

**INTERNATIONAL JOURNAL OF SCIENCE FOR GLOBAL SUSTAINABILITY****Extraction of Heavy Metal in Tannery Effluent Using Abundant Agricultural Wastes**

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ABSTRACT

Removal of chromium from tannery effluent was conducted successfully using untreated noncarbonated rice husk biomass, maximum removal was observed at pH 4, indicating that agricultural wastes could be economically used in purification of tannery effluent, adsorbent dosage has no significant impact on the removal of chromium from the solution since there was full adsorption in some instances and partial in others. Furthermore, natural pH tends to fluctuate between the range of 2-1.6, indicating that there is need for a naturally available base and a little knowledge that can be used to adjust pH level before addition of the untreated rice husk.

Keywords: Extraction, heavy metal, tannery effluents, pH, untreated rice husk.

1.0 INTRODUCTION

Pollution is the introduction of contaminants into the natural environment that cause adverse change. It can take the form of chemical substance or energy, such as noise, heat or light pollutants, the components of pollution, can be either foreign substance/energies or naturally occurring contaminants. It is often classed as point source or non-point source pollution. In 2015, pollution killed 9 million people in the world major forms of pollution include: Air pollution, light pollution, littering, noise pollution, plastic pollution, soil pollution, radioactive contamination, thermal pollution, visual pollution and water pollution. (Merriam- Webster.com 2010).

Water pollution occurs in water bodies including lake, rivers, oceans, aquifers and ground when contaminants are introduced into the natural environment. For example, releasing inadequately treated waste water into natural water bodies can lead to degradation of aquatic ecosystem. It is also one of the leading worldwide causes of death and disease as it may contain many substances such as organic matter, inorganic matter as well as heavy metal (Harland *et al.*, 2005).

Tanning industry use different dyeing materials mainly made up of transition elements and are

referred to as heavy metals, which run into rivers thereby polluting the water bodies. This polluted water is used for agricultural and domestic purposes and as such there is the need to assess the level of heavy metals in it as they are toxic to their users. Trace quantities of heavy metals, such as nickel, manganese, chromium, cadmium, zinc, copper, and iron find their way into water. Some of these metals in very small concentrations are necessary for the growth of biological life, but harmful in higher concentration (Sirius, 2008).

1.1.1 Zinc

Zinc is a trace element that is essential for human health. It is important for the physiological functions of living tissue and regulates much biochemical process; however too much zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia (Oyoro *et al.*, 2007).

1.1.2 Copper

Copper does essential work in animal metabolism. But the excessive ingestion of copper brings about pervious toxicological concerns, such as vomiting, cramps, convulsions or even death. (Pauli *et al.*, 2006).

1.1.3 Nickel Exceeding

Nickel exceeding its critical level may bring about lung and kidney problems aside from gastro intestinal distress, pulmonary fibrosis and skin dermatitis. (Borba et al., 2006)

1.1.4 Mercury

Mercury is a neurotoxin that can cause damage to the central nervous system. High concentrations of mercury cause impairment of pulmonary and kidney function. Chest pain and dyspnoea. (Namasivayam and Kidivelv, 2000).

1.1.5 Lead

Lead can cause central nervous system damage, kidney, liver, reproductive system, basis cellular processes and brain functions. The toxic symptoms are anemia, insomnia, headache, dizziness, irritability, weakness of muscles hallucination and renal damages. (Naseem and Tahir, 2001).

1.1.6 Chromium

Chromium exists in the aquatic environment mainly in two states: Cr (III) and Cr (VI). In general, Cr (VI) is more toxic than Cr (III). Cr (VI) effects human physiology accumulates in food chain and causes severe health problems ranging from simple skin irritation to lung carcinoma. (Khezami and Capart, 2005).

1.2.0 Heavy Metal Wastewater Treatment Techniques

1.2.1 Chemical Precipitation

Chemical precipitation is effective and by far the most widely used process in industry, because of its relative simplicity and inexpensive to operate. In precipitation process, chemicals react with heavy metal ions to form insoluble precipitates. The forming precipitate can be separated from the water by sedimentation or filtration. And the treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide and sulfide precipitation. (Ku and Lung, 2001).

1.2.1.1 Hydroxide Precipitation

The most widely used chemical precipitation technique is hydroxide precipitation due to its relative simplicity, low cost and ease of pH control. (Heisman et al., 2006)

Solubility of various metal hydroxides is minimized in the pH range of 8.0 -11.0, the metal

hydroxide can be removed by flocculation and sedimentation (Baltpurvins et al., 2010).

1.2.1.2 Sulfide Precipitation

Sulfide precipitation is also an effective process for the treatment of toxic heavy metals ions. One of the primary advantages of using sulfide is that the solubility of the metal sulfide precipitate is generally lower than hydroxide precipitates and sulfide precipitates are not amphoteric. Hence, sulfide precipitation process can achieve a high degree of metal removal over a broad pH range compared with hydroxide precipitation.

1.2.2 Activated Carbon Adsorbent

Activated carbon (Ac) adsorbents are widely used in the removal of heavy metal contaminants; its usefulness derives mainly from its large micro pore and meso pore volumes and the resulting high surface area. Nowadays, the depleted source of commercial coal-based activated carbon results in the increase of price to make progress in heavy metals adsorption and activated carbon without the expense of decline in the pollutants adsorption, additives and activated carbon composite could be an alternative additive of alginate. (Park et al., 2006).

1.2.3 Carbon Nanotubes Adsorbents

Carbon nanotubes (CNTs) discovered by Iijima in 1991, have been widely studied for the excellent properties and applications, as relatively new adsorbents. CNTs have been proven to possess great potential for removing heavy metals ions, such as lead, cadmium, chromium, copper and nickel from wastewater. The results of this studies shown that CNTs are promising candidates for adsorption of heavy metal. (Wong et al., 2007), (Kabbashiet al., 2009), (Kua and Lin, 2009), (Pillay et al., 2009), (Li et al., 2010), (Kandah and Muenier, 2007). CNTs are divided into two types: (1) single-walled carbon nanotubes (SWCNTs) and (2) multi-walled carbon nanotubes (MWCNTs) say by Odom et al in 1998.

1.2.4 Low-Cost Adsorbents

AC has been the most used adsorbent, nevertheless it's relatively expensive. Searching for low-cost and easily available adsorbent to remove heavy metal ions have become a main research focus, to

date hundreds of studies on the use of low-cost adsorbents have been published.

1.2.5 Biosorbents

Biosorption of heavy metals from aqueous solutions is a relatively new process that has been confirmed a very promising process in the removal of heavy metals contaminants. The major advantages of biosorption are its high effectiveness in reducing the heavy metal ions and the use of inexpensive biosorbents. Biosorption process is particularly suitable to treat dilute heavy metal wastewater. Typical biosorbents can be derived from three sources are follows:

1. Non-living biomass, such as bark, lignin, shrimp, krill, squid, crab shell e.t.c
2. Algal biomass.
3. Microbial biomass, e.g. bacteria, fungi and yeast.

1.2.6.0 Membrane Filtration

Membrane filtration technologies with different types of membranes show great promise for heavy metal removal in their high efficiency, easy operation and space saving. The membrane processes used to remove metals from the waste water are ultrafiltration, reverse osmosis, nano- filtration and electro dialysis. (Landaburu-aguirre *et al.*, 2009)

1.2.6.1 Ultrafiltration

Ultra filtration (UF) is a membrane technique working at low transmembrane pressure for the removal of dissolved and colloidal material. Since the pore size of UF membrane are larger than dissolved metal ions in the form of hydrated ions or as low molecular weight complexes. These ions would pass easily through ultra-filtration membranes, to obtain high removal efficiency of metal ions.

1.2.6.2 Reverse osmosis

The reverse osmosis (RO) process uses a semi permeable membrane, allowing the fluid that is being purified to pass through it, while rejecting the contaminants. Reverse osmosis is one of the techniques able to remove a wide range of dissolved species from water. It accounts for more than 20% of the world's desalination capacity. (Shahalamet *al.*, 2002).

RO is an increasingly popular wastewater treatment option in chemical and environmental engineering, using appropriate RO systems to remove heavy metals have been investigated, but these have yet to be widely applied. Cu^{2+} and Ni^{2+} ions were successfully removed by the RO process and the rejection efficiency of the two ions increase up to 99.5% by using Na_2EDTA . (Mohsen-Nia *et al.*, 2007).

1.2.6.3 Nano filtration

Nanofiltration (NF) is the intermediate process between ultra filtration and reverse osmosis. NF is a promising technology for the rejection of heavy metal ions, such as nickel, chromium, copper and arsenic from wastewater. (Murthy and Chaudari, 2008), (Muthuk-rishnan and Guha, 2008), (Csefalvayet *al.*, 2009, Ahmad and Ooi, 2010), (Nguyen *et al.*, 2009, Figoliet *al.*, 2010).NF process benefits from ease of operation, reliability and comparatively low energy consumption as well as high efficiency of pollutant removal. (Erikson, 2008).

1.2.7 Electrodialysis

Electro dialysis is another membrane process for the separation of ions across charged membrane from one solution to another, using electric field. In most electro dialysis process, ions exchange membranes are actually two basic types: cation exchange and anion exchange membranes. This process has been widely used for the production of drinking and process water from brackish water and seawater, treatment of industrial effluents, recovery of useful materials from effluents and salt production. (Sadrazadeha *et al.*, 2009).

1.2.8 Coagulation and Flocculation

Coagulation and Flocculation followed by sedimentation and filtration are also employed to remove heavy metal from wastewaters. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Many coagulants are widely used in the conventional wastewater treatment processes, such as aluminum, ferrous sulfate and ferric chloride, resulting in the effective removal of wastewater particulates and impurities through charge neutralization of particles. Investigation shown that removal of heavy metal by coagulation of combined sewer overflow with two commercial coagulants, a ferric

chloride solution and a poly aluminum chloride (PAC), found to be an excellent heavy metal elimination and achieved within a narrow range of coagulant around optimum coagulant concentration. (El-samrani *et al.*, 2008).

1.2.9 Flotation

Flotation has nowadays found extensive use in wastewater treatment. Flotation has been employed to separate heavy metal from a liquid phase using bubble attachment, originated in mineral processing; dissolved air flotation (DAF), ion flotation and precipitation flotation are the main flotation processes for the removal of metal ions from solution. Dissolved air flotation is to allow micro-bubbles of air to attach to the suspended particles in the water, developing agglomerates with lower density than water, causing the flocks to rise through the water and accumulating at the surface where they can be removed as sludge. (Lundhet *et al.*, 2000). Dissolved air flotation had been widely studied to remove heavy metal in 1990s. (Waters, 2006) and (Tassel *et al.*, 2007 & 2008).

1.2.10 Electro-Chemical Treatment

Electro-chemical methods involve the plating out of metal ions on a cathode surface and can recover metals in the elemental metal state. Electro-chemical wastewater technologies involve relatively large capital investment and the expensive electricity supply, so they haven't been widely applied. However, with the stringent environmental regulations regarding the wastewater discharge, electro-chemical technologies have regained their importance worldwide during the past two decades. (Wang *et al.*, 2007).

1.2.11 Biosorption Mechanism

The biosorption process involves a solid phase (sorber or biosorbent, biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions) due to higher affinity of the sorber for the sorbate species, the later is attracted and removed by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remained in the solution. The degree of sorber affinity for sorbate determines its distribution

between the solid and liquid phases. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency, minimization of chemical and biological sludge, regeneration of biosorbent and possibility of metal recovery (Krachthovil and Volesky, 2008). While disadvantages of biosorption are: Early saturation, the potential for biological process improvement, nonpotentially biological altered metal valiancy state (Ahluwalia and Goyal, 2007).

1.3. Factors Affecting Biosorption

The major factors that affect the biosorption processes include; Initial metal ion, concentration, Temperature, pH and Biomass concentration in solution. Aksu *et al.*, (2002) reported that temperature does not influence the biosorption process in the range 20-35°C. However, pH seems to be the most important parameter in the biosorption processes, it affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of the metallic ions. (Friis and Kerith, 2008). Biomass concentration in the solution seems to influence the specific uptake; for lower values of biomass concentration leads to interference between the binding sites. (Fourest and Roux, 2002).

1.4.0 Biosorption Equilibrium Models

The equilibrium of the biosorption process is often described by fitting the experimental points with models. (Gadd G M, White C & De Rome'L, 2008). The two widely accepted and linearised equilibrium adsorption isotherm models for single solute system are given by the following equation:

$$\text{Langmuir: } q = \frac{Q_{max}bceq}{1+bceq}$$

where q is milligrams of metal accumulated per gram of the biosorbent material; ceq is the metal residual concentration in solution; q_{max} is the maxi-saturation and b is the ratio of adsorption and desorption rates as the theoretical model for monolayer adsorption (Gadd *et al.*, 2008).

1.5. Waste Materials Of Food And Agricultural Industry As Biosobents

Agricultural bye products have been widely studied for metal removal from water, peat, wood, pine bark, banana pith, soybean, cotton hulls, rice bran,

saw dust, wool, orange peel have been demonstrated to remove heavy metals wastewater (Ozer, 2004). These agricultural waste biosorbents are inexhaustible, cheap and non-hazardous materials, which are specifically selective for heavy metals and can be easily disposed by incineration (Kartel *et al.*, 2009).

The objective of this research is to investigate the removal of chromium from tannery effluent using

2.1 Samples Collection

The rice husk was obtained from kalambaina area at wamakko Local Government Sokoto State. The tannery industry wastewater was obtained from Leather Industry (Marina area) Sokoto North Local Government Sokoto State.

2.2 Determination of Heavy Metals

The tannery wastewater collected in a clean container (1 litre), each was acidified with 2ml HNO₃ solution immediately, shaken homogeneously and then carefully refrigerated at 4°C prior to use. The water sample was then filtered using Whatman filter paper No. 1 to remove suspended materials (Das *et al.*, 2011). The concentration of heavy metals (Pb, Cd, Cr, Cu, Ni, As and Zn) were determined by atomic absorption spectrophotometer (AA240FS), which will serve as the initial concentration of the heavy metals in the subsequent Batch adsorption studies. The data were expressed as mean \pm standard deviation of the replicated samples.

Metal uptake q (mg/ml) = $V(C_i - C_e)/S$ where C_i and C_e Initial and equilibrium concentration of mg/L, V = Volume of solution (L), S = weight of Biosorbent (g).

3.0 RESULTS

3.1 Chromium Concentration

Figure 1: Portrays chromium adsorption in rice husk at different pH level and different adsorbent dosage of selected contact time of 30 minutes at 40 degrees centigrade, from the chart below it shows that at pH 2 there was 98.6%, 85.7% and 62.9% for 5g, 10g and 15g respectively, while that of pH 4 showed 100% adsorption in all the samples. However, pH 6 had 100%, 100% and 81.4% removal of chromium at 5g, 10g, and 15g

untreated noncarbonated rice husk biomass and agricultural wastes materials.

2.0 MATERIALS AND METHOD

The instruments used include atomic absorption Spectroscopy (Alpha 4), Hot plate (Gerherd), Magnetic stirrer, oven (Gallen Kamp), pH meter (3015) and weighing balance (Mettler balance DT 100).

Chemicals used are Sodium Hydroxide and Tetraoxosulphate (VI) acid

2.3 Preparation/Activation of Rice Husk

The rice husk was washed several times with distilled water to remove all dirt. The clean rice husk was dried at 100°C (Napi *et al.*, 2011). The sample was transferred in a clean container and store prior to use.

2.4 Batch Adsorption Studies

Batch adsorption experiments were carried out in 250ml Erlenmeyer flask containing 200ml of tannery wastewater and rice husk which was varied (5g, 10g and 15g). Mixtures were shaken at 120 rpm at contact time of 30, 60 and 90 minutes on magnetic stirrer. At pH 2, 4 and 6 under the same temperature of 40 degrees centigrade. The solution was allowed to equilibrate for 1 hour, filtered using Whatman filter paper (No. 1). The filtrate was analysed for equilibrium metal concentration using AA240FS Atomic Absorption Spectrophotometry (Varian medical System Inc., USA) (Volesky, 2003; Sahabi *et al.*, 2010).

respectively. Therefore, the least adsorption occurred at 62.9% in TE 2 (15g). From the above it can be seen that there was maximum and absolute adsorption at pH 4 even though other pH ranges gave an excellent adsorption.

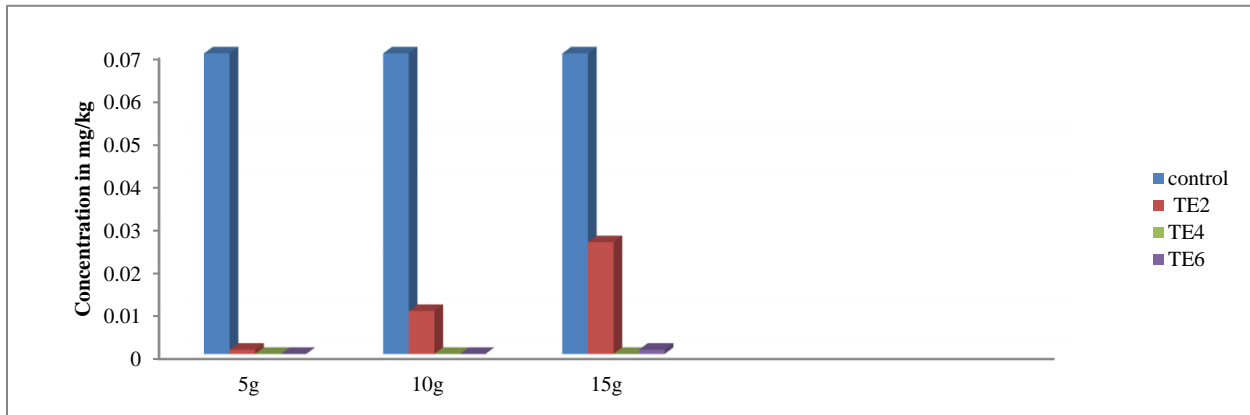


Figure 1: Chromium Concentration in Treated Tannery Effluent at 30mins Contact Time, Chromium

3.2 Concentration

Figure2 shows adsorption capacity of rice husk at different dosage level in various pH though under same contact time and temperature of 40 degrees centigrade. At pH 2 there was adsorption of 100%,

14.3% and 100% for 5g, 10g, and 15g respectively. At pH 4 there was absolute adsorption in all the three samples, whereas pH 6 had 100%, 85.7% and 100% for 5g, 10g and 15g respectively with least adsorption in TE2(10g).

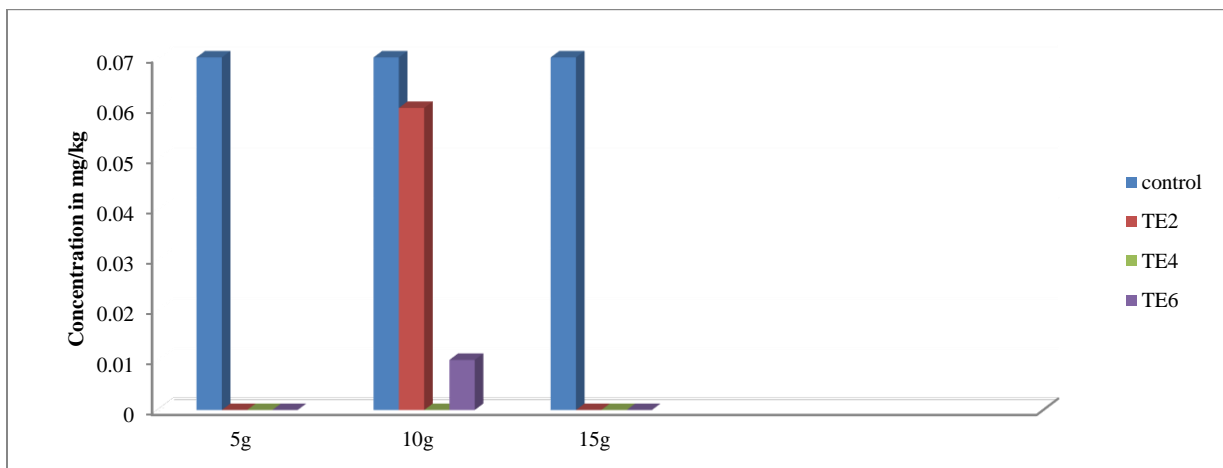


Figure 2: Chromium Concentration in Treated Tannery Effluent At 60mins Contact Time

Figure 3: Chromium Concentration

Figure 3: Reveals the adsorption of chromium at 40 degrees centigrade in 90 minutes. At pH 2 there was 100%, 100% and 91.4% removal of chromium in 5g, 10g and 15g respectively, and pH 4 medium was fully cleared of chromium after treatment in all samples while the pH 6 medium had 42.9%, 75.7%

and 100% adsorption in 5g, 10g and 15g respectively with least adsorption in TE 6 (5g).

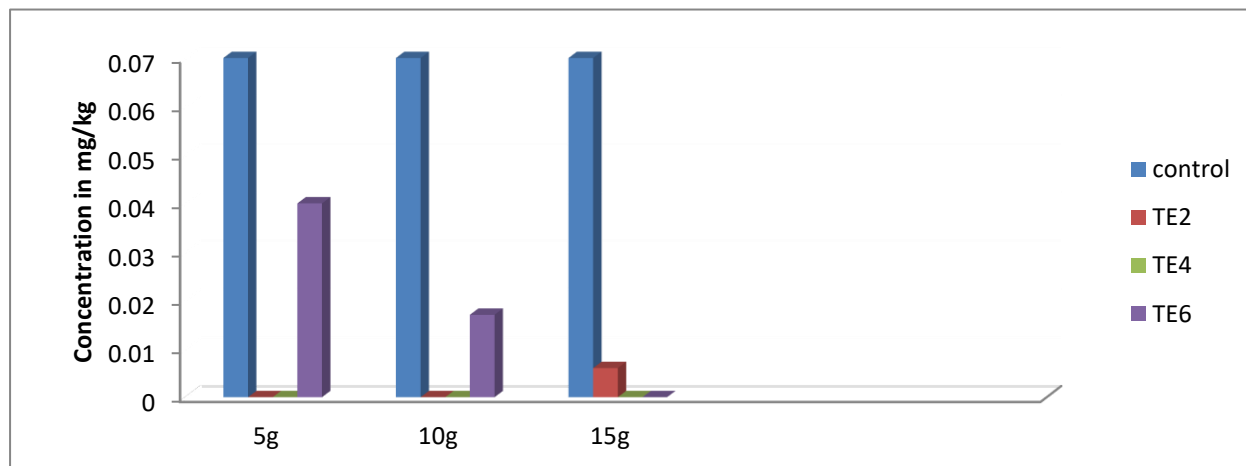


Figure 3: Chromium concentration in treated tannery effluent at 90minutes contact time

3.4 Effect of Adsorbent Dosage

The dosage of the husk was varied in order to assess at what rate the highest adsorption is achieved, from the charts above it can be deduced that adsorbent dosage has no significant impact on the removal of chromium from the solution since there was full adsorption in some instances and partial in others.

3.5 Effect of pH

The effect of pH on removal of chromium being the only heavymetal detected in the tannery effluent under investigation showed that, at pH 2 there is uptake of the metal and even full adsorption in some cases following the charts above, it could be seen that at pH2 only three samples showed full adsorption all across the three contact time and adsorbent dosages, whereas samples from pH 4 had full adsorption showing no trace of chromium at all and finally pH6 had four samples that showed traces of chromium, from this information conclusion can be drawn that pH 4 is much more suitable for adsorption of chromium from tannery effluent, which is in compliance with bishnoi et al., 2007, Blaquez et al., 2009, Dias et al., 2000 and Fahim et al., 2006.

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3.5 Effect of Contact Time

Four samples showed traces of chromium content under contact time of 30 mins, and at 60 mins two samples showed traces of chromium whereas at 90mins three samples had traces of chromium content, so from the observation here it could be seen that contact time has no much impact on the removal of heavymetals from the effluent which could be due to low concentration of the chromium in the solutions.

4.0 CONCLUSION

Removal of chromium from tannery effluent was successful using untreated uncarbonised rice husk biomass, maximum removal was at pH 4, indicating that agricultural wastes could be economically used in purification of tannery effluent only that in this case the effluent's natural pH in use tend to fluctuate between a range of 2-1.6, therefore there is the need for a naturally available base that can be used to adjust pH level before addition of the untreated rice husk and a little knowledge on how to adjust pH level.

5.0 RECOMMENDATION

Further work can be done to improve the rate at which adsorption of heavymetals can be increased using various agricultural wastes and conditions that may give better adsorption.

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