Using Nanotubes in Processes Photocatalytic for the Removal of Organic Matter in Tanning Effluent

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Abstract

Several environmental problems are related to tanning, among them we highlight the issue of bad odors and effluent generation. The use of chemicals as low biodegradability of dyes, tannins and sulfonated oils and potentially polluting, such as chromium, makes the treatment of these effluents complex and expensive. In this sense, it is necessary to develop alternatives that might enable not only the treatment, but the reuse and conservation of water resources receivers. The heterogeneous photocatalysis using nanotubes of transition metal oxides have been implicated in the degradation of organic compounds dispersed in water. This work aimed to study the use of nanotubes in photocatalytic processes for the removal of organic matter in effluents from tanneries. The nanotubes used consisted of sodium titanate, cerium and cobalt. They were applied to clarified effluent, in a photo-reactor, after treatment with the flocculant consisting of aluminum polychloride. The measurement of the organic material was made by analysis of COD within 12 hours for each experiment. Early experiments showed that among the nanotubes used in the Cobalt Titanate showed the best photocatalytic activity. For removal of COD, the proposed conditions, nanotubes titanates cerium, cobalt and sodium are not efficient and not competitive compared with the advanced oxidation processes such as photo-Fenton.

Keywords: tannery wastewater; nanotubes; photocatalysis.

Introduction

The leather industry has a unique importance to the Brazilian economy. According to Cunha (2011), Brazil's share of world trade in leather is impressive, from 6.5% in 2004 to 8.8% in 2008 and 8.0% in 2009, placing the country third in the list the largest exporters in 2008-2009. Looking at the data from the Brazilian Leather (2012), the Brazilian leather exports reached a figure of approximately $ 2.05 billion, including monetary amounts accrued in the year 2011.

According to the IBGE (2012), the effective national cattle in 2010 reached 212.8 million head. In 2011, Brazil ranked 2nd position worldwide in herd of cattle, behind India, whose flock was 324, 5 million, about 1.5 times higher than the Brazilian. Following stood out China and the United States.

However, the growing debate about the environmental impacts arising from the tanning activity has led to greater oversight and control by environmental agencies, mainly with respect to effluent quality, odor generation and disposal of sludge.

The challenge of producing within the concept of sustainable development is important for the leather industry, so that they may broaden their perspectives of experience in domestic and foreign markets, and greater access to credit lines.

Observing the international market for leather is remarkable displacement of large tanneries for the least developed countries. For Santos et al. (2002), the reasons for this market shift to regions like South America reside in search of lower labor costs and more stringent restrictions on the environmental policies of the traditional producer countries.

The called developed countries have focused their production on finishing the imported raw material in the underdeveloped countries (wet blue or crust), ie, the most polluting production process ends up being more economically developed countries unfavorable. In this sense, Correa (2001) notes that in relation to the environmental aspect is important to note that the production of leather to the wet blue stage produces 85% of the environmental waste of the productive chain, while the processing of wet blue leather shoes produced in the 15% remaining.

According to Guterres (2006), the leather market was a rise in the period from 1970 to 2000, especially in developing countries. However, the alliance between the economic development of this activity, with environmental conservation and its adaptation to new market trends is to ensure their survival and their resistance to market fluctuations.

There are several challenges for the effective control of pollution caused by tanneries. In this research the focus will be directed to the treatment of effluents generated by this activity. According to Lofrano et al. (2011), are raised about 30 - 35m³ sewage on average per ton of rawhide.

To Di Iaconi et al. (2002), a large quantity and low biodegradability of various chemicals, such as coloring agents, natural or synthetic tannins, sulfonated oils, makes the treatment of effluents from tanneries an environmental problem and technology. According to Schrank et al. (2005), it is necessary to study new alternatives, which may not only enable efficient treatment of the effluents of the leather industry, but the reuse of treated wastewater, as they are large consumers of water, thus contributing to the consequent rationing and conservation water resources.

As the constitution of effluents from tanneries, Karahan et al. (2008) claim that the COD of tannery effluents is constituted by 60% of particulate organic matter suspended in the range soluble 25% and 15% remaining in the colloidal range. Thus giving us, subsidies for a treatment planning system.

According to Schrank et al. (2004) and Sauer et al. (2006), TiO_2/UV heterogeneous system has been widely studied, but little used in the treatment of tannery effluents. According to Gogate and Pandit (2003), the major advantage of photocatalytic oxidation based processes is the ability to effectively use the sunlight near UV radiation, which should result in considerable cost savings for large scale operations.

The processes of photocatalysis has gained prominence in the scientific community, especially with the development of nanometer-scale structures. They have a large surface area, allowing a wide range of applications involving surface phenomena. The nanometric carbon structures are among the most studied in the scientific community. However, the development of nanomaterials based on inorganic compounds has attracted the attention of academia. Among them there are the TiO_2 based nanostructures, especially titanates.

The potential use of the base titanate nanotubes is presented by Viana et al. (2009). They were able to remove 70% Total Organic Carbon (TOC) and 65% color solution of textile dye Reactive Blue 19 formed of titanate nanotubes using exchanged with cerium (Ce-TiNT).

According to Lee et al. (2007), sodium titanate nanotubes have potential as adsorbents for the removal of basic dyes from an aqueous solution by ion exchange mechanisms. In this case it was discovered that the adsorption capacity can reach up to 380mg/g of TNT.

This work aimed to study the use of titanate nanotubes, exchanged with cerium, cobalt and sodium in photocatalytic processes for the removal of organic matter in effluents from tanneries.

Materials And Methods

Characterization of the study área

The effluent was collected in the city of Teresina, Piauí State, Brazil, at coordinates 4 ° 59 '10.07 "S, 42 ° 50' 52.04" W (WGS84 datum). The samples were collected at the end of the season emissary of the tannery effluent treatment, after treatment physicochemical and biological, as shown in Figure 1.

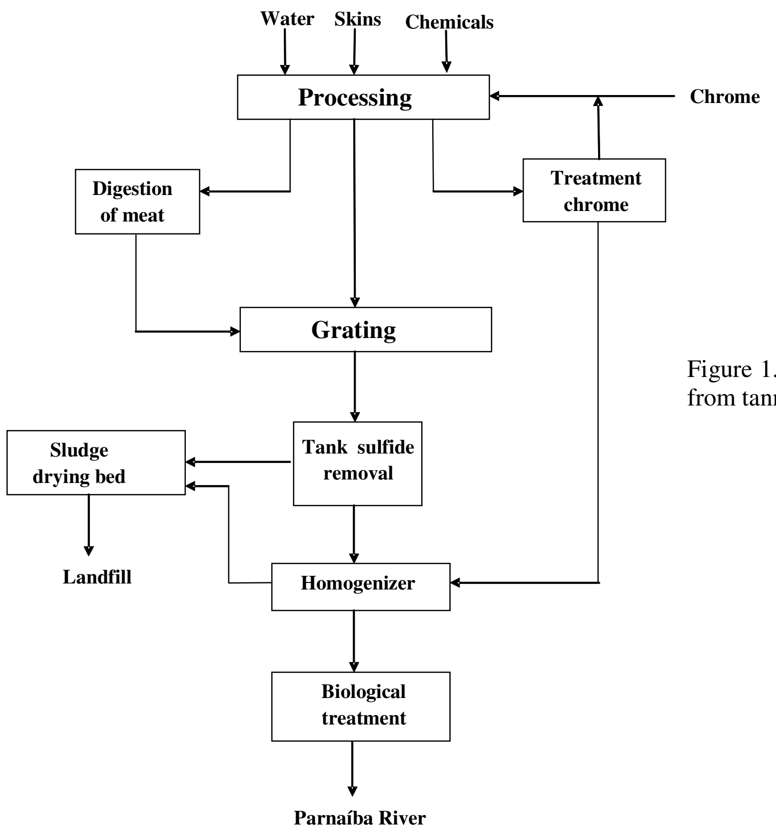

Figure 1. Scheme of treatment plant effluents from tannery.

Preparation of nanotubes

Titanate nanotubes were prepared by the hydrothermal method described by Ferreira (2006). In summary, according Viana (2009), were used 2.00 g (25mmol) of TiO_2 (anatase) and 60mL of an aqueous solution of 10mol / L NaOH. The TiO_2 was suspended in aqueous NaOH solution for 30min. The white suspension formed was transferred to a Teflon container with a volume of 90ml and this was placed in a stainless steel autoclave, which was maintained at 165 ± 5°C for 170h in a muffle furnace type. After 170h of heat treatment the autoclave was removed from the oven and cooled naturally to room temperature. When has cooled, the precipitated white solid was removed and washed several times with deionized water to remove excess sodium ions and other impurities from the surface of the material to reach a pH between 11 and 12.

Titanate nanotubes with cerium and cobalt were made from ion exchange reactions of sodium titanate nanotubes with cerium nitrate (Ce^{4+}) and cobalt (Co^{2+}).

The ionic exchange reactions of titanate nanotubes with metal ions were performed as Viana (2009), through a suspension of 100mg of TNT-Na aqueous solution (100mL) with concentration of 0.05 mol / L of the metal salt. Was used $(NH_4)_2Ce(NO_3)_6$ to ion exchange reaction with sodium titanate nanotubes with cerium. Subsequently, the suspension was magnetically stirred for 24h at room temperature. The solid product was isolated by centrifugation at 3000rpm, and washed with deionized water several times to remove remaining soluble ions (Ce^{4+}, NH^{4+}, NO_3) precursor. The solid product was dried under vacuum for 6h then to obtain nanotubes intercalated with cerium titanate.

Oxidation reactions

Before starting the photocatalytic processes, the effluent passed through coagulation and flocculation processes, to clarify the sample. This was necessary to allow greater penetration of UV radiation in the medium. As a reagent used was a commercial flocculant, whose composition (% W/V) was 26.4% basic aluminum chloride/aluminum polychloride (Al_2Cl_6) in water.

The photocatalytic processes were applied to tannery wastewater in photo-reactor with a capacity of 1000 ml, as shown in Figure 2. The irradiation system consisted of a mercury vapor lamp, high pressure 80 W, Philips, model HPLN80W without the original bulb and encapsulated by a quartz tube of 23mm in diameter and 140mm in height.

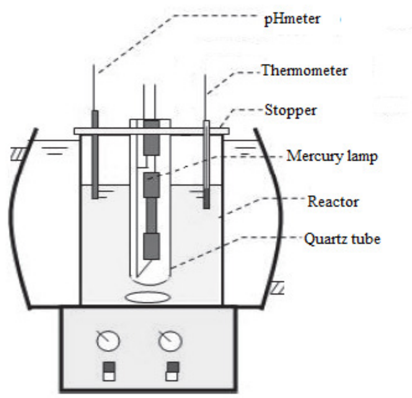

Figure 2. Photo-reactor used in the process of photocatalysis.

The homogeneity of the solution was maintained through a magnetic stirrer and to keep the isothermal conditions around 25 ± 2°C was used a thermostatic bath. The samples were collected at predetermined intervals, between 0 and 120 minutes, measuring the chemical oxygen demand (COD) in these intervals, through the closed reflux method as APHA (1999).

Results And Discussion

The effluent collected in the wild had a pH = 8.6. After clarified by a process of coagulation-flocculation medium acidificava reaching 6.9. This environment was created for the beginning of the photocatalytic process.

It was observed that it is possible to reduce the COD of the medium 30 - 50% with the process of coagulation-flocculation by adjusting only the reagent dosing. But the pollutants are transferred only phase, creating a liability (sludge) that need remediation.

In all experiments we used the TNT concentration 200 mg/L. The results, shown below in Figures 3, 4 and 5 show a small effect of titanate nanotubes in the decay of COD.

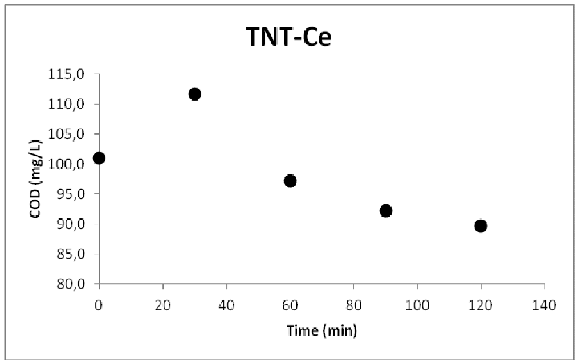

Figure 3. Degradation of COD by TNT-Ce.

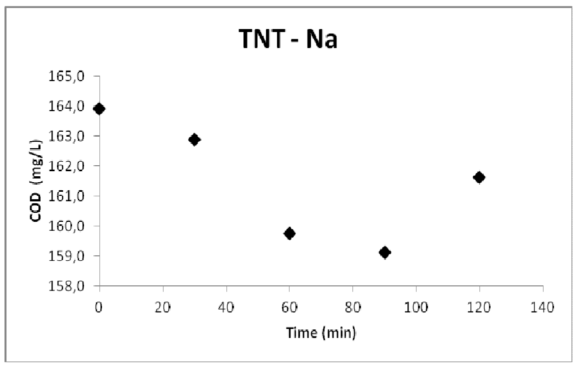

Figure 4. Degradation of COD by TNT-Na.

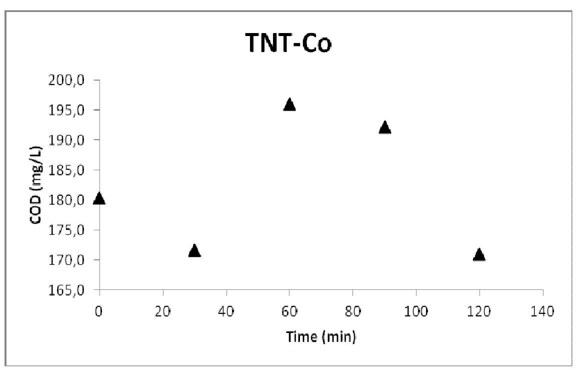

Figure 5. Degradation of COD for TNT-Co.

The process efficiency was he who used the TNT-Ce in the process of photocatalytic degradation of organic matter. The obtained even 11% removal. Since the Co-TNT and TNT-Na had 5.2% and 2.5%, respectively.

The process of advanced oxidation type photo-Fenton is still one of the most efficient in this type of situation. Martins and Moita Neto (2012) found 94% removal of COD in 120 minutes of reaction using the photo-Fenton, in tannery wastewater clarified by aluminum polychloride (Al_2Cl_6).

Conclusion

For removal of COD, under these conditions, nanotubes titanates cerium, cobalt and sodium are not efficient and not competitive compared with the advanced oxidation processes such as photo-Fenton.

It is necessary to evaluate the use of nanotubes before the process of flocculation/coagulation when the pH would be theoretically more favorable for photocatalysis. At this stage, there is evidence of efficiency in removal of dyes and surfactants middle, contributing in reducing the use of reagents in the photo-Fenton process.

It is suggested the use of new sources of UV radiation and insertion of H_2O_2 in the middle in order to assess the interaction of titanate nanotubes therewith. Furthermore, it should evaluate the use of iron titanate nanotubes II in photo-Fenton process as a source of Fe^{2+}.

Acknowledgements

The autors acknowledge the CAPES for a PhD scholarship granted.

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