JIMMA UNIVERSITY

COLLEGE OF NATURAL SCIENCE

DEPARTMENT OF CHEMISTRY



RESEARCH THESIS

ON:

ADSORPTION OF Pb(II) FROM AQUEOUS SOLUTION ONTO MICROWAVE AND CONVENTIONAL METHOD PREPARED ACTIVATED CARBON FROM TEFF HUSK USING Zncl₂ AS AN ACTIVATED AGENT

BY

JAMES SIMON ABALLA

OCTOBER,2018

JIMMA, ETHIOPIA

ADSORPTION OF Pb(II) FROM AQUEOUS SOLUTION SOLUTION ONTO MICROWAVE AND CONVENTIONAL METHOD PREPARED ACTIVATED CARBON FROM TEFF HUSK USING Zncl₂ AS AN ACTIVATED AGENT

BY

JAMES SIMON ABALLA

ADVISOR: Dr. KHALID SIRAJ (PhD)

CO-ADVISOR: BIRTUKAN ADANE(M.Sc.)

A THESIS SUBMITTED TO SCHOOL OF GRADUATE STUDIES JIMMA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE IN PHYSICAL CHEMISTRY.

Supervisor signature of appr	oval for defense	
Advisor	Sign	Date
Dr. Khalid Siraj (PhD)		
Assistant professor		
Department of chemistry		
College of Natural Science		
Jimma University		
Co-advisor		
Mrs. Birtukan Adane (M.Sc.)	
Department of chemistry		
College of Natural Science		
Jimma University		
External examiner:		
Internal examiner:		
<u> </u>		
Head, department:		

ACKNOWLEDGEMENT

First, my appreciation goes to Authors, for he/her ideas, inspirations and guidance towards the actualization of this work. Secondly, my deepest appreciation goes to my advisor Dr Khalid Siraj, Co-advisor Birtukan Adane (M.Sc.) and Demisachew Shitaw (M.Sc.) for their intellectual contributions, constructive, immeasurable assistance and further advice towards the completion of this thesis. I also want to thank Chemistry department, Jimma University for allowing me to use their research laboratory and ICT lab freely. Finally, I extend my warmest appreciation to my postgraduate colleague in physical chemistry department namely: Asrese Dara and others field of chemistry to mention for their individual contributions towards the success of this thesis. Thank you all for your contributions.

Table of Contents

Acknowledgementi
List of tablei
List of figureii
List of abbreviationiv
Abstractv
1. Introduction
1.1 Background of the study1
1.2. Statement of the problem
1.3. Objective of the study
1.3.1. General objective
1.3.2. Specific objective
1.4. Significance of the study
2. Literature review
2.1 Introduction
2.2. Iodine number
2.3. Adsorption kinetics
2.3.1. Pseudo first order
2.3.2. Pseudo second order7
2.3.3. Intraparticle diffusion model
2.3.4. The liquid film diffusion model7
2.3.5. Elovich kinetic model
2.4 Adsorption thermodynamic
2.5 Adsorption isotherm
2.6 Surface characterizations
2.7 Microwave method of carbonization10
2.8 Conventional method of carbonization11
3. Material and method12
3.1 Materials
3.1.1 Chemicals

3.1.2 Apparatus	12
3.1.3 Instruments	12
3.2. Methods	12
3.2.1. Cleaning of Sample containers	12
3.2.2. Digestion of wastewater sample for determining concentration level of Pb(II)	13
3.2.3. Preparation of activated carbon as adsorbent from teff husk	13
3.2.3.1 Method of collected sample	13
3.2.3.2. Activated carbon preparation	13
3.2.3.3. Preparation of stock solution	15
3.2.3.4. Determination of the λ max onto activated carbon prepared from teff husk	15
3.3. Adsorption equilibrium	16
3.3.1 Effect adsorbent dosage	16
3.3.2. Effect of initial Pb(NO ₃) ₂ concentration	17
3.3.3. Effect of contact time	17
3.3.4. Effect of pH	17
3.3.5. Effect of temperature	
3.4. Adsorption Isotherm	18
3.5. Adsorptions kinetic studies	18
3.6. Adsorption thermodynamic Studies	18
4. Result and discussion	19
4.1. Analyzed of parameter that influence adsorption capacities	19
4.1.1. Proximate analysis onto teff husk activated carbon	19
4.2. Determination λ max onto activated carbon prepared from teff husk	20
4.2.1 UV-visible absorption spectrum of carbon on teff husk activated carbon	20
4.3. Characterization of adsorbent	21
4.3.1. XRD diffraction analysis	21
4.3.2. FTIR spectra analysis	23
4.4. Adsorption equilibrium study	26
4.4.1. Effect adsorbent dosage on removal efficiency Pb(II)	26
4.4.2. Effect of initial concentration on efficiency of teff husk activated carbon	27

4.4.3. The effect of contact time on removal efficiency of Pb(II)
4.4.4. Effect of pH on removal efficiency of Pb(II)
4.4.5. Effect of temperature on removal efficiency of Pb(II)
4.5. Adsorption isotherms study
4.6. Kinetic analysis
4.6.3. Intraparticle diffusion model
4.6.4. The liquid film diffusion model
4.6.5. Elovich kinetic model
4.7. Adsorption thermodynamic parameter on removal of Pb(II)
4.8. Comparison of the efficiency of teff husk activated carbon for removal of Pb(II) ions
from the wastewater with the maximums permissible limited in drinking water
4.9. Comparison of adsorption capacity of teff husk adsorbent with other adsorbent
4.10. Desorption experiment
5. Conclusion and recommendation
5.1. Conclusion
5.2. Recommendation
References
Appendix

LIST OF TABLE

Table 1: Proximate analysis of teff husk prepared activated carbon	19
Table 2: Show the changing functional group before and after adsorption onto microw	ave
assisted	24
Table 3: Show the changing functional group before and after adsorption onto conventiona	ıl25
Table 4: Show the isotherm model onto activated carbon	.31
Table 5: all calculated value of kinetic model onto teff husk activated carbon	.36
Table 6: Show the thermodynamic parameter onto teff husk activated carbon	.37
Table 7: Comparisons of adsorption capacity of teff husk adsorbent for removal of Pb(II) i	ons
from aqueous solution with other adsorbent	40

LIST FIGURE

Figure 1: Schematic representation for preparation of activated carbon using conventional
method14
Figure 2: Schematic representation for preparation of activated carbon using Microwave
method15
Figure 3: Calibration plot for the Pb(II) ions at each adsorbent20
Figure 4: X-ray diffractogram for the prepared adsorbent using microwave assisted and
Conventional method. (a) and (b) showing XRD spectrum for conventional method prepared
AC before and after loading Pb^{2+} ions; (c) and (d) showing XRD spectrum for microwave
assisted prepared AC before and after loading Pb^{2+} ions respectively22
Figure 5: FTIR spectrum for microwave-assisted activated carbon; (a) Before adsorption; (b)
After adsorption
Figure 6: FTIR spectrum for conventional method prepared activated carbon; (a) Before
adsorption; (b) After adsorption25
Figure 7: Effect of adsorbent dosage onto AC at temperature = 348 K, initial conce = 0.25
ppm, pH=6 and contact time=20 minute
Figure 8: Show the effect of initial concentration of Pb(II) ions onto at dosage =2 g,
temperature =348 K, contact time =20 minute and pH= 627
Figure 9. Show the effect of contact time onto AC at temperature =348 K, $pH = 6$ dosage =2
g and initial conce =0.25 ppm
Figure 10: Show the effect of pH onto AC and at dosage =2 g, initial conce =0.25 ppm,
contact time =20 minute and temperature = 348 K
Figure 11: Show the effect of temperature onto AC at dosage =2 g, contact time =20 minute,
initial conce = 0.25 ppm, pH= 630
Figure 12: The Freundlich isotherm plot for the removal of Pb(II) ions onto activated carbon
Figure 13: The Langmuir isotherm plot for the removal of Pb(II) ions onto activated carbon32
4.6. Kinetic analysis
Figure 14:(a) show pseudo second order on microwave and (b) on conventional33
Figure 15: (c) Shown pseudo first order on microwave and (d) pseudo first order on
conventional

Figure 16: Plot of intraparticle diffusion the intraparticle diffusion on teff husk activated
carbon
Figure 17: Plot of liquid film diffusion for Pb(II) removal by teff husk activated carbon35
Figure 18: Plots of Elovich model for the Pb(II) ion removal by teff husk activated carbon on
(a) microwave and (b) conventional
Figure 19: show the plot of lnk_d vs 1/T onto microwave activated carbon
Figure 20: Show the plot of lnk_d vs 1/T onto conventional activated carbon
Figure 21: Comparison of the efficiency teff husk activated carbon for removal of Pb(II) ions
from wastewater by MWAC and CMAC with MPL of Pb(II) ions in drinking water =0.01
mg/L and in surface water =0.05 mg/L
Figure 22: Plot of the desorption experiment onto activated carbon

LIST OF ABBREVIATION

AC- activated carbon CMACAA- conventional activated carbon after adsorption CMACBA- conventional activated carbon before adsorption EPA- Environmental protection agents FTIR- Fourier transforms Infrared IQ-Intelligence quotient SMPL- Standard maximums permissible limit MWACAA- microwave activated carbon after adsorption MWACBA- microwave activated carbon before adsorption WWATCMAC-Wastewater after treatment with conventional activated carbon WWATCMAC-Wastewater after treatment with microwave activated carbon WWBTCMAC-Wastewater before treatment with conventional activated carbon WWBTCMAC-Wastewater before treatment with microwave activated carbon WWBTCMAC-Wastewater before treatment with microwave activated carbon WWBTMWAC-Wastewater before treatment with microwave activated carbon WHO-World Health Organization XRD-X-ray diffraction

ABSTRACT

Various agricultural wastes can be used as an adsorbent for heavy metal removal after chemical modification by heating into activated carbon due to increasing it efficiency. Teff husk wastes were considered as low cost, environmentally friendly and easily available materials. Until now, the removal efficiency of Pb(II) ions on activated carbon prepared from teff husk was not reported. Therefore, this work was done in order to evaluated the removal efficiency of Pb(II) ions on activated carbon prepared from teff husk using ZnCl₂ as an activating agent. The activation process was done in order to increase the adsorption capacities for removal of Pb(II) from aqueous solutions. The proximate analysis of adsorbent on microwave were I_2 (805 mg/g), moisture contents (7.83%), ash contents (2.96%), volatile matter (12.4%), fixed carbon (76.81%) and on conventional were I₂ (576 mg/g), moisture contents (9.29%), ash contents (12.56%), volatile matter (20.98%), fixed carbon (57.17%). Activated carbon was characterized by FTIR and XRD, it was determined used UV/visible spectrophotometer. The effect of parameter onto teff husk activated carbon was conducted by range as adsorbent dosage (0.25 g to 3.5 g) initial concentration (0.25 ppm to 5.5 ppm), contact time (5 minute to 30 minute), pH (2 to 14) and temperature (318 K to 358 K). As a result, adsorption equilibrium was adsorbent dosage (2 g), initial concentration (0.25 ppm), contact time (20 minute), pH (6) and temperature (348 K). The best fitted of adsorption isotherms and kinetic model for the adsorption of Pb(II) were selected based on R². Finally, Langmuir isotherms (0.993), pseudo second order (0.993), intraparticle diffusion (0.983), Elovich model (0.909), Liquid film diffusion (0.984) were the best fitted. The thermodynamic parameters on microwave activated carbon were ΔG° (-0.3939 KJ/mol to -16.72 KJ/mol), ΔH° (256.611 KJ/mol), ΔS° (0.858 KJ/K*mol) and on conventional activated carbon were ΔG° (-5.5002 KJ/mol to 9.8179 KJ/mol), ΔH° (81.751 KJ/mol), ΔS° (0.28808 KJ/K*mol). The adsorption capacity of teff husk activated carbon for removal of Pb(II) from aqueous solution is 10.31(mg/g) and it desorption is 85%. The adsorption is chemisorption, particle diffusions, endothermic in nature, randomly motion to the adsorbent and spontaneous in nature. In conclusion, teff husk activated carbon was efficient for removal of Pb(II) ions from aqueous solution and it is recycling process.

Key word: Teff husk, Adsorption, adsorption isotherm, adsorbent, adsorption equilibrium

1. INTRODUCTION

1.1 Background of the study

Lead is a heavy metal, which is absorbable to human body through drinking water in the form of corrosion and plating from cooking material. It is root cause of carcinogenesis, mutagenesis and tetratogenesis to the human [1, 2]

Lead exposure can cause anemia because it inhibits the body's ability to make hemoglobin. Many reports also have shown an association between lead exposure and increases in blood pressure. Lead readily crosses the placenta and there is evidence that exposure to high levels increases the risk of spontaneous abortion, miscarriage and stillbirth. There is also evidence of less strength that fetal lead exposure can increase the risk of reduced birth weighed and premature birth. Human studies indicate the lead may have toxic effects on sperm starting at Pb(II) levels of $40\mu g/L$ [2]

In case of children and fetuses, it is more susceptible than adults are because their bodies are smaller, so the same dose of lead that an adult receives would have a greater effect on a child. In addition to these, the toxicological response can depend on the development of receptors to various chemicals, which developed at various stages. The brain is especially vulnerable during the brain growth spurt, which is the period when the brain undergoes several fundamental changes, like dendritic and axonal growth, synaptogenesis, and rapid myelination [3].

In children, even low levels of exposure can result in reduced IQ, learning disabilities, attention deficit disorders, behavioral problems, stunted growth, hyperactive behavior, impaired hearing, and kidney damage. The incidence of childhood cancer has increased, especially for acute lymphocytic leukemia, brain tumor and Wilm tumor. The last one suspected to be in relation with paternal exposure to lead [4].

At high levels of exposure, a child may become mentally retarded, fall into a coma, and even die from lead poisoning. A level of concern for children is a lead concentration exceeding 10 μ g/L of blood. For adults, the level of concern is a concentration above 25 μ g/L[5].

Since, various methods of treating effluents containing Pb(II) developed such as chemical precipitation, Chemical oxidation or reduction, electrochemical treatment, ion exchange, reverse osmosis, filtration, evaporation recovery and electro coagulation [6, 7]. Though the methods have been significant, still and all it has disadvantages including high-energy requirements, inefficient metal removal, generation of toxic sludge and expensive equipment [8, 9]. In addition to, there is a need to develop efficient and rapid from less cost, environment friendly and easily available material by chemical modification and heating into activated carbon for the removal of Pb(II) from aqueous solution. Until now, the efficiency of Pb(II) removal by teff husk activated carbon from aqueous solution was not investigated. Therefore, this studies was an effort to determine the efficiency of removal of Pb(II) by teff husk activated carbon from aqueous solution. The effects of different parameters such as adsorption equilibrium, adsorption isotherm, adsorption kinetic and adsorption thermodynamic were evaluated. Additionally, the sample was determined using UV/visible spectrophotometer and characterized by XRD, FTIR.

1.2. Statement of the problem

All Living things depend on water. However, human being through different activity could release organic and inorganic effluent containing lead in water; this is great role to polluted water body [10,11]. Lead poisoning in humans body causes severe damage to organ of the body, which result sterility, abortion, stillbirth and deaths [12]. Though lead ion are toxic to human being, there are many agricultural waste used for treatment of heavy metal from aqueous solution in the form of activated carbon, but the removal of lead ions by teff husk activated carbon onto microwave and conventional method was not determined. Therefore, this work was done to focus on the Pb(II) removal using activated carbon prepared from teff husk by tries to answered the following question.

- What was the efficiency of activated carbon prepared from teff husk for remove Pb(II)?
- What kind of adsorption isotherms, kinetics and thermodynamics feasible, proper for adsorption of Pb(II) by activated carbon prepared from teff husk?
- How much amount of Pb(II) adsorb by activated carbon from teff husk using activating agent?

1.3. Objective of the study

1.3.1. General objective

The general objective of this study was to determine the adsorption capacity of Pb(II) on activated carbon prepared from teff husk by using $ZnCl_2$ as an activating agent.

1.3.2. Specific objective

The specific objective of this thesis was:

- To synthesize activated carbon from teff husk by microwave and conventional method using ZnCl₂ as an activating agent for removal of Pb(II) from aqueous solution.
- To evaluate the adsorption capacity of Pb(II) on activated carbon prepared from teff husk.
- To determine the effect of pH, contact time, adsorbent dosage, initial metal ions concentration, and the temperature on prepared activated carbon.
- To investigate the proper adsorption isotherm, kinetics and thermodynamics feasibility for adsorption of Pb(II) from aqueous solution by using teff husk

1.4. Significance of the study

Now a day the world is going to develop new technology for the processing raw material into useful product, which is useful for survivals of human being worldwide. Meanwhile, all the processes are passes through different stage that contains many organic and inorganic compounds. Furthermore, the concentration of Pb(II) ions is constituent in their products as electroplate. For that case, our generation are already affected by Pb(II) ions from different source includes corrosion, industrials effluent etc. Our lives are vastly different now than they would have been before due to various extrinsic factors such as synthetics dyes, increasing industrials, increasing population and other factors, it's too numerous to mention that caused water polluted. Therefore, to safe our future generations the system need to develop, in order to be accessible for everyone. Finally, this method is used:

- For wastewater treatment
- For purification of industrial effluent and adsorbs the corrosion of heavy metal from lead pipe and other water supply.
- In the field of electroplating industry for adsorption of heavy metal concentration from various product

2. LITERATURE REVIEW

2.1 Introduction

Heavy metals represented a large group of chemical elements (> 40) with atomic mass> 50 carbon units [13]. Although there is, no clear definition of what a heavy metal is. Density is in most cases taken to be defining factor. Heavy metals commonly defined, as those having a specific density above $5g/cm^3$ and that are capable of forming polyvalent cations [14-16].Trace elements, which include all the elements in the periodic system except bulk elements and macro minerals best classified in to two categories. Those elements whose essentiality established are accepted standards and those for which proof of essentiality does not exist. By simplest definition an element is essential when meets the following criteria:

- The element must be presence in all tissues of a given animal.
- Its concentration in a given tissue must be constant from one animal to the next.
- Its withdrawals from the diet must lead to a specific deficiency syndrome.
- The deficiency syndrome must be associated with pertinent biochemical changes.
- Syndrome and biochemical changes prevented the administration of the element.

Based on the above criteria, V, Cr, Mn, Fe, Co, Cu, As, Ni, Zn and Mo now considered essential in animals. These metals are an indispensable part of biomolecules, and one third of enzymes need metal ions for their catalytic activity [17]. These are essential micronutrients with a human requirement of no more than a few milligrams per day. However, micronutrients may become harmful when their ingestion rates are too high [18]. In addition, a metal can be toxic or be a micronutrient depending on its chemical form or speciation (e.g. Cr-VI and Cr-III) [17].Other elements have no proven essential functions in humans and are likely to have adverse physiological effects.

Lead (Pb) are well known as toxic even when taken in small amount and have become serious environmental hazards for plants, animals and human.

They are extremely persistent in the environment, they are non-biodegradable and non-thermo-degradable in to less harmful constituents and thus their accumulation readily reaches to toxic levels [19, 20]

2.2. Iodine number

Iodine number is a fundamental parameter used to increase activated carbon performance. It is a measure of the micro pore content of the activated carbon and obtained by the adsorption of iodine from a solution by the activated carbon sample. The mesopores are responsible for the large surface area of activated carbon particles and created during heating technique. It is the mesopores that adsorption largely takes place [21]. Activated carbon referred to as a good adsorbent because of its high degree of porosity and an extensive surface area. The adsorption capacity of activated carbon determined not only by the textural properties but also by the chemical nature of its surface. The surface of activated carbon contains a number of oxygen containing functional groups. The nature of surface area of any activated carbon destroyed by different treatments [22, 23]

2.3. Adsorption kinetics

The kinetics of the system controls the adsorption residence time and reactor dimensions. As a result, predicting the rate at which adsorption take place for a given system is probable the most importance factor in adsorption system design [24]. In order to design an effective model, investigation has been made on the adsorption rate. Several kinetics models (pseudo first order, pseudo-second order, Elovich model, liquid film diffusion and intraparticle diffusion are used to test the experimental data such as the examination of the controlling mechanism of the adsorption process [25].

2.3.1. Pseudo first order

The kinetic model that enable to known whether the adsorbed is only one binding site. This kinetic model can be analysis by the following linear form of model

$$log(q_e - q_t) = \log k_1 - \frac{1}{2.303}t$$

Where q_e and q_t (mg/g) are the amount of adsorbed heavy metals on the adsorbent at equilibrium and at time t (min) and k_1 (1/min) is the rate constant of first-order sorption

2.3.2. Pseudo second order

The kinetic model that enable to known whether the adsorbed is two binding site. This kinetic model can be analysis by the following linear form of model

$$\frac{t}{q_t} = \frac{1}{K_2 q_2} + \frac{t}{q_e} - 2$$

Where q_e and q_t are the amounts of Pb(II) adsorbed onto adsorbent (mg/g) at equilibrium and at time t, and k_2 is the rate constant of pseudo second-order kinetic model

2.3.3. Intraparticle diffusion model

1 /

The adsorption mechanisms on the adsorbent are investigated used intraparticle diffusion model. The applicability fitting of the model shown more into mechanism of Pb(II) ions adsorption onto adsorbent prepared. The parameter on intraparticle diffusion can be analysis by following linear form.

Where K_{id} (mg/g^{1/2}) is the intraparticle diffusion rate constant and Ci is stand for intercept.

2.3.4. The liquid film diffusion model

Liquid film diffusion is used in this study in order to understand, if transports of adsorbate from the liquid phase to solid phase boundary play a role in adsorption process. It can be determine using following formula.

Where f is the fraction attainment of equilibrium, $f = \frac{q_t}{q_e}$, Kid is liquid film diffusion

constant and t is time.

2.3.5. Elovich kinetic model

The Elovich model is another kinetic model that described the adsorption and desorption process of purity metal by a solid in an aqueous medium. The linear form of the Elovich equation is as follows

$$qt = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t - ---5$$

Where α and β are the Elovich coefficients that represented the initial adsorption rate [g/(mgmin)] and the desorption coefficient [mg/(gmin)] respectively

2.4 Adsorption thermodynamic

Adsorption thermodynamic is the parameter, which determines the spontaneities and endothermic or exothermic nature of adsorbent. These parameters actually lead the understanding of better adsorbent which give the randomly motion of adsorbate to adsorbent [26]. The parameters on the adsorption are determined using the following formula below

Where, change in enthalpy (Δ H), entropy (Δ S), Gibbs frees energy (Δ G).

2.5 Adsorption isotherm

Adsorption isotherm is a curve obtained by plotting at constant temperature the quantity of adsorbate against the concentration of the substance (adsorbent). The application of adsorption isotherms is very useful to describe the interaction between the adsorbate and the adsorbent of any system. The parameters obtained from modeling of isotherm data provided important information's for the proper analysis and design of adsorption system. Freundlich and Langmuir equation are the two parameters [27, 28].

Freundlich isotherm model is a empirical model, assuming that adsorptions can occur at infinite number of delocalized site (heterogeneous) and adsorption is physiosorption.

The layer of adsorbed is multilayer. The freundlich model is fitted the experimental data with the linear analysis given below

Where, K_f and 1/n are the measured of adsorption capacity and intensity of adsorption respectively. qe is the amount adsorbed per unit mass of adsorbent (in mg/g). Langmuir isotherm model is a rational model, assuming that adsorption can occur only at finite number of localized site (homogeneous) and adsorption is chemisorptions. The layer is monolayer or one molecule in thickness adsorption. Langmuir model is fitted the experimental data with the linear analysis given below

$$\frac{Ce}{qt} = \frac{1}{Q0b} + \frac{Ce}{Q0} - \dots - 9$$

 Q_o and b are Langmuir constants, which are the measures of monolayer adsorption capacity (in mg/g) and Surface energy (L/mg), respectively

2.6 Surface characterizations

Surface characterization is microscopy techniques, which probe and map the surface and subsurface structure of a material. These techniques can use photons, electrons, ions or physical cantilever probes to gather data about a sample's structure on a range of length scales. Surface characterization of activated carbons in terms of functional groups presence at the surface is a quite complicated task. Elemental constituents of the carbon surface can be finding out quantitatively and qualitatively with the help of some easily and convenient instrumental techniques such as XRD. However, these techniques are not enabling to give any information about the surface functional groups. Hence, the results obtained with the help of these tests cannot treat as the reflection of surface chemistry [19]. On other hand, surface functional group is an important characteristic of any activated carbon. To know the surface functional group Fourier transforms infrared (FTIR) spectroscopy technique have been use since its introduction, FTIR spectroscopy has found a wide application to both qualitative and quantitative analysis of the carbon materials[25]

2.7 Microwave method of carbonization

Microwaves are a technique designed to convert applied energy into heat by electric component of the wave with charge particles in the material. Broadly, microwave is the component electromagnetic spectrum in the range from 300 MHz to 300 GHz, (λ =1 mm to100 cm), which lie in the segment between infrared and radio wave. Alternatively, microwaves can supply energy to carbon particles, and this energy is converted into heat within the particles themselves by dipole rotation and ionic conduction, and, in fact, microwave heating has been recently employed for the preparation of AC[29]. Junior et al. synthesized a highly porous AC from macadamia nut endocarp by chemical activation with ZnCl₂ via microwave radiation [30]. Njoku et al. also introduced a microwave induced activation process to prepare a high-surface area AC from rambutan peel [31]. Hesas et al. revealed AC production from oil palm shells through microwave-induced ZnCl₂ activation [32].

The microwave technique means that it is possible to produce AC easily and quickly, while also providing benefits over conventional heating, such as minimizing of oxidize, short treatment time, low energy cost, high heating rate, selective heating, and a controllable heating process [33, 34]. All recent reports have validated the use of a microwave- induced activation process, citing faster activation rate and higher carbon yield. Therefore, microwave heating is rightly considers as a viable alternative for conventional heating methods.

2.8 Conventional method of carbonization

Conventional methods are advice that produces energy using electric for recovering process that has the potential to generate char, and steam as by-products [36]. A thermal treatment of the precursor materials removes the moisture and the volatile organic matter contents of the biomass and remains with solid. The remaining solid char shows different properties than the parent's precursor biomass materials. The remarkable differences observed in the materials are mainly in porosity, surface area, and pores structures such as microporous, mesoporous and macro porous, and physicochemical properties such as composition, elemental constituents, ash and the volatile matter contents of the precursor biomass. During carbonization, most of the non-carbon elements such as oxygen, hydrogen, nitrogen and sulphure are eliminated as volatile gaseous products by the pyrolytic decomposition of the source raw material. The residual elementary carbon atoms group themselves into stacks of aromatic sheets cross-linked in a random manner.

3. MATERIAL AND METHOD

3.1 Materials

3.1.1 Chemicals

The following chemicals were used during this study:

ZnCl₂,95.99% (Riedeldehaen,Germany), HCl,37% (Riedeldehaen,Germany), NaOH, 35.5% (SigmaAldrich,USA), KI, 25% (Mumbai,india),I₂,23% (Mumbai,india), Starch, 97% (Riedelde,Germany), Pb(NO₃)₂, 95.99% (Riedel-de Haen, Germany), Na₂S₂O₃, 98% (FINKEM, England)

3.1.2 Apparatus

The apparatus used during this study were plastic bottle, volumetric flask, conical flask, Mortar and pestle, Electronic balance, Measuring cylinder, Burret and pippet, Magnetic stirred and cuvett

3.1.3 Instruments

The instrument used for this studies were:

Sanyo 800W compact microwave (EM-S1053,china), Thermostatic water bath (Grant GLS400,England),UV/Visible spectrophotometer single beam (6705 jenway,UK) 304-stainless steel (SEAL,franch) Hot plate (CB162,UK), pH meter (ATC 353,UK) Sieve (ASTME11,UK), X-ray diffraction (Shimadzu,japan),FT-IR (Shimadzu,japan)

3.2. Methods

3.2.1. Cleaning of Sample containers

A sample container was cleaned in order to avoid contaminant with interferents. This is of particular importance when determined trace or ultra trace analyses levels. Accordingly, the following cleaning sequence has been performs to be adequately minimizing contamination in the sample bottle. At the beginning, plastic bottle was washed with distill water followed by H_2O :HNO₃ and finally rinsed with H_2O : HCl.

3.2.2. Digestion of wastewater sample for determining concentration level of Pb(II)

The entire samples was acidified at the time of collection with 2 mL conc.HNO₃.Then 100 mL of well-mixed acidified sample were measured into a 125 mL beaker and to the sample 5 mL of conc.HCl was added. The sample was heated on a hot plate in a well-ventilated hood until the volume was reduced to 20 mL, the sample were cooled and filtered through a suitable filter into 100 mL volumetric flask and was adjusted to volume. Finally, the samples were determined using UV/visible spectrophotometer.

3.2.3. Preparation of activated carbon as adsorbent from teff husk

3.2.3.1 Method of collected sample

Teff husk was collected randomly from Jimma zone, kebele 05 Ginjoo Guduro were mill available. It was transport to Jimma University, analytical and physical chemistry laboratory research.

3.2.3.2. Activated carbon preparation

The collected teff husk was washed repeatedly with tap water. Consequently, rewashed with distilled water, this husk was sun dried for 4-day and kept again at 105 0 C oven for 2-hour. Therefore, it was grinded and sieved to 250-mesh size. For carbonization, half portion of powder was loaded in stainless steel and put on hot plate. As a result, the temperature was ramp from room temperature to 450 0 C for 5 hour. The obtained charred materiel was soaking into 95% of ZnCl₂ anhydrate with an impregnation of 1:2(w/w %) for 24 hours in order to activate. The resultant activated carbon was kept in 20 mL concentration HCl solution for 24 hour followed by washing with distilled water repeadly until the pH was nearly constant. The washed AC was dried again at 105 0 C oven for 2 hour. Finally, the obtained AC was stored in airtight bottle for further use by labeling the sample as conventionally chemical activated carbon.

Secondly, half of the powder was kept in conical flask (Approx) and installing onto glass tray in Sanyo 800W compact microwave. For instant, the heating time was set to 3-minute and adjusted the input power to 1200W, based on the technique and run the system until the time was complete. After that, carbon powder was soaked into 95% of ZnCl₂ anhydrate with an impregnation of 1:2(w/w %) for 24 hour to activate. The resultant activated carbon was kept in 20 mL HCl solution for 24 hour, and washing repeadly with distilled water until the pH was nearly constant. The obtained AC dried again at 105 $^{\circ}$ C oven for 2 hour. Lastly, it was stored in airtight bottle for further use by labeling the sample as microwave-assisted chemically activated carbon [35]



Figure 1: Schematic representation for preparation of activated carbon using conventional method



Figure 2: Schematic representation for preparation of activated carbon using Microwave method

3.2.3.3. Preparation of stock solution

1000 mg/L stock solution of Pb^{2+} ions was prepared by dissolving 1.5 g $Pb(NO_3)_2$ in 1000 mL volumetric flask and made up to calibration mark. For various experiment, serial dilution were made from stock solution using distilled water.

3.2.3.4. Determination of the $\lambda \max$ onto activated carbon prepared from teff husk

Determination of λ max onto microwave and conventional method were carried out by weighing 2 g of activated carbon from each and put in different conical flask. 20 mL of stock solution was added to each conical flask. All conical flasks were stir at room temperature then were shaken at 150-rpm. The solution was filtered with watmann filter paper. Finally, it was calibrated from 200 nm-400 nm

3.3. Adsorption equilibrium

The adsorption experiment were conducted in a set of 250 mL volumetric flask containing 2 g of adsorbent dosage and 20 mL of Pb(II) ions solution was added to each. Initial concentration were various amount of Pb(NO₃)₂ and fixed 2 g of adsorbent to each. The flasks were agitated in a thermostatic shaker at 150-rpm at room temperature until the equilibrium was reached. Pb(II) concentration in the supernatant solution was measured using UV-Visible spectrophotometer. Pb(II) uptake at equilibrium q_e(mg/g) and percentage were determined by formula respectively



Where C_0 and Ce (mg/L) are liquid phase concentrations of Pb(II) at initial and equilibrium, respectively V (L) is the volume of the solution and W(g) is the mass of adsorbent[35].

3.3.1 Effect adsorbent dosage

Amount of activated carbon from 0.25, 0.5, 1, 1.5, 2.0, 2, 2.5, 3.0, 3 and 3.5 g were accurately weighed from sample and transferred into different beakers (25 mL). 20 mL of $Pb(NO_3)_2$ prepared stock solutions was add to each beaker. The pH of the solution was adjusted to constant by adding 0.1M HCl. All beakers were tightly cover with aluminum foil and shaken at 150-rpm. At the end of agitation, the suspension was filtered using Whatman filter paper. The solution was analyzed using UV/visible spectrophotometer.

3.3.2. Effect of initial Pb(NO₃)₂ concentration

Effect of initial concentration was determined by prepared stock solution from 0.25,0.5, 1, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 and 5.5 ppm of $Pb(NO_3)_2$ into conical flask (25 mL), then 2 g of activated carbon was measured from the sample into different beakers while labeled. Then each prepared stock solution was placed to labeled beakers.

The pH of the solution was adjuste to constant by added 0.1M HCl. The suspension was agitated at 150-rpm on a shaker by keeping other parameters constant. The sample was filter through filter paper. Pb^{2+} concentration in the filtrate were analyzed using UV/Visible spectrophotometer.

3.3.3. Effect of contact time

2 g of activated carbon was weighed accurately from the sample and introduced into different conical flasks (25 mL). 20 mL of $Pb(NO_3)_2$ prepared stock solutions were added' to each activated carbon. The pH was adjusted to constant by adding the solution of 0.1M HCl. The flask was tightly covered with aluminum foil and shaken for 5, 10, 15, 20, 25 and 30 minute at speed 150-rpm by keeping the other parameter constant, the suspension was filtered using Whatman filter paper. Then the solution was analyzed using UV/visible spectrophotometer.

3.3.4. Effect of pH

2 g of activated carbon was weighed accurately from the sample and introduced into different conical flasks (25 mL). 20 mL of $Pb(NO_3)_2$ prepared stock solutions were added' to each activated carbon. The pH was adjusted from 2 to 14 by adjusting the solution with 0.1M HCl or 0.1M NaOH .The flask was tightly covered with aluminum foil and shaken for 20 minute at speed 150-rpm by keeping the other parameter constant, the suspension was filter using whatman filter paper. Then the solution was analyzed using UV/visible spectrophotometer

3.3.5. Effect of temperature

2 g of activated carbon was weighed and placed into different conical flask (25 mL). Then 20 mL of stock solution prepared from of $Pb(NO_3)_2$ was added to each sample. The pH was adjusted to constant value by adding 0.1M HCl .The flask were agitated at speed of 150-rpm and kept at 45 0 C, 55 0 C, 65 0 C, 75 0 C and 85 0 C temperature by kept the other parameters constant. The suspension was filter using whatman filter paper. Then, solution was analysis by UV/visible spectrophotometer.

3.4. Adsorption Isotherm

20 mL of adsorbate solution was taken from prepared stock solution of $Pb(NO_3)_2$, put into different conical flask (25 mL) containing 2 g of activated carbon and then it was shaken at 150-rpm by keeping the other parameters constant. The flask was being agitated at different concentration and filtered by whatman filter paper followed by calibrated using UV-visible spectrophotometer.

3.5. Adsorptions kinetic studies

20 mL of adsorbate solution was taken from prepared stock solution of $Pb(NO_3)_2$, put into different conical flask (25 mL) containing 2 g of activated carbon and then it was shaken at 150-rpm by keeping the other parameters constant. The flask was being agitated at 5, 10, 15, 20, 25, 30 minute and filter by whatman filter paper followed by calibrated using UV/visible spectrophotometer.

3.6. Adsorption thermodynamic Studies

20 mL of adsorbate solution was taken from prepared stock solution of $Pb(NO_3)_2$, put into conical flask(25 mL) containing 2 g of activated carbon. It was shaken at 150-rpm by keeping the other parameters constant and various temperature from 45 $^{\circ}C$, 55 $^{\circ}C$, 65 $^{\circ}C$, 75 $^{\circ}C$ and 85 $^{\circ}C$ then filter by whatman filter paper followed by calibrated used UV/visible spectrophotometer.

4. RESULT AND DISCUSSION

4.1. Analyzed of parameter that influence adsorption capacities

4.1.1. Proximate analysis onto teff husk activated carbon

The sample were found to be less in moisture content, ash content, volatile matter and high fixed carbon, iodine number for microwave activated carbon. This may be the heating effect remove the light organic compound and created the maximum pores on the surface of the adsorbent. During heating process, microwave methods start heat from the inner part of the sample to outer part and then converted powder into charcoal with in 3 minute by releasing more gas from the sample. In conventional method burning started from the surface of the sample and not burn completely after 5 hour. According to [36] much heating process, caused organic substance unstable as a result break their bond. During activation process volatile matter are released as a gas and liquid then leaving the material with high carbon content and iodine number. The maximum amount of ash content, moisture content, and volatile matter can reduce the overall activity of the activated carbon and lower the efficiency of activated carbon [36]. Therefore, proximate analyses clearly indicate that, high fixed carbon, iodine numbers are successfully increased the efficiency of teff husk activated.

Parameter	MWAC	CMAC
Fixed carbon%	76.81	57.17
Moisture content%	7.83	9.29
Ash content%	2.96	12.56
Volatile matter%	12.4	20.98
Iodine number(mg/g)	805	576

Fable 1: Proximate	e analysis c	of teff husk	prepared	activated	carbon
---------------------------	--------------	--------------	----------	-----------	--------

4.2. Determination λ max onto activated carbon prepared from teff husk

4.2.1 UV/Visible absorption spectrum of carbon on teff husk activated carbon

UV-visible spectrophotometer is the electronic device, which are used UV-Visible electromagnetic spectrum to detect the concentration of analyte in the sample molecule at a certain wavelengths. In this studies, the sample was determined before and after adsorption in order to understand the light absorb by the concentration of Pb(II) at certain wavelength. Figure 3: Shows the dependence of the absorbance vs wavelength in UV region. The spectrum shows that, less absorbance of incident light in all wavelengths before adsorption, which indicated that the presence of only concentration of adsorbent. After adsorption there is maximum absorbance at 300 nm for microwave activated carbon this implied that during adsorption there is electron transition between π – π * in the range of UV spectrum that lead to sorbed. While in conventional, maximum absorbance is at 250 nm, which indicated that there is decreasing of electron transition in conventional activated, which indicated that less interaction of adsorbed [37].



Figure 3: Calibration plot for the Pb(II) ions at each adsorbent

4.3. Characterization of adsorbent

4.3.1. XRD diffraction analysis

XRD diffraction is the tool, which have been used in order to understand the transformation of amorphous to crystalline of adsorbent if the interaction between adsorbent and adsorbate took place. This sample was evaluated as before adsorption and after adsorption to understand whether there is formation of crystal. As show in Figure 4, before adsorption both contain broadband from $2\theta = 10$ to 30, which is well defined amorphous for the quality of adsorbent. On the other hand, three peaks at different angle; this may indicate that the presence of high electron density in the sample [38].

However, after adsorption, more change from broadband to sharp peak in microwave chemical assisted, which presence the transformation of amorphous to crystalline according to [39]. Moreover, the peaks, which indicate the presence of the electron density, are reducing in microwave chemical assisted and produced other intend peak. This may be the interaction between the lone pair and cations on the adsorbate caused the electron density to reduce and produced the crystal. This implied the presence of Pb(II) on the surface of adsorbent[40]. Secondly, conventional activated carbons contain few sharp peaks. This stated that the concentration of Pb (II) on the surface of adsorbent is less crystal [41]. Another important thing is the maximums intensity may indicate that higher interaction of adsorbate [42]



Figure 4: X-ray diffractogram for the prepared adsorbent using microwave assisted and Conventional method. (a) and (b) showing XRD spectrum for conventional method prepared AC before and after loading Pb^{2+} ions; (c) and (d) showing XRD spectrum for microwave assisted prepared AC before and after loading Pb^{2+} ions respectively.

4.3.2. FTIR spectra analysis

FTIR is the machine, which is used infrared, light to vibrate or rotated the functional group presence in the sample. In this study, it was characterized as before and after adsorption to differentiated whether the presence of Pb(II) on the surface of adsorbent lead to other organometalic compound which cannot be vibrated or rotated by the infrared light. According to [43] on perusal of FT-IR; the functional group in Table 2 recorded from Figure 5, as for microwave activated carbon before and after adsorption of lead ions. It is noted that the band at; 891.05, 833.19, 2318.28, 2109.98, 3186.18.3278.76 pertained to -C-H, C-C, $-C \equiv N$, $-C \equiv C^{-}$, $\equiv CH$ and $=CH_2$ organic compound respectively deformation were not observed after adsorption this indicated that the interaction between each functional group with Pb(II) ions are change to other compound which can't be vibrated or rotated by infrared radiation. On other hand the band at 2727.16, 1458.08, 2318.23 pertained to -HS,-C=C, C-C-H organic compound are changed to 2677.01, 1461.94, 2314.42 respectively which implied that during interaction Pb (II) ions with organic compound in the sample there is bending and stretching of the bond molecule in sample.

Secondly, FTIR spectra in the Table 3, are recorded from Figure 6, for conventional activated before and after adsorption of lead ions. It is recorded that the band at 3186.18, 1600.81 pertained to $\equiv CH$ and C=C are not seen after adsorption, indicated that formation of functional group during interaction cannot be rotated or vibrated by infrared radiation. However, the band at 2677.01 pertained to -HS increased to 2680.87 which meaning during adsorption there is changing of bond angle and bond length



Figure 5: FTIR spectrum for microwave-assisted activated carbon; (a) Before adsorption; (b) After adsorption

Table 2: Show the changing functional group before and after adsorption onto microwave assisted

Molecule	peak before	Peak after adsorption
	adsorption	
-C-H	891.05	No peak
C-C	833.19	No peak
-C=C	1458.08	1461.94
-C-O	1072.35	1072.35
$\equiv CH$	3186.18	No peak
С-С-Н	2318.23	2314.42
$=CH_2$	3278.76	No peak
-CH-	2923.88	2923.88
-SH	2727.16	2677.01
$-C \equiv N$	2318.28	No peak
$-C \equiv C -$	2109.98	No peak



Figure 6: FTIR spectrum for conventional method prepared activated carbon; (a) Before adsorption; (b) After adsorption

Table 3: Show the changing functional group before and after adsorption onto conventional

Molecule	Peak before adsorption	Peak after adsorption
$\equiv CH$	3186.18	No peak
-HS	2677.01	2680.87
$-C \equiv N$	2322.13	2310.56
$-C \equiv C -$	2194.84	2167.84
C=C	1600.81	No peak
-C-F	1072.35	1072.35
-C-Cl	721.33	721.33
C-0,C-N	1311.08	1311.08

4.4. Adsorption equilibrium study

4.4.1. Effect adsorbent dosage on removal efficiency Pb(II)

Effects of adsorbent dosage on teff husk activated carbon were range from 0.25 to 3.5 g. With increasing of dosage from 0.25 g to 1.5 g, the percentage removal of Pb(II) ions is increase from 10% to 60% rapidly as shows in the Figure 7. This may be due to the availability of more active site on the surface of both adsorbent. As the amount of dosage increased from 1.5 g to 2 g, the adsorption of Pb(II) ions is slowly increased upto 80% removal, beyond 80% the removal was observed constant. As a result no more adsorption, this is because the limit amount of Pb(II) ions on the surface of adsorbent. This observation is agree with reported in literature for the adsorption of Pb(II) ions by different material [44]



Figure 7: Effect of adsorbent dosage onto AC at temperature = 348K, initial conce = 0.25ppm, pH=6 and contact time=20 minute

4.4.2. Effect of initial concentration on efficiency of teff husk activated carbon

The effect of initial concentration was studies in the range of concentration of lead (II) ions from 0.25 to 5.5 ppm, and then 2 g of adsorbent was kept in each. According to Figure 8, as the concentration of Pb(II) increase from 0.25 to 0.5 ppm, the percentage removal is decrease from 90% to 88% for conventional and 95% to 90% for microwave. This is because, the active sit on adsorbent can detect the smallest concentration of Pb(II) from aqueous solution. As the amount of Pb(II) ions increase from 0.5 to 5.5 ppm, there is decreasing of adsorption of pb(II) ions . The decreasing may be due to the limited number of available active sites on the surface of AC to accommodate higher concentration of Pb(II) ions[45].



Figure 8: Show the effect of initial concentration of Pb(II) ions onto at dosage =2 g, temperature =348 K, contact time =20 minute and pH= 6

4.4.3. The effect of contact time on removal efficiency of Pb(II)

The effects of contact time on teff husk activated carbon are shown in Figure 9. From 5 to 15 minute, the rate of removal of Pb(II) ions was increased from 20% to 60% for microwave and 20% to 50% for conventional. With increasing the time from 15 minute to 20 minute the percentage removal slower from 60% to 70% for microwave while 50% to 60% for conventional, due to the different available of more active site on the surface created by heating technique. Beyond 20 minute equilibrium established, this might be due to the concentration of adsorbate in the pores and concentration of adsorbate in the bulk coexists. Similar results have been report in literature for the removal of metal ions [46] by adsorbent



Figure 9. Show the effect of contact time onto AC at temperature =348 K, pH = 6 dosage =2 g and initial conce =0.25 ppm

4.4.4. Effect of pH on removal efficiency of Pb(II)

The effect of pH was range from 2.0 to 14.0 as shown in Figure 10. On the removal of Pb(II) ions by teff husk activated carbon from aqueous solution. As the pH, value increase from 2 to 6 there is increment of percentage removal from 10% to 70%, this is due to the repulsing of H^+ from acid and cations from adsorbate create the highly increment of pH. Beyond pH= 6, no adsorption was observed; this may be due to the formation of metal hydroxide. As a result, adsorption and precipitation occur simultaneously and adsorption was not exactly differentiated [47].



Figure 10: Show the effect of pH onto AC and at dosage =2 g, initial conce =0.25 ppm, contact time =20 minute and temperature = 348 K

4.4.5. Effect of temperature on removal efficiency of Pb(II)

The adsorption of Pb(II) onto activated carbon was increased from 40% to 70% when temperature increase from 318 K to 338 K. This due to the mobile of adsorbate from bulk to the surface of adsorbent increased. As the temperature increased from 338 K to 358 K, caused adsorption capacity remain constant according to Figure 11. This is due the mobile of adsorbate on the pores and adsorbate in the bulk reached at equilibrium [48].



Figure 11: Show the effect of temperature onto AC at dosage =2 g, contact time =20 minute, initial conce = 0.25 ppm, pH= 6

4.5. Adsorption isotherms study

The results of linear analysis from Figure 12 and 13 are summarized in Table 4. This result are corresponding the isotherm parameter and their correlation coefficient (\mathbb{R}^2) for each isotherm. According to correlation coefficient, the Langmuir is fitted this experimental data with linear analysis. This result indicated that the adsorption of adsorbent is chemisorption; monolayer and all active site are at equilibrium.

Furthermore, the essential characteristics of the Langmuir isotherm have been described' by separation factor, R_L , which is define as the following equation [50-52].

The separation factors, R_L indicated the shape of isotherm and nature of adsorption process as given below

R _L value	Nature of the process	
R _L >1	unfavorable	
$R_L=1$	Linear	
R _L <1	Favorable	
R _L >0	Irreversible	

 Table 4: Show the isotherm model onto activated carbon

Model	Isotherm parameter	MWAC	CMAC		
Langmuir	Q _m (mg/g)	10.31	9.41		
	K _L (L/mg)	1.564	0.076		
	R _L	0.610	0.929		
	R^2	0.993	0.837		
Freundlich	n	1.38	3.27		
	$K_{id}(mg/g)(L/mg)^{1/n}$	4.63	2.26		
	R^2	0.912	0.826		



Figure 12: The Freundlich isotherm plot for the removal of Pb(II) ions onto activated carbon



Figure 13: The Langmuir isotherm plot for the removal of Pb(II) ions onto activated carbon

4.6. Kinetic analysis

Pseudo second order is the kinetic model that enable to known whether the adsorbed is two binding site [54]. Result of pseudo second order obtained from Figure 14a and 14b are given Table 5. This kinetic model can be analysis by the following linear form of model The plot of $\frac{t}{qt}$ Vs t may give R² (0.993), which implied that the accepted of flow

of rate.



Figure 14:(a) show pseudo second order on microwave and (b) on conventional

Pseudo first order the kinetic model that described whether the adsorbed site only one site [55]. This can be obtained from the linear plot of logqe/qt versus t show in the Figure 15c and 14d. The obtained values from the plots were given in Table 5



Figure 15: (c) Shown pseudo first order on microwave and (d) pseudo first order on conventional

4.6.3. Intraparticle diffusion model

This can be evaluating from the slope of the linear plots of qt vs $t^{1/2}$. The q_t is the amount of solute adsorb per unit weighed of adsorbent per time (mg/g) and $t^{1/2}$ the half adsorption time (g/hmg). The intercept of the plots indicated the boundary layer effect. The larger the intercept is the great contribution to the surface of the sorption. As shown in Figure 16, if the q_t vs $t^{1/2}$ is linear and passes through the origin, the intraparticle is particle diffusion were as if not passes through the origin the intraparticle diffusion is film diffusion according to [56, 57]. The calculated value of intraparticle are show in Table 5.



Figure 16: Plot of intraparticle diffusion the intraparticle diffusion on teff husk activated carbon

4.6.4. The liquid film diffusion model

The liquid film diffusion of $-\ln(1-f)$ versus t was also use for investigation of transport of adsorbate from bulk to the surface of adsorbent. The value in Table 5, are calculate from the plot of the Figure 17. The film diffusion parameter were obtained and given the intercept Pb(II) on adsorbent. Hence, the intercept values were higher than zero, but closer to origin, which indicated that the significant of liquid film of the adsorption process, similar to the report in [58]



Figure 17: Plot of liquid film diffusion for Pb(II) removal by teff husk activated carbon

4.6.5. Elovich kinetic model

The Elovich coefficients were calculated from the plots q_t versus lnt. As show in Figure 18, The Elovich coefficients α and β which all calculated from slope and intercept were given in Table 5. The correlation coefficients of the Elovich plots were satisfactory on activated carbon, which indicated, that the suitability of the Elovich on teff husk activated carbon [60]



Figure 18: Plots of Elovich model for the Pb(II) ion removal by teff husk activated carbon on (a) microwave and (b) conventional

Kinetic model	Parameter	onto MWAC	onto CMAC	
Pseudo first order	k ₁ (1/min)	0.0894	1.626	
	Qe(mg/g)	1.297	1.33	
	\mathbb{R}^2	0.932	0.935	
Pseudo second order	k ₂ (g/mgmin)	1.669	0.0178	
	Qe(mg/g)	0.759	29.41	
	\mathbb{R}^2	0.993	0.938	
Intraparticle diffusion	$K_{id}(mg/gmin^{1/2})$	0.052	0.243	
	C(mol/kg)	0.058	-0.328	
	\mathbb{R}^2	0.983	0.939	
Liquid film diffusion	K _{id} (mg/g)	0.072	0.09	
	b(g/L)	0.656	0.661	
	R^2	0.984	0.849	
Elovich model	$\alpha_{(mg/(gmin))}$	3.47	1.72	
	β (g/min)	0.234	2.22	
	\mathbb{R}^2	0.909	0.785	

Table 5: all calculated value of kinetic model onto teff husk activated carbon

4.7. Adsorption thermodynamic parameter on removal of Pb(II)

The values of thermodynamic parameter in Table 6 were obtained from the plot of lnk_d vs 1/T that is shown in the Figure 19 and 20. The increasing positive value of ΔH indicated that, Process is endothermic in nature [61]. The increasing positive value for ΔS , suggesting that during adsorption process at the interface, the degree of freedom of adsorbate to word the adsorbent is the most favorable and increase diffusion rate of adsorbate across the external bounder layer and internal pores of adsorbent on AC. The rapid increment negative value of ΔG , is better spontaneous according to [62]

Adsorbent	Temperature (K)	K _d (L/g)	∆G (KJ/mol)	ΔH (K J/mol)	∆S (KJ/K*mol)	\mathbf{R}^2
	318	1.171	-0.3939			
	328	2.221	-2.01			
MWAC	338	13.806	-6.72	256.611	0.858	0.944
	348	165.2	-14.47			
	358	456.01	-16.72			
	318	9.21	-5.5002			
CMAC	328	14.5	-6.7437			
	338	18.5	-7.3509	81.751	0.288	0.873
	348	26.6	-8.4886			
	358	36.61	-9.8179			

Table 6: Show the thermodynamic parameter onto teff husk activated carbon



Figure 19: show the plot of lnk_d vs 1/T onto microwave activated carbon



Figure 20: Show the plot of lnk_d vs 1/T onto conventional activated carbon

4.8. Comparison of the efficiency of teff husk activated carbon for removal of Pb(II) ions from the wastewater with the maximums permissible limited in drinking water

As shown in Figure 20, Lead concentrations in wastewater was found higher than the maximum permissible limit of lead in drinking water according to WHO guidelines and EPA. This could be due to a result of runoff, city street runoff, construction sites, discharging of organic compound into environment. After treatment process the concentration of lead reduced to less than the maximum permissible limit during in microwave activated carbon whereas conventional does not detect the concentration of heavy metal less than the standard. Finally, the efficiency of teff husk activated carbon can reduced the level of heavy metal in wastewater.



Figure 21: Comparison of the efficiency teff husk activated carbon for removal of Pb(II) ions from wastewater by MWAC and CMAC with MPL of Pb(II) ions in drinking water =0.01 mg/L and in surface water =0.05 mg/L

4.9. Comparison of adsorption capacity of teff husk adsorbent with other adsorbent

Adsorption capacity is the ability of the active site on the surface, which required the maximums amount of of Pb(II) ions from aqueous solution. In these studies, the capacities of lead(II) ions on adsorbent from aqueous solution were comparing with other adsorbent. As the adsorption capacity of other adsorbent are given in Table 7, the capacity on teff husk activated carbon is 10.31 mg/g of Pb(II) from aqueous solution, this may be due to the heating technique created active site on the surface of adsorbent. It is better as compared to baobab fruit, china clay and wollastoninte [63, 64]. However, a Ceiba pantandra hull is null [65]. But capacity of Pb(II) ions onto teff straw from aqueous solution is 17.5 mg/g adsorption capacity[66], this may be due to different factor including activating agent used, impregnations ratio and nature of different part of teff. But,. Therefore, teff husk are good alternative adsorbent for removal of Pb(II) from aqueous solution.

Table 7: Comparisons of adsorption capacity of teff husk adsorbent for removal of Pb(II) ions from aqueous solution with other adsorbent

Activated carbon	Q _m (mg/g)			
Baobab fruit	7.65			
China clay	0.415			
Wollastonite	0.308			
Ceiba pantandra hulls	-			
Teff straw	17.5			
Teff husk	10.31			

4.10. Desorption experiment

Desorption is the process whereby the adsorbent is reused by recovered of metals using HNO₃ or HCl as desorbing agent [67]. In this study, HCl was used as desorbing agent for desorption of Pb(II) from adsorbed. The quantitative recovered of lead and recycling of pure carbon was obtained by plotted Desorption vs HCl concentration. Desorption of Pb(II) ions by HCl was approached to 85% as shown in Figure 22.





Figure 22: Plot of the desorption experiment onto activated carbon

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

In this paper, the activated carbon prepared from teff husk were determined using UV/visible spectrophotometer, characterized by; FTIR and XRD to evaluated changing concentration, changing functional group and formation of crystal after adsorption respectively. According to correlation coefficient ($r^2=0.993$) obtained from the experimental data, Langmuir isotherm model was fitted with this adsorption. The adsorbent was 10.31 mg/g adsorption capacity for removal of Pb(II) ions from aqueous solution by chemisorptions process and 85% of desorption process. In conclusion, teff husk activated carbon as an alternative for removal of Pb(II) ions from aqueous solutions.

5.2. Recommendation

Technology is going on worldwide in order to survive human being. This is great role for water pollution due to various effluent discharges in water bodies, which contain the concentration of organic and inorganic heavy metal. As a result, human being may affect by Pb(II) ion direct or indirectly. Therefore, in this paper it would be recommend that; the rule and regulation need to be formulate by government to used activated carbon for cleaning the deposited of heavy metal concentration on the surface of other substance: case of water pipe and cooking materials for safe the future generation. Secondly, the knowledge of activated carbon needs to provide for the society in order to be accessible for everyone at home.

REFERENCES

- [1].Enb, A.; Abou, M.A.; Abd-Rabou, N.S.; Abou-Arab, A.A.K.; and El-Senaity, M.H. Chemical composition of raw milk and heavy metals behavior during processing of milk products, Global Veterinaria.2009, 3(3), 268-275
- [2].Spivey, M.R .Assessment of cadmium, lead and vanadium status of large animals as related to the human food chain, food and drug administration Washington. D.C. Journal of animal sci. 2004, 65, 1744-1752
- [3].Agneta, O.; Palminger, I.; Sundberg, J.; Petersson, K. Risk assessment in relation to neonatal metal exposure. Analyst .1998, 123, 19–23.
- [4].Vilena, K.; Ruzica, R.; Aleksandra, F.; Veda, M.; Martina, P. Lead acetate genotoxicity in suckling rat biological. J of Hazard .2004, 59,779-785.
- [5].Canfield, R.L.; Henderson, C. R.; Cory-slechta, D. A.; Cox, C.; Jusko, T. A.; Lanphear,
 B. P. Intellectual impairment in children with blood lead concentrations below 10 micro per deciliter. New England, Journal of Medicine. 2003, 348, 1517–1526.
- [6].Esalah,M.E.Removal of lead,cadmium and zinc from aqueous solution by precipitation with sodium di-(n-octyl)phosphinate.Canadian Journal of Chemical Engineering, 2000,78(5), 948–954.
- [7].Amer, F. I.Adsorption of lead,zinc and cadmium ions on polyphosphate-modified kaolinite clay. Journal of EnvironmentalChemistry and Ecotoxicology.**2010**, 2(1),1–8.
- [8].Miebaka,N.O.Chromium (VI) adsorption rate in the treatment of liquid phase oil based drill cuttings. African Journal of Environmental Science and Technology.2008,2(4),68–674.
- [9].Ahmed, T. Y.Sorption behaviour of lead(II) ions from aqueous solution onto haro river sand. Adsorption Science and technology.2006, 24, 6, 475–486.
- [10].Manahan, S. Environmental Chemistry, Brooks/Colei California, USA.1984.
- [11].Subramaniam, K.S.; C, J. Lead contamination of drinking water, J. Environ. Sci. Health.1991,54, 29-33.
- [12].Goyer, R.A.; C. Metallic Contamination and Human Health, Lee D.H.K. (ed.). New York and London.1972 (academic press)

- [13].Galiulina.R.As, R.F.; Bashkin, V.N.; Galiulina.R.A. Kucharski, R. Airborne soil contamination by heavy metals in Russia and Poland, and its remediation: Land contamination & Reclamation. 2002, 10:179-187
- [14].Foulkes, E. Transport of toxic heavy metals across cell membrane: Society for Experimental biology and medicine.2000, 223, 234-240
- [15].Cruz, G.; Din, Z.; Feri, D.; Ballooning, M.; Gonzales, G.; Navidad, M.; Schlaaff, M.F.; Winter, J. Analysis of toxic heavy metals (Arsenic, Lead, and Mercury) in selected infant formula milk commercially available in the Philippines by AAS. International, scientific research Journal. 2009, 1, 40-51.
- [16].Lars, J. hazards of heavy metal contamination: department of epidemiology and public health, imperial college, London, UK.British medical bulletin. 2003, 68, 167–182.
- [17].Mingli, H.; Zhou, S.; Sun, B.; Zhao, Q. Heavy metals in wheat grain: Assessment of Potential health risk for inhabitants in Kunshan, China. Science of the total environ.2008, 405, 54 – 61
- [18].Santos, E.E.; Lauria, D.C.; Silveira, C.L. Removal of malachite green from aqueous solution by activated carbon prepared from the pericarp Ricinus communis by adsorption. Journal of hazard mater. Science of the total environs. 2009, 327,69–79
- [19].Lucio, A.E. Risk assessment as complementary tool for environmental permit systems when toxic air pollutants are involves. A Journal on Integrated Management of Occupational health and the Environment.2008, 3, 1-19
- [20].Sajjad, K.; Faroo, R.; Shahbaz, S.; Khan M.; and Sadique, M. Health risks assessment of heavy metals for population via Consumption of VegeTables. Institute of Information technology, Abbott bad, pakistan. World Applied Sciences Journal.2009, 6,1602-1606
- [21].Bello, O.S.; Ahmad, M.A.; Siang, T.T. Utilization of cocoa pod husk for the removal of Remazol Black B Reactive dye from aqueous solutions: kinetic, equilibrium and thermodynamic studies. Trends Appl Sci Res .2011, 6(8):794–812
- [22].Santhi, T,; Monomania, S,; smith a T. Removal of malachite green from aqueous solution by activated carbon prepared from the epicure of Ricinus communis by adsorption. J Hazard Mater .2010, 179:178–186

- [23].Al-Ghouti, M.A.; Khraisheh, M.A.; Allen, S.J.; Ahmad, M.N. The removal of dyes from textile wastewater: study of the physical characteristics and adsorption mechanisms of diatomaceous earth. J Environ Manag. 2003, 69, 229
- [24].Hameed, B.H. and Dau, F.B.M. Adsorption studies of basic Pb(NO₃)₂ on activated carbon derived from agricultural waste: Heveabrasiliensis straw/husk coat, Chem. Eng. J. 2008, 139, 48-55
- [25].Hameed, B.H.; Chin,L.H.; Rengaraj,S. Adsorption of 4-chlorophenol onto activated Carbon prepared from rattan sawdust: Desalination. **2008**, 225, 185–198
- [26].Lua, A.C.; Lau, F.Y.; Guo, J. Influence of pyrolysis conditions on pore development of oil-palm shell activated carbon. J. Anal. Apply Pyrol. 2006, 76, 96-102
- [27].Langmuir, I. The constitution and fundamental properties of solid and liquid. Journal of Am. Chem. Soc. 1916, 38, 2221–2295.
- [28].Freundlich, M.F. Über dies adsorption in lösungen, Z. Phys. Chem. 1906, 385–47
- [29].Ozhan, A; Sahin, O,; Saka, C,; Kucuk, M.M.Study on extraction of cellulose and removal of hemicelluloses and lignin from peanut hull. Cellulose.**2014**, 21, 2457–2467.
- [30].Junior, O.P.; Cazetta, A.L.; Gomes, R.C.;Barizao, E.O.; Souza, A.F.; Martins, A.C.; Asefa, T.; Almeida, V.C. Surface and porous characterization of activated carbon prepared from pyrolysis of biomass by two-stage procedure at low activation temperature and it is the adsorption of iodine. Anal. App Pyrol. 2014, 105, 166–176.
- [31].Njoku, V.O.; Foo, K.Y.; Asif, M.;Hameed, B.H. Preparation of activated carbons from rambutan (NepHeliumLappaceum) peel by microwave-induced KOH activation for acid yellow 17 dye Adsorption, Chem. Eng. J. 2014, 250, 198–204.
- [32].Hesas, R.H.; Arami-Niya, A.; Daud, M.A.;Sahu, J.A.New method on producing high surface area activated carbon: the effect of salt on the surface area and the pore size distribution of activated carbon prepared from pistachio shell. Chem. Eng. Res. Des.2013, 91, 2447–2456.
- [33].Xiao, X.M.; Tian, F.; Yan, Y.J.; Wu, Z.S. J.Preparation characterization and evaluation of adsorptive properties of orange peel based activated carbon via microwave induced K₂CO₃ activation. Shihezi Univ. 2014, 4, 485–490.

- [34].Xiao, X.M.; Tian, F.; Yan, Y.J.; Wu, Z.S.; Wu, Z.L.; Cravotto, G. Korean J.Utilization of rice husks as a feedstock for preparation of activated carbon by microwave induced KOH and K₂CO₃ activation. Chem. Eng. 2015, 32, 1129–1136.
- [35].Yammer, J.; Yadava, O. P.; Kebede, T.; Mohammed, J.Kinetics and Equilibrium study of adsorption of phenol red on Teff (eragrostisteff) husk activated carbon, International Journal of Innovation and Scientific Research. 2014, 11(2), 471-476.
- [36].Ahmad,M.A; Alrozi,R.Optimization of preparation conditions for mango stem peelbased activated carbons for removals of Remazol Brilliant Blue R using response surface methodology. Chem. Eng.J.2011, 165, 883-890
- [37].Ahmed,N.A,;Elham,M.;Alrufuie and haider,N.Thermodynamic and spectrophotometric studies on complexes formation of properties of quercetin and curcumin within Ni(II) and Pb(II) determination of stability by spectrophotometric method .Int.J.chem.techol.2017,10,716-725
- [38].Cauhan, A.; Kaith, B. X-Ray powder diffraction studies to evaluate the transition in Graft-copolymers. Malaysian polymers procured from Roselle fiber. Journal of natural fiber.2012, 9, 87-97
- [39].Cauhan, A.; Kaith, B.X-Ray Diffraction Studies and Assessment of Roselle Graft-Coplymers.Malaysian polymer journal.2011, 6,155-164
- [40] Cauhan, A.; Singh, B. X-Ray powder diffractions Studies to Acredit the morphological transformation in hibiscus sabdariffa Graft-Copolymers. International Journal of Polymer Analysis and Characterization.2011, 16,319-328
- [41].Chauhan, A.; Kaith.B. XRD and Physico-chemical Evaluations of Hibiscus sabdariffa cellulose -Butyl acrylate-co-vinyl monomer graft. American Journal of Biochemistry and Molecular Biology.2013, 3, 61-70
- [42].Cauhan, A.;Kaith, B.XRD Elaborate the Metamorphosis in Graft Copolmers.J.Anal Bioana Tech.2012, 3, 1-6
- [43].Ravulapalli, S.; Kunta, K.Removal of Pb(II) ions from wastewater using active carbon of caryota urens seeds and its embedded calcium alginate beads as adsorbent.J.Environ.Chem.Eng.2018,6,4298-4309

- [44]. Quazene,N.; Sahmuna,M.N.Equilibrum and kinetic modeling of astrapon yellow adsorption by sawdust: effect of important parameter.Int .J. Chem. React. Eng. 2010,8, 151
- [45].Kannan, N and Meenakshisundaram, M.water air soil poll.2002, 138,189
- [46].Kannan, N and Xavier, A.Toxico Environ Chem.2001, 19, 95
- [47].Kannan and Raja Kumar, A.Toxico Environ Chem.2003, 84(14), 7
- [48].Connell, D.W.O.; Birkinshaw, C.; Dwyer, T.F.A modified cellulose Adsorbent for the Removal of Nickel (II) from Aqueous solutions, J.Chem.Technol.Biotechnol.2006, 81, 1820-1828
- [49].Moradi,O.;Aghaie,M.;Zare,K.;Monajjemi,M.;Aghaie,H.The. The study of Adsorption characteristics Cu(II) and Pb(II) Ions onto PHEMA and P(MMA-HEMA) surface from aqueous single solution,J.Hazard .mater.2009,170,673-679
- [50].Immamuglu,M.;Tekir,O.Removal of copper(II) and lead (II) ions from aqueous solution by adsorption on activated carbon from a new precursor hazelnut husk,Desalination.2008,228,108-113
- [51].Lagergren, S, Zur theorie sogennanten adsorption geloester stoffe, Vetern science.1898, 24, 1-39
- [52].Ho,Y.S. and McKay,G. Pseudo second order model for sorption process. proc.Biochem.1999, 34, 451-465
- [53].Gupta,N.;Kushwaha,A.K.'Chattop dhyaya,M.C.Kinetics,thermodynamicof malachite green adsorption on banana pseudo stem fibers.J.Chem.Res.**2011**,3,284-296
- [54].Aharoni,C.; Ungarish,M. Kinetics of activated chemisorptions. Part I: the non-Elovich and part of the isotherm, J.Chem.Soc.Farad.Trans.**1976**, 72, 265-268
- [55].Weber, W.J; Morris, J.C. Kinetics of adsorption on carbon from solution. J.Sanit. Eng. Div.1962, 89, 31-59. (ASCE)

- [56].Srivastava, V.C.; Swamy, M.M.; Mall, I.D.; Prasad and Misha, I.M. Adsorptive removal of Phenol by Bagasse fly ash and activated carbon: Equilibriums, kinetics and Thermodynamics. Colloid and Surfaces a physicochemical engineering aspect. 2006, 272, 89-104
- [57].McKay, H.Y. Application of kinetics model to the sorption of copper (II) onto peat.Adsorpt Sci technol. 2002, 20,797-815
- [58].Bello,O.S.;Ahmad,M.A.;Ahmad,N.Adsorptive features of banana(Musa paradisiacal) stalk based activated carbon for malachite green dye removal,chem.Ecol. 2012, 28,153-167
- [59].Bello, O.S.; Fatona, T.A.; Falaye, F.S.; OSuolale, O.M.; Njoku, V.O. Adsorption of eosindyy from aqueous solution groundnut hull based activated carbon: kinetic, equilibrium and thermodynamic studies, Environ. Eng. Sci. 2012, 29,186-194
- [60].Baraka,A.;Hall,P.J.;Heslop,M.J.Preparation and characterization of Melamine-Formaldehyde-DTPA Chelating Resin and its use as an Adsorbent for heavy metals Removal from wastewater,React.Funct.Polymer.2007,67,585-600
- [61].Mihwa, B.; agbemi, B.C.O.; Jin,O.Se.;Kim,D.S. Removal of malachite green from aqueous using degreased coffee bean.J.Hazard.Mater.**2010**,176,820-828
- [62].Onala,Y.;Akmil-Basara,C.;Diem,E.;Sozdemira,C.;Tolga,D.Adsorption kinetic of malachite green onto activated carbon prepared from tunc bile lignite .J. Hazard mater.2006,128,150-157
- [63].Chigondo,F.;Nyamunda,B.C.;Sithole,S.C.;Gwatidzo.Removalof of lead(II) ions and Copper(II) ions from aqueous solution by baobab (Adononsia digitations) fruit.Journal of Envirn.2013,5,43-50
- [64]. Yadava, K.P.; Tyagi, B.S. Effect of temperature on the removal of Lead (II) by adsorption on China clay and Wollastonite. Journal of Chem techno and Biotechnol. 1991, 52, 47-60
- [65]. Rao.M.M; Ramesh, A.; Rao, G.P.C.; Seshaiah, K.Removal of lead(II), copper and Cadmiums from the aqueous solution by activated carbon derived from Ceiba pantandra hulls.J.Has.Mat.2006, 129,123-129

- [66].Mulu, B.D.Langmuir and freundlich study for the adsorption of textile metal ion onto teff straw(Eragrosis tef) agricultural waste.J of thermodymic.**2013**,6,45-52
- [67].Dela Rosa, G.; eynel-Avila,H.E.;Bonilla-Petriciolet,A.;Cano-Rodriguez I,Velasco-Santos,C.Martinez-Hernandaez,A.L.Recycling poultry feathers for Pb(II) removal from wastewater: Kinetic and equilibrium studies.Int.J .Chem.BioEng.2008,1(4),185-193

APPENDIX

18	-	-									
1.6	\wedge		СВА. С+Р6(NO3)2	Pb(NO3)2+MWAC				MWAC			
1.2	1.4 1.2 2 4 1				0/7	0		41-	0/7	-	
§ 1-			Wavelength	Abs	%1	Conce	Wavelength	Abs	%1	Conce	
1 0.8	÷ 0.3			200	0.28	52.48	0.001405	200	0.124	75.16	0.00062
0.6 -			250	0.35	44.67	0.001412	250	0.258	55.08	0.001032	
0.4		1.		300	1.67	2.14	0.005578	300	0.304	49.66	0.001013
0.2				350	0.23	58.88	0.000657	350	0.207	62.09	0.000591
200	250 300	350	400	400	0.09	81.28	0.00023	400	0.132	73.79	0.00033
	λ, nm										
	Pb(NO3)2 + CMAC							CMAC			
	Wavelength	Abs	%т	Conce				Wavelength	Abs	%Т	Conce
	200	0.16	69.18	0.0008				200	0.863	13.71	0.00415
	250	0.714	19.32	0.002856				250	0.016	96.38	0.000064
	300	0.163	68.71	0.000543				300	0.529	29.58	0.00176
	350	0.125	74.99	0.000357				350	0.447	35.27	0.001278
	400	0.038	91.62	0.000095				400	0.406	39.26	0.001015

Appendix (1): Shown the unknown concentration in the sample solution