

**Remediation of Surface Water Polluted by Effluent Discharges from Mining
Activities in the Eastern Region of Ghana**

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By

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DECLARATION

This thesis is the result of research work undertaken by Samuel Kusi in the department of Nuclear Engineering, School of Nuclear and Allied Sciences, University of Ghana, under the supervision of Andrew Nyamful (PhD) and Vincent Agbodemegbe (PhD).

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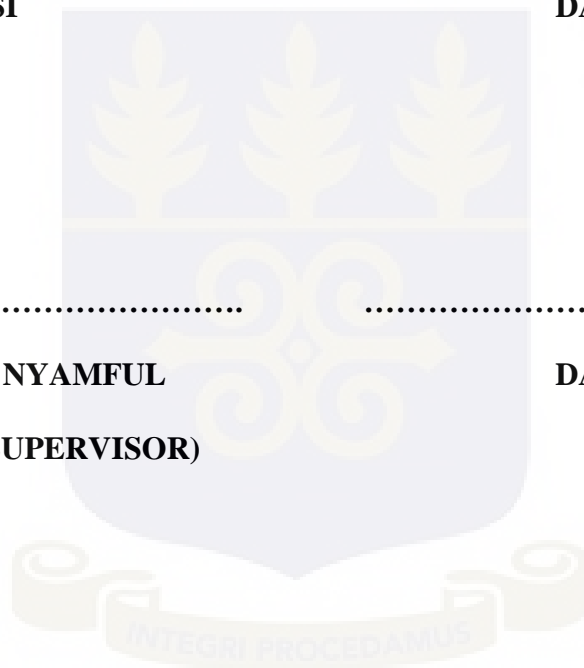
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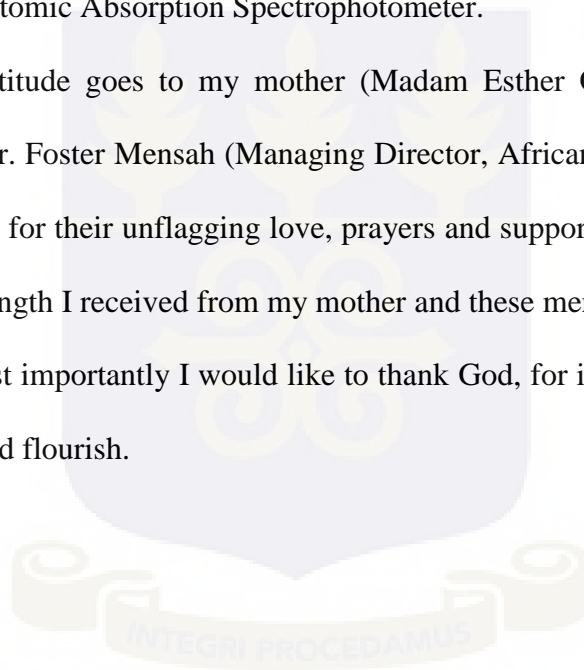
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ABSTRACT

Heavy metals are very toxic to the environment and humans at large. Exposures to heavy metals have significant health disorders. In this research, the mandate to find novel adsorbent to reduce lead and mercury concentrations from water samples from Birim River in the Eastern Region of Ghana was studied. The turbidity of the water samples from Kibi, Anyinam and Kade indicated that, the river is very turbid (an average of 355 NTU) and therefore not recommended for domestic use without treatment. The modification of rice husk and orange peels with tartaric acid showed that modified rice husk had better binding efficiency for Pb and Hg. A series of batch experiments using tartaric acid modified rice husk (RH-TAM), tartaric acid orange peel modified (OP-TAM), unmodified rice husk (UM-RH) and unmodified orange peel (UM-OP) for the removal of Pb and Hg showed that the sorption processes depended on pH, contact time and adsorbent dosage. A pH of 5 with 0.5 g/20 ml of adsorbent solution maintained at a temperature of $35^{\circ}\text{C} \pm 2$ for a period of four (4) hours yielded the highest adsorption efficiency for both modified and unmodified adsorbents. The adsorption efficiencies recorded for RH –TAM and UM-RH were 75.56 % and 69.93 % respectively for Pb. Similarly, Hg adsorption efficiencies for both RH-TAM and UM-RH were 53.26 % and 45.11 % respectively. The adsorption efficiencies of OP –TAM was 62.03 % for Pb and 44.57% for Hg. The unmodified orange peel (UM-OP) had the least adsorption efficiencies of 51.88 % for Pb and 42.39% for Hg. The Langmuir isotherm fitted the experimental data for Pb and Hg better than the Freundlich isotherm.

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CHAPTER ONE

INTRODUCTION

Living things cannot live without water. Water is used every day for many activities including and not limited to drinking, cooking, industrial and agricultural processes, human recreation and waste disposal. Humans face two major problems with water; these are the quantity and quality of water (Zubia *et al.*, 2015). Reduction in surface water and groundwater quality is mainly caused by both anthropogenic pressures and natural processes (Carpenter *et al.*, 1998).

Natural weathering of the earth's crust, mining, industrial discharge, pesticides applied to plants and air pollution are some of the major sources that lead to reduction in water quality (Ming-Ho, 2005).

Mining activities impact negatively on agriculture and water bodies (which in extent pose threat to humans and animals) because of the complex interactions that occur as waste becomes part of the ecosystems into which they are deposited. Large quantities of tailings and waste which contain heavy metals are released from mining activities into water bodies, agricultural soils and contaminate food crops (Amune *et al.*, 2012).

In a typical mining industry, contaminants in various forms are generated and introduced to water bodies. These include inorganic chemicals such as heavy metals, acids, alkalis, cyanide, dissolved salts and also organic chemicals such as oil and grease, soaps and detergents, dyes and phenolic compounds. The presence of these contaminants in water bodies show physical effects such as turbidity, colour, taste, odour etc on the water body.

Mining activities generate heavy metal contaminated wastewater, and because lead and mercury have high solubility in water, living organisms absorb them and become part

of the food chain. Once they become part of the food chain, they go through the food chain cycle (M.A. Barakat., 2010).

The implications of accumulating heavy metals in the body are so devastating and can even result in death. Diseases such as cancer, organ damage, nervous system damage, reduced growth in both plants and animals often occur when there are high levels of heavy metals. (M.A. Barakat., 2010).

Mercury and lead have the ability to affect a person's own immune system to attack itself when ingested in large concentrations. Due to these damaging effects to humans and the environment, regulatory bodies such as the World Health Organization (W.H.O) have set up limits for these heavy metals. (M. A. Barakat., 2010).

Mining industries that are regulated treat the wastewater they generate in order to reduce heavy metal and other physical, organic and biological contamination before releasing their effluents into the environment. Due to the cost involved in treatment of these effluents, some industries however make efforts to treat their waste water but not always to the highest degree. Unregulated mining industries, however do not employ any treatment technologies to the wastewater they generate before releasing them into the environment. This expose mankind and the aquatic life to higher risk to all the dangers associated with untreated wastewater.

Polluted water from mining activities and other sources that render water unsafe for human usage, industrial usage and to the environment need to be treated to reduce the possible these effects they cause to humans and the environments (Maria *et al.*, 2004).

In the quest to prevent exposure of these heavy metals to humans and the environment, treatment processes have been developed to treat effluents from industries before being

discharged into river bodies and the environment at large. These treatment techniques normally come with high cost of operation and hence a lot of industries that generate these heavy metals find it difficult to adopt them. Some of these treatment processes are ion exchange, precipitation, coagulation, and flocculation, membrane filtration, etc.

Comparing all the treatment processes, adsorption is economically beneficial when low cost adsorbent like agricultural waste are used. The most common adsorbent which has good capacity of adsorbing heavy metals is activated charcoal. The cost of producing activated charcoal is quite high and hence poses financial challenge to industries that depend on it. Synthetic polymers and silica-based adsorbents have been used to remove heavy metals, but these materials are also expensive. (Mathew Frency., 2008)

Finding cost effective materials that can reduce substantially the heavy metals concentrations in water bodies have been of growing interest to scientist and engineers all over the world. This research is therefore aimed at helping to identify such adsorbents for heavy metal in effluents to prevent their deleterious effects on man.

1.1 Statement of Problem

Industrial wastewater contains high levels of heavy metals. The metals include arsenic, chromium, copper, zinc, cadmium, lead, iron, nickel, mercury, silver etc. Heavy metals are elements that have more than five times the specific gravity of water and are toxic even at low concentrations. They are one of the most toxic types of water pollutants. They are emitted into the environment in quantities that are hazardous to the environment and human health.

The rampant illegal mining activities in Ghana have also contributed to the pollution of water bodies by heavy metals. This is because most of these mining activities are performed in rudimental manner and the waste generated are often not treated before

discharge into the water bodies. Many treatment processes such as precipitation coupled with coagulation and flocculation, ion exchange, complexation of biomass, membrane filtration and adsorption have been used in the past to remove heavy metals from wastewater. However, there are limitations: (i) Precipitation produces large quantities of heavy metals rich waste sludge; (ii) ion exchange and biomass methods are costly and cannot be readily applied to large scale applications. Adsorption is commonly done with activated carbon, which adsorbs dissolved organic substances water. Although activated carbon has advantages of effectively removing colours and applicable for a wide variety of organic compounds, it has limitations that prevents it from treating highly soluble organics and high concentrations of organic and inorganic compounds. In addition to the above, the cost of operation in using activated charcoal is very high and industries face challenges with this process. Other adsorbents that have been used include synthetic polymers and silica-based substances. However, these materials are much more costly when compared to activated carbon. Due to these limitations, and regulations brought about by governmental agencies, newer technologies are needed to remove these metals. Hence, there is a perceived necessity and growing interest in finding adsorbents that are more cost-effective and with fewer limitations including high temperatures and pressures. Therefore, finding suitable materials and operating conditions are essential to addressing the concerns of heavy metal pollution.

1.2 Justification

Heavy metals concentrations at even low levels are toxic to humans and the aquatic system. Water bodies are destroyed and crop productions are lowered when there are high levels of heavy metals in the water and in the soil. Mining activities have been one of the major routes for introducing heavy metals into the environment and which

eventually enter the food chain due to the complex interactions that occur as waste becomes part of the ecosystems into which it's deposited. Large quantities of tailings and waste which contain heavy metals are released from mining activities into water bodies, agricultural soils and food crops (Amune *et al.*, 2012).

When these heavy metals enter the food chain, humans and living organisms are exposed to, eventually they accumulate in the human body and cause severe health problems such as cancer, kidney diseases, diseases related to the circulatory and nervous systems, stunted growth of plants, damage to the fetal brain etc. (M.A. Barakat., 2010).

Since the cost of reducing these heavy metals are so high, most mining industries do not treat their waste water before releasing to the environment. For those who apply some form of treatment, they do not always achieve the standard set by regulatory bodies.

It is therefore imperative to determine the levels of heavy metal in river bodies and find a cost-effective method to reduce their concentrations (if they are more than) to the permissible levels set by the World Health Organization (WHO).

The reduction of heavy metal concentrations will also enhance crop yield, since the water used for irrigation purposes will no longer be contaminated with heavy metals to cause stunted growth, reduction in seed germination, reduced shoot growth, decrease in chlorophyll concentration, reduction in plant nutrient content etc. Economically this process will be beneficial, since the adsorbents employed in this work are all agricultural waste and they are readily available. This research will also contribute to achieving the Sustainable Development Goal (SDGs) 6, set by the United Nations (i.e

making sure that water is available to all and the management of water and sanitation is also adhered to)

1.3 Objectives

1.3.1 Main Objective

The objective of this research is to determine the adsorption capacities of rice husk and orange peels and their tartaric acid modified form for the removal of mercury and lead from the Birim River, in the eastern region of Ghana.

1.3.2 Specific Objectives

1. To determine the physicochemical parameters of Birim River in three main unregulated or illegal mining areas in the eastern region of Ghana.
2. To determine the adsorption capacities of rice husks and orange peels for the removal of lead and mercury in the polluted water.
3. To predict the optimum operating conditions of each adsorbent and its modified version under specific conditions.

CHAPTER TWO

LITERATURE REVIEW

Artisanal and small-scale mining involves the extraction of minerals using rudimentary techniques. In most rural communities, small scale mining is the major source of income (UNEP, 2016). The operation is often carried out on a small scale and the people have not sufficient knowledge about the chemicals used in the extraction of minerals. Mercury has been the major chemical used by these miners to separate the metal from the ore. Introduction of heavy metals into the environment has been attributed to mining because, the ore bodies contain both heavy metals and essential minerals. Two major techniques, opencast and underground mines methods are often used to extract these minerals from the earth ((Sneha et al, 2012).

Downstream water users are faced with poor water quality due to poorly planned stockpiling, mining activities, dumping of overburnt and chemical/fuel spills. This is because the activities are not controlled and the tailings are often released into streams. The cost of treating this water is often very high since several treatment procedures have to be used. The aquatic systems are also poisoned as a result of these activities (M. Naveen Saviour and P. Stalin., 2012).

Also, the small-scale mining activities affect stream reserve –habitat by reducing penetration of light, decreases primary production and feeding opportunities. In the distribution and breeding of aquatic life, physicochemical parameters of water are of extreme significance, because they control chemical, biological and physical processes taking place in the environment (Zubia et al., 2015)

2.1 Physicochemical Parameters of Water

The following water quality parameters have been chosen to determine the quality of the mining effluents. They include:

2.1.1 pH

In the geochemical equilibrium calculations, hydroxonium ion concentration (pH) is considered an important ecological factor because of the information it provides for geochemical equilibria and solubility calculations (M. Prasad et al., 2014). Odour and taste are also affected by pH, especially at the point where the pH controls the equilibrium concentrations of the neutral and ionized forms of a substance in solution (Olumuyiwa et al., 2012). Due to the absence of any thermodynamically valid method to measure the activity of the hydrogen ion, pH becomes a unique parameter among all the physicochemical parameters of wastewater.

2.1.2 Temperature

Temperature is generally considered as coldness or hotness of a substance. Temperature is one parameter that affects the growth rate of micro –organisms. It also has influence on the odour of a substance due to the relation between odour and vapour pressure. Another great effect of temperature on water is the changes it can cause to the density of water. The density of water changes with varying temperature and it becomes less in warming up and more in cooling (M. Prasad; 2014)

2.1.3 Electrical Conductivity

The ability of water to carry electric current is measure of its electrical conductivity. Conductivity is inversely related to the resistivity of a substance. The amount of total dissolved salts in water is mainly demonstrated by the electrical conductivity of the water. In determining the purity of water, electrical conductivity is a major parameter that needs to be determined (Dahiya and Kaur, 1999).

2.1.4 Total Hardness

Water hardness is a major parameter that is often used to determine in analyzing the purity of water. This is because; the ability of water to lather with soap is affected by the hardness of water. When water is of a higher hardness value, it causes an increase in the boiling point of such water. The amount of calcium and magnesium is the main cause of water hardness. (M. Prasad et al., 2014)

2.1.5 Colour and Odour

Wastewater from mining activities usually exhibits the colour of the heavy metals that have corroded in them. Most of these wastewater from the mines are green and blue due to lead and copper corrosion. In wastewater treatment plants, odour is mostly caused by the emission of sulphur and volatile organic compounds (VOCs). In most cases hydrogen sulphide is the common odorous gas encountered in wastewater treatment systems.

In the formation of hydrogen sulphide, sulphate is reduced to hydrogen sulphide by bacteria under anaerobic conditions. The equation below shows the process for the hydrogen sulphide formation. (Olumuyiwa et al., 2012)



2.1.6 Biochemical Oxygen Demand (BOD)

In the aquatic environment, dissolved oxygen is an important parameter required in the decomposition of organic matter and also for oxidation of inorganic materials such as iron and sulphides. This amount of dissolved oxygen required is what is termed as biochemical oxygen demand. It also determines the organic material contaminations in water (Patil et al., 2012).

2.1.7 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. COD measurements are commonly made on samples of waste or natural waters contaminated by domestic or industrial wastes. Chemical oxygen demand is measured as a standardized laboratory assay in which a closed water sample is incubated with a strong chemical oxidant under specific conditions of temperature and for a particular period of time.

A commonly used oxidant in COD assays is potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) which is used in combination with boiling sulfuric acid (H_2SO_4). Because this chemical oxidant

is not specific to oxygen-consuming chemicals that are organic or inorganic, both of these sources of oxygen demand are measured in a COD assay.

Chemical oxygen demand is related to biochemical oxygen demand (BOD), another standard test for assaying the oxygen-demanding strength of waste waters. However, biochemical oxygen demand only measures the amount of oxygen consumed by microbial oxidation and is most relevant to waters rich in organic matter (Patil et al., 2012).

2.1.8 Turbidity

The amount of cloudiness in water is what is referred to as turbidity. In most cases, turbidity is caused by silt, sand, mud, bacteria and other chemical precipitates.

High turbidity is often observed in rivers in which this unregulated mining activities take place. A high level of turbidity also affects the treatment of water systems by blocking filters and reduces their efficiency. Pipes and tanks are most often filled with silt due to high level of turbidity. In a system where chlorination is used to purify water, high turbidity can even prevent the chlorine from killing the germs effectively (O.D Ansa-Asare and K. A Asante., 2000)

2.2 Heavy Metals

Heavy metals are generally defined as metals with relatively high densities, atomic weights, or atomic numbers. The definition can be based on either density, atomic number or the chemical behaviour of that metal. The main route to which most heavy metals enter the environment is either natural or anthropogenic. Examples of these

sources are mining, weathering of the earth's crust, industrial discharge, air pollution fallout, pest and disease control processes applied to plants (Simone et al., 2012). The main route of exposure of heavy metals to people is through food and water. The chain of contamination assumes a cyclic manner starting from industrial discharges to the atmosphere, then to the soils and water and then to food and eventually to man. Due to the adverse health effects of these heavy metals, there has been an increase concern about exposure, intake and absorption of heavy metals by human. Regulatory bodies have therefore researched into and set standards for maximum exposure.

The following are heavy metals which are mostly associated with wastewater from mining activities.

2.2.1 Lead

One of the natural constituent of the earth crust is lead. Lead is believed to have an average concentration of about 16 mg/kg (Olumuyiwa et al., 2012). The amount of lead in water is increased by corrosion when water has low pH values. The main exposure routes are through foods, drinking water and air (Ming-Ho, 2005). Lead is very toxic and has low geochemical mobility (Morais et al., 2012).

2.2.2 Arsenic

Arsenic is abundant in the earth crust with an average terrestrial concentration of about 5 g/ton. It exists as an inorganic oxy-anion which is similar in chemical nature to nitrogen, phosphorus, antimony and bismuth. For the physicochemical parameters of water, arsenic is referred to as a metal, though it's a metalloid. Due to the high toxic

nature of this metal and also, it's persistent nature; bio- accumulative nature, the World Health Organization (WHO) considers it as one of the main contaminant in wastewater. Mining processes generate wastewater that are rich in toxic metals or their oxy-anions. Exposure of arsenic is mainly through drinking water (Simone et al., 2012). High level of arsenic exposure can lead to very severe toxicity including acute toxicity, developmental and reproductive toxicity and chronic toxicity (Simone et al., 2012).

2.2.3 Mercury

Mercury can exist as ionic, metallic and organic in its chemical form. Most at times the toxicity of mercury exposure depends on the nature of exposure. The level of mercury toxicity is in the order, ionic < metallic < organic (Clarkson T.W and Magos L., 2006).

In artisanal mining activities, mercury is one of the main chemicals used to extract the essential metals. This has resulted in its abundance in the environment when the wastes generated by these miners are released to the environment.

When mercury is introduced into the soil or water bodies, micro-organisms converts it to methyl-mercury: a very bio-accumulating toxin. Mercury is considered by W.H. O as very toxic because, even short-term exposure can lead to lung damage, skin rashes, eye irritation, damage to kidneys, developing fetus damage and permanent damage to the brain (Clarkson T.W and Magos L., 2006).

2.2.4 Cadmium

Cadmium is found in rocks, coal and mineral fertilizers. Mining activities expose this metal to the environment and the aquatic system. Cadmium and its compounds are known carcinogens and they also cause damage to the kidney, lungs and fragile bones. (Abdelnaeim, Mohamed Y et al., 2016).

2.2.5 Nickel

Nickel is a dietary requirement for many organisms, but may be toxic in larger doses. The human body contains approximately 100 mg of nickel (Matthew Frency., 2008). Acute nickel toxicity includes gastrointestinal symptoms like nausea, vomiting, abdominal discomfort and diarrhoea and neurological symptoms like headache, giddiness, cough and shortness of breath. Many people develop dermatitis upon skin contact with nickel. Nickel salts affect the pulmonary and digestive tract of humans. Exposure to soluble nickel compounds also causes respiratory tract cancer if the dosage exceeds 1 µg of Ni/ L.

Chronic health effects of nickel include chronic bronchitis and lung disease which is caused by reduced lung function. Nickel also affects the blood, liver, kidney and immune systems. Metallic nickel is teratogenic and carcinogenic to mammals (Zhao, Z. et al., 2010).

2.2.6 Copper

Copper has both acute and chronic effect on aquatic organisms that can result in death. They are known to bio-concentrate in some aquatic species. In mammals, overexposure to copper can damage the liver and kidney. Acute exposure to copper causes gastrointestinal effects such as nausea, vomiting and diarrhoea. In the aquatic system, the younger fishes are affected the most by the toxicity of copper. The adult fishes can tolerate lower concentrations for a short period of time (Xue-Song Wang., 2007).

2.3 Conventional Methods for Reducing Heavy Metal Concentration in Wastewater

2.3.1 Chemical Precipitation

In this method a chemical additive is added to the effluent to make the metal that is to be removed from the wastewater insoluble. After the metal precipitates in the solution it is removed from the water by filtering or settling. Most of the metals are precipitated as metal hydroxides by raising the pH to a neutral or an alkaline level. However, this method is not effective enough to meet the discharge effluent standards. Another problem with this method is that chelated metal ions do not precipitate at all. So, for metal hydroxides, a more advanced treatment such as reaction with organic or inorganic sulphides are employed. Chemical precipitation uses hydroxide, carbonate or sulphide reagents for precipitation. One of the many disadvantages of this process is that the precipitation process is often left incomplete and has many side effects. Another disadvantage of this process is that it generates huge amounts of water rich sludge which needs to be disposed (Upadhyay Kanjan., 2006).

2.3.2 Coagulation/Flocculation

It is a process in which the metal to be removed is separated out from the solution as flocs or flakes which can then be easily removed. Flocculation is often preceded by coagulation where, by the addition of a coagulant, substances are aggregated into microscopic particles which then flocculate into larger flocs. In this process the destabilized suspension is mixed very slowly to provide an opportunity for the particles to come into contact with one another and form flocs. The most commonly used coagulants-flocculants in wastewater treatment are aluminium sulphate, calcium oxide, iron (III) chloride, iron (II) sulphate and sodium silicate. The disadvantage of this

process is that it has a moderately higher total operation and maintenance cost which is mainly due to sludge handling (Semerjian, L., 2003).

2.3.3 Ion Exchange

Ion exchange has a high capacity of removing heavy metals from wastewater up to the ppb level of concentration in large volumes. This makes the method one of the best for heavy metal removal, but the cost in operating and managing is very high. The ion exchanger is normally a solid with the ability to exchange cations and anions from the surrounding material. Synthetic organic ion exchange resins are the commonly used matrices in this method. In the process of ion exchange, the matrices get fouled by organics and other solids in the water and hence preventing concentrated metal solution from being treated well. The method is very sensitive to pH of the adsorbate solution (Amam et al., 2015).

2.3.4 Membrane Filtration

Membrane filtration is one method that focuses on the size of particle that can be retained. Based on this, different types of membrane filtration methods can be applied in treating wastewater. The main advantage of this method is its ability to remove suspended solids in addition to the heavy metals. Methods such as ultra-filtration, nano-filtration and reverse osmosis falls under this method of treatment of wastewater.

In the reverse osmosis, which is used often by most industries, most of the separation occurs in the polymer matrix where there is a dense barrier layer. The semipermeable nature of the membrane used in this method allows the passage of solvent but not for metals. Many types of molecules and ions can be removed from solutions, including bacteria and this makes this method useful in the industries. The separation efficiency

of this method is dependent on solute concentration, pressure, and water flux rate because of the diffusive nature of the reverse osmosis (Gunatilake S.K., 2015).

2.3.5 Biosorption

This is a biological sorption method used for heavy metal removal from wastewater. Live or dead microorganisms or their derivatives are used in biosorption. In this method the metal ions are complexed by the functional groups present on their outer surfaces through the action of ligands. It is an effective and a cheaper method compared to the other removal techniques. Biosorption is a time demanding process, because it requires a very long time to remove the metals. Also, regeneration of the material for further biosorption is not possible. Drawbacks such as high capital and operational costs and problem of disposal of residual metal sludge are faced by this method also. (Amam et al., 2015)

2.3.6 Adsorption

To better the quality of water by removing heavy metals using adsorption process, researchers are constantly reviewing the process of adsorption with different materials to gain a more economically sustainable adsorbent.

These researches have been very beneficial, but there is the need to better still find the most cost-effective material for heavy metal adsorption. (Gupta S. and Babu B.V., 2009)

While cost effective adsorbent were also been searched for, isotherms to model and design the adsorption process were also been studied. Scientist like Langmuir, Fleundlich, Temkin, Dubinin-Radushkevich , BET (Branauer, Emmett, and Teller) have developed isotherms under certain assumptions to describe the adsorption process.

Langmuir's model corresponds to ideal and localized layer practically. Branauer, Emmett, and Teller (BET) developed a multilayer adsorption model, and they used the same assumption as Langmuir. The BET theory became the bases that created a universal theory of physical attraction. For monolayer and multilayer adsorption process, the Langmuir and BET isotherms fits them respectively (Ramalingam, S. et al., 2011).

Freundlich also developed a model for heterogeneous surfaces and this model is best used in wastewater analysis.

The main advantages of adsorption are the inexpensive nature of the adsorbents, the simple designing process and its high adsorption efficiency.

2.3.6.1 Adsorption Mechanism

The interaction between the adsorbent and the adsorbate is either physi-sorption or chemisorption. Physical adsorption or physi-sorption is controlled by Van der Waals forces. For a process where there are strong forces of attraction, chemisorption occurs. These strong forces of attraction bind the adsorbent and the adsorbate together. Chemisorption and physi-sorption can occur successively or at the same time under specific conditions (Grassi, et al. 2012).

One of the difficulties encountered in the study of adsorption mechanism is the ability to determine whether the adsorption is due to physi-sorption or chemisorption. Hence the term sorption is used to explain all adsorption processes.

Several mechanisms are also encountered during adsorption process. The mechanisms encountered have different characteristics due to the adsorbent type, its origin and method of processing before usage.

In all this, the adsorption process takes place in three steps. The adsorbate from the bulk solution is transferred to the outer surface of the adsorbent by molecular diffusion. This process is normally known as external or film diffusion. Internal diffusion process is followed up by this and this process transport the adsorbate from the particle surface to the interior sites of by diffusion within the pores and migration along the solid surface of the pores. Finally, adsorption of the solute occurs on the active sites on the interior of the pores (IAW Tan., 2008)

2.3.6.2 Adsorption Isotherm

To determine the adsorption isotherm of any adsorption process, the amount of solute adsorbed per unit weight of the adsorbent, q_e , is plotted against the concentration of the solute still remaining in the solution.

The capacity of the adsorbents determines the amount of heavy metal that has been attracted onto the surface of the adsorbent. The amount adsorbed can be calculated using the equation below:

$$q_e = \frac{(C_o - C_e)V}{m}$$

In this equation q_e is the adsorbent concentration after equilibrium has been attained. The variable V also represent the total volume of the solute solution (in L), whereas C_o is the initial concentration of the solute (in mg/L). The residual equilibrium

concentration of the solute after adsorption is also represented by C_e (in mg/L), and, m denotes the mass of the adsorbents used (in g).

2.3.6.2.1 Langmuir isotherm model

For a surface containing a finite number of identical sites, Langmuir adsorption model is used, because it assumes uniform energies of adsorption on the surface. The nonlinear form of Langmuir's isotherm equation is:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$$

In this equation, q_e is the amount of metal adsorbed at equilibrium (in mg/g), q_m and K_a are the maximum adsorption capacity and the Langmuir constant respectively.

Calculation of q_m and K_a can be done by plotting $\frac{1}{q_e}$ vs $\frac{1}{C_e}$, where q_m is $\frac{1}{intercept}$ and K_a is the $intercept \times \frac{1}{slope}$. (Dada, A.O., 2012).

2.3.6.2.2 Freundlich isotherm model

For heterogeneous surface, Freundlich model is the best isotherm model for determining the adsorption capacities of metals. Freundlich isotherm can be represented as $q_e = K_f C_e^{1/n}$.

The K_f and n are constants, K_f is the Freundlich constant and it indicates the relative adsorption capacity of the adsorbent, and is also proportional to $RT_n b e^{\Delta H/RT}$ and with $n > 1$ (Gupta S. and Babu B.V. (2009). Taking the logarithms of the isotherm yields

$\log q_e = \log K_f + \frac{1}{n} \log C_e$ with an intercept of K_f and a slope of $\frac{1}{n}$, where K_f is the adsorption capacity, and $\frac{1}{n}$ the adsorption intensity.

2.3.6.2.3 Dubinin-Radushkevich isotherm model

Another important isotherm for determining the adsorption capacity is the Dubinin–Radushkevich isotherm model. This isotherm model does not assume a homogenous surface and a constant adsorption potential; hence it has a wide range than the Langmuir’s model. It is used to determine whether the sorption process is chemical or physical.

The Dubinin–Radushkevich isotherm is expressed as:

$$q_e = q_m \exp(-K[RT \ln(1 + 1/C_e)]^2)$$

$$q_e = q_m \exp(-K \varepsilon'^2)$$

Its linear form can be represented as:

$$\ln q_e = \ln q_m - K \varepsilon'^2$$

ε'^2 is the Polanyi potential, K is the Dubinin–Radushkevich constant which is related to mean free energy of adsorption. A plot $\ln q_e$ versus ε'^2 gives a straight line from which K and q_m can be evaluated from the slope and intercept.

The parameter ε can be calculated as $\varepsilon = RT \ln[1 + \frac{1}{C_e}]$

To calculate the mean free energy, the relation below is used:

$$E_s = \frac{1}{\sqrt{2K}}$$

If the magnitude of E_s is between 8 and 16 KJ / mol, then we have an ion-exchange or chemisorption process. On the other hand, if the value of E_s is less than, the adsorption process is of a physical nature (Dada A. O. et al., 2015)

2.3.6.2.4 Temkin isotherm model

As a result of adsorbent – adsorbate interaction, Temkin isotherm model, takes into account a decrease in the heat of sorption. The model can be represented mathematically as shown below:

$$q_e = \frac{RT}{b_T} \ln(K_T C_e)$$

$$q_e = \frac{RT}{b_T} \ln(K_T) + \frac{RT}{b_T} \ln(C_e)$$

K_T is the Temkin isotherm constant (L/g), R is ideal gas constant (8.314 J/mol K), T is absolute temperature (K), b_T is constant related to the heat of sorption (J/mol). Plotting q_e versus $\ln(C_e)$ gives a straight line from which K_T and b_T can be evaluated from the slope and intercept. (Dada A. O. et al., 2015).

2.3.6.3 BET (Brunauer, Emmett and Teller) isotherm:

The BET isotherm represents a more generalized form because of the assumption it makes from the Langmuir's model. It also assumes that there is equal energy of adsorption for each layer except for the first layer. The BET equation is represented as follows:

$$q_e = \frac{K_B \cdot C_e \cdot Q_a^o}{(C_s - C_e) [1 + (K_B - 1) \left(\frac{C_e}{C_s}\right)]}$$

where C_s is the saturation (solubility limit) concentration of the solute (mg/L) and K_B is a parameter related to the intensities of all layers.

Rearranging the above equation results to a linear form as shown below:

$$\frac{C_e}{(C_s - C_e)q_e} = \frac{K_B - 1}{K_B \cdot Q_a^0} \left(\frac{C_e}{C_s} \right) + \frac{1}{K_B \cdot Q_a^0}$$

A plot of $\frac{C_e}{(C_s - C_e)q_e}$ versus C_e gives a slope of $\frac{K_B - 1}{K_B \cdot Q_a^0} \left(\frac{1}{C_s} \right)$ and an intercept of $\frac{1}{K_B \cdot Q_a^0}$

These isotherms are important because they predict the competence of the adsorbent on the adsorbates. Also, they provide interpretation of the practical reliance of the adsorbent capability on the concentration of the adsorbate. (Dada A. O. et al., 2015).

2.3.7 Adsorbent

Adsorbents are materials onto which surface adsorption occurs. Activated carbon, synthetic polymers, and silica are the most widely known and used adsorbents.

Due to the high cost of these adsorbents, many of them are not widely used.

In the search for cheap natural adsorbents that are easily available and are effective in removing the toxic heavy metals in the mining wastewaters, studies have been conducted on natural wastes where materials such as rice sawdust, soybean hulls, cotton seed hulls, sago waste, sugarcane bagasse, orange peels, coconut coir, rice husk etc have been studied to determine their ability to reduce or lower the concentrations of heavy metals. In general, they have good adsorption capacities. These unconventional natural adsorbents have advantages other than being abundant in nature (Ahluwalia, S.S. and Goyal, D., 2005)

Most of them need less prior processing and are waste by-products from some other industry and they also have high carbon or oxygen content for efficient adsorption. Due to the chemical nature of these agricultural waste materials, they contain multiple functional groups which aid the adsorption process. Most of these materials have high

content of hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch. Though agricultural waste can be used as adsorbent, it can also be treated or modified to enhance effective adsorption (Ahluwalia, S.S. and Goyal, D., 2005).

So, they become alternative to costlier adsorbents like activated carbon, or synthetic polymers (Ahluwalia and Goyal., 2005).

In the present studies, the adsorbents being used are rice husk and orange peels.

2.3.7.1 Rice Husk

One of the most interesting agricultural waste materials which seem to have a very high capacity for adsorbing heavy metals is rice husk. In the dry form it is composed of about 70-80 % of organic matter (lignin, cellulose, sugars etc). In its cellular membrane is also contains about 20 % silica (Pavan G. D., 2015). Unmodified forms and modified forms of rice husk have been used by different researchers to study the removal ability of some specific metals. The main component of the rice husk which makes it a good adsorbent in its raw form is the organic constituent which gives multiple functional groups. In its ash form, silica is the main constituent which enhances the adsorption processes. The table below are some of the works done on rice husk by different researchers all over the world.

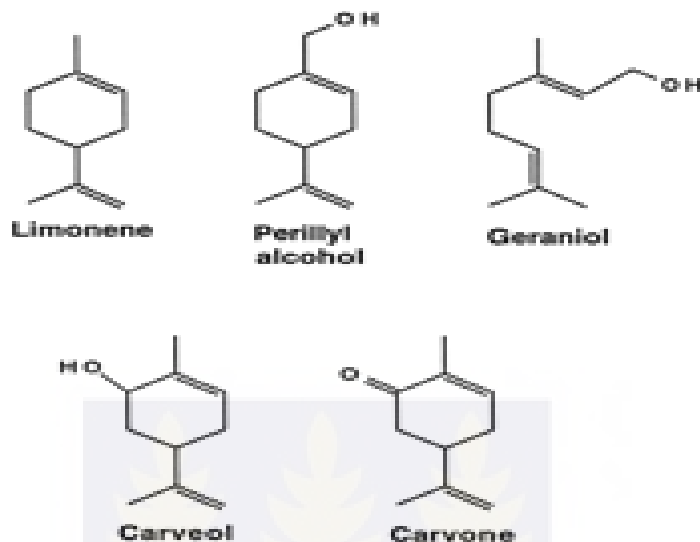
Table 1. Work done by other researchers on the adsorption capacities of Rice Husk

Adsorbent	Metal used for	Researchers	Year of Research
Tartaric acid modified rice husk	Pb and Cu	Wong et al	2003
Untreated and phosphate treated rice husk	Ni ²⁺ , Zn ²⁺ , Cd ²⁺ , and Cr ⁶⁺	Ajmal et al	2003
KOH treated rice husk	Fe, Mn, Zn, Cd and Pd.	Daifullah et al	2003
Micro and mesoporous rice husk-based activated carbon	Cr ⁶⁺	Guo et al	2003
Raw rice husk	Cr ⁶⁺	Subramaniam et al	2004
Rice hulls coated with reactive dye procion red(PR) or procion yellow(PY)	Pb ²⁺ and Hg ²⁺	Suemitsu R et al.,	1986
Rice husk with sulphuric acid followed by carbon dioxide (CO ₂) activation	Cr ⁶⁺	Srinivasah et al	1998
Raw rice husk	Cr ⁶⁺ , Zn ²⁺ , Cu ²⁺ and Cd ²⁺	Munaf E and Zein R	1997
Green algae and rice hulls	Sr, Cd, Ni, Pb, Zn, Co, Cr, As ions	Roy D et al	1993

In all the research conducted, significant amount of not less than 50 % of the metals were removed. This shows that rice husk has the potential to act as an adsorbent for heavy metal removal in effluents.

2.3.7.2 Orange Peel

Orange peel is mainly composed of the compounds below.



It is the hydroxyl and the carboxyl functional groups in the orange peels that have an affinity for the adsorbate, either through metal exchange reaction or chemical bonding or both.

2.3.7.3 Advantages of using agricultural waste adsorbents

- Wide availability of sorbents.
- They are very cheap compared to other raw materials for adsorption.
- They have high adsorption capacities.
- They do not generate toxic sludges.
- The metals can be recovered through desorption process.

CHAPTER THREE

METHODOLOGY

3.1 Experimental setup

This research was divided into two main parts. The first part deals with determining the physicochemical parameters of the water samples from Birim River at Kibi, Kade and Anyinam and compared to the WHO Standard for Potable Water intake levels. The second part focuses on reducing lead (Pb) and mercury (Hg) concentrations in the water samples using agricultural waste as adsorbent and also to determine the optimum conditions for this adsorption process in batch tests.



3.2 Sample collection.

3.2.1. Map showing sampling points

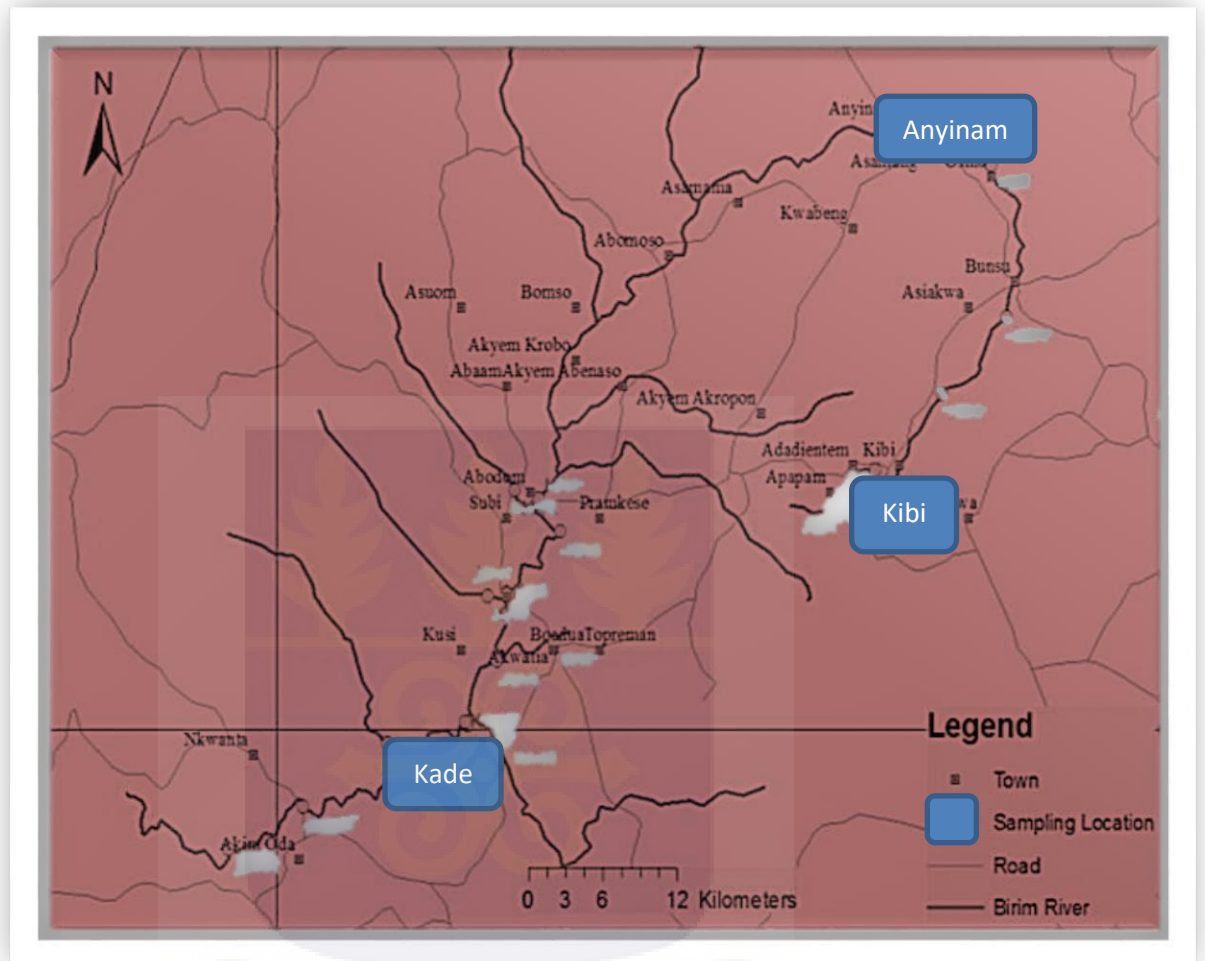
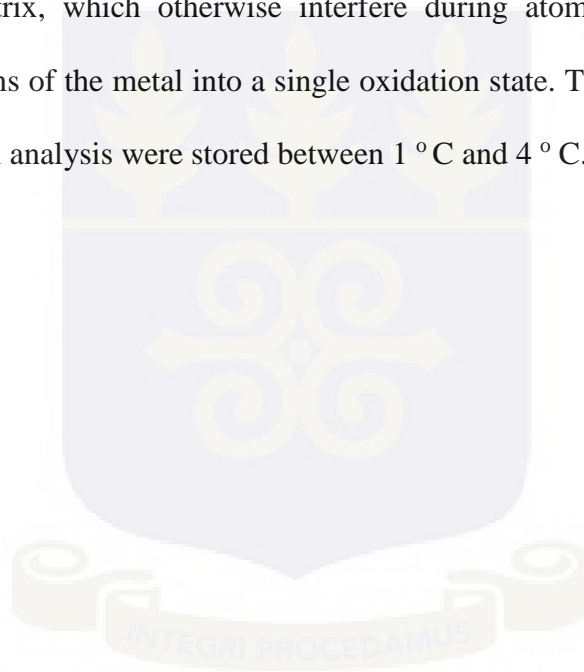


Figure 1. Map of Birim River showing sampling sites for this work.

3.2.2 Sampling and Preservation.

The water samples were collected from the Birim River at Kibi, Anyinam and Kade in the eastern region of Ghana. The points of sampling were chosen near areas where small scale mining activities takes place and the wastewaters generated by these miners are released into this river. The samples were collected into airtight polypropylene bottles

cleaned and rinsed with distilled water. The samples for heavy metal analysis were acidified with nitric acid at the time of collection to reduce the pH of the samples to less than 2. This is because, below a pH of 2, precipitation and adsorption to the walls of the container are minimized. Any acid can be used to oxidize the samples but, HNO_3 is preferred because of its oxidizing nature. When HNO_3 is added to the samples, it converts the metal ions in the samples to their nitrate salts, which are highly soluble. Another important reason for choosing HNO_3 over other acids is that, sample digestion is required before Atomic Adsorption Spectroscopic analysis, and the purpose is to destroy the matrix, which otherwise interfere during atomization. Digestion also converts all forms of the metal into a single oxidation state. The other samples for the physicochemical analysis were stored between 1°C and 4°C .



3.2.3 Appearance of Birim River at the time of sampling



Figure 2. Appearance of Birim River at Kibi at the time of sampling.

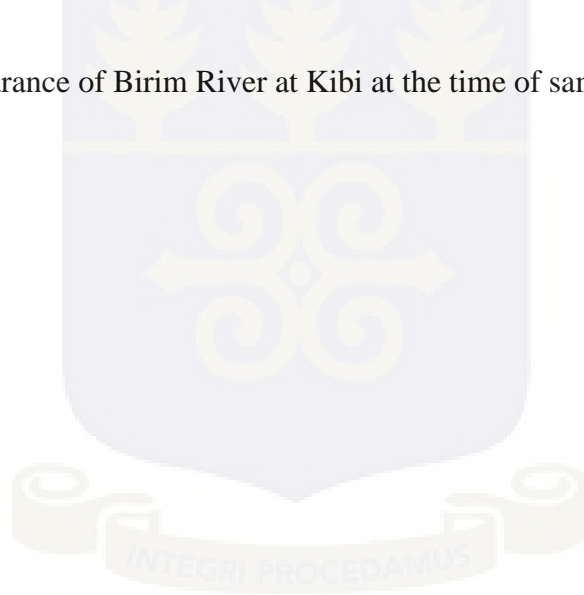




Figure 3. Appearance of Birim River at Kade at the time of sampling.

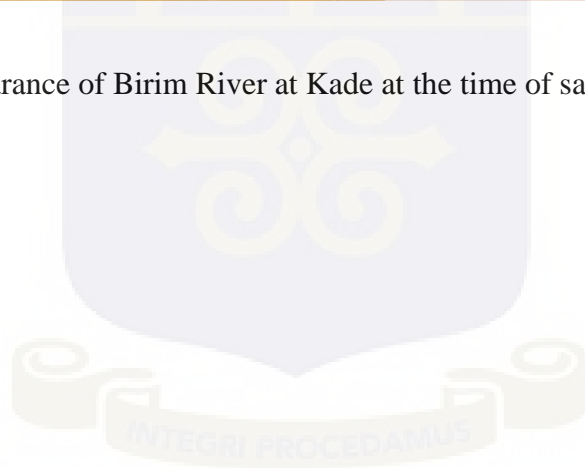
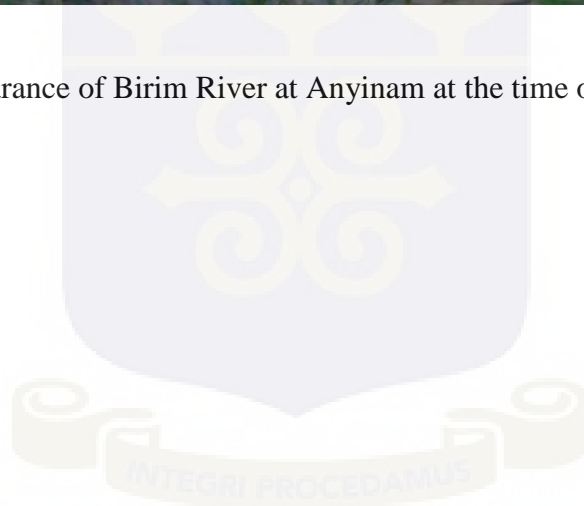




Figure 4. Appearance of Birim River at Anyinam at the time of sampling.



3.3. Adsorbent Collection

3.4 Materials

Rice husks were obtained from a rice mill at Dawenya, Tema, in Ghana. Orange peels were obtained from farms at Nsawam-Adoagyiri Municipality in Ghana. Water samples were obtained from Birim River in the eastern region of Ghana.

3.4.1 Chemicals

- Tartaric acid (Merck, Germany).
- Hydrochloric acid (Merck, Germany).
- Sodium hydroxide (Merck, Germany).
- Nitric acid (Merck, Germany).
- Mercury reference standard solution, 1000 ppm \pm 1 % /certified (Fisher Scientific, USA)
- Lead reference standard solution, 1000 ppm \pm 1 %/ certified (Fisher Scientific, USA)

3.4.2 Equipment

- Atomic Absorption Spectrophotometer (AAS), Perkin-Elmer Pin Acclle 900T model.
- Digital thermometer
- pH meter.
- Conductivity meter.
- Turbidity meter.
- UV/VIS Spectrophotometer.
- Shaker.

3.5. PHYSICOCHEMICAL PARAMETERS

The physicochemical parameters as well as the methods used in the present study are shown in Table 2.

Table 2. Physicochemical Parameters and the methods used for their analysis.

Parameter	ASTM Codes/CSRI –WRI SOP No:	Parameter	ASTM Codes/CSRI –WRI SOP No:
Turbidity	3	Chloride	D512 - 12
Colour (apparent)	2	Sulphate (SO ₄)	D516 - 16
pH	D1293 - 12	Phosphate (PO ₄ -P)	17
Conductivity	1	Manganese	D858 - 17
Total Suspended Solids (SS)	5	Nitrite (NO ₂ -N)	D3867 - 16
Total Dissolved Solids (TDS)	D1293 - 12	Nitrate (NO ₃ -N)	D3867 - 16
Sodium	D4191 - 15	Total Hardness (as CaCO ₃)	D1126 - 12
Potassium	D4192 - 15	Total Alkalinity (as CaCO ₃)	D1067 - 16
Calcium	D511 - 14	Calcium Hardness (as CaCO ₃)	D1126 - 12
Magnesium	D511 - 14	Magnesium (as CaCO ₃)	D1126 - 12
Total Iron	D1068 - 15	Fluoride	D1179 - 16
Ammonia (NH ₄ -N)	D1426 - 15	Bicarbonate	22
Carbonate	22		
Magnesium	D511 - 14	Magnesium (as CaCO ₃)	D1126 - 12
Total Iron	D1068 - 15	Fluoride	D1179 - 16
Ammonia (NH ₄ -N)	D1426 - 15	Bicarbonate	22
Carbonate	22		

Table 3. ASTM and CSRI-WRI Protocols used for the water analysis.

Designation	Title
D511 - 14	Standard test methods for calcium and magnesium in water
D512 - 12	Standard test methods for chloride ion in water
D516 - 16	Standard test method for sulfate ion in water
D858 - 17	Standard test methods for manganese in water
D1067 - 16	Standard test methods for acidity or alkalinity of water
D1068 - 15	Standard test methods for iron in water
D1126 - 12	Standard test method for hardness in water
D1179 - 16	Standard test methods for fluoride ion in water
2	Standard test method for colour determination in wastewater
D1426 - 15	Standard test methods for ammonia nitrogen in water
D3867 - 16	Standard test methods for nitrite-nitrate in water
D1293 - 12	Standard test methods for ph, conductivity, tds and turbidity of water
D4191 - 15	Standard test method for sodium in water
D4192 - 15	Standard test method for potassium in water
5	Determination of total suspended solids in wastewater
17	Determination of phosphate in wastewater using uv/vis spectrophotometer
22	Determination of carbonate and bicarbonate in wastewater
1 & 3	Determination of conductivity (1) and turbidity (3) of water

3.6 ADSORBENT PREPARATION

3.6.1 Preparation of Rice Husk and Orange peel Adsorbents

The rice husk was cleaned with distilled water. The cleaned rice husks were dried in an oven at 50°C for 12 hours. It was crushed using mortar and pestle and sieved to a particle size of 1 mm. The sieved particles were placed in a clean airtight polypropylene bottle and labelled **UM-RH (Unmodified Rice Husk)**.

The above procedure was repeated using orange peels and the clean airtight polypropylene bottle was labelled **UM –OP (unmodified orange peel)**.

5 g of the prepared **UM-RH** were mixed with 35 ml of 1.2 M tartaric acid and stirred to obtain a homogenous mixture. The homogenous mixture was dried at 50 °C for 12 hours and was placed in a clean airtight polypropylene bottle and labelled **RH-TAM (Rice Husk Tartaric Acid Modified)**.

The above procedure was repeated using 5 g of UM –OP and the clean airtight polypropylene bottle was labelled **OP-TAM (Orange peel tartaric acid modified)**.

3.6.2 Standard Preparation

Standard solutions of Pb and Hg were prepared from the 1000 mg/L reference solutions of Pb and Hg. The standards were diluted to the concentrations ranging from 0.1 mg/L to 2.5 mg/L and stored in polypropylene bottles.

3.6.3 Digestion Process

About 50 ml of the water sample from Birim River were placed in a round bottom flask; 5 ml of conc. HNO₃ (69 %) were added. The mixture was boiled and evaporated on a hot plate to the lowest volume possible (about 10 ml). The flask was washed down with distilled water after the digestion and filtered using Whatman filter paper of 0.45µm. 5

ml of the filtrate was transferred into a 10 ml volumetric flask, and diluted to the mark with distilled water. A portion of this solution was taken for lead and mercury analysis using the Atomic Absorption Spectrophotometer (AAS).

3.6.4 Blank Preparation

About 50 ml of distilled water was placed in a round bottom flask; 5 ml of conc. HNO₃ (69 %) were added. The mixture was boiled and evaporated on a hot plate to the lowest volume possible (about 10 ml). The flask was washed down with distilled water after the digestion and filtered using Whatman filter paper of 0.45µm. 5 ml of the filtrate was transferred into a 10 ml volumetric flask, and diluted to the mark with distilled water. A portion of this solution was taken for lead and mercury analysis using the Atomic Absorption Spectrophotometer.

3.7 BATCH TEST

3.7.1 Variation of pH

0.1 g of the UM-RH were added to 20 ml of the water sample and mixed to obtain a homogenous mixture. A similar homogenous mixture of 0.1 g of unmodified orange peel was prepared. The pH of each of the mixtures was adjusted to 5 using 0.1M HCl or 0.1 M NaOH solutions. The two mixtures were placed on the same shaker at a speed of 175 rpm in an oven at 35 °C ± 2 for 4 hours. The mixtures were filtered using 0.45µm Whatman filter paper. 10 ml of each solution were digested (as described earlier) and the filtrate of the digest was analyzed using AAS. The process was repeated for pH 6, 7, 8 and 9. The above procedure was repeated for RH-TAM and OP –TAM by modifying the method described by 2010 Wong *et al.*, 2003.

3.7.2 Variation of Contact Time

0.1 g of the UM-RH were added to 20 ml of the water sample and mixed to obtain a homogenous mixture. A similar homogenous mixture of 0.1 g of unmodified orange peel was prepared. Each mixture was adjusted to an optimum pH of 5; and the two mixtures were placed on the same shaker at a speed of 175 rpm in an oven at $35\text{ }^{\circ}\text{C} \pm 2$ for 4 hours. 10 ml of each solution were digested (as described earlier) and the filtrate of the digest was analyzed using AAS. The process was repeated for contact time of 1, 2, 3 and 5 hours. The whole procedure was repeated for both OP-TAM and RH-TAM following the procedure used by Ajmal *et al* in 2003.

3.7.4 Variation of Adsorbent Dosage

0.1 g of the UM-RH were added to 20 ml of the water sample and mixed to obtain a homogenous mixture. A similar homogenous mixture of 0.1 g of unmodified orange peel was prepared. Each mixture was adjusted to an optimum pH of 5; and the two mixtures were placed on the same shaker at a speed of 175 rpm in an oven at $35\text{ }^{\circ}\text{C} \pm 2$ for 4 hours. 10 ml of each solution were digested (as described earlier) and the filtrates were analyzed using AAS. The process was repeated for dosage of 0.2 g, 0.3 g, 0.4 g and 0.5 g. The whole procedure was repeated for both OP-TAM and RH-TAM following the procedure used by Siew –Teng *et al.*, and Munaf and Zein, 1997.

3.7.5 Analysis of Lead and Mercury Concentrations

An Atomic Absorption Spectrophotometer (AAS), Perkin-Elmer Pin Accle 900T model, at the Ecological Laboratory, University of Ghana, was used to determine the concentrations of Pb and Hg in the water samples from Birim River at each variation

process at wavelengths 283.3 nm and 253.7 nm respectively. The concentrations of the metals were analyzed using the air-acetylene flame for lead and the hydride generation/cold vapour technique for mercury with their respective hollow cathode tubes. The concentrations of Pb and Hg were determined with reference to the corresponding standard solutions. The initial concentrations of Pb and Hg from the Birim River were 0.266 ppm and 0.185 ppm respectively.

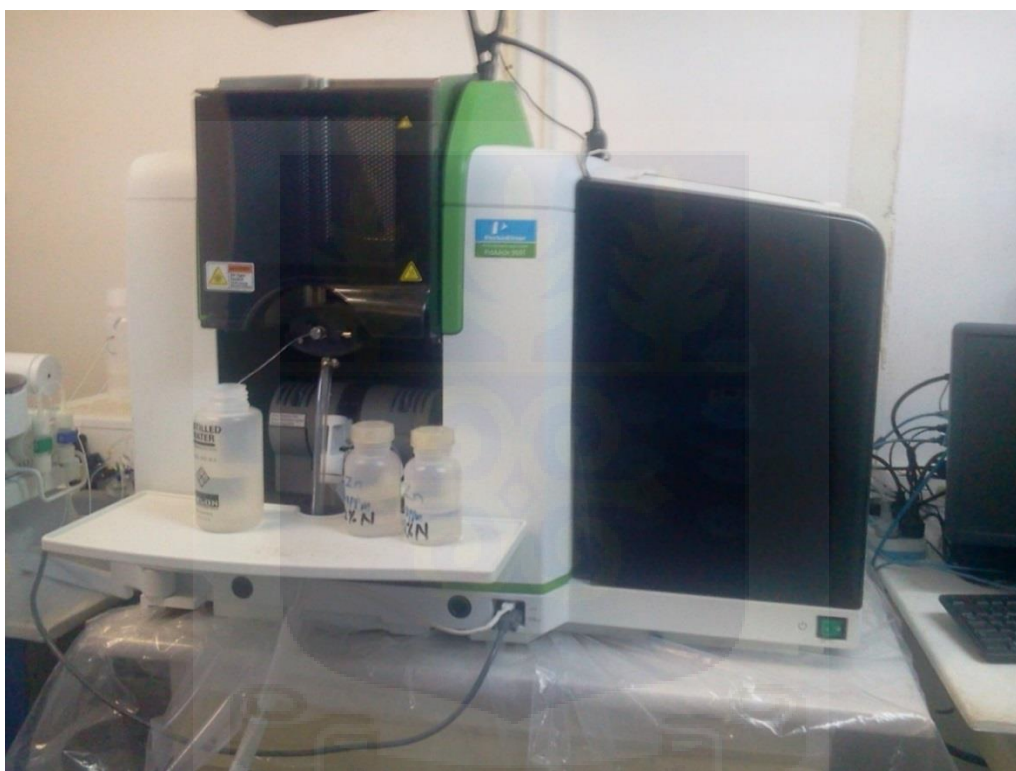


Figure 5. Pelkin Elmer Atomic Adsorption Spectrophotometer.

3.8. ADSORPTION ISOTHERM

The samples from Birim River were spiked to obtain different concentrations for both Pb and Hg. The concentrations of Pb and Hg ranged from 0.5 mg/L to 2.5 mg/L. The Langmuir and Freundlich adsorption isotherms were used to determine the adsorption capacities of rice husk, orange peel and their modified forms. The adsorption process was carried out at pH of 5, contact time of 4 hours and adsorbent dosage of 0.5 g /20 ml at $35^{\circ}\text{C} \pm 2$.

The amount of Pb and Hg adsorbed was calculated using the equation below:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

In this equation q_e is the adsorbent concentration after equilibrium has been attained. The variable V also represents the total volume of the solute solution (in L), whereas C_0 is the initial concentration of the solute (in mg/L). The residual equilibrium concentration of the solute after adsorption is also represented by C_e (in mg/L), and, m denotes the mass of the adsorbents used (in g).

3.8.1. Langmuir Adsorption Isotherm.

Langmuir's isotherm equation is given as:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$$

In this equation, q_e is the amount of metal adsorbed at equilibrium (in mg/g), q_m and K_a are Langmuir constants.

Calculation of q_m and K_a was done by plotting $\frac{1}{q_e}$ vs $\frac{1}{C_e}$, where q_m is $\frac{1}{\text{intercept}}$ and K_a is the $\text{intercept} \times \frac{1}{\text{slope}}$.

3.8.2. Freundlich Adsorption Isotherm

Freundlich isotherm is represented as $q_e = K_f C_e^{1/n}$.

The K_f and n are constants, K_f is the Freundlich constant. Taking the logarithms of the isotherm yields $\log q_e = \log K_f + \frac{1}{n} \log C_e$ with an intercept of K_f and a slope of $\frac{1}{n}$, $\log q_e$ was plotted against $\log C_e$ where K_f is the adsorption capacity, and $\frac{1}{n}$ the adsorption intensity.



CHAPTER FOUR

EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Results from Physicochemical Analysis

Table 4. below show the results of the physicochemical parameters from the three sampling sites compared with the W.H.O Guidelines for Potable Water.

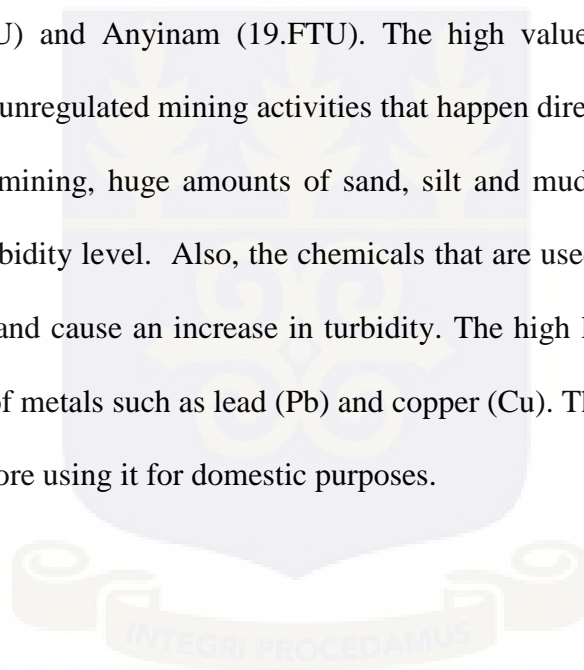


Table 4. Physicochemical parameters of Birim river at Kibi, Kade and Anyinam

BIRIM RIVER					
PARAMETER	UNIT	KIBI	KADE	ANYINAM	WHO
Turbidity	NTU	356	360	350	5
Colour (apparent)	Hz	150	161	159	15
pH	pH Units	7.31	7.5	7.61	6.5 - 8.5
Conductivity	µS/cm	108	115	110	1500
Total Suspended Solids (SS)	mg/L	1	1.2	1.08	-
Total Dissolved Solids (TDS)	mg/L	59.4	60.9	61	1000
Sodium	mg/L	3.1	3.3	3.5	200
Potassium	mg/L	1.2	1.08	1.3	30
Calcium	mg/L	7.46	7.35	7.6	200
Magnesium	mg/L	6.65	7.01	7.02	150
Total Iron	mg/L	0.581	0.591	0.6	0.3
Ammonia (NH ₄ -N)	mg/L	0.11	0.114	0.109	0.00 – 1.5
Chloride	mg/L	9.93	10.01	9.89	250
Sulphate(SO ₄)	mg/L	11.5	10.9	11.35	250
Phosphate (PO ₄ -P)	mg/L	0.054	0.049	0.072	-
Manganese	mg/L	0.496	0.501	0.508	0.4
Nitrite (NO ₂ -N)	mg/L	0.013	0.013	0.012	1.0
Nitrate (NO ₃ -N)	mg/L	0.116	0.115	0.113	10
Total Hardness (as CaCO ₃)	mg/L	46	44	48	500
Total Alkalinity (as CaCO ₃)	mg/L	26.4	26.5	27	-
Calcium Hardness (as CaCO ₃)	mg/L	18.6	18.6	18.9	-
Magnesium (as CaCO ₃)	mg/L	27.4	28	27.7	-
Fluoride	mg/L	0.156	0.154	0.156	1.5
Bicarbonate	mg/L	32.2	32.2	32.2	-
Carbonate	mg/L	0	0	0	-

4.2 Physicochemical Parameters

From the experimental results for the three sampling stations shown in the Table 4, it could be observed that, most of the physicochemical parameters are within the WHO guideline for potable water. However, iron, turbidity, colour and manganese have values that exceed the WHO guidelines for potable water. In O.D Ansa-Asare and K.A Asante's research on "The Quality of Birim River in South- East Ghana", in 2000, similar results of high turbidity were observed from this same river at Kibi (51.0 FTU), Kade (35.0 FTU) and Anyinam (19.FTU). The high value of turbidity might be attributed to the unregulated mining activities that happen directly in this river. This is because during mining, huge amounts of sand, silt and mud are generated and this increases the turbidity level. Also, the chemicals that are used in this mining activity also precipitate and cause an increase in turbidity. The high level of colour could be from corrosion of metals such as lead (Pb) and copper (Cu). The water therefore needs to be treated before using it for domestic purposes.



4.3. Initial Concentrations of Pb and Hg before treatment with adsorbents.

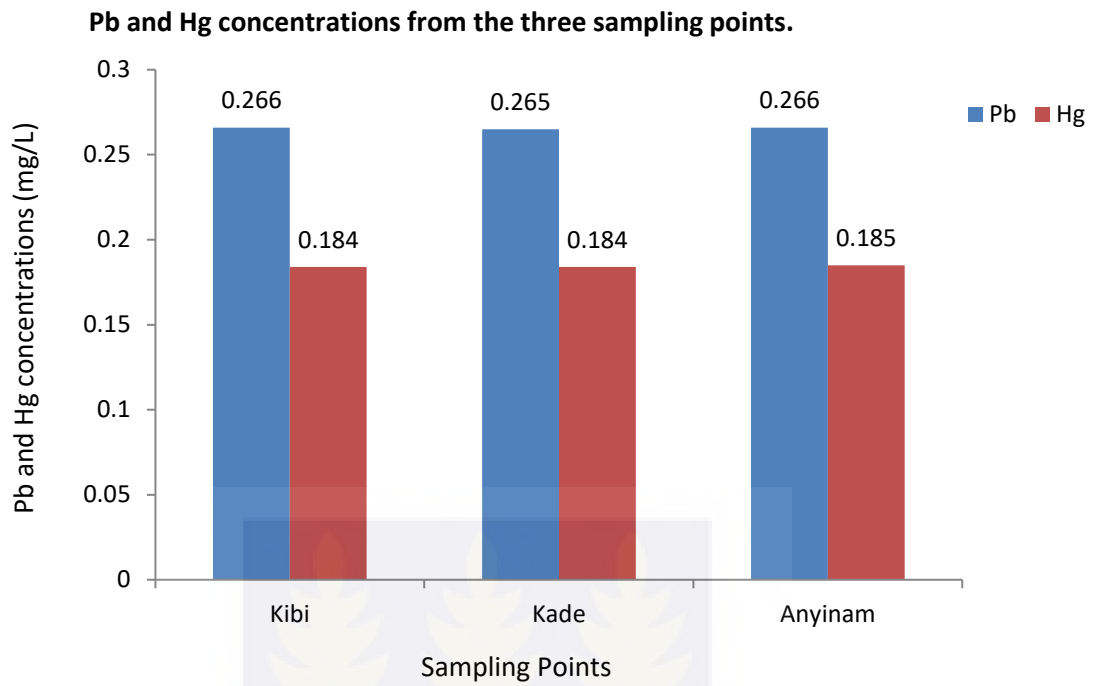


Figure 6. Pb and Hg concentrations from the three sampling points before treatment with adsorbents.

4.4. Results from Batch Test

The results obtained from the batch test are graphically represented below, showing the effect of contact time, pH and adsorbent dosage on each adsorbent.

4.4.1 Effect of pH

FTIR spectrum of orange peel showed the presence of carboxyl and hydroxyl functional groups as the main groups responsible for metal adsorption (Perez-Marín et al., 2008). In rice husk, the main group responsible for metal adsorption is silica (Lee et al., 1994). Sorption of Pb and Hg by rice husk and orange peel adsorbents depends on the pH of the solution (Wong *et al.*, 2003). Figure 7 generally shows that, the uptake of Pb and Hg is higher at pH 5 for both modified and unmodified adsorbents. A similar work conducted by Wong *et al.*, 2003 showed a higher adsorption of Pb at pH 5.3. However, as pH increased the amount of Pb and Hg adsorbed decreased. This may be due to the fact that as the pH increased, it rendered the surfaces of the adsorbents and the metal ions negatively charged and hence repulsion occurred instead of attraction. The modified adsorbents have greater adsorption efficiencies compared to the unmodified counterparts. This could be the additional carboxyl and hydroxyl functional groups from tartaric acid which increased the adsorption sites.

pH versus adsorbent efficiency

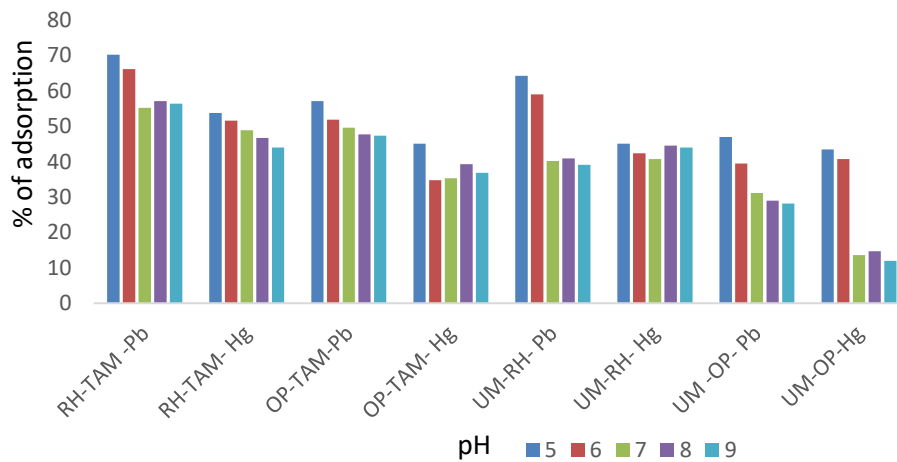


Figure 7: Effect of pH on RH-TAM, OP-TAM, UM-RH and UM-OP

4.4.2. Effect of Contact time

Figure 8 shows that, the optimum time at which maximum adsorption of Pb and Hg occurred for both modified and unmodified adsorbents was 4 hours. The least time at which adsorption of Pb and Hg occurred was 1 hour. Averagely, adsorption efficiency of the adsorbents increased with increase in contact time. A similar work carried out by Rajkumar V. Raikar., 2015 and Wong et al., 2003 confirmed the observed trend. As the metal ions stayed in contact with the adsorbent, an equilibrium was established where the rate at which the metal ions bonded with the adsorbents became equal to the rate at which the bond between the metal ions and the adsorbent dissociated. At this point, the adsorption efficiency of the adsorbent became steady with no significant change in adsorption; and maximum adsorption of metal ions by the adsorbent depended much on the time at which the equilibrium was established.

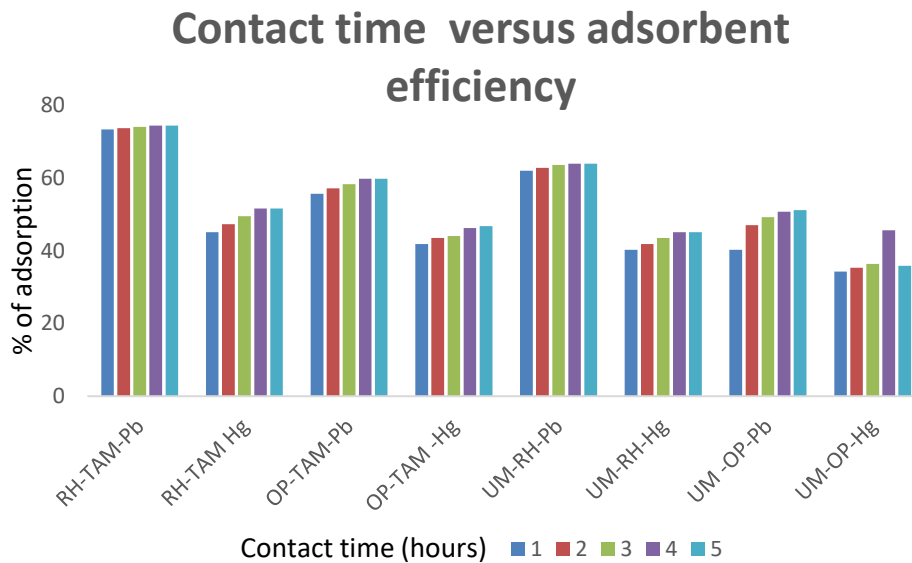


Figure 8: Effect of contact time on RH-TAM, OP-TAM, UM-RH, and UM-OP

4.4.3. Effect of adsorbent dosage

Figure 9 depicts that the optimum dosage at which maximum adsorption of Pb and Hg occurred for both modified and unmodified adsorbents was 0.5 g. However, the least dosage at which adsorption of Pb and Hg occurred was 0.1 g. Generally, adsorption efficiency of the adsorbents increased with increase in adsorbent dosage and this observation had been confirmed by Wong *et al.*, 2003; Arivoli *et al.*, 2009 and Ladhe *et al* 2011 who carried out similar experiments. The increased in adsorption efficiency with respect to increase in adsorbent dosage could be as a result of increased in surface area of the adsorbent, increased in active functional groups and hence increased in adsorption sites.

Adsorbent dosage versus adsorbent efficiency.

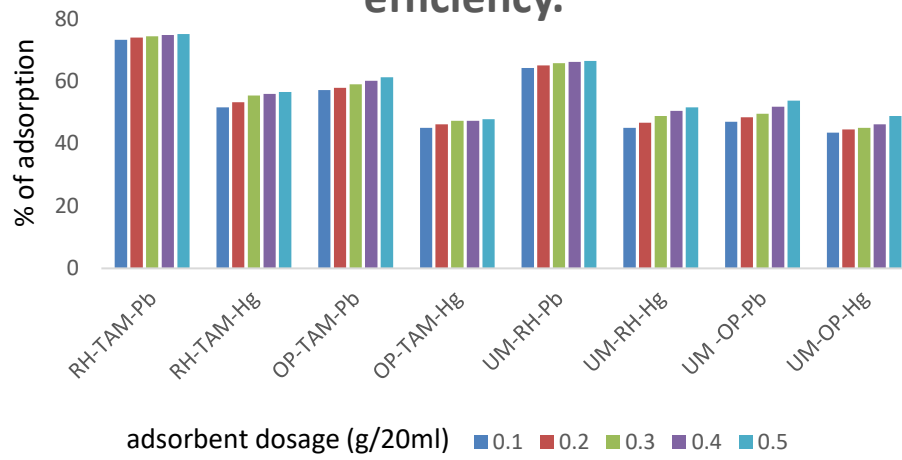
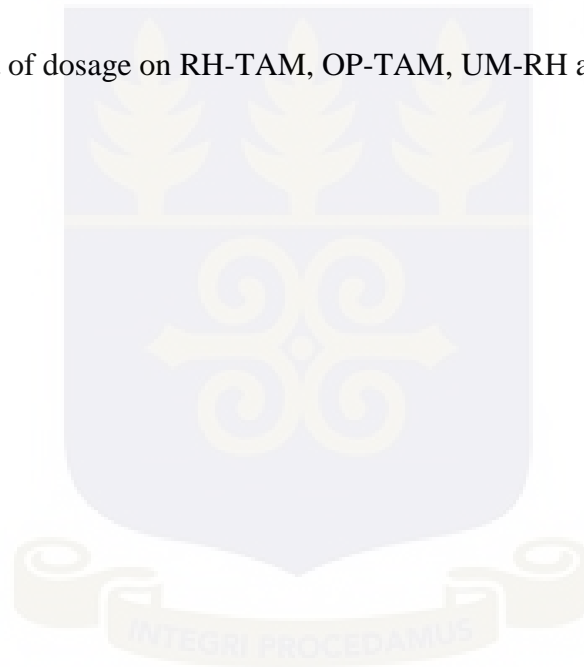


Figure 9: Effect of dosage on RH-TAM, OP-TAM, UM-RH and UM-OP



4.5 Adsorption Isotherms

4.5.1 Langmuir Adsorption Isotherm for RH-TAM

Figures 10 (a) (i) and 10 (a) (ii) show Langmuir adsorption isotherms for RH-TAM for Pb and Hg respectively.

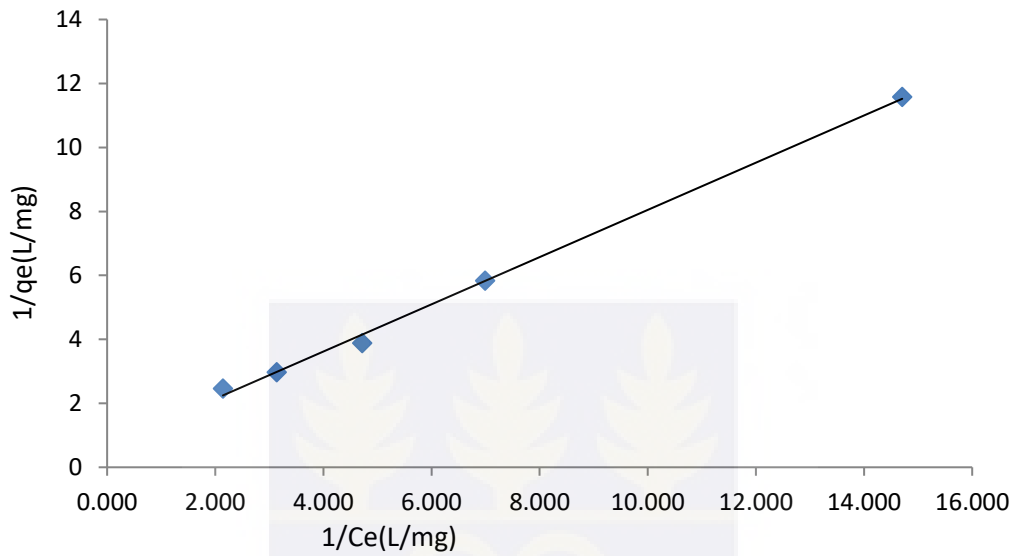


Figure 10 (a) (i): Langmuir isotherm for Pb adsorption using RH-TAM

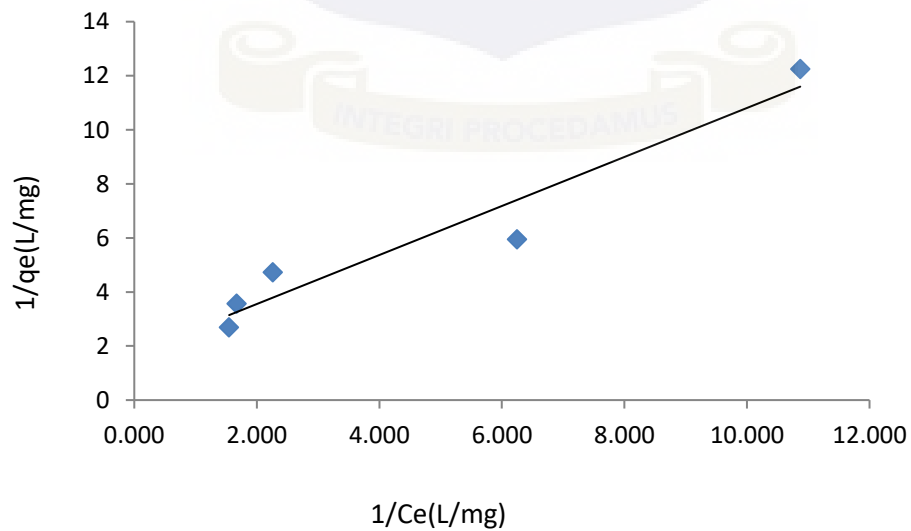


Figure 10 (a) (ii): Langmuir isotherm for Hg adsorption using RH-TAM

4.5.2 Langmuir Adsorption Isotherm for UM-RH

Figures 10 (b) (i) and 10 (b) (ii) show Langmuir adsorption isotherms for UM-RH for Pb and Hg respectively.

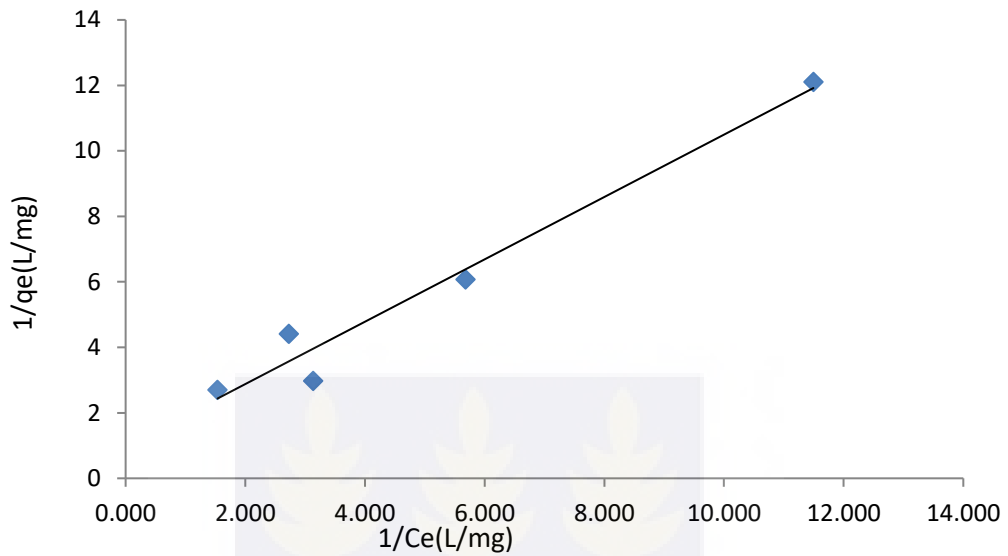


Figure 10 (b) (i): Langmuir isotherm for Pb adsorption using UM-RH

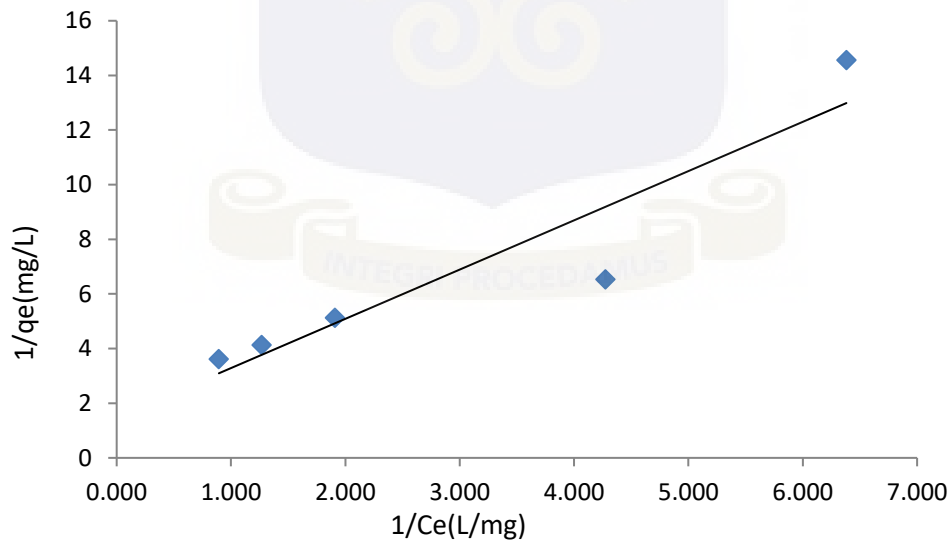


Figure 10 (b) (ii): Langmuir isotherm for Hg adsorption using UM-RH

4.5.3 Langmuir Adsorption Isotherm for OP-TAM

Figures 11 (a) (i) and 11 (a) (ii) show Langmuir adsorption isotherms for OP-TAM for Pb and Hg respectively.

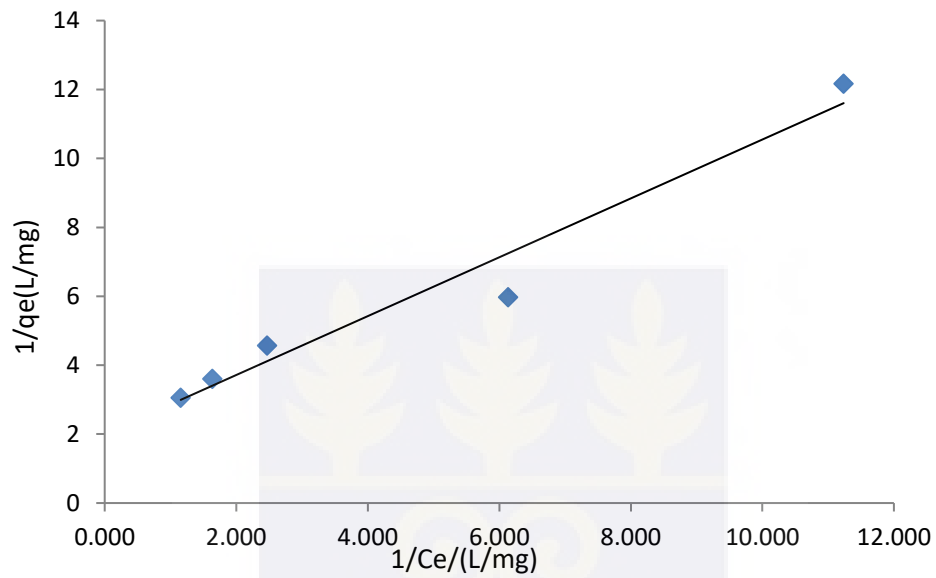


Figure 11 (a) (i): Langmuir isotherm for Pb adsorption using OP-TAM

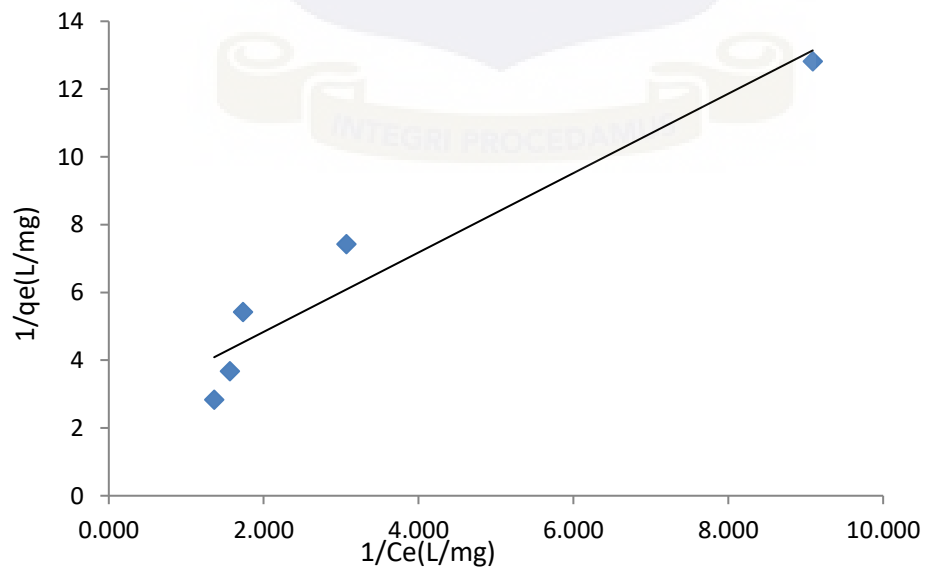


Figure 11 (a) (ii): Langmuir isotherm for Hg adsorption using OP-TAM

4.5.4 Langmuir Adsorption Isotherm for UM-OP

Figures 11 (b) (i) and 11 (b) (ii) show Langmuir adsorption isotherms for UM-OP for Pb and Hg respectively.

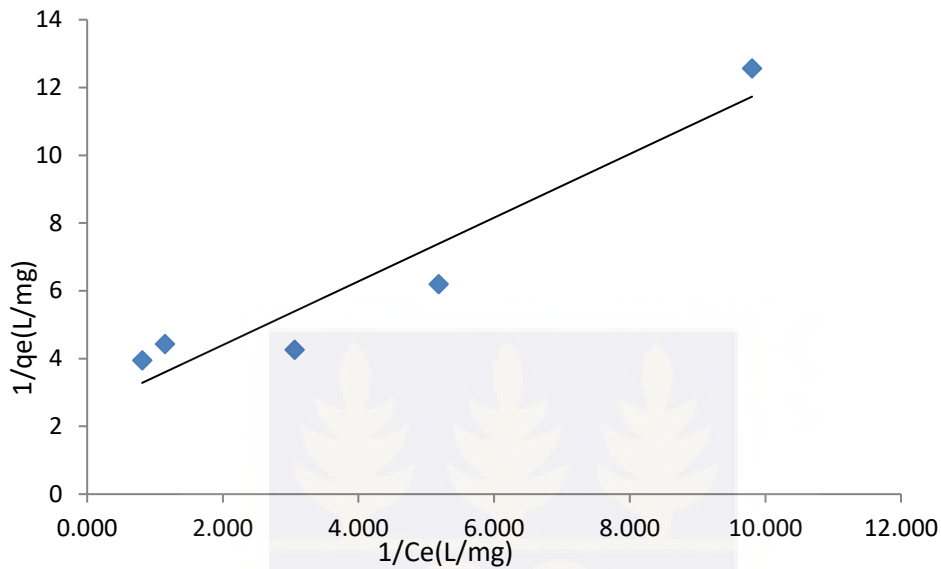


Figure 11 (b) (i): Langmuir isotherm for Pb adsorption using UM-OP

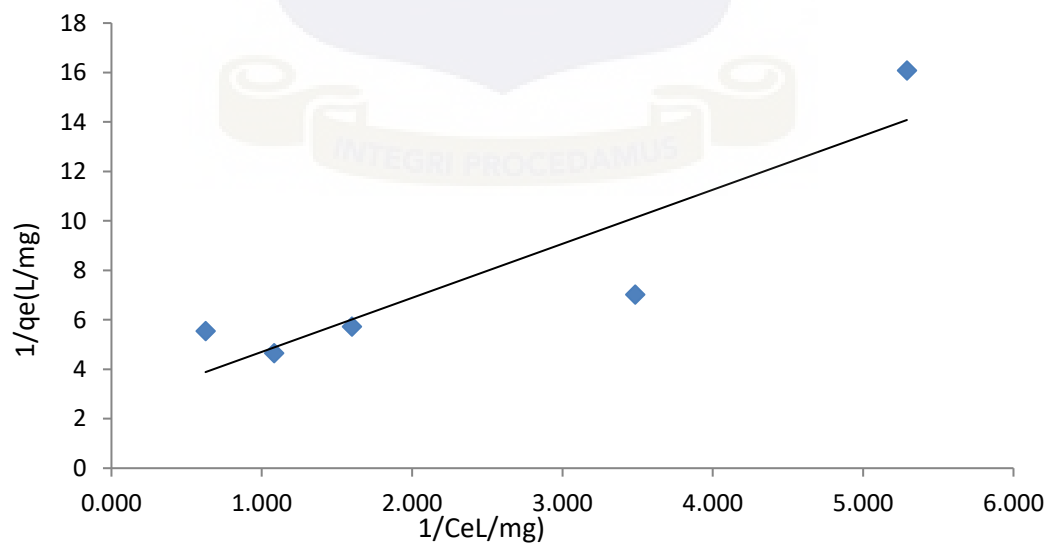


Figure 11 (b) (ii): Langmuir isotherm for Hg adsorption using UM-OP

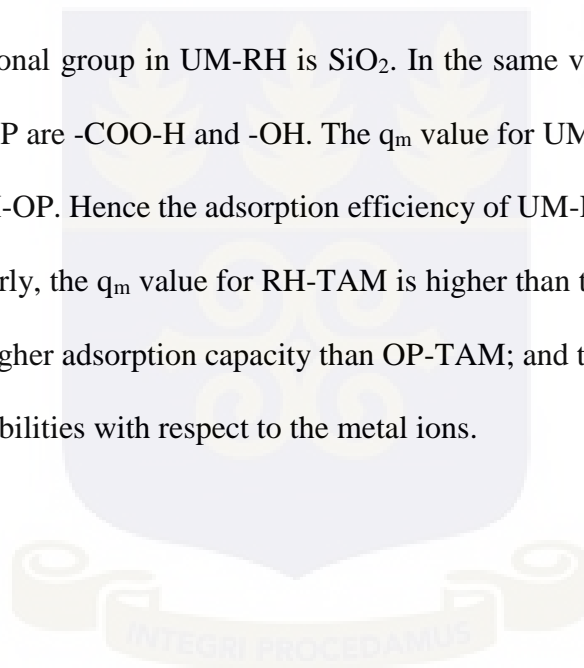
Table 5. Langmuir isotherm parameters for Pb and Hg for RH-TAM, OP-TAM, UM-RH and UM-OP

Langmuir Isotherm for Pb adsorption for RH-TAM				
Intercept	Slope	q_m (g/g)	K_a	R^2
0.5734	0.7466	1.74398326	0.768015	0.9989
Langmuir Isotherm for Pb adsorption for OP-TAM				
Intercept	Slope	q_m	K_a	R^2
2.0073	0.8541	0.49818164	2.35019319	0.9599
Langmuir Isotherm for Hg adsorption for RH-TAM				
Intercept	Slope	q_m	K_a	R^2
1.7402	0.9068	0.57464659	1.91905602	0.9353
Langmuir Isotherm for Hg adsorption for OP-TAM				
Intercept	Slope	q_m	K_a	R^2
2.4933	1.1712	0.40107488	2.12884221	0.9262
Langmuir Isotherm for Pb adsorption for UM-RH				
Intercept	Slope	q_m	K_a	R^2
0.9744	0.9521	1.02627258	1.02342191	0.9681
Langmuir Isotherm for Hg adsorption for UM-RH				
Intercept	Slope	q_m	K_a	R^2
1.4847	1.8025	0.67353674	0.82368932	0.8755
Langmuir Isotherm for Pb adsorption for UM-OP				
Intercept	Slope	q_m	K_a	R^2
2.5224	0.9393	0.39644783	2.68540402	0.9136
Langmuir Isotherm for Hg adsorption for UM-OP				
Intercept	Slope	q_m	K_a	R^2
2.5177	2.1853	0.39718791	1.15210726	0.8123

Table 5 above shows that adsorption of Pb and Hg with RH-TAM fits the Langmuir isotherm better than the adsorption of Pb and Hg with UM-RH; because the R^2 value for RH-TAM is closer to one than that for UM-RH. Similarly, the adsorption of Pb and Hg with OP-TAM fits the Langmuir isotherm better than the adsorption of Pb and Hg with UM-OP.

The additional functional groups (-COOH and -OH) from tartaric acid increased the available sites for adsorption in the modified forms of the adsorbents. This is evident in the q_m values (i.e the available sites for adsorption) for all the modified adsorbents.

The main functional group in UM-RH is SiO_2 . In the same vein, the main functional groups in UM-OP are -COO-H and -OH. The q_m value for UM-RH (Table 5) is higher than that for UM-OP. Hence the adsorption efficiency of UM-RH is higher than that of UM-OP. Similarly, the q_m value for RH-TAM is higher than that for OP-TAM; hence RH-TAM has higher adsorption capacity than OP-TAM; and this could be due to their relative bond stabilities with respect to the metal ions.



4.6 Freundlich Isotherms

4.6.1 Freundlich Adsorption Isotherm for RH-TAM

Figures 12 (a) (i) and 12 (a) (ii) show Freundlich adsorption isotherms for RH-TAM for Pb and Hg respectively

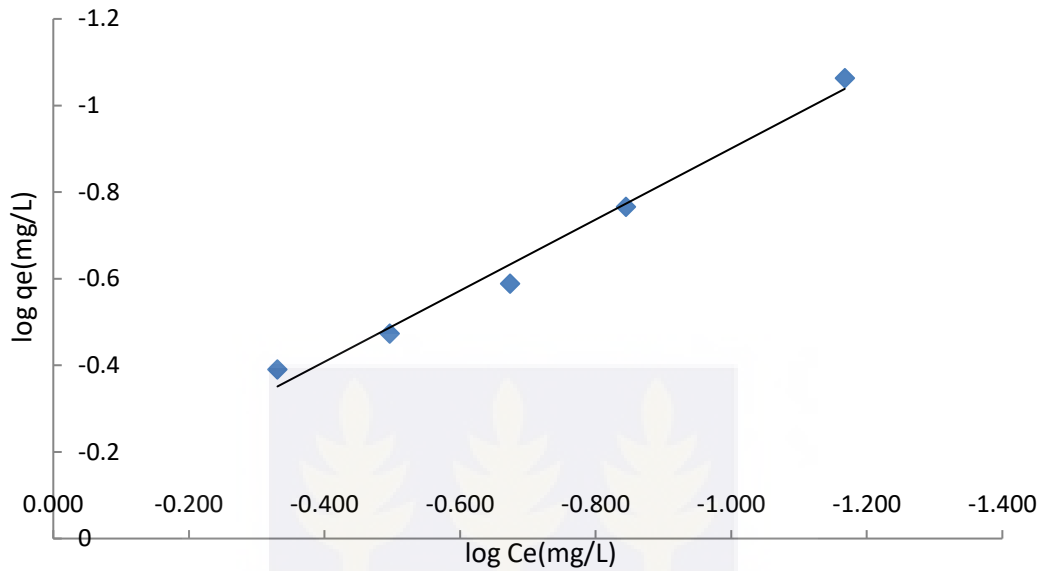


Figure 12 (a) (i): Freundlich isotherm for Pb adsorption using RH-TAM

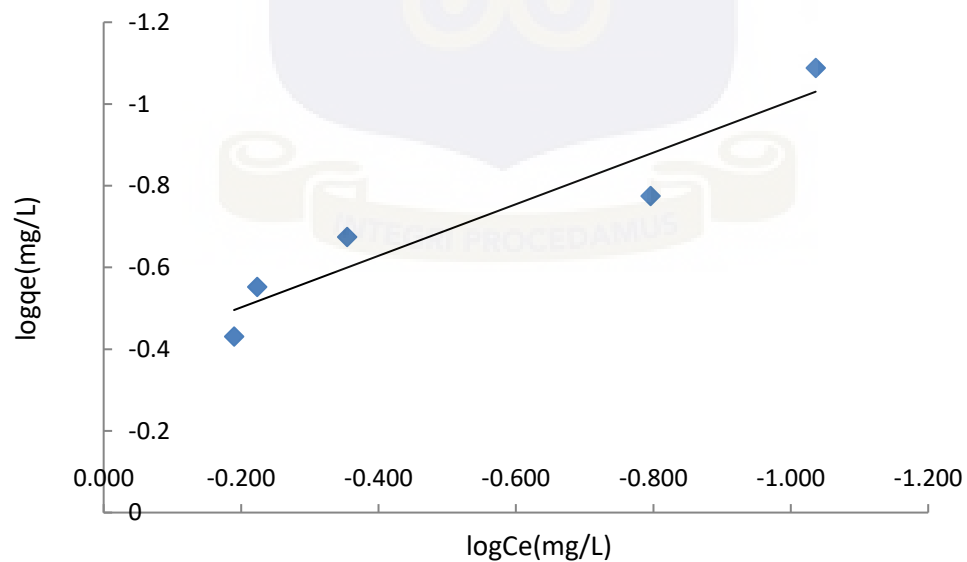


Figure 12 (a) (ii): Freundlich isotherm for Hg adsorption using RH-TAM

4.6.2 Freundlich Adsorption Isotherm for UM-RH

Figures 12 (b) (i) and 12 (b) (ii) show Freundlich adsorption isotherms for UM-RH for Pb and Hg respectively.

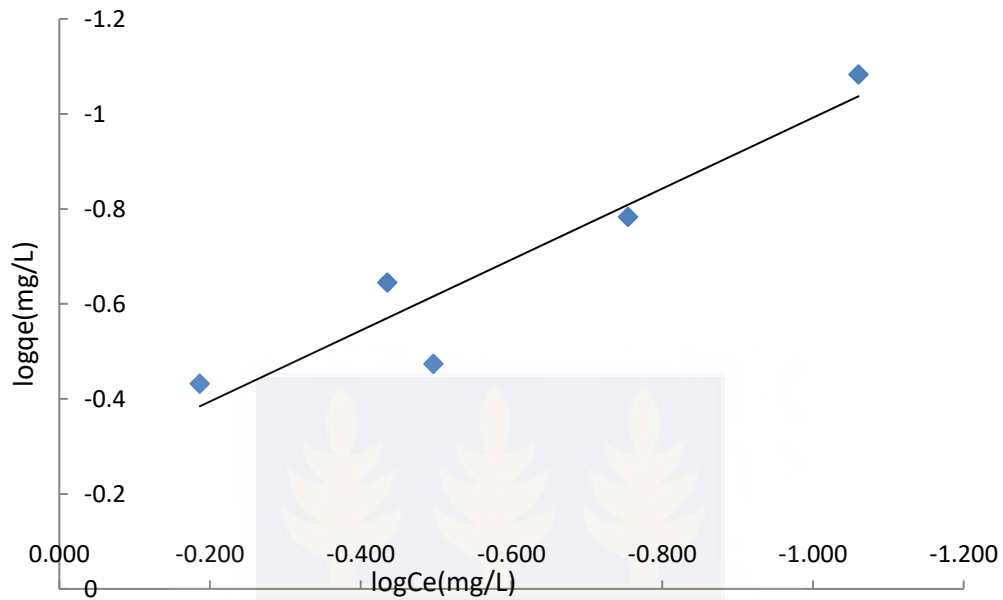


Figure 12 (b) (i): Freundlich isotherm for Pb adsorption using UM-RH

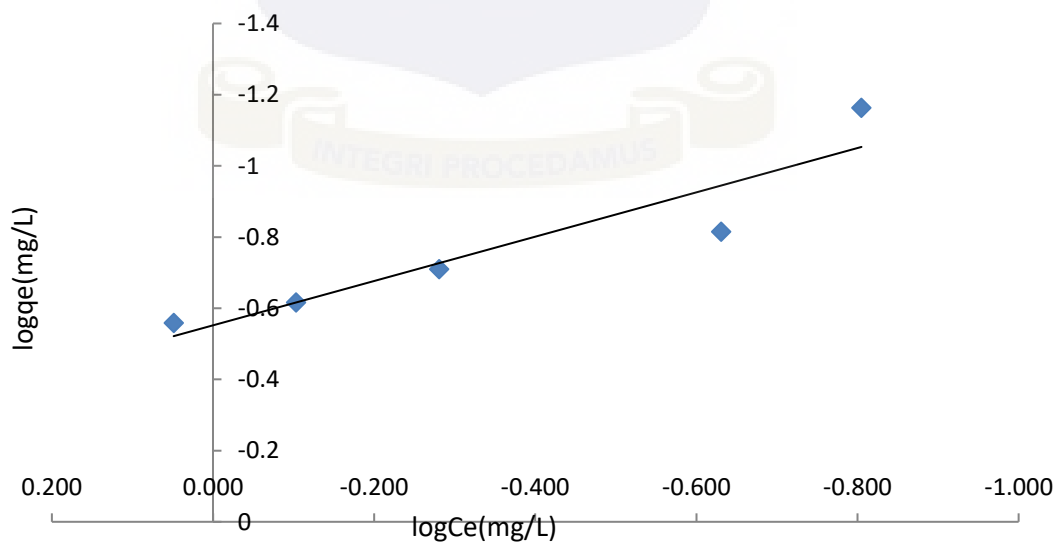


Figure 12 (b) (ii): Freundlich isotherm for Hg adsorption using UM-RH

4.6.3 Freundlich Adsorption Isotherm for OP-TAM

Figures 13 (a) (i) and 13 (a) (ii) show Freundlich adsorption isotherms for OP-TAM for Pb and Hg respectively.

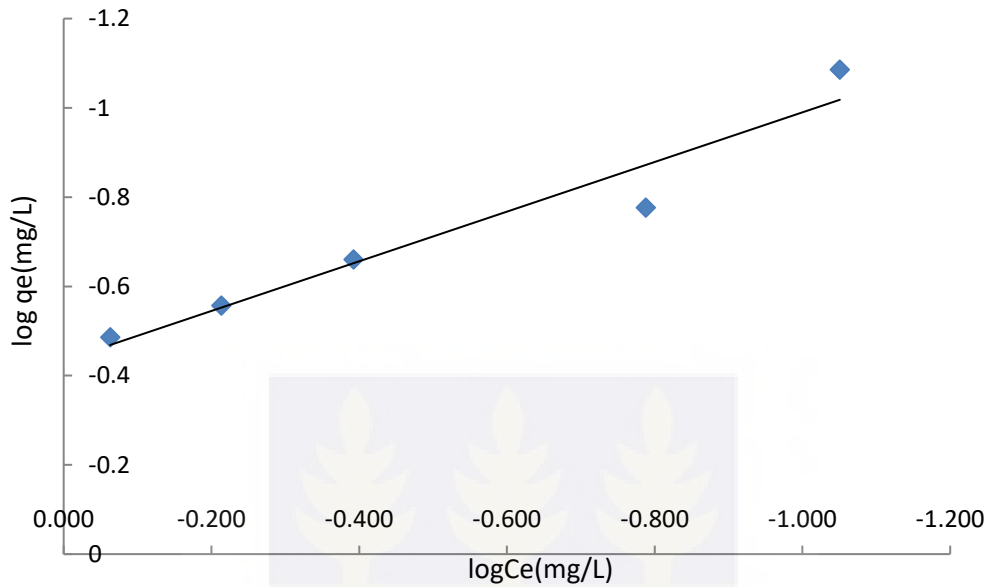


Figure 13 (a) (i): Freundlich isotherm for Pb adsorption using OP-TAM

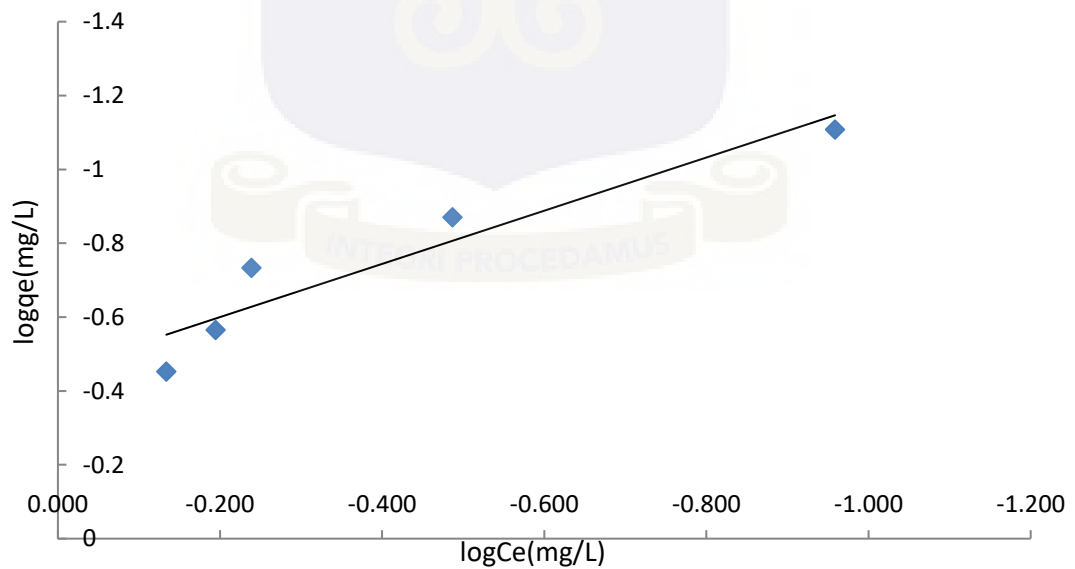


Figure 13 (a) (ii): Freundlich isotherm for Hg adsorption using OP-TAM

4.6.4 Freundlich Adsorption Isotherm for UM-OP

Figures 13 (b) (i) and 13 (b) (ii) show Freundlich adsorption isotherms for UM-OP for Pb and Hg respectively.

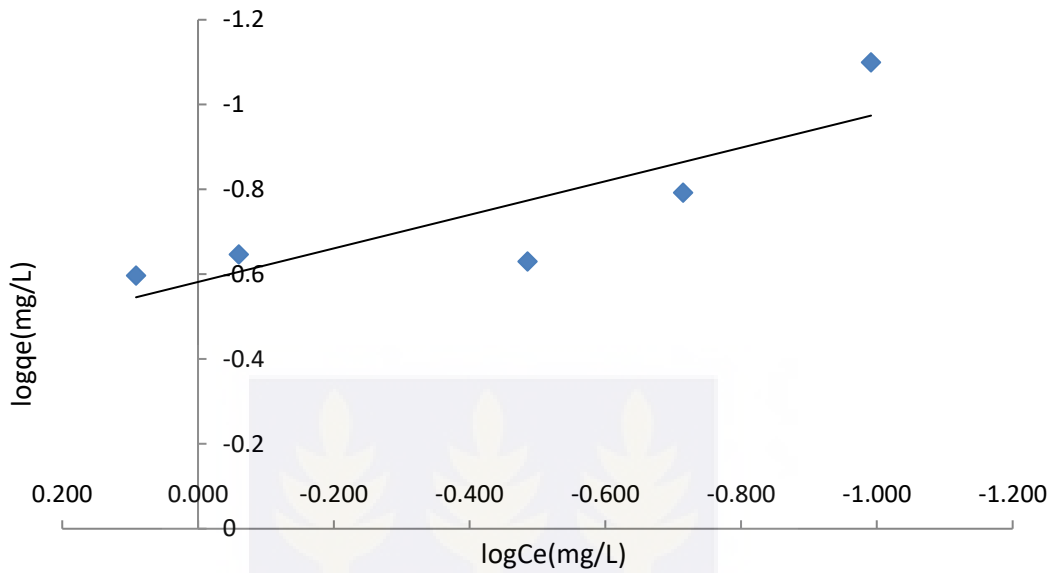


Figure 13 (b) (i): Freundlich isotherm for Pb adsorption using UM-OP

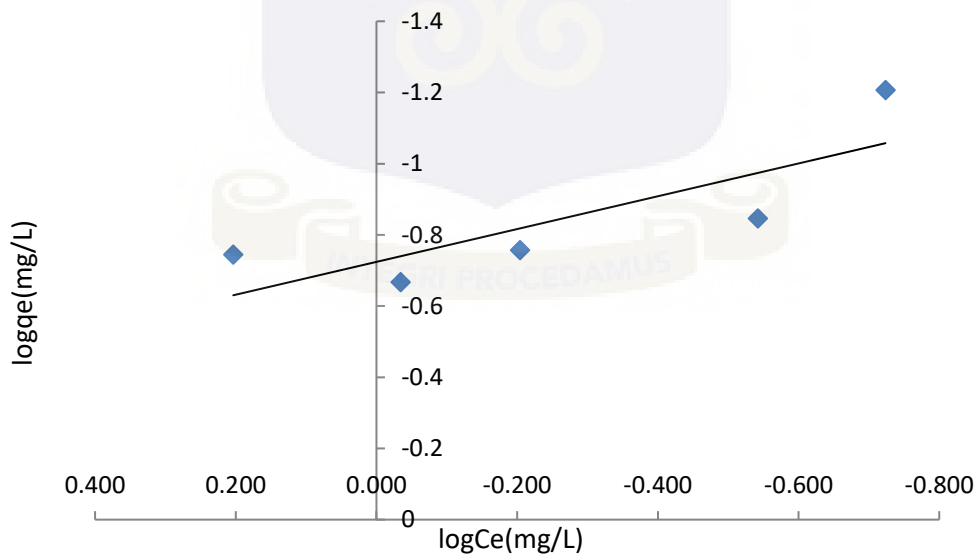


Figure 13 (b) (ii): Freundlich isotherm for Hg adsorption using UM-OP

Table 6. Freundlich isotherm parameters for Pb and Hg for RH-TAM, OP-TAM, UM-RH and UM-OP

Freundlich Isotherm for Pb adsorption for RH-TAM				
Intercept	Slope	K_f	n	R^2
-0.0796	0.8212	0.83253021	1.217730151	0.9848
Freundlich Isotherm for Pb adsorption for OP-TAM				
Intercept	Slope	K_f	n	R^2
-0.4336	0.5563	2.71393849	1.797591228	0.9368
Freundlich Isotherm for Hg adsorption for RH-TAM				
Intercept	Slope	K_f	n	R^2
-0.3758	0.6314	0.42092042	1.583782072	0.8998
Freundlich Isotherm for Hg adsorption for OP-TAM				
Intercept	Slope	K_f	n	R^2
-0.456	0.7202	0.34994517	1.388503194	0.8998
Freundlich Isotherm for Pb adsorption for UM-RH				
Intercept	Slope	K_f	n	R^2
-0.2452	0.7468	0.56859102	1.339046599	0.8892
Freundlich Isotherm for Hg adsorption for UM-RH				
Intercept	Slope	K_f	n	R^2
-0.5519	0.6227	0.28060797	1.605909748	0.8657
Freundlich Isotherm for Pb adsorption for UM-OP				
Intercept	Slope	K_f	n	R^2
-0.5818	0.3957	0.2619389	2.527167046	0.7337
Freundlich Isotherm for Hg adsorption for UM-OP				
Intercept	Slope	K_f	n	R^2
-0.7241	0.4609	0.18875567	2.169668041	0.6645

Table 6 presents the Freundlich adsorption isotherm parameters for RH-TAM, OP-TAM, UM-RH and UM-OP obtained for Pb and Hg. The R^2 value for RH-TAM is closer to 1 than that for UM-RH. Therefore, the RH-TAM fits the Freundlich model better than the UM-RH. The adsorption capacity (K_f) for RH-TAM is higher than that for UM-RH. In the same vein, the adsorption capacity for OP-TAM is higher than that for UM-OP since K_f value for OP-TAM is greater than that for UM-OP. Finally, the K_f value for OP-TAM is greater than that for RH-TAM, hence the adsorption capacity for OP-TAM is higher than that for RH-TAM.



CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The adsorption of Pb and Hg by rice husk, orange peel and their modified forms were studied under different conditions. RH-TAM recorded adsorption capacities of 75.56 % and 53.26 % for Pb and Hg respectively. The unmodified form of rice husk also showed significant adsorption efficiencies of 69.92 % and 42.39 % for Pb and Hg respectively. The orange peel and its modified form was able to adsorb Pb and Hg but with lower adsorption efficiencies as compared to rice husk and its modified form (i.e OP-TAM-Pb: 62.03 %, OP-TAM-Hg: 44.57%, UM-OP- Pb: 51.88% and UM-OP-Hg: 42.39%).

In general, rice husk and its modified form exhibited higher adsorption capacities than orange peel and its modified form. Pb adsorption was favoured by both adsorbents and their modified forms than Hg. The two adsorbents had high adsorption efficiencies at pH of 5, adsorbent dose of 0.5 g/20 mL for 4 hours at 35°C. The Langmuir adsorption isotherm provided better correlation for the adsorption of Pb and Hg than the Freundlich isotherm.

The turbidity of the water sample from Birim River at Kibi (356 NTU), Kade (360 NTU) and Anyinam (350 NTU) were far greater than the WHO acceptable limit (5 NTU). Also, the initial concentrations of Pb (0.226 ppm) and Hg (0.185 ppm) were also higher than the WHO acceptable limits of 0.01 ppm for Pb and 0.001 ppm for Hg.

5.2 Recommendations

The adsorption of other heavy metals from wastewater should also be studied with these same adsorbents. Column adsorption should also be conducted to study the adsorbent capacity on an industrial scale. For effective removal of mercury, rice husk modified with dyestuffs such as Procion Red and Yellow should also be studied.



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APPENDICES

Abbreviations.

ASTM- American Standard for Testing Materials.

CSRI –WRI- Center for Scientific and Industrial Research- Water Research Institute,
Ghana.

NTU - Nephelometric turbidity unit.

