ADSORPTIVE REMOVAL OF Cr (VI) FROM TANNERY WASTEWATER USING BIOCHAR DERIVED FROM ORGANIC FRACTION OF MUNICIPAL SOLID WASTE

BY

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A THESIS SUBMITTED TO THE DEPARTMENT OF ENVIRONMENTAL HEALTH SCIENCE AND TECHNOLOGY, COLLEGE OF HEALTH SCIENCES, JIMMA UNIVERSITY, IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN ENVIRONMENTAL SCIENCE AND TECHNOLOGY

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Adsorptive Removal of Chromium from Tannery Wastewater Using Biochar Derived From Organic Fraction of Municipal Solid Waste

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A Thesis Submitted To The Department Of Environmental Health Science And Technology, College Of Health Sciences, Jimma University, In Partial Fulfillment Of The Requirements For The Degree Of Master Of Science In Environmental Science And Technology

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The undersigned to accept responsibility for the scientific ethical and technical conduct of the research project and for provision of required progress reports as per terms and conditions of the college of Health Sciences in effect at the time of grant is forwarded as the result of this application.

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Abstract

This work aimed to investigate the potential use of pyrolysed organic fraction of municipal solid waste as an adsorbent agent for removal of Cr (VI) from aqueous and tannery wastewater. We adopted a pyrolytic process to produce biochars from dried organic fraction of municipal solid waste at different temperatures (350°C, 450°C and $700°$C). Cr (VI) adsorptive potential of the manufactured biochars was assessed via batch adsorption experiment. The influence of contact time, co-existing ions, effect of pyrolytic temperature, the initial chromium concentration, pH and adsorbent doses were assessed. The model fitness was determined using Langmuir and Freundlich isotherm model as well as kinetic equilibrium experiments. In this study removal efficiency increased with time until equilibrium time reached at 30 min. The adsorption of Cr (VI) on the biochars was greatly dependent on the pH of the solution. Optimum pH for maximum Cr (VI) removal was at 2. The amount of Cr^{6+} ions adsorbed increase until it reached the optimum dose 1g, and it became constant with increasing the dose of the adsorbent from 2g to 10 g. Maximum removal efficiency of 98.2%, 99.5% and 98.8% for Cr (VI) was achieved using 1g/L of BC-350°C, BC-450°C and BC-700°C respectively. The removal efficiency of Cr (VI) decreased from (99.9 to 51%), (100 to 56.6%) and (99.9 to 52.5%) with increasing the initial Cr^{6+} concentration from 1mg/L to 40mg/L for BC-350°C, BC-450°C and BC-700°C respectively. Anions such as phosphate, nitrate, chloride and their mixture had affected the adsorption of Cr (VI) ions on the biochars. The influence of phosphate ions was higher when compared with other anions, but lower than their mixtures effect. Desorption of Cr (VI) increased as the concentration of NaOH increased from 0.1 to 1M solution. The Cr (VI) adsorption kinetics data followed the pseudo-second order equation with the correlation coefficient, $R^2>0.99$, for all adsorbents. The equilibrium adsorption data was well described by Freundlich isotherms with correlation coefficient R^2 value of greater than 0.98 for all tested biochars. Overall the study results indicated that the potential use of biochar derived from OFMSW as adsorbent for Cr^{6+} removal are feasible.

Keywords: Biochar, Hexavalent Chromium, Adsorption, Adsorption Isotherms

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Acronyms and Abbreviations

BC-350 - Biochar manufactured at 350 °C

BC-450-Biochar manufactured at 450 °C

BC-700- Biochar manufactured at 700 °C

OFMSW –Organic fraction of municipal solid waste

EEPA - Ethiopia Environmental Protection Authority

EGSL - Ethiopian Geological Survey Laboratory

EPA - Environmental Protection Authority

USPHS - United State Public Health Service

WHO - World Health Organization

IARC - International Agency for Research on Cancer

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Chapter One: Introduction

1.1   Background

The presence of heavy metals in the environment is of global concern due to possible adverse effects on human health, as well as on aquatic flora and fauna(Agrafioti, Kalderis, & Diamadopoulos, 2014). Heavy metals are natural constituent on earth known with properties such as having persistence, high toxicity and non-biodegradable pollutants. They accumulate in the ecosystem that have an atomic density greater than 4 g/cm^3 or 5 times or more than water. They are classified into three different types including toxic metals (Hg, Cr, Pb, Zn, Cu, Ni, Cd) precious metals (Pd, Pt, Ag, Au) and radionuclide's (U, Th, Ra, Am) (Teknologi & Perlis, 2013). Heavy metals are introduced into the environment by human activities such as agriculture, industrial activities and waste disposal (Chantawong*et al*., 2004).

Chromium salts are widely used in several industrial processes such as tanneries, electroplating, textile, dyeing and metal finishing industries that makes chromium a common pollutant found in industrial effluents (Ajouyed *et al*., 2011). Naturally chromium exists in two most stable oxidation states i.e. trivalent and hexavalent forms in aqueous systems. At trace level the trivalent form is considered as an essential nutrient whereas hexavalent form of chromium is toxic, carcinogenic and mutagenic (Abdel *et al*., 2012).Hexavalent chromium is one of the most known toxic contaminants which enter the water streams through various industrial operations such as metallurgy, electroplating, leather tanning, textile dyeing, paint, ink and aluminum manufacturing industries (Singh *et al.,* 2012). It is also toxic to all life forms and considered as a priority pollutant that the International Agency for Research on Cancer (IARC) has classified inhaled Cr (VI) as a human carcinogen (Dubey *et al*., 2015).

Chromate ions are toxic to living organisms, non-degradable and persistent in the environment, therefore, its removal from wastewater is important to protect public health and the environment. In most cases adsorption is considered as very effective and economical process for metal ion removal from wastewaters (Zhao *et al*., 2011).

According to WHO the permissible limit of Cr (VI) for potable water is 0.05ppm and for industrial wastewater discharge is 0.1ppm (Devi & Manonmani, 2015). The Ethiopian

Environmental Protection Authority (EPA) also has set a permissible level to be 0.1 mg/L for hexavalent chrome containing industrial wastewater effluents. To obey with these legal requirements, and protect the environment removal of chromium from industrial effluents is highly desirable (Werkneh, Habtu, & Beyene, 2014). Therefore, development technology for chromium treatment and removal is badly needed that can offer a significant advantages like the low-cost, availability, profitability, ease of operation, and efficiency. This reckless action is causing aquatic ecosystem contamination with heavy metal ion–including chromium ion ($Cr_2O_7^2$). Chromium is an essential nutrient for plant and animal metabolism, but the increasing accumulation of chromium in the environment from industrial effluents has caused great concern (Dubey *et al*., 2015). The current chromium treatment technologies available are unaffordable and in some cases they are very expensive, complicated and sometimes inefficient especially when the concentrations of heavy metal ions is less than 10 mg/L (Akpomie*et al*., 2013). Chromium removal from industrial wastewater is mandatory task. Therefore, developing of low-cost and easily operated technology is in a prime importance for such industries.

Presently, the methods used for heavy metal removal from water include adsorption on activated carbon, precipitation, use of ion exchange resins and membrane filtration. However, lately there is an intense interest regarding heavy metal immobilization using biochar technology in water and wastewater. Biochar, a solid materials obtained from thermochemical conversion of biomass, are currently receiving increasing attention due to their soil improvement potential, and ability to function as carbon sequester as well as biosorbent of environmental pollutants (Lehmann *et al*., 2011). Biochar's ability to adsorb heavy metals is possibly attributed to electrostatic interactions between carbon negative surface charge and metal cations, as well as to exchange of ions between biochar surface protons and metallic cations. Biochar technology nowadays have a wide application due to its simplicity, low-cost and easy operational conditions (Agrafioti *et al*., 2014).

Biomass wastes such as agricultural residues, municipal solid waste, sewage sludge, bioprocess wastes, and animal wastes are being recognized as valuable feedstock for biochar production (Zielińska*et al.,* 2015). However, the suitability of each type of biomass as feedstock is dependent on the nature, chemical composition, environmental, as well as economic factors. In addition, pyrolysis conditions largely control the physical and chemical properties (e.g.

composition, particle and pore size distribution) of the resulting biochar to trap dissolved pollutants (e.g. heavy metals) from waste streams. The pyrolysis conditions and feedstock type largely control the physical and chemical properties of the resulting biochars to adsorb dissolved pollutants (Lehmann and Rondon, 2007; Shackley*et al*., 2010). Here, in this study, the potential use of biochar made from organic fraction of municipal solid waste for adsorption of chromium ions from tannery wastewater aiming to develop low-cost chromium removal technology for tannery wastewater.

1.2 Statement of the problem

Industrialization, and civilization has resulted a geometrical increasing in water demand worldwide. Further, wastewater produced from such industries needs to be purified and recycled for the purpose as alternative sources of water as well as to protect the environment. Worldwide, linked with industrial expansion, environmental pollution by toxic heavy metals is a critical problem (Shadreck & Tawanda, 2013). Especially in developing countries the problem is severe as inadequate environmental protection and monitoring program exist. In Ethiopia large amount of waste products from industries are discharged directly into water sources without any treatment − where sewage treatment coverage ranges from very low to non existence. In most cases, industries do not treat their wastes unless it contains recyclable products which could be reprocessed or sold to generate additional income (Ademe & Alemayehu, 2014).

Nowadays, various sorbents have been developed, ranging from natural materials to synthetic products for chromium removal from water and wastewater. Adsorption is widely used as effective physical method of separation in order to eliminate or lower the concentration of pollutants (heavy metals) in the polluted waters by application of most common adsorbents, such as silica gel, activated carbon, and aluminium oxide (Technology *et al.*, 2012). Among those sorbents developed, the C-based sorbents have proven to be most cost-effective in removing inorganic as well as organic pollutants from wastewater. This suggests an opportunity to evaluate biochar technology as adsorbent for heavy metals removal from water and wastewater effluent.

The application of biochars technology is effective for removal of heavy metal due to porous structure, organic nature and large-scale availability (Ash *et al*., 2006). A number of studies have demonstrated effective removal of heavy metals from aqueous solutions by biochars and, in

some cases, significant ability of Biochars to activated carbons for heavy metals (Fri *et al*., 2015). A few studies have indicated that the effectiveness of biochars in retaining heavy metals varied with different biochars and metals. Furthermore, the underlying mechanisms for the sorption of different metals by biochars are not fully yet understood (Cui, Hao, Zhang, He, & Yang, 2016). Hence, evaluation of the effect of the pyrolysis condition and feedstock type is needed if the biochar is going to be used as adsorbent for heavy metals.

Compared with activated carbon, biochar appears to be a new potential, low-cost and effective adsorbent (Nguyen & Lee, 2015). The production of activated carbon needs higher temperature and additional activation process. Comparatively, production of biochar is cheaper with lower energy requirements (Nguyen *et al*., 2015). In addition; the feedstocks of biochar production are abundant and low-cost, which mainly obtained from waste matter. The converting waste matter into biochar can improve the waste management and protect the environment (Sensoz, Demiral, Gercel, 2006). Therefore, the conversion of biomass into biochar as a sorbent is a ''win–win'' solution for both improving waste management and protecting the environment.

A number of studies have been done on the removal of chromium (III) from tannery wastewater using different adsorbents from wastewater (Fahim*et al*., 2006) and removal of Cr (VI) from aqueous solution was studied by natural, low-cost materials such as sphagnum mass peat, saw dust, leaf mould, sugar beet pulp, bagasse, maize cob, biogas residual slurry (Werkneh*et al*., 2014). However, up to my knowledge no articles describe the use of biochar manufactured from organic fraction of municipal solid waste for the removal of chromium in aqueous solution. Therefore, scientific research and future engineering applications of biochar for the purification of chromium pollutants in water and wastewater is needed urgently. In addition, effect of ageing process on biochar properties has not been studied in detail so far; for example, adsorption capacities of biochar changes with time (Parmar, Nema, & Agarwal, 2014). Furthermore, while different researches have been done on adsorption of chromium in Ethiopia, there is limited study on the removal of chromium from wastewater using biochar derived from organic solid waste. Therefore, this study aims to conduct a study on adsorptive removal of Cr (VI) from aqueous solution and real tannery wastewater using biochar derived from organic fraction of municipal solid waste.

1.3   Significance of study

In Ethiopia, solid wastes from municipal and domestic have little or no market value, making their disposal uneconomic and environmentally unsustainable. In most cases, the majority of organic wastes generated are left to decay on-site, and dumped in open spaces. These waste disposal strategies cause significant water and air pollution. In this study biochar technology is advocated aimed to minimize environmental degradation and improve the environmental performance of tannery industry. Overall, the study result is not only instrumental to meet the current challenges of growing climate change and water pollution, but also to tackle the high health burden related to water and sanitation via recycling organic waste. More specifically, the outcome of this study would help to save society live downstream from wastewater contamination of chromium cations and also serve the issued organization how to purify wastewater with cost effective method using biochar derived from organic solid waste. So far many researchers had used different types of adsorbents for chromate removal from aqueous solutions. However biochar is not tested before based on our knowledge. Thus, the study result will help further to develop biochar based technology as adsorbent for Cr (VI) ion removal from wastewater.

1.4.   Research Questions

➢ Can biochar prepared from OFMSW at different temperature remove Cr (VI) from wastewater?

CHAPTER TWO: LITERATURE REVIEW

2.1. Chromium (Cr $^{6+}$)

Water contamination with heavy metal ions is a very harsh environmental problem all over the world and chromium is a toxic pollutant that causes severe environmental and public health problems (Al-sou, 2012).

Pollution of the environment especially water with toxic substances is a major problem to humans, plants and aquatic health as well as environmental quality. Cr(VI) is known to be one of the most dangerous to the ecosystem among different toxic substances released into the environment (Akpomie *et al*., 2013).

Toxic heavy metals are released into soils and water has been widespread among these chromium is one of the concerned heavy metals due to its high toxic and carcinogenic properties (chulsung kim, 2007).Although many heavy metals are necessary in small amounts for the normal development of the biological cycles most of them become toxic at high concentrations (Chantawong, 2004). According to WHO the maximum threshold level of Cr (VI) in water is 0.05 mg/L (Megharaj MallavarapuA *et al*., 2010). Most of heavy metal ions are toxic to living organisms, non-degradable and are persistent in the environment therefore elimination of them from wastewater is important to protect public health (Zhao *et al*., 2011).

Invertebrate species such as polychaete worms, insects, and crustaceans are more sensitive to the toxic effects of chromium than vertebrates such as fish and lethal chromium level for several aquatic and terrestrial invertebrates has been reported to be 0.05 mg/L (Baysl *et al*., 2013).

Although Several industrial wastewater streams may contain heavy metals such as Sb, Cr, Cu, Pb, Zn, Co, Ni, etc. toxic metals exist in high or low concentrations must be effectively treated from the wastewaters (Suleyman *et al*.,2013).

Conventional methods for heavy metal removal include precipitation, evaporation, electroplating and ion exchange have been known however, these methods have several disadvantages such as only limited to certain concentrations of metals ions, generation of large amount of toxic sludge and the capital costs are much too high to be economical. Hence adsorption using low cost adsorbents is found to be more environmentally friendly (Teknologi & Perlis, 2013).

Heavy metal adsorption through biochar is considered as surface complexion with carboxyl and hydroxyl groups and surface precipitation. Agriculture waste, wood waste, etc. are generally burned. Biochar can be produced from these waste materials; it is used as an adsorbent and it provides many other benefits to soil. So, Problem of burning is solved, It gives energy production in the form of syngas (Agrafioti et al., 2014).

2.2. Occurrence and nature of Chromium

Chromium was discovered by the French chemist Louis Vauquelin in 1798 (Hyder, 2013). It is a group 6th element in the latest IUPAC periodic table that exist in the aqueous environment mainly in +III and +VI states. Cr (III) is non-toxic, and an essential species to mammals that helps the body to control blood-sugar levels in trace concentrations, but toxic to fish when present in water above 5.0 mg/ℓ (S. Goswami& Ghosh 2005). Chromium exists in oxidation states from +2 to +6, but only two states trivalent and hexavalent are of environmental significance. Trivalent chromium, Cr (III), is considered to be a trace element that is essential for the functioning of living organism but at high concentration, it can be dangerous to health as it can coordinate with organic compounds which in turn lead to inhibition of some metallo enzyme systems. Hexavalent chromium (strong oxidizing agent) which is primarily present in the form of chromate (CrO_4^{2-}) in alkaline and dichromate ($Cr_2O_7^{2-}$) in acidic environment poses significantly higher levels of toxicity than the other valence states (Bajpai et al., 2015).

Cr (III) occurs naturally and is an essential micronutrient requirement is 50 to 200 µg per day that assists the body in metabolizing sugar, protein and fat. Cr (VI) is usually of anthropogenic origin and rarely occurs naturally (Bojic et al., 2004).

Chromium contamination is common in soil, ground and surface waters in industrial areas. Cr compounds have been released to the environment due to improper disposal and leakage e.g. in ore processing, manufacture and usage of alloys, and in the galvanic, ceramic, dye, and tannery industries (Buerge& Hug, 1999).

Many minerals contain high percentages of chromium however chromites ($FeCr_2O_4$) is the only economically important ore mineral. Processing of the ore for the manufacture of Cr (V) compounds involves roasting the ore with soda ash (Na_2CO_3) and lime. The material is then leached with water to remove the soluble Na_2CrO_4. This process may be repeated a second time

to recover additional Cr (IV). At the end of the process there is a waste residue or mud that contains $CaCrO_4$, calcium aluminochromate ($3CaO\text{-}Al_2O_3CrO_4$), tribasic calcium chromate [Ca_3 ($CrO_4)_2$], and basic ferric chromate [$Fe(OH)CrO_4$] that dissolve in and add hexavalent chromium to percolating waters (Wittbrodt*et al*., 1991).

Chromium is one of the most abundant inorganic groundwater contaminants at hazardous waste sites. As Compared to its trivalent, hexavalent Cr forms chromate (CrO_4^{2-}) or hydrogen chromate ($HCrO_4^-$) that is more toxic and more soluble under different pH. Hexavalent chromium (CrO_4^{2-}) is an antibiofoulant and anticorrosive agent and is common in industrial waste waters (Resch *et al*., 1987). Although Cr (III) is strongly retained onto biochar Cr (VI) species such as chromate (CrO_4^{2}-), bichromate ($HCrO_4$-) and dichromate ($Cr_2O_7^{2}$-) are weakly sorbed to biochar under alkaline to slightly acidic conditions leading to their movement to sub surface environments (Mallavarapu*et al.,* 2010).

2.3. Source of chromium

Effluents from textile, leather, tannery, electroplating, galvanizing, pigment and dyes, metallurgical and paint industries and other metal processing and refining operations at small and large scale sector contain considerable amounts of toxic chromate ions (Abdus-Salam and Adekola, 2005)**.**

Heavy metals are introduced in aquatic environments by atmospheric deposition, weathering and erosion of the geological environment or through anthropogenic sources (Hong *et al*., 2008). Hexavalent chromium is one of the most known toxic contaminants which enter the water streams through various industrial operations such as: metallurgy, electroplating, leather tanning, textile dyeing, paint, ink, and aluminum manufacturing industries (Access *et al*.,2012). Chromium plating processes are the main source of Cr(VI) pollution (Boji*et al*., 2004). Almost all the hexavalent chromium in the environment is a result of human activities (Baysl *et al.*, 2013). The increased industrial activities, indiscriminate use of organic and inorganic fertilizers and pesticides, and disposal of industrial effluents enhance the possibility of pollution and toxicity of heavy metals in environment. Although due to their extended persistence in biological systems and tendency to bioaccumulation the contamination of water by toxic chromate is a worldwide environmental hazard (Fruit *et al*., 2014).

2.4. Chromium mobility in the environment and toxicity

The degree of toxicity of metals depends on their chemical forms and oxidation states (Shadreck&Tawanda, 2013).According to its toxicity, chromium was classified as a primary pollutant and ranked as second among many toxic metals in the environment for frequency of occurrence at Department of Energy (DoE) sites (Junyapoon*et al,.* 2006). Because of severe toxicity of hexavalent chromium the Agency for Toxic Substances and Diseases Registry classifies it as the top sixteenth hazardous substance (Ajouyed*et al.*, 2011). The permissible limit of chromium for drinking water is 0.1 mg/L (as total chromium) in EPA standard (EPA, 2009).

All heavy metals can affect human and environment by different ways**.** Chromium is potential toxins that enter the environment in elevated levels primarily due to anthropogenic activities (Goethite & Sparks, 1997). Chromium (VI) is highly toxic in nature due to the fact that the reduction products of Chromium (VI) is Chromium (V) a known carcinogen and will gatehouse in any tissue to form cancerous growths. It is a very strong oxidizing agent therefore very fast in reacting and likely to form complexes. Chromium (VI) is not a very stable state when compared to Cr (III). Chronic inhalation of Chromium (VI) compounds increases the risk of lung, nasal and sinus cancer. Severe dermatitis skin ulcer can result from contact with Chromium (VI) compounds. It can cause mild to severe liver abnormalities. Chromium (VI) compounds are teratogenic to animals (Devi *et al.*, 2012).

 Although Chromium is used as Cr (VI) in timber treatment and as Cr (III) in tannery industry, hexavalent chromium is highly toxic, carcinogenic, mutagenic and teratogenic. The oxidation state of Cr in contaminated site is an important indicator of toxicity (Bolan *et al.*, 2010). It has a number of adverse effects ranging from causing irritation to cancer. Hexavalent chromium is in general more toxic to organisms in the environment than the trivalent chromium. Cr (VI) is one of the most toxic contaminants recognized as a carcinogenic and mutagenic agent and needs complete removal from wastewater before disposal (Dubey *et al.*, 2015).

 Chromium (VI) has been released to the environment via leakage, poor storage or improper disposal practices (Khatoon*et al*, 2013). It cause direct toxicity to humans and other living beings due to their presence in aquatic environment above the permissible limits so that these metals affect the aquatic life when discharged in water bodies through wastes and harmful to human

health because of bioaccumulation (Khan *et al.,* 2008). Waste streams contain toxic heavy metals such as chromium, cadmium, lead, mercury, nickel, and copper though chromium is a common pollutant which occurs in the surface or groundwater due to the discharge of a variety of industrial wastewaters and other human activities (Trochimczuk, 2011). Increasing levels of chromium in the environment pose serious threats to water quality, human health and living organisms. Cr (VI) has high toxicity for humans and animals and commonly interferes with beneficial use of effluents for irrigation and industrial applications (Attar, 2010).

2.5. Technological options to remove chromium

Nowadays water pollution raises a great concern since water constitutes a basic necessity in life and is essential to all living things (Al-sou, 2012). Various treatment technologies have been developed for the removal of heavy metals from water and wastewater but the most widely used conventional methods for removing chromate from wastewater include ion exchange, chemical precipitation, reverse osmosis, evaporation and membrane filtration (Ajmal *et al*., 2008). All these treatments lead to certain disadvantages such as incomplete removal of heavy metals, high-energy requirements and production of toxic sludge (Teknologi& Perlis, 2013). Adsorption of heavy metals such as chromium (VI) is an efficient technology in industrial waste water treatment and this method is cheap and applicable for small scale industries (Gandhi *et al*., 2014).

A conventional treatment methods for the removal of toxic metal ions from wastewater involves various chemical, biological, electrolytic and adsorption methods which includes chemical reduction, ion exchange, electro dialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation, coagulation, adsorption on solid organic waste (Technology & Mishra, 2012). Except adsorption other methods are expensive and it may produce large amount of sludge. Adsorption of heavy metals such as chromium (VI) is an efficient technology in industrial waste water treatment. This method is cheap and applicable for small scale industries (Gandhi *et al.*, 2014).

2.6. Adsorption Review

Adsorption using low-cost adsorbents like biochar is found to be more environmental friendly however high adsorption capacities, cost effectiveness and their abundance in nature are the important parameters which explain why the adsorbent is economical for chromate removal (Abas & Ismail, 2013).

As stated by Abdel et al., 2012 the % removal was 73% for activated carbon and 77% for bentonite after 120 min. It is clear that, at the beginning % removal increased rapidly in few minutes, by increasing contact time, % removal increased lightly and slowly till reach maximum value and this can be explained on the basis that as initially a large number of vacant surface sites are available for adsorption of metal ions but with passage of time the surface sites become exhausted.

As stated by (Nameni, Moghadam, & Arami, 2008) olive stone and egg husk was examined in the pH range of (2-11). The experiment of adsorption as a function of pH was conducted at known initial concentration of 5 mg/L Cr^{6+}, dose of 2 g/100 mL for wheat bran at 25 °C. The result was showed that the adsorption capacity of Cr^{6+} ions onto adsorbent increased significantly with decreasing pH value and the maximum removal of Cr^{6+} ions by adsorbent for contact time (60 min) was carried out at pH (2.0). The improved removal of chromium (VI) at low PH value is probably due to reduction of hexavalent chromium to trivalent chromium ions:

$$Cr_2O_7^{2-}+14H+6e-12Cr^{+3}+7H_2O$$
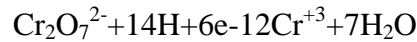
Also at low pH, there is presence of a large number of H^+ ions, which in turn neutralize the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion of dichromate ions.

2.7. Nature and Source of Organic solid waste

Municipal refuse can be divided into two parts: organic or biodegradable waste, and non- organic or non-biodegradable waste. Organic waste includes kitchen waste, food leftovers, rotten fruit and vegetables and peelings, straw and hay, leaves and garden trimmings, crop residues, rags, paper, animal excreta, bones and leather. Typical industrial organic waste includes coffee husks, coconut waste and sawdust. The non-organic components of solid waste include earth, including

ash, stone and bricks, coal and cinders, glass, plastics, rubber, and ferrous and non-ferrous metals(Bash, 2015).

Solid wastes from agriculture, agro-industrial processing, municipal and domestic and sludge from wastewater treatment plants have little or no market value, making their disposal uneconomic and environmentally unsustainable. In most cases, the majority of organic wastes generated are left to decay on-site, and dumped in open spaces (McElligott, 2011). Municipal solid waste (MSW) consists of all types of solid waste generated by households and commercial establishments, and collected usually by local government bodies. Many cities in developing countries face serious environmental degradation and health risks due to the weakly developed MSW management system. As one of the fast-growing cities in this part of the world, Jimma city, Ethiopia is also facing the same problem(Getahun et al., 2012).

As stated by (Getahun et al., 2012) daily average generation rate of solid waste was found to be 12,118 kg, which amounts to an annual average amount generation rate of ca. 32,000 tons. Eighty-seven percent of this waste was generated by households. Remarkably, only a negligible fraction (0.1%) was generated by street sweepings. The waste generation per household was 2.7± 1.0, 3.1±1.1, and 3.8±1.1 kg/day in the dry, in between and in the wet seasons, respectively. The volume of the generated waste was observed to be 146 m^3/day, and the density was 600 kg/m^3. Considering the local average household size, the average per capita waste generation for Jimma city was 0.55± 0.17 kg/cap/day,

The interest in the application of biochar as a method for mitigating the global-warming effects is steadily increasing. In addition to the studies on the use of biochar for carbon sequestration, a number of reports have focused on alternative applications of biochar for the improvement of soil fertility, plant growth, and decontamination of pollutants such as pesticides, heavy metals, and hydrocarbons(Jindo, Mizumoto, Sawada, Sanchez-Monedero, & Sonoki, 2014)

2.8. Biochar

Utilizing residual biomass from agriculture and agro- processing industry to produce biochar is economically a more viable solution to manage waste from these sectors, which is otherwise being used inefficiently (Parmar *et al*., 2014). Thermochemical decomposition of organic matter in the absence of oxygen at high temperature is termed as pyrolysis (Parmar *et al*., 2014).

Pyrolysis is the thermal decomposition of fuel into liquids, gases, and char (solid residue) in the absence of oxygen. It is usually understood to be anhydrous (without water). Pyrolytic products can be used as fuels, with or without prior upgrading, or they can be utilized as feedstock for chemical or material industries (Sadaka, n.d.). Utilizing residual biomass from agriculture and agro- processing industry to produce biochar is economically a more viable solution to manage waste from these sectors, which is otherwise being used inefficiently.

CHAPTER THREE: OBJECTIVE

3.1.   General Objective

To investigate adsorptive removal of Cr (VI) from tannery wastewater using biochar derived from organic fraction of municipal solid waste.

3.2.   Specific Objectives:-

➤ To determine Cr (VI) removal efficiency of biochars produced at 350°C, 450°C and 700°C from OFMSW.

➤ To study the effect of contact time, pH, adsorbent dose and initial concentration of Cr^{+6} metal ions adsorption on OFMSW.

➤ To describe the experimental data of adsorption isotherms through Langmuir and Freundlich models

➤ To investigate the adsorption properties of Cr^{+6} and to discuss mechanism of kinetic adsorption

CHAPTER FOUR: METHODS AND MATERIALS

4.1. Study Area and Period

The study was conducted at Environmental Health Science and Technology Graduate and Staff Laboratory, Jimma University from January 2016 to October 2016.

4.2. Experimental Design

Laboratory based batch experimental study was conducted. For the experiment organic fraction of the municipal solid waste was collected from Jimma town waste recycling Abdi enterprise. The collected OFMSW was oven dried at 105 °C for 2 h and the proximate properties were determined. Then subsequently three biochars were manufactured at 350, 450 and 700°C in a Tube Furnace in Addis Ababa University institute of Technology. The resulting biochars were pulverized before initiating char characterization. For comparison, the resulting products produced at the prescribed temperatures were referred to as BC-350°C, BC-450°C, and BC-700°C. Real wastewater sample was collected from Batu tannery in Addis Ababa, Ethiopia. The effect of parameters such as contact time, pH, adsorbent dose and initial concentration of Cr^{+6} metal ions were optimized with aqueous solution. Below Fig. 1 shows the experimental working package for the adsorption experiments.
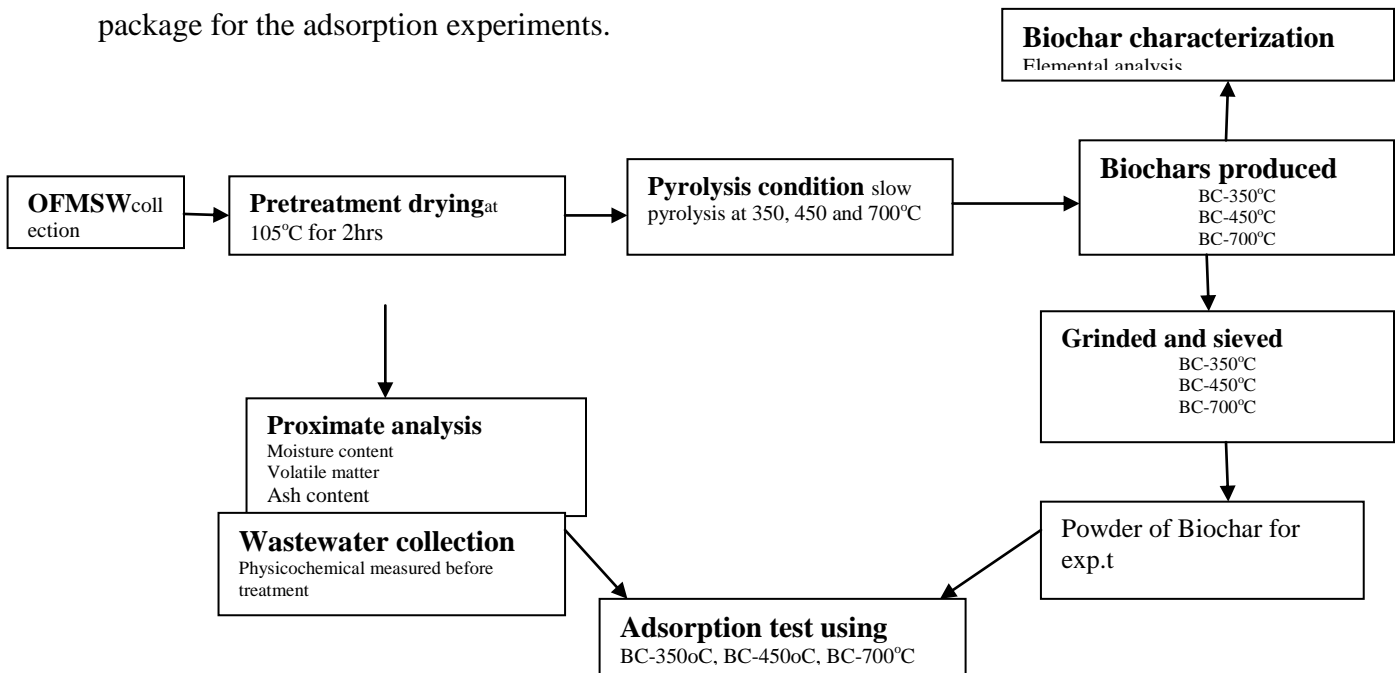
Figure 1: Experimental working package for adsorption experiment

4.3.   Study Parameters

4.3.1. Independent parameters

The independent variables in the study are pH, contact time, Initial Cr^{6+} concentration, and adsorbent dose.

4.3.2. Dependents parameters

The dependent variables of the study are removal efficiency and adsorption capacity.

4.4.   Adsorbent
4.4.1.   Feedstock collection

The study was conducted in Jimma town aimed to create sustainable sanitation system for biomass waste via assessing resource recovery options. Organic fraction of municipal solid wastewas collected from the town waste recycling Abdi enterprise.

Figure 2: Collection of organic solid waste

4.4.2. **Proximate Analysis of the Feedstock**

The collected OSW was air dried at room temperature and then dried in oven until the moisture of had been removed. The moisture content of the OSW was determined by taking a measured weight of the OSW in a previously weighed crucible and placing it in an electric hot air oven maintained at about $105^{o}C$ for 2 hrs. The moisture content was calculated using the equation:

$$\%\text{Wet mass moisture content} = \frac{\text{Loss in weight on drying}}{\text{Initial sample weight}} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The standard test method for ash content-ASTM D2866-94 was used. A crucible was pre-heated in a muffler furnace to about $550^{o}C$, cooled in desiccators and weighed. 1.0g of dried organic solid waste was transferred into the crucibles and reweighed. The crucibles containing the samples were then placed in a cold muffler furnace and the temperature was allowed to rise to $550^{o}C$. It was removed and allowed to cool in desiccators to room temperature and reweighed again. The ash content was calculated using the equation:

$$\%\text{Ash} = \frac{\text{Weight of residue after ignition}}{\text{Weight of dry solid waste}} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The applicable ASTM standard E-872 for determination of volatile matter was used. The previous sample used for moisture determination, was again heated in a covered crucible to avoid contact with air during devolatilization. The covered crucible was placed into a furnace at $950℃$ for two hour. Then the crucible was taken out, cooled in desiccators and weighed.

Volatile matter was calculated using the equation:

$$\%\text{Volatile matter} = \frac{\text{Weight (dry solid waste – residue after ignition)}}{\text{Weight of dry solid waste}} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

4.4.3. Biochar Production

The oven dried OFMSW was crushed and homogenized before pyrolysed. The homogenized OFMSW was pyrolysed in tube furnace at Addis Ababa University Institute of Technology at different temperatures (350°C, 450°C and 700°C) (Figure 3) under a nitrogen flow of 5 L h^{-1} to produce biochars, the biochars produced at different temperatures were crushed in a grinder, and sieved to a uniform size of 250μm sieve. For comparison, the resulting products produced at the prescribed temperatures from each feedstock were referred as BC-350°C, BC-450°C, and BC-750°C.

Figure 3: Tube Furnace: experimental set-up of Biochar production at 350°C, 450°C and 700°C temperature for 2hrs. (1 N$_2$ cylinder,2valve,3 pressure meter;4 flow meter, 5 furnace, 6 sample, 7 stainless steel tube and 8 trap)

4.4.4. Characterization of Biochar

Analyses of elements of carbon (C) hydrogen (H), and nitrogen (N) were carried out on the resulting products (i.e., BC-300°C, BC-450°C and BC-750°Cbiochars) with element analyzer (Vario EL III Element Analyzer; Elementar Co., Germany). Prior to the measurement, the standard sample was also analyzed for checking the experimental error within ± 1%.Oxygen is a calculated value and is the summation of percentage carbon, hydrogen, nitrogen, and sulfur subtracted from 100 (Liu et al. 2014). The yield of biochar was calculated using equation 4.

$$Y_{biochar} = F_{biochar} \Big/ F_{imput} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(4)}$$

Where, Y $_{biochar}$ is the yields of biochar; F $_{input}$ and F $_{biochar}$ are the weight of input dry OFMSW and collected biochar after pyrolysis, respectively.

4.5. Real wastewater sampling

Industrial wastewater sample was collected from Batu Tannery, Addis Ababa Ethiopia, according to standard methods for water and wastewater sampling procedures(Myers, 2006). The sample was collected in acid washed plastic bottles. The sample was acidified using sulfuric acid pH < 2 to prevent complexation of Cr (VI) ions by organic matters in the wastewater. The physicochemical properties of the sample were determined according to standard method for water and wastewaters analysis (APHA, 2005).

The adoptability of the technique expanded with the new organic sorbent in this work for Cr (VI) removal was carried out with some actual chromium waste water samples. The hexavalentChromium water pH and concentrations were measured before application with adsorbent. In order to study the efficiency of the adsorbent for this real sample, The Cr (VI) water sample was diluted many times and the resulting solution was stirred with appropriate 1g of biochars for 30min at initial pH.

Then this sample was subjected for extraction of chromate using the natural sorbent developed at optimum conditions of pH, equilibrium time and sorbent dose.

Figure 4: Batu Tannery Waste water sampling

4.6. Chemicals

All the chemicals used were analytical grade reagents. A stock solution of 100 mg/L Cr (VI) was prepared by dissolving and$K_2Cr_2O_7$ in distilled water (Merck, Darmstadt, Germany). The stock solution was further diluted in distilled water in order to obtain two working solutions. The pH of the solution was adjusted using 0.1 M NaOH and/or 1M H_2So_4. Overall, three sets of experiments were conducted: adsorption kinetic, equilibrium and desorption experiments.

4.7. Cr (VI) ions adsorption procedures

A series of duplicate batch adsorption experiments was conducted at room temperature in acid washed polyethylene plastic bottles with blank (only Biochar) and control only with the desired concentrations of Cr (VI) working solutions experiment. A 100 mL of the working solution with desired dose of the adsorbent was agitated on horizontal shaker at 200 rpm at room temperature for specific time intervals. At the end of each time interval, samples was withdrawn and subsequently filtered through Whatman GF/C filters.The filtrate was then analyzed for their chromium concentration with an UV visible spectrophotometer. The adsorbed heavy metal concentration was calculated as the difference of initial and final metal concentration of the liquid phase.

4.7.1. Effect of contact time

To determine the equilibrium contact time at which the adsorption completed, the agitation time was varied from (15, 30, 40, 60, and 120) min until equilibrium is achieved. A known concentration of the adsorbate in aqueous solutions at desired pH was shaken with a desired amount of the adsorbent at a fixed rpm for a predetermined contact time. The amount of the Cr ions adsorbed per unit mass of the adsorbent media, and the percentage adsorption was computed using respectively eqs. (1) And (2) given below

$$q_t = \frac{(C_0 - C_t)}{M} * V$$ …………………………………………………………………………..…. (5)

$$A = \frac{(C_0 - C_t)}{C_0} * 100$$ …………………………………………………………………... (6)

where, q_t (mg/g) is the amount of Cr ions adsorbed at any time, t (min); $A(\%)$ is the percentage of ions adsorbed; C_0 (mg/L) is initial Cr ions concentration ; C_t (mg/L) is concentration of Cr in the aqueous phase at any time, t; V (L) is volume of the aqueous solution; and M (g) is mass of the adsorbent media used in the experiment (Fruit et al., 2014).

4.7.2. Effect of solution pH

The effect of solution pH was investigated to determine the optimum pH for maximum adsorptive removal of heavy metal over the initial pH range (2, 3, 4, 5, 6, 7, 8, 9 and 10) by allowing a known dose of the adsorbent to adsorb a desired concentration of heavy metal ions in the aqueous solution.

Figure 5: procedures of adsorption for pH adjustment

4.7.3. Effect of adsorbent dose

To determine the optimum dose required for the reduction of average heavy metal concentration in the industrial wastewater to a desired level, different adsorbent doses ranging from (1, 2, 4, 6, 8, 10) g/L was separately added into aqueous solution of known pH containing a desired adsorbate concentration. The mixture was agitated at a fixed rpm (revolution per minute) for equilibrium contact time determined by time series experiments.

4.7.4. Effect of initial concentration

The effect of initial concentration was examined varying the concentration of hexavalent chromium ions (0.5 - 40) mg/L while maintaining the solution pH, adsorbent dose and shaking speed at optimum and contact time at equilibrium.

4.7.5. Effect of co-existing ions

The influence of co-existing ions at different concentration levels on the removal efficiency were examined in such a way that each ion separately and in a mixture added to a container of 150mL solution of a known concentration of heavy metal ion at optimum solution pH and desired adsorbent dose.

In order to determine the effects of competitive anions, different concentrations of Phosphate, Nitrate, chloride and their mixture as the most abundant anions present in natural waters were prepared and adsorption tests of hexavalent chromium was repeated under the influence of these competing anions at optimum time. Measurement anions were done according to the procedures described in Standard Methods (APHA, 2005). The model of visual spectrophotometer used for these analyses was PerkinElmer and before analyses, all of the water samples had been filtered by use of 0.45 μm Whatman filter paper. The percentage (%) of extraction was calculated from the data obtained.

4.8.   Desorption experiment

The residues on the filters paper was used for the desorption experiments. The Whatman GF/C filters used for the adsorption experiments would be placed in bottles containing 100 ml

deionized water and the mixture was agitated at 200 rpm at room temperature. It was assumed that desorption equilibrium was reached at the same time as adsorption equilibrium. After reaching equilibrium time, the samples were then filtered with the filters described above and the filtrate metal content adsorbent was oven dried for 12 hrs and was measured by means of the atomic adsorption spectrophotometer. The pH values of the solutions were measured with a pH-meter, before and after adsorption as well as after desorption experiments, in order to record any significant changes. Similarly, all the experiments were carried out in duplicate to reliable the result.

4.9.   Data Analysis
4.9.1. Adsorption kinetics

The Pseudo first-order and second-order kinetic models are the most popular models used to study the sorption kinetics of heavy metals and to quantify the extent of uptake in sorption kinetics. In order to evaluate the kinetics of Cr (VI) adsorption and potential rate controlling steps, the pseudo first and pseudo second order models was checked. This was obtained by taking 2 mg/g Cr (VI) concentration at the same dose of adsorbent 1g/L.

4.9.1.1. **Pseudo first order kinetics**

The pseudo first-order rate expression is:

$$\text{Log } (qe - qt) = \log qe - \frac{k_1}{2.303} t \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(7)}$$

Linear plots of $Log(qe - qt)$ versus t indicate the applicability of this model

4.9.1.2. **Pseudo second order kinetics**

The pseudo second-order rate expression is:

$$\frac{t}{qt} = \frac{1}{K2qe2} + \frac{t}{qe} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(8)}$$

If the pseudo second-order kinetics is applicable, the plot of t/qt versus t should give a linear relationship (Deng et al., 2013).

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4.9.2. Adsorption isotherms

Langmuir and Freundlich isotherms were used to study adsorption mechanism and to determine maximum adsorption capacity of the adsorbents. Development of adsorption isotherms for this study was done by exposing known concentrations of chromium (1-40 mg/L) to a fixed dosage of adsorbent (1 g/L) in the optimum pH 2.

4.9.2.1. Langmuir isotherm

Langmuir isotherm is based on the assumption that the point of valance exists on the surface of the adsorbent and that each of these site is capable of adsorbing one molecule. It is assumed that the adsorption sites have equal affinities for molecules of adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site.

The general equation:

$$\frac{Ce}{qe} = \left(\frac{1}{qmb}\right) + \left(\frac{1}{qm}\right)C \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (9)$$

Ce is the equilibrium concentration (mg/L) and qe the amount adsorbed at equilibrium (mg/g).The Langmuir constants qm (mg/g) represent the monolayer adsorption capacity and b (l/mg) relates the heat of adsorption (Gandhi et al., 2014).

In order to evaluate the feasibility of the process, the Langmuir isotherm can be described in terms of the dimensionless constant; separation factor or equilibrium parameter;

$$R_L = \frac{1}{1+bCo} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (10)$$

b(Lmg−1) is the Langmuir isotherm constant and Co (mg /L) is the initial concentration of chromate. There are four probabilities for the RL value:

For favorable adsorption $0 < R$L < 1

For unfavorable adsorption RL > 1

For linear adsorption RL $= 1$ and

For irreversible adsorption RL $= 0$ (Foo & Hameed, 2010).

4.9.2.2. Freundlich isotherm

Freundlich isotherm provides the detailed idea about the effectiveness of the adsorbent and the maximum amount of adsorbate will get adsorbed by the adsorbent. The Freundlich equation is basically empirical but it is often useful as a means for data description. It describes the heterogeneous surface energies by multilayer adsorption.

The general equation:

$$\ln qe = \ln Kf + \left(\frac{1}{n}\right)\ln C \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (11)$$

Kf indicates adsorption capacity (mg/g) and 1/n an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. For values in the range $0.1 < 1/n < 1$, adsorption is favorable. The greater the values of Kf better is the favorability of adsorption (Attar, 2010).

The amount of metal ion adsorbed per unit mass of adsorbent was obtained using the equation:

$$qe = (Ci - Ce)\frac{V}{m} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. \quad (12)$$

where qe is the mass of adsorbate (metal ion) adsorbed per unit mass of adsorbent (mg adsorbate/g adsorbent), C_i is the initial concentration (mg /L) of metal ion in solution, Ce is the final (equilibrium) concentration (mg /L) of metal ion in solution, V is the volume (L) and m is the mass of adsorbent (g) (Chantawong, 2004).

Generally, the removal efficiency of Cr (VI) was calculated as

$$\%R = \left[\frac{(Co - Ce)}{Co}\right] \times 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.. \quad (13)$$

C^0 and Ce is the initial and equilibrium metal ion concentrations (mg/L). The linear plots of ln Ceq vs. ln q show that the adsorption of metal ions onto the adsorbent follows the Freundlich isotherm model. Finally, the simulation of sorption isotherm of Cr (VI) on the two biochars was assessed based on the Langmuir and Freundlich models. All the results of proximate analyses were expressed as the average of three experiments by standard deviations.

Duplicate experiments were carried out to avoid any discrepancy in results with the reproducibility and the relative deviation of the orders. Blank samples without ions was used as Control and average data was reported

Chapter Five: Results

5.1. Proximate Analysis

The proximate analyses as presented in table 1 showed that the percentage of moisture content, volatile matter and ash content (82.94%, 14.1%, 2.97%) %, respectively. Ash content can also affect activated carbon i.e. it reduces the overall activity of activated carbon. It also reduces the efficiency of reactivation, the lower the ash value therefore the better the activated carbon for use as adsorbent.

Table 1: Proximate analysis of OFMSW

Parameters	Mean ± SD
Moisture contents (wt %)	82.94±1.015
Volatile matter (wt%)[a]	14.1±0.5
Ash content (wt%)[a]	2.97±0.34

[a] Results relative to dry basis

5.2. Characterization of biochar

The effect of pyrolysis temperature on the ultimate and proximate analysis of biochars was given in Table 3. As indicated from the table when the pyrolysis temperature was increase from 350°C to 700°C; the char yield was decrease from 60% to 29% and the fixed carbon content of the biocharsdecreased. Consequently, the Hydrogen and Nitrogen content was decrease from (7.01% to1.32%), (7.1% to 1.9%), respectively.

Table 2: Char Yield and Elemental Composition of organic MSWF char produced at various temperatures (300°C, 450°C and 700°C)

Composition	BC-350	BC-450	BC-700
Char yield (wt%)[a]	60 ± 0.23	35 ± 0.2	29 ± 1.5
Carbon (wt%)[b]	53.23	49.67	39.03

| Hydrogen(wt%)[b] | 7.01 | 2.82 | 1.32 |
| Nitrogen(wt%)[b] | 7.10 | 3.06 | 1.90 |

[a]based on dry mass results relative to dry basis
[b] results relative to dry basis free of ash
[c] calculated by $100-C\%-H\%-N\%-S\%$

5.3. Effect of contact time

Contact time is one of the important parameters for the adsorption process and the optimization of contact time in the adsorption process is necessary to develop cost effective procedure. The effect of contact time on the adsorption of Cr(VI) by biochars were examined using 4 g of biochars produced at different temperatures and 100 ml of 2 mgL^{-1} Cr (VI) solution (pH 7). The adsorption experiment was carried out for 2 hours to determine the adequate adsorption time and the result is presented in Figure 6.

The amount of the adsorbed Cr (VI) onto the biochar slow increase up to 15 min and rapidly increased from 15 min to 30 min for BC-350°C and BC-700°C. For BC-450 the removal efficiency was increased up to 15 min and slow increase from 15 to 30 min. It reached a constant value after 30 min. The percent removal of initial Cr (VI) using BC-350°C was 61.25, BC-450°Cwas 68.5% and BC-700°Cwas 64.5% at 30 min contact time. The adsorption capacity of Cr (VI) from 15 min to 30 min was also increase from (0.0285 to 0.1225), (0.1 to 0.137) and (0.1175 to 0.129) for BC-350°C, BC-450°C and BC-700°C.Even though, the removal efficiency and adsorption capacity of all biochars was different, the equilibrium time for all the adsorbents was similar (30min).
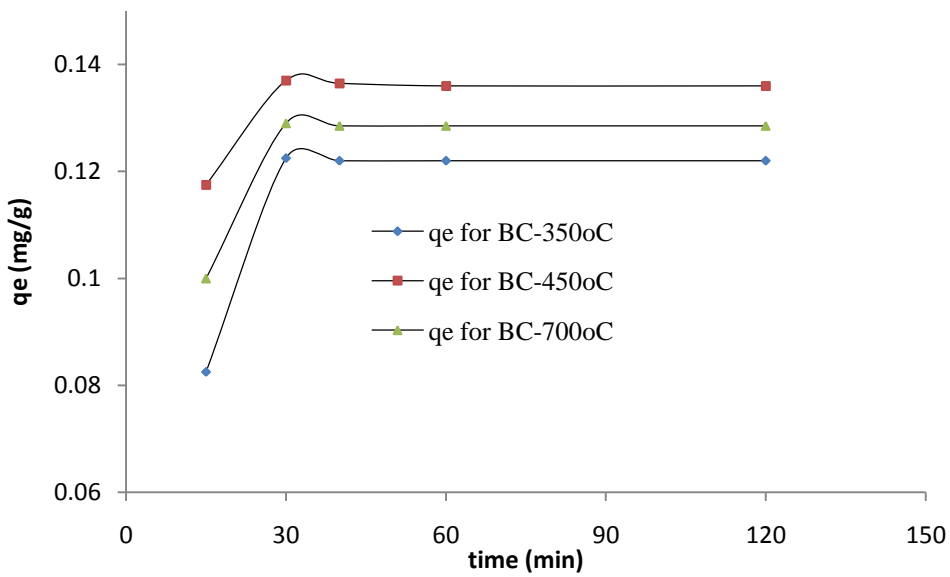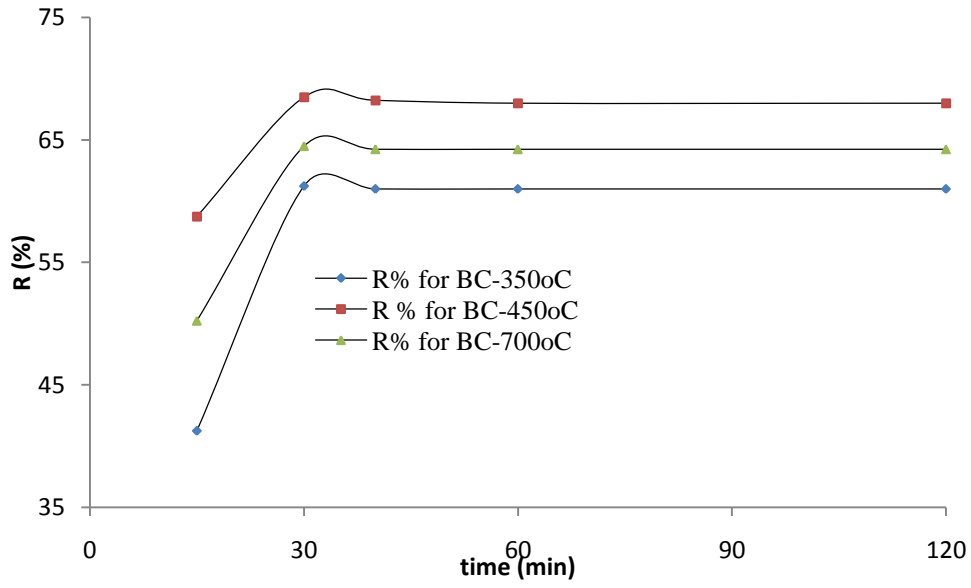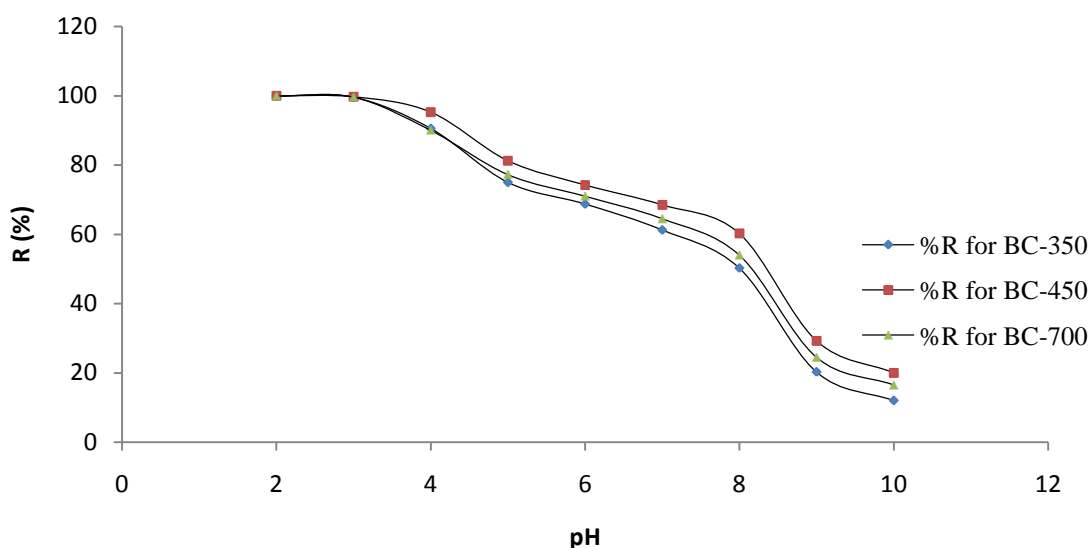
Figure 6: Cr (VI) removal efficiency versus time (initial chromium concentration: 2 mg/L, adsorbent dose: 1 g/L, PH: 7, shaking speed: 200 rpm)

5.4.Effect of pH

The effect of pH on removal of Cr (VI) was investigated by varying pH from 2.0 to 10.0. As indicated from the figure 7, a progressive decrease in Cr (VI) adsorption was observed with increase from pH 2 to pH 10. A maximum removal efficiency of initial Cr (VI) was 99.92%, 100% and 99.95% for BC-350°C, BC-450°C and BC-700°C respectively at pH 2. The removal efficiency of biochars showed a slight decrease between pH 2 to pH 4 (i.e. from 99.92% to 90.57%, 100% to 95.3% and 99.95% to 90.05% for BC-350°C, BC-450°C and BC-700°C respectively. when the pH was increase from 2 to 10 the adsorption capacity was decrease from (0.19985 to 0.02 mg/g) for BC-350°C, (0.2 to 0.04mg/g) for BC-450°C and (0.1999 to 0.033 mg/g) for BC-700°C. Hence the optimum removal efficiency and adsorption capacity was observed at pH 2.
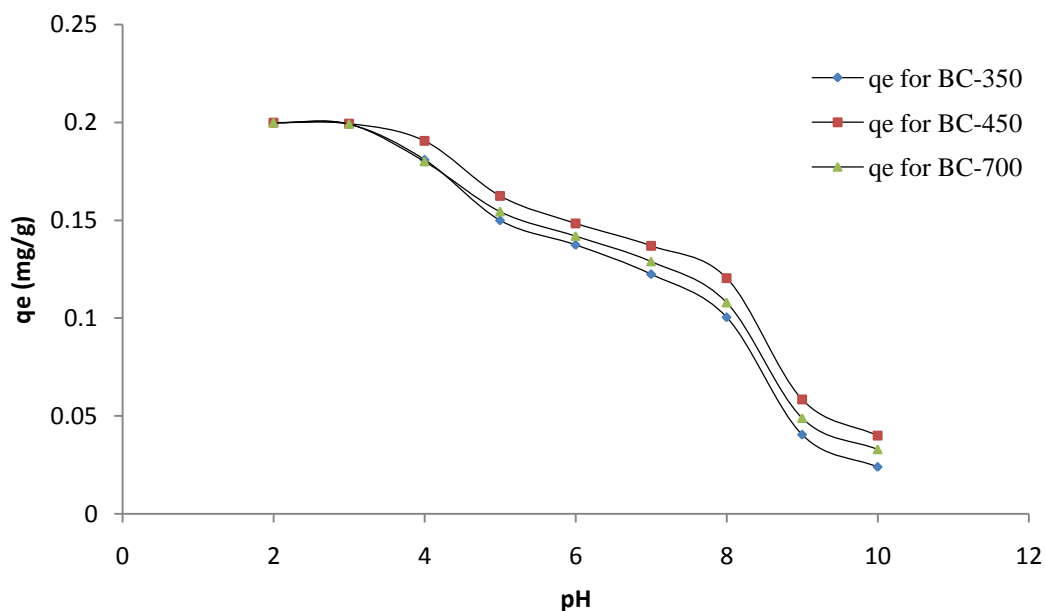
Figure 7: Cr (VI) removal efficiency versus PH (initial Cr^{6+} concentration: 2mg/L, adsorbent dose: 1 g/L, contact time: 30min, shaking speed: 200 rpm)

5.5. Effect of adsorbent dose

The pattern of Cr (VI) adsorption with varying biochars dose is presented in Figure 8. The result of this study showed that the Cr (VI) loading capacity (the amount of Cr (VI) adsorbed per unit mass of biochars) progressively decreased from (0.196 mg/g to 0.019 mg/g), (0.2 mg/g to 0/01956 mg/g) and (0.2 mg/g to 0.0194 mg/g). The removal efficiency became constant when the adsorbent dose increased from 1g to 10 g. The efficiency of Cr (VI) removal increased rapidly from 85.6% to 98.2%, 87.5% to 99.5%, and 86.8% to 98.8% as the adsorbent's dose increased from 0.5 to 1 g/L for BC-350°C, BC-450°C and BC-700°C respectively. Therefore 1g/L was the optimum dose for 2 mg/L (Cr VI) at pH 2 and 30 min contact time.
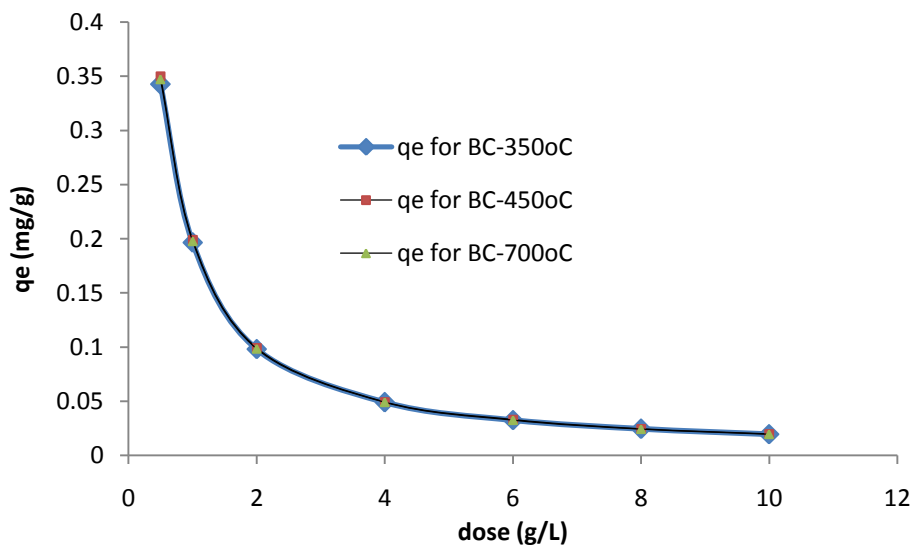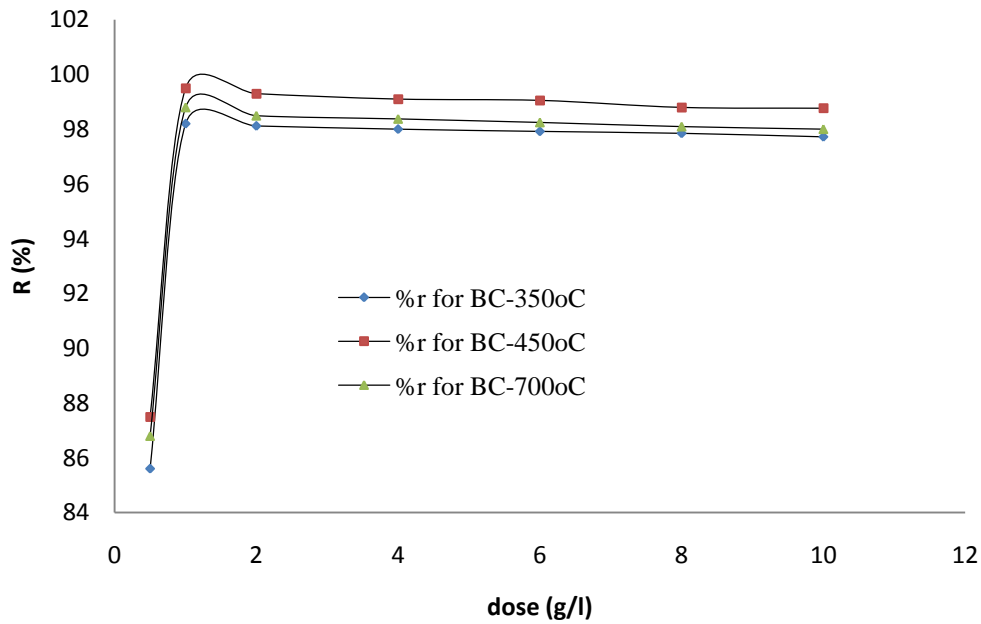
Figure 8: Cr (VI) removal capacity as a function of adsorbent dose (initial Cr^{6+} concentration: 2mg/L, contact time: 30 min, pH: 2, agitation speed: 200 rpm)

5.6.Effect of initial Cr (VI) concentration

The removal of Cr (VI) using BC-350°C, BC-450°C and BC-700°C was investigated by varying initial Cr (VI) concentration, optimum pH (2), contact time of 30 min and 1g dose. The results presented in Figure 8 showed that the removal efficiency of Cr (VI) decreased at all adsorbents: from (99.9% to 51%), (100% to 56.6%) and (99.9% to 52.5%) forBC-350°C, BC-450°C and BC-700°C, however the adsorption capacity was increase from (0.09995mg/g to 2.04mg/g,), (0.1 mg/g to 2.18 mg/g) and (0.09995 mg/g to 2.1 mg/g) respectively as the initial Cr (VI) concentration increased from 1 mg/L to 40 mg/L. All the adsorbents removed both higher and lower concentrations of Cr (VI). However, BC-450°C had more removal efficiency than both BC-350°C and BC-700°C biochars. The equilibrium concentration of BC-450°C was 10 mg/g with removal efficiency of 99%. Hence, 10 mg/L was an equilibrium concentration at 1g/L dose. The equilibrium initial concentration of Cr (VI) for BC-350°C and BC-700°C was 4 mg/L and 6 mg/L with a removal efficiency of 97.5% and 98.3% respectively.
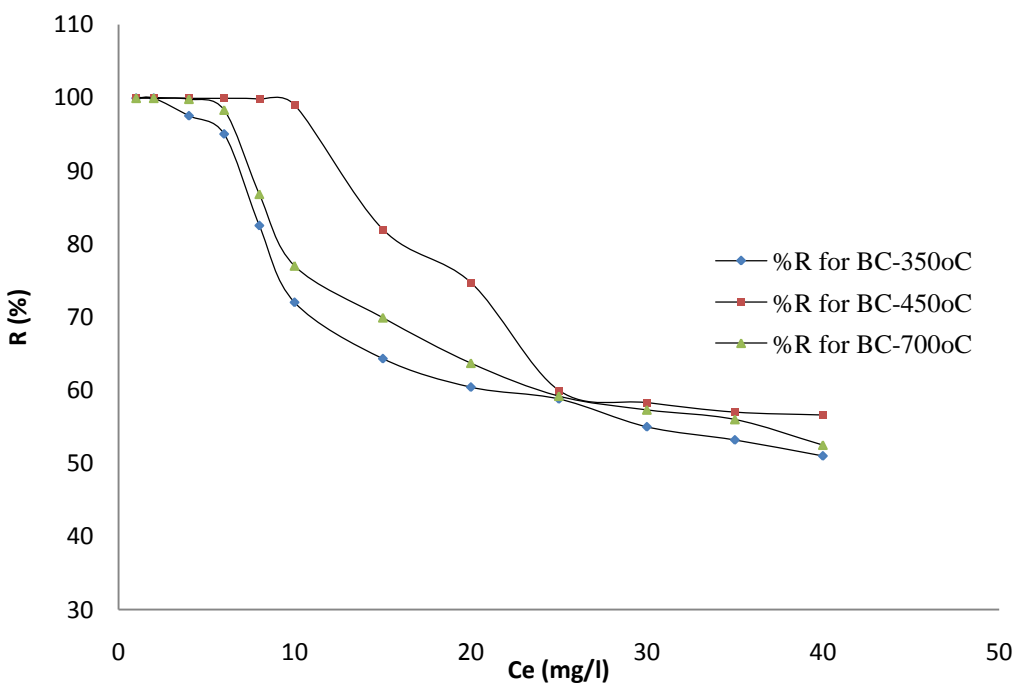
Figure 9: Cr (VI) removal efficiency versus initial concentration (adsorbent dose: 1 g/L, pH: 2, contact time: 30 min, shaking speed: 200 rpm)

5.7.   Effect of Co-existing ions

In order to assess the potential applicability of biochars as an adsorbent for Cr (VI) removal from tannery waste water, adsorption capacity was evaluated as a function of various competing ions such as chloride, nitrate, phosphate, and their mixture. The influences of the presence of these anions separately and in a mixture in the solution on the efficiency of Cr (VI) adsorption on biochars in Figure 9 showed that phosphate, among the three anions, caused the decrease in the removal rate of Cr (VI). However; the mixture of anions had greater influence on the adsorption capacity of Cr (VI) when compared with the phosphate. The influence these anions had similar result on BC-350°C, BC-450°C and BC-700°C.
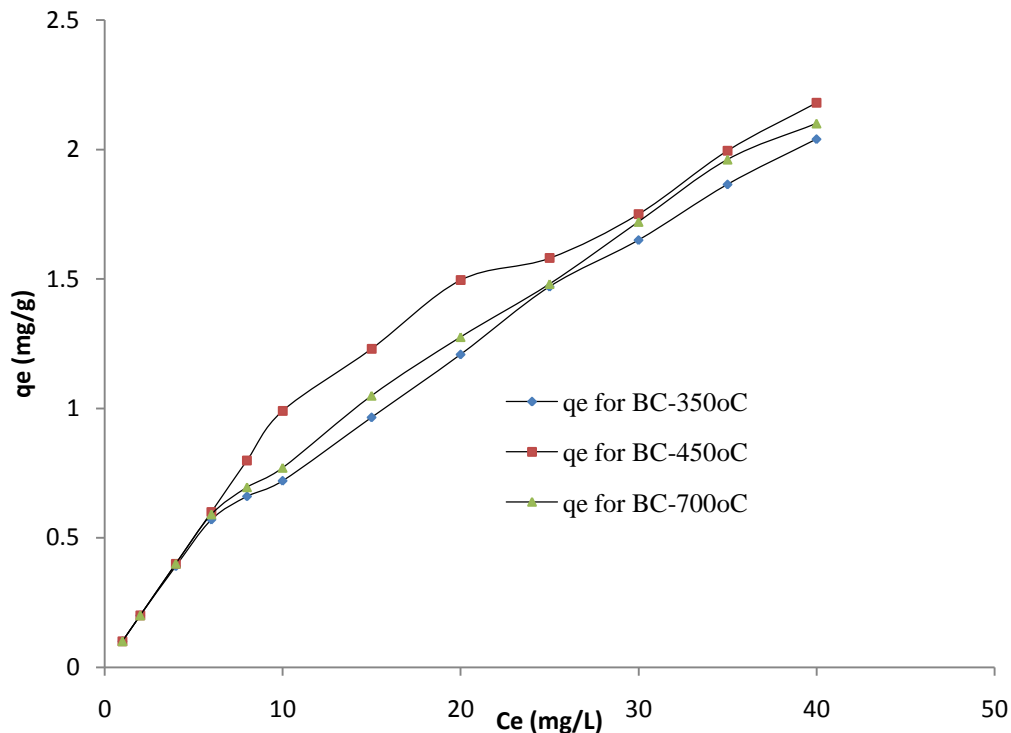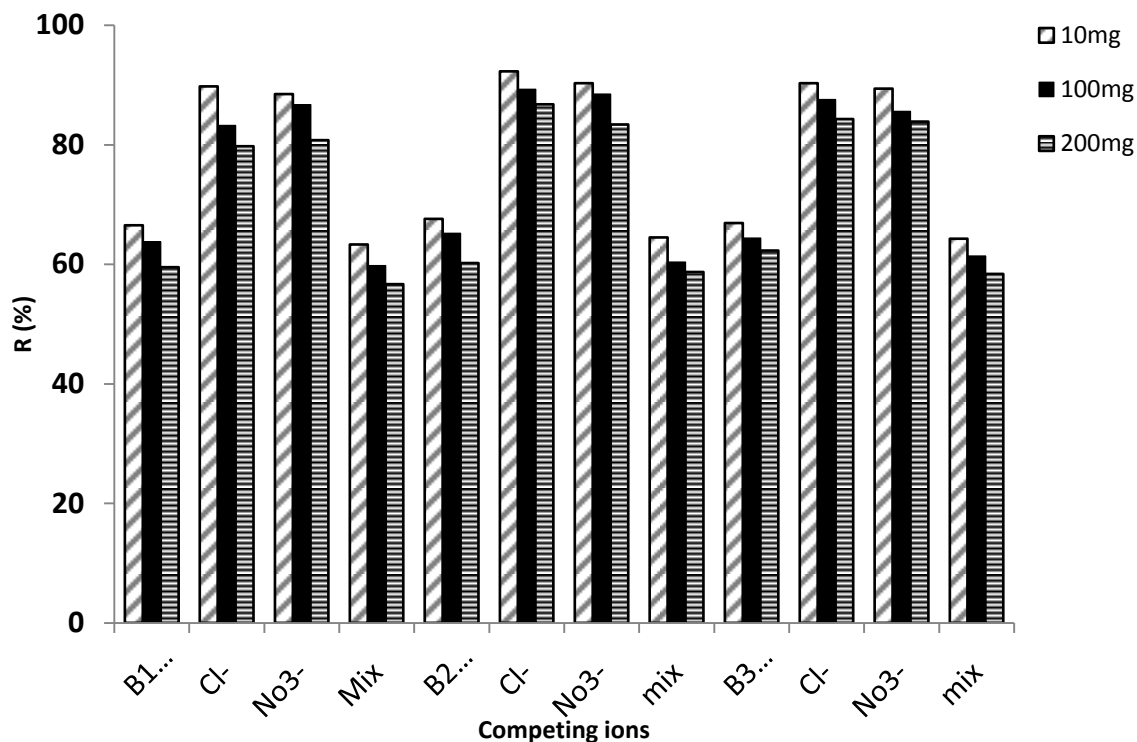
Figure 10: Cr (VI) removal efficiency versus interfering ions (adsorbent dose: 1 g/L, PH: 2, contact time: 30 min, agitation speed: 200 rpm)

5.8. Desorption study

The effect of strength of regeneration solution (NaOH) on the recovery of Cr (VI) is shown in the figure 10 that, when the strength of regeneration solution increased from 0.1 to 1 M, percentage recovery of Cr(VI) increases from 36.6% to 68%, 23.25% to 57.75 25% to 63% for BC-350°C, BC-450°C and BC-700°C respectively. The percentage recovery of Cr (VI) on BC-450°C is less when compared with both BC-350°C and BC-700°C. BC-350°C had greater desorption rate with 68%.
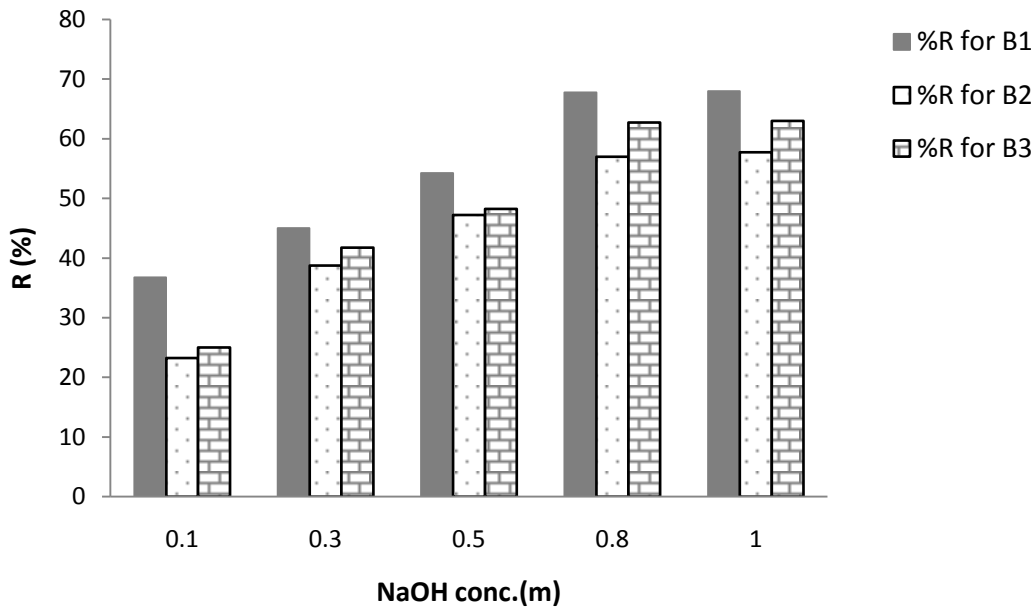
Figure 11: Percentage of Cr (VI) desorbed

5.9.   Data Analysis

5.9.1. Kinetic Equilibrium

The kinetics gives information about reaction pathways and times to reach equilibrium. Sorption kinetics shows a large dependence on the physical and /or chemical characteristics of the sorbent material.

Times determined contact times for the subsequent sorption isotherm studies. The pseudo-second order rate constant, k_2 (mg/g.min) and the calculated equilibrium adsorption capacity were computed from the slope and intercept of the plot of t/qt and t. The Cr (VI) adsorption kinetics data were followed the pseudo-second order kinetics model with the correlation coefficient, R^2 greater than 0.99 (Figure 12, 13 and 14). The values of the pseudo-second order parameters are given in Table 3.

Table 3: Parameters of pseudo-second order kinetic model for Cr (VI) adsorption onto BC-350°C, BC-450°C and BC-700°C.

Biochars	K_2	R^2
B1	0.054	0.99
B2	0.055	0.99
B3	0.045	0.99

Figure 12: Plot of pseudo-second order kinetics of Cr (VI) adsorption at BC 350°C (initial Cr6+ concentration: 2 mg/L, adsorbent dose; 1 g/L, pH: 2, contact time: 30 min and agitation speed: 200 rpm) for BC-350°C

Figure 13: Plot of pseudo-second order kinetics of Cr (VI) adsorption at BC 450°C (initial Cr^{6+} concentration: 2 mg/L, adsorbent dose; 1 g/L, pH: 2, contact time: 30 min and agitation speed: 200 rpm) for BC-450°C
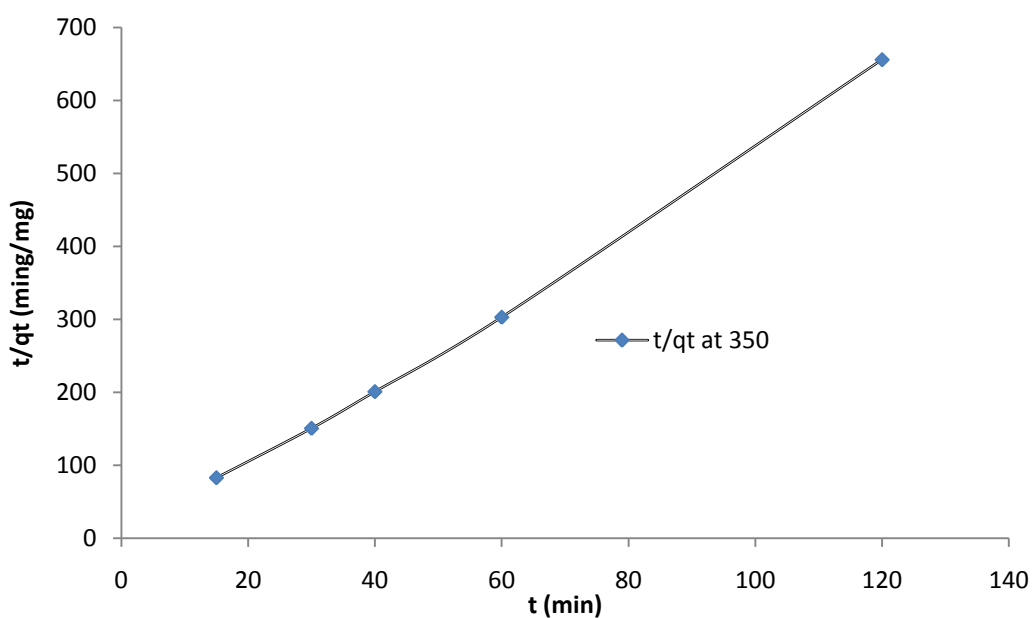

Figure 14: Plot of pseudo-second order kinetics of Cr (VI) adsorption at BC 700°C (initial Cr^{6+} concentration: 2 mg/L, adsorbent dose; 1 g/L, pH: 2, contact time: 30 min and agitation speed: 200 rpm) for BC-700°C
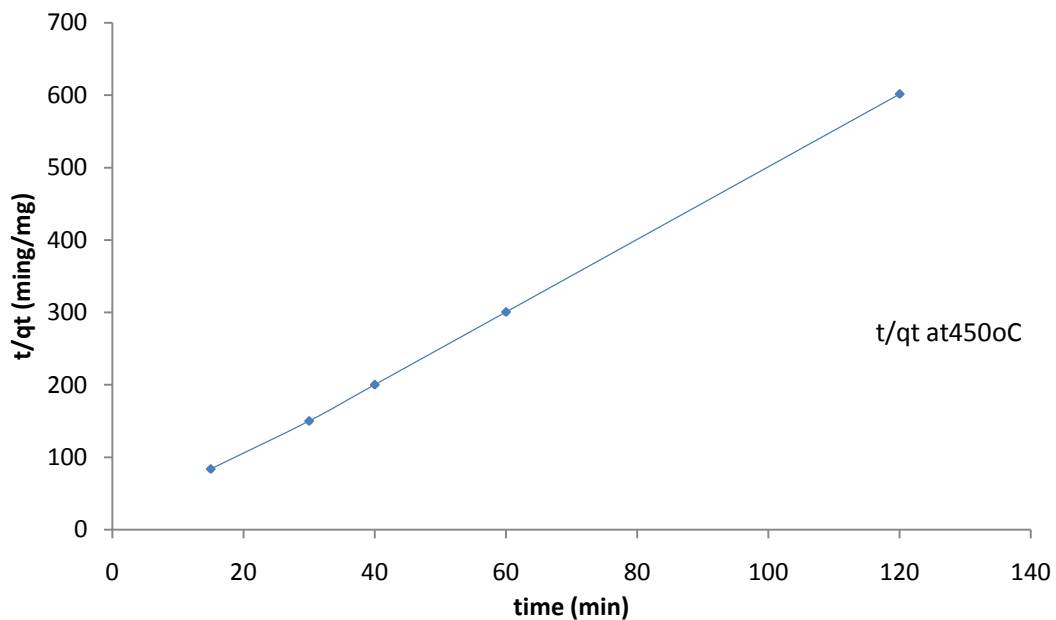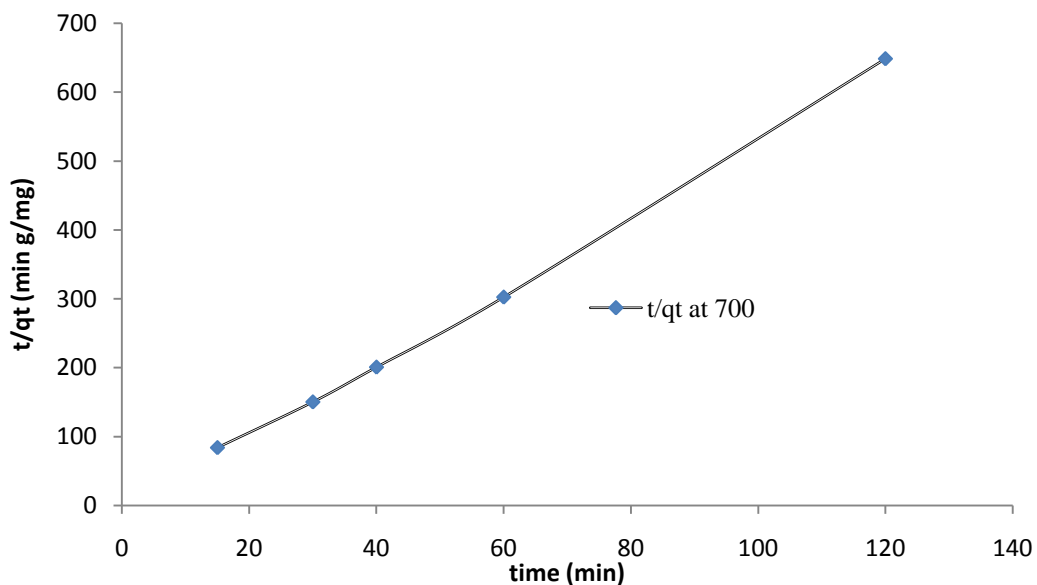
5.9.2. Isotherm

The Langmuir and Freundlich adsorption models were used for mathematical description of adsorption of Cr (VI) ions. The results of the Cr (VI) adsorption isotherm are given in Figure and table. Experiments were carried out by varying the initial Cr (VI) ion concentrations at pH 2, 1g dose and 30 min. To analyses the adsorption data, the Langmuir and Freundlich isotherm equations are used and calculated parameters from the fitting plots. The results of the study showed that Freundlich models follow Cr (VI) adsorption for BC-350°C, BC-450°C and BC-700°C with all R^2 values over 0.98. However, the correlation coefficients of Langmuir model are lower and the R^2 value for BC-350°C, BC-450°C and BC-700°C was 0.96, 0.81 and 0.97 respectively; Suggesting that the Freundlich isotherm correlation had better fit than Langmuir model for all adsorbents. The R^2 value for Freundlich correlation was 0.985, 0.981 and 0.99 for BC-350°C, BC-450°C and BC-700°C respectively. This indicates the applicability of heterogeneous surface and multilayer adsorption process of the Cr (VI) on the surface of biochars.

Table 4: Non-linear estimated isotherm parameters for chromate adsorption

Biochars produced at different temperature	qe(mg/g)	Freundlich Isotherm			Langmuir Isotherm		
		KF (mg/g)	1/n (mg/L)	R^2	Q_{max}(mg/g)	B (mg/L)	R^2
350°C	2.04	0.37	0.56	0.985	1.5	0.05	0.96
450°C	2.26	1.09	0.2	0.981	0.83	0.08	0.81
700°C	2.03	0.59	0.41	0.99	0.67	0.07	0.97
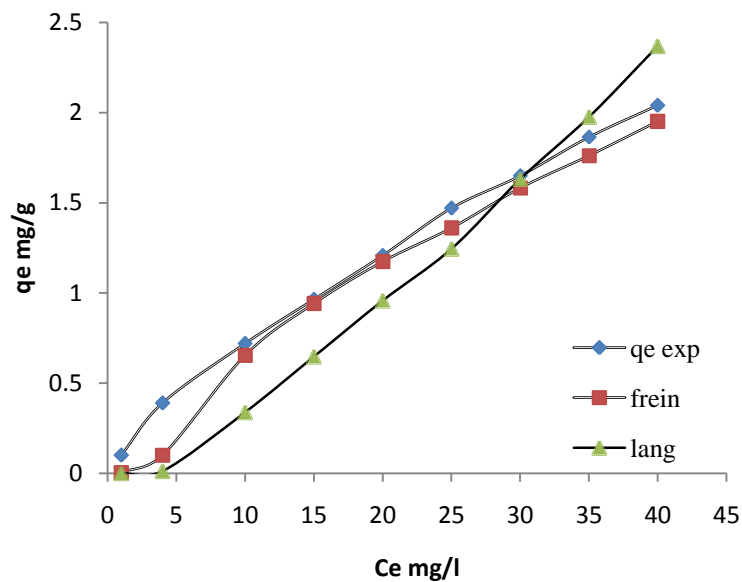
Figure 15: Freundlich and Langmuir isotherms for Cr (VI) adsorption (initial Cr^{6+} concentration: 1 to 40 mg/L, adsorbent dose: 1 g/L, pH: 2, contact time: 30 min, agitation speed: 200 rpm) for BC-350°C.
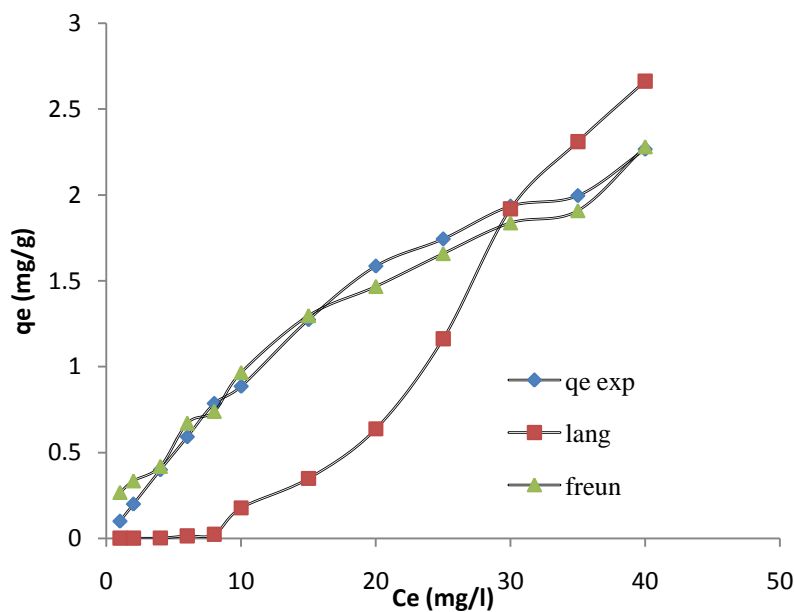
Figure 16: Freundlich and Langmuir isotherms for Cr (VI) adsorption (initial Cr^{6+} concentration: 1 to 40 mg/L, adsorbent dose: 2 g/L, pH: 2, contact time: 30 min, agitation speed: 200 rpm) at BC-450°C.
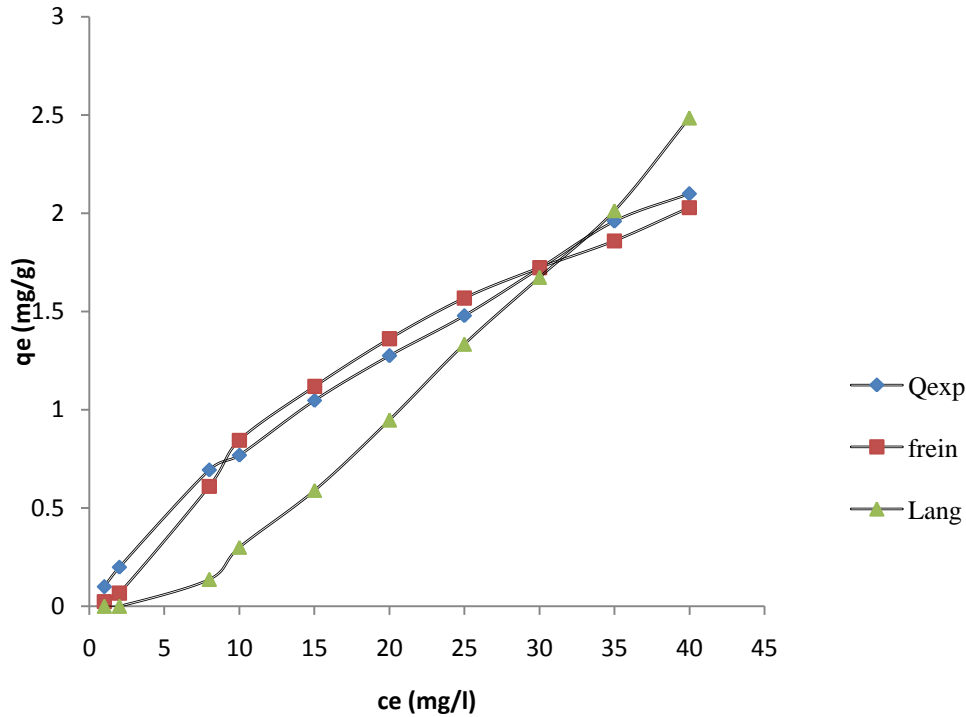
Figure 17: Freundlich and Langmuir isotherms for Cr (VI) adsorption (initial Cr (VI) concentration: 2 to 10 mg/L, adsorbent dose: 2 g/L, pH: 3, contact time: 60 min, agitation speed: 200 rpm at BC-700°C).

5.10. Removal of Cr (VI) from real wastewater

The characteristics of wastewater sample collected from Batu tannery are summarized in Table 4. The wastewater contained chromium ion and other chemicals such as NO_3^-, PO_4^{3-}, Cl^-, COD, BOD and etc. The amount of Chromium ions in this waste water were 0.8 mg/L and this was reduced 0.0124 mg/L using 1 g/L of the adsorbent within 30 min of contact time at pH 2 of the sample. Consequently 98.45% of the 0.8mg/L Cr (VI) concentration of the wastewater was removed.

Table 5: Physicochemical characteristics of waste water from Batu Tannery

Composition	Value
Cr^{+6}	0.8 mg/L
NO_3^-	0.449 mg/L
PO_4^{3-}	13.5 mg/L
COD	746 mg/L
BOD	1738 mg/L
Cl^-	349 mg/L
pH	7.86
Temperature (^{o}c)	25.4^{o}C

CHAPTER SIX: DISCUSSION

6.1. Discussion

In this study there are three adsorbents produced at different temperatures from OFMSW using pyrolysis for activation to investigate the removal efficiency of biochars for (Cr VI). As indicated from the result BC-450°C had high removal efficiency of (Cr VI) when compared with BC-350°C and BC-700°C. Similar studies with this results as reported (Esentepe, 2014) surface areas were slightly increase while increasing pyrolysis temperature up to 550°C and decreased thereafter. Structural ordering and micropore coalescence are found to be responsible for the decrease in the value of the surface area observed at 700^{0}C, resulting in a thermal deactivation of the biochar.

The same trends are observed in micropore volume and area data (Guerrero, 2005). The Micropore volume and area of biochars increased with the pyrolysis temperature (550°C) and reached a maximum. At the temperature of 700°C, the surface area and total pore volume were lowered. According to (Liu, 2010) due to the high temperature, the porous structure cracked and the pores might be partially blocked, which could to a low surface area. As gonz'ales(2005) stated that an increase of the temperature does not improve the textural properties of the biochars. This might be due to a sintering effect, following by shrinkage of the biochar and realignment of the biochar structure which leads to a decrease of the mean-size and volume of the pores. Therefore, from the above result the BC-450°C had high efficiency to remove Cr (VI) due to the high surface area and pore volume of the adsorbent.

Proximate and elemental analysis of biochars was used to determine the characteristics of biochars produced at different temperature. As revealed from the table 1 the amount of moisture content was 82.94%, volatile matter was 14.1% and ash content was 2.79%. As indicated from the result the volatile matter and ash content of organic fraction of solid waste was low. Similar investigation with this result reported by (Ekpete, Harcourt, Chemistry, & Harcourt, 2011) Low amount ash and volatile matter, indicating that the particle density is relatively small and that the biomaterial should be an excellent raw material for adsorbents to be used. The ash content is a measure of the non-volatile matter and non-combustible component of the biochar (Esentepe, 2014). The elemental analysis of biochars from table 2 indicated that when the temperature of pyrolysis was increase the carbon, Hydrogen and nitrogen was decrease. This was to be expected

because the increased devolatilization during pyrolysis resulted in biochar(Esentepe, 2014).These were also a decrease in the hydrogen content; this might be due to the great proportion of hydrogen compounds in the volatile matter (Sanchez, 2009). The increased ash content is due to the reduction in the content of other elements during pyrolysis. Elements such as C, H, N, O, and S are volatilized during heating while the inorganic salts such as quartz and calcite are not fully volatilized (Claoston, Samsuri, Ahmad Husni, & Mohd Amran, 2014).Therefore, this biochar could be used in application of activated carbon production. This trend in the elemental analysis were found similar in biochar produced from other biomass sample such as wheat grains, cotton stalk, pitch pine (Chen 2012; Kim . 2012).

6.2. Effect of contact time

The experiment, concerning the influence of reaction time on removal efficiency, was carried out keeping all other parameters constant. Removal of Cr (VI) at varying contact time of (15, 30, 40, 60, and 120 min) was studied. As it can be seen in figure 6 removal efficiency increased with an increase in contact time before equilibrium is reached. After equilibrium is reached removal efficiency would be constant at all biochars. Cr (VI) uptake rate was rapid up to 15 min and slow from 15 to 30 min of contact time for BC-450°C and slow increase up to 15min and then rapid increase from 15 to 30 min for BC-350°C and BC-700°C; become constant after equilibrium.

This could be due to the large number of vacant spaces on the adsorbent surface and, the initial strong attraction between adsorbent positive sites and the negatively charged chromate species which is similar with an observation of (Abdel *et al*., 2012).Hence equilibrium contact time is reached at 30min; similar study with this was observed that adsorption rate equilibrium was reached after 30 min. The initial faster rate of metal sorption may be explained by the large number of sorption sites available for adsorption. For the initial bare surface, the sticking probability is large, and consequently adsorption proceeded with a high rate and the Cr (VI) uptake rate by adsorbent is decreased significantly, due to the decrease in the number of adsorption sites (Sobhanardakani, Parvizimosaed, &Olyaie, 2013).

6.3. Effect of pH

The pH value is an important factor for controlling the process of adsorption as it affects the surface charge of the adsorbents, the degree of ionization and the species of the adsorbate. The effect of pH on adsorption of Cr^{6+} at different initial concentrations is shown in Figure6. The maximum percentage removal of Cr (VI) (99.92, 100 and 99.95%) for BC-350°C, BC-450°C and BC-700°C is reported at pH value of 2.

As K. Ranganathan, Shreedevi D. Kabadgi (2011)stated that the behavior for better adsorption at low pH by biochar might be attributed to the large number of H^+ ions present at low pH values which in turn neutralize the negatively charged adsorbent surface.This observation was similar with study of (Yarkandi, 2014). On the other hand, at lower pH 2, dominant form of Cr (VI) is $HCrO_4^-$ while the surface of adsorbent is charged positively. Hence the maximum chromium removal was observed at lower pH 2. Higher removal efficiency of chromium at low pH may also be due to reduction of chromium (VI) to chromium (III), which was then adsorbed by the adsorbent (Namasivayam and Yamuna, 1995). Increase in pH shifts concentration of $HCrO_4^-$ to other forms, CrO_4^- and $Cr_2O_7^{2-}$. It can be concluded that the active form of Cr (VI) that can be adsorbed by biochar was $HCrO_4$-. The increase in pH with contact time explained by hydrolysis of the adsorbent in water, which will create positively, charged sites. Upon adsorption of $HCrO_4^-$, a net production of hydroxide ions will occur (Saliba, 2002).

Every mole of $HCrO_4^-$ adsorbed results in the release of two moles of hydroxyl ions in the solution, which raises the solution pH (Namasivayam*et al*, .2004). Hence pH 2 was optimum pH for the maximum removal efficiency of this study.

6.4. Effect of Dose

As indicated from the result percent removal was increased from 0.5 g/L to 1 g/L dose of all the biochars. The increase in the removal percentage with the increase in the adsorbent dose can be attributed to the increase in the number of the adsorption sites as the amount of adsorbent increased (Aryal and Liakopoulou, 2011). After 1 g/L dose of adsorbent percent removal of Cr (VI) become constant. The adsorption capacity was slowly decrease as the biochars dose increase from 1 to 10 mg/L. Similar result with this study was showed that according to (Thole, 2011) the progressive decrease in the loading capacity was possibly due to the lower ratio of Cr (VI) ions to the available active binding sites with the increase in the mass of the adsorbent. The decrease

in size of adsorbent results in the increase of the surface area and thereby the number of active sites is better exposed to the adsorbate(Krishna & Sree, 2013).

6.5. Effect of Initial Concentration

The initial concentration of metal ion provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases (Malkoc 2006). When the initial Cr (VI) ions increase from 1 mg/L to 40 mg/L the removal efficiency was decrease from 99.9% to 51%, 100 to 56.6% and 99.9% to 52.2% for BC-350°C, BC-450°C and BC-700°C respectively. Even though all the biochars had efficient to remove Cr (VI), BC-450°C equilibrium removal rate was greater than the two biochars; this is due to surface area and pore volume of the biochar depending on the pyrolysed temperature. According to Esentepe(2014), Biochars produced at all pyrolysis temperatures did slightly increase while increasing pyrolysis temperature up to 550°C and decreased thereafter.

In case of low chromium concentrations, the ratio of the initial number of moles of chromium ions to the available surface area of adsorbent is large and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of metal ions which depends upon the initial concentration, decreases (Yu *et al*., 2010).

6.6. Effect of Co-existing ions

The interference anions were determined to measure the effect of ions in the wastewater on the removal efficiency of Cr (VI). As shown from figure 12 Po$_4$$^{3-}$ ions influence the adsorption capacity of Cr (VI) on to biochars while other anions had less influence on the adsorption capacity on to all biochars. Even though the removal efficiency of biochars are different; the Po$_4$$^{3-}$ ions effect was the same at all biochars. The presences of tenfold excess existence of interfering ions reduce removal efficiency of chromate in waste water treatment (Ravindhranath. 2012). Phosphate anions in the concentration range of 20 to 200 mg/L decrease the removal efficiency of chromium ions on the adsorbent under the present experimental conditions. This could be due to the binding of Cr^{+6} ions by outer sphere complexation process on the surface of an adsorbent, and the higher affinity of the phosphate towards an adsorbent decrease the adsorption of the Cr (VI) ions (Pigna, 2010, Wang et al., 2013)

6.7. Desorption

The saturated adsorbent which contains Cr (VI) is not safe for disposal due to the stringent environmental constraints. It is important and appropriate to propose a method for regeneration and reuse of adsorbent so as to reduce the load on environment in terms of disposal of polluted adsorbent(Chemistry, Harcourt, & Harcourt, 2006).

As indicated from the result batch desorption experiments were conducted in order to investigate whether Chromium adsorption on biochars is reversible or not. The high desorption rates 68% was observed using 1M of NaOH for BC-350°C. However; when the normality of NaOH was decrease desorption rate also decrease (for example; the 0.1m NaOH desorption rate was 36.75% 23.25%and 25% for BC-350°C, BC-450°C and BC-700°C) respectively. However, when the concentration of NaOH was increased the rate of desorption also increase to 68%, 57.75% and 63% for BC-350°C, BC-450°C and BC-700°C respectively. This may be due to that, at high strength of regeneration solution (NaOH) the abundance of hydroxide ions (OH-) increases hindrance to diffusion of Cr (VI) anions, thereby increasing detachment of the anion from the surface(Werkneh et al., 2014).

6.8. Kinetic equilibrium

When an adsorbent comes into contact with a metal ion solution, the concentration of metal ions on the adsorbent surface increased until a dynamic equilibrium is reached; at this point, there is a clearly defined distribution of metal ions between the solid and liquid phases. The kinetic sorption of Cr (VI) was analyzed with the pseudo-first and pseudo-second order kinetic model. For Cr (VI) and adsorbents examined the pseudo-second order kinetic model gave a better fit and provided the best correlation to the data (R^2 > 0.999) for all biochars when compared to pseudo first order. Pseudo-second order kinetic model constants are presented in Table 3. Based on pseudo-second order kinetic model assumptions, the reaction rate is proportional to the number of active sites on the adsorbent's surface and the rate-limiting step may be a chemical sorption between the adsorbate and the adsorbent (Agrafioti et al., 2014). Cr (VI) adsorption equilibrium was achieved at 30min.

The equilibrium chromate adsorption data analysis showed that chromate adsorption process can be well described by the Freundlich than the Langmuir isotherm models with the correlation

coefficient, R^2 value of 0.99, 0.98, and 0.98 for BC-350°C, BC-450°C and BC-700°C respectively. The Langmuir isotherm model R^2 value was ($R^2 = 0.96$, $R^2 = 0.82$, $R^2 = 0.97$) for BC-350°C, BC-450°C and BC-700°C respectively. Therefore, the best fit Isotherm model for the study of biochars to remove Cr (VI) was Freundlich which assumes surface heterogeneity of adsorbent.

CHAPTER SEVEN: CONCLUSION AND RECOMMENDATION

7.1. Conclusion

Biochars derived from OFMSW showed a high capacity for metal adsorption, suggesting that biochar production using organic solid waste could generate efficient metal adsorbents from metal-contaminated water and wastewater.The adsorption data referred to BC-450°C had more adsorption capacity for Cr (VI) removal than BC-350°C and BC-700°C. The tested biochars efficiently worked for Cr (VI) removal at pH 2. The equilibrium was achieved for the three biochars at the same time (30min) and the optimum dose for maximum removal was 1 g/L; when the adsorbent dose increase the efficiency become slowly decrease.The increasing of initial chromium concentration was reduced removal efficiency and increased amounts of chromate uptake. The anions occurred in the waste water had interfere the adsorption capacity. Maximum percentage of Cr (VI) desorption was achieved using 1M NaOH solution. BC-350 had high desorption capacity when compared with the two biochars. The removal rate of chromium in the real wastewater sample (0.8mg/L) using1g/L for all biochars was 98%.The kinetic adsorption characteristics were well described by the pseudo second-order model, which indicates that the chemisorptions mechanism controls the chromium adsorption onto biochars.The adsorption isotherm of metal adsorption onto biochars was well fitted by Freundlich than Langmuir isotherm. Generally, asbiocharsderived from OFMSW were effective to remove Cr (VI), easily available, it is expected to be an economical adsorbent material for removal and recovery of Cr(VI) from tannery wastewater.

Inadequate urban sanitation continues to pose a major threat to public health. The gradual increase in industrialization in developing country leads to emission of heavy metals to the environment which causes ecological/environmentaldegradation. Solutions for waste management and providing affordable waste treatment techniques are a timely issue. Therefore, in this regard application of biochar technology made from waste material for waste cleanup is a win-win solution, which is proofed in this study.

7.2.   Recommendation

All Biochars produced from organic fraction of municipal solid were efficient to remove the tested heavy metal from wastewater. Desorption rate was almost the same and BC-450°C had greater removal efficiency 10mg/l. Hence BC-450 was better applicability for removal of the heavy metal as well as for environment.

An adsorption of heavy metal using biochar derived from OFMSW that has the major importance in its: locally available, environmentally friendly, high adsorption capacities, high removal efficiency and the possibility of metal recovery. Further investigation is also required to investigate the adsorption capacity of the adsorbent under continuous flow conditions.

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ANNEX I

Materials

All chemicals used in this work (including Potassium dichromate, Diphenylcarbazide, Phosphoric acid, Sulfuric acid, Sodium hydroxide, potassium chloride, sodium chloride were used. The used organic solid waste (OSW) contain food and fruit waste, fruit peels, paper and wood, garden waste, pea and bean waste, coffee husk, saw dust and residual vegetables.

Apparatus

The tube furnace used for pyrolysis is shown in Fig. 1. Thermoanalyzer (Setaram, Model STA BAHR503), Measuring cylinder (100ml), Drying Ovens, Funnel, Spatula, Dropper, 250ml Erlenmeyer flask, 100ml Conical Flask, 120ml amber glass, wide mouth jar, PVC gloves, pH Meter (EUTECH pH510), orbital shaker (Stuart SSLI), spectrophotometer, Whatman 0.45µm filter paper, mechanical sieve and analytical balance, stirrer.

Reagents and standards

Use reagents and distilled water free from Chromium contamination.

i. Stock chromium solution: Dissolve 141.4 mg $K_2Cr_2O_7$ in water and dilute to 100ml; 1ml = 500µg Cr.on curve.

ii. Standard chromium solution: Dilute 1ml stock chromium solution to 100ml; 1ml = 5µg Cr. iii. Nitric acid: HNO_3, conc.

iv. Sulphuric acid: H_2SO_4, conc.; H_2SO_4, 1+1 (18N); H_2SO_4 (6N)

v. Sulphuric acid: H_2SO_4, 0.2N: Dilute 17ml6N H_2SO_4 to 500ml with water.

vi. Phosphoric acid: H_3PO_4, conc.

vii. Diphenylcarbazidesolution: Dissolve 250mg 1,5-diphenylcarbazide (1,5-diphenylcarbohydrazide) in 50 ml acetone. Store in a brown bottle.Discard when solution becomes discoloured.

viii. Sodium hydroxide 1N: Dissolve 40g NaOH 1L water. Store in plastic bottle.

Procedure

Preparation of calibration curve:

To compensate for possible slight losses of chromium during analytical operations, treat chromium standards by the same procedure as the sample. Accordingly, pipette measured volumes of standard chromium solution (5µg/l) ranging from 2 to 20ml, to give standards for 10 to 100 µg Cr, into 250ml beakers or conical flasks.

Color development and measurements:

Add 0.25ml (5 drops) H_3PO_4. Use 0.2N H_2SO_4 and pH meter to adjust solution to pH ± 0.5. Transfer solution to a 100 mlvolumetric flask, dilute to 100ml and mix. Add 2 Ml Diphenylcarbazide solution mix and let stand 5 to 10 min for full color development. Transfer an appropriate portion to 1 cm absorption cell and measure its absorbance at 540nm, using reagent water as reference. Correct absorbance of a blank carried through the method. From the corrected absorbance, determine micrograms chromium present by reference to the calibration. Construct a calibration curve by plotting corrected absorbance values against micrograms chromium in 102ml final volume. Repeat the experiment with samples.

 Calculation

mg Cr/l = [mg Cr (in 102ml final volume) / A] x 100

Where: A = ml original sample