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Tannery Wastewater Treatment Using Coconut Shell for Small-Scale Irrigation Scheme

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Abstract: *The research was carried out to analyses some selected physical and chemical properties of Industrial effluent of tannery industry in Maiduguri. Coconut shell powder was applied in three varied doses of 5, 10, and 15 mg to one litre of industrial effluent designated as sample TC1, TC2 and TC3 respectively. Each sample has three replicate. The coconut shell was cleaned using tap water to eradicate possible strange material present in it (dirt and sands). Washed material was sun dried for 2 to 5 hrs and then crushed with mortar and pestle to reduce the size of the shell. Finally, the shell was oven dried for 40mins and at last received the coconut shell activated carbon. 20 litres of industrial effluent was collected in one jerry can and nine litres were measured in nine different plastic bottles designated as TC1R1, TC1R2, TC1R3 TC2R1, TC2R2, TC3R3, TC3R1, TC3R2, TC3R3 and another designated as TC4R1, TC4R2, TC4R3 which served as the control sample respectively. The dosages 5,10 and 15 mg of activated coconut shell was added to effluent in duplicate respectively, and allowed to stay for 24 hrs then taken to NAFDAC laboratory for analysis, the parameters analysed were total dissolved solid, electrical conductivity, pH value, calcium content, magnesium content and nitrate. The result revealed that there is significances reduction in values of those parameters in all the treatment.*

Key words: *Tannery: Effluent and Coconut shell*

1.0 INTRODUCTION

1.2 Background of the Study

Most toxic chemicals in the environment are discharged by industries into water, air and soil. Once they get involved in biological process, it becomes difficult to eliminate them from the environment and they disturb various biochemical processes, leading to undesirable results. Numerous potentially mutagenic chemicals have been studied because they can cause mutagenic, damaging and inheritable changes in the genetic material (Khanna and Sharma, 2013, p. 105). Wastewaters discharged from tanning industries contains high level of BOD, COD, electrical conductivity and heavy metals especially Cr above permissible limit as recommended by various regulatory agencies making it potentially toxic (Lal, 2009). Usually tanning industries discharge their wastewater on land and into nearby rivers and indirectly is being used for irrigation of crops and vegetables. This practice has ultimately led to movement of potentially toxic metals from water to plant system and ultimately to human beings Sinha *et al*., (2008). It is well known that Cr (VI) is a potent carcinogen to humans and animals as it enters cells via surface transport system and gets reduced to Cr (III) inducing genotoxicity Matsumoto *et al*., (2006). Thus, Cr loaded effluent used for irrigation disrupts several physiological and cytological processes in cells. Chidambaram *et al*., (2009) leading to reduced root growth, biomass, seed germination, early seedling development Irfan and Akinici (2010), and induces chlorosis, photosynthetic impairment and finally leading to plant death. The current pattern of industrial activity alters the natural flow of materials and introduces novel chemicals into the environment. The released organic compounds and heavy metals are one of the key factors that exert negative influences on man and environment, causing toxicity to plants and other forms of biotics and abiotics that are continually exposed to potentially toxic heavy metals Puthur, (2010). In tanning industries, the raw hide undergoes a series of chemical treatments before it turns into flattening leather. This includes soaking, liming, dehairing, deliming, bating, degreasing and pickling. For all these steps the chemicals like sodium sulphide, ammonium chloride, sodium sulphite, hydrogen peroxide, formate, sodium bicarbonate, chromate and chloride are used which are quite toxic. Thus due to these multifarious operations with an array of chemicals, the leather processing industry is one of the worst offenders of the environment (Murugan and Sohaibani, 2010). These chemical substances produce varying anomalies in mitosis, germination and growth of plants. It could also give rise to allergy at early ages, respiratory disorders, coronary problems and even cancer in middle ages Morales (2008).

1.3 Tanning Process

Leather tanning is the process of converting raw hides or skins into leather. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent decaying, make them resistant to wetting (Verma, Pramod, Ramteke and Kumar, 2008). Tanning involves a complex combination of mechanical and chemical processes. Central to the process is the tanning operation itself in which organic or inorganic materials become chemically bound to the protein structure of the hide and preserve it from deterioration. The substances generally used to accomplish the tanning process are chromium or extracts from bark of trees, such as chestnut. These tanning agents give rise to the two predominant types of tanning operations modern chrome and traditional vegetable tanning processes (Federal Ministry of Environment, 2012).

1.4 Tannery Waste Waters

Tanneries generate waste waters that are typically high in organic and inorganic pollutants. Since tanneries employ a sequence of batch processes, and use a wide range of raw materials, their effluent is complex in nature, with variations in characteristics from time to time, process to process and tannery to tannery (IPPC, 2013). Waste water from tannery industry is considered as a serious environmental threat throughout the world (Gupta and Sinha, 2007). The tannery industries discharge large quantities of common salt during the process of tanning and deposition of this salt into the soil takes place when the water comes in contact with the soil. Besides chlorides, toxic substances like chromium, sodium sulphide, sodium carbonate and ammonium sulphate are present in the discharged effluent which manifolds the soil pollution (Rajan and Arias, 2007). Pre-tanning processes contribute 80-90 percent of the toxic pollution in the industry and generates noxious gases such as hydrogen sulphide, as well as solid wastes and chrome sludge (Thanikaivelan, Vaidya, and Desai, 2004).

1.5 Effect of Tannery waste water on the components of the biosphere

Environmental concerns in a tannery include the prevention and control of emissions to water, air, and soil. A range of process chemicals is used, some of which may require special treatment in the effluent. The environmental effects that have to be taken into account in any tannery comprise not merely the load and concentration of the classic pollutants, but also the use of certain chemicals, e.g., biocides, surfactants, and organic solvents (IPPC, 2013). Tannery industry is a primary polluter of the environment and has a strong potential to cause soil, water pollution (with its high oxygen demand, discolouration and toxic chemical constituents (Song, as cited in Tadesseand Guya, 2017)), plants, vegetables, terrestrial and atmospheric systems owing to the discharge of untreated effluent.

1.6 Effect of tannery waste water on soil

Soil pollution by metals is essentially different from air or water pollution because the persistence of heavy metals in soil is reportedly much longer than in other compartments of the biosphere. Removal of heavy metals from polluted soil is difficult. Once deposited on the soil certain metals such as lead and chromium may be virtually permanent (Okeyode and Moshood, 2010). Although heavy metals like iron, molybdenum, manganese, zinc, copper, magnesium, copper, selenium and nickel play major roles in the growth and development of plants, but may be toxic beyond certain level (Edday, Odoemelan andMbaba, 2006).The most common heavy metals found in the soil are cadmium, chromium, copper, mercury, lead and zinc (Marques *et al.,* 2008). Moreover, using sodium chloride as raw material in tanneries releases a high concentration of chloride and nitrate (Babyshakila, 2009) as the end product of oxidation of nitrogen whereas sodium carbonate, sodium bicarbonate, sodium chloride and calcium chloride in tanning causes the alkalization of the soil resulting to increase in pH (Mondal, Saxena, and Sinha, 2005).

1.7 Effect of Tannery waste water on plant growth

Repeated metal exposure of plants affects its physiological processes such as photosynthesis, water relations and mineral nutrition (Patton, Dauble and Mckinstry, 2007). The impact of toxicity was evident as visible symptoms of chlorosis, yellowing and immature fall of leaves, poor growth and retarded flower, fruit and green yields. Metabolic alterations by metal exposure have also been described in plants either by direct effect on enzymes or other metabolites. This was possibly attributed to the imbalance of nutrients and nutritional disorders in the plants due to metal interactions with plant nutrients

(Chunillal, Kindness and Jonnaladda, 2005). The effluent is an inevitable consequence of industrial process. In arid and semi-arid regions of the country, where shortage of water becomes limiting factor, the effluent is being used for irrigational purposes by the farmers in agriculture and agro-forestry practices. Since the production of wastewater is a continuous process, it can cater for substantial irrigation requirements. This alternative use of wastewater will not only prevent the waste from becoming an environment hazard but also will serve as a potential source of fertilizer if used rationally and at appropriate concentration (Saxena and Srivastava, 2002). Therefore, there is need, for the current study, to evaluate the effect of company treatment on biotoxicity of tannery waste water using coconut shell.

2.0 Materials Methods

The materials used for this research work are the cocanut shell obtained from a local mill area and tanning wastewater obtained from a tanning area in Maiduguri. The experimental work was conducted in the Ramat polytechnic Maiduguri in AE laboratory. Following are equipment/tools used for the practical's.

1. Blender
2. Containers
3. Desiccated
4. Digital weighing balance
5. Distilled water
6. Filter paper
7. Glass cups
8. Measuring cans
9. Measuring cylinder
10. Oven
11. Pestle and mortar
12. Plastic Bottle
13. Coconut shell powder
14. Sensitive Balance
15. Sieve size 425
16. Stop watch
17. Tannery wastewater

2.1 Characterization of the adsorbents

The characterization of coconut shell powder was carried out by determining the following physical and chemical parameters:

2.2 Moisture content

The moisture content of the adsorbents was determined by weighing 10g of coconut shell into

cans. This was placed in an oven and heated for 5hour at constant temperature of 105°C.The sample was then removed and put rapidly into desiccators in order to prevent more moisture uptake from atmosphere. The sample was re-weighed; the difference in the mass constitutes the amount of moisture content=w2-w3/w2-w1

Where:

W1= Weight of can

W2= Initial weight of can with sample

W3= Final weight of can with sample

2.3 Adsorbent pH

The determination of the adsorbent pH was carried out by weighing 1g of coconut shell, then boil
in a beaker containing 100 cm3 of distilled water for 5minutes, the solution was diluted to 200
cm3 with distilled water and cooled at room temperature, the pH of each was measured using
a pH meter (model ATPH-6).

2.4 Bulk density

The bulk density of the adsorbent was determined using archimenpdes's principle by weighing at 10 cm^3 measuring cylinder before and after filling with the adsorbent. The measuring cylinder was then dried and the adsorbent was then packed inside the measuring cylinder, leveled and weighed. The weight of the sample packed in a measuring cylinder was determined from the difference in weight of the filled and empty measuring cylinder. The volume of water in the container was determined by taking the difference in weight of the empty and water filled measuring cylinder. The bulk density was then determined using Equation 3.3

$$\text{bulk density} = \frac{w2-w1}{v} \qquad \text{Equation 3.3}$$

Where:

W1 = Weight of empty measuring cylinder
W2 = Weight of cylinder filled with sample
V = Volume of cylinder

2.5 Preparation of the Adsorbent

Homogeneous mixture of coconut shell was thoroughly washed with distilled water to clean dirt and mud and heated to the temperature of 104°C for 3 hours. The coconut shell was grinded into powder using pestle and mortal and sieves using Steve size N. 425μ.

2.6 Batch experiment

Coconut shell was obtained from a small local milling area in Zabarmari ward Jere local government and the tannery wastewater was collected from tannery industry Lawan Bukar and experiment was conducted in Agricultural Engineering laboratory at University Maiduguri Borno state. The experiment helps us to investigate the adsorption capacities of coconut shell powder on removal of chromium (Cr) from tannery wastewater. The experiment was conducted for different process like adsorbents dosage of 5, 10, 15g, and 20g contact time of 30, 60, 90, and 120min, blender speed of 650 and 950 rpm. Tannery industry wastewater was collected 3 glass cups capacity and was put on the blender for different adsorbent dosage, contact time and different speeds. The treated samples with various processes was filtered and the settled particles removed. The clear samples after settlement (24 hours) was further tested by a Digital spectrophotometer to find out the reduction in concentrations of chromium (Cr) in the tannery wastewater.

The adsorption removal percentage was calculated by using Equation 3.4

$$\text{Percentage Removal} = [(Co-Ct)/Co \times 100] \qquad \text{Equation 3.4}$$

Where:

Co= Initial concentration; Ct= Concentration after adsorption by adsorbent.

2.7 Spectrophotometer test on Chromium

The test was conducted by NAFDAC in Maiduguri using universal sample holder, following procedures below;

1. Press and hold ON button until spectrophotometer turns on
2. Scroll to and select PROGRAMMED TESTS from menu.
3. Scroll to and select ALL TESTS (or another sequence containing 22 chromium)
4. Scroll to and select 22 chromium from menu.
5. Rinse a clean tube (0290) with sample water. Fill to 10mL line with sample.
6. Insert tube into chamber, close lid and select SCAN BLACK.
7. Remove tube from Spector. USE the 0.1g spoon (0699) to add one measure of ×Chromium
Reagent Powder (V-6276). Cap and shake until powder dissolves. Wait 3 minutes for full color development.
8. During waiting period, fold a piece of filter paper (0465) in half then half again to form a cone. Push corners together to open end, and insert into funnel (0459).
9. At the end of 3 minutes waiting period, filter sample into a clean tube. Mix. Insert tube chamber, close lid and select SCAN SAMPLE. Record result.
10. Press OFF button to turn spectrophotometer off or press EXIT button to exit to previous menu or make another menu selection.

2.8. Data analysis

The chemical concentration of the tannery wastewater samples was analyzed using excess spreadsheet package.

3.0 Result and Discussion

The results on the experimented cocanut shell on the treatment of the tannery was water for irrigation purposed was presented below.

Table 1: Characterization of the Effluent

Parameters	Concentration	FAO Standard
Ca	1.92	40.1
Mg	1.89	24.3
Na	0.87	23
Cr	0.93	0.05
Tds	669	500
Ec	31.0	26.4
Temp	30.7	26.2
pH	6.95	6.5 – 9.2

The Characterization of the Effluent shows that all the parameters were within the FAO standard of Irrigation water quality except electric conductivity, temperature and toxic dissolve solid which were above the standard limit as shown in the table 1 above.

Table 2: Mean Concentrations of Waste Quality parameters

Treatment	PH	TDS	EC	Temp	Ca	Cr	Mg	Na
T5	6.4 [a]	872 [a]	4764 [a]	27.367[a]	1.36[b]	18.78 [a]	1.4 [b]	0.2467 [b]
T10	6.24 [a]	883 [a]	4764 [a]	27.467 [a]	1.35[b]	0.8325 [b]	1.28 [b]	0.1967 [b]
T15	6.57 [a]	872 [a]	4764 [a]	26.367[b]	1.38[ab]	0.7367 [b]	1.34 [b]	0.34 [ab]
TC	6.49 [a]	882 [a]	4764 [a]	26.875[ab]	1.605[a]	0.6067 [b]	1.865[a]	0.53 [a]
FAO	6.5-9.2	500	99	26.2	40.1	0.05	24.3	23

Table 2 shows the result of concentration of the following parameters, Total dissolve solid, Electric Conductivity, Temperature, pH, Calcium, Magnesium, Sodium and chromium in the treatment. The concentration of total dissolve solid decreases with increased in dosage of the absorbent from T5 to T10, but generally has increased when compared with the control TC. However, the value does not fall to the FAO standard of irrigation water quality. The concentration of electric conductivity neither increases nor decrease compared to the control and finally it does not fall within the FAO standard of irrigation water quality. The concentration of temperature decreases with increased in dosage of the absorbent from T5 to T10 and then decreased in T15 which has the highest absorbent but, generally has increased when compared with the control TC.

However, the values are above the FAO standard of irrigation water quality, the concentration of pH decreases with increased in dosage of the absorbent from T5 to T10 and increased in T15, but generally has increased when compared with the control TC. However, the values fall within FAO standard of irrigation water quality. The concentration of Calcium decreases with increased of the absorbent from T5 to T10 and increased in T15, but generally has decreased when compared to the control TC. However, the values fall within FAO standard of irrigation water quality.

The concentration of Magnesium decreases with increased of the absorbent from T5 to T10 and increased in T15, but generally has decreased when compared with the control TC. However, the values fall within FAO standard of irrigation water quality. concentration of sodium decreases with increased of the absorbent from T5 to T10 and then increased in T15 which has the highest absorbent but generally has decreased when compared with the control TC. However, the value falls within FAO standard of irrigation water quality. concentration of chromium decreases with increased of the absorbent from T5 to T10 and then decreased in T15 which has the highest absorbent but generally has increased when compared with the control TC. However, the value does not fall within FAO standard of irrigation water quality.

Table: 3 Correlations Matrix Among the Parameters

	PH	TDS	Temp	Ca	Cr	Mg	Na
PH	1						
TDS	-0.5272	1					
Temp	-0.9101	0.37194	1				
Ca	0.37024	0.49308	-0.2604	1			
Cr	-0.1245	-0.5767	0.46282	-0.3661	1		
Mg	0.38563	0.389541	-0.2014	0.982483	-0.18737	1	

As illustrated from table 3, the correlation in the table above shows there is relationship between Ca to Ca and Ec to Ca and EC to Ec and there is relationship Mg to Mg which is 1 and there is relationship between cr to Mg and cr to cr the result shows there is relationship between Na to Mg, cr and Na and there is relationship between pH to Mg, NO3, Na and pH there is relationship between TDS to Ca, EC and TDS and there is relationship between TEMP to TDS and TEMP respectively. And there is no relationship between the remaining parameter that has negative values in the table 3 above.

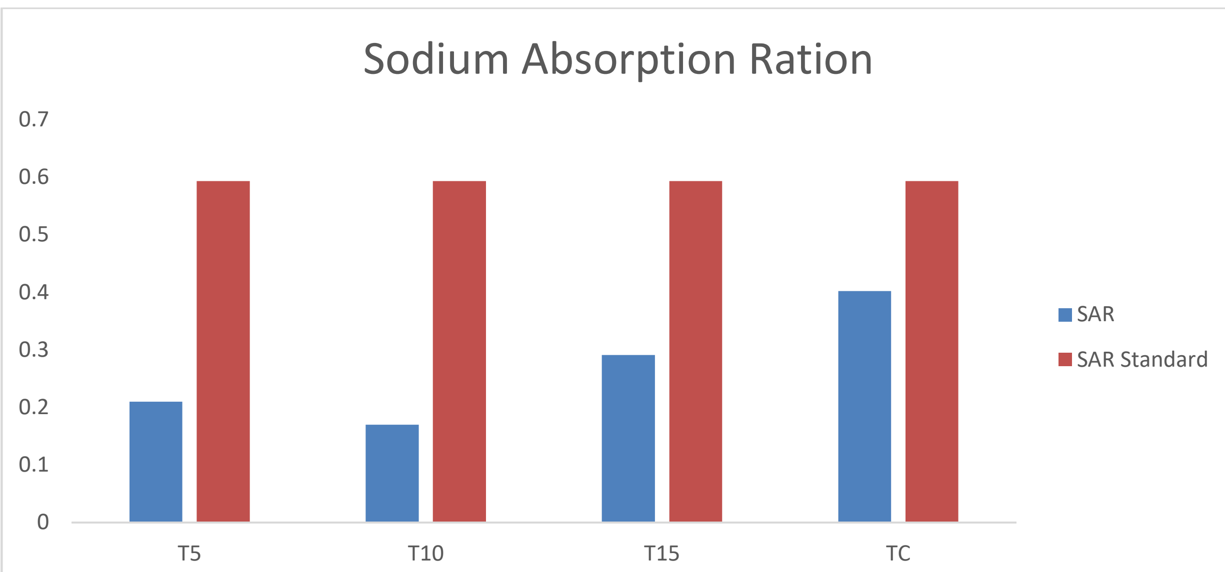

Figure: 1 Shows the Comparison between Calculated and Standard Value Sodium Absorption Ratio

The Characterization of the effluent shows that all the treatments experimented were within Sodium absorption ratio (SAR) standard of irrigation water quality.

3.0 CONCLUSION AND RECOMMENDATION

3.1 Conclusion

In the present study, experiments have been conducted forth removal of Cr (VI) in tannery industrial wastewater using coconut shell silica powder as an adsorbent. Took now the ability of coconut shell silica powder for removing Cr(VI) in the tannery industrial wastewater, the experiments were conducted with varying adsorbent dosage, contact time and pH against the initial concentration of 292mg/L. There salt showed that the maximum percentage removal of Cr(VI) in the tannery industrial wastewater at an optimum adsorbent dosage of 15 g, contact time of 120 min., pH of 4 respectively, using coconut shell silica powder was 88.3%. The experimental data on removal of Cr(VI) from tannery industry wastewater is validated with the Cr(VI) in an aqueous solution of same initial concentration of tannery industry waster. Also, the obtained maximum removal percentage of Cr (VI) in a tannery industry wastewater using coconut shell silica powder with an optimum process parameters were verified with the other physic-chemical parameters, COD, BOD, and SO_4^{2-} in a tannery industry wastewater. This study concluded that the experimental investigation done for this study may be reproduced for removing Cr (VI) from tannery wastewater or from any chromium based water and industrial wastewater.

3.2 Recommendation

It is therefore recommended that

1. Environmental managers implement and enforce laws to further subject industrial influence toxicity evaluation, hence ensuring complains to permissible limit before they are finally discharge.
2. The ministry of agricultural and rural development should carry out sensitization on the use of coconut shell further for treatment of tannery waste water.
3. That further researcher should have carried out to compare the results of coconut shell to another agricultural waste such as bagasse (sugarcane), and banana peels.

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