

Effectiveness of Crushed Egg Shell, Orange Peel and Charcoal to Minimize the Pollution Caused by Tannery Industry in Ranipet District Tamilnadu

Palaar river walaja Anaicut Dam, Beautiful view of nature

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Abstract: This research was conducted to study the effectiveness of Crushed egg shell (*Gallus gallus domesticus*) residue, orange peel (*Citrus sinensis*) and charcoal (*Mahogany*; *Swietenia mahagoni*) as the bio-adsorbents to minimize the pollution of Palaar River caused by tannery industry at Ranipet in Tamilnadu. Tannery industries discharged effluents containing huge pollutants. Crushed egg shell, orange peel and charcoal are available bio-adsorbents and are abundant in Bangladesh. These adsorbents are low cost for adsorption of organic and inorganic pollutants from water and wastewater. From the points of view of multipurpose utilization and environmental protection, utilization of Crushed egg shell, orange peel and charcoal were in important. Therefore, this study could help in converting these wastes into useful product by investigating its effectiveness for wastewater pollution minimization. Tannery wastes were treated with these three types of bio-adsorbents mentioned above. The results revealed that using of Crushed egg shell; orange peel and charcoal were very helpful to minimize the pollution of heavy metals. Among the analyzed heavy metals, the concentration of chromium (Cr) decreased the most by the organic adsorbents. The effectiveness of these organic residues can be ranked as: Crushed egg shell \geq orange peel \geq charcoal

Keywords: Palaar river, bio-adsorbent, charcoal, developing country, Crushed egg shell

I. INTRODUCTION

The environment is under increasing pressure from the direct discharge of industrial effluents and municipal wastewaters into soils and water. This has become a growing environmental problem. The water is being polluted with different types of industries especially tannery industry. Tannery industry is recognized as a serious environmental threat all over the world (Tariq et al., 2005). Huge amounts of tannery effluents are directly discharged to the river or to the nearby open lands. This effluent adversely affects the water quality, soil and ground water rendering them unsuitable for viable human use as well as the soil flora and fauna (Farooque et al., 1984). Tannery effluents contain toxic chemicals such as sulfide (S²⁻), chromium (Cr)-salts and other toxic trace metals (Thiagaragan, 1992). Tannery effluents are normally highly colored, foul smelling liquids containing both acidic and alkaline liquors (United Nations Environment Programme; UNEP 1994). The introduction of heavy metals in various forms in the environment can produce considerable modifications of the microbial communities and their activities (Aleem et al., 2003).

Tannery waste contains large quantities biological oxygen demand (BOD), chemical oxygen demand (COD), sodium sulphide (Na₂S) and suspended solids (SS; Vijayaraghavan and Murthy, 1997). Wastewater of tannery contains high organic matter, high BOD (210 - 4,300 mg L⁻¹), high COD (180 - 27,000 mg L⁻¹). The concentration of SS is 925 - 36,000 mg L⁻¹, Cr is 3 - 350 mg L⁻¹, S²⁻ is 1 - 500 mg L⁻¹, chloride (Cl⁻) is 1,500 - 28,000 mg L⁻¹, total phenolic (TF) compounds is 0.4 - 100 mg L⁻¹, ammonium (NH₄⁺) is 17 - 380 mg L⁻¹, Kjeldahl nitrogen (N) is 90 - 630 mg L⁻¹ fats and oils is 49 - 620 mg L⁻¹ and the pH range is 1 - 13 (Vlyssides and Israilides, 1997). Wastewater of tannery industry



also contains high concentration of heavy metals like iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), nickel (Ni), lead (Pb), mercury (Hg), Cr and etc. Many of these are severe toxic to plants and animal (Ullah and Islam, 1995).

Some heavy metals cannot be degraded and destroyed like Fe, Mn, Zn, Cu, Ni, Pb, cadmium (Cd), and Cr. At high concentrations, these elements are very toxic to soils, water, plants and even to animals. Various methods are applied to remove these heavy metals from wastewater to reduce the severity and its adverse effect on environment including human health. Besides the conventional methods, the bio-sorption and separation techniques are effectively used in industry for wastewater treatment (Datta et al., 2013).

The main features of bio-sorption are low cost, high efficiency, minimization of chemical and biological sludge, no additional nutrient requirement, and possibility of metal recovery (Kratochvil, 1998). Due to the presence of abundant chelating functional groups, all biological materials have greater affinity for metal ions (Volesky, 2007). Therefore, there is increasing research interest in using alternative low cost adsorbents.

Charcoal is known to adsorb a huge variety of substances e.g. paints, dyes and many different kinds of ions. Moreover, the amount of adsorption at normal pressure and temperature is high. This is because charcoal has an amazingly big surface area. Once activated, it gains the property of further large surface area. It is largely used because it is quite cheap. Activated charcoal is a great adsorbent because of its huge surface area. Activated carbon is usually made by more specialized processes that guarantee the final product will have a very large surface area (often >1,000 m² g⁻¹). Bamboo charcoal could be used for the removal of Cd²⁺ ions in water treatment. Batch adsorption experiments showed that adsorption of Cd²⁺ ions from aqueous solution by bamboo charcoal was very high and the equilibrium time is 6 h (Wang et al., 2010). Therefore, it will be a good trial to use charcoal available in Ranipet to purify the tannery wastewater for removal of toxic metals' from tannery wastes.

Orange is widely consumed fruit in Tamilnadu. Before eating, the peel is removed by hands or with a sharp knife from white membrane. Orange peels are also agro-industrial waste residues of the orange juice and soft drink industries (Namasivayam et al., 1996). Peels are used to remove a number of dyes such as direct blue-86 (El-Nemr et al., 2009), direct N-blue-106 (Khaled et al., 2009), direct yellow (Khaled et al., 2009), direct red-23 and direct red-80 (Arami et al., 2005), acid violet-17 (Sivaraj et al., 2001) and methyl orange, methylene blue, rhodamine-B, congo red, methyl violet and amido black 10B (Annadurai et al., 2002). Therefore, use of orange peels could be another trial to purify contaminated wastewater discharged from the tannery industries.

Tea is widely preferred drink in Tamilnadu. As a result, huge quantities of residues are produced throughout Tamilnadu including local city Ranipet. The use of this residue could be a better option to remove pollutants from the contaminated wastewater discharged from industries. Trace metals such as Zn, Cu, Ni, Pb, Cd, Hg and Cr are released to the environment which generates concern because of their potential toxicity. There are many conventional methods for removing these metals from wastewater e.g. chemical precipitation, ion exchange, membrane technologies and electrochemical treatment. But these processes are very expensive. Thus in recent years. There has been increasing interest to use low cost adsorbent such as banana peels, rice husks, coals and Crushed egg shells. These types of low cost wastes are easily available in Ranipet and can be used to save the environment from pollution. Palar river pollution caused by tannery effluents is very severe in Ranipet. Therefore, the objectives of this study were: (1) to determine the physical, chemical and biological characteristics of the effluent of some leather industry and (2) to observe the effectiveness of Crushed egg shell, orange peel and charcoal to reduce the concentration of pollutants before discharge to the river.

EXPERIMENTAL SECTION

Study Area: The tannery leather industry is situated at of Ranipet district. The effluent as collected from this industry site. **Preparation of Crushed egg shell:** The Crushed egg shell (*Gallus gallus domesticus*) residue was collected from the nearby tea stall of Bazaar, Ranipet on 30 December 2023. The residue was washed with tap water first and then with distilled water for several times until a colored component and other soluble dirtiness removed. After washing, the residues were filtered and were dried in an electric oven at 55°C for 48 hours and then air dried for another 24 hours. After that the



residues was grinded with the electric blender and were sieved (150-mesh size). The fine residues were preserved in airless container, so that they could not react with neighboring environment.

Preparation of Orange Peel: Oranges (*Citrus sinensis*) were collected from a local market Barobazar, Ranipet on 30 December 2023. Then the oranges were washed with tap water first and then with distilled water and air dried. After that, the peels were removed with clean hands and were sun dried for 4 days. The dried peels were grinded with the help of electric blender till fine size. The fine peels were sieved (150-mesh size) and then preserved in small clean plastic jar, so that the peels could not react with neighboring environment.

Preparation of Charcoal: Homemade charcoals were collected from, a Bazaar of Ranipet District on 1st week of January 2024. The charcoal was prepared by burning the dried young branch of Mehogony (*Mahogany*; *Swietenia mahagoni*). The charcoal was washed with tap water first and then with distilled water properly. After air drying, the charcoal was crushed in the particular size (150-mesh) with hammer in a clean sealed cloth bag. The particular size charcoal was preserved in airless container, so that charcoal could not react with neighboring environment.

Effluent Collected from Tannery Leather Industry: The effluent was collected from the source point of the leather industry. Plastic bottles were collected and shocked in 0.1 N HCl for overnight and then rinsed with distilled water about 3 to 4 times. Before sampling, the bottles were rinsed with sample water 2 or 3 times, so that the sample could represent the total characteristics of polluted water. After sampling, the bottles were tightened properly with sealed cap to avoid air bubbles. The samples were labeled properly showing the location name, date and time of sample collection and were preserved immediately in refrigerator at 4°C. The sampling time was between 4.00 pm - 4.30 pm on 9 May, 2017. The Tannery leather industry releases its polluted effluent directly into the Palaar river at around 4.00 pm every day.

Place of Experiment and Analysis: The experiment was set up in the Environmental Chemistry Laboratory, Department of Environmental Science and Technology, Ranipet

University of Science and Technology, Ranipet 7408, Bangladesh. The color, odor, electrical conductivity (EC), total dissolved solids (TDS), nitrate (NO_3^-) and phosphate (PO_4^{3-}) were determined in our Laboratory. The heavy metals Fe, Mn, Cu, Pb and Cr were determined by atomic absorption spectroscopy (AAS; Loeppert and Inskeep, 2001) in the Laboratory of Asia Arsenic Network, Ranipet 7400. This study was conducted during the period of January ,2024 - February 2024 .

Experimental Design: The volume of the sterilized plastic bottle was 500 mL. In each bottle, 250 mL effluent and 5.0 g bio-adsorbent of each (Crushed egg shell, orange peel and charcoal) were taken. There were 12 bottles [3 (control) + 3 (for 3 days) + 3 (for 6 days) + 3 (for 9 days) for each bio-adsorbent. Therefore, the total numbers of the bottles were $12 \times 3 = 36$ for 3 types of bio-adsorbent. All these bottles were placed carefully in the safe place and investigated for days' time period. The bottles were shaken carefully (by hand) and almost similarly for mixing up the adsorbents with effluents. **Statistical Analysis:** The experiment was arranged in a randomized blocks with three replications in the Laboratory. The data were subjected to statistical analysis of variance (ANOVA) with Student-Neuman-Keuls multiple-range test and the means were tested using uncan's Multiple Range est MR at % level of significance. The data were presented in Tables as means \pm standard error (SE) of three replicates.

Determination of NO_3^- and PO_4^{3-} : Nitrate was measure by developing the color with the help of Nitrate Reagent 1. Phosphate was measure by developing the color with the help of Phosphate Reagents 1 and Phosphate Reagents 2 (Water Testing Kit, Nice Chemicals Pvt. Ltd., Kochi-682024, Kerala, India). The color intensity was compared with the color chart presented in the box of water testing kit.

II. RESULTS AND DISCUSSION

Physico-Chemical Parameters

Color: At the initial stage, the color of the effluent was bottle green. But after application of treatments the effluent becomes clearer with time. At the end of the experiment, the solution was almost clear. This was most probably, due to the fact that the adsorbent may adsorb the chemical dyes and made the solution clear. This was only the result of physical appearance. Its needs to be determined with turbidity meter. Color is the vital parameter for most water users e.g.- in



domestic or industrial purpose everybody usually uses colorless water. Pure water has no color. The presence of humic acids, fulvic acids, metallic ions, suspended matter, phytoplankton and industrial effluents may cause color in natural water (Gupta et al., 2009). Determination of color can help in estimated costs related to discoloration of the water. Colored industrial waters may require color removal before discharge into watercourses (Jones, 1952).

Odor: Before treatment, the odor of the collected samples were high pungent. It was very difficult to take the breath at 0 day after treatment (DAT), but after 9 DAT it was improved as compared to odors of 0 DAT. The wastewater that was collected as discharged was pretty bad, that is, it was smelly. The intensity of the odor reduced substantially after the treatment was applied. We do not know the exact reason of the reduction of odor, but it was reduced substantially.

Electrical Conductivity (EC): On 0 DAT, the initial EC value was 10,070 $\mu\text{S cm}^{-1}$ (Table 1). After the application of the organic adsorbent, the EC values did not decrease much (Table 1). After using charcoal, the EC value decreased only by 4.87% at 3 DAT, 5.16 % at 6 DAT, and 6.36% at 9 DAT. Similar results were also found in the case of orange peel and Crushed egg shell (Table 1).

It was supposed to decrease the EC value after using the adsorbent, but we did not have so impressive result. Therefore, we need to accept this result and need to do further research. Conductivity shows significant correlation with the parameters of temperature, pH value, alkalinity, TH, Ca, TS, TDS, COD, Cl and Fe concentration of water (Bundela et al., 2012).

Total Dissolved Solid (TDS): It was observed that TDS concentration decreased after using Crushed egg shell and charcoal (Table 1). Charcoal decreased the TDS by 5.16% at 3 DAT, 12.32% at 6 DAT and 13.32% at 9 DAT. Similar results were found in the case of Crushed egg shells (Table 1). The reduction of TDS was most probably due to the fact that the organic adsorbent may adsorbed a number of metals from the solution and therefore, responsible for the reduction of TDS in the aqueous solution. In the case of orange peel, the TDS increased significantly (Table 1). In this case, the decomposition of orange peel may be occurred resulting in the dissolution of solids in the aqueous solution, which ultimately increased the TDS in the aqueous solution.

Hydrogen ion Concentration (pH): The initial pH of the collected sample was 7.86, indicating that the effluent was alkaline in character. It may be due to the fact that during the processing of the leather, some alkaline substances might be used. After introduction of Crushed egg shell and charcoal with the samples, the pH increased further (Table 2). The increase of pH was most probably due to the fact that the Crushed egg shell and charcoal might release such substances which may responsible for the increase of pH of the samples. The observed higher pH values suggested that carbon dioxide, carbonate-bicarbonate equilibrium was affected more due to change in physico-chemical condition (Karanth, 1987). After introduction of orange peel, the pH of the solution decreased as compared to the initial value. It is well known that the orange contain sufficient quantities of citric acid. Therefore, after introduction of orange peels some citric acid may be released into the solution and decreased the pH. This supposition needs to be verified with the experimental results and with scientific logics. As the pH of the effluent is high, therefore, there is highly possibility to remove the pollutants effectively. It was found that high pH

(≥ 8.0) was favorable for the adsorption and removal of Cd^{2+} ions. Higher initial Cd concentrations led to lower removal percentages but higher adsorption capacity. It is also found that the removal of Cd increased with the increase of adsorbent dose (Wang et al., 2010).

Nitrate (NO_3^-): The initial concentration of NO_3^- was 5.00 mg L⁻¹ (Table 2). After 3 DAT, the concentration did not change very much. However, after 6 DAT, the NO_3^- concentration was almost 0. It means the effectiveness of Crushed egg shell; orange peel and charcoal were almost similar in the case of NO_3^- removal. The other explanation might be that the NO_3^- concentration in the solution might be also disappeared due to denitrification in the solution. In this case, some microbial bacteria might be involved with disappearance.

Phosphate (PO_4^{3-}): At 0 DAT, the initial concentration of PO_4^{3-} was 1.00 mg L⁻¹ in effluent solution (Table 2). After 3 DATS, the concentration of PO_4^{3-} decreased almost 50% in the solution for all the treatments. After 6 DATS, the concentration PO_4^{3-} in the solution was almost 0. It means, the PO_4^{3-} could be removed by the organic bio-adsorbents within 6 DAT. This results need to be verified with appropriate experimental data. It was reported that, P could be



removed from aqueous solution by using activated carbon loaded with Fe (III) oxide (Shi et al., 2011). Municipal wastewaters may contain total phosphorous from 5 to 20 mg L⁻¹ of which 1 to 5 mg L⁻¹ is organic and the rest is in inorganic form. Considering the concentration, the phosphorus data were not so important for our current research, though we analyzed the samples.

Table 1: The Physical Properties Varied in the Adsorbent Treated Solution with Time

DAT	EC(μScm^{-1})				TDS(mgL^{-1})			
	Cont.	TR	OP	Char	Cont.	TR	OP	Char
0	10,070a			5,030a				
3	9,790a		9,790a	9,580a	4,770a	4,770a		4,470b
6	9,500a		9,500a	9,550a	4,411ab	9,500b		4,410b
9	9,430a		9,430a	9,430a	4,359b	9,430b		4,360b

DAT = Days after treatments; Cont. = Control means concentration of the parameters at the time of sample collection; Char. = Charcoal; OP = Orange peels; CES = Crushed egg shells; EC = Electrical conductivity; TDS = Total dissolved solids.

Table 2: The Chemical Properties of the Effluents Varied in the Adsorbent Treated Solution with Time

DAT	pH				NO ₃				PO ₄ (mg L)			
	Cont.	TR	OP	Char	Cont.	TR	OP	Char	Cont.	TR	OP	Char
0	7.86a				5.00a				1.00a			
3		8.23b	6.88c	8.52b	5.00a	5.00a	5.00a	5.00a	0.50b	0.50b	0.50b	0.50b
6		8.25b	6.20c	8.55b	0.00b	0.00b	0.00b	0.00b	0.00b	0.00b	0.00b	0.00b
9		8.27b	5.90c	8.55b	0.00b	0.00b	0.00b	0.00b	0.00b	0.00b	0.00b	0.00b

DAT= Days after treatments; Cont. = Control means concentration of elements at the time of sample collection; Char. = Charcoal; OP = Orange peels; CES = Crushed egg shells.

Table 3: The Concentration of heavy Metals in the Effluents Varied with Time in the Adsorbent Treated Solution

DA T	Fe(mgL^{-1})				Mn(mgL^{-1})				Cu(mgL^{-1})				Cr(mgL^{-1})			
	Cont.	TR	OP	Char	Cont.	TR	OP	Char	Con	TR	OP	Char	Con	TR	OP	Char
0	5.00d				0.57a				0.02a				27.7d			
3	3.00a	3.00a	3.00a	3.00a	0.53a	0.53a	0.54a	0.54a	0.22a	0.22a	0.29a	0.29a	7.39a	8.09a	11.28a	11.28a
6	1.00b	1.00b	1.00b	1.00b	0.53a	0.52a	0.52a	0.52a	0.19a	0.17a	0.23a	0.23a	6.39b	8.39a	8.92b	8.92b
9	0.30c	0.30c	0.30c	0.30c	0.52a	0.53a	0.52a	0.52a	0.17ab	0.19a	0.19a	0.19a	5.36ab	6.36b	6.71c	6.71c



DAT= Days after treatments; Cont. = Control means concentration of elements at the time of sample collection; Char. = Charcoal; OP = Orange peels; CES = Crushed egg shells

Removal of Heavy Metal

Iron (Fe): The collected effluent contained 5.0 mg L⁻¹ Fe (Table 3). After 3 DAT, Crushed egg shell, orange peel and charcoal decreased about 60% concentration of Fe in the solution. Again, after 6 DAT, the concentration decreased almost 80% and after 9 DAT the concentration decreased by 94% with the treatments (Table 3). The United Nations Food and Agriculture Organization recommended level of iron in irrigation waters is 5 mg L⁻¹. The United States Environmental Protection Agency (US EPA) secondary drinking water standard maximum contamination level (MCL) is 0.30 mg L⁻¹ (US EPA, 1994). Considering the Fe concentration in the aqueous solution, the Fe concentration in the wastewater was not harmful for agricultural purposes. In this research, the only significant information was that Fe concentration in wastewater could be reduced by using Crushed egg shell, orange peel and charcoal. Bio-sorption is an alternative technology to remove heavy metals from the dilute aqueous solutions using inactive and dead biomasses to bind and accumulate these pollutants by different mechanisms such as physical adsorption, complexation, ion exchange, and surface micro-precipitation (Aksu et al., 1991).

Manganese (Mn): At 0 DAT, the concentration of Mn was 0.57 mg L⁻¹ in the effluents (Table 3). The Mn concentration did not vary significantly up to 9 DAT with the treatments. It means, Mn could not be removed with the Crushed egg shell, orange peel and charcoal to clean up wastewater used as bio- adsorbents. Recently we presented our research in an international conference (Shaibur et al., 2018).

Copper (Cu): The effluent contained 0.02 mg L⁻¹ Cu at the time of sample collection (Table 3). Surprisingly, the concentration of Cu increased significantly in all the treatments of Crushed egg shell, orange peel and charcoal. We do not know the exact reason why such result did occur but it was our result. The possible cause may be due to the fact that all the used bio- adsorbents might contain sufficient content of Cu in them which is easily soluble in water. Therefore, when the bio-adsorbent came in contact with the alkaline water, it might release Cu in the solution, resulting in increased Cu concentration in the solution. Copper is considered as an essential trace element for plants and animals. Some compounds of Cu are toxic by ingestion or inhalation. The United Nations Food and Agriculture Organization recommended level for copper in irrigation water is 200 mg L⁻¹ (US EPA, 1994).

Lead (Pb): After collection of the samples, Pd concentration was measured at 0 DAT. Fortunately, we could not determine the Pb in the samples (Table 3). It means, the Pb concentration was below detection limit. This was most probably, there was no substances used for the processing of leather in the tannery leather industry. Lead in water supply is come from industrial, smelter discharge and mine or from the dissolution of plumbing and plumbing fixtures. It is too toxic by ingestion and is cumulative poison (Ashbolt et al., 2001). The use of fruit peel in adsorption of heavy metals has extensively been investigated including banana and orange peel (Mandina et al., 2013). The advantages of using fruit peel as the adsorption material is that they are readily available and less costly (Thirumavalavan et al., 2010). Research studies on banana peel shows potential to adsorb ions including Zn, Cu, Ni and Pd (Annadurai et al., 2002).

Chromium(Cr): The initial concentration of Cr was 27.65 mg L⁻¹ in the effluents at 0 DAT (Table 3). The concentration decreased more than 73-81% by Crushed egg shell; almost 68-76 % by orange peel and 60-75% by charcoal (Table 3). Specifically, Crushed egg shell decreased the concentration of Cr by 73.27% at 3 DAT, 76.88% at 6 DAT and 80.81% at 9 DAT.

Similarly, the values were 67.92%, 68.17% and 75.80% for orange peel; by 59.20%, 67.73% and 75.73%, respectively. Among the used bio-adsorbents, Crushed egg shell showed the highest effectiveness. The Cr removal capacity can be ranked as Crushed egg shell \geq orange peel \geq charcoal.

Banana peel contains cellulose, hemicelluloses, chlorophyll pigments and pectin substances. These chemical substances contain galacturonic acid, arabinose, galactose, and rhamnose. Galacturonic acids help the pectin to bind the metal ions strongly because of the carboxyl group of the sugar (Thirumavalavan et al., 2010). Cellulose also allows heavy metals to bind (Thirumavalavan et al., 2010). Additionally, banana peel contains amine, hydroxyl and carboxylic groups



(Thirumavalavan et al., 2010). These structural groups of peels may responsible to bind the toxic metals and may remove them from tannery wastewater. We do not know the structure of Crushed egg shells. We suspect that the surfaces of Crushed egg shells are irregular and highly porous. The pores of the surface may exhibit a micro-rough texture with crater-like pores, which may promote the adsorption process.

The wood carbons consist of slit like voids and macropores. It is used in certain metallurgical processes and as a filter to remove organic compounds and other toxic chemicals from water and air (Baker, 1985). There are various reports on the use of charcoal and activated charcoals in heavy metal removal (Hamidi et al., 2005). A batch experiment showed that oak wood charcoal adsorbs 30.10 mg g⁻¹ Cr at pH 2 (Pehlivan and Kahraman, 2011). The use of charcoal in removal of Zn, Ni, Pb and Cd heavy metals was also observed to have efficiencies of 80% (Hamidi et al., 2005).

Generally, heavy metals are adsorbed as a result of physico-chemical interactions. During the process a complex is formed between metal ions and functional groups cell surface. The functional groups of Crushed egg shell which are responsible for Cr adsorption need to be studied. Chromium is known as non-essential for plants, but an essential trace element for animals with very low concentration. Hexavalent compounds have been shown to be carcinogenic by inhalation and are corrosive to tissue. The United Nations Food and Agriculture Organization recommended level for irrigation water is 0.10 µg L⁻¹. The USEPA primary drinking water standard MCL is 0.10 mg L⁻¹ (USEPA, 1994).

III. CONCLUSION AND RECOMMENDATIONS

It can be concluded that the effluent discharged from the tanneries to the river or water bodies may contaminate the water bodies. Large amounts of effluents are discharged without any treatment, with high pH, BOD, TSS, TDS, NO₃⁻, PO₃⁻ and very low DO as well as high 4 levels of some heavy metals all exceeding the values of the standard EPA guidelines. The presence of high levels of Cr and other heavy metals in industrial wastewater poses serious problems when discharged into water bodies. The Palar River receives highly polluted wastewater from the tannery industry. In the discarded effluents, the concentration of Fe was 5 mg L⁻¹, Mn was 0.57 mg L⁻¹, Cu was 0.02 mg L⁻¹, Pd was nil and Cr was 27.65 mg L⁻¹. Among the analyzed heavy metals, the concentration of Cr was unexpectedly very high. Therefore, removal of Cr from wastewaters was obligatory to prevent the water pollution. This has led to the need for removal of Cr from wastewaters before discharge. Using Crushed egg shell, orange peel and charcoal as bio-adsorbent for Cr and other heavy metals removal is a potential alternative to existing methods for their recovery from industrial wastewaters. Our result showed that biological reduction of Cr from wastewater is a good technology for low cost bioremediation especially in developing countries like Tamilnadu where discharge of industrial wastes poses environmental threats. The study also provides a foundation for the implementation of indigenous technology for rapid and effective removal of Cr and other heavy metals from untreated wastewater. The effectiveness of the bio-adsorbent can be ranked as Crushed egg shell ≥ orange peel ≥ charcoal. We suggested the following recommendations:

- a), Crushed egg shell, orange peel and charcoal can easily be used in industry as a bio-adsorbent.
- b), Functional groups of Crushed egg shell, orange peel and charcoal need to be characterized for determining effectiveness of those bio-adsorbents individually.
- c), Since tannery industries wastewater contain a mixture of heavy metals and other organic and inorganic pollutants, further study should be conducted on the performance of tea waste, orange peel and charcoal in removing of organic and other inorganic pollutants.
- d), The tannery industry has no ETP and therefore the Crushed egg shell, orange peel and charcoal could be applied to minimize the pollution as a local technology.

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