longrightarrow 4OH^{-} \qquad (4)$$

An apparent current efficiency of the indirect cathodic oxidation of organic pollutants (expressed as the current efficiency of the reduction in COD, assumes that 96 500 C corresponds to 8 g of O_2) for 30, 60 and 120 min of the process was relatively low and equalled: 34.6, 20.3 and 10.6%, respectively. The effectiveness of the process referred to the content of H_2O_2 remaining in the solution after a specified time could be calculated based on reaction (2).

For 30, 60 and 120 min of the process, the effectiveness was: 18.8, 11.0 and 6.3%, respectively. The total efficiency of H_2O_2 synthesis and of oxidation of organic pollutants was also not high and for 30 min of the process equalled 53.4%. The current efficiency of H_2O_2 synthesis determined with the use of KJ solution was much higher – 87.7%. This difference in the current efficiency described above was probably caused by decomposition of H_2O_2 due to the phenomena discussed above.

Due to cathodic reactions described with Eqs. (2) and (4), some increase in pH was observed, thus strong acid had to be added to maintain pH between 3.0–4.5. Theoretical amount of strong acid required to neutralize OH^- ions is 229 mmol/h but in practice it was ca. 3% lower. Increase in temperature was slightly higher than in the case of anodic oxidation, probably due to a need of higher voltage (9.2–14.0 V) to obtain the current density of 2 A/dm^2, caused by a diaphragm increasing electrical resistance. During the cathodic process, no decrease in ammonia concentration was observed. However, in anodic oxidation ammonia was removed after 55 min. Under flow conditions, the retention time for catholyte and anolyte must be the same (the same volume). It can be therefore assumed that optimum conditions for the coupled process should include the EF process lasting 55 min at the current density of 2.0 A/dm^2, followed by anodic indirect oxidation, also in 55 min at 2.1 A/dm^2.

The time dependences of COD during anodic electrooxidation in the coupled process, as well as during electrooxidation of wastewater after classical Fenton process [21] are also shown in Fig. 1. Both curves are very close to each other. The final COD removal in the coupled process was 72.9%. For the Fenton process accompanied with electrooxidation, corresponding to the time of ammonia removal, the final effect is a little higher – 73.8% COD removal [1]. Anodic electrooxidation (Fig. 1) of coagulated wastewater resulted in 43 min for complete ammonia removal and 39.3% for COD removal (to 428 mg/dm^3) [1]. The effect was much less outstanding than in the coupled process.

Ammonia concentrations during the anodic oxidation of wastewaters after EF process are shown in Fig. 3, being similar to those observed for anodic oxidation of wastewaters only after coagulation, presented elsewhere [1]. The current efficiency of electrooxidation of ammonia was by 1.3% lower (41.1%) and reduction of COD was by 0.5% higher (43.5%) than those in wastewater only after coagulation. The current efficiency of COD removal was 8.8% being also higher than that in previous studies (8.5%) [1].

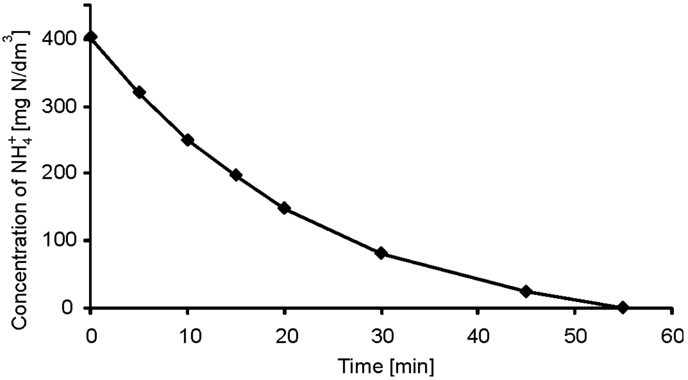

Fig. 3. Ammonia concentration during electro-Fenton process

The main disadvantage of the coupled electrooxidation process is a significant energy consumption, due to high electrical resistance caused by the presence of a diaphragm. Energy consumption per 1 kg of N-NH_4 was 130.5 kW/h, being almost twice higher than that for the electrooxidation. Another disadvantage of the coupled process is a need of adding acid or base solutions. The principal advantage of the coupled process is much higher COD removal and possibility to conduct the process in one reactor.

Due to scarce literature data, the results presented above cannot be compared with those of other authors. Do and Yeh [29] used a sintered glass disc as a diaphragm, graphite cathode and SPR anode. They found that the cathodic efficiency of phenol oxidation is higher than the anodic one and it decreased with an increase in the amount of electrical charge. The increase from 300 to 2500 C resulted in the decrease in the cathodic current efficiency from 83.5 to 56.1% and in the anodic one – from 80.4 to 57.4%. Those efficiencies were relatively high but mostly due to a high initial concentration of phenol (3222 mg/dm^3). Degradation of phenol was below 40%. This significant decrease in the current efficiency has been explained by degradation of hydroxyl radicals on the cathodic surface. The authors investigated also the influence of temperature on the effectiveness of cathodic and anodic process and they found that the optimum is about 35 °C. Similar results were obtained by Sudoh at al. [27] with the use of Pt anode and graphite cathode.

REFERENCES

[1] NAUMCZYK J., *Electrooxidation of Some Impurities in Its Application to Tannery Wastewater*, Publ. Office Warsaw Univ, Techn., Res. Pap., Envirironment. Eng., Warsaw, 2001 (in Polish).
[2] SZPYRKOWICZ L., NAUMCZYK J., ZILIO-GRANDI F., Wat. Res., 1995, 29, 517 .
[3] NAUMCZYK J., SZPYRKOWICZ L., ZILIO-GRANDI F., Trans. J. Chem. E. B. 1996, 74, 59.
[4] SZPYRKOWICZ L., KAUL S.N., NETI R.N., SATYANMARANAN, Water Res. 2005, 39, 1601.
[5] SZPYRKOWICZ L., NAUMCZYK J., ZILIO-GRANDI F., Toxicol. Environ. Chem., 1994, 44, 189.
[6] NAUMCZYK J., RUSINIAK M., Polish J. Environ. Stud., 2005, 6, 789.
[7] KASPRZYK-HORDERN B., RACZYK-STANISŁAWIAK U., NAWROCKI J., Ochr. Środ., 2006, 28 (1), 23.
[8] PERKOWSKI J., SIDOR M., Ochr. Środ., 2007, 29 (1), 19.
[9] DĘBOWSKI M., KRZEMIENIEWSKI M., Environ. Prot. Eng., 2007, 33 (1), 65.
[10] RACYTE J., RIMEIKA M., BRUNING H., Environ. Prot. Eng., 2009, 35 (3), 167.
[11] MARCIOCHA, D., FELIS, E., SURMACZ-GÓRSKA, J., Environ. Prot. Eng., 2007, 33 (2), 165.
[12] VENTURA A., JACQUET G., BERMOND A., CAMEL V., Wat. Res., 2002, 36, 3517.
[13] MORENO A.D., FRONTANA-URIBE B.A., RAMIREZ ZAMORA R.M., Water Sci. Techn., 2004, 50 (2), 83.
[14] DA POZZO A., DI PMERLI C., PETRUCCI E., J. Appl. Electrochem., 2005, 35, 413.
[15] BRILLAS E., MUR E., SAULEDA R., SANCHEZ L., PERAL J., DOMENECH X., CASADO J., Appl. Catal. B: Environ., 1998, 16, 31.
[16] ZHOU M., YU Q., LEI L., BARTON G., Separ. Purif. Techn., 2007, 57, 380.
[17] PANIZZA M., CERISOLA G., Electrochim. Acta, 2008, 54, 876.
[18] LIN S.H., CHANG C.C., Water Res., 2000, 34(17), 4243.
[19] KURT U., APAYDIN O., GONULLU M.T., J. Hazard. Mater., 2007, 143, 33.

[20] ATAMACA E., J. Hazard. Mater., 2009, 163, 109.
[21] BRILLAS E., CASSADO J., Chemosphere, 2002, 47, 241.
[22] FORTI J.C., NUNES J.A., LANZA M.R.V., BERTAZZOLI R., J. Appl. Electrochem., 2007, 37, 527.
[23] ZHANG H., ZHANG D., ZHOU J., J. Hazard. Mater., 2006, B135, 106.
[24] PANIZZA M., CERISOLA G., Water Res., 2001, 35 (16), 3987.
[25] DO J-S., YEH W-C., J. Appl. Electroch., 1998, 28, 703.
[26] MARTINS A.F., WILDE M.L., VASCONCELOS T.G., HENRIQUES D.M., Separ. Purif. Technol., 2006, 50, 249.
[27] SUDOH M., KODERA T., SAKAI K., ZHANG J.Q., KOIDE K., J. Chem. Eng. Jpn., 1986, 19, 513.
[28] SONG-HU Y., XIAO-HUA L., J. Hazard. Mater., 2005, B118, 85.
[29] DO J.-S., YEH W.-C., J. Appl. Electrochem., 1996, 26, 673.