REMOVAL OF WATER POLLUTANTS FROM TANNERY WASTE EFFLUENT CONTAMINATNS BY ADSORTION USING ACTIVATED CARBON METAL CHLORIDE ($BaCl_2$) AS AN ADSORBENT

G. ANBUKKARASI[1*], A.THAMINUM ANSARI ABUBACKER[2]

1. P.G. & Research Department of Chemistry, Muthurangam Govt. Arts College, Vellore, Tamil Nadu,

2. Assistant Professor, P.G. & Research Department of Chemistry, Muthurangam Govt. Arts College, Vellore, Tamil Nadu

*__Corresponding author E-mail__: anbulak.07@gmail.com

ABSTRACT

In this investigation, the activated carbon was modified with some metal chlorides like $BaCl_2$ by using co-precipitation, sol gel and green synthesis method. These activated carbon was modified with some metal chlorides are used to lessen the various physico chemical parameters such as pH, TDS, TSS, COD, BOD, organic pollutants and heavy metals dissolved in tannery waste water by sorption. The physicochemical status and the evaluation of statistics of obtained physicochemical data of tannery industrial effluent were studied. We observed that this Modified metal chloride $BaCl_2$ activated carbon much efficient than other ordinary activated carbons used as adsorbent.

Key words: *Tannery effluents, Metal chloride, activated carbon, adsorption, Physicochemical.*

1.0. INTRODUCTION

In India, the major industries contributing of water pollution include food and agro based, pulp and paper, textiles, chemicals and tanneries [1]. Pollution is a gift of Industrial civilization. Leather industry is one of the oldest industries in India and one of the leading foreign exchange earners for the country. Tannery wastewater is considered to be one of the most polluting effluents due to it containing a large variety of toxic heavy metals that range from chromium, lead, cadmium, cobalt, nickel, selenium to arsenic. As consequence of most tannery wastewater treatments, the tannery sludge that is produced contains considerable amounts of heavy metals, which are harmful to the environment and human health. Hence, tannery wastewater and sludge treatments have become a serious environmental issue [3]. However, heavy metals in the tannery sludge often outweigh the soil's heavy metal content, and the application of sludge can indeed increase the concentration of heavy metals in the agricultural soil and affect the crop production owing to uptake of the metals. Thus the leather industries relieve the disposal problem of uneatable hide and skins. Cleaner technology adoption in the tannery process reduces the pollution load to an extent [4]. Industrial waste is generated from different processes and the amount and toxicity of wastes released varies with its own specific industrial processes. Tannery effluents are ranked as the highest pollutants among all industrial wastes [5].

Tannery effluents again compromise the physical, chemical and biological properties of aquatic environment. The chemical impurities of tannery effluents mostly includes the following dissolved substances such as inorganic salt cations (Cr, Pb, Fe, Zn, Cu, Ca, Na, etc.);anions such as $SO_4,^{2-}$, $NO_3,^{-}$, $PO_4,^{3-}$ Cl^{-} and parameters such as, pH, BOD, COD, TSS, TDS, pH etc. Every tanning process step, with exception of the crust finishing operations, produces a huge amount of wastewater [6-8]. Tannery wastewater has widely varying characteristics resulting from the nature of the tanning process adopted, the amount of water used and in-plant measures for pollution reduction. The Minimum Acceptable Standards (MINAS) set by the Central Pollution Control Board (CPCB), India for the discharge of effluents to surface water bodies are also given in the **Table –1.1** [20].

Table: 1 Characterization of untreated (Raw) Waste Water

S.No	Parameters	CPCB Discharge Norms	Untreated waste water
1	**Colour**	Colourless	Blockish
2	**Odour**	Odourless	Odour
3	**pH**	6 – 8	9.0
4	**Turbidity (NTU)**	10	450
5	**Salinity**	-	15200
6	**EC (µs/cm, 25ºC)**	0.288	27.3
7	**COD (mg/L)**	250	4318
8	**BOD (mg/L)**	30	1260
9	**TSS (mg/L)**	2000	13653
10	**TDS (mg/L)**	2100	15675
11	**Total Hardness(mg/L)**	300	950
12	**Chloride (mg/L)**	1000	1570
13	**Nitrate (mg/L)**	2	46
14	**Sulphate (mg/L)**	2	752
15	**Dissolved oxygen**	4-6	1.75
16	**Chromium (mg/L)**	2.0	198
17	**Hexavalent chromium (mg/L)**	0.1	0.768
18	**Lead (mg/L)**	0.5	0.597
19	**Copper (mg/L)**	1.0	1.758
20	**Iron (mg/L)**	2	14.53
21	**Cadmium (mg/L)**	0.3	0.485
22	**Nickel (mg/L)**	1.0	0.157
23	**Sodium (mg/L)**	1000-1500	4890
24	**Surfactants**	10	23

Adsorption

Adsorption is defined as a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid–solid interface.

- Surface area of the adsorbent material
- Nature and concentration of adsorbate
- pH of the solution
- Temperature
- Properties and dose of the sorbent

The adsorption process of the adsorbate molecules from the bulk liquid phase into the adsorbent surface is presumed to involve the following stages (**Figure -1.5**).

1. Mass transfer of the adsorbate molecules across the external boundary layer towards the solid particle.
2. Adsorbate molecules transport from the particle surface into the active sites by diffusion within the pore–filled liquid and migrate along the solid surface of the pore.
3. Solute molecules adsorption on the active sites on the interior surfaces of the pores.
4. Once the molecule adsorbed, it may migrate on the pore surface trough surface diffusion.

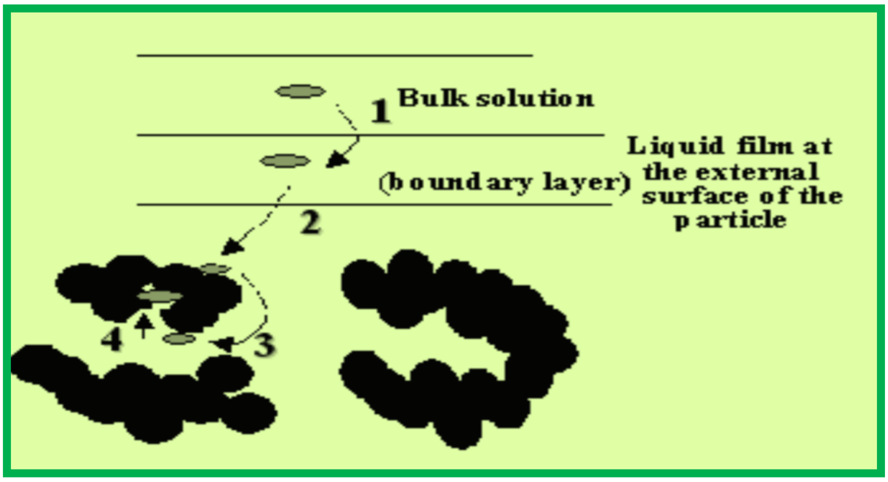

Fig 1: Processes and Terms involved in Adsorption Technology

Activated carbon as sorbent to remove dyes in wastewater because of its excellent adsorption ability. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies .However, although activated carbon is a preferred sorbent, its widespread use is restricted due to high cost. Recently, numerous approaches have been studied for the development of cheaper and effective adsorbent [9 – 11].

In this study, the activated carbon was modified with some metal chlorides by using co-precipitation, sol gel and green synthesis method. These activated carbon was modified with some metal chlorides are used to reduce the various physico chemical parameters such as pH, TDS, TSS, COD, BOD, organic pollutants and heavy metals dissolved in tannery waste water by sorption. The physicochemical status and the evaluation of statistics of obtained physicochemical data of tannery industrial effluent were studied.

2.0. MATERIALS AND METHOD

2.1 Collection of Tannery wastewater sample

This research entailed the collection of 15 tannery effluent samples from the final discharge point (outlet) of different leather tanning unit located in Ambur, Vaniyambadi, Pernambut and Ranipet, Vellore district, Tamilnadu, India. Effluent samples by lowering a pre-cleaned 4L glass bottle (previously washed with 0.1M HNO_3 before rinsed with distilled water) into different depths of the effluent, allowed to overflow, withdrawn, sealed and stored in Polythene containers at 4°C till required for further analysis. pH, total dissolved solids, and conductivity were determined [12 – 14].

Table 2: The Physico-chemical characteristics of tannery effiuent (before and after sand filtration process) and compare with standard permissible limits

S.No	Parameters	Std. limits (ISI-2000/ ISWBDS)	Untreated effluent's (Raw effluent)	Sand-stone filtered Effluents (SSF)
1	**Colour**	Colourless	Blockish	Light grey
2	**Odour**	Odourless	Odour	Odour
3	**pH**	5.5 – 8.0	9.0	7.2
4	**EC (µmhos/cm)**	400	8720	7430
5	**BOD (mg/L)**	30	1565	1415
6	**COD (mg/L)**	250	4857	2137
7	**TDS (mg/L)**	2100	15674	13438
8	**TH (mg/L)**	300	1355	1150
9	**Chloride (mg/L)**	1000	2860	2116
10	**Sulphate (mg/L)**	2.0	752	624
11	**Nitrate (mg/L)**	10	121	93
12	**Cr (VI) (mg/L)**	0.1	0.968	0.573
13	**Surfactants**	10	22	16

2.3 Physico chemical study

The experiments were performed at least three times to minimize analytical error. The color of the tannery effluent was observed visually and recorded, and the odor was detected by smelling. pH was measured using Eutech pH meter on the site. Other physicochemical parameters such as electrical conductivity (EC), dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), total suspended solids (TSS), SO_4^{2-}, NO_3^-, PO_4^{3-} Cl^-, surfactants, etc., were measured as per standard methods of APHA (1985). .The heavy metal such as Chromium from tannery effluent were analyzed in the laboratory using Flame Atomic Absorption spectrometer (AAS) [15 – 17].

2.4. Treatment of wastewater through adsorption process by the use of activated carbon modified metal chlorides.

Tannery effluent samples were treated through adsorption (coagulation) process by using activated carbon modified $SrCl_2$ **(**1.0 g, 2.0 g,3.0 g 4.0 g ,5.0 g in 1 lit**)** in Jar test system by maintaining process parameters as agitation speed 100 rpm, agitation time 60 min, temperature 30º C and settling time 1 hour. After settling of flakes, coagulated samples were filtered through vacuum filtration system and were analyzed. Again coagulated effluent samples were treated through adsorption process by use of activated carbon at different doses. This treatment was conducted in Jar test system by maintaining parameters such as agitation time 60 minutes,28ºC temperature, agitation speed 250 rpm and settling time 1 hour. After adsorption process, treated samples were filtered by use of Whatman No.4 filter papers with a pore size of 20 to 25 µm through vacuum filtration system. These treated effluent samples were analyzed according to the standard laboratory protocols. The same procedure was carried out with activated modified $BaCl_2$ and $CaCl_2$ adsorbents. These treated effluent samples were analyzed according to the standard laboratory protocols.[18 & 19]

2.5. Color, Odour and Appearance

The average color range of the untreated tannery industry effluent was found to be 15 Hazen units; which was higher than all the recommended values of standard (5 Hazen units). The color appearance of untreated effluent was found blackish. The analysis results indicate that the untreated effluents contained highly colored compound which has the potential to pollute the environment. The original blackish color of the effluent (15 hazen units) was reduced to 10 hazen units after sand-stone filtration, indicating the effectiveness (40 %) of the filter media. The color appearance of this filtered effluent was dull-white. The effluents' blackish color has turned Colourless, when the activated carbon modified metal chloride doses increased above 4.0 g/L. The study results show that 4.0 g/L of activated carbon modified metal chloride dose was the most effective for removal of coloring agent. Research reports showed that the effluents temperature depends on the process of production in the industry and it is usually with a range of 32 – 40°C [15 & 16].From the result of physico-chemical properties of tannery effluent after adsorption with activated carbon modified metal chlorides, it was found that the each parameter (pH, TOC, EC and TDS) was changed significantly ($p < 0.05$) from their respective initial content.

2.6. Effect of synthesized activated carbon modified metal chlorides (AC_$BaCl_2$) on tannery effluent.

At first, optimization of coagulant (Activated carbon modified metal chlorides) dose was determined and then optimization of pH was made. The dependency of pH on coagulation process was examined using a wide pH range from 2 to 9. The pH was adjusted with 0.1 M NaOH or 0.1 M HCl as required in the beginning of the experiment. Finally the optimization of coagulation period was determined by analyzing the removal efficiencies for each parameter of 0.5 – 4 days. However, this work presents only the results of 1-day's treatment as the results obtained after two or more days treatment did show any significant difference from those obtained in 1- day treatment. The entire experiments were conducted at room temperature (28 $\pm$ 2°C).

The pH value of the untreated tannery effluent and treated (sand-stone filter) effluents were 8.9 and 8.1 respectively. After filtration, pH value slightly increased due to add 0.1 M NaOH during the settling period. After filtration, the effluents were treated with different doses (100 – 500 mg/ L) of activated carbon metal chlorides. The study results observed that the pH of the treated effluents was decreased with increasing adsorbents dose as expected.

The physico chemical parameters and heavy metals like chromium in the tannery effiuent was reduced gradually with the addition of 100 - 500 mg/L of activated carbon metal chlorides like $Cacl_2$.It can be seen that ,the highest removal efficiencies for different parameters achieved were 41% (EC), 76% (BOD), 47%(COD) , 72% (TDS), 87% (total hardness), 45% (chlorides), 63% (Sulphate), 58% (nitrates), 70%(Cr) , 32% (Surfactants) as shown in Table 3.3 and Fig 2..

The physico chemical parameters and heavy metals like chromium in the tannery effiuent was reduced gradually with the addition of 100 - 500 mg/L of activated carbon metal chlorides like $Bacl_2$.It can be seen that ,the highest removal efficiencies for different parameters achieved were 44% (EC), 79% (BOD), 51%(COD) , 76% (TDS), 89% (total hardness), 48% (chlorides), 66%(Sulphate), 60% (nitrates),75% (Cr) , 44% (Surfactants) as shown in Table 3.3 and Fig 2..

The physico chemical parameters and heavy metals like chromium in the tannery effiuent was reduced gradually with the addition of 100 - 500 mg/L of activated carbon metal chlorides like $Srcl_2$.It can be seen that ,the highest removal efficiencies for different parameters achieved were 51% (EC),84% (BOD),58% (COD) , 82% (TDS),92% (total hardness), 56% (chlorides), 73% (Sulphates),68% (nitrates),80% (Cr) , 57%(Surfactants) as shown in Table 3.3 and Fig 2.

Table 3: The physico-chemical characteristics of tannery effluents (before and after filtration processes) and addition of AC- $Cacl_2$ adsorbent

S. No	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)
1.	**Colour(Hazen)**	Colourless	Blockish	Light grey	Dull-white	Dull-white	Dull-white	Dull-white	Dull-white
2	**Odour**	Odourless	Odour	Odour	Odour	Odour	Odour	Odour	Odour
3	**pH**	5.5-8.0	8.9	8.1	7.8	7.5	7.2	6.9	6.7
4	**EC(µmhos/cm)**	400	9830	8429	7729	7024	6327	5629	4998
5	**BOD (mg/L)**	30	1359	1328	1128	928	726	525	321
6	**COD (mg/L)**	250	4187	2185	1960	1745	1523	1300	1159
7	**TDS (mg/L)**	2100	13680	12883	10983	9083	7183	5283	3615
8	**TH (mg/L)**	300	1175	1056	875	696	517	338	140
9	**Cl (mg/L)**	1000	3250	2116	1914	1710	1522	1320	1180
10	**Sulphate (mg/L)**	2.0	687	615	545	472	396	304	229
11	**Nitrate (mg/L)**	10	103	89	78	71	59	43	38
12	**Cr (VI)(mg/L)**	0.1	1.017	0.098	0.080	0.071	0.056	0.042	0.031
13	**Surfactants**	10	24	16	15.5	14	13	12.5	11

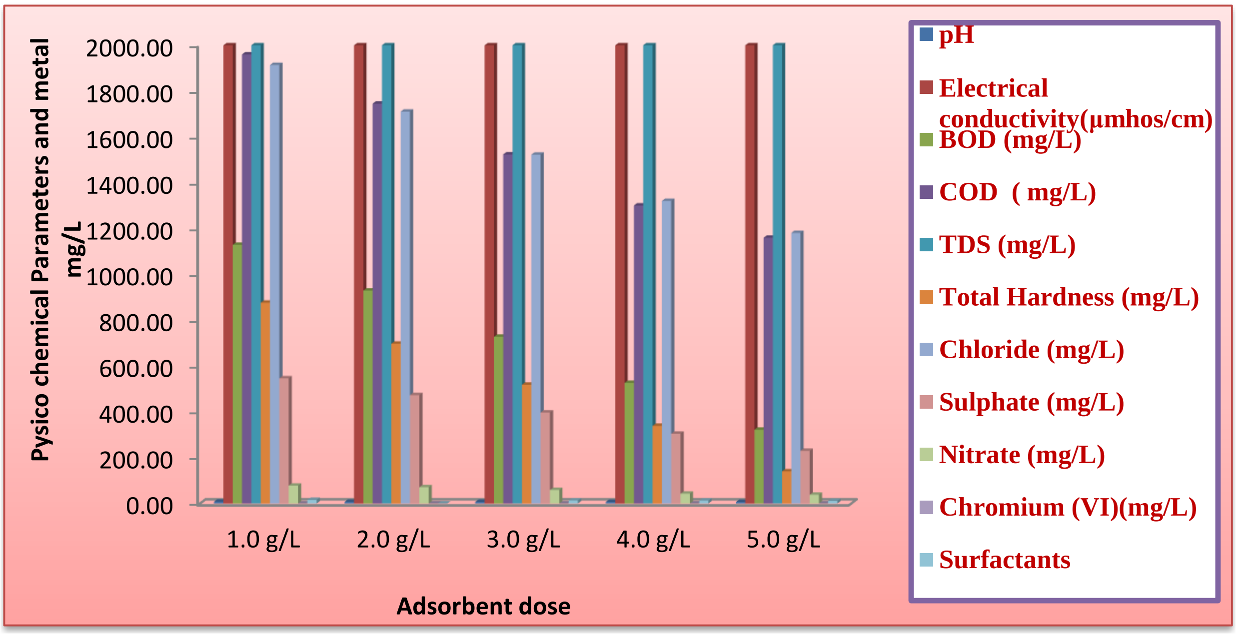

Fig 2: The physico-chemical characteristics of tannery effluents (before and after filtration processes) and addition of AC- Bacl2 adsorbent

The study illustrate that the sand stone filtration process could reduce certain pollution levels but not sufficient enough to consider the process alone using in effluent treatment. In the jar test experiments,adsorption as carried out with adsorbent dosages ranging 1.0 g to 5.0 g activated carbon metal chlorides, while other variables were constant. Removal of chromium ion increased with increasing adsorbent dosage. Five grams of activated carbon metal chlorides adsorbed almost all the chromium ions (70-80%) in the effluent, because large amount of activated carbon metal chlorides provides a larger amount of reaction sites for adsorption. Chromium removal with 1.0 g to 5.0 g activated carbon metal chlorides was significantly different from those of the other treatments. After adsorption with synthesized activated carbon metal chlorides the pH and turbidity reached acceptable values.

3. CONCLUSION

The chromium removal efficiency only was (70-80%) within one hour of batch adsorption with adsorbent of activated carbon metal chlorides where as other cations such as (45-56%) chlorides,(63-73%) Sulphate,(58-68%) nitrates ,(32-57%) surfactants was observed. In this study, increasing adsorption time did not provide any remarkable difference in chromium metal removals, as the reaction reached its equilibrium point within one hour. So 5.0 g of synthesized activated carbon metal chlorides have provided enough adsorption site to bind chromium and adsorption time did not affect the adsorption efficiency of activated carbon metal chlorides in the effluent. We observed the increase of pH after addition of 6.0 g of adsorbents probably caused by excess metal hydroxide remained in the effluent solution..The result showed that the maximum removal percentage of heavy metal like chromium and other physic chemical parameters in the tannery industrial waste water at an optimum adsorbent dosage of 1.0 g o 5.0 g ,contact time of 30-240 min and Ph of 3 o 7 were observed. The highest removal efficiencies for different parameters achieved were 41% (EC), 76% (BOD), 47%(COD) , 72% (TDS), 87% (total hardness), 45% (chlorides), 63% (sulphates), 58% (nitrates), 70%(Cr) , 32% (Surfactants) after adsorption was significantly changed ($p<0.05$) from the initial value of effluent was observed.

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