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A Simple Treatment of Tannery Wastewater using Modified Activated Carbon by Metal Chloride

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Tannery wastewaters are exceedingly complex and characterized by high contents of organic, inorganic and nitrogenous compounds, chromium, sulfides, suspended solids and dissolved substances. Treatment of tannery wastewater was carried out by using activated carbon modified metal chlorides approaches. Effluent from an existing tannery was used as the test medium. The characteristics of the influent and effluent after the chemical treatment were determined. Modified activated carbon mixed with clarified tannery effluent then the various constituents of the effluent were re-investigated. The results indicated a very good deduction of physico-chemical parameters and heavy metals such as chromium were gradually reduced with the introduction of 100-500 mg/L of activated carbon metal chlorides, including $CaCl_2$, which were 41% (EC), 76% (BOD), 47% (COD) (72%) (TDS), 87% (total hardness), 45% (chlorides), 63% (sulphate), 58% (nitrates), 70% (Cr), 32% (surfactants).

Keywords: Tannery wastewater, Activated carbon, Metal chloride, Physico-chemical parameters.

INTRODUCTION

Tanning is one of the oldest industries in the world. During ancient times, tanning activities were organized to meet the local demands of leather footwear, drums and musical instruments. With the growth of population, the increasing requirement of leather and its products led to the establishment of large commercial tanneries [1-3]. Two methods are adopted for tanning of raw hide/skin *viz.* vegetable tanning and chrome tanning. The production processes in a tannery can be split into four main categories: (i) hide and skin storage and beam house operations, (ii) tanyard operations, (iii) post-tanning operations and (iv) finishing operations.

Tanneries are typically characterized as pollution intensive industrial complexes which generate widely varying, high-strength wastewaters. Variability of tannery wastewaters are not only from the fill and draw type operation associated with tanning processes, but also from the different procedures used for hide preparation, tanning and finishing. These procedures are dictated by the kind of raw hides employed and the required characteristics of the finished product. Tanning industry also has one of the highest toxic intensity per unit of output [4-7]. During tanning process at least about 300 kg chemicals are added per ton of hides [8]. Tannery effluent is among one of the hazardous pollutants of industry. Major problems are due to wastewater containing heavy metals, toxic chemicals, chloride, lime with high dissolved and suspended salts and other pollutants (Ruberoid) [9].

Tannery waste has a good variety (black to dark brown), lower BOD, high pH and small dissolved solids. Tannery effluents, puerile, pollute the receiving stream when emitted unchecked and, if permitted to enter into the field for an extended period, seriously affect the locality's soil water table. It has been noticed that a single tannery pollutes the groundwater in the area of 7 to 8 km. Total dissolved solids in freshwater in some places [TNWDB] are as high as 17,000 mg/L. Sodium chloride is the dominant element of freshwater, rendering it unsafe for consumption and agriculture. Na^+, Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-} are more than the dissolved ingredients required for either alcohol. Such factories did not initially perform effluent treatment, before it was released into the environment. The surface water (Palar river) and land is severely contaminated [10-12]. After several years, even the irrigation supplies spread the disease. The factories soon developed a local effluent treatment plant (CETP), which was supported by Tamil Nadu State. Total wastewater is emitted from 35 to 45 L/kg of covering. This effluent is sent to one of the CETPs from the study area where, the emission levels are very harmful in this water-shed [13].

The uncontrolled discharge of industrial waste into the rivers, which combine with groundwater, causes water contamination. Metals constitute an intrinsic part of nature and perform an integral role in living organisms' life cycles [14]. Many heavy metals are well-known toxic and carcinogenic agents that pose a significant threat to the people and the flora and fauna in the water bodies that collect them. Heavy metals appear to bioaccumulate and are eventually introduced to the climate. If waste water is released to water bodies without heavy metals being extracted, it could be dangerous for both human and marine organisms because it is non-degradable and permanent. Copper, copper, zinc, cadmium, gold, mercury, chromium, lead, steel, nickel, titanium, arsenic, selenium, molybdenum, cobalt, manganese and aluminum are known as following components. Due to strict regulations, the elimination of heavy metals from drainage has recently become a significant subject of interest. Heavy metal industrial wastewater should be processed prior to injection into the water stream, but its handling is very costly [15-17].

The study deals with the reduction, through the use of an adsorbent, of heavy metals such as chromium or other essential physico-chemical parameters such as total solid dissolved (TDS), total biochemical oxygen (BOD), chemical oxygen demand (COD), total hardness and electrical conductivity from the tanning wastewater. The research carried out by using the activated carbon modified with cadmium chloride was evaluated in the post treatment of tannery wastewater effluents, collected from Vellore district of India where large number of tanneries is located. The characteristics of the influent and effluent after the chemical treatment were determined. Modified activated carbon mixed with clarified tannery effluent then the various constituents of the effluent were re-measured. This research deals with the reduction, through the use of an adsorbent, of heavy metals such as chromium or other essential physico-chemical parameters such as total solid dissolved (TDS) total biochemical oxygen (BOD), chemical oxygen demand (COD), total hardness and electrical conductivity from the tanning wastewater.

EXPERIMENTAL

Synthesis of activated carbon modified metal chlorides: Chemicals and reagents were obtained from Merck, India for alteration and adsorption tests. The chemical alteration of activated carbon surface was carried out using calcium chloride, barium chloride and strontium chloride. In 500 mL beaker, a solution of 500 mg/L was prepared, including calcium chloride, barium chloride and strontium chloride. Then, it added 10 g of GAC and stirred the solution for 3 h. After the water was purified, the carbon retained by the filter was dried for 24 h in a 150 ºC vacuum oven [18].

Collection of tannery effluent sample: Tannery effluent is a major source of heavy metals and dissolved organic waste discharged directly into the Palar river in Vellore district, India. In the process of this inquiry, the identified tanneries throughout four areas, namely Vaniyambadi, Ambur, Pernambut and Ranipet, were obtained from the outlet (predischarge drain to the sedimenting tank). Discharged effluents have been obtained with washed airtight plastic bottles and processed in the cooling system by 4 ºC and measurements of pH, total dissolved solids (TDS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), maximum hardness, electrical conductivity and dissolved anions such as chloride, sulfate, phosphate, nitrite, and heavy metals have been analyzed [19].

Preparation of tannery effluent for adsorption study by digestion: Tannery effluent contains a large amount of suspended solids, which can render atomic absorption spectroscopy (AAS) measurements. It is therefore necessary to digest the sample before treatment. In beaker, 50 mL of effluent was added to 15 mL of conc. HNO_3. The fluid was then heated at 60-75 ºC to reduce the amount of $HClO_4$ to half, 7.5 mL of $HClO_4$ was dissolved to the solution and heated until all acids were extracted. The clear solution was then diluted with water to achieve the required volume and the sample was finally ready for further analysis. At first, the concentration of the digested samples was analyzed using AAS and used as a tannery effluent stock solution which was diluted in 1.00, 2.00 and 3.00 ppm solutions. The physico-chemical properties of chrome tanning raw effluents are provided in Table-1. The limit prescribed by the Central Pollution Control Board (CPCB), India [20].

Characterization of tannery effluent: The sampled effluent has been analyzed for its physico-chemical parameters following procedures described in the standard water/water testing methods [21]. Such parameters include pH, electric conductivity, total dissolved solids, biochemical oxygen demand (BOD), chemical oxygen demand, SO_4^{2-}, NO_3^-, PO_4^{3-}, Cl^-, surfactants and so forth. Flame atomic absorption spectrometer was utilized to analyzed the presence of heavy metals like Cr(VI).

Effect of physical settling: The disposal of tannery waste water is extremely contaminated and challenging in the presence of toxic compounds. Pretreatment to minimize the concentration of these contaminants must therefore be applied before discharge, a particular problem being the removal of COD, BOD and heavy metals, particularly chromium. In this phase, the probability of sedimentation emission control utilizing sand filters was investigated. During the preliminary tests, the most relevant parameters of the single sedimentation (BOD, COD, pH, conductivity, TDS and sulfides) were evaluated. The option of processes for treating wastewater depends on various factors such as performance, cost and environmental capacity [22]. However, before conducting studies to explore the cost effective disposal methods for tannery wastewater, the dye effluent of the pretreatment must first be studied.

Pretreatment process (sand filtration): Tannery effluent sample was collected in 5 L jar, 5 mg/L NaOH was applied to minimize the solubility of the effluent cations and allowed to settle for 24 h. Complete suspended solids (TSS) were thus settled by flock forming. The supernatant liquids were passed through a sand-stone filter after settling. The filtration cycle is

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS OF TANNERY EFFLUENT (BEFORE AND AFTER SAND FILTRATION PROCESS) AND COMPARE WITH STANDARD PERMISSIBLE LIMITS

Parameters	Standards limits (ISI-2000/ISWBDS)	Untreated effluents (raw effluent)	Sand-stone filtered effluents (SSF)	Methods
Colour	Colourless	Blockish	Light grey	Pt–Co colour unit Spectrophotometer, Merck
Odour	Odourless	Odour	Odour	–
pH	5.5-8.0	9.0	7.2	Merck pH meter
Elect. conductivity (µmhos/cm)	400	8720	7355	Electrometric instrument
BOD (mg/L)	30	1565	1438	Incubating the sample at 30 °C for 5 days followed by titration
COD (mg/L)	250	4857	2100	Closed reflux method
TDS (mg/L)	2100	15674	12483	Gravimetric, oven drying at 105 °C
Total hardness (mg/L)	300	1355	1235	Digital titrimetric
Chloride (mg/L)	1000	2860	2015	Argentometric titration
Sulphate	2.0	752	617	UV spectrophotometer (barium chloride)
Nitrate (mg/L)	10	121	87	AA Spectrophotometer, Merck
Chromium(VI) (mg/L)	0.1	0.968	0.529	AA Spectrophotometer, Merck
Surfactants	10	22	15	Partition-gravimetric method

the primary process in which organic materials, such as complete organic carbon (TOC), biochemical oxygen needs (BOD), chemical oxygen demand (COD) and nutrients (ammonia) have been extracted from tannery effluents. The efficiency and durability of the process depends on the extent of hydraulic loading and sandstone and other filter regeneration. Four-layer sandstone filter beds were engineered to optimize the extract organic matter, BODs, CODs and nutrients. The extraction products composed of sand and stones are ranged from 10 to 12 cm per sheet. The sand deposits composed of two inches, field sands (1 mm in diameter) at the surface and small sand on the edge (around 0.15 mm in diameter). The stone layers often consist of two layers of larger stones (a diameter of 5 mm) on the surface and smaller ones (a diameter of 5 mm) on the bottom, which were used to eliminate blockages in the sand filter. A report suggested that the multiple dose of sand filters provided superior treatment output capacity and filter speed [23]. The sandstone beds used could be reused and refurbished by cleaning and boiling freshwater and saline water at 100-102 ºC [24]. The supernatant solvent was added to the top of the filter after the settling cycle and allowed to pass through the different layers and the percolated water was eventually deposited at the base of the pipe. Experiments including coagulation-floculation and sedimentation strategies were performed in lots.

Physico-chemical studies: The experiments have been performed at least three times to eliminate the observational faults. Visually, the colour of the tannery effluent was examined and the scent was detected. The pH on the field was determined with the Eutech pH meter. Other physico-chemical parameters such as electrical conductivity (EC) and the need for biological oxygen (BOD) were measured using standard APHA methods [25]. Other physico-chemical parameters include total dissolved solids (TDS), full hardness, SO_4^{2-} and NO_3^-, surfactants, PO_4^{3-} and Cl^-. In the laboratory, heavy metals such as tannery effluent chromium have been analyzed using a flame atomic absorption spectrometer (AAS). The physico-chemical parameter values following the standard procedures are shown in Table-2.

Tannery wastewater characteristics: Tannery wastewater characteristics vary significantly from tannery to tannery, based

TABLE-2
PHYSICO-CHEMICAL CHARACTERISTICS OF TANNERY EFFLUENTS (BEFORE AND AFTER FILTRATION PROCESSES) & ADDITION OF AC- $CaCl_2$ ADSORBENT

Parameters	Standards limits (ISI-2000/ ISWBDS)	Untreated effluents	Sand-stone filtered effluents (SSF)	1.0 (g/L)	2.0 (g/L)	3.0 (g/L)	4.0 (g/L)	5.0 (g/L)
Colour (Hazen)	Colourless	Blockish	Light grey	Dull white	Dull white	Dull white	Dull white	Dull white
Odour	Odourless	Odour	Odour	Odour	Odour	Odour	Odour	Odour
pH	5.5-8.0	8.9	8.1	7.6	7.4	7.0	6.9	6.9
EC (µmhos/cm)	400	9830	8420	7722	7024	6325	5626	4998
BOD (mg/L)	30	1359	1328	1128	928	726	525	321
COD (mg/L)	250	4187	2185	1960	1745	1523	1300	1159
TDS (mg/L)	2100	13680	12870	10980	9083	7183	5283	3615
Total hardness (mg/L)	300	1174	1056	875	696	517	338	140
Chloride (mg/L)	1000	3250	2110	1914	1710	1522	1320	1180
Sulphate (mg/L)	2.0	687	615	545	470	396	304	229
Nitrate (mg/L)	10	103	89	78	71	59	43	38
Chromium(VI) (mg/L)	0.1	1.017	0.098	0.080	0.070	0.056	0.042	0.031
Surfactants	10	24	16	15.5	14	13	12.5	11

on tannery scale, the chemicals used for a particular operation, the amounts of water used and the form of final product provided by a tannery. Tannery wastewater is primarily distinguished by biochemical oxygen demand measures (BOD), chemical oxygen demand (COD), suspended solid (SS) and total dissolved solids (TDS), chromium and sulfides, *etc*.

Treatment of wastewater through adsorption process by the use of modified activated carbon with $CaCl_2$: Samples of tannery effluent is treatment by method of adsorption, using $CaCl_2$ adjusted activated carbon (1.0 g, 2.0 g, 3.0 g, 4.0 g, 5.0 g and 1 L) in jar test systems by retaining process parameters such as 100 rpm agitation level, 60 min agitation, 30 ºC and 1 h adjustment period. Coagulated samples were filtered *via* a vacuum filtration system after the flakes have been settled and analyzed. Once again, coagulated effluent samples have been tested at different doses using activated carbon by adsorption. The treatments were conducted with parameters such as turbulence 60 min, 28 ºC, instability 250 rpm and settling time 1 h in the jar test system. After adsorption, collected samples have been purified by the vacuum filtration system using Whatman No. 4 filter paper with the pore size 20 to 25 μm (125 mm, Whatman Manufacturing Company, U.K.). Such samples were examined in keeping with the normal laboratory protocols. The same process was conducted with adjusted adsorbents $SrCl_2$ and $CaCl_2$. Such samples were examined in compliance with normal laboratory procedures.

Effect of synthesized activated carbon modified metal chlorides on tannery effluent: The first dosage was calculated by adjusting coagulant (activated carbon-modified MCl_2) and pH control. The pH dependency on the coagulation cycle was examined with a broad pH range of 2 to 9. The pH was adjusted at the beginning of the experiment with 0.1 M NaOH or 0.1 M HCl. The final analysis of removal efficiencies for each parameter of 0.5 to 4 days determined the efficiency of the coagulation cycle. This work presents only the results of 1 day treatment, however, since the results after two or more days of treat-ment show a considerable difference from the results obtained during one-day treatment. Both tests were performed at room temperature (28 ± 2 ºC). The pH of the tannery effluents and the treated effluent (sandstone filter) were 8.9 and 8.1. Following filtration, the pH value increased marginally due to the addition of 0.1 M NaOH. Upon filtration, specific concentrations (100-500 mg/L) of activated carbon metal chlorides were contained in the effluents. The results of the study showed that the pH of the handled effluents was decreased as predicted by the increased dose of adsorbents. The physico-chemical parameters and heavy metals such as chromium were gradually reduced with the introduction of 100-500 mg/L of activated carbon metal chlorides, including $CaCl_2$, which were 41% (EC), 76% (BOD), 47% (COD) (72%) (TDS), 87% (total hardness), 45% (chlorides), 63% (sulphate), 58% (nitrates), 70% (Cr), 32% (surfactants).

RESULTS AND DISCUSSION

While tanning is an important industry for the economic and social development of any nation, it is troubling that waste water is directly discharged by such factories into the surrounding polar water body with insufficient manner. Most of the chemical physical parameters tested in this analysis have shown that almost all effluent properties are higher than the IS (Indian Standard) and CPCB (Central Pollution Control Board) temporary emission cap (Table-1). Results showed that chemical effluents from tannery are not appropriate to discharge surface water bodies that pose the possible health and environmental risks.

It is also observed that the filtration cycle of sand stone could minimize some levels of pollution but not enough for the treatment of effluents (Table-2). Chromium ion reduction improved with an elevated dosage of adsorbents, since large quantities of activated carbon-metal chlorides provide a greater number of adsorption reaction sites. The pH and turbidity also exceeded appropriate values following adsorption with synthesized activated carbon metal chlorides.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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