Jr. of Industrial Pollution Control 34(1)(2018) pp 1882-1887
www.icontrolpollution.com
Research Article

TREATMENT OF TANNING WASTEWATER WITH NANO-PHOTOCATALYSIS

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(Received 16 June, 2017; accepted 23 April, 2018)

Key words: Tannery waste water, Pollutants, Nanomaterials.

ABSTRACT

This work, aimed at studying treatment of waste water from leather industries to determine the removal and reducing of pollutants by using nanomaterials. Tannery waste water was treated with photocatalysis process involved titanium dioxide, zinc sulphide, cadminum sulphide in core shell nanocomposite materials. The synthesized nanomaterials were characterization with XRD, TEM, SEM, EDX and FTIR. All the results show that these materials were in nanomaterials range. XRD pattern for titanium dioxide and composite material were 30 nm and 3.3 nm respectively. TEM images of titanium dioxide and composite material particles size were 20 nm and 5 nm respectively. The SEM images of titanium dioxide and composite material particles size were 100 nm for all them. The SEM image of nanocomposite material indicated that its core shell material. The EDX and FTIR of the materials show the purification of these materials. The tannery processes generated high polluted wastewater, when the pH, turbidity, COD, TDS, chromium, sulphide, chloride and sulphate were found 7, 13900 ntu, 10155 ppm, 462 ppm, 28950 ppm, 412 ppm, 6471.5 ppm and 5995 ppm respectively, which exceeds the existing Sudanese standards. The best removal efficiency of tannery waste water with photocatalysis method at pH 7 and 3 h, which removed 99.8%, 82.7%, 57.1%, 99.9% and 88.3% from Turbidity, COD, TDS, Chromium and Sulphide respectively. photocatalysis was not removed chloride and sulphate from tannery waste water.

INTRODUCTION

The conventional leather tanning technology is highly polluting as it produces large amounts of inorganic and organic chemical pollutants. These pollutants, which are mostly contained in the effluent discharged by tanneries, are a serious threat to the environment. The tannery effluent, if not treated properly, can cause serious damage to soil and water bodies. The high amount of salt contained in the effluent, for example, can increase soil salinity, reduce fertility and damage farming in large areas. Tanneries also produce harmful gases, dust and a large amount of solid waste. Industrial pollution is considered as one of the major issues in environmental protection (Supply and Demand survey on the leather industry – Sudan, 2010).

An average of 30–35 m^3 of wastewater is produced per ton of raw hide. However, wastewater production varies in wide range (10–100 m^3 per ton hide) depending on the raw material, the finishing product and the production processes. Organic pollutants (proteic and lipidic components) are originated from skins (it is calculated that the raw skin has 30% loss of organic material during the working cycle) or they are introduced during processes. The parameters of tannery effluent were found to be high and exceeding the legal ranges of selected parameters discharge to inland water and to sewer.

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The difficulty in treatment of tannery wastewater is due to complex nature of the industry and a large number of chemicals employed in the leather processing. The segregation of each sectional stream and separate treatment therefore requires very high investments in terms of equipment, land etc. hence eliminating or reducing the wastage at the source i.e., at the stage of leather processing, is a promising option for the tanneries (Elnasri, 2003). The wastes are collected in aseptic tank, in some tanneries were treated with alum, but in other tanneries were pumped without treatment.

Several methods have been developed for the treatment of tannery wastewater, including biological and physicochemical processes. Among these methods, currently, nanotechnology has been extensively studied as it offers potential advantages like low cost, reuse and high efficiency in removing and recovering the pollutants (Akbari, *et al.*, 2011).

Photocatalytic oxidation is an advanced oxidation process for removal of trace contaminants and microbial pathogens. It is a useful pretreatment for hazardous and non-biodegradable contaminants to enhance their biodegradability (Mondal and Sharma, 2014).

The semiconductor has the electronic configuration which is characterized by a filled valence band and an empty conduction band divided by an energetic gap. Absorption of a photon with an energy hv greater or equal than the band gap energy generally leads to the formation of an electron/hole pair in the semiconductor particle. If a suitable scavenger or surface defect state is available to trap the electron or hole, recombination is prevented and subsequent redox reactions may occur. The valence band holes are powerful oxidants (+ 3.5 V vs. NHE for TiO_2), while the conduction band electrons are good reductans (+0.5 V vs. NHE). Most organic photodegradation reactions utilize the oxidizing power of the holes. The oxidative degradation process goes on through two initial steps that generate free radicals •OH which attack the organic molecules degrading in CO_2 and H_2O. (Fig. 1) shows schematically the mechanism of photocatalysis. The essential reactive species are oxygen as anions OH- which behave respectively as electron attractor and electron donator, acquiring and giving only one electron (Domenico, *et al.*, 2013).

The main objectives of this work are to: prepare and characterize titanium dioxide, zinc sulphide and cadmium sulphide nanocomposite materials and use it in tanneries wastewater treatment with photocatalysis in the treatment of highly polluted effluents from these industries.

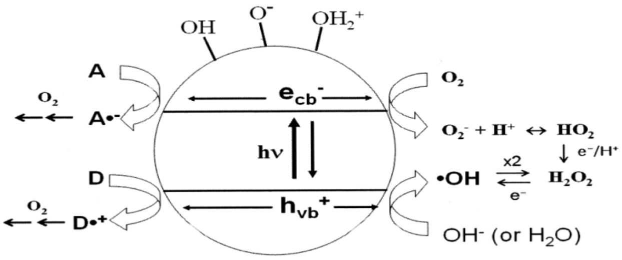

Fig. 1 Principle mechanism of photocatalysis.

EXPERIMENTAL WORK

A composite sample of the tannery wastewater was collected in a plastic container from the White Nile tannery, These samples were analyzed for COD, total dissolved solids, turbidity, pH, Chromium content, sulphide, sulphate and chloride content before and after treatment according to Standard Methods for the Examination of Water and Wastewater (SMWW4000 - 6000) (APHA, 2000), and compared with the Indian (Indian Standards 3025-10, 2002; Indian Standards 3025-29, 2003; Indian Standards 3025-52, 2003; Indian Standards 3025-58, 2006; SSMO 173/2008, 2008), Sudanese, ISO and WHO specification.

Synthesis of titanium dioxide nanoparticles TiO_2

50 ml of $TiCl_4$ solution were slowly added to 200 ml of distilled water in an ice bath. After the addition completed, the mixture was stirred for 30 minutes at room temperature. The solution was heated in water bath for 90 minutes under refluxing. Then, it was filtered using vacuum pump and calcined at 600°C in the muffle furnace for 2 hours (Parthasarathi and Thilagavathi, 2009).

Synthesis of nanocomposite particles of TiO_2, CdS and ZnS

50 ml of 0.1 M cadmium chloride and 50 ml of 0.1 M zinc chloride were mixed and stirred with glass rod for 1 minute (solution A).1.5 g of thiourea and 0.5 g of TiO_2 NPs were added with continuous stirring to 50 ml of 0.2 M sodium sulphide (solution B). Solution A was added slowly to solution B with stirring. The reaction mixture was heated to the boiling temperature under stirring for 3 hours. The product was filtered and washed with distilled water and ethyl alcohol then dried overnight at room temperature (Vaidyaa, *et al.*, 2012; Štengl and Králová, 2011).

Application of photocatalysis in of tannery wastewater treatment

0.6 grams of the nanocomposite material, TiO_2/CdS/ZnS, were suspended in the 1 L beaker containing 600 ml of tannery waste water. The pH was adjusted and the solution was continuously stirred with magnetic stirrer. The solution was exposed to visible light from the sun directly. 200 ml of wastewater samples were collected every 60 min, filtered and analyzed in order to determine the process efficiency in this treatment, the efficiency of treatment at pH of 3, 7 and 10 and time intervals of 1, 2 and 3 hours was determined.

RESULTS AND DISCUSSION

The particle size of the of titanium dioxide nanoparticles was estimated using Sherrer' s equation:

$$D = k\lambda / \beta \cos\phi$$

The particle size of titanium dioxide was found to be 30 nanometer; when comparing the obtained spectrum with the standard pattern (Morris, *et al.*, 1981), the following peaks were found 25, 38, 48, 54, 55, 64 and 69 degree**;** the same peaks appeared in the prepared TiO_2 (Fig. 2).

The particle size of composite nanoparticles was calculated from the 2 theta of the most intense peak in the XRD pattern. The sizes were found 3.3 nm , 1.7 nm and 2.3 nm for TiO_2, CdS and ZnS respectively. As shown in (Fig. 3) when comparing the obtained spectrum with the standard pattern, the following peaks were found 25, 38, 48, 54, 55, 64 and 69 degree for TiO_2 particles.26.7, 45 and 51 for CdS particles. 29, 34, 50 and 69.7 for ZnS particles. All the above peaks are present in the standard pattern (Wang and Zhang, 2014; Daskalaki, *et al*., 2010; Ohama and Gemert, 2011; Chen, *et al*., 2009, Chuong, *et al*., 2008).

(Fig. 4a and 4b) describe the images of titanium dioxide. From the figures it is clearly evident that the particle size is about 30 nm. (Fig. 5a and 5b) showed that the images of composite materials for cadmium sulphide, zinc sulphide and titanium dioxide indicating the heterogeneity of the composite nanomaterials.

(Fig. 6a and 6b); describes the morphology of

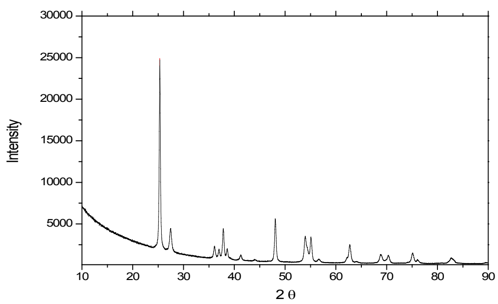

Fig. 2 XRD pattern of titanium dioxide nanoparticles.

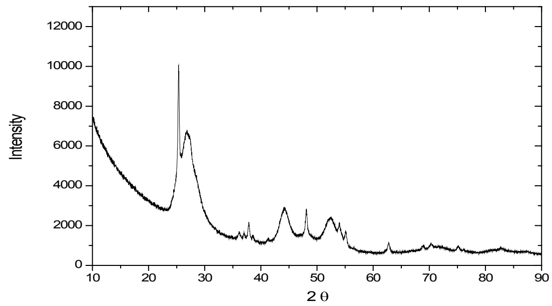

Fig. 3 XRD pattern of composite (CdS/ZnS/TiO_2) nanoparticles.

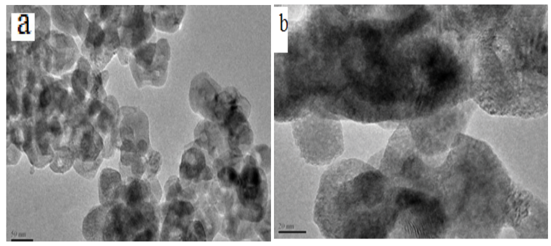

Fig. 4a and 4b TEM image of the titanium dioxide TiO_2 nanoparticles.

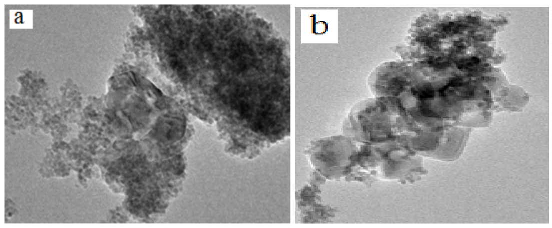

Fig. 5a and 5b TEM image of the composite CdS/ZnS/TiO_2 nanoparticles.

titanium dioxide nanoparticles. From the images it is clearly that the milling of the prepared powders brought the required nanosize. The SEM images show that the titanium dioxide was nearly spherical in shape of regular granules; this may increase the surface area available for the contact in the treatment experiments.

(Fig. 7a and 7b); describes the images of composite sample. The images showed the clustered-shape particles of the composite materials nanoparticles. The homogenous powder indicates complete mixing of the three compounds in one composite particle.

Experimental results indicated that the photocatalysis process was effective in removing some pollutants from the sample of tannery wastewater. To check the accuracy of the results the whole experiment was repeated three times and the average values were calculated.

The results of present study revealed that Turbidity level from different tanning processes reached a value of 13900 ntu as shown in Tables 1 and 2.

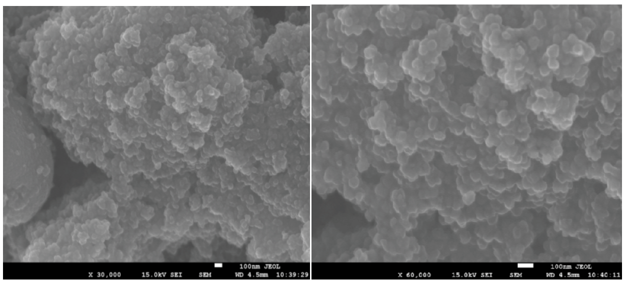

Fig. 6a and 6b SEM image of titanium dioxide nanomaterials.

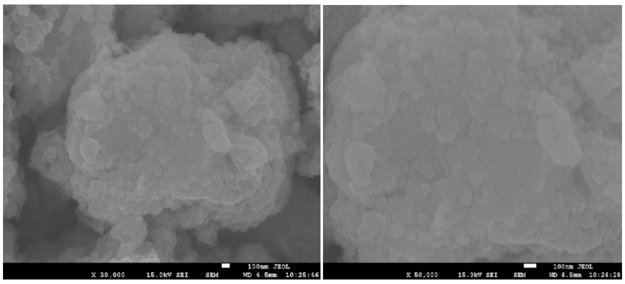

Fig. 7a and 7b SEM image of nanocomposite materials.

(Fig. 8) illustrate the effect of pH on the reduction of turbidity during the 1, 2 and 3hours of the batch run at the photocatalysis process. High removal efficiency of turbidity of 99.9%, 99.8% and 99.9% was found at 3 hours period when the pH of the TWW was 3, 7 and 10 respectively, also all the turbidity values at 2 and 3 hours period in all the pH values were in range of the standard value (Table 3).

Before treatment the COD value is 10155 ppm which is over of the Sudanese industrial wastewater standard 1000 ppm (Fig. 9).

The high removal efficiency of COD was found at 3 hours period at pH 3, 7 and 10 where 74.1%, 82.7% and 64.7% were achieved respectively. All the COD values were over range of the standard value, but the considerable reduction achieved can be used as a pre-treatment step for the COD (Table 4).

TDS value before treatment is 28950 ppm, Fig. 10 illustrates the effect of pH on the reduction of TDS during the 1, 2 and 3 hours of the photocatalysis process (Fig. 10).

The high removal of TDS was reached at 3 hours period in all pH 3, 7 and 10 where 43.8%, 57.1% and 52.1% removal percentages were achieved respectively. The remaining TDS values were over range of the standard limit (Table 5) (Fig. 11).

The removal of sulphide was studied at pH range 3, 7 and 10, keeping all other experimental conditions constant. All the sulphide values were over permissible value of the standard. Maximum removal (92.7%) was achieved at 3 h at pH 3 and this due to liberated sulphide in acidic media. In pH 7 and 10 the removal efficiency were 88.3% and 86.4% respectively. Sulphide from the composite nanomaterials may result in an increase in the values the total sulphide (Table 6).

Table 1. Initial characterization of the tannery waste water and standard limits.

No	Parameters	Concentration	STD value
1	pH	7	6 - 9
2	Turbidity	13900 NTU	40 NTU
3	COD	10155 ppm	1000 ppm
4	Chromium	462 ppm	1.5 ppm
5	TDS	28950 ppm	2500 ppm
6	Sulphide	412 ppm	2 ppm
7	Sulphate	5995 ppm	300 ppm
8	Chloride	6471.5 ppm	1000 ppm

Table 2. Turbidity in TWW at different pH values and time.

pH / Time	3	7	10
1 hour	16	82	44
2 hours	13	30	28
3 hours	12	24	12

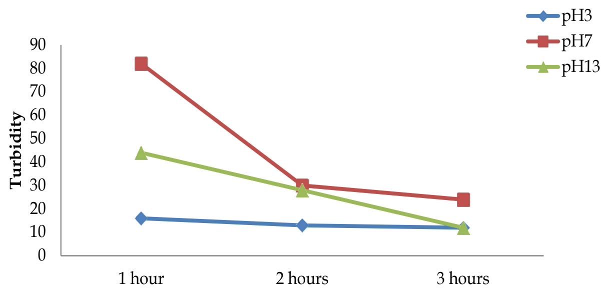

Fig. 8 Turbidity values at different time periods and pH.

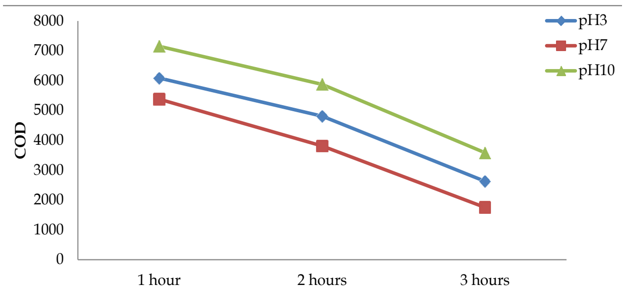

Fig. 9 COD at different values of time and pH.

Table 3. COD in TWW at different pH values and time periods.

pH / Time	3	7	10
1 hour	6088	5380	7152
2 hours	4812	3812	5876
3 hours	2628	1752	3584

The analysis of the TWW sample revealed that chloride level was 6471.5 ppm (Table 1) and the levels exceed the permissible chloride level of 1000 mg/L of effluent discharge into inland surface waters (Fig. 12).

Photocatalysis was not effective in removing chloride content and this due to the high activity of the chloride ions. In pH 3 increasing of chloride value due to acidification of the samples with hydrochloric acid (Table 7).

The sample analysis showed that, the sulphate content in the TWW was 5995ppm Table 1. High levels of sulphate in the tannery effluent could be attributed to the pickling and tanning processes (Fig. 13) (Table 8).

The chromium content in the TWW was found to be 462 ppm (Table 1) much higher than the permissible levels of the chromium, 1.5 ppm, of effluent discharge into inland surface waters (Fig. 14).

At pH 3 the remaining chromium is over the permissible value, and the high removal reached 78.1% at 3 hours.

At pH 7 and 10, the content of chromium was

Table 4. TDS in TWW at different pH values and time periods.

Time \ pH	3	7	10
1 hour	24624	22082	23462
2 hours	19864	17358	18626
3 hours	16260	12416	13872

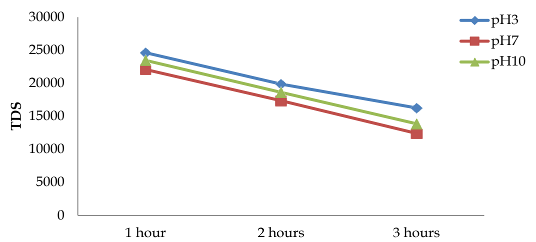

Fig. 10 TDS of the TWW at different values of time and pH.

Table 5. Sulphide in TWW at at different pH values and time periods.

Time \ pH	3	7	10
1 hour	76	86	84
2 hours	58	62	68
3 hours	30	48	56

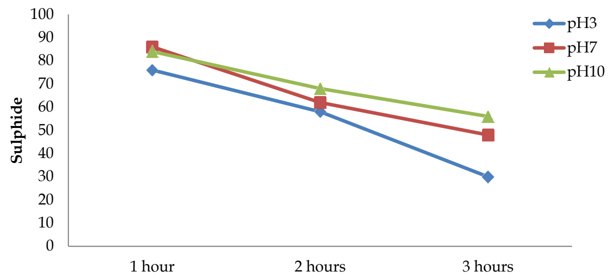

Fig. 11 Sulphide at different values of time and pH.

Table 6. Chloride in TWW at different pH values and time periods.

Time \ pH	3	7	10
1 hour	9256	5963	5340
2 hours	9167	5874	5162
3 hours	9160	5963	5251

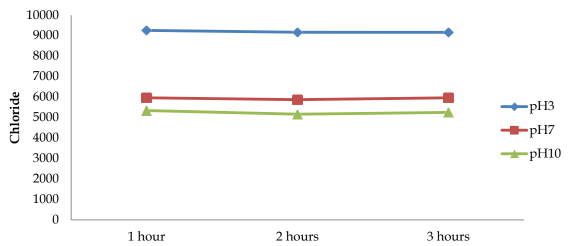

Fig. 12 Chloride values at different values of time at pH.

Table 7. Sulphate in TWW at different pH values and time periods.

Time \ pH	3	7	10
1 hour	5349	6237	6105
2 hours	5478	5991	6244
3 hours	6010	6097	5927

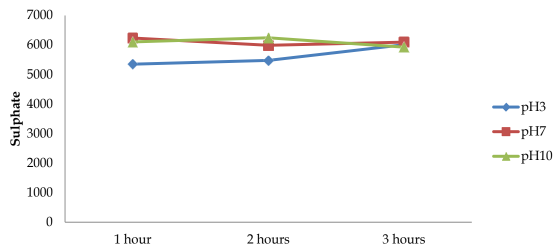

Fig. 13 Sulphate values at different values of time at pH.

Table 8. Chromium in TWW at different pH values and time periods

Time \ pH	3	7	10
1 hour	103.4	0.749	1.337
2 hours	102.4	0.531	0.385
3 hours	101.2	0.312	0.352

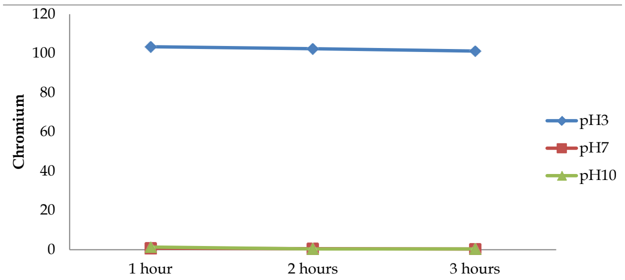

Fig. 14 Chromium values at different values of time and pH.

below the permissible value, and the high removal efficiency was 99.9% at 3 hours.

CONCLUSION

The processing of leather production generates a large amount of liquid waste from pits, drums or paddles containing several soluble and insoluble components. The results of the analysis indicate that the White Nile tannery discharge is highly polluted liquid waste. The photocatalysis technique was reduced the turbidity, COD, chrome and sulphide to the level of satisfaction, among the primary treatments for tannery wastewater. It was not acceptable technique in removing sulphate and chloride from tannery wastewater.

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