Journal of Chemistry and Nutritional Biochemistry
https://jcnb.sabapub.com
E ISSN: 2709-5932

2023 Volume 4, Issue 2: 35–50
DOI: https://doi.org/10.48185/jcnb.v4i2.923

Preparation and Characterization of Adsorbent From Leather Off-Cuts: A Potential Wastewater Decontaminant

Muhammad Lawan Anas[1]*, Feka Danauta Paschal[1], Alpha Samuel Ojochenemi[1], Benjamin Cynthia[1]
[1]Nigerian Institute of Leather and Science Technology Samara Zaria, Kaduna State, Nigeria

Received: 06.11.2023 • Accepted: 27.12.2023 • Published: 29.12.2023 • Final Version: 31.12.2023

Abstract: The preparation and characterization of Adsorbent from leather off-cuts was prepared by cutting the off-cuts and then pulverize into powder using grinding. The treatment which was used to characterized the leather off-cuts in NaOH, EDTA, and H_2SO_4 at different molarity, subsequent characterization using FTIR was done. The result obtained varies at different molarity treatment. The NaOH treatment shows a progressive reduction to amine absorption of dechroming frequencies of 3254.61 CM^{-1}, 3247.20 CM^{-1}, 2917.61 CM^{-1}, 2918.30 CM^{-1}, 2917.63 CM^{-1} correspond to 0.2M, 0.4M, 0.6M, 0,8M, and 1.0M respectively. For H_2SO_4 , a similar trend was observed with a little fluctuation in the absorption band. For EDTA, the absorption from 3525.91 CM^{-1} , 3366.53 CM^{-1}, 3522.24 CM^{-1} and 3517.45 CM^{-1} respectively was observed.

Keywords: Leather off-cuts, Pulverize, dechroming, Treatment, characterization, absorption.

1. Introduction

Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. This process differs from absorption, in which a fluid (the absorbate) is dissolved by or permeates a liquid or solid (the absorbent) [1].

Decontamination is the process of removing contaminants on an object or area, including chemicals, micro-organisms or radioactive substances. This may be achieved by chemical reaction, disinfection or physical removal. It refers to specific action taken to reduce the hazard posed by such contaminants, as opposed to general cleaning [2].

Adsorption method of metal removal has proved to be one of the reliable and cost-effective methods, which is uncomplicated, cheap and selective for the remediation of metal polluted wastes [3]. One of the heavy metals that have been a major focus in wastewater management is chromium; this metal is introduced into the environment via industrial discharges from leather tanning, textiles, paint and pigment, electroplating, canning, glass and ceramic industries. At high concentrations, all

*Corresponding author: Email: ahmadinamla@gmail.com

compounds of chromium are toxic, its ingestion may result to diarrhea and severe vomiting, nausea and epigastric pains [4].

Due to increased population growth, there has been an increase in the number of industries to meet the day to day demands of the mankind. Along with the useful products, these industries generate a large amount of toxic materials in various forms of solid, liquid and gaseous contaminations. The quantity and toxicity of these hazardous releases vary and depends on the type of industries. In 1991, Sehn et al., analyzed that among all the industrial wastes, tannery effluents are the top ranked toxic releases. A significant part of the chemicals used in leather processing is not actually absorbed or consumed in the process and hence it is discharged into the environment. Due to industrial enlargement, huge amounts of industrial wastes are accruing in the environment and can't be disposed[5]. Liquid effluents from light leather processing comprises about 10 to 100 mg/L of organic matter, chromium, sulphide, and solid waste including fleshing, trimmings, shavings and, buffing dust [6].

As estimated, the total wastewater discharge from tanneries runs to about 400 million m3 each year. This industry has been painted negatively in the society owing to its high pollutant composition. The difficulty in treating tannery effluent results from the complex nature of the wastewater produced, leading to various environmental regulations and laws in many developing countries being passed especially in the last ten years. The tannery industry is known for its deterring impact on the environment. High quantities of polluted water are discharged containing large amounts of chemicals which include lime, sodium chloride and chromium salts from which the discharge of heavy metal (Cr) into the environment is known [7]. It is noteworthy that the chromium present in chrome tan by-products is in the trivalent state and considered harmless, which under non-controllable conditions, however, the Cr (III) can be oxidized to the mutagenic chromium (VI) and become threatening to man and the environment [8]

Chromium is a chemical element with the symbol Cr and atomic number 24. It is the first element in group 6. It is a steely-grey, lustrous, hard, and brittle transition metal. Throughout the world, heavy metals are one of the most widespread origins of industrial water pollution, because of their toxicity, non-biodegradable nature and accumulation in living organisms [9].

Chromium is such a major toxic heavy metal for both humans and the environment and often found in industrial wastewater, which is introduced into water streams from mining, tanning, electroplating, wood preservatives, paints, textile dyeing, and plants producing industrial inorganic chemicals and pigments. Chromium occurs most frequently as both trivalent [Cr (III)] and hexavalent [Cr (VI)] states in aquatic environment. Trace amounts of Cr (III) is an essential micronutrient for sugar, protein and fat metabolism in mammals, while Cr (VI) is a primary contaminant, which is considered potential carcinogen that induces primary liver cancer. Hence, it is necessary to treat industrial wastewater containing chromium before being discharged to the environment [9].

The chemical characterization of adsorbent focuses on the elemental composition and chemical compounds of the adsorbent materials and also the functional groups on the active sites of the adsorbent. Acidicsurface have the potential for cationic exchange due to the presence of carboxylic compounds on the surface of the adsorbent. Elemental analysis of the prepared adsorbent materials can be achieved using the energy dispersive X-ray (EDX) incorporated in SEM (JOEL-JSM 6400). Prior to the investigation, adsorbent materials are coated to enhance the conductivity of the adsorbent material in order to achieve better resolution of the microstructure of the adsorbent and to avoid the accumulation of electrostatic charge. Some of the materials used for coating to enhance the conductivity of the sample include gold, platinum, chromium, and tungsten. The coating material on the surface is usually conducted at low-vacuum sputter coating or by high vacuum evaporation. The images produced by SEM are as a result of the interaction between electron beams of the samples obtained at various depths. The images are transmitted in form of signals. Some of the most common types of signals produced by SEM include the secondary electrons, back-scattered electrons and transmitted electrons. Nonconductive sample to be analyzed by the SEM obtain charges when scanned by the electron beam can result to improper scanning of the material. The elemental compositions of the adsorbents were achieved as percentage atomic contents in the adsorbents. This was used to determine the heavy metals before and after the batch adsorption study. The emission of secondary X-rays from an excited material involves the bombardment with high-energy X-rays. This is achieved by the radiation of the element at different electronic orbital by the removal of the electron inside the orbitals by an energetic photon which is provided by a primary source of radiation. For the excitation of the atoms, a source of radiation with sufficient energy is needed to expel tightly held inner electrons. X-ray transmitters in the range of 20–60 kV are used to obtain atomic information of the excited material [10]

Commercial Sorbents and Applications

Only four types of generic sorbents have dominated the commercial use of adsorption: activated carbon, zeolites, silica gel, and activated alumina. Estimates of worldwide sales of these sorbents are [11].

Activated carbon	**$1 billion**
Zeolites	**$100 million**
Silica gel	**$27 million**
Activated alumina	**$26 million**

Some other reported figures are (according to 2001 demand) zeolites ($1,070 million), silica gel ($71 million), activated alumina ($63 million), and clays ($16 million) [12]. Activated carbon has been used as an all-purpose sorbent. It is “hydrophobic.” Its precedent, charcoal, was first used in the sugar industry in England in 1794 to decolorize sugar syrup. The major development of activated carbon took place during World War I, for use in filters to remove chemical agents from air. The commercial activated carbon has taken its present form since the 1930's [13]. Silica gel and activated alumina are used mainly as desiccants, although many modified forms are available for special purification applications. Synthetic zeolites, the youngest type among the four[14]. The zeolites that are in commercial use today are mainly the types in Milton's invention, i.e., types A, X, and Y. It is remarkable that most of the $100 million annual sales of zeolites and the businesses associated with the zeolites are generated by a single invention. Zeolites are used for their special adsorption properties due to their unique surface chemistries and crystalline pore structures. It should be noted, however, that a sizable portion of the commercial zeolites is used for ion exchange and as catalysts. Polymeric resins are used increasing use in potable water purification, because for some organics they can remove to lower concentration levels than activated carbon does. Acid-treated clays and pillared clays are used for treatments of edible and mineral oils.

Statement of Research problem

Production of adsorbent is quite expensive and difficult to produce. There is need to find a possible way of producing an absorbent that is less expensive but yet efficient. More also, leather off-cuts causes' environmental pollution which is a thread to human health.

Justification

Most common adsorbent are prepared from wood, thereby encouraging deforestation and amplifying oxides of O,N and S in the atmosphere. Similarly, absorbents have been synthesized using metal oxides (MgO, ZnO, CuO etc.), which are quite expensive and complicated to achieve hence, the need for a cheaper, environmentally friendly and sustainable adsorbent. Leather wastes (as off-cuts, old shoes, bags, belts, wallets e.t.c) which are not easily biodegradable, and on putrefaction, may cause menace to human. This research intends to reduce these wastes and find a more useful application for it as adsorbents for the removal of contaminant in industrial waste water.

Aim

The research study is aimed for preparation and characterization of adsorbent from leather off-cuts: a potential wastewater decontaminant.

Objectives

To prepare Nano powder from leather off-cuts.

To characterize the unmodified Nano powder using FTIR.

To determine the removal efficiency of parametric factors applied by the use of isotherm transport mode and kinetic studies.

To study the significant difference amongst set of data generated in the treatment process using ANOVA tool.

2. Materials and Methods

Batch shaker (model no: Hy-4C), conical flask, beaker, measuring cylinder, volumetric flask, distilled water, NaOH, EDTA, H2SO4, grinding machine, weighing balance, 250ml Erlenmeyer flasks.

Sample collection and off-cuts preparation

Leather off-cuts were collected from footwear Department, Nigerian Institute of Leather and Science Technology, Samaru Zaria. Those samples were separated into different colors, size, then washed and cut into smaller pieces for easy grinding. The leather off-cuts were then pulverized into powder in the control laboratory (NILEST).

Preparation of standard solution of NaOH, EDTA and H2SO4

A standard solutions was prepared into five different molarity each of NaOH, EDTA and H2SO4 ; 0.2M, 0.4M, 0.6M, 0.8M and 1.0M.

Leather off-cut treated with NaOH, EDTA and H2SO4

1g of off-cuts was poured into five different conical flasks, the standard solutions were added into the various conical flask, a shaker was used for an hour to shake the prepared absorbent The conical flask containing solutions of off-cuts and standard solution of different molarity were filtered and further analysis was carried out.

Preparation of Absorbent

A standard solution of H2SO4 (500ml) was prepared, 25 g of off-cuts was measured and transferred into 100ml flask and then the prepared solutions was transferred into the off-cuts, stirred thoroughly. The absorbent was left for a period of one week, then filtered and allow to dry for almost five days. The prepared absorbent was taken for analysis.

3. Results

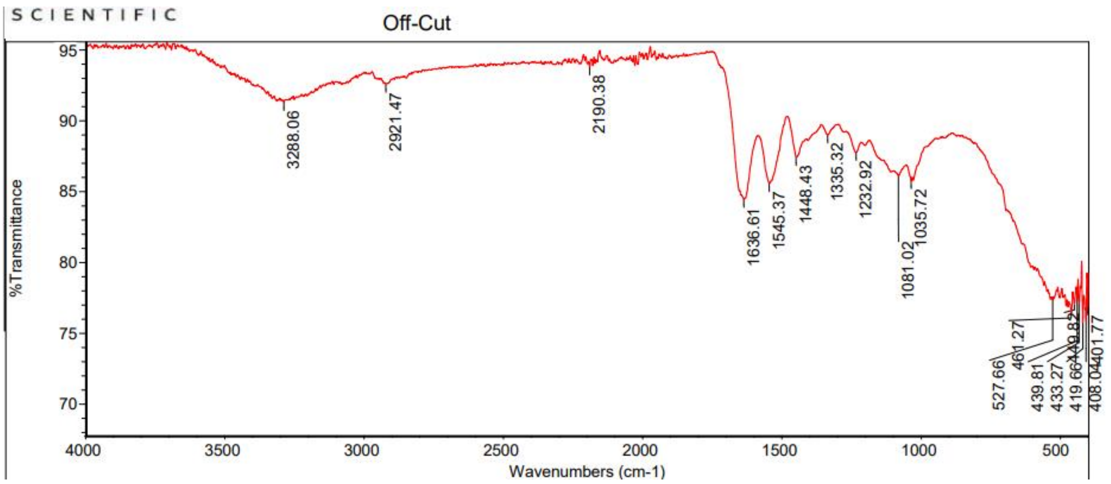

Figure 1: FTIR graph of Leather off-cuts

Signal at3288.0 cm^{-1} a major group of Amide, 2929.49 cm^{-1} and 2190.38 cm^{-1} correspond to Alkane and Alkyne. The presence of Amide indicate Amino acid which is gotten as a result of tanning, thus the molarity 1.0M is not the best for removal.

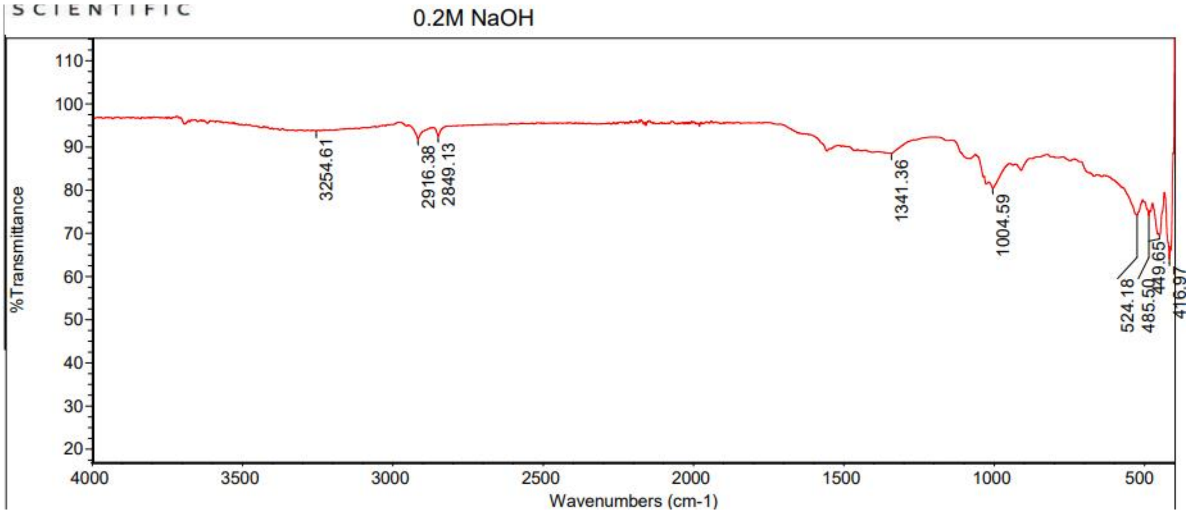

Figure 2: FTIR graph of Leather off-cuts treated with 0.2M NaOH

Spectral of 0.2M H_2SO_4 with a major group of Amide at a signal of 3075.112 cm^{-1} ,2916.49 cm^{-1}, 2849.95 cm^{-1} corresponding to Alkane. Presence of many Amino group shows that it is not the best for removal (0.2M)

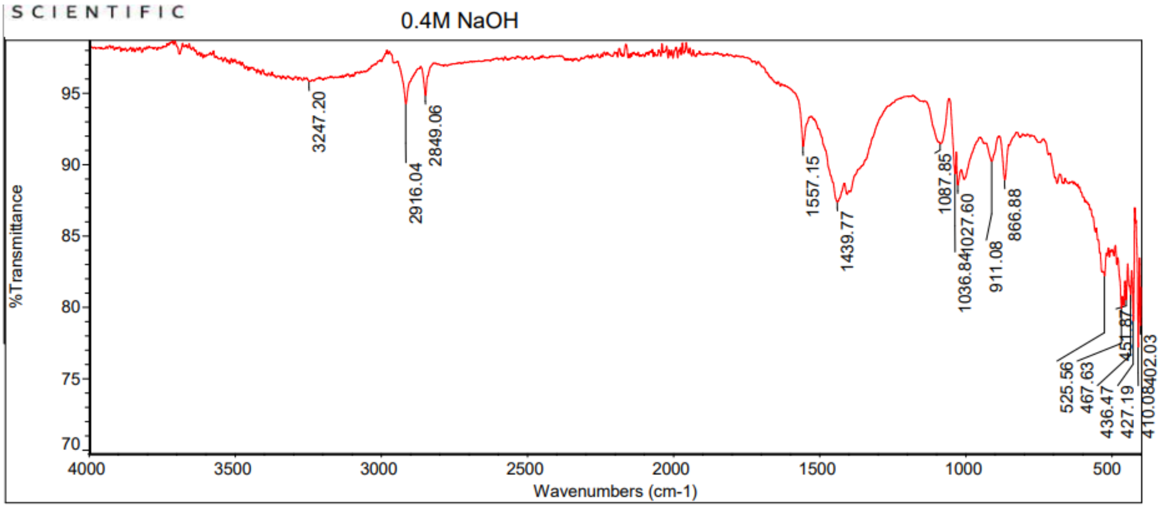

Figure 3: FTIR graph of Leather off-cuts treated with 0.4M NaOH

Spectral 3247.20 Cm-1 represent Amide, 2916.04 represent Alkane and 2849.06 Alkane. The removal of many functional group like Amide, Anhydride and many shows that 0.4M of Sodium hydroxide is the best a good removal.

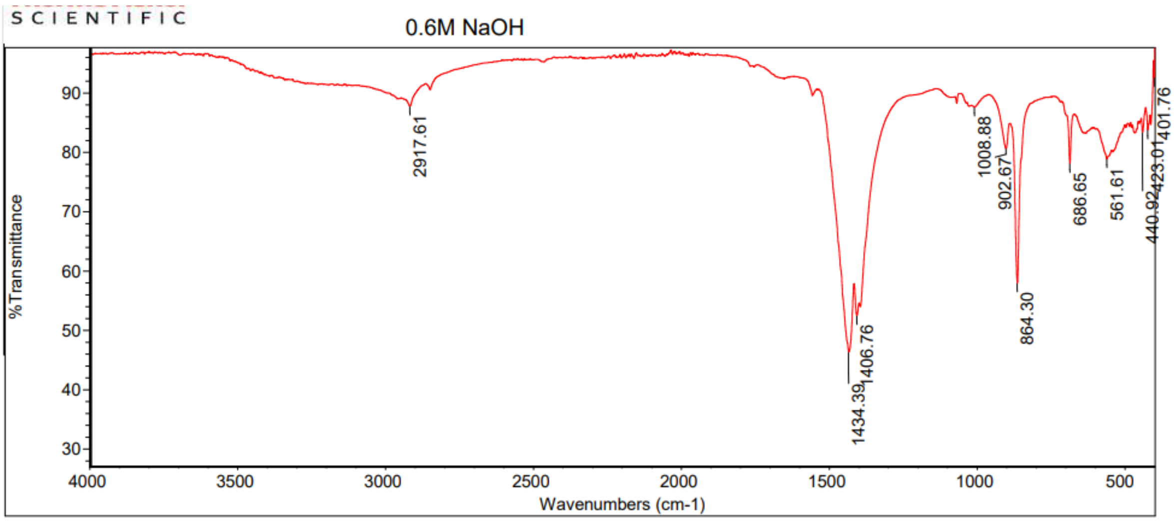

Figure 4: FTIR graph of Leather off-cuts treated with 0.6M NaOH

Spectral of 2917.61 cm^{-1} represent Alkane. Absence of functional group indicate that it is a good removal

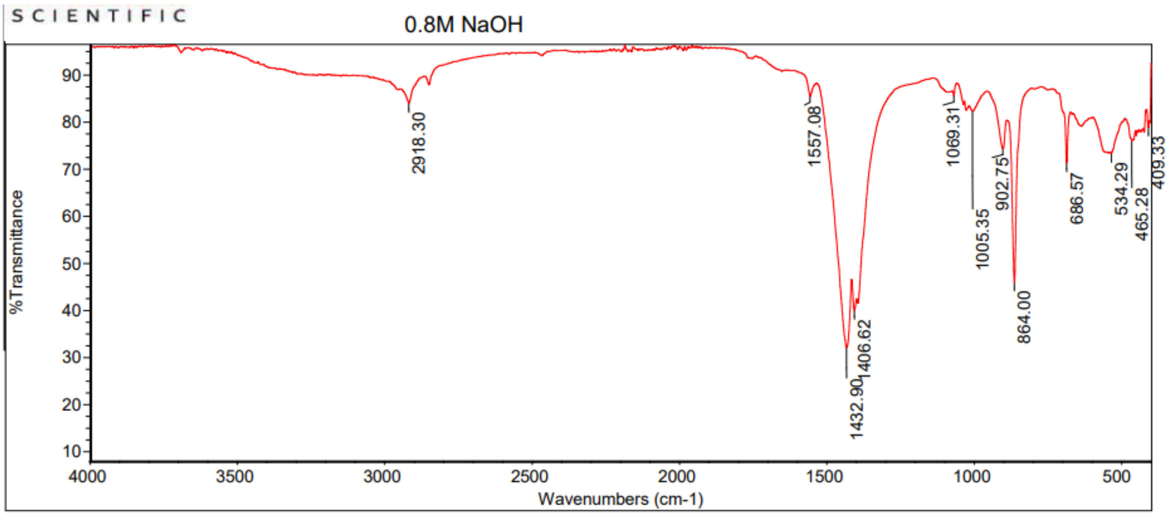

Figure 5: FTIR graph of Leather off-cuts treated with 0.8M NaOH

Spectral 2918.30 **(**Cm^{-1}) represent Alkane. Removal of functional groups indicate that Sodium hydroxide is a good removal

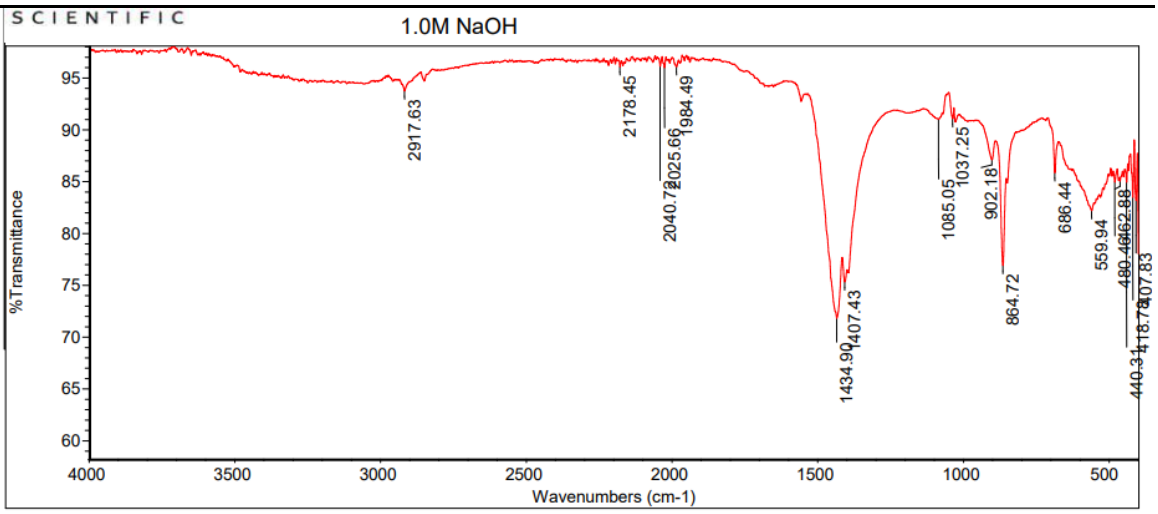

Figure 6: FTIR graph of Leather off-cuts treated with 1.0M NaOH

spectral 2917.63 (Cm^{-1}) represent Alkane, 2178.4(Cm^{-1}), 2040.78 (Cm^{-1}), 2025.66 (Cm^{-1}) and 1984.49 (Cm^{-1}) represents Alkynes and Anhydrides respectively. The higher the molarity the less effective in removal of functional group in sodium hydroxide.

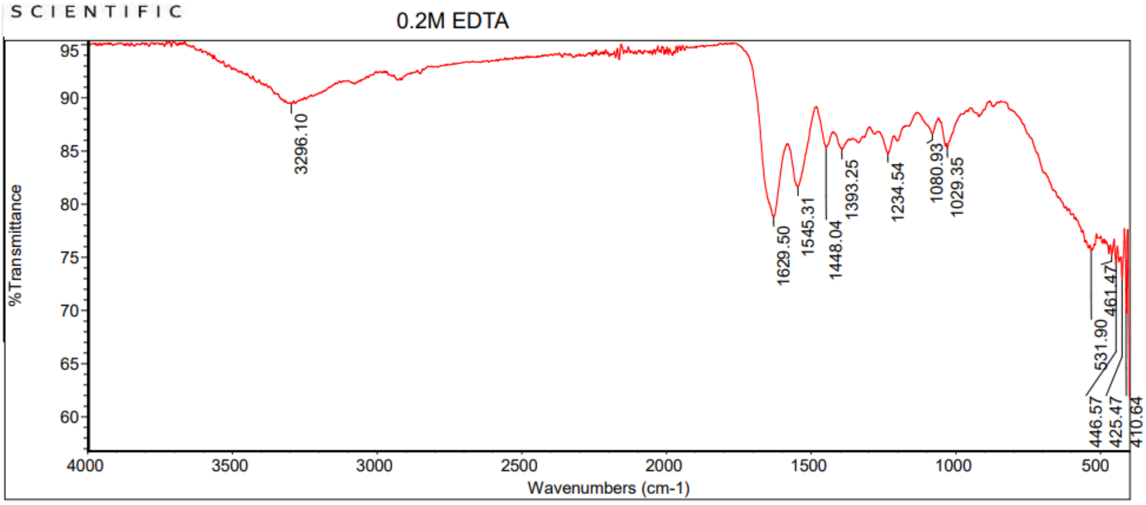

Figure 7: FTIR graph of Leather off-cuts treated with 0.2M EDTA

signal at 3296.10 cm^{-1}, 1629.50 cm^{-1}, 1545.31 cm^{-1} are mostly C-H stretch, C=H and NO stretch. The presence of these functional groupindicates the less effective the removal is.

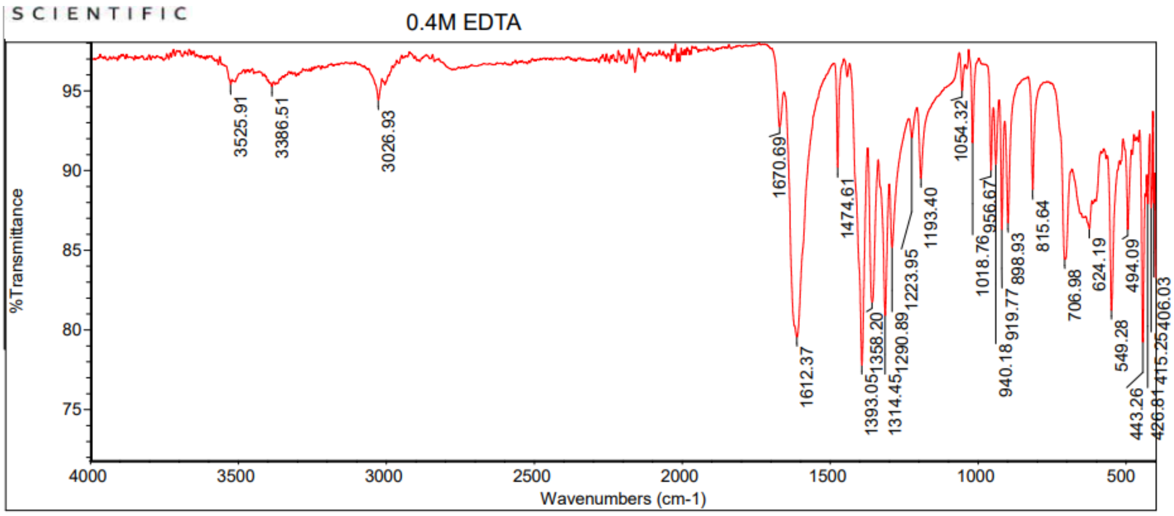

Figure.8: FTIR graph of Leather off-cuts treated with 0.4M EDTA

Spectral 3525.91 (Cm^{-1}), 3386.51 (Cm^{-1}), 3026,93 (Cm^{-1}), 1670.69 (Cm^{-1}), 1612.37 (Cm^{-1}) represents Amides, Amides, Alkene and Alkene respectively. The removal of Amino group is less and not effective in EDTA

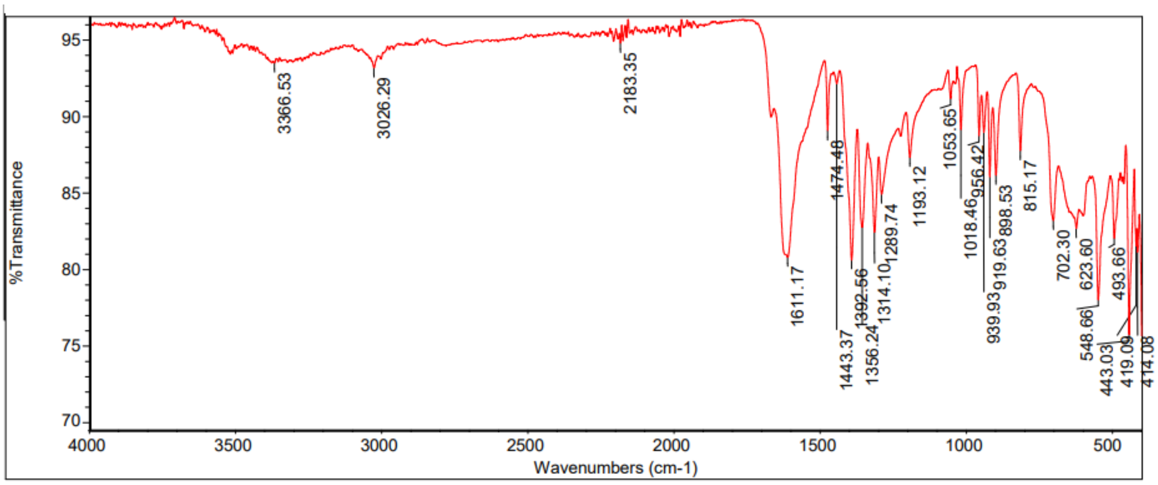

Figure 9: FTIR graph of Leather off-cuts treated with 0.6M EDTA

Spectral 3366.53 (Cm^{-1}) represents Amides, 3026.29 (Cm^{-1}), 2183.35 (Cm^{-1}), 1611.7 (Cm^{-1}) represents Amides, Aromatic compound, Alkyne and Alkene respectively. Presence of the above functional group shows how less effective EDTA at a molarity of 0.6M is in removal.

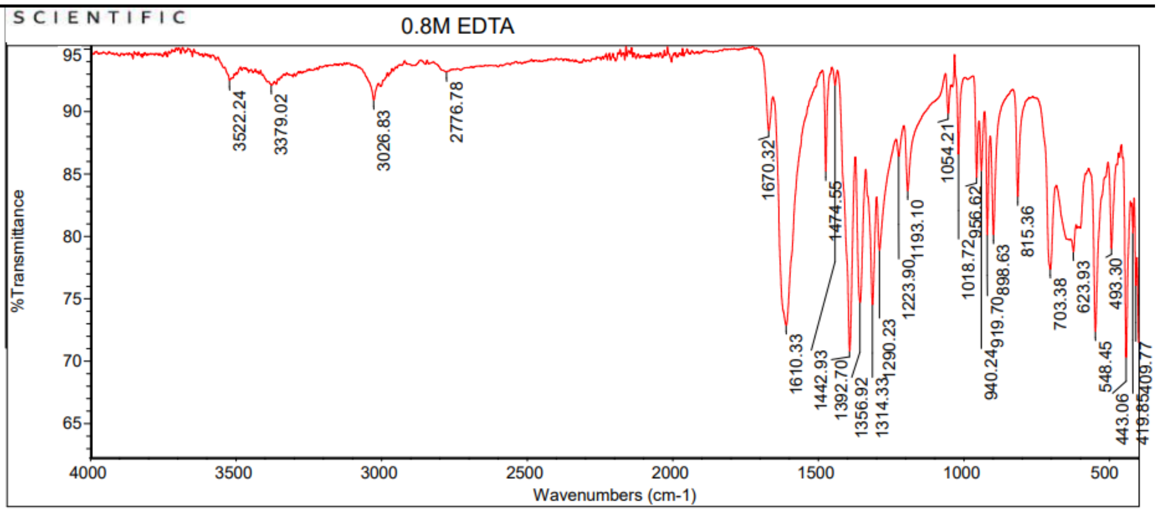

Figure 10: FTIR graph of Leather off-cuts treated with 0.8M EDTA

3522.24 (Cm^{-1}), 3379.02 (Cm^{-1}), 3026.83 (Cm^{-1}), 2776.78 (Cm^{-1}) spectral represents Amides, Amides, Alkene and Aldehydes respectively. This molarity is able to removal few functional group which shows it's inability in removal.

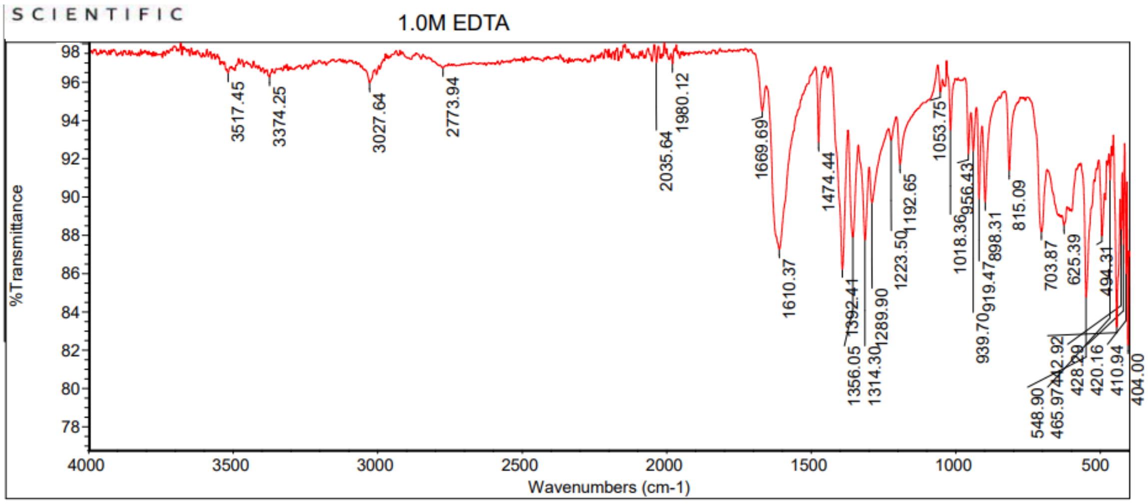

Figure 11: FTIR graph of Leather off-cuts treated with 1.0M EDTA

3517.45 (Cm^{-1}), 3374.25 (Cm^{-1}), 3027.64 (Cm^{-1}), 2773.94 (Cm^{-1}), 2035.64 (Cm^{-1}) spectral represents Amides, Amides, Alkene, Aldehydes and Nitriles respectively. Few removal of functional group in this molarity

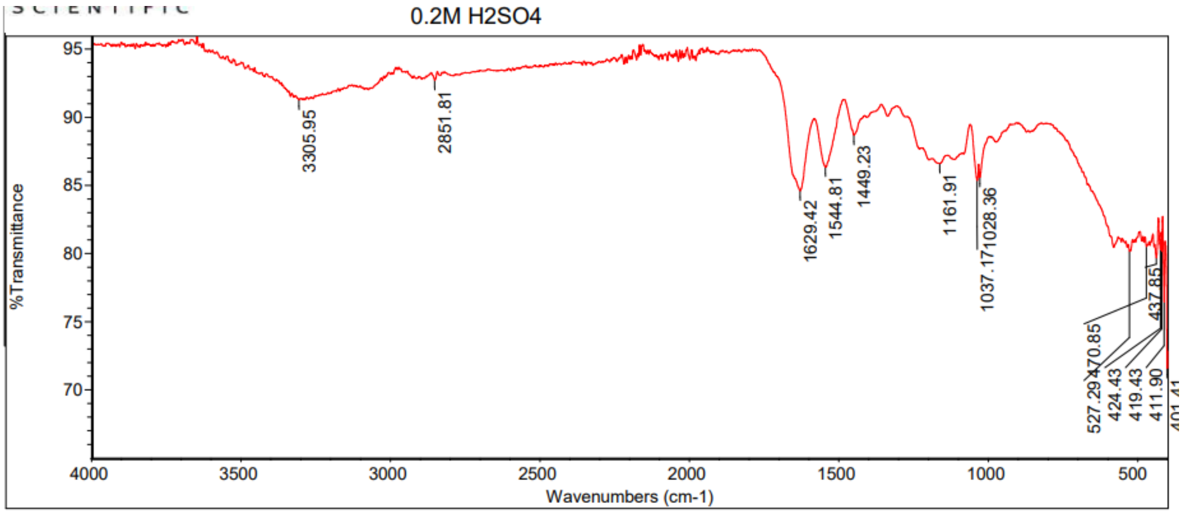

Figure 12: FTIR graph of Leather off-cuts treated with 0.2M H_2SO_4

3305.95 (Cm^{-1}), 2851.81 (Cm^{-1}), 1629.42 (Cm^{-1}), 1544.81 (Cm^{-1}) spectral represents Alkyne, Alkane, Alkyne and Nitro compound. Acid is not a good removal of functional group like Amino group that is why the removal is not likely to happened.

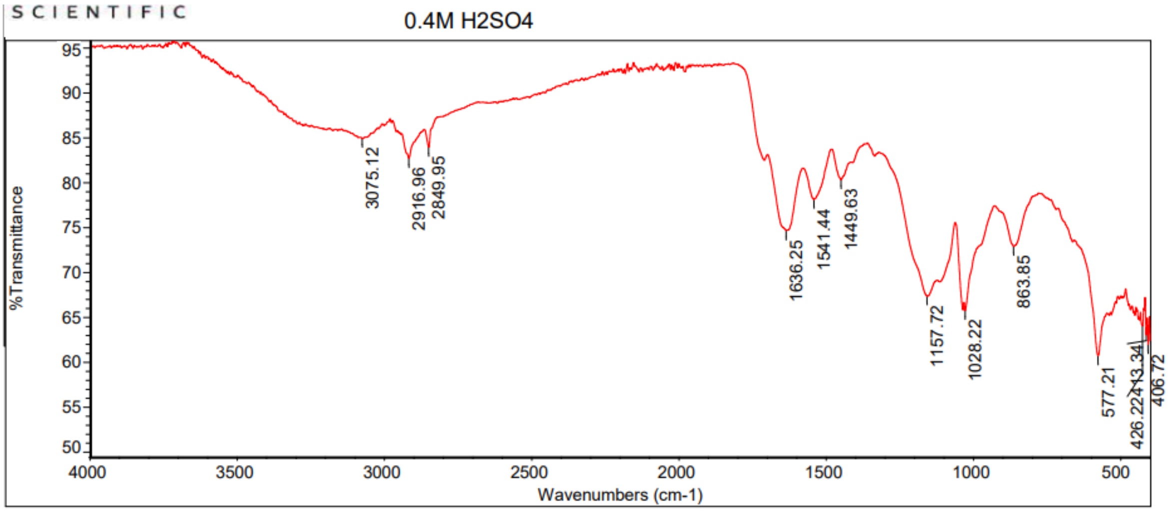

Figure 13: FTIR graph of Leather off-cuts treated with 0.2M H_2SO_4

3075.12 (Cm^{-1}), 2916.96 (Cm^{-1}), 2849.95 (Cm^{-1}), 1635.25 (Cm^{-1}), 1544.81 (Cm^{-1}) spectral Alkene, Alkane, Alkane, Aromatic compound and Nitro compound respectively. Acid cannot be neutralize by acid that is why the removal is not effective.

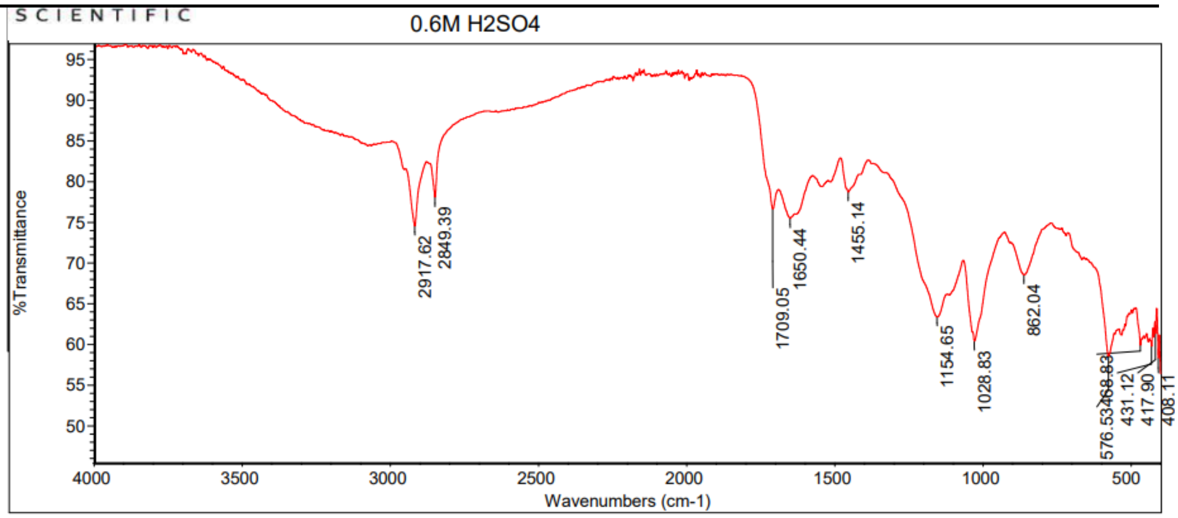

Figure 14: FTIR graph of Leather off-cuts treated with 0.6M H_2SO_4

2917.62 (Cm^{-1}), 2849.39 (Cm^{-1}), 1709.05 (Cm^{-1}), 1650.44 (Cm^{-1}) spectral represents Alkane, Alkane, Ketone and Alkene respectively. The functional group present in the off-cut as a result of tanning cannot be neutralize and removed by acid.

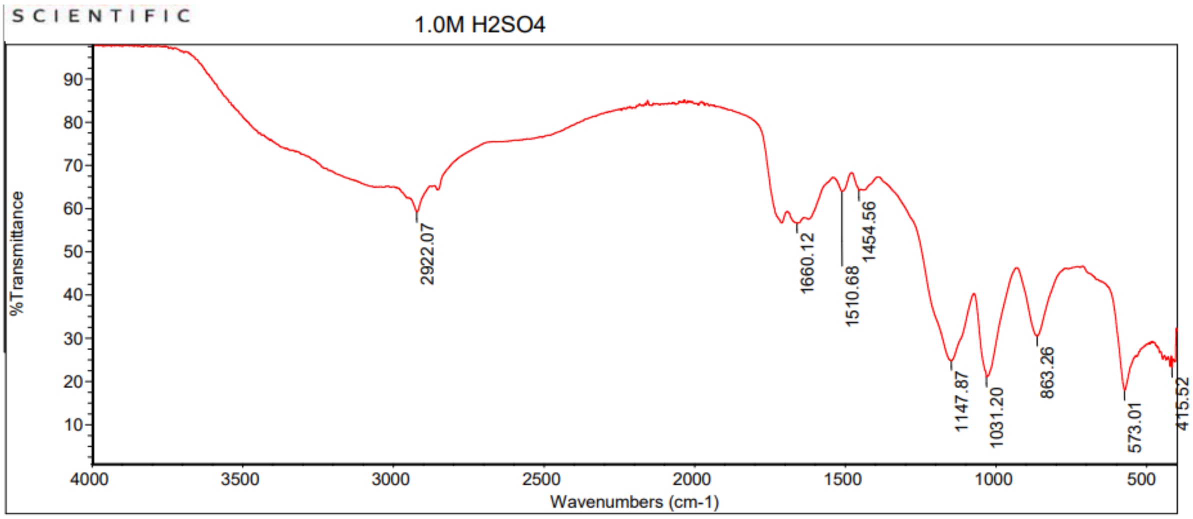

Figure 15: FTIR graph of Leather off-cuts treated with 1.0M H_2SO_4

2922.07 (Cm^{-1}), 1660.12 (Cm^{-1}) spectral represent Alkanes. Acid cannot removal the functional group because acid can only be neutralize by base.

4. Discussion

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a largely used technique to identify the functional groups in the materials (gas, liquid, and solid) by using the beam of infrared radiations. An infrared spectroscopy measured the absorption of IR radiation made by each bond in the molecule and as a result gives spectrum which is commonly designated as % transmittance versus wave number (cm^{-1}). A diverse range of materials containing the covalent bond absorbed electromagnetic radiation in the IR region. The IR region is at lower energy and higher wavelength than the UV-visible light and has higher energy or shorter wavelength than the microwave radiations. For the determination of functional groups in a molecule, it must be IR active [15]. An IR active molecule is the one which has dipole moment. When the IR radiation interacts with the covalent bond of the materials having an electric dipole, the molecule absorbed energy, and the bond starts back and forth oscillation. Therefore, the oscillation which caused the change in the net dipole moment of the molecule should absorbed IR radiations. A single atom doesn’t absorb IR radiation as it has no chemical bond [15]. Symmetrical molecules also do not absorbed IR radiation, because of zero dipole moment. For instance, H2 molecule has two H atoms; both canceled the effect of each other and giving zero dipole moment to H2 molecule. Therefore, H2 molecule is not an IR active molecule. On other hand, H-F (hydrogen fluoride) is an IR active molecule, because when IR radiation interacts with H-F molecule, the charge transferred toward the fluorine atom and as a result fluorine becomes partial negative and hydrogen becomes partial positive, giving net dipole moment to H-F molecule. It should be noted here that a particular IR radiation (frequency) will be absorbed by a particular bond in the molecule, because every bond has their particular natural vibrational frequency. For instance, a molecule such as acetic acid (CH3COOH) containing various bonds (C-C, C-H, C-O, O-H, and C=O), all these bonds are absorbed at specific wavelength and are not affected by other bond. We can say that two molecules with different structures don’t have the same infrared spectrum, although some of the frequencies might be same [15]

Basic Principle of FTIR

When infrared radiation is bombarded on a sample, it absorbs the light and creates various vibration modes. This absorption relates precisely to the nature of bonds in the molecule. The frequency ranges are measured as wave numbers typically over the range of 4000–600 cm^{-1}. The

FTIR spectrum is measured as wave number because wave number is directly related to the energy and frequency, thus providing an easy way for interpreting the spectrum. Prior to the sample analysis, the background is recorded, to avoid air and water vapor contamination peaks. The proportion of the background and the sample spectrum are directly related to the absorption spectrum of the sample. The absorption spectrum indicating various vibrations of the bonds presents in the sample molecule. Several modes arise due to the various bond vibrations. So, in this way one can easily identify the functional group in a molecule [15]

Figure 1 shows the FTIR spectral of untreated leather with a major group of Amide at a signal of 3288.06 cm^{-1} other at 2929.49 cm^{-1} and 2190.38 cm^{-1} corresponding to Alkane and Alkyne respectively. The Amide functional group can be related to as Tennis used in tanning and other chemical process influence on the leather. Other absorption below the functional group region are 1545.37 cm^{-1}, 1448043 cm^{-1} represent the elements present on the leather and its composition. The signals at 3247.20 $cm^{-1}$is mostly assigned to N-H bending vibration, signals at 2916.04 cm^{-1}, 2849.06 cm^{-1} is mostly C-H at figure 2 signal at 2917.61 cm^{-1} is mostly C-H stretch.

Figure 7 signal at 3296.10 cm^{-1}, 1629.50 cm^{-1}, 1545.31 cm^{-1} are mostly C-H stretch, C=H and NO stretch.

Figure 13 shows the FTIR spectral with a major group of Amide at a signal of 3075.12 cm^{-1} other at 2916.49 cm^{-1}, 2849.95 cm^{-1} corresponding to Alkane. The result decrease as the molarity increase. Its shows decrease at 0.4M, 0.6M, 0.8M and 1.0M respectively.

Figure 14 shows the FTIR spectral of 2917.62 cm^{-1} with a major group of carbon-Hydrogen stretch, 2849.39 cm^{-1}, 1709.05 cm^{-1} and 1650.44 cm^{-1} with a major group of Carbon Hydrogen, Carbon oxygen and Carbon carbon respectively.

Figure 16 shows the FTIR spectral of prepared absorbent with a major group of Alkane at a signal of 2919.10 cm^{-1} other at 2091.49 cm^{-1} and 1633.42 cm^{-1} corresponding to Alkyne and ketone respectively. The Amide functional group which related to as Tennis used in tanning have been treated with 1.0M H_2SO_4.

5. Conclusion

The preparation and characterization of Adsorbent from leather off-cuts was prepared by cutting the off-cuts and then pulverize into powder using grinding, treatments using NaOH, EDTA and H_2SO_4 at a concentration of 0.2M, 0.4M, 0.6M, 0.8M and 1.0M was further characterize using FTIR. The result shows 0.4M of NaOH have the highest percentage removal.

6. Recommendations

Analysis like SEM should be done, in order to know the morphology best treatment for adsorbent preparation.

Carbonization of the leather off-cuts could be also be determined.

Preparation of adsorbent should be done

Commercial adsorbent should be as control, to determine the best between the commercial and prepared adsorbent.

7. REFERENCES

1. Brownfields (2008). The Glossary And Land Revitalization Technology Support Center. Retrieved 2009-12-21.
2. McGraw Hill (2004). "Water Decontamination", in Yearbook of Science and Technology. p 372 Mwinyihija M, Quiesenberry W. (2013) Review of the challenges towards value addition of the leather sector in Africa; 2(11):518-528.
3. Hassan Z, Abdorrahman H, Vahdat J. (2012) Studies of the adsorption thermodynamics and kinetics of Cr(III) and Ni(II) removal by polyacrylamide. J. Serbia. Chem. Soc.; 77(3):393–405.
4. Krishnamoorthy A, Joseph CJ. (2004). Adsorption of chromium (VI) ion onto activated amla dust: Adsorption inotherms and kinetics. Indian Journal of Chemistry. ; 42:45-50.
5. Badar U., Ahmed N., Beswick AJ., PattanapipitpaisalP,Macaskie LE., (2000). Reduction
6. Kocaoba, S. and G. Akin, 2002. Removal and recovery of chromium and chromium
7. Mandi L, Souad T, Abderrahim J. (2009) Depuration of tannery efluent by phytoremediation and infiltration percolation under arid climate. Options Méditerranéennes; 88:199-205.
8. VassilikiGP, Dimitris K, Ersi V. A (1998). Method for the removal of chromium from tanned leather wastes. Journal of the Air & Waste Management Association; 48(9):846-852. DOI: 10.1080/10473289.1998.10463735
9. Cecilia W. M. (2015). Evaluation of Banana Peels, Pumice and Charcoal Potential to Adsorb Chromium Ions from Tannery Wastewater Cecilia WangechiMuriukiA Thesis submitted in partial fulfillment for the Degree of Masters in Environmental Engineering and Management in the Jomo.
10. Mohamed, O. A., El Sayed, N. H., Abdelhakim, A. A.; Preparation and characterization of polyamide-leather wastes polymer composites. J. Appl. Polym. Sci. 118(1), 446-451. 2010.
11. Humphrey, J. L. and Keller, G. E., II. (1997) Separation Process Technology. McGraw- Hill, New York, NY.

12. Chemical Engineering, February 2000, p. 59
13. Jankowska, H., Swiatkowski, A., and Choma, J. (1991) Active Carbon. Ellis Harwood, New York, NY.
14. Milton, R. M. U.S. Patents 2,882,243 and 2,882,244 (1959).
15. Shahid Ali Khan, Sher Bahadar Khan, Latif Ullah Khan, Aliya Farooq, Kalsoom Akhtar, and Abdullah M. Asiri ‘Fourier Transform Infrared Spectroscopy: Fundamentals and Application in Functional Groups and Nanomaterials Characterization Springer International Publishing AG, part of Springer Nature 2018 S. K. Sharma (ed.), Handbook of Materials Characterization, https://doi.org/10.1007/978-3-319-92955-2_9