EFFECT OF ORANGE PEEL, WATERMELON PEEL, AND THEIR SYNERGISTIC EFFECT ON THE REMOVAL OF HEAVY METALS FROM DYE WASTEWATER

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A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER'S DEGREE IN WATER RESOURCES AND ENVIRONMENTAL ENGINEERING

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MARCH, 2021

DECLARATION

I hereby declare that the work in this dissertation titled "**Effect of orange peel, watermelon peel, and their synergistic effect on the removal of heavy metals from dye wastewater**" has been performed by me in the Department of Water Resources and Environmental Engineering. All information derived from the literature has been duly acknowledged in the text and list of references provided. No part of this work has been previously presented for another degree or diploma at this or any other institution.

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Name of Student	Signature	Date

CERTIFICATION

This dissertation tittled Effect of orange peel, watermelon peel, and their synergistic effect on the removal of heavy metals from dye wastewater by Zainab Baba-Mai ALI (P16EGWR8023) meets the regulations governing the award of the degree of Master of Science in Water Resources and Environmental Engineering of the Ahmadu Bello University, and is approved for its' contribution to knowledge and literary presentation.

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DEDICATION

Dedicated to my late parents, Baba Mai Ali and Professor Hauwa Baba-Mai Ali for the unconditional love, inspiration and mentorship.

ABSTRACT

Modernization of our surrounding has resulted to widespread pollutants being disposed amidst which are heavy metals into the surroundings. Heavy metals are toxic to both human health and the environment even at low concentrations. Biosorption studies is considered as a method for the removal of heavy metals from dye wastewater due to its simple design, specific affinity, low cost, effectiveness, reduced chemical and biological sludge, no further nutrient requirement, revitalization of biosorbent, and potentiality of metal recovery. This research investigated the feasibility of using orange peel (OP) and watermelon peel (WP) and their combination (CP) as biosorbents for the removal of cadmium (Cd), lead (Pb) and mercury (Hg) metal ions from dye wastewater. The analysis was performed to study the effects of time, biosorbent dosage and initial pH of the biosorbents on the removal efficiency of the heavy metals, an ANOVA analysis, adsorption kinetics and isotherm modelling were also used. The materials were obtained and prepared in a laboratory where 2.0g of the adsorbent was equilibrated with 50 ml of the dye. From the study, OP had the highest adsorption efficiency for Hg at 96.9%, Cd at 88.8% and Pb at 93.1% in relation to time; OP had the highest adsorption efficiency for Hg at 93.4% and Cd at 98.9% while WP had the highest adsorption efficiency for Pb at 91.4% in relation to dosage. For pH variations the equilibrium was achieved around wastewater pH levels of 6.8-7.7 for the sorption of all metal ions by using all adsorbents. Ranking the adsorption ability of the measured metal ions, the following series was obtained: for OP, $Hg\ (II) > Cd\ (II) > Pb\ (II)$; for WP, the ranking was $Cd\ (II) > Pb\ (II) > Hg\ (II)$, and for the CP it's $Cd\ (II) > Pb\ (II) > Hg\ (II)$. The research shows that both biosorbents can be used to perform metal ions adsorption successfully, they proved to have high adsorption capacities and appeared to have a universal application for adsorption of the metal ions. The research showed the adsorption of metal ions is dependent on contact time, biosorbent dosage and pH. Using the three adsorbents at respective time duration, Cd adsorption was found to be the most effective, with Fischer (F) and Probability (P) values of 13802.04 and 3.2×10^{-29} respectively. Similarly, at respective weight variation, Cd adsorption was also found to be the most effective, with F and P values of 9262.98 and 5.5×10^{-15} respectively. While, at pH levels, Hg adsorption was found to be the most effective, with F and P values of 201.31 and 1.41×10^{-14} respectively. This research also showed that the adsorption kinetics modelling studies for the biosorbent dosage followed the first order kinetic models. The isotherm equilibrium studies confirmed that Freundlich adsorption isotherms well fitted models and revealed that adsorption of metals ions is multi-layer and heterogenous. The results from the research indicated that the process used to adsorb metal ions from wastewater has a possible application for a proper plant design.

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CHAPTER ONE

INTRODUCTION

1.1 Background

Paucity of water and water pollution remains to be a dilemma of utmost interest worldwide. Due to toxicity to the environment and its life forms, pollution by heavy metal has grown to be a severe environmental issue for number of years. In developing countries, heavy metals removal from drinking water, industrial water and water use for irrigation is a recurrent problem (Vhahangwele and Khathutshelo, 2018).

Environmental pollution is the adverse modification of the environment chiefly by actions of man, directly or indirectly, which impact changes in the energy pattern, the levels of radiation, chemical and physical constitution and death of microorganisms (Prabhat, 2016). Environmental pollution can have injurious and fatal consequence on man and his environment. The actions of man as a result of urban sprawl, modernization, mining, and expedition are the leading cause of environmental pollution (Prince *et al.,* 2020)

Despite technological advances in recent times, environmental pollution still constitutes one of the most important contemporary problems of our time. Apart from air pollution, industries have enormous capability, to instigate pollution in lakes, streams, rivers and seas. Flourishing modernization has ushered rise in disposal of pollutants amidst which are heavy metals into the environment. Pollution by heavy metals occurs in aqueous waste streams of numerous industries, such as mining, metal finishing, electroplating, metallurgical work, pesticides, fertilizers, chemical manufacturing, tanning, battery, dyes and textile manufacturing (Kang *et al*., 2007 and Lesmana *et al*., 2009).

The World Bank (1995) revealed that roughly 19, 000 tonnes of perilous waste is generated yearly in Nigeria and that the waste comes majorly from steel, metal processing,

pharmaceuticals, textiles, tanneries, and oil refining industries. The processes in industries give rise to extensive diversity of contaminants.

Heavy metals have been described as leading contaminants, as a result of their unsteadiness in aquatic ecosystems. Their existence and toxicity even in low concentrations and compatibility in the environment has resulted in grievous environmental catastrophe. They are not ecofriendly and tend to buildup in human tissue and living creatures, resulting in several ailments and irregularities. For example, cadmium exposure can cause serious damage to human health which may include desecration to bones, worsening of cancer, impairment of mucus membrane and influence the manufacture of progesterone and testosterone (Rahate *et al*., 2013).

Lead is one of three utmost lethal heavy metals that has the capacity to ascribe reposing and permanent adverse consequences on health, resulting to hepatitis, anemia, nephritic syndrome, destruction to brain, intellectual or cognitive insufficiency, malnutrition, throwing up, restlessness and brain disorder (Shaibu-Imodagbe *et al*., 2013). Also, mercury poisoning can lead to shivering, alteration in emotions, restlessness, tiredness, shrinking of muscle, trembling, migraines, interruption in sensitivity, alterations in nerve reactions, shortfall in capabilities on examination of mental activity and intense subjections may affect the kidney, floppy breathing and could be fatal (Olson, 2016).

Various techniques have been exploited for the extraction of heavy metals from water and wastewater in the past few decades. Chemical precipitation, ultrafiltration, ion exchange, reverse osmosis, electro winning, carbon adsorption and phytoremediation are the frequent techniques used for extraction of heavy metals from polluted water. Most of these techniques seem to be unsuccessful, highly costly and take extended time for heavy metal ion to be extracted from water and industrial wastewater (Joshi, 2017). Thus, several pioneering procedures have been researched on, so as to enhance cost effective and more structured heavy metal extraction

methods. Biosorption is believed to be convenient, useful purifying and separation technique for the extraction of heavy metals from contaminated water from industries (Gunatilake, 2015).

Due to quest for groundbreaking techniques involving removal of heavy metals from wastewater, this has steered interest to biosorption, due to its advantage of metal binding capabilities to different organic constituents. Biosorption referred to as the capability of materials which has biological origin to agglomerate heavy metals from wastewater (by the use of Adenosine Triphosphate-ATP) or physio-chemical routes of utilization (Shamim, 2018). According to Michalak *et al*., (2013) the intriguing properties of biosorption over traditional methods of treatment include: affordability, great effectiveness, reduced chemical and or biological sludge, no further nutrient demand, revitalization of biosorbent, and potentiality of recovering metal.

The activities involve in biosorption includes a solid state (sorbent or biosorbent, biological material) and a liquid state (solvent, usually water) comprising a dissolvable specie to be sorbed (sorbent, metal ions). Owing to strong bond of the sorbent for sorbate species, the later is drawn and surrounded there by various techniques. The activity prevails until balance is achieved between the quantity of solid-bound sorbent and its fragment left over in the solutions. The sequence between the solid and liquid phases is dependent on the amount of sorbent affinity for the sorbate (Thakur *et al*., 2015)

Waste from agriculture is being harnessed as adsorbents due to their plentiful handiness and affordability due to their large solid carbon content and the existence of absorbent composition.

1.2 Statement of Research Problem

The flourishing number of dyeing activities, combined with a lack of technology for the efficient wastewater treatment and lack of enforcement by law enforcement agencies, have led to increase in generation of complex chemical by-products. This has serious consequences, for

surface and ground waters receiving dyeing wastewater. Wastewaters from dyeing activities are very complex, because it contains high organic load, heavy metals and contaminants, which are toxic to both human health and the environment even at low concentrations. Also, the discharge of polluted dye wastewater promotes gradual depletion of dissolved oxygen (DO) in soil and water. This constitutes severe danger to the lives of aquatic animals and micro-organisms.

In view of these, the need to assess the degree to which these contaminants (heavy metals) can be removed from dye wastewater through biosorption before being discharged to receiving water bodies becomes paramount as biosorption has been identified to be efficient and cost-effective wastewater treatment technique.

1.3 Aim and Objectives

The aim of this research is to investigate the feasibility of using orange peel, watermelon peel, and their synergistic effect as biosorbent for the removal of cadmium (Cd), lead (Pb) and mercury (Hg) metal ions from dye wastewater.

The specific objectives are:

i. To investigate the effect of orange peel (OP) as a biosorbent in the removal of heavy metals (Lead [Pb], Mercury [Hg] and Cadmium [Cd]) from contaminated dye wastewater.
ii. To ascertain the effect of watermelon peel (WP) as a biosorbent in the removal of heavy metals (Pb, Hg and Cd) from contaminated dye wastewater.
iii. To ascertain the effect of combination of orange peel and watermelon peel (CP) as biosorbent in the removal of heavy metals (Pb, Hg and Cd) from contaminated dye wastewater.

iv. To analyse the comparative effects of OP, WP and CP at constant time, dosage and pH for Hg, Cd, and Pb heavy metals removal efficiency

v. To evaluate the adsorption properties of OP, WP, CP using kinetics modelling

vi. To examine the equilibrium adsorption behaviour of OP, WP, CP by applying adsorption isotherm models

1.4 Justification for Using Orange and Watermelon Peels

The best part of these biosorbents (i.e., orange and watermelon peel and its combination peel) is their non-toxic nature. Despite the advantages of using chemical precipitation, coagulation-flocculation, ion exchange and membrane filtration in the removal of heavy metals from contaminated wastewater as detailed in the literature review, they have their problems and limitations in application such as chemical precipitation demands for a huge quantity of chemicals so as to decrease metals to a permissible level for release, manufacture of enormous sludge that will necessitates advance purification and continuing negative effects on surrounding sludge disposed. For coagulation-flocculation, it has expensive cost of operation because it uses chemicals and harmful sludge is produced which will require alteration to prevent heavy metals from escaping into the environment. Similar to coagulation-flocculation, ion exchange is expensive and before it is done, suitable pre-treatment system for secondary effluent which include removal of suspended solids from wastewater are needed. Membrane filtration decline in performance due to membrane fouling and concentration polarization.

Based on the aforementioned limitations of physico-chemical treatments and adsorption, the need was felt to investigate the use of biosorption materials mainly agricultural by-products which are residues of agriculture in the removal of these heavy metals in dye wastewater as well as helping to sustainably manage these agricultural solid wastes.

1.5 Scope and Limitations of the Research

The scope of this study is limited to orange and watermelon peels used as biosorbents to remove heavy metals (mercury, cadmium and lead) from dye wastewater.

Characterization of the biosorbents were not done and it is important to explore the suitability of the peels as an adsorbent.

CHAPTER TWO

LITERATURE REVIEW

2.1 Wastewater

Wastewater referred to any water which has been negatively afflicted in terms of quality as a result of anthropogenic activities. It encompasses aqueous used water released by homes, business premises, manufacturing industries and/or agribusiness and comprise a broad stretch of potential pollutants (Kushwa *et al*., 2011).

2.2 Water Pollution

Water pollution originates as a result of discharge of extrinsic contaminants in water body or poured in the watershed of water. The most likely familiar origin of water pollution is clearly discarding of waste, garbage, refuse into water body. Pollution from disease causing agent (bacteria, worms and viruses) is graver existing in sewage. Likewise, wastewater emptied by dye and textile companies have to be refined as a result of their influence on water bodies and increasing civic worry over their harmful and health hazards to be specific (Hamel, 2012).

Dyes normally have artificial source and intricate aromatic molecular structures (Tripathi and Srivastava, 2011). Artificial dyes are considerably employed by industries including dye bleach process, paper printing industries, fabric dyers, colour snapshot and as added ingredient in petroleum products. By-products from these companies are mostly colour-washed and discard of these wastewater within the surrounding can be eminently damaging. Their existence in water bodies is seemly intolerable and may be detectable at concentration below 1 ppm. Furthermore, the action of photosynthesis could further be influenced by decreasing spreading of sunlight (Hamel, 2012).

2.3 Various Methods for the Removal of Heavy Metals

Pollution caused by heavy metals is turning a pressing concern all over the globe due to rise in exploitation and handling of heavy metals in the course of pursuit to reach the demand of the speedily multiplying populace. While there are numerous origins of water pollution, industrialization and urbanization are two of the contributors for spread of heavy metal water pollution (Vhahangwele and Khathutshelo, 2018).

2.3.1 Physicochemical treatments

i. Chemical precipitation is extensively applied for inorganic heavy metal extraction from effluent (Benefield and morgan, 1999). According to Wang *et al.,* (2004), when pH is adjusted to very basic conditions, (pH 10), the dissolved metal ions are converted to the insoluble solid phase through a chemical reaction. Typically, the metal precipitated from the solution is in the form of hydroxide (Tunay, 2003). As a result of ease of access in many nations, calcium hydroxide or lime is utmost used as agent of precipitation. Precipitation using calcium hydroxide can be used to completely purify inorganic discharges with a metal concentration of greater than 1000 ppm. Akin supremacy of exploiting precipitation by calcium hydroxide comprises; clarity of the procedure, low-cost tools needed and suitable and secured set-ups, compelling it to be a conventional approach embraced for metal removal from polluted wastewater (Parmar and Thakur, 2013).

Despite its merits, chemical precipitation has some demerit, which consist of – the demand for a huge quantity of chemicals so as to decrease metals to a permissible level for release (Juttner *et al*., 2000); manufacture of enormous sludge that will necessitates advance purification; metal precipitation is dawdling; low settling; agglomeration of metal precipitates and also continuing negative effects on surrounding sludge disposed (Yang *et al*., 2001).

ii. **Coagulation-flocculation** wastewater packed with heavy metals can be treated using this method. Chiefly, a physical process disrupts suspended colloidal fragments by attaching to a coagulant and ensuing settling (Shammas, 2004). Generally, coagulation-flocculation can purify chemical discharges with a metal concentration below 100ppm or greater than 1000ppm. Similar to chemical precipitation, pH varying from 11.0 to 11.5 has been established to completely enrich the removal of heavy metal by this process. The major merits of lime-base coagulation comprise of; sludge settling better, power to subdued bacterial capacities, firmness of sludge and dewatering characteristics (Cheng *et al.,* 1994) and (Edwards, 1994).

Despite this merits, coagulation-flocculation has restrictions such as expensive cost of operation as a result of utilization of chemical and high quantity of sludge produced which could inhibit its selection as a worldwide blueprint for purification of discharges. This can be ascribed due to the harmful sludge which should be altered into a sustainable outcome to restrict heavy metals from escaping into the surrounding (Ayoub *et al*., 2001).

To gain mastery of the issues linked with ordinary coagulation, electro-coagulation could be an improved substitute, as it capable of removing the tiniest colloidal fragments and bring forth, just a little quantity of sludge (Vik *et al*., 1984). Notwithstanding, this method also give rise to floc of metallic hydroxides, which will necessitate additional treatment (Persin and Rumean, 1989), resulting in the reclamation of valuable heavy metals almost unrealizable.

iii. **Ion exchange** is one of the commonly used technique globally for treatment of wastewater full of heavy metals. In this method, there is a reversible exchange of ions around the solid and liquid phases, these occurs when an indissoluble matter (resin), eliminates ions from a solution of decomposition reaction and unleash other ions of same charge, in a chemically equivalent amount, without any alteration in configuration of the resin (Rengaraj *et al*., 2001; Vigneswaran *et al*., 2004).

In acidic environment with pH spanning between 2 to 6, removal of heavy metal by ion exchange method works excellently, depending on the attributes of the ion exchanger. Unlike chemical precipitation, ion exchange does not pose any sludge disposition issues and consequently lessen the running charges for the discarding of the remaining metal sludge (Dobrevsky *et al*., 1996). Other merits comprise its ease for research, for as much as the needed tools is handy, the speciation outcomes are effective, and the investigation can be done promptly. Additionally, Resins have some specific ligands that can carefully bind with specific metal cations, making ion exchange simple to apply and shorter time being used (Korngold *et al*., 2003).

Regardless of these merits, ion exchange also has some demerits. Before ion exchange, suitable pretreatment system for secondary effluent which include removal of suspended solids from wastewater are needed, desirable ion exchange resins are not handy for all heavy metals, the funds and running estimate is immense (Ahmed *et al*., 1998).

iv. Membrane filtration this method has the capacity of not just eliminating suspended solid and biotic compounds but also inorganic pollutants like heavy metals. This technique has been given substantial consideration for purification of inorganic effluent. Considering the magnitude of fragments that can be hold on to, different kind of membrane filtration such as Ultra filtration (UF) and Reverse Osmosis (RO) can be used for the removal of heavy metal.

Also considering membrane classifications, Ultra Filtration can realize over 90% removal efficiency with metal concentration ranging from 10 to 112 ppm, at a pH ranging from 5 to 9.5 and at pressure of 2.5 bar. Several merits of Ultra Filtration include lesser driving force and a lesser space interval needed as a result of its immense packing density. Although, the decline in performance of Ultra Filtration is as a result of membrane fouling which has stopped it from extensive use in purification of wastewater. Fouling has numerous unfavorable impacts on the

membrane system examples are decrease in flux, an improve Trans Membrane Pressure (TMP) and environmentally safe membrane materials (Choi *et al*., 2005). Increased operational cost for the membrane system is caused by fouling.

v. **Reverse Osmosis** is more advantageous for heavy metal removal from inorganic solution compared to Ultra Filtration, as shown by the declining percentage of 97% with a metal concentration ranging from 21 to 200 ppm. As determined by the characteristic of membrane, which include porousness, non-ionic material, stratification, toughness and charge of membrane (Madaeni and Mansourpanah, 2003). Reverse osmosis operates excellently at a wide pH range of 3 to 11 and at 4.5 to 15 bars of pressure. Contrary to chemical precipitation, rather than pH, the pressure is the important variable that influences the degree of heavy metal removal by Reverse Osmosis. In Reverse Osmosis, the higher the pressure is, the higher the metal removal efficiencies and thus the soaring the amount of energy consumed. Other merits of this method consist of great flux rate, great salt rejection, hostility to biological attack, routine strength, chemical stability and the capacity to resist great temperatures (Ujang and Anderson, 1996).

Despite the benefits of Reverse Osmosis, it has several constraints. Owing to the suspended solids or oxidized compounds for example chlorine oxides, the minute voids of the membrane structures it to be more susceptible to fouling (Potts *et al*., 1981). Any cations such as cadmium Cd (II) and copper Cu (II) existing in the polluted wastewater enhances fouling of membrane, which may be irremediable. The membrane may then have to be restored, thereby making cost of operation to increase. The performance of membrane tends to decline with time, ensuing in declining flow rate of filter (Ning, 2002). Other disadvantages are the great power usage, the scaling of $CaCO_3$ or $CaSO_4$ and the urgency for skilled personnel to drive the process (Slatter *et al*., 1983).

Thus, majority of these techniques may be costly or not effective when metals are dissolved at moderately little concentration (Rorrer, 1998).

2.3.2 Adsorption

Adsorption is a mass removal method, which entails the assemblage of materials at the boundary of two phases, such as, liquid–liquid, gas–liquid, gas–solid or liquid–solid boundary. The materials that is been adsorbed is the adsorbate and the adsorbing substances is known as the adsorbent. The adsorbates and adsorbents are quite distinct and rely on their components. If the interactivity connecting the solid plane and the adsorbed fragments has a physical classification, the activity is called physisorption. Under these circumstances, the attraction association are van der Waals forces and, as they are fragile the process outcome is changeable. In addition, it happens at the bottom or at the final critical temperature of the adsorbed material.

Contrasting, it is referred to as chemisorption when forces of attraction between the molecules adsorbed and the solid surface are as a result of chemical bonding. Chemisorption take place on a single layer, contrary to physisorption. In addition, due to stronger forces which is at stake, materials chemisorbed on solid surface are scarcely eliminated. In favorable conditions, physisorption and chemisorption take place concurrently. Physisorption occurs as a result of decline in free energy and orderliness of the adsorption system and consequently, this process releases heat (De Gisi *et al*., 2016).

The most common adsorbents used are clay, fly ash, coal, natural oxide, activated carbon, among others (Babel and Kurmiawan, 2003). Activated carbon (AC) is known to have considerable removal efficiency of impurities, as its practical application is restricted as a result of issues linked with its restoration or disposal, sludge generation and beneficial to the economy in terms of profitability (Singh *et al*., 2017). Though activated carbon is widely used, it remains as a

costly material as its price surges with the quality. The industrial grade activated carbon is very expensive. Complexing agents are needed to ameliorate its removal performance for mineral materials (Rahate, 2010).

2.3.2.1 Effect of pH in adsorption

The pH of wastewater is the major dominant parameter which has control in adsorption process (Ajmal *et al*., 1998). This is chiefly as a result of the protons being the major contending adsorbate ions, and partially as a result of pH of a solution affecting the chemical speciation of the metal ions in the solution and ionization of the functional groups of the adsorbents (Bozie *et al*., 2009).

As a result of hydrolysis, decline in the uptake of metal was observed at elevated pH. The number of available sites can differ with pH due to protonation-deprotonation of weekly acidic site (Perez- Marin *et al*., 2007). At low pH, there is minimal adsorption of metal ion which could be due to elevated concentrations and the protons being mobile, which functions as a competitor and preferentially adsorbed instead of metal ions on the active binding site (Annadurai *et al*., 2002).

Carboxylate groups normally have pK_a values between 3 and 5 (Buffle, 1990). Phenolic functional groups could be responsible for one of the intermediate pK_a values (Lee *et al*., 1999). Lignin on the other hand comprises two main classification of functional groups that have firm interactions with metal ions- carboxylic and phenolic groups (Ravat *et al*., 2000).

2.3.3 Biosorption

Expensive operation charges, secondary contamination likelihood, adoption of harmful reagents and lengthy operation time associated with the physicochemical and electrochemical treatment methods outlined above, coupled with public concern toward the conservation of the

environment placed restriction on the usage of these conventional methods in wastewater treatment. Thus, a strong urgency is felt to develop a low cost and eco-friendly process for treatment of wastewater. This need has made us considered biosorption as an alternative method of wastewater treatment, due to its metal binding capabilities of numerous biological materials.

Different researchers have used the term “biosorption” for varieties of processes which include bioadsorption, bioabsorption, and biosorption by living or dead biomass, bio accumulation and a variety of substance such as metals, radionuclides and organics. In Sorption, one substance gets fixed to another since it is a physico-chemical process. Regardless of the ‘bio’ prefix that signifies the participation of a biological unit, biosorption is simply known as the removal of substances/materials from fluid by biological substance and it is a physico-chemical process (Fomina and Gadd, 2013).

Materials of biological origin can be beneficial biosorbents for metal segregation excluding mobile alkali metal cations like sodium and potassium ions, and this can be an important passive process in living and lifeless organisms a number of affordable biosorbents for the removal of metals chiefly fall underneath the following classification: bacteria, fungi, algae, plants, industrial wastes, agricultural wastes and other polysaccharide materials. Generally, all types of biomaterials utilized for biosorption were established to have great biosorption capabilities with regard to all types of metal ions (Mustapha and Halimoon, 2015).

2.4 Adsorption Potential of Agricultural Waste

Many research efforts have been expended in studying the biosorption of heavy metal removal involving the use of either laboratory-grown microorganism or biomass created by varieties of processing industries or wastewater treatment units. Since the 1990’s the adsorption of heavy metal ions by affordable materials of biological origin has received great drive (Bailey *et al*.,

1999; Rao and Parwate, 2002). The utilization of seaweeds, molds, yeasts, and other dead microbial biomass and agricultural by products for removal of heavy metals has been investigated (Sudha and Abraham, 2003).

Recently however, there is a shift in attention towards materials with biological origin which are outgrowth from extensive industrial activities and agricultural by-products. The usage of these biological materials in purification technology is very propitious given the near zero-cost for the synthesis of those adsorbents. The biomass mostly used include Banana, orange, and potato peels and they have been outlined in literatures. Although, other peels have been used as possible adsorbents examples are pomegranate, citrus, grapefruit, yam, and garlic (Anastopoulos and Kyzas, 2014).

These rising agricultural byproducts are utilized in the removal of metal ions either in their natural form or after it has been modified physically or chemically. The coming section will present reviews of the utilization of some of these agricultural byproducts as biosorbents for removal of toxic heavy metal ions.

2.4.1 Potato Peel

Chemically modified potato peels treated with $HCHO$ (PP) and H_2SO_4(APP) were analysed for the biosorption of MG from aqueous solution (Sharma *et al.*, 2014). PP and APP exhibited optimum adsorption ambience at $pH 12.0$ (pH ranges between 2 and 12) and using $2.5\ g/L$ biosorbent dosage (tested in the range of 0.1 to 0.25 g/100 ml solution). The percentage removal of dye in the case of PP was establish to decrease from 93.3 to 87.5% as concentration increased from 50 to $250\ mg/L$, while contrasting discovery were spotted for APP (from 82.2 to 86 %).

Okem *et al*., (2012) used potato peel as adsorbent for the removal of Methylene Blue from aqueous solution. The kinetic experiments showed that the process equilibrated after 60 min

(optimum pH was equal to 8). FTIR spectra showed that several functional groups such as hydroxyl and carboxylic get involved in dye adsorption.

2.4.2 Banana Peel

Moubarak *et al.* (2014) researched on the adsorption of methane blue dye onto banana peel powder. The influence of particle size ($d < 80\mu m$and $80\mu m < d < 2mm$), solution temperature (22 and $50\ ^{\circ}C$) and biosorbent's mass were examined. Highest adsorption was found for $d < 80\mu m$ using $0.1\ g$ mass of adsorbent. The quantity of dye absorption was established to be uninfluenced by changing the temperature. The decolourization of biologically treated pal oil mill using natural, methylated and activated carbon taken from banana peels was assessed by Mohammed and Chong (2014). Experiments were performed as a function of adsorbent's dosage ($5-30\ g/100\ mL$), pH ($2.0-12.0$) and contact time ($2-36\ h$). The highest colour removal was detected using $30\ g$ of biosorbent per $100\ mL$ of solution at $pH = 2.0$ ($30\ h$ as contact time). Chemical activated carbon was established to be more structured in the removal colour than other forms of banana peel due to manufacture of high surface area carbons by chemical activation.

2.4.3 Watermelon Peel (Watermelon Rind)

Watermelon peel contains an impressive concentration of nutrients like oxalates ($128.4\ mg\ \%$), hydrogen cyanide ($121.02\ mg\ \%$), alkaloids ($10.09\ \%$) phytates (0.7%) with a total phenolics content of $0.91\ \%$. In terms of mineral composition, watermelon peel is composed of $11.21\ mg/100g$ dry peel of calcium, $3.78\ mg/100g$ dry peel of zinc, $45.58\ mg/100g$ dry peel of iron and $1.25\ mg/100g$ dry peel of manganese (Feumba *et al.*, 2016).

Watermelon peel was used as an adsorbent for the removal of Cr^{3+}ions from aqueous solution (Reddy *et al*., 2014). Researches using batch mode adsorption were carried out using different parameters such as pH, contact time, adsorbent dose and initial metal ion concentration. Maximum loading capacity of watermelon rind was established to be $172.6\ mg/g$1for Cr^{3+}ions at $pH\ 3$. Kinetic studies revealed that removal of Cr^{3+}ions was rapid and followed a pseudo-second order model. The study reveals that watermelon can be an inexpensive sorbent for the removal of heavy metals from aqueous solution.

Lakshmipathy and Sarada (2013) exploited the usage of watermelon as a sorbent for the removal of nickel and cobalt from aqueous solution. Investigations were carried out by changing the pH, adsorbent dose, contact time, and initial metal ion concentration. Desorption and regeneration research were carried out to study the workability of watermelon rind. The maximum sorption capability of watermelon rind was determined as 35.3 and $23.3\ mg/g$for $Ni^{2+}$and Co^{+2}ions, accordingly. Ni^{2+}ions exhibited greater affinity and adsorption rate beyond comparison with Co^{+2}ions under the experimental circumstances. Extraction of $Ni^{+2}$and Co^{+2} ions was established to be undoubtedly influenced by the existence of other metals as a result of competitiveness. The same authors evaluated the potential of protonated watermelon rind (PWR) as an inexpensive and structured adsorbent for the removal of $Pb^{+2}$and Cu^{+2}ions from aqueous solution. Protonation of watermelon peel was done with $0.1\ M\ HCl$ as protonating agent. It was discovered that the adsorption process was unconstrained and there was release of heat. The maximum loading capacity of PWR was found to be 116.2 and $39.2\ mg/g$for Pb^{+2} and Cu^{+2}ions, respectively. Results from the research suggested that watermelon rind can be effectively exploited as adsorbent for the removal of heavy metal ions from aqueous solution.

2.4.4 Orange Peel (OP)

Orange peels (OP) are the main by-product of the citrus processing industry. These by-products are loaded in pectin, cellulose, and hemicellulose, but poor in protein (5.8%), and constitute roughly 50% of the fresh fruit weight Ahmadi *et al*., 2014; Bampidis and Robinson (2006); Mamma *et al*., 2008). Orange peels contain approximately 13.12% of oil which has been shown to be effective in countering micro pathogen that include *Aeromonas hydrophila, Klebsiella pneumonia, Psudomonas aeruginosa, Ecsherichia coli, Psudomonas fluorescenes, Proteus spp. Enterococcus feacalis, Staphylococcus aureus, Candidia albicans* and *Listeria.*

Orange peel comprises largely of cellulose pectin; hemi-cellulose, lignin and other low molecular weight compounds including limestone, the effectiveness of orange peel as a well-organized and affordable bio-adsorbent for removing dyes metals and organic contaminants from industrial wastewater has been explored in a number of studies. Abdurrahman *et al*., (2013) studied the possibility of utilizing orange peel as adsorbent for the removal of dyes from wastewater and to introduce it, as a standard wastewater treatment process for textile company. The key objectives of the study were to ascertain the quantity and effects of adsorbent (orange peel), determine the pH and retention time on the removal of dyes from the wastewater. The results from the research revealed that the removal percentage was $60-70\%$ at $pH=7$ with a retention time of 120 minutes. The ideal quantity of dose of adsorbent was found to be $1.5g/25mL$. The equilibrium adsorption behavior was examined by applying Langmuir adsorption isotherm model. However, this work is limited to studying dye removal using orange peel only, it did not study the removal of heavy metals. The adsorption capability of orange peel was found to be comparable to the other available adsorbents. In a related study by (El-Said and Gamal, 2012), orange peel was exploited as an inexpensive native wastewater adsorbent treatment for textile effluent. The efficacy of the orange peel in adsorbing; C.I. Direct Red 79

(DR 79) and C.I. Direct Yellow 27 (DY27) from dye baths was researched on as a function of pH, solid/liquid ratio, agitation time and initial dye concentration. The sorption isotherms were assessed using Langmuir and Frendlich models. The results show that acidic solution favored the adsorption of the researched dyes in the orange peel.

A comparative study to determine the suitability of orange and banana peel as adsorbents in diary wastewater using carbonization and dehydration (biosorption) methods was undertaken by (Al Khusabi *et al*., 2015). The removal of contaminants existing in pasteurizing plant wastewater was evaluated with respect to pH, contact time, adsorbent dosage, and adsorbent particle. The research revealed that banana peels were not as effective as the orange peels in the removal of contaminants from the pasteurizing plant wastewater. The method of carbonization was discovered to be more structured in contrast to the de-hydration technique for the pair of orange and banana peels. The orange peel was discovered to be more well organized in both techniques with greater percentage removal of 50.1% and 14.3% accordingly. In contrast to the banana peels where the percentage removal was found to be 44.1% and 8.2% for the carbonization and de-hydration techniques accordingly.

Foo and Hameed (2012) explored the possibilities of using orange peel, a citrus processing biomass as a substitute precursor for preparation of activated carbon (OPAC) through microwave assisted K_2CO_3 activation. Findings from the studies revealed that orange peel is a possible raw precursor for preparation of high-quality activated carbon. Integration of microwave heating has enhanced porosity development in a short heating period. The optimum condition for preparation of OPAC has been pointed out at IR of 1.25, heating power of 600 W and irradiation time of 360 seconds in a liquid-phase adsorption removal of Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+}. Annadurai *et al*., (2003) used orange and banana peels in the concentration range of $5-25ng/L$ at $30°C$.

Under comparable conditions, the amount of adsorption decreased in the order $Pb^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+}$ for both adsorbent.

In order to enhance the mesopore and enlarge the biophile capability of activated carbon and ameliorate it for adsorption of macromolecular pollutants and advance the growth of bacteria for wastewater purification. Xie *et al*., (2014), produced activated carbon in a one-step activation with orange peel as raw material, and zinc chloride as activator. The study established that natural void arrangement of orange peel is advantageous for the development of mesoporous active carbon. The yield of the as-prepared biological activated carbon is 50.9%. A static adsorption evaluation connoted that orange peel activated carbon has a good adsorption to deal with leachate biochemical tail water. The removal rate of UV_{254} is 63.0% and TOC is 59.7% accordingly.

2.5 Adsorption Mechanism of Orange and Watermelon Peel

A number of factors which affects metal biosorption may include chemisorption, complexation, adsorption-complexation on surface and pores, ion exchange, micro precipitation, heavy metal hydroxide condensation onto the bio surface, and surface adsorption, since it is rather a complex process (Gardea-Torresdey *et al*., 2009).

For the pursuance of comprehending the manner with which metal stick to the biomass, it is important to determine the functional groups behind metal binding. Majority of the functional groups engaged in the binding process are established in cell walls. Plant cell walls are normally regarded as structures assembled by cellulose molecules, arranged in microfibrils and adjoined by hemicellulosic substances (xylans, mannans, glucomannans, galactans, arabogalactans), lignin and pectin throughout with small quantities of protein (Godwin and Mercer, 1972) and (Al-Asheh and Duvnjak, 1997).

Orange peel is made up of cellulose, pectin, hemicellulose, chlorophyll pigments and other little molecular weight compounds, comprising of limonene. Several studies have reported the functional carboxylic groups of pectin and the alcoholic hydroxyl groups of the celluloses as the active binding sites for metals (Ghimire *et al*., 2003).

The orange peel can absorb metal ions via ion exchange or complexation or a combination of both processes. As cadmium, lead and mercury ions belong to transition metals, which have empty orbitals that can be occupied by electrons to form complex and considering steric hindrance, both ion exchange and complex formation are the most possible adsorption processes (Liang *et al.*, 2009).

Watermelon peels basically consist of cellulose, hemicellulose, lignin, pectin, silica, and silica free minerals (Singh *et al.*, 1975). According to research conducted by the ARS laboratory the peel consists of amino acid citrulline (Campbell, 2006). Lignin is a natural amorphous cross-linked resin that has an aromatic three-dimensional polymer structure consisting of a sizeable functional group such as phenolic, hydroxyl, benzyl alcohol, methoxyl and aldehyde groups (Sarkanen and Ludwig, 1971), setting it up as potential beneficial adsorbent material for removal of heavy metals from wastewater. A number of researches revealed that ion-exchange mechanisms could be behind the sorption of metal ions on lignin (Lalvani *et al*., 1997). Lignin also accommodates plenty polyhydric phenols, other oxygenated functions and sulfur-containing groups at its surface. These are engrossed in the breaking down of adsorbate.

No particular mechanism could interpret the process involve in metal removal by lignin as proposed by some researchers (Srivastava *et al*., 1988; (Mohan *et al*., 2006). A number of processes encompassing ion exchange, surface adsorption and complexation have been insinuated to define the processes used. Other researchers revealed that metal ion sorption was aassisted by stoichiometric liberation of protons and existing metals and inferred that ion

exchange mechanisms over saw for the removal of metals by lignin (Crist *et al*., 2002); (Crist *et al*., 2003); (Al-Saadi *et al*., 2009).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials and equipment

Table 3.1: Materials, equipment and software used for the analysis

S/N	Materials / Equipment	Model
1	Atomic absorption spectrophotometry (AAS)	AA-6800 SHIMADZU, Japan.
2	Centrifuge	MPW-251 model
3	Electric weighing balance	MP 300 model England
4	Blender	Clarkson CB 15E
5	pH meter	PHS-3C, England.
6	Oven	DFO 36-240
7	Shaker	SK-L330-Pro linear shaker
8	Filter paper, (125mm Ø)	GE Healthcare, UK
9	Test tubes, (100ml and 200ml)	Pyrex England
10	Beakers	Pyrex, England
11	Pipette	Hexa PharmaChem, India
12	Sieve	EI-496 Technolab, India
13	Spatula	Fischer Sci brand, EU
14	Microsoft Excel 2016	

Table 3.2: Reagent used for the analysis

S/N	Reagent	Supplier	Concentration
1	Nitric Acid	BDH Chemicals, England	
2	Sodium Hydroxide (NaOH)	BDH Chemicals, England	0.1M
3	Hydrochloric Acid (HCl)	BDH Chemicals, England	1M

3.1.1 Biosorbents

The biosorbent used in this work are Orange Peel (OP), Watermelon peel (WP) and combination of orange and watermelon peel (CP). The peels were obtained from different fruit stalls within Kaduna metropolis, Kaduna State.

3.1.2 Wastewater sample

Wastewater was obtained from a local dyeing place in Tudun Wada, Kaduna, Kaduna State.

3.2 METHODS

3.2.1 Laboratory test

The general method used for this laboratory study is as described as follows:

The orange and watermelon peels were collected and washed with distilled water, then dried in an oven (at 90^{o}C for 45 minutes), blended into powder, and sieved using a 150µm sieve.

The sample of local dye wastewater was collected and levels of three heavy metals - cadmium, lead and mercury in the wastewater were determined by using Atomic Absorption Spectrophotometry (AAS). Exactly 50 ml of the local dye wastewater was poured into four (4) beakers (three [3] for the treatment and one [1] as control) was used for the study.

Exactly 2 g of each of the adsorbent (orange, watermelon, and a combination of the two peels) was poured into the 50 ml local dye wastewater. For the effect of biosorbents dosage, known dose of 0.5 g, 1 g, 1.5 g, 2 g and 2.5 g of the biosorbent was added to 50 ml of the wastewater for 60 minutes and the adsorption was determined for each dosage.

For the effect of pH, 0.1M sodium hydroxide (NaOH) and 1M hydrochloric acid (HCl) were used to adjust the pH. The pH meter was inserted in 250 ml of the wastewater and the pH was noted each time HCl or NaOH was dropped into the wastewater. Using a pipette, a drop at a time of HCl was added to decrease the pH of the wastewater and same process was used with NaOH to increase the pH. Exactly 2.0 g of each biosorbent was added to 50 ml of the wastewater for 60 minutes with different known pH levels (1.0, 2.5, 4.6, 5.7, 6.8, 7.7, 9.1 and 10.6) and the adsorption was determined for each pH.

Adsorption process was performed for a predetermined time (between 10 to 120 minutes) using 2.0g of each of the three biosorbents added to 50 ml of the wastewater so as determine the effect of time.

Each sample was shook using an electric shaker at 130 rpm for 2 minutes. Then each sample was transferred to 60ml pre-labeled centrifuge tubes and centrifuged for 8 minutes at 6,000 rpm after which it was filtered using a micron filter and a few drops of concentrated nitric acid were added to each filtrate to prevent any contamination in the filtrates. Then, the concentrations of metal ions in all the filtrates were analyzed using the AAS. The average of the result from the three samples was used as the equilibrium concentration while the result for the control is the initial concentration.

The removal efficiency (RE) was then calculated from the experiment data using the relationship expressed by Eqn. (3.1).

$$RE(\%) = \frac{(C_i - C_e) * 100}{C_i} \qquad (3.1)$$

Where C_i is the initial concentration of the metal ions in the wastewater, C_e is the equilibrium concentration of the metal ions in the aqueous solution.

3.2.2 Statistical Analysis

Analysis of Variance (ANOVA) was done to statistically analyze the comparative effects of orange peel (OP), watermelon peel (WP) and combination peel (CP) at constant time, dosage, and pH for heavy metals (Mercury [Hg], Cadmium [Cd], and Lead [Pb]) removal efficiency using Microsoft Excel software. The results were used to determine the level of significance among the three adsorbents considered. Based on Fisher (F) value and Probability (P) value.

Using the data analysis tool in the software, the two-way ANOVA analysis was used to show the descriptive statistical analysis of the three adsorbents at the same time, do, and pH.

The confidence interval used in the study was 95%, this gives a significance level of P = 0.05. The model term having the largest F-value is identified as the term having the most significant effect on the response.

3.2.3 Adsorption isotherm modelling

Adsorption isotherms were used to examine the equilibrium adsorption behaviour of the heavy metals using Langmuir and Freundlich Isotherms.

3.2.3.1 Langmuir isotherm

The Langmuir model is expressed as;

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{3.2}$$

Where;

Q represents the maximum monolayer adsorption capacity, **(mg/g)**;

K_L represents the Langmuir equilibrium constant, **(l/mg).**

The linear transformed Langmuir-type 2 is given as;

$$\frac{1}{Q_e} = \frac{1}{Qm2} + \left(\frac{1}{K_{L2} Q_{m2}}\right) \frac{1}{Ce} \tag{3.3}$$

$$Slope = \frac{1}{K_{L2} Q_{m2}} \tag{3.4}$$

(3.5)

$$Intercept = \frac{1}{Qm2}$$

- Taking the inverse of intercept gives the value of Q_m
- Taking the inverse of (*Slope* multiplied by Q_m) gives the value

3.2.3.1 Freundlich Isotherm

The Freundlich model is given as;

$$Q_e = K_F C_e^{1/n} \tag{3.6}$$

It can be linearized (FR-L) by taking the logarithm of both sides (Ho *et al.*, 2005) and is given as;

$$lnQe = lnK_F + \frac{1}{n} lnC_e \tag{3.7}$$

The plot of $ln\ q_e$ versus lnC_e gives a straight line with slope of $1/n$ and intercept of $log\ K$

- Taking antilog of $log\ K_F$ gives the value of K_F
- Taking inverse of slope (1/n) gives the value of n

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 ANOVA Analysis

4.1.1 Comparative ANOVA analysis for OP, WP and CP at varying time durations

Table 4.1 represents the total removal efficiencies by using Orange Peel (OP), Watermelon Peel (WP) and Combination Peel (CP) for sorption of Mercury (Hg), Cadmium (Cd) and Lead (Pb) metal ions at constant Time intervals (0, 10, 20, 30, 40, 60, 80, 100, 120 minutes) respectively. It is shown from Table 4.1, that the time variations (across the Rows) were significant all through for the sorption of Hg, Cd and Pb metal ions by using OP, WP and CP at respective time durations, especially for the WM adsorbent.

Table 4.1: Effect of Orange Peel (OP), Watermelon Peel (WP) and Combination Peel (CP) on the Sorption of Mercury (Hg), Cadmium (Cd) and Lead (Pb) Metal Ions at Respective Time Durations.

Time (mins)	Removal Efficiencies (%)								
	Mercury (Hg)			Cadmium (Cd)			Lead (Pb)		
	OP	WP	CP	OP	WP	CP	OP	WP	CP
0	0	0	0	0	0	0	0	0	0
10	85.03	78.99	84.7	93.24	93.37	94.12	82.54	85.85	84.58
20	96.77	79.90	86.52	94.46	93.43	93.69	87.46	86.61	93.22
30	94.62	83.21	84.03	93.05	93.46	93.30	87.71	86.10	91.36
40	96.94	83.62	87.09	93.67	94.01	94.29	91.36	88.81	85.08
60	84.37	84.86	88.58	95.19	94.27	93.56	92.88	88.31	87.71
80	96.44	84.45	88.75	95.21	94.40	94.27	92.80	88.48	93.14
100	96.27	84.74	88.50	95.30	94.21	94.40	92.97	88.31	92.12
120	96.36	84.70	88.42	95.28	94.29	94.36	93.14	88.64	93.05

Although, Table 4.1 shows that the highest adsorption efficiencies of Hg obtained for OP, WP and CP were 96.94 %, 84.86 % and 88.75 % at 20, 60 and 80 mins respectively. This

characteristic proves OP as the most effective adsorbent for Hg adsorption, its effect is also noticed in the CP when considering the lower WP adsorption efficiencies.

For Cd, the highest removal efficiencies obtained were 95.30 %, 94.40 % and 94.40 % at 100, 80 and 100 mins for OP, WP and CP respectively. This also shows OP as the most efficient adsorbent for Cd removal from dye wastewater.

Also, the highest adsorption efficiencies obtained for Pb were 93.14 %, 88.81 % and 93.22 % for OP, WP and CP at 120, 40 and 20 mins respectively. Although this shows CP as the adsorbent with the highest removal efficiency, OP also shows a significantly similar removal efficiency but at a higher constant time.

Table 4.2 shows that for time variation across the rows, Cadmium (Cd) is having the highest P-value ($3.2x10^{-29}$) and F-value (13802.04), this indicates that using the three adsorbents, the removal efficiencies were more significant for the sorption of Cd ions followed by Lead (Pb) at P-value ($2.02x10^{-17}$) and F-value (459.8777) then Mercury (Hg) with the least P-value ($6.36x10^{-15}$) and F-value (222.6376) at constant time variations.

Table 4.2: ANOVA Analysis Showing the Effect of Orange Peel (OP), Watermelon Peel (WP) and Combination Peel (CP) on the Sorption of Hg, Cd and Pb Metal Ions at Time Durations of 60 mins.

Heavy Metal	Factor	Source of Variation	Sum of Squares	df	Mean Square	F-value	P-value	Variance of Adsorbents		
								OP	WP	CP
Hg	Time	Rows	20696.59	8	2587.074	222.6376	$6.36x10^{-15}$	993.65	771.23	845.44
		Columns	382.6284	2	191.3142	16.46406	0.000131			
Cd	Time	Rows	23627.66	8	2953.458	13802.04	$3.2x10^{-29}$	991.50	980.48	981.91
		Columns	1.022674	2	0.511337	2.38957	0.123577			
Pb	Time	Rows	21365.87	8	2670.734	459.8777	$2.02x10^{-17}$	915.14	854.72	912.49
		Columns	28.04241	2	14.0212	2.414332	0.121246			

Table 4.2 also indicates that across the three (3) adsorbents (i.e., across Columns), the level of variance indicates that orange peel (OP) had the highest level of significant variance for the sorption of Hg, Cd and Pb metal ions followed by combination peel (CP) then watermelon peel (WP) with the lowest level of significant variance. This shows that the WP has a low significant level of stability in heavy metals adsorption for the time intervals considered.

4.1.2 Comparative ANOVA analysis for OP, WP and CP at varying adsorbent dosage

Table 4.3 shows the total removal efficiencies by using OP, WP and CP for sorption of Hg, Cd and Pb metal ions at constant adsorbent dosage intervals (0, 0.5, 1.0, 1.5, 2.0 and 2.5 grams) respectively at a constant time of 60 mins. It can be seen that the removal efficiency for all 3 bio-sorbents had higher removal efficiencies for Cd ion followed by Hg then Pb. Also, as the dosage increased the removal efficiencies also increased all through for the three heavy metals, especially for the WP adsorbent.

Table 4.3: Effect of Orange Peel (OP), Watermelon Peel (WP) and Combination Peel (CP) on the Sorption of Mercury (Hg), Cadmium (Cd) and Lead (Pb) Metal Ions at Respective Adsorbent dosage Intervals.

Adsorbent dosage (g)	Removal Efficiencies (%)								
	Mercury (Hg)			Cadmium (Cd)			Lead (Pb)		
	OP	WP	CP	OP	WP	CP	OP	WP	CP
0	0	0	0	0	0	0	0	0	0
0.5	75.02	67.98	76.09	96.20	95.00	94.25	72.29	74.32	70.00
1.0	82.55	77.30	78.16	96.40	94.16	95.02	73.90	75.68	72.71
1.5	83.62	84.86	83.37	97.34	94.98	95.04	74.92	82.80	79.75
2.0	91.56	91.50	87.01	98.93	95.13	95.97	88.64	91.02	82.97
2.5	93.38	91.70	87.59	97.73	95.69	96.07	91.10	91.36	83.22

Table 4.3 also shows that the highest adsorption efficiencies of Hg obtained for OP, WP and CP were 93.38 %, 91.70 % and 87.59 % all at 2.5 g respectively. This proves OP as the most

effective adsorbent for Hg adsorption, although its effect is not noticed in the CP when considering the lower WP adsorption efficiencies.

For Cd, the highest adsorption efficiencies obtained were 98.93 %, 95.69 % and 96.07 % at 2.0, 2.5 and 2.5 g respectively for OP, WP and CP respectively. This also shows OP as the most efficient adsorbent for Cd removal from wastewater, its effect is noticed in the CP when considering the lower WP adsorption efficiencies.

Also, the highest adsorption efficiencies obtained for Pb were 91.10 %, 91.36 % and 83.22 % for OP, WP and CP all at 2.5 g respectively. Although this shows WP as the adsorbent with the highest removal efficiency, OP also shows a significantly similar removal efficiency, its effect is not noticed in the CP even when considering OP adsorbent with similar adsorption efficiencies. This could be as a result of the different properties of WP and OP competing instead of complementing each other.

Table 4.4 shows that for adsorbent dosage variation across the rows, Cadmium (Cd) was having the highest P-value ($5.5x10^{-18}$) and F-value (9262.983), this indicates that using the three adsorbents, the removal efficiencies were more significant for the sorption of Cd ions followed by Mercury (Hg) with P-value ($8.26x10^{-12}$) and F-value (536.3781) then Lead (Pb) with the least P-value ($8.91x10^{-12}$) and F-value (528.2414) at constant time of 60 minutes. This indicates that the removal efficiencies were more significant for the sorption of Cd ions as compared to that of Hg and Pb at constant dosage variation.

Table 4.4 also shows that across the adsorbent dosage intervals, the three (3) adsorbents (i.e., across Columns), the level of variance indicates that orange peel (OP) had the highest level of significant variance for the sorption of Hg and Cd metal ions, while the watermelon peel (WP) had the highest level of significant variance for the sorption of Pb metal ion. The combination

peel (CP) had the lowest level of significant variance for Hg and Pb metal ions, while the watermelon peel (WP) had the lowest level of significant variance for Cd metal ion.

Table 4.4: ANOVA Analysis Showing the Effect of Orange Peel (OP), Watermelon Peel (WP) and Combination Peel (CP) on the Sorption of Hg, Cd and Pb Metal Ions at Respective Adsorbent dosage Intervals.

Heavy Metal	Factor	Source of Variation	Sum of Squares	df	Mean Square	F-value	P-value	VARIANCE of Adsorbents		
								OP	WP	CP
Hg	dosage	Rows	18081.01	5	3616.202	536.3781	$8.26x10^{-12}$	1254.7	1220.8	1154.2
		Columns	19.90703	2	9.953517	1.476369	0.274279			
Cd	dosage	Rows	22979.25	5	4595.849	9262.983	$5.5x10^{-18}$	1579.5	1504.2	1513.2
		Columns	13.47134	2	6.735672	13.57582	0.001413			
Pb	dosage	Rows	16803.16	5	3360.631	528.2414	$8.91x10^{-12}$	1135.2	1201.8	1036.3
		Columns	58.77943	2	29.38972	4.619628	0.037937			

4.1.3 Comparative ANOVA analysis for OP, WP and CP at varying pH intervals

Table 4.5 presents the total removal efficiencies by using Orange Peel (OP), Watermelon Peel (WP) and Combination Peel (CP) for sorption of Mercury (Hg), Cadmium (Cd) and Lead (Pb) metal ions at pH variations (0, 1.0, 2.5, 4.6, 5.7, 6.8, 7.7, 9.1, 10.6) respectively.

It is observed from Table 4.5, that the removal efficiencies for pH variations (across the Rows) were more significantly stable around wastewater pH levels of 6.8-7.7 for the sorption of Hg, Cd and Pb metal ions by using OP, WP and CP at respective pH, especially for the WP and CP adsorbents.

Table 4.5: Effect of Orange Peel (OP), Watermelon Peel (WP) and Combination Peel (CP) on the Sorption of Mercury (Hg), Cadmium (Cd) and Lead (Pb) Metal Ions at Respective pH Intervals.

pH	Removal Efficiencies (%)								
	Mercury (Hg)			Cadmium (Cd)			Lead (Pb)		
	OP	WP	CP	OP	WP	CP	OP	WP	CP
0	0	0	0	0	0	0	0	0	0
1.0	73.61	92.31	86.85	28.97	89.70	50.22	35.51	98.14	60.00
2.5	81.97	91.65	89.41	81.76	93.35	88.03	94.75	93.98	93.31
4.6	92.89	91.56	92.39	85.84	94.42	92.98	95.34	92.97	94.66
5.7	93.71	92.06	96.86	93.99	93.99	94.29	90.68	97.46	95.42
6.8	91.65	91.98	94.38	87.55	93.56	95.86	91.78	97.54	95.93
7.7	92.97	88.58	92.89	92.49	95.92	93.71	93.56	98.56	93.48
9.1	90.74	91.73	92.14	86.48	95.28	92.47	94.83	97.37	92.80
10.6	89.99	89.91	93.88	83.91	95.71	92.90	92.63	98.98	91.86

Table 4.6 shows that for adsorbent pH variation across the rows, Mercury (Hg) had the most significant P-value ($1.41x10^{-14}$) and F-value (201.3134), this indicates that using the three adsorbents, the removal efficiencies were more significant for the sorption of Hg ions followed by Cadmium (Cd) with P-value ($2.06x10^{-08}$) and F-value (31.8975) then Lead (Pb) with the least P-value ($3.91x10^{-08}$) and F-value (29.9356) at constant time variations. This shows that the removal efficiencies were more significant for the sorption of Hg ions as compared to that of Cd and Pb at pH variation at a constant time of 60 minutes and a biosorbent dosage of 2.0 g.

Table 4.6: ANOVA Analysis Showing the Effect of Orange Peel (OP), Watermelon Peel (WM) and Combination Peel (CP) on the Sorption of Hg, Cd and Pb Metal Ions at Respective pH Intervals.

Heavy Metal	Factor	Source of Variation	Sum of Squares	df	Mean Square	F-value	P-value	VARIANCE of Adsorbents		
								OP	WM	CP
Hg	pH	Rows	22136.31	8	2767.039	201.3134	$1.41x10^{-14}$	912.58	926.08	955.87
		Columns	57.56429	2	28.78214	2.094019	0.155671			
Cd	pH	Rows	23653.57	8	2956.697	31.89175	$2.06x10^{-08}$	1101.7	985.04	1055.4
		Columns	684.9454	2	342.4727	3.694006	0.047975			
Pb	pH	Rows	24416.53	8	3052.066	29.23643	$3.91x10^{-08}$	1192.8	1046.9	1021.1
		Columns	425.8712	2	212.9356	2.039758	0.16253			

Table 4.6 also indicates that the pH variations across the three (3) adsorbents (i.e., Columns), the level of variance indicates that combination peel CP had the highest level of significant variance for the sorption of Hg metal ions, while OP had the highest level of significant variance for the sorption of Cd and Pb metal ion. Table 4.6 also showed that OP, WP and CP had the least degree of variance for the sorption of Hg, Cd and Pb metal ions respectively.

4.2 Adsorption Kinetics

The dye wastewater containing lead, mercury and cadmium metal ions was used to carry out the experiments. The initial concentration of the heavy metals was determined and noted, the volume of dye wastewater was kept constant at all times during the investigation at 50ml and all experiments were conducted at ambient temperature.

For most of the experiment the equilibrium concentration of adsorbent material was chosen to be 2.0g based on the results of the result of the laboratory analysis conducted with respect to dosage of biosorbent. The average dosage at the maximum removal efficiencies of the metal ions was chosen. The time considered was 60mins also based on the results obtained for OP, WM and CP at constant time intervals. This is further explained in detail below.

The following parameters of the processes were changed and then studied during the experiments: absorption time, biosorbent dosage and pH (using sodium hydroxide and nitric

acid) so as to study effect of adsorption of mercury, lead and cadmium metal ions present in dye wastewater using orange peel, watermelon peel and a combination of the two peels.

4.2.1 Adsorption time

The influence of time on sorption of metal ions by orange peel, watermelon peel and combination peel were studied by taking 2.0g biosorbent with 50ml of the dye wastewater.

4.2.1.1 Effects of time with orange peel as biosorbent

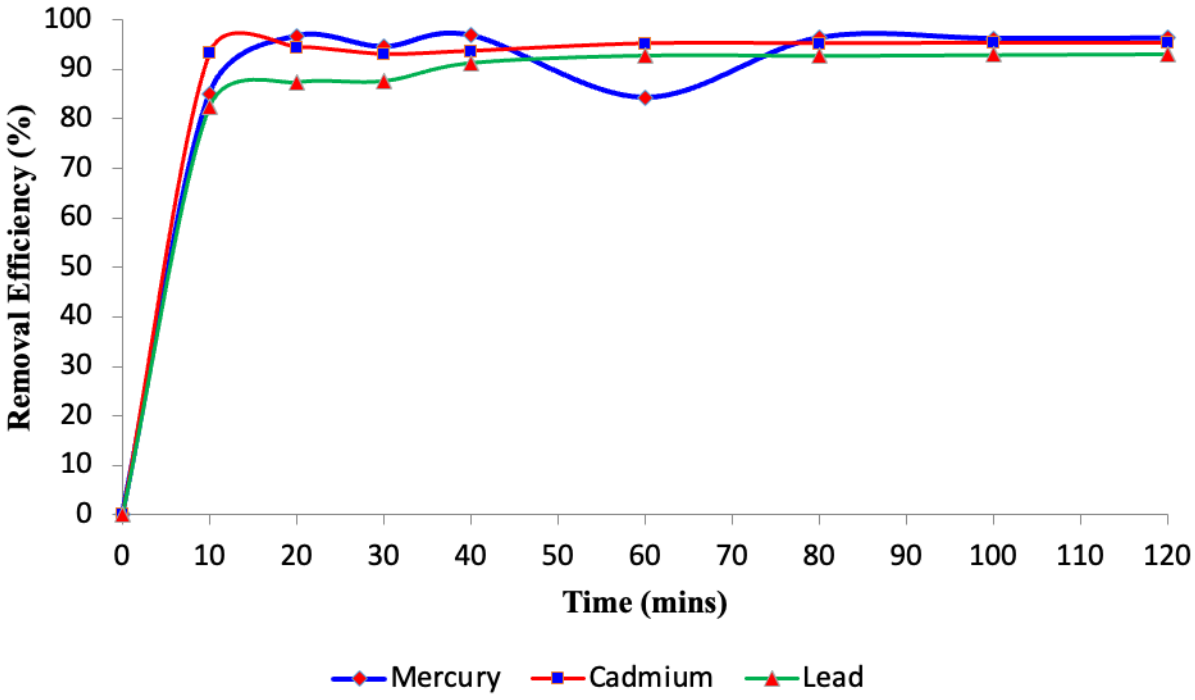


Figure 4.1: Comparison of the Effects of Equilibrium Time on the Sorption of Mercury, Cadmium and Lead Metal Ions Using Orange Peel.

The findings for effect of time using orange peel as biosorbent on the sorption of the three metal ions are shown in Table 4.1 and Figure 4.1. The graph shows that initial removal occurs rapidly as soon as the wastewater and the peels come in contact but after that, when some of the easily available active sites engaged, dye wastewater needs time to find more active sitesfor building. The results indicate that the removal efficiency for mercury, lead and cadmium is very high even in 10 minutes of adsorption time for OP. The results indicated that sorption increased with time

of equilibrium, and it became nearly constant at 60 mins for all the metal ions, denoting attainment of equilibrium. The differences in the uptake of metal ions could be as a result of all active sites of adsorbent which were vacant in the first 10 mins, and the solute concentration was great at the start. The quick equilibrium time is as a result of the small particle size as the effectual surface area is great for small particles (Zhexian *et al.*, 2006). After that, only a very little increment in the metal ions uptake was observed as there are few surface-active sites on the biosorbent. It is concluded that the wastewater and peels should be in contact for at least 60 minutes in order to get maximum removal percentage

4.2.1.2 Effects of time with watermelon peel as biosorbent

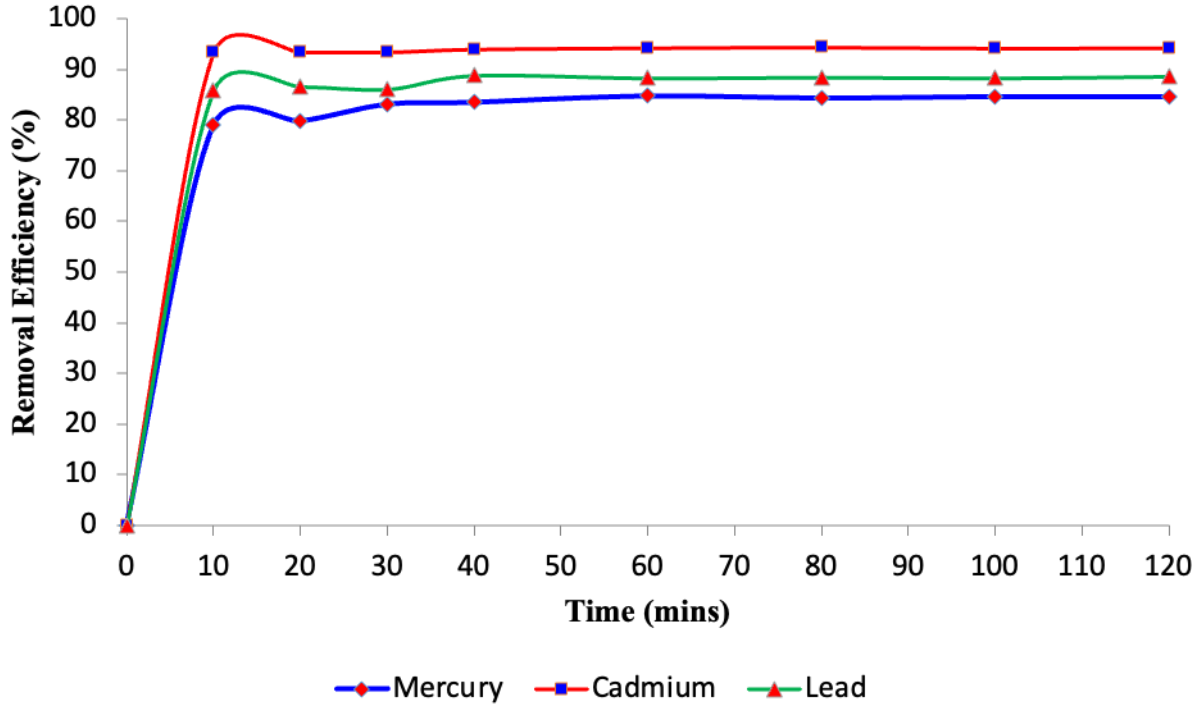


Figure 4.2: Comparison of the Effects of Equilibrium Time on the Sorption of Mercury Metal Ions, Cadmium Metal Ions and Lead Metal Ions Using Watermelon Peel

The result for influence of time on the sorption of Hg, Cd and Pb metal ions on watermelon peel are shown in Table 4.1 and Figure 4.2. The WP results indicate similar OP initial rapid adsorption efficiency within the first 10 mins as bio-sorbent. The results indicated that sorption

increased with time of equilibrium and it became almost constant from 60 mins for all the metal ions, denoting attainment of equilibrium. This phenomenon indicates that either closing of adsorbent internal pores occurs as adsorbate particles are being adsorbed over the adsorbent surface with remaining molecules in the solution or accumulation and integration of adsorbent particles occur, as a result led to decrease of active sites for adsorption (Shi *et al.*, 2013).

4.2.1.3 Effects of time with combination peel as biosorbent

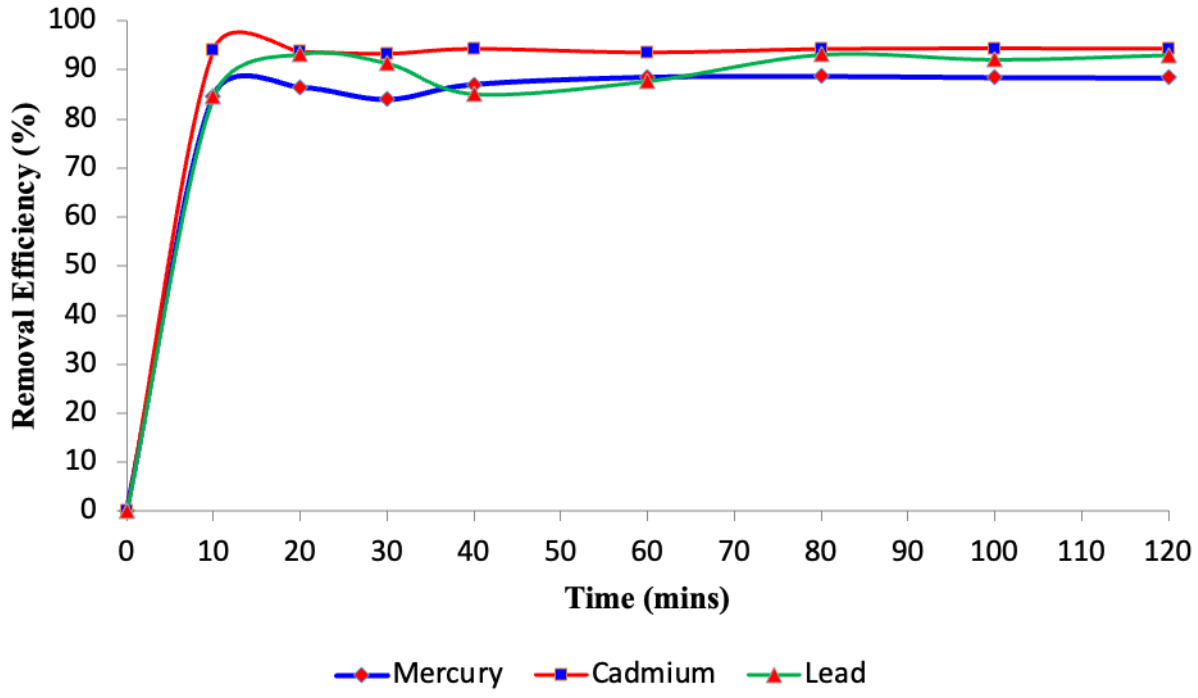


Figure 4.3: Comparison of the Effects of Equilibrium Time on the sorption of Mercury Metal Ions, Cadmium Metal Ions and Lead Metal Ions using Combination Peel

The effect of time on sorption of mercury, cadmium and lead metal ions using combination peel as indicated in Table 4.1 and Figure 4.3 shows similar trend as OP and WP within the initial 10 mins. The results indicate that the removal efficiency for mercury, lead and cadmium is also very high within the first 10 minutes of adsorption time. The sorption increased with time and became almost constant at 60 mins for mercury metal ion and 80mins for cadmium and lead metal ions, thereby attaining equilibrium.

4.2.1.4 Comparing the three biosorbents

For mercury the maximum removal efficiencies were found to be 96.94% at 40 mins, 84.94% at 100 mins and 88.75 % at 80 mins for OP, WP and CP respectively. This indicates that orange peel has the greatest absorption effect for mercury. Similarly, for cadmium, the maximum removal efficiencies were found to be 95.30 % at 100 mins, 94.40 % at 80 mins and 94.40 % at 100 mins for OP, WP and CP respectively. Also, for lead, the maximum removal efficiencies were found to be 93.14 % at 120 mins, 88.81 % at 40 mins and 93.22 % at 20 mins for orange peel, watermelon peel and combination peel respectively, combination peel was observed to have the maximum removal efficiency in the case of lead metal ion. These high adsorption efficiencies for OP for the three metal ions were achievable as a result of smaller pore sizes obtained from the OP, thereby providing more surface area for adsorption as shown by Zhexian *et al.*, 2006.

4.2.2 Biosorbent Dosage

The effect of biosorbent dosage on sorption of metal ions by orange peel, watermelon peel and combination peel were studied by taking 2.0 g biosorbent with 50 ml of the wastewater. Table 4.10 and Figures 4.4 are the results of the analysis carried out with each biosorbent. This can be explained by the increase in biosorption sites for metal ions due to the increase in surface area (Schiewer and Volesky, 2000).

4.2.2.1 Effects of biosorbent dosage with orange peel as biosorbent

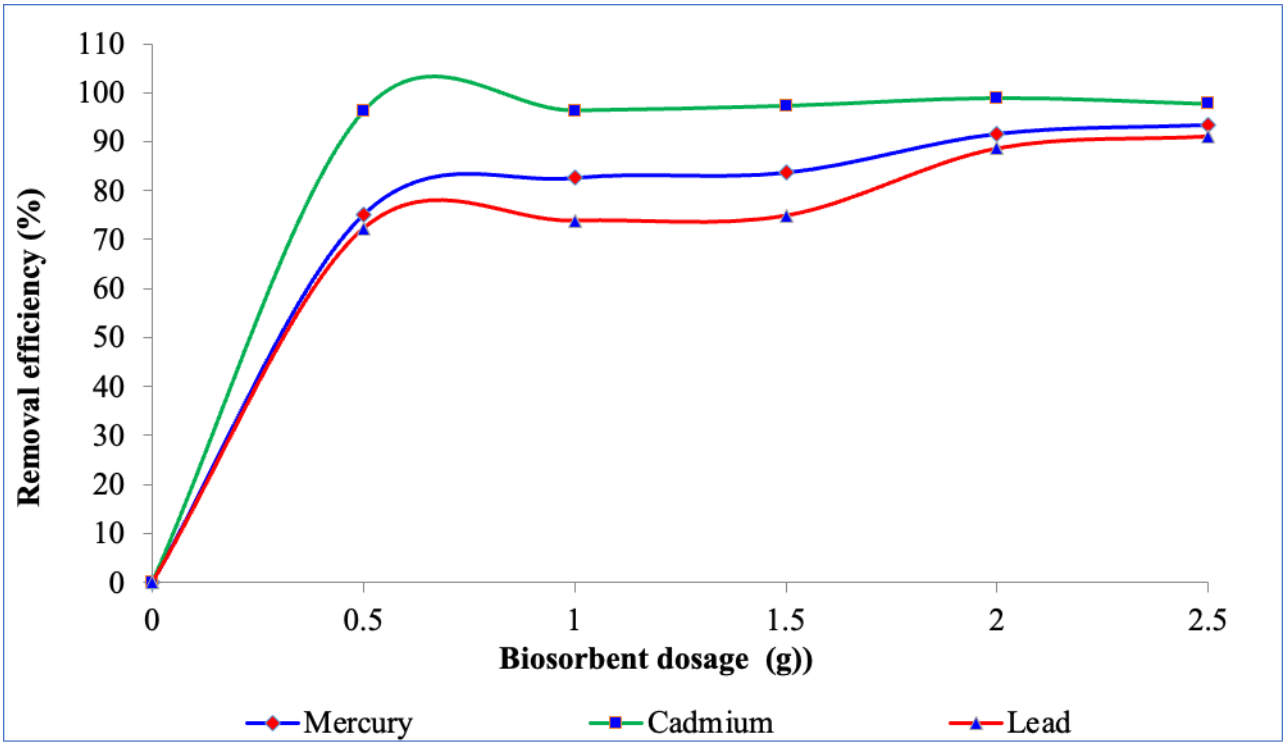


Figure 4.4: Comparison of the Effects of Biosorbent Dosage on the Sorption of Mercury, Cadmium and Lead Metal Ions Using Orange Peel

The findings for effect of biosorbent dosage using orange peel as the biosorbent on the sorption of the three metal ions are shown in Table 4.3 and Figure 4.4 above. The results indicate that the removal efficiency for cadmium is very high even at 0.5 g of biosorbent for OP while for mercury and lead, the removal efficiency got to 90 % as the dosage was increased to 2.0 g and 2.5 g respectively. The results indicated that sorption of the three metal ions by all the biosorbents increased with an increase in the dosage. The changes in the metal ions uptake as observed may also be due to the fact that; the more the active sites of adsorbent were vacant the higher the adsorption. The removal efficiency increased with increase in biosorbent dosage which was consistent with the findings of (Banerjee *et al.*, 2012) and (Ben-ali *et al.*, 2017).

4.2.2.2 Effects of biosorbent dosage with watermelon peel as biosorbent

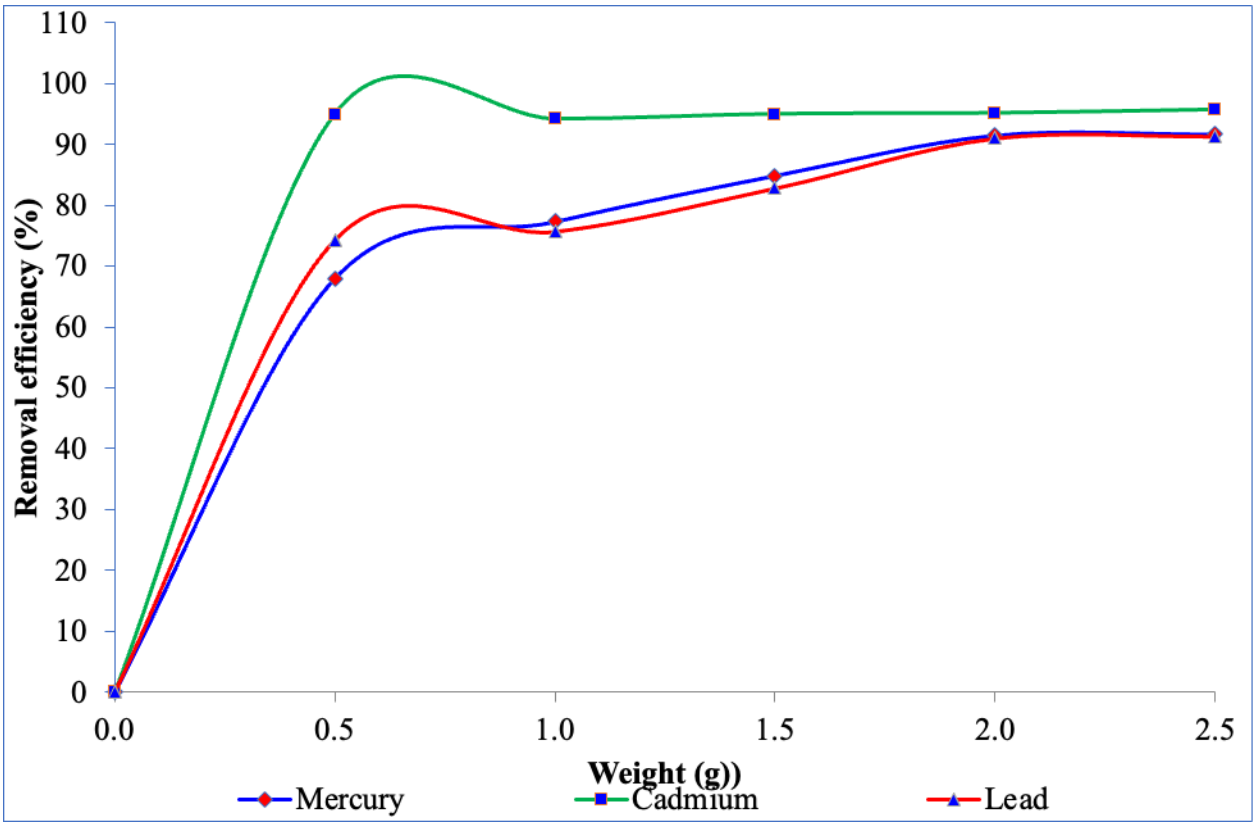


Figure 4.5: Comparison of the Effect of Biosorbent Dosage on the Sorption of Mercury, Cadmium and Lead Metal Ions Using Watermelon Peel

The results observed for the effect of biosorbent dosage using watermelon peel as the biosorbent on the sorption of the three metal ions are shown in Table 4.3 and Figures 4.5. The analysis indicates that the removal efficiency for all the three metal ions increase with an increase in dosage. Just as in the case of OP, cadmium is very high even at 0.5g of biosorbent for WP. The results indicated that sorption of the three metal ions by all the biosorbents increased with an increase in the dosage as well.

4.2.2.3 Effects of Biosorbent Dosage with Combination Peel as Biosorbent

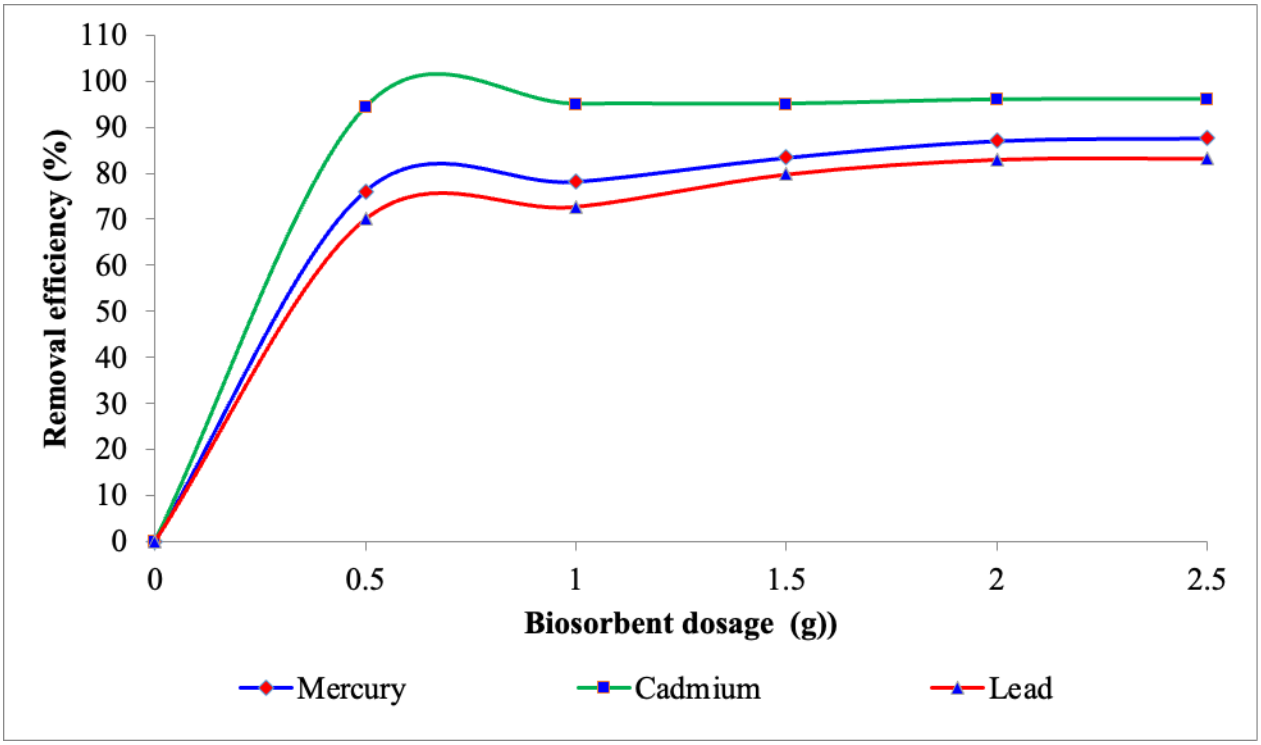


Figure 4.6: Comparison of the Effect of Biosorbent Dosage on the Sorption of Mercury, Cadmium and Lead Metal Ions using Combination Peel

The findings for effect of biosorbent dosage using combination peel as the biosorbent on the sorption of the three metal ions are shown in Table 4.3 and Figure 4.6 above. The results of the analysis indicate a similar pattern with the OP and WP as biosorbents. The removal efficiency for cadmium is very high even at 0.5g of biosorbent for CP while for mercury and lead, the removal efficiency increased with increase in the biosorbent dosage. Based on the similar pattern of adsorption, it can be said that changes in the metal ions uptake as observed is due to the presence of more active vacant sites of the adsorbent.

4.2.2.4 Comparing the three biosorbents

Comparing the three biosorbents, it can be seen that the maximum removal efficiencies using orange peel as biosorbent were found to be 93.38 %, 98.93 % and 91.10 % for mercury, cadmium and lead metal ions at biosorbent dosage of 2.5 g, 2.0 g and 2.5 g respectively. Also,

with the watermelon peel as biosorbent, the highest adsorption was found to be 91.70 %, 95.69 % and 91.36 % for mercury, cadmium and lead metal ions at biosorbent dosage of 2.5 g for all. While for the combination peel, it was found to be 87.59 %, 96.07 % and 83.22 % for mercury, cadmium and lead metal ions at biosorbent dosage of 2.5 g for each metal ion. It can be seen that cadmium metal ion uptake is higher in all the three biosorbent. Based on the maximum removal efficiencies obtained in the experiment and also considering the increase in adsorption with the dosage an average of 2 g was chosen to conduct the analysis for effect of time and pH.

It is clear from the analysis that the quantity of metal ions absorbed by biosorbent differed with the amount of biosorbent and adsorption increases with an increase in biosorbent dosage. This can be easily explained by an increase in surface area (i.e. due to more availability of active adsorption site) with an increase in biosorbent dosage. Several factors affecting adsorption are number of sites in the biosorbent material, the chemical state of site (i.e. availability), the accessibility of the sites and the affinity linking the sites and the metal (i.e. binding strength). Related attributes on the influence of biosorbent dosage on metal adsorption was detected in the literatures, for a diversity of adsorbents (Agrawal *et al.,* 2004).

4.2.3 Initial pH

The effect of initial pH on adsorption of metal ions by orange peel, watermelon peel and combination peel were studied, and the following were arrived at;

4.2.3.1 Effects of initial pH with orange peel as biosorbent

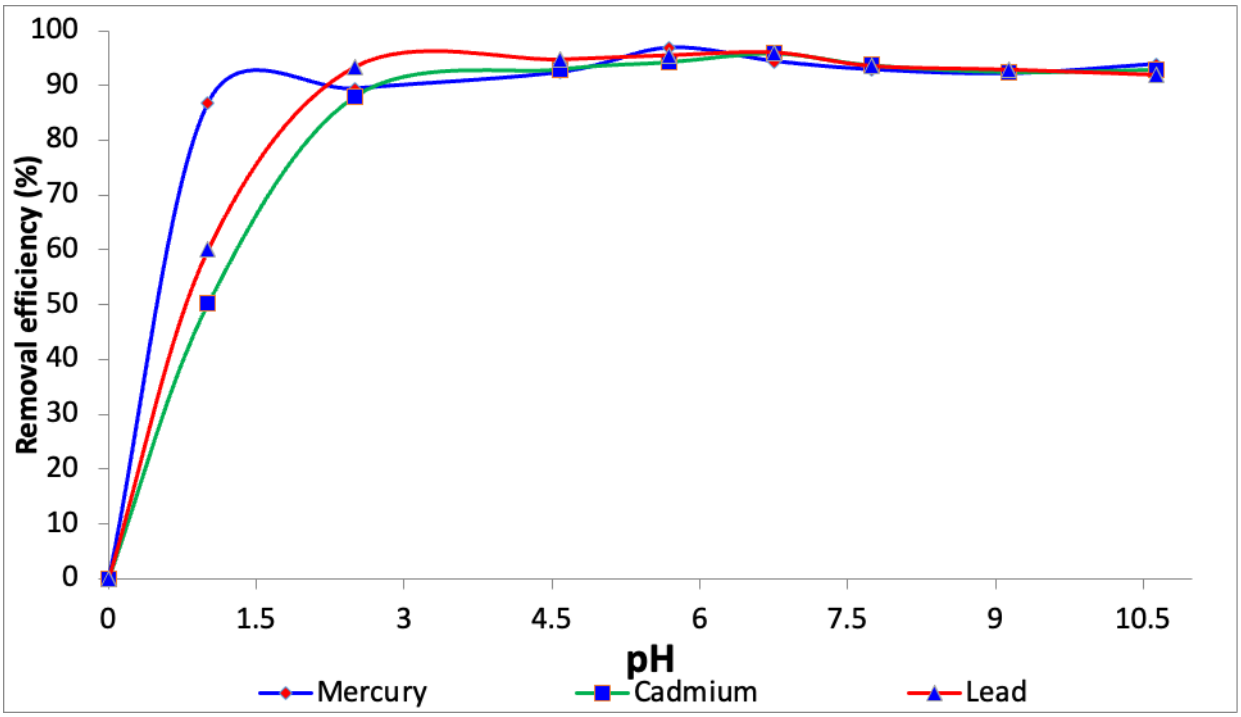


Figure 4.7: Comparison of the Effect of pH on the Sorption of Mercury. Cadmium and lead metal ion on Orange Peel

Using orange peel as biosorbent, it was discovered that the maximum adsorption of mercury was found to be 93.71 % at a pH of 5.70; for cadmium it was found to be 93.99 % at a pH of 5.70 and for lead it was 95.34 % at a pH of 4.60. It can be said that the effect of pH affects the adsorption by orange peel of mercury, cadmium and lead metal ions.

As orange peels are rich in pectin, it is only to be expected that carboxylate groups are among the main functional groups, that might be responsible for metal ions adsorption at a pH range of 3-9.

4.2.3.2 Effects of Initial pH with watermelon peel as biosorbent

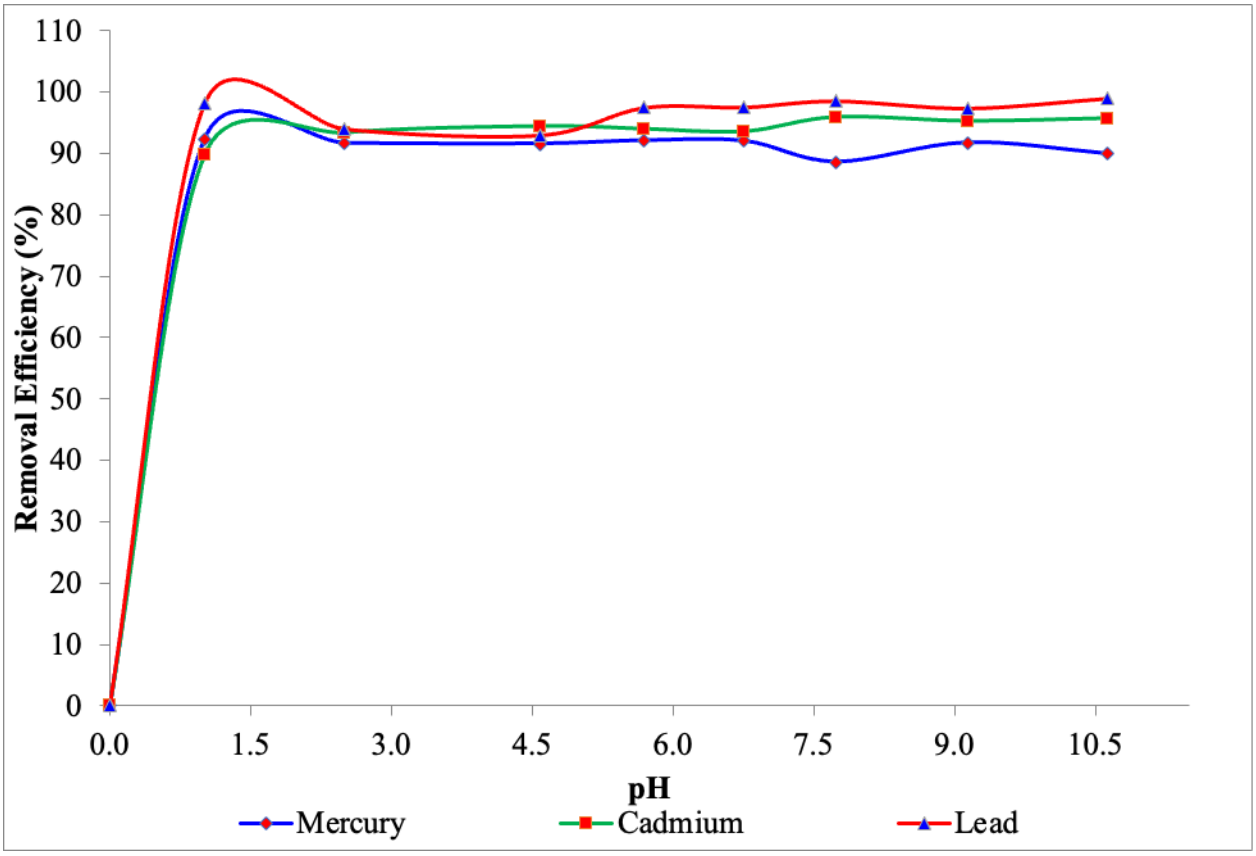


Figure 4.8: Comparison of the Effect of pH on the Sorption of Mercury, cadmium and lead metal ion Using Watermelon Peel

For watermelon peel, the maximum removal efficiencies were 92.06 % at a pH of 5.69, 95.92 % at a pH of 7.74 and 98.98 % at a pH of 10.63 for mercury, cadmium and lead metal ions respectively. It was discovered that the lower the pH the higher the removal efficiency for mercury metal ion but vice versa for cadmium ion. In the case of lead, the removal efficiency fluctuated at different pH. Watermelon peels basically contains lignin. Based on this study, it is reasonable to assume that these lignin groups might be responsible for the efficient adsorption of all the metal ions in wide range of pH.

4.2.3.3 Effects of Initial pH with combination peel as biosorbent

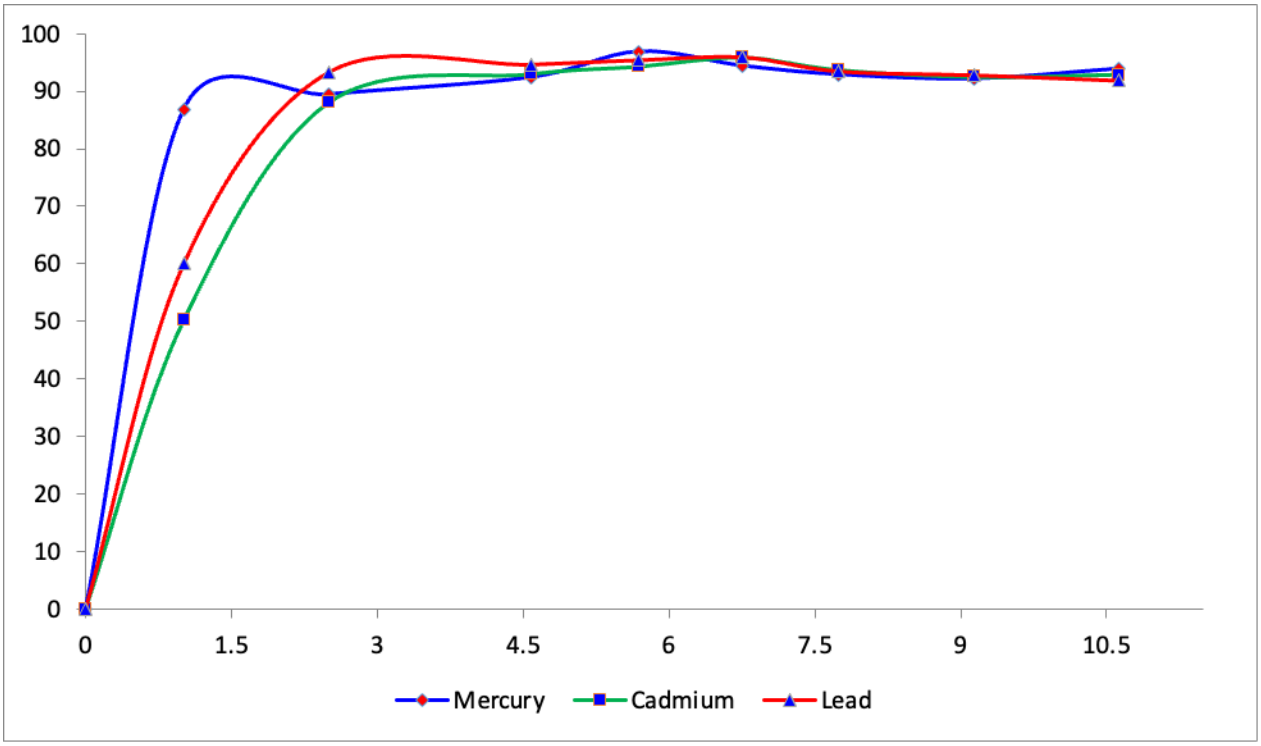


Figure 4.9: The Effect of pH on the Sorption of mercury, Cadmium and lead metal ion on Combination Peel

On the other hand, for the combination peel, the maximum removal efficiencies were found to be maxima at a pH of 5.69 for mercury metal ion and 6.76 for both cadmium and lead metal ions. These pH levels for combination peel shows high adsorption effectiveness around a more neutral wastewater pH level.

4.2.3.4 Comparing the three biosorbents

Comparing the results from the three biosorbents; it is clear that the pH of the wastewater affects the adsorption of the metal ions by the biosorbent. Using orange peel as biosorbent it can be said that for maximum removal efficiency the pH ranges from 5.69 to 7.74 for the three metal ions, even though the range is wider for lead.

In the case of watermelon peel the pH ranges between 4.58 and 7.74 for mercury and cadmium metal ions while for lead metal ion it ranges from 1.01 and 10.63.

Finally, for combination peel the pH ranges between 5.69 and 6.76 for all the metal ions.

4.3 Effect of Ion Species on the Adsorption – Selectivity of the Process

From the engineering stance, it is paramount to acquire validation regarding the potential of the absorbent to mop up varieties of heavy metal ions. The removal efficiency at the plateau values differs for various metal ions, displaying proof about the adsorption capability of the adsorbent which can be accomplished for each of the appraised metal ion species. From the research of the preceding parameters, it is obvious that the greatest adsorption capability by orange peel was for cadmium, mercury and then lead, in other words ranking the adsorption ability of the measured metal ions, the following series was obtained: $Cd\ (II) > Hg\ (II) > Pb\ (II)$. Also, for watermelon peel, the ranking for the adsorption ability of measured metal ions was found to be $Cd\ (II) > Pb\ (II) > Hg\ (II)$, and for the combination peel it's $Cd\ (II) > Pb\ (II) > Hg\ (II)$.

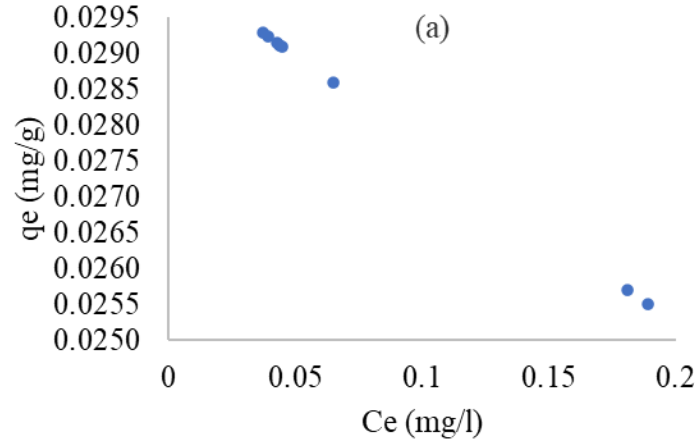
4.4 Adsorption Isotherms

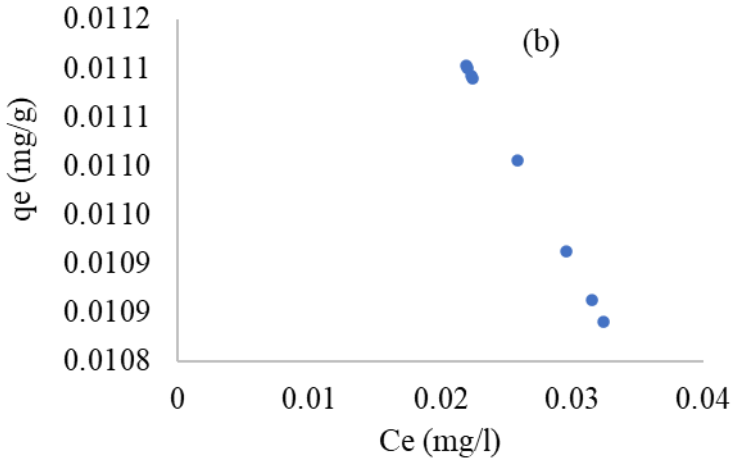
Adsorption isotherms were used to describes how the pollutants' (Hg, Cd and Pb ions) concentration interact with adsorbent (OP, WP, CP) surfaces. Langmuir and Freundlich isotherms were used.

The results of the batch experiments are presented in Appendix C while the sorption isotherms for Hg, Cd, and Pb on OP, WP and CB are presented in Figures 4.10 to 4.18 respectively. The fittings of the isotherms using linear regressions that obtained the isotherm parameters are presented in Appendix E for the mercury, cadmium and lead ions using the biosorbents.

It can be observed that the isotherm's curves follow similar patterns for effect of time and pH (Figures 4.10 - 415) on the sorption of all the ions on the biosorbents except for the effect of dosage (Figures 4.16 - 4.18) which follows a different pattern.

In general, it can be observed for the isotherms of Figures 410 to 4.15, that at lower equilibrium concentrations (Ce), the sorption capacities (qe) are higher but drastically drops down with increase in in the equilibrium concentration. This suggests the lack of availability of sorption sites or inadequate dosages of the biosorbents to adsorb metal solutes from the solution thereby leading the exhaustion of the sorption sites and the biosorbents. Hence, a drastic drop in the equilibrium sorption capacities was observed.





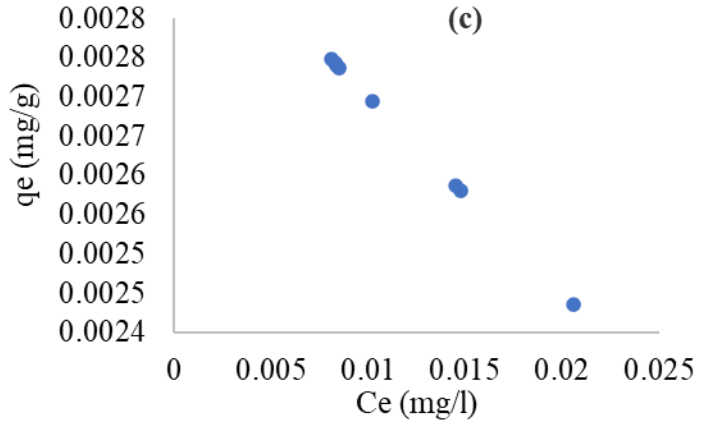
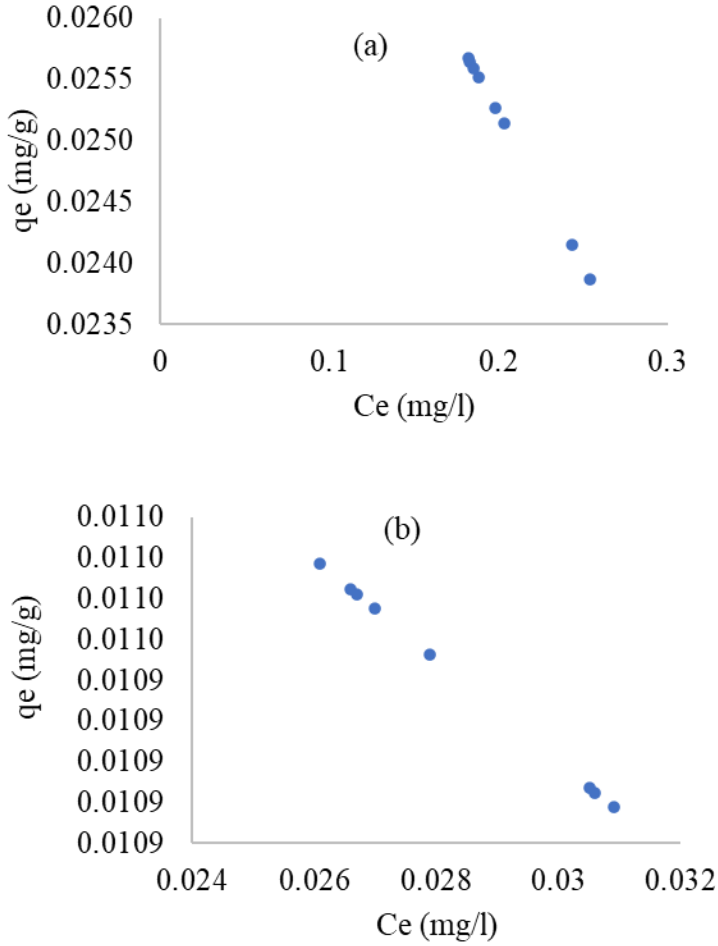


Figure 4.10: Isotherm on the effect of time on the sorption of (a) mercury (b) cadmium and (c) lead using orange peel respectively



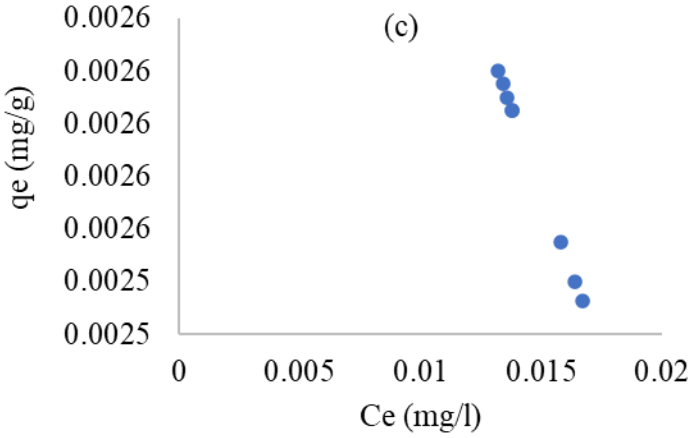
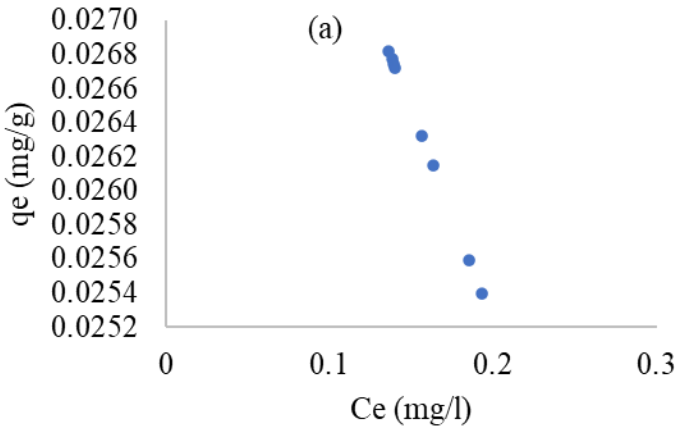
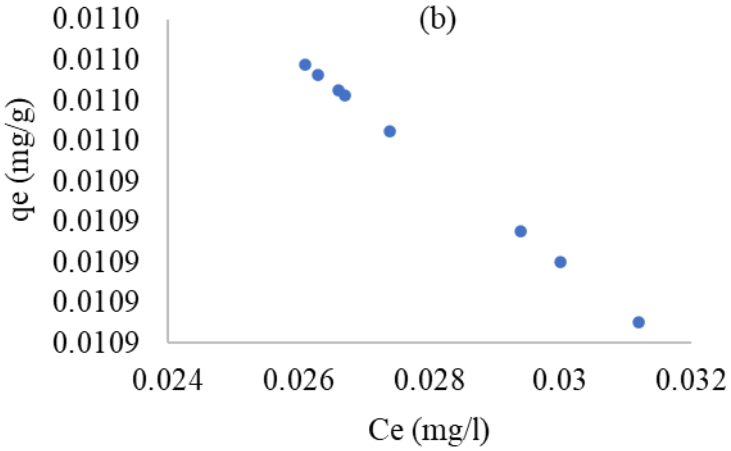


Figure 4.11: Isotherm on the effect of time on the sorption of (a) mercury (b) cadmium and (c) lead using watermelon peel respectively





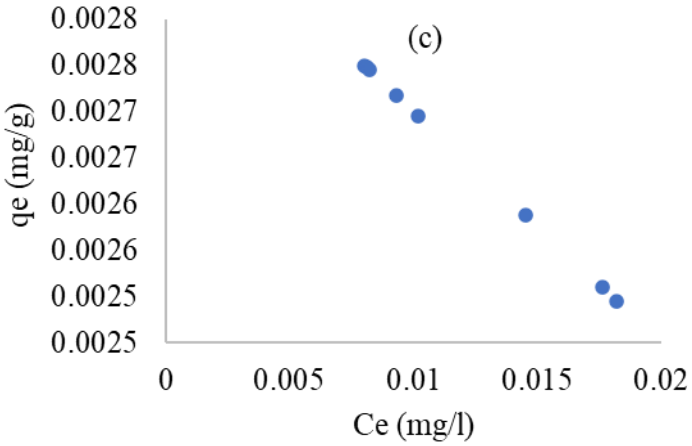
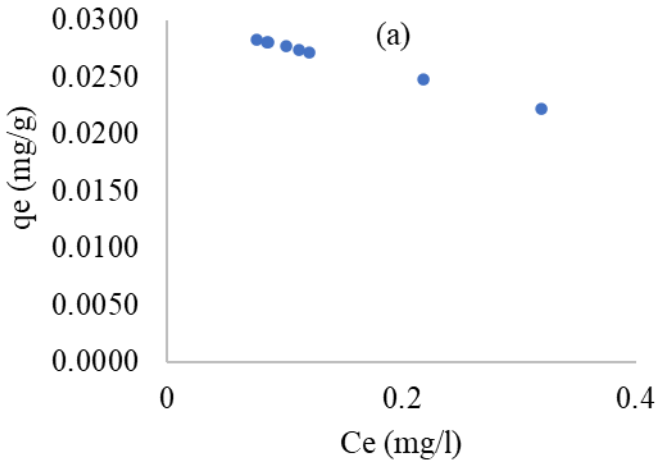
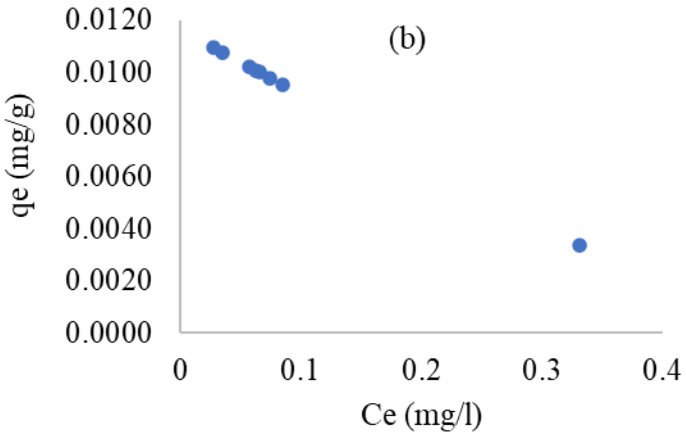


Figure 4.12: Isotherm on the effect of time on the sorption of (a) mercury (b) cadmium and (c) lead using combination peel respectively





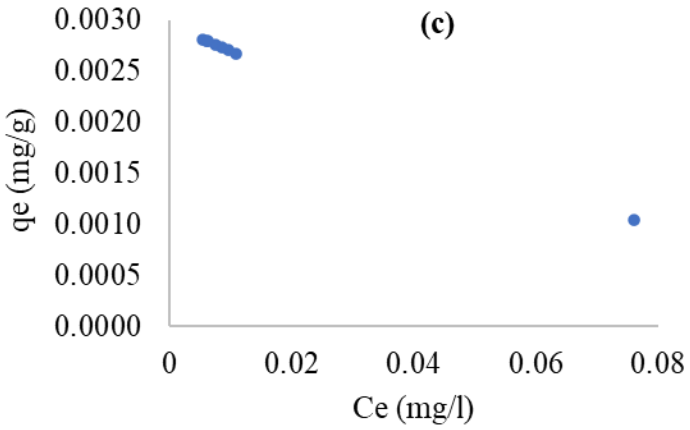
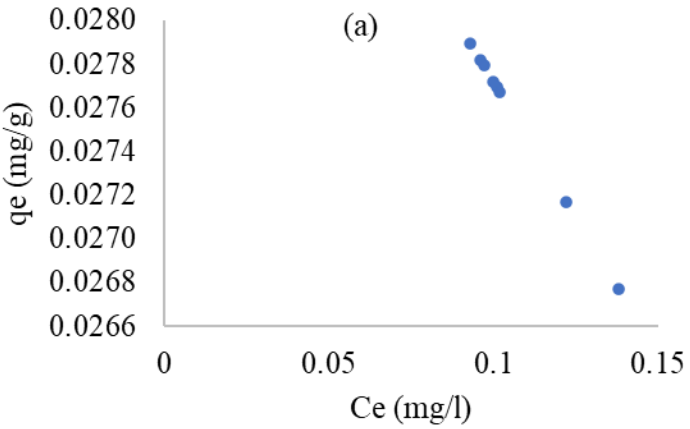
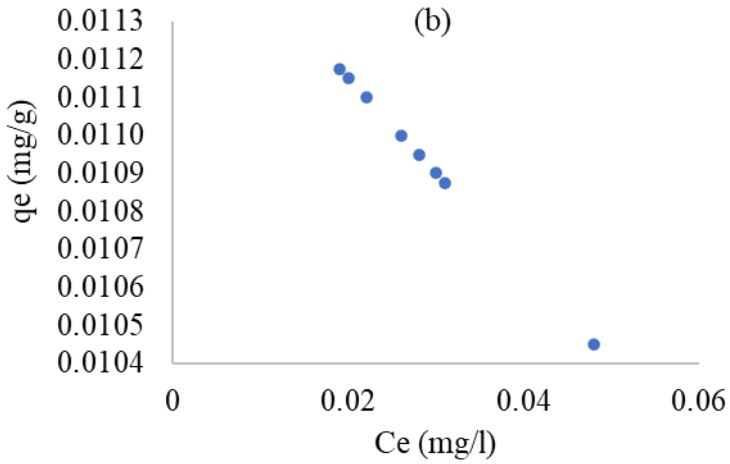


Figure 4.13: Isotherm on the effect of pH on the sorption of (a) mercury (b) cadmium and (c) lead using orange peel respectively





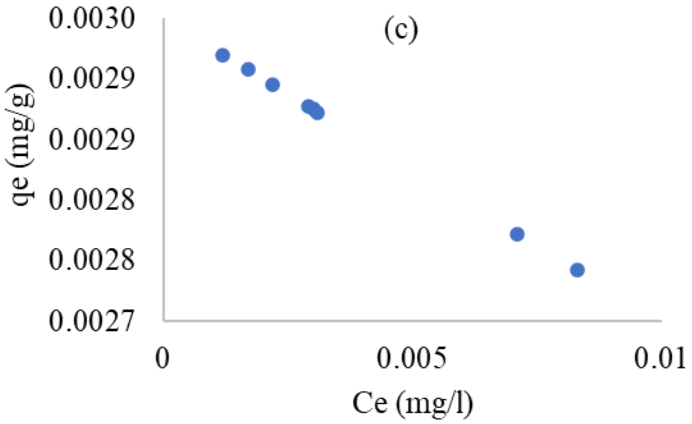
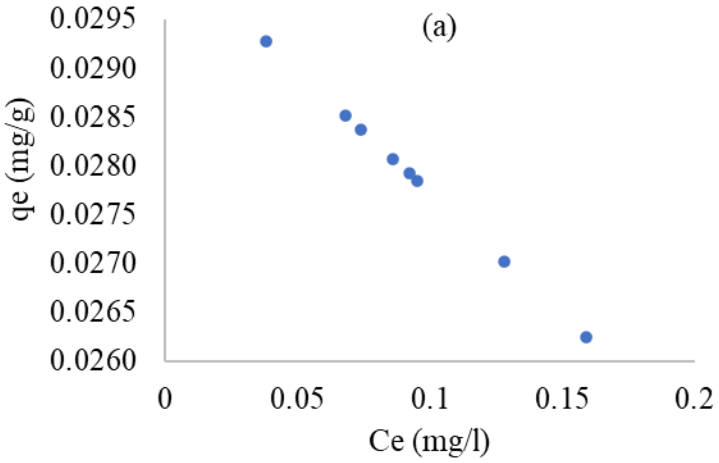
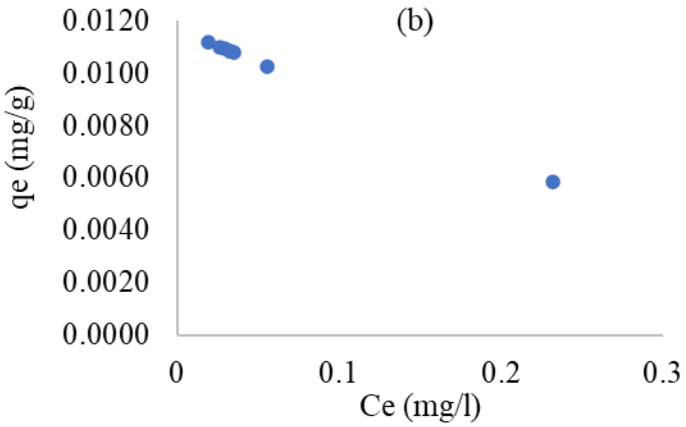


Figure 4.14: Isotherm on the effect of pH on the sorption of (a) mercury (b) cadmium and (c) lead using watermelon peel respectively





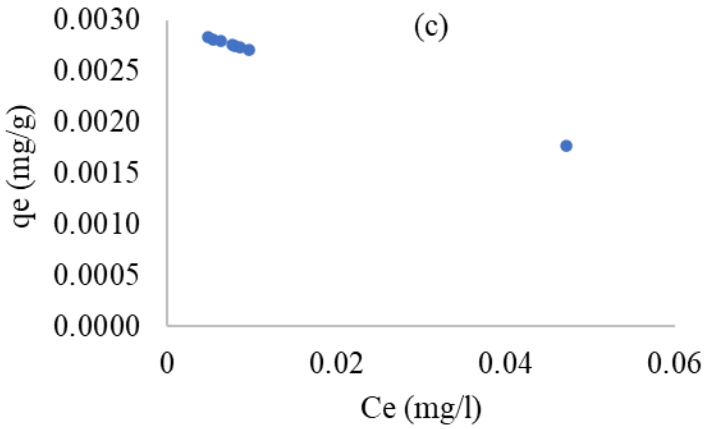


Figure 4.15: Isotherm on the effect of pH on the sorption of (a) mercury (b) cadmium and (c) lead using combination peel respectively

In the case of the effect of dosages of the biosorbents (Figures 4.16 – 4.18) on the sorption of the three ions (Hg, Cd and Pb), which shows a different pattern from those of effects of contact time and pH, it can be observed that the shape of the isotherms tends to appear sigmoidal. There were rises in the sorption capacities as the equilibrium concentrations increase. This suggests the availability of sorption sites as a result of increase biosorbent's dosages which favours more sorption and hence resulted in the increase in the equilibrium sorption capacities (qe).

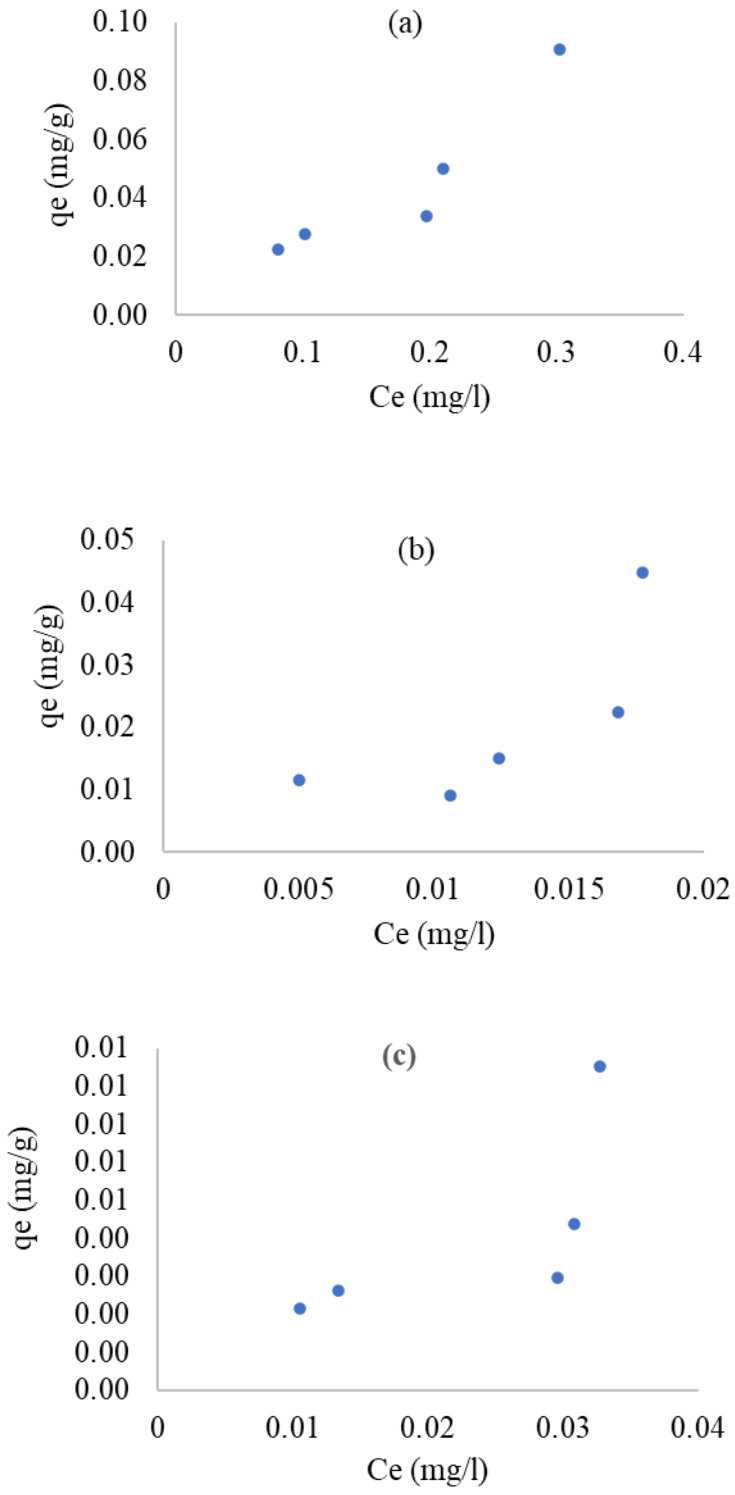


Figure 4.16: Isotherm on the effect of dosage on the sorption of (a) mercury (b) cadmium and (c) lead using orange peel respectively

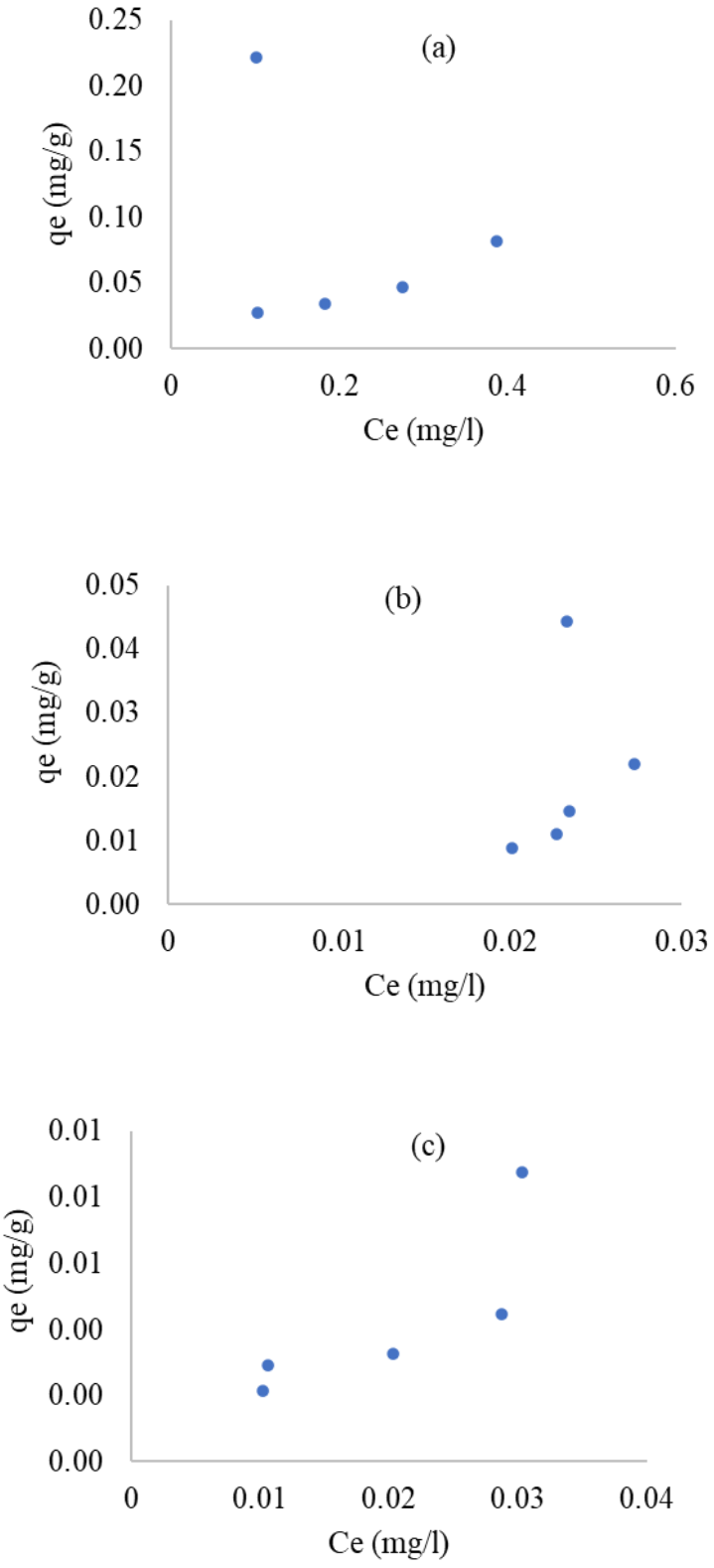


Figure 4.17: Isotherm on the effect of dosage on the sorption of (a) mercury (b) cadmium and (c) lead using watermelon peel respectively

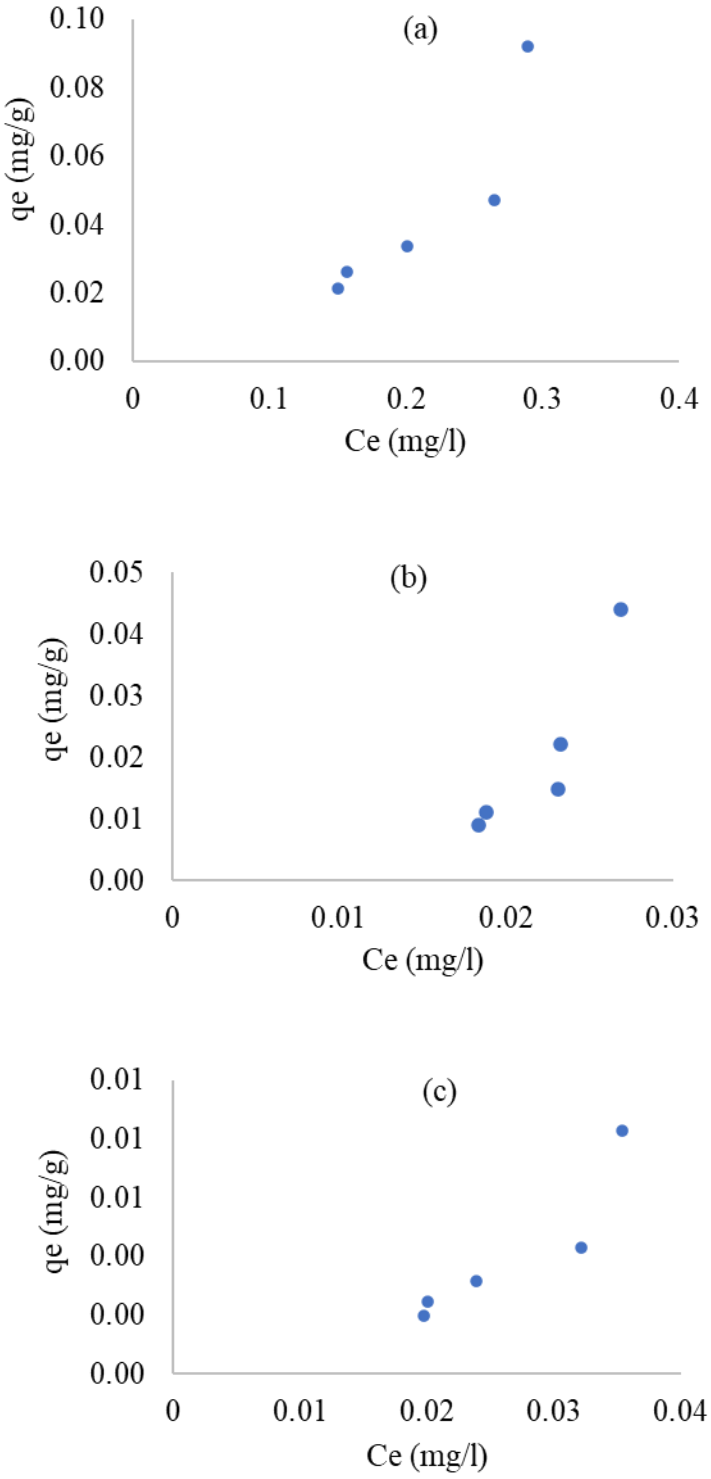


Figure 4.18: Isotherm on the effect of dosage on the sorption of (a) mercury (b) cadmium and (c) lead using combination peel respectively

4.4.1 Linear Transformed Isotherm Models

The plots of the linear transformations of the Langmuir and Freundlich models are presented in Appendix E while the isotherm parameters are presented in Tables 4.7 to 4.15. The isotherm parameters were obtained through linear regression methods using Microsoft Excel. The model with the highest R^2 value was selected as the best fit to represent the sorption process.

Table 4.7: Isotherm parameters for the effect of time on the sorption of mercury using orange peel, watermelon peel and combination peel

Model	Parameters	Orange Peel	Watermelon Peel	Combination Peel
LANGMUIR	Q_m	0.0250	0.0203	0.0226
	K_L	-166.30	-26.27	-46.78
	R^2	0.9182	0.9925	0.9182
FREUNDLICH	$1/n$	-0.0871	-0.2174	-0.1546
	K_F	0.0222	5.14	0.020
	R^2	0.9837	0.9974	0.9837

Table 4.8: Isotherm parameters for the effect of time on the sorption of cadmium using orange peel, watermelon peel and combination peel

Model	Parameters	Orange Peel	Watermelon Peel	Combination Peel
LANGMUIR	Q_m	0.0103	0.0102	0.01027
	K_L	-671.26	-572.44	-577.54
	R^2	0.9989	0.9989	0.9982
FREUNDLICH	$1/n$	-0.0604	-0.0653	-0.065
	K_F	113.42	9.67	0.0086
	R^2	0.9997	0.9997	0.9997

Table 4.9: Isotherm parameters for the effect of time on the sorption of lead using orange peel, watermelon peel and combination peel

Model	Parameters	Orange Peel	Watermelon Peel	Combination Peel
LANGMUIR	Q_m	0.002	0.002	0.002
	K_L	-533.77	533.77	-827.48
	R^2	0.998	0.998	0.9641
FREUNDLICH	$1/n$	-0.1222	-0.1446	-0.1171
	K_F	0.0015	0.0014	0.0016
	R^2	0.9306	0.9306	0.9306

Table 4.10: Isotherm parameters for the effect of dosage on the sorption of mercury using orange peel, watermelon peel and combination peel

Model	Parameters	Orange Peel	Watermelon Peel	Combination Peel
LANGMUIR	Q_m	0.16	0.05	-0.05478
	K_L	1.79	53.30	-1.93469
	R^2	0.8658	0.0087	0.9399
FREUNDLICH	$1/n$	0.9306	0.1436	3.6958
	K_F	0.21	0.05	0.693426
	R^2	0.7798	0.0105	0.8884

Table 4.11: Isotherm parameters for the effect of dosage on the sorption of cadmium using orange peel, watermelon peel and combination peel

Model	Parameters	Orange Peel	Watermelon Peel	Combination Peel
LANGMUIR	Q_m	0.04	0.04	0.04
	K_L	54.17	54.17	54.17
	R^2	0.5631	0.0576	0.9196
FREUNDLICH	$1/n$	0.897	3.4895	3.6958
	K_F	0.96	3086.74	23507.15
	R^2	0.619	0.2897	0.8869

Table 4.12: Isotherm parameters for the effect of dosage on the sorption of lead using orange peel, watermelon peel and combination peel

Model	Parameters	Orange Peel	Watermelon Peel	Combination Peel
LANGMUIR	Q_m	0.0097	0.0146	0.16
	K_L	26.99	19.1	1.79
	R^2	0.7005	0.7649	0.8658
FREUNDLICH	$1/n$	0.7757	0.8619	0.9306
	K_F	0.072061	0.121311	0.21
	R^2	0.5791	0.721	0.7798

Table 4.13: Isotherm parameters for the effect of pH on the sorption of mercury using orange peel, watermelon peel and combination peel

Model	Parameters	Orange Peel	Watermelon Peel	Combination Peel
LANGMUIR	Q_m	0.021994	0.0248	0.026295
	K_L	-51.8959	-94.19	-223.574
	R^2	0.8445	0.9897	0.7431
FREUNDLICH	$1/n$	-0.164	-0.1043	1.8287
	K_F	0.018897	0.02	0.693426
	R^2	0.9603	0.9974	0.9292

Table 4.14: Isotherm parameters for the effect of pH on the sorption of cadmium using orange peel, watermelon peel and combination peel

Model	Parameters	Orange Peel	Watermelon Peel	Combination Peel
LANGMUIR	Q_m	0.005	0.010178	0.007
	K_L	-45.99	-550.415	95.19
	R^2	0.3945	0.8902	0.6035
FREUNDLICH	$1/n$	-0.4843	-0.0708	-0.2743
	K_F	0.0024	0.008474	0.0042
	R^2	0.8333	0.9603	0.8869

Table 4.15: Isotherm parameters for the effect of pH on the sorption of lead using orange peel, watermelon peel and combination peel

Model	Parameters	Orange Peel	Watermelon Peel	Combination Peel
LANGMUIR	Q_m	0.0012	0.003	0.0019
	K_L	-256.46	-12548.26	-500.08
	R^2	0.6762	0.6991	0.6808
FREUNDLICH	$1/n$	0.3914	-0.0334	0.9306
	K_F	0.0004	0.0024	0.0009
	R^2	0.9444	0.9306	0.7798

4.4.1.1 Evaluation of the isotherm models

Generally, fairly high R^2 values were obtained for the models across the three biosorbents as presented in Tables 4.7 to 4.15. These R^2 values were shared between the Langmuir and Freundlich models. For the effect of pH, the Freundlich model provided the best fitted model of the sorption process all through for Hg, cd, and Pb across the three biosorbents. This suggests multi-layer adsorption occurring over heterogenous surfaces. Similar results were obtained for the effect of dosage, as Freundlich proved the best fit for orange and watermelon peels for Cd and watermelon for Hg with the exception of combination and orange peel for Hg which appeared to be Langmuir. This means the sorption processes of combination and orange peels for Cd is a monolayer adsorption that occurred over homogeneous surfaces. In terms of dosage on Pb sorption, the process follows the Langmuir model. For the effect of time, the process appears to be Freundlich for Hg and Cd but Langmuir for lead.

4.5 Adsorption Kinetics Modelling

Adsorption kinetics was carried out using 1st order kinetic, 2nd order kinetic, Langmuir isotherm and Freundlich isotherm. The rate of adsorption is high at initial times of adsorption and most of

adsorption takes place within 10 mins which indicate that the rate of dye adsorption by all three peels is high in 2nd order kinetics.

4.5.1 Adsorption Kinetics Modelling for Biosorbent Dosage of Orange Peel

From the results obtained, orange peel favors the removal of lead and follows the first and second order kinetic. R^2 value for Langmuir and Freundlich isotherm were not too close to 1 as compared to the first and second order kinetics shown in Figures 4.10 to 4.13 below;

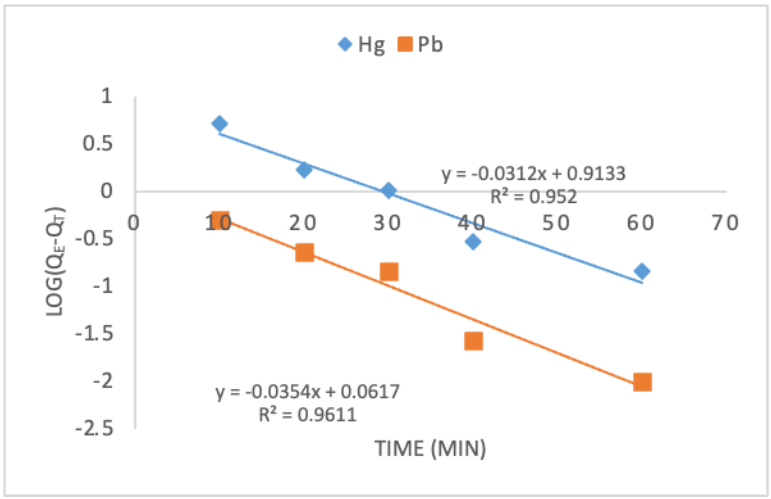


Figure 4.19: The Effect of adsorbent dosage on the sorption of Mercury, Cadmium and Lead ions on orange peel using First Order Kinetic.

Figures 4.10 and 4.11 showed that the first and second order kinetics model were the closest to unity, each models having an R^2 value of atleast 0.95 were obtained for the metal ions considered. This indicates a more stable and consistent models as compared to Langmuir and Freundlich models.

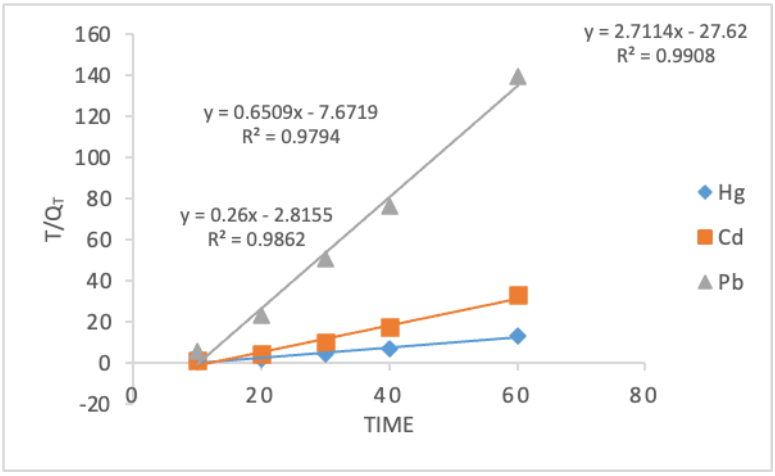


Figure 4.20: The Effect of adsorbent dosage on the sorption of Mercury, Cadmium and Lead metal ions on orange peel using Second Order Kinetic

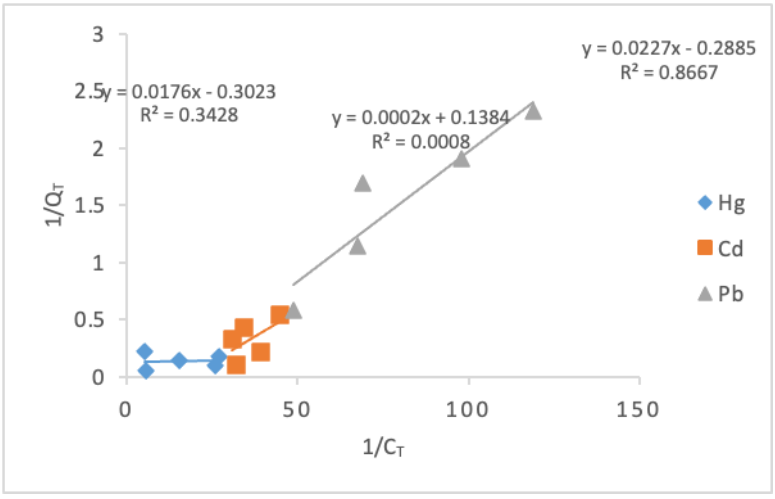


Figure 4.21: The Effect of adsorbent dosage on the sorption of Mercury, Cadmium and Lead metal ions on orange peel using Langmuir Isotherm

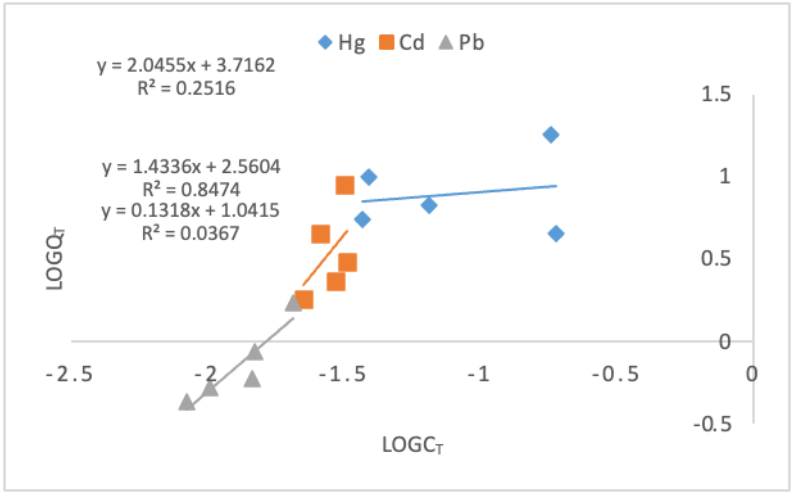


Figure 4.22: The Effect of adsorbent dosage on the sorption of Mercury, Cadmium and Lead metal ions on orange peel using Freundlich Isotherm.

Meanwhile, the highest R^2 values obtained for Langmuir and Freundlich models were 0.8667 and 0.8474 respectively. Which are both farther from unity as compared to the first and second kinetic models.

4.4.2 Adsorption Kinetics Modelling for Biosorbent Dosage of Watermelon Peel

Watermelon peel favors the removal of Lead for the second order kinetic (with R^2 value 0.9855) as well as Langmuir and Freundlich isotherm with R^2 value of 0.9435 and 0.9092 respectively. The process can be described as physicochemical adsorption as shown in Figures 4.14 to 4.16;

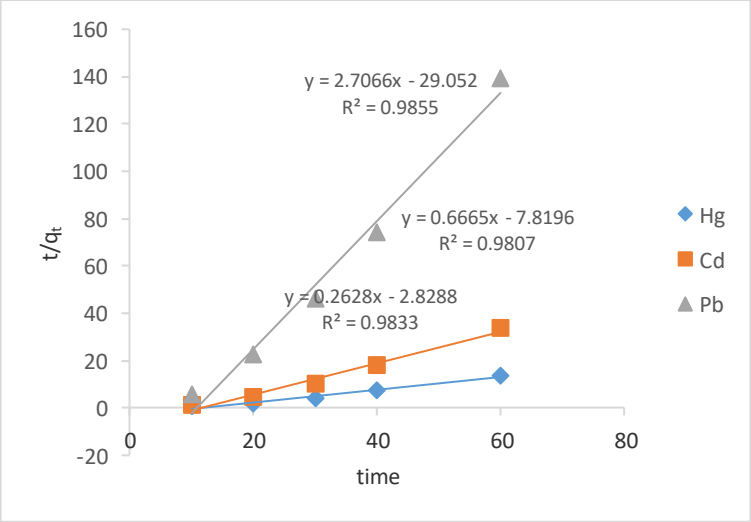


Figure 4.23: The Effect of adsorbent dosage on the sorption of Mercury, Cadmium and Lead metal ions on watermelon peel using Second Order Kinetic

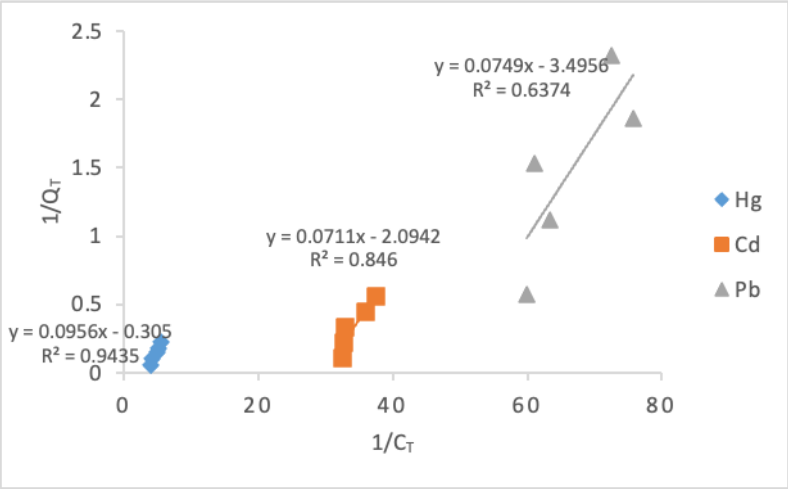


Figure 4.24: The Effect of adsorbent dosage on the sorption of Mercury, Cadmium and Lead metal ions on watermelon peel using Langmuir Isotherm

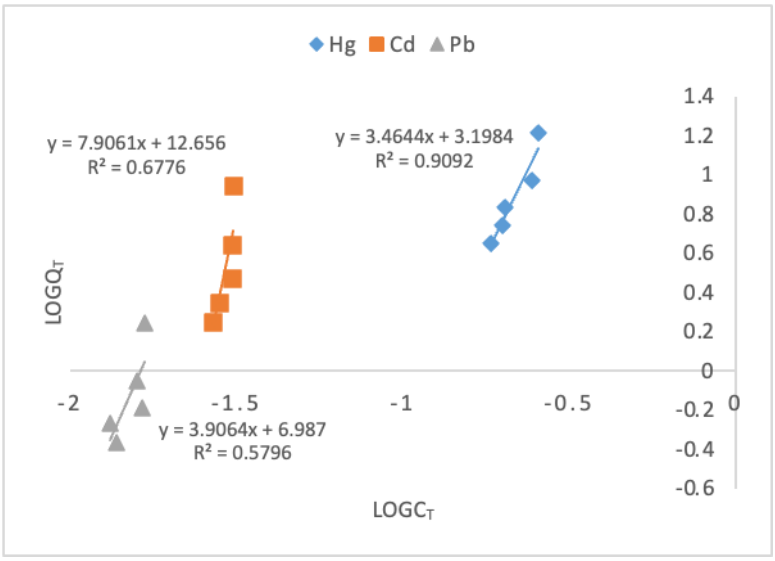


Figure 4.25: The Effect of adsorbent dosage on the sorption of Mercury, Cadmium and Lead metal ions on watermelon peel using Freundlich Isotherm.

Similarly, the WP follows the second order kinetic model for mercury, cadmium and lead adsorption, indicating a more stable and consistent models as compared to Langmuir and Freundlich models which are both farther from unity as compared to the second kinetic models.

4.4.3 Adsorption Kinetics Modelling for Biosorbent Dosage of Combination Peel

Combination peel favours the removal of mercury and follows the first and second order kinetic, with both models having R^2 values ranging from 0.8771 to 0.9930 were obtained for the metal ions considered. R^2 values for Langmuir and Freundlich isotherms were not close to 1 (it cannot be clearly predicted if this a chemical or physical process) as shown in Figures 4.17 to 4.20 below;

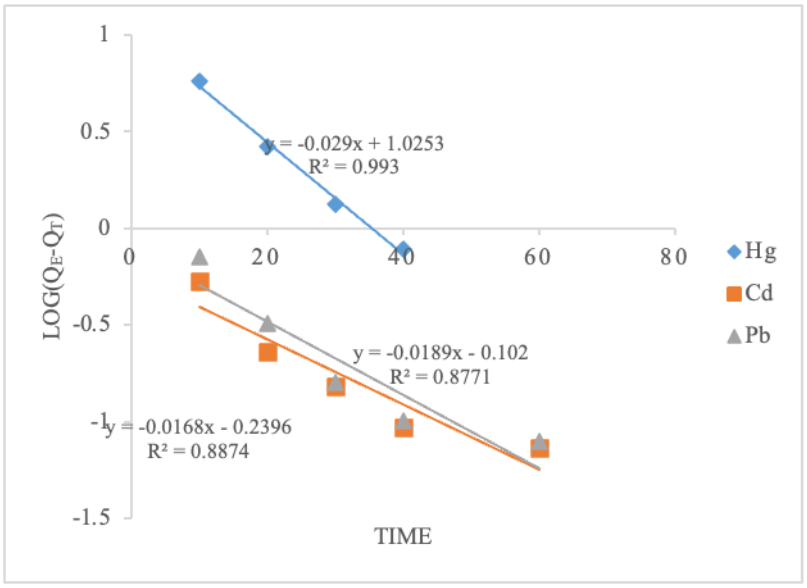


Figure 4.26: The Effect of adsorbent dosage on the sorption of Mercury, Cadmium and Lead metal ions on combination peel using First Order Kinetic

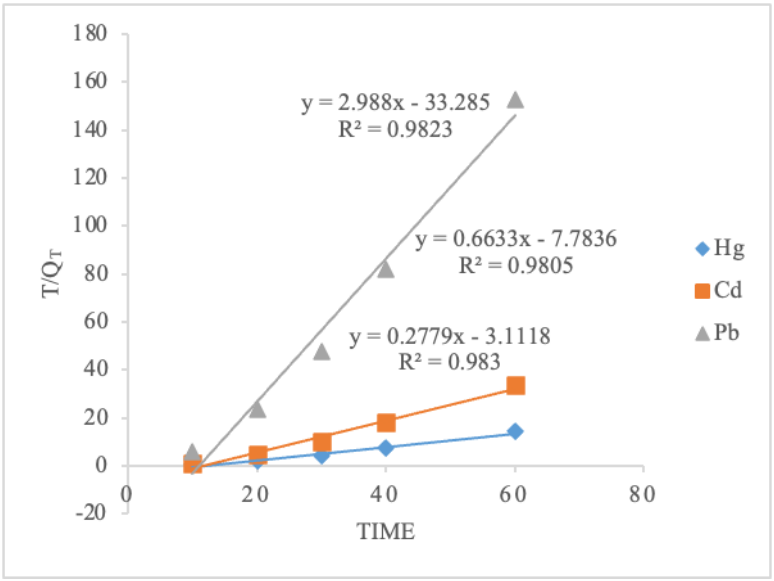


Figure 4.27: The Effect of adsorbent dosage on the sorption of Mercury, Cadmium and Lead metal ions on combination peel using Second Order Kinetic

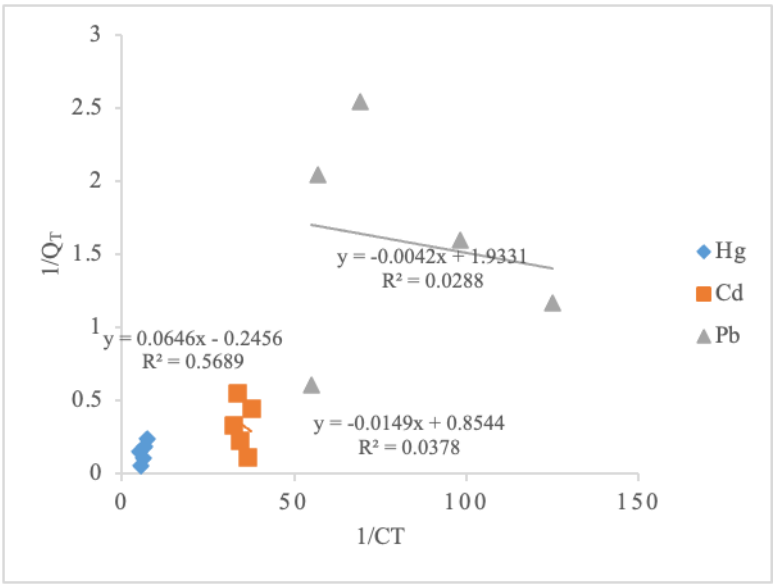


Figure 4.28: The Effect of adsorbent dosage on the sorption of Mercury, Cadmium and Lead metal ions on combination peel using Langmuir Isotherm

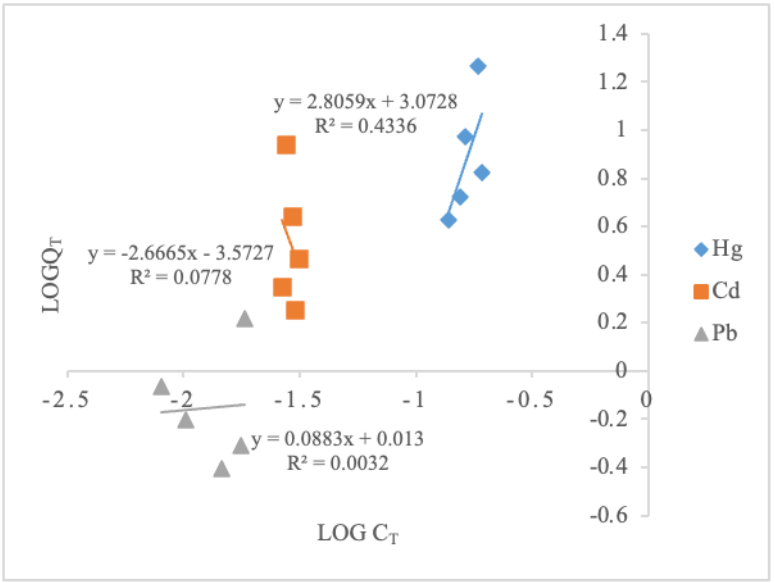


Figure 4.29: The Effect of adsorbent dosage on the sorption of Mercury, Cadmium and Lead metal ions on combination peel using Freundlich Isotherm.

In general, the closer the R^2 value is to unity, and the smaller the standard deviation, the better the model is in predicting the response (Alam, *et al.*, 2009).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this investigation analytical parameters were studied for the adsorption of mercury, cadmium and lead metal ions by using orange peel, watermelon peel and combination peel as adsorbents. The variables studied during the course of the research included adsorption time, biosorbent dosage and pH.

From the investigation of the adsorption process and ANOVA analysis, the following conclusions were drawn:

1. The research shows that both biosorbents i.e., orange peel and watermelon peel can be used to perform metal ions adsorption successfully. The biosorbents proved to have high adsorption capacities.
2. Both biosorbents and its combination appeared to have a universal application for adsorption of the metal ions considered. These materials showed a great tendency for uptake of mercury (II), cadmium (II) and lead (II) metal ions.
3. Adsorption of metal ions is dependent on contact time, biosorbent dosage, pH and particle size. Using the three adsorbents at respective time duration, cadmium adsorption was found to be the most effective, with F and P values of 13802.04 and 3.2×10^{-29} respectively. Similarly, at respective dosage variation, cadmium adsorption was also found to be the most effective, with F and P values of 9262.98 and 5.5×10^{-15} respectively. While at respective pH levels, mercury adsorption was found to be the most effective, with F and P values of 201.31 and 1.41×10^{-14} respectively.
4. The adsorbent to adsorbate interactions is quick. The maximum adsorption appears to occur in less than 60 minutes of adsorption time.

5. No single mechanism can explain the process of metal removal by these biosorbents. Mechanisms involved in the biosorption process might be chemisorption, complexation, adsorption-complexation on surface and pores, ion exchange, micro precipitation, heavy metal hydroxide condensation onto bio surface and surface adsorption.
6. This research also showed that the adsorption kinetics modelling studies for the biosorbent dosage of OP, WP and CP followed the second and first order kinetic models.
7. The results obtained from the research indicate that the batch process used to adsorb metal ions from wastewater has a possible application for a proper plant design. The material could be used in big lakes and ponds of water to eliminate metals from the water source.

5.2 Recommendations

The other parameter of importance in adsorption process is to investigate the effect of anions and cations present together in a solution, the effect of temperature and the complex nature of adsorption mechanism needs to be investigated too, as well as the regeneration and reuse of the biosorbent materials.

A further investigation is needed such as generalized adsorption model applicable to sorption phenomenon followed by these materials.

REFERENCES

AbdurRahman, F. B., Akter, M., & Zainal Abedin, M. (2013). Dyes Removal From Textile Wastewater Using Orange Peels. *International journal of scientific & technology research, Volume 2*(9).

Ahmadi, F., Zamiri, M. J., Khorvash, M., Banihashemi, Z., & Bayat, A. R. (2014). Chemical composition and protein enrichment of orange peels and sugar beet pulp after fermentation by two Trichoderma species. *Iranian Journal of Veterinary Research, Shiraz University, 16*(1/50), 25-30.

Ahmed, S., Chughtai, S., & Keane, M. A. (1998). The Removal of Cadmium and Lead from Aqueous Solution by Ion Exchange with Na-Y Zeolite. *Separation and Purification Technology, 13*, 57-64.

Ajmal, M., Khan, A. H., Ahmad, S., & Ahmad, A. (1998). Role of Sawdust in the Removal of Copper (II) from Industrial Wastes. *Water Research, 32(10)*, 3085-3091.

Al-Asheh, S., & Duvnjak, Z. (1997). Sorption of Cadmium and other Heavy Metals by Pine Bark. *Hazardous Material, 56*, 35-51.

Al-Saadi, N. H. M., Ahmad, N. S., & Sa´eed, S. E. (2009). Determination of some chemical compounds and the effect of oil extract from orange peel on some pathogens. *Journal of Kerbala University, 7*(2).

Al Khusaibi, T. M., Dumaran, J. J., Devi, M. G., Rao, L. N., & Feroz, S. (2015). Treatment of Dairy Wastewater using Orange and Banana Peels. *Journal of Chemical and Pharmaceutical Research, Volume 7*(4), 1385-1391.

Alam, M.Z., Ameem, E.S., Muyibi, S.A., and Kabbashi, N.A., (2009): "The factors affecting the performance of activated carbon of prepared from oil palm empty fruit bunches for adsorption of phenol". *Chemical Engineering Journal*, vol. 155, no.1-2, pp. 191-198.

Anastopoulos, I., & Kyzas, G. (2014). Agricultural peels for dye adsorption: A review of recent literature. *Journal of Molecular Liquids, xxx*. doi: http://dx.doi.org/10.1016/j.molliq.2014.11.006

Annadurai, G., Juang, R. S., & Lee, D. I. (2002). Use of Cellulose-Based Waste for Adsorption of Dyes from Aqueous Solutions. *Hazardous Materials, 3(92)*, 263-274.

Annadurai, G., Juang, R. S., & Lee, D. J. (2003). Adsorption of Heavy Metals from Water using Banana and Orange Peels. *Water Science and Technology, Volume 47*(1).

Ayoub, G. M., Semerjian, L., Aera, A., El Fadel, M., & Koopman, B. (2001). Heavy Metal Removal by Coagulation with Seawater Liquid Bittern. *Environmental Engineering, 127(3)*, 196-202.

Babel, S., & Kurniawan, T. A. (2003). Low-Cost Adsorbent for Heavy Metal Uptake from Contaminated Water: A review. *Hazardous Materials, B97*, 219-243.

Bailey, S. E., Olin, T. J., Bricka, R. M., & Adrian, D. D. (1999). A review of potentially low-cost sorbents for heavy metals. *Water Research, 33*, 2469–2479.

Bampidis, V. A., & Robinson, P. H. (2006). Citrus by-products as ruminant feeds: a review. *Anim. Feed Sci. Technol., 128*, 175–217.

Banerjee, K., Ramesh, S.T., Gandhimathi, R., Nidheesh, P.V. & Bharathi K.S (2012) A novel agricultural waste adsorbent, watermelon shell for the removal of copper from aqueous solutions *Iran. J. Energy Environ., 3 (2), pp. 143-156*

Ben-Ali, S., Jaouali, I., Souissi-Najar, S., Ouederni A. (2017). Characterization and adsorption capacity of raw pomegranate peel biosorbent for copper removal. *J. Clean. Prod., 142, pp. 3809-3821*

Benefield, L. D., & Morgan, J. M. (1999). *Chemical Precipitation in Water Quality and Treatment*. New York: McGraw Hill Inc.

Bozie, D., Stankovic, D., Gorgievski, M., Bogdanovic, G., & Kovacevic, R. (2009). Adsorption of heavy metal ions by sawdust of deciduous trees. *Hazardous Materials, 171*, 684-692.

Buffle, J. (1990). *Complexation of Reactions in Aquatic Systems-An Analytical Approach*. Chichester: Ellis Howard Limited.

Campbell, M. (2006). Extraction of Pectin from Watermelon Rind.

Cheng, R. C., Liang, S., & M.D, W. H. C. a. B. (1994). Enhanced coagulation for arsenic removal. *American Water Works Association, 86(9)*, 79-90.

Choi, H., Zhang, K., Dionysiou, D. D., Oerther, D. B., & Sorial, G. A. (2005). Effect of Permeate Flux and Tangential Flow on Membrane Fouling for Wastewater Treatment. *Separation and Purification Technology, 45*, 68-78.

Crist, D. R., Crist, R. H., & Martin, J. R. (2003). A New Process for Toxic Metal Uptake by a Kraft Lignin. *Chemical Technology and Biotechnology, 78*, 199-202.

Crist, R. H., Martin, J. R., & Crist, D. R. (2002). Heavy Metal Uptake by Lignin: Comparison of Biotic Ligand Models with an Ion-Exchange Process. *Environmental Science and Technology, 36*, 1485-1490.

Davis, M. L., (2010). Water and Wastewater Engineering; Design Principles and Practice. McGraw-Hill Inc., USA.

De Gisi, S., Lofrano, G., Grassi, M., & Notarnicola, M. (2016). Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. *Sustainable Materials and Technologies, Volume 9*, 10-40.

Dobrevsky, I., Todorova, D. M., & Panayotova, T. (1996). Electroplating Rinse Wastewater Treatment by Ion Exchange. *Desalination, 108*, 277-280.

Edwards, M. (1994). Chemistry of Arsenic Removal during Coagulation and Fe-Mn Oxidation. *The American Water Works Association, 86(9)*, 64-78.

El-Said, A. G., & Gamal, A. M. (2012). Potential Application of Orange Peel (OP) as an Eco-friendly Adsorbent for Textile Dyeing Effluents. *Journal of Textile and Apparel Technology and Management, Volume 7*(3).

Feumba, D. R., Ashwini, R. P., & Ragu, S. M. (2016). Chemical Composition of some selected Fruit Peels. *European Journal of Food Science and Technology, 4*(4), 12-21.

Fomina, M., & Gadd, G. M. (2013). Biosorption: current perspectives on concept, definition and application, (2013), . *Bioresource Technology*. doi: http://dx.doi.org/10.1016/j.biortech.2013.12.102

Foo, K. Y., & Hameed, B. H. (2012). Preparation, characterization and evaluation of adsorptive properties of orange peel based activated carbon via microwave induced K2CO3. *Bioresource Technology, 104*, 679–686. doi: doi:10.1016/j.biortech.2011.10.005

Gardea-Torresdey, J. L., de la Rosa, G., & Peralta-Videa, J. R. (2004). Use of Phytofiltration Technologies in the Removal of Heavy Metals: A Review. *Pure and Applied Chemistry, 76(4)*, 801-813.

Ghimire, K. N., Inoue, K., Yamaguchi, H., Makino, K., & Miyajima, T. (2003). "Adsorptive separation of arsenate and arsenite anions from aqueous medium by using orange waste". *Water Research, Vol 37*, pp.4945-4953.

Godwin, T. W., & Mercer, E. I. (1972). *Introduction to Plant Biochemistry*. Oxford: Pergamon press.

Green Materials for Sustainable Water Remediation and Treatment. (2013). Cambridge: RSC Publishing.

Gunatilake, S. K. (2015). Methods of Removing Heavy Metals from Industrial Wastewater. *Journal of Multidisciplinary Engineering Science Studies, 1*(1), 12-18.

Hamel, G. (2012). How Does Water Pollution Affect the Environment. *eHow Healthy living.* Retrieved 14/12/2012, 2012, from http://www.ehow.com/how-does_4709768_water-pollution-affect-environment.html

Joshi, N. C. (2017). HEAVY METALS, CONVENTIONAL METHODS FOR HEAVY METAL Removal, Biosorption and the Development of Low Cost Adsorbent. *European Journal o f Pharmaceutical and Medical Research, 4*(2), 388-393.

Juttner, K., Galla, U., & Schmieder, H. (2000). Electrochemical Approaches to Environmental Problems in the Process Industry. *Electrochimica Acta, 45*, 2575-2594.

Kang, M. S., Lee, D. H., & Kima, H. (2007). Biosorption of Cr (III) and Cr (IV) onto the Cell Surface of Pseudomonas Aeruginosa. *Biochemical Engineering, 36*, 54-58.

Kalavathy, M.H., Regupathi, I., Phillai, M.G., and Miranda, L.R., (2009): "Modelling, analysis and optimization of adsorption parameters for H3PO4 activated rubber wood sawdust using response surface methodology (RSM)". *Colloids and Surfaces B: Biointerfaces,* vol. 70, no. 1, p. 35-45.

Khan, S., Farooqi, A., Danish, M. I., & Zeb, A. (2013). Biosorption of Copper (II) from Aqeous Solution using Citrus Sinensis Peel for Purification of Drinking and Waste Water. *International Journal of Research and Reviews in Applied Sciences, 16*(2), 296-306.

Korngold, E., Belayev, N., & Aronov, L. (2003). Removal of Chromates from Drinking Water by Anion Exchangers. *Separation and Purification Technology, 33*, 179-187.

Kushwa, R. K., Bajpai, A., & Malik, S. (2011). Performance of Sewage Treatment Plant with Special Reference to Badwai (STP) Bhopal, (INDIA). *Chemical and Pharmaceutical Research, 3(5)*, 51-55.

Lakshmipathy, R., & Sarada, N. C. (2013). Application of watermelon rind as sorbent for removal of nickel and cobalt from aqueous solution. *International Journal of Mineral Processing, 122*(Supplement C), 63-65. doi: https://doi.org/10.1016/j.minpro.2013.03.002

Lalvani, S. B., Wiltowski, T. S., Murphy, D., & Lalvani, L. S. (1997). Metal Removal from Process Water by Lignin. *Environmental Technology, 18*, 1163-1168.

Lee, S. H., Shon, S. J., Chung, H., Lee, M. Y., & Yang, J. W. (1999). Effect of Chemical Modification on Carboxylate Groups in Apple Residues on Metal Ion Binding. *Korean Journal of Chemical Engineering, 16*, 576-580.

Lesmana, S. O., Febriana, N., Soetaredjo, F. E., Sunarso, J., & Ismadji, S. (2009). Studies on Potential Applications of Biomass for Separation of Heavy Metals from Water and Wastewater. *Biochemical Engineering, 44*, 19-41.

Lima, L.S., Araujo, M.D.M., Quinaia, S.P., Migliorine, D.W. and Garcia, J.R., (2011): "Adsorption modelling of Cr, Cd and Cu on activated carbon of different origins by using fractional factorial design". *Chemical Engineering Journal,* vol. 166, p. 881- 889.

Madaeni, S. S., & Mansourpanah, Y. (2003). COD Removal from Concentrated Wastewater using Membranes. *Filtration and Separation, 40*(6), 40-46.

Mamma, D., Kourtoglou, E., & Christakopoulos, P. (2008). Fungal multienzyme production on industrial by-products of the citrus-processing industry. *Bioresour. Technol., 99*, 2373–2383.

Michalak, I., Chojnacka, K., & Witek-Krowiak, A. (2013). State of the Art for the Biosorption Process—a Review. *Applied Biochemistry and Biotechnology, 170*(6), 1389-1416.

Mohammed, R. R., & Chong, M. F. (2014). Treatment and decolourization of biologically treated Palm Oil Mill Effluent (POME) using banana peel as novel biosorbent,. *J. Environ. Manag, 132*, 237–249.

Mohan, D., Pittman, C. U. J., & Steele, P. H. (2006). Single, Binary and Multicomponent Adsorption of Copper and Cadmium from Aqueous Solutions on Kraft Lignin-a Biosorbent. *Colloid and Interface Science, 297*, 489-504.

Moubarak, F., Atmani, R., Maghri, I., Elkouali, M., Talbi, M., & Latifa, M. (2014). Elimination of Methylene Blue dye with natural adsorbent "Banana Peels Powder. *Glob. J. Sci. Front. Res. B Chem, 14*, 39–44.

Mustapha, M. U., & Halimoon, N. (2015). Microorganisms and Biosorption of Heavy Metals in the Environment: A Review Paper. *Microbial & Biochemical Technology, Volume 7*(5), 253-256. doi: http://dx.doi.org/10.4172/1948-5948.1000219

Ning, R. Y. (2002). "Arsenic Removal by Reverse Osmosis". *Desalination, Vol 143*, pp.237-241. Öktem, Y. A., Pozan Soylu, G. S., & Aytan, N. (2012). The adsorption of Methylene Blue from aqueous solution by using waste potato peels; Equilibrium and kinetic studies. *J. Sci. Ind. Res., 71*, 817–821.

Olson, D. A. (2016). Medscape. *emedicine*. http://emedicine.medscape.com/article/1175560-overview

Parmar, M., & Thakur, L. S. (2013). Heavy Metal CU, NI AND ZN: Toxicity, Health Hazards and their removal techniques by low cost adsorbent: A short overview. *International Journal of Plant, Animal and Environmental Sciences, 3*(3), 143 - 152.

Perez-Marin, A. B., Mesegaer, Z. V., Ortuno, J. F., Aguilar, M., Saez, J., & Liorens, M. (2007). Removal of Cadmium from Aqueous Solutions by Adsorption onto Orange Waste. *Hazardous Material, B139*, 122-131.

Persin, F., & Rumean, M. (1989). Electrochemical Treatment of Waters and Effluents. *Water Tribune, 3*(42), 45-46.

Potts, D. E., Ahlert, R. C., & Wang, S. S. (1981). A Critical Review of Fouling of Reverse Osmosis Membranes. *Desalination, 36*, 235-264.

Prabhat, K. R., (2016). Particulate Matter and its Size Fractionation - Biomagnetic Monitoring of Particulate Matter, https://www.sciencedirect.com/topics/earth-and-planetary-sciences/environmental-pollution

Prince, O. U., Ugochukwu, E. and Chibuzo, V. O., (2020) Environmental pollution: causes, effects, and the remedies - Microorganisms for Sustainable Environment and Health Ch 21, Pg 419-429

Rahate, M. V. (2010). "Green Approach for Low Cost Treatment of Water". 12-22.

Rahate, M. V., Deshmukh, P., Labhasetwar, P., Shukla, S., & Mhaisalkar, V. (2013). Low Cost Efficient Treatment for Contaminated Water. *13th edition of the World Wide Workshop for Young Environmental Scientists*.

Rao, M., & Parwate, A. V. (2002). Utilization of low-cost adsorbents for the removal of heavy metals from wastewater – a review. *J. Environ. Pollut. Control, 5*, 12-23.

Ravat, C., Monteil-Rivera, F., & Dumoneeau, J. (2000). "Metal ions binding to natural organic matter extracted from wheat barn: Application of surface complexation model.". *Journal of Colloid and Interface Science, Vol 225*, pp.329-339.

Reddy, N. A., Lakshmipathy, R., & Sarada, N. C. (2014). Application of Citrullus lanatus rind as biosorbent for removal of trivalent chromium from aqueous solution. *Alexandria Engineering Journal, 53*(4), 969-975. doi: https://doi.org/10.1016/j.aej.2014.07.006

Rengaraj, S., Yeon, K. H., & Moon, S. H. (2001). "Removal of Chromium from Water and Wastewater by Ion Exchange Resins". *Journal of Hazardous Materials, Vol 87*, 273-287.

Rorrer, G. L. (1998). “Heavy Metal Ions Removal from Wastewater” *Encyclopedia of Environmental Analysis and Remediation* (Vol. Vol 4, pp. pp.2104-2128).

Roy, P., Mondal, N.K. and Das, K., (2013): "Modelling of the adsorptive removal of arsenic: A statistical approach". *Journal of Environmental Chemical Engineering,* http://dx.doi.org/10.1016/j.jece.2013.10.014.

Sarkanen, K. V., & Ludwig, C. H. (1971). *“Lignins: Occurrence, Formation, Structure and Reactions"*. New York: Wiley Interscience.

Schiewer, S. & Volesky, B. (2000). Biosorption processes for heavy metal removal Environmental Microbe-metal Interactions, *American Society of Microbiology, pp. 329-362*

Shamim, S., (2018). Biosorption of Heavy Metals, Biosorption, Jan Derco and Branislav Vrana, IntechOpen, DOI: 10.5772/intechopen.72099. Available from: https://www.intechopen.com/books/biosorption/biosorption-of-heavy-metals

Shammas, N. K. (2004). *"Coagulation and Flocculation in Physicochemical Treatment Processes"* (Vol. Vol 3). Totowa: The Humana Press.

Sharma, N., Tiwari, D. P., & Singh, S. K. (2014). The efficiency appraisal for removal of Malachite Green by potato peel and neem bark: isotherm and kinetic studies. *Int. J. Chem. Environ. Eng*, *5*, 84–88.

Shuaibu-Imodagbe, E. M., Okuofu, C. A., & Unyimadu, J. P. (2013). Water Quality and Syndicated lead Burden of a Community Drinking Water. *Ethiopian Journal of Environmental Studies and Management*, *6*(4), 405.

Shi, M., Wang, Z., and Zheng, Z., (2013): "Effect of Na^+ impregnated activated carbon on the adsorption of NH^+_4N from aqueous solution". *Journal of Environmental Science,* vol. 25: p. 1501-1510.

Singh, H., Chauhan, G., Jain, A. K., & Sharma, S. K. (2017). Adsorptive potential of agricultural wastes for removal of dyes from aqueous solutions. *Journal of Environmental Chemical Engineering, Volume 5*, 122-135.

Singh, R., Kumar, J. C., & Nandpuri, K. S. (1975). “A Study on the Influence of the Structural Chemical Constituents of the Skin of Water Melon (Citrullus Lanatus Sch.) Fruit on the Incidence of its Blossom-End-Rot and Cracking”. *The Indian Journal of Horticulture, Vol 32*(1/2), pp98-101.

Slater, C. S., Ahlert, R. C., & Uchrin, C. G. (1983). “Applications of Reverse Osmosis to Complex Industrial Wastewater Treatment”. *Desalination, Vol 48*, pp171-187.

Srivastava, S. K., Bhattacharjee, G., Tyagi, R., Pant, N., & Pal, N. (1988). “Studies on the Removal of Some Toxic Metal-Ions from Aqueous Solutions and Industrial Waste. Part 1(Removal of Lead and Cadmium by Hydrous Iron and Aluminum Oxide)”. *Environmental Technology Letters, Vol 9*(10), pp1173-1185.

Sudha, B. R., & Abraham, E. (2003). Studies on chromium (VI) adsorption using immobilized fungal biomass. *Biores. Technol, 87*, 17-26.

Thakur, Y., Kumar, M., & Singh, S. (2015). Microbial Biosorption as a Green Technology for Bioremediation of Heavy. *Research Journal of Pharmaceutical, Biological and Chemical, 6*(3), 1717-1724.

Tripathi, A., & Srivastava, S. K. (2011). *International Journal of Bioscience, Biochemistry and Bioinformatics, Vol 1*(1).

Tunay, O. (2003). “Developments in the Application of Chemical Technologies to Wastewater Treatment”. *Water Science and Technology, Vol 48*, pp.43-52.

Ujang, Z., & Anderson, G. K. (1996). "Application of Low-Pressure Reverse Osmosis Membrane for Zn2+ and cu2+ Removal from Wastewater". *Water Science and Technology, Vol 34*(9), pp247-253.

Vhahangwele Masindi and Khathutshelo L. Muedi (2018). Environmental Contamination by Heavy Metals, Heavy Metals, Hosam El-Din M. Saleh and Refaat F. Aglan, IntechOpen, DOI: 10.5772/intechopen.76082. Available from: https://www.intechopen.com/books/heavy-metals/environmental-contamination-by-heavy-metals

Vigneswaran, S., Ngo, H. H., Chaudhary, D. S., & Hung, Y. T. (2004). *"Physico-Chemical Treatment Pocesses for Water Reuse". In L.K. Wang, Y.T. Hung and N.K. Shammas (Eds.)* (Vol. Vol 3). New Jersey: Humana Press.

Vik, E. I., Carlsoon, D. A., Eikum, A. S., & Gjessing, E. T. (1984). "Electrocoagulation of Portable Water". *Water Research, Vol 18*, 1355-1360, .

Wang, L. K., Vaccari, D. A., Li, Y., & Shammas, N. K. (2004). *"Chemical Precipitation, in L.K. Wang, Y.T. Hung, N.K. Shammas (Eds.), Physicochemical Treatment Processes"* (Vol. Vol 3). New Jersey: Humana Press.

Xie, Z., Guan, W., Ji, F., Song, Z., & Zhao, Y. (2014). Production of Biologically Activated Carbon from Orange Peel and Landfill Leachate Subsequent Treatment Technology. *Journal of Chemistry, 2014*. doi: http://dx.doi.org/10.1155/2014/491912

Yang, X. J., Fane, A. G., & Mac Naughton, S. (2001). "Removal and Recovery of Heavy Metals from Wastewater by Supported Liquid Membranes". *Water Science and Technology, Vol 43*, pp.341-348.

World Bank (1995). Nigeria Strategic Options for Redressing Industrial Pollution World Bank, Industry and Energy Division. 1st Edn, West Central Africa Department, Annexes, pp: 60-62.

Zhexian, X., Yanru, T., Xiaomin, L., Yinghui, L., & Fang, L. (2006). "Study on the Equilibrium, Kinetics and Isotherm of Biosorption of Lead Ions onto Pretreated Chemically Modified Orange Peel". *Biochemical Engineering Journal, Vol 31*(2), pp.160-164.

APPENDICES

APPENDIX A: EFFECT OF EQUILBRIUM TIME ON THE SORPTION OF MERCURY, CADMIUM AND LEAD METAL IONS USING BIOSORBENTS

A1: Results of the effect of equilibrium time on the sorption of mercury, cadmium and lead ions using orange peel

Time	**Mercury**			**Cadmium**			**Lead**		
(Mins)	**C_i**	**C_e**	**R_e (%)**	**C_i**	**C_e**	**R_e (%)**	**C_i**	**C_e**	**R_e (%)**
10	1.208	0.181	85.02	0.466	0.031	93.24	0.118	0.0206	82.54
20	1.208	0.039	96.77	0.466	0.026	94.46	0.118	0.0148	87.45
30	1.208	0.065	94.62	0.466	0.032	93.04	0.118	0.0145	87.71
40	1.208	0.037	96.94	0.466	0.029	93.67	0.118	0.0102	91.35
60	1.208	0.189	84.36	0.466	0.022	95.19	0.118	0.0084	92.88
80	1.208	0.043	96.44	0.466	0.022	95.21	0.118	0.0085	92.79
100	1.208	0.045	96.27	0.466	0.022	95.30	0.118	0.0083	92.96
120	1.208	0.044	96.36	0.466	0.022	95.28	0.118	0.0081	93.13

A2: Results of the effect of equilibrium time on the sorption of mercury, cadmium and lead ions using watermelon peel

Time	**Mercury**			**Cadmium**			**Lead**		
(Mins)	**C_i**	**C_e**	**R_e (%)**	**C_i**	**C_e**	**R_e (%)**	**C_i**	**C_e**	**R_e (%)**
10	1.2088	0.254	78.9874	0.466	0.0309	93.3691	0.118	0.0167	85.8475
20	1.2088	0.243	79.8974	0.466	0.0306	93.4335	0.118	0.0158	86.6102
30	1.2088	0.203	83.2065	0.466	0.0305	93.4549	0.118	0.0164	86.1017
40	1.2088	0.198	83.6201	0.466	0.0279	94.0129	0.118	0.0132	88.8136

60	1.2088	0.183	84.8610	0.466	0.0267	94.2704	0.118	0.0138	88.3051
80	1.2088	0.188	84.4474	0.466	0.0261	94.3991	0.118	0.0136	88.4746
100	1.2088	0.182	84.9437	0.466	0.0270	94.2060	0.118	0.0138	88.3051
120	1.2088	0.185	84.6956	0.466	0.0266	94.2918	0.118	0.0134	88.6441

A3: Results of the effect of equilibrium time on the sorption of mercury, cadmium and lead ions using combination peel

Time	**Mercury**			**Cadmium**			**Lead**		
(Mins)	**C_i**	**C_e**	**R_e (%)**	**C_i**	**C_e**	**R_e (%)**	**C_i**	**C_e**	**R_e (%)**
10	1.2088	0.185	84.6956	0.466	0.0274	94.1202	0.118	0.0182	84.5763
20	1.2088	0.163	86.5156	0.466	0.0294	93.6910	0.118	0.0080	93.2203
30	1.2088	0.193	84.0338	0.466	0.0312	93.3047	0.118	0.0102	91.3559
40	1.2088	0.156	87.0946	0.466	0.0266	94.2918	0.118	0.0176	85.0847
60	1.2088	0.138	88.5837	0.466	0.0300	93.5622	0.118	0.0145	87.7119
80	1.2088	0.136	88.7492	0.466	0.0267	94.2704	0.118	0.0081	93.1356
100	1.2088	0.139	88.5010	0.466	0.0261	94.3991	0.118	0.0093	92.1186
120	1.2088	0.140	88.4183	0.466	0.0263	94.3562	0.118	0.0082	93.0508

APPENDIX B: EFFECT OF BIOSORBENT DOSAGE ON THE SORPTION OF MERCURY, CADMIUM AND LEAD IONS

B1: Results of the effect of biosorbent dosage on the sorption of mercury, cadmium and lead ions using orange peel

Dosage	**Mercury**			**Cadmium**			**Lead**		
(g)	**C_i**	**C_e**	**R_e (%)**	**C_i**	**C_e**	**R_e (%)**	**C_i**	**C_e**	**R_e (%)**
0.5	1.2088	0.3020	75.0165	0.466	0.0177	96.2017	0.118	0.0327	72.2881
1.0	1.2088	0.2110	82.5447	0.466	0.0168	96.3948	0.118	0.0308	73.8983

1.5	1.2088	0.1980	83.6201	0.466	0.0124	97.3391	0.118	0.0296	74.9153
2.0	1.2088	0.1020	91.5619	0.466	0.0050	98.9270	0.118	0.0134	88.6441
2.5	1.2088	0.0800	93.3819	0.466	0.0106	97.7253	0.118	0.0105	91.1017

B2: Results of the effect of biosorbent dosage on the sorption of mercury, cadmium and lead ions using watermelon peel

Dosage	**Mercury**			**Cadmium**			**Lead**		
(g)	**C_i**	**C_e**	**R_e (%)**	**C_i**	**C_e**	**R_e (%)**	**C_i**	**C_e**	**R_e (%)**
0.5	1.2088	0.3870	67.9848	0.466	0.0233	95.0000	0.118	0.0303	74.3220
1.0	1.2088	0.2744	77.2998	0.466	0.0272	94.1631	0.118	0.0287	75.6780
1.5	1.2088	0.1830	84.8610	0.466	0.0234	94.9785	0.118	0.0203	82.7966
2.0	1.2088	0.1028	91.4957	0.466	0.0227	95.1288	0.118	0.0106	91.0169
2.5	1.2088	0.1003	91.7025	0.466	0.0201	95.6867	0.118	0.0102	91.3559

B3: Results of the effect of biosorbent dosage on the sorption of mercury, cadmium and lead Ions using combination peel

Dosage	**Mercury**			**Cadmium**			**Lead**		
(g)	**C_i**	**C_e**	**R_e (%)**	**C_i**	**C_e**	**R_e (%)**	**C_i**	**C_e**	**R_e (%)**
0.5	1.2088	0.289	76.0920	0.466	0.0268	94.2489	0.118	0.0354	70.0000
1.0	1.2088	0.264	78.1602	0.466	0.0232	95.0215	0.118	0.0322	72.7119
1.5	1.2088	0.201	83.3719	0.466	0.0231	95.0429	0.118	0.0239	79.7458
2.0	1.2088	0.157	87.0119	0.466	0.0188	95.9657	0.118	0.0201	82.9661
2.5	1.2088	0.15	87.5910	0.466	0.0183	96.0730	0.118	0.0198	83.2203

APPENDIX C: EFFECT OF pH ON THE SORPTION OF MERCURY, CADMIUM AND LEAD METAL IONS

C1: Results of the effect of pH on the sorption of Mercury, Cadmium and Lead Ions using Orange Peel

pH	Mercury			Cadmium			Lead		
	C_i	C_e	R_e (%)	C_i	C_e	R_e (%)	C_i	C_e	R_e (%)
1.01	1.2088	0.319	73.6102	0.466	0.331	28.9700	0.118	0.0761	35.5085
2.50	1.2088	0.218	81.9656	0.466	0.085	81.7597	0.118	0.0062	94.7458
4.58	1.2088	0.086	92.8855	0.466	0.066	85.8369	0.118	0.0055	95.3390
5.69	1.2088	0.076	93.7128	0.466	0.028	93.9914	0.118	0.0110	90.6780
6.76	1.2088	0.101	91.6446	0.466	0.058	87.5536	0.118	0.0097	91.7797
7.74	1.2088	0.085	92.9682	0.466	0.035	92.4893	0.118	0.0076	93.5593
9.14	1.2088	0.112	90.7346	0.466	0.063	86.4807	0.118	0.0061	94.8305
10.63	1.2088	0.121	89.9901	0.466	0.075	83.9056	0.118	0.0087	92.6271

C2: Results of the effect of pH on the sorption of mercury, cadmium and lead ions using watermelon peel

pH	Mercury			Cadmium			Lead		
	C_i	C_e	R_e (%)	C_i	C_e	R_e (%)	C_i	C_e	R_e (%)
1.01	1.2088	0.093	92.3064	0.466	0.048	89.6996	0.118	0.0022	98.1356
2.50	1.2088	0.101	91.6446	0.466	0.031	93.3476	0.118	0.0071	93.9831
4.58	1.2088	0.102	91.5619	0.466	0.026	94.4206	0.118	0.0083	92.9661
5.69	1.2088	0.096	92.0582	0.466	0.028	93.9914	0.118	0.0030	97.4576
6.76	1.2088	0.097	91.9755	0.466	0.030	93.5622	0.118	0.0029	97.5424
7.74	1.2088	0.138	88.5837	0.466	0.019	95.9227	0.118	0.0017	98.5593
9.14	1.2088	0.100	91.7273	0.466	0.022	95.2790	0.118	0.0031	97.3729

10.63	1.2088	0.122	89.9073	0.466	0.020	95.7082	0.118	0.0012	98.9831

C3: Results of the effect of pH on the sorption of mercury, cadmium and lead ions using combination peel

pH	Mercury			Cadmium			Lead		
	C_i	C_e	R_e (%)	C_i	C_e	R_e (%)	C_i	C_e	R_e (%)
1.01	1.2088	0.159	86.8465	0.466	0.232	50.2146	0.118	0.0472	60.0000
2.50	1.2088	0.128	89.4110	0.466	0.0558	88.0258	0.118	0.0079	93.3051
4.58	1.2088	0.092	92.3891	0.466	0.0327	92.9828	0.118	0.0063	94.6610
5.69	1.2088	0.038	96.8564	0.466	0.0266	94.2918	0.118	0.0054	95.4237
6.76	1.2088	0.068	94.3746	0.466	0.0193	95.8584	0.118	0.0048	95.9322
7.74	1.2088	0.086	92.8855	0.466	0.0293	93.7124	0.118	0.0077	93.4746
9.14	1.2088	0.095	92.1410	0.466	0.0351	92.4678	0.118	0.0085	92.7966
10.63	1.2088	0.074	93.8782	0.466	0.0331	92.8970	0.118	0.0096	91.8644

APPENDIX D: SORPTION ISOTHERM MODELLING OF MERCURY, CADMIUM AND LEAD IONS

D1: Isotherm modelling of the effect of time on the sorption of mercury ions using orange peel

Co	Ce	qe	1/Ce	1/qe	log Ce	log qe
1.2088	0.181	0.0257	5.525	38.918	-0.742	-1.590
1.2088	0.039	0.0292	25.641	34.194	-1.409	-1.534
1.2088	0.065	0.0286	15.385	34.971	-1.187	-1.544
1.2088	0.037	0.0293	27.027	34.136	-1.432	-1.533
1.2088	0.189	0.0255	5.291	39.223	-0.724	-1.594
1.2088	0.043	0.0291	23.256	34.311	-1.367	-1.535
1.2088	0.045	0.0291	22.222	34.370	-1.347	-1.536

1.2088	0.044	0.0291	22.727	34.341	-1.357	-1.536

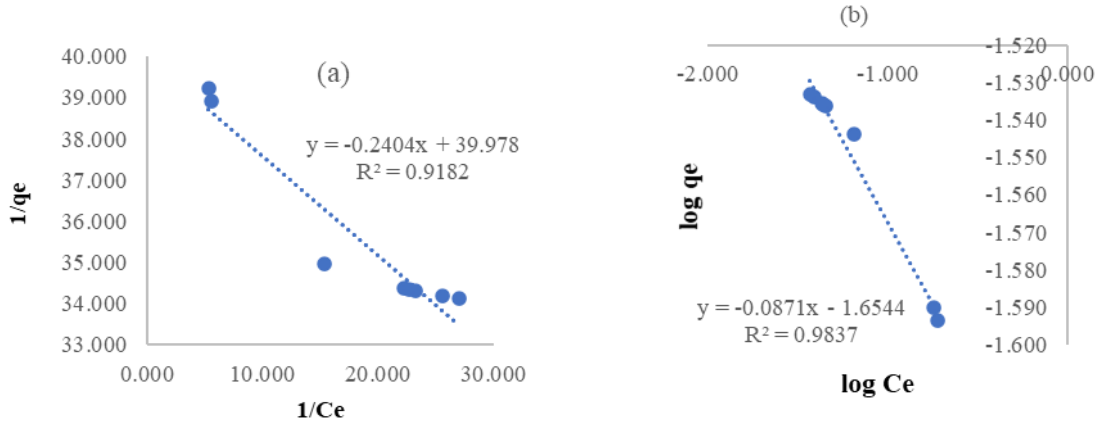
D2: Isotherm modelling of the effect of time on the sorption of cadmium ions using orange peel

Co	Ce	qe	1/Ce	1/qe	log Ce	log qe
0.466	0.0315	0.0109	31.746	92.060	-1.502	-1.964
0.466	0.0258	0.0110	38.760	90.868	-1.588	-1.958
0.466	0.0324	0.0108	30.864	92.251	-1.489	-1.965
0.466	0.0295	0.0109	33.898	91.638	-1.530	-1.962
0.466	0.0224	0.0111	44.643	90.171	-1.650	-1.955
0.466	0.0223	0.0111	44.843	90.151	-1.652	-1.955
0.466	0.0219	0.0111	45.662	90.070	-1.660	-1.955
0.466	0.022	0.0111	45.455	90.090	-1.658	-1.955

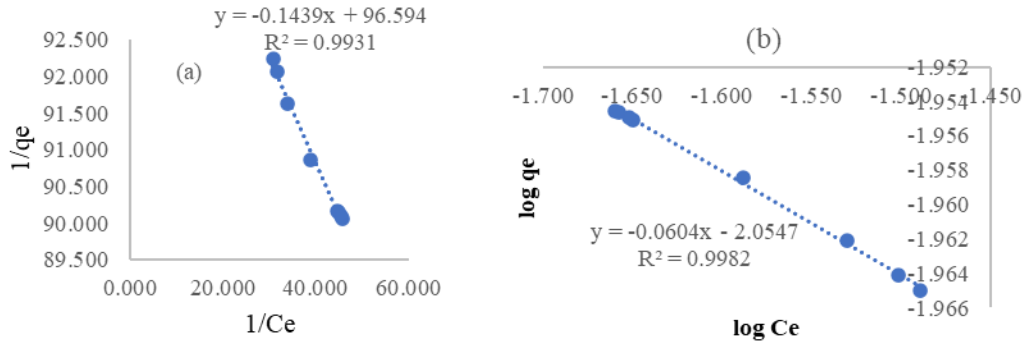
D3: Isotherm modelling of the effect of time on the sorption of lead ions using orange peel

Co	Ce	qe	1/Ce	1/qe	log Ce	log qe
0.118	0.0206	0.0024	48.54369	410.6776	-1.686	-2.6135
0.118	0.0148	0.0026	67.56757	387.5969	-1.830	-2.58838
0.118	0.0145	0.0026	68.96552	386.4734	-1.839	-2.58712
0.118	0.0102	0.0027	98.03922	371.0575	-1.991	-2.56944
0.118	0.0084	0.0027	119.0476	364.9635	-2.076	-2.56225
0.118	0.0085	0.0027	117.6471	365.2968	-2.071	-2.56265
0.118	0.0083	0.0027	120.4819	364.6308	-2.081	-2.56185
0.118	0.0081	0.0027	123.4568	363.9672	-2.092	-2.56106

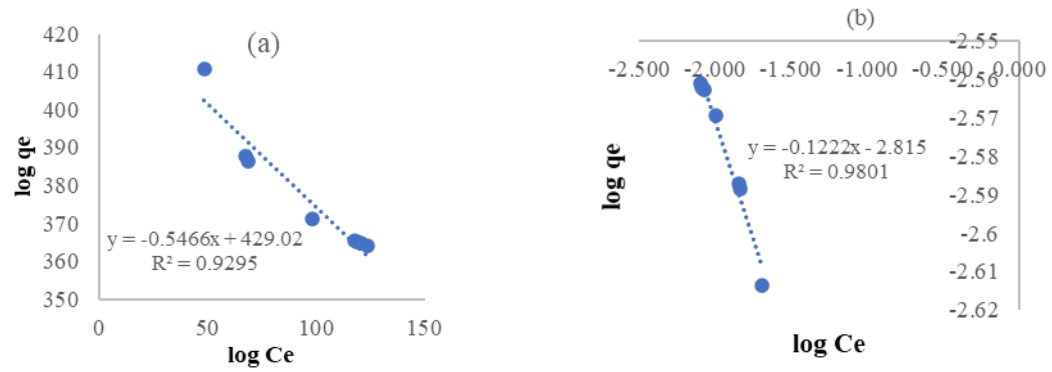
APPENDIX E: LINEAR FITTINGS OF THE ISOTHERMS OF MERCURY, CADMIUM AND LEAD IONS USING THE BIOSORBENTS



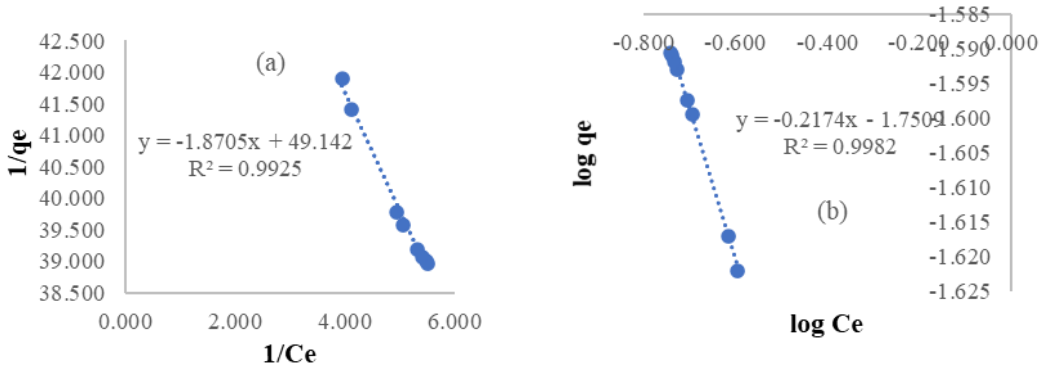
E1: Fitting of isotherm time data for mercury on orange peel using (a) Langmuir and (b) Freundlich



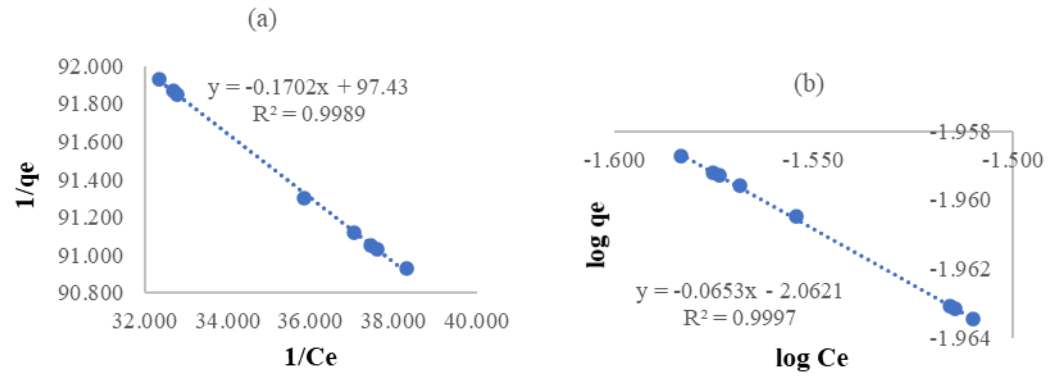
E2: Fitting of isotherm time data for cadmium on orange peel using (a) Langmuir and (b) Freundlich



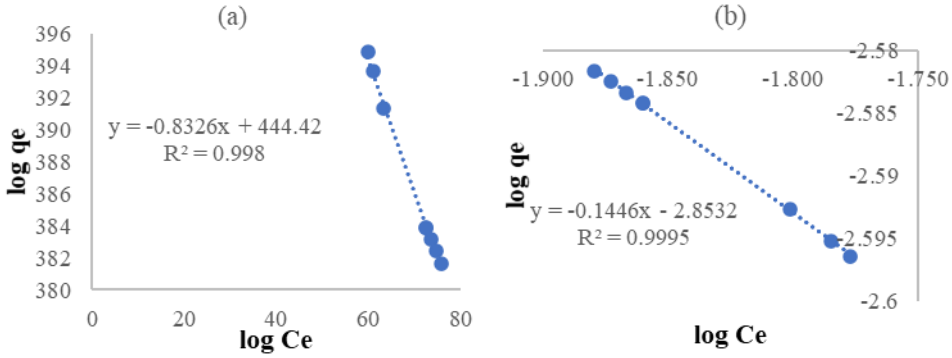
E3: Fitting of isotherm time data for lead on orange peel using (a) Langmuir and (b) Freundlich



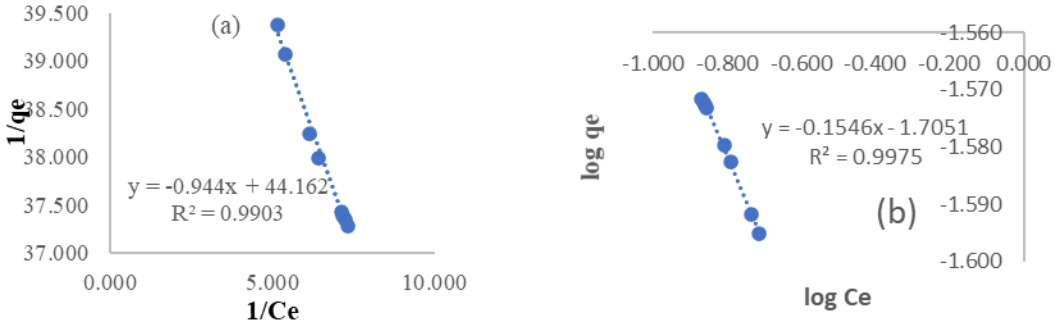
E4: Fitting of isotherm time data for mercury on watermelon peel using (a) Langmuir and (b) Freundlich



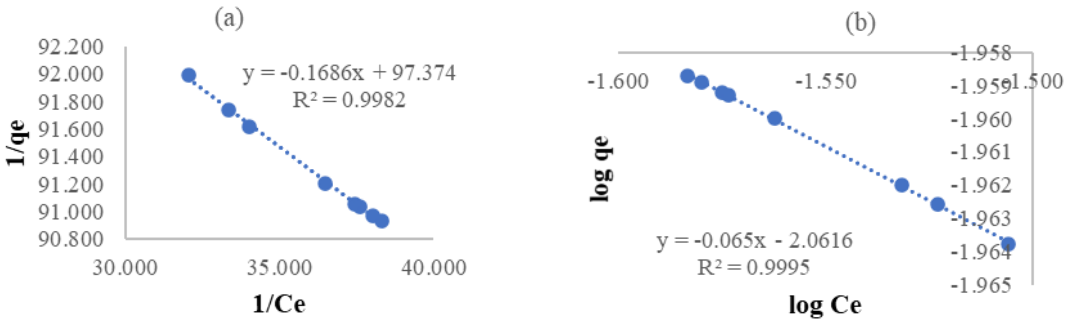
E5: Fitting of isotherm time data for cadmium on watermelon peel using (a) Langmuir and (b) Freundlich



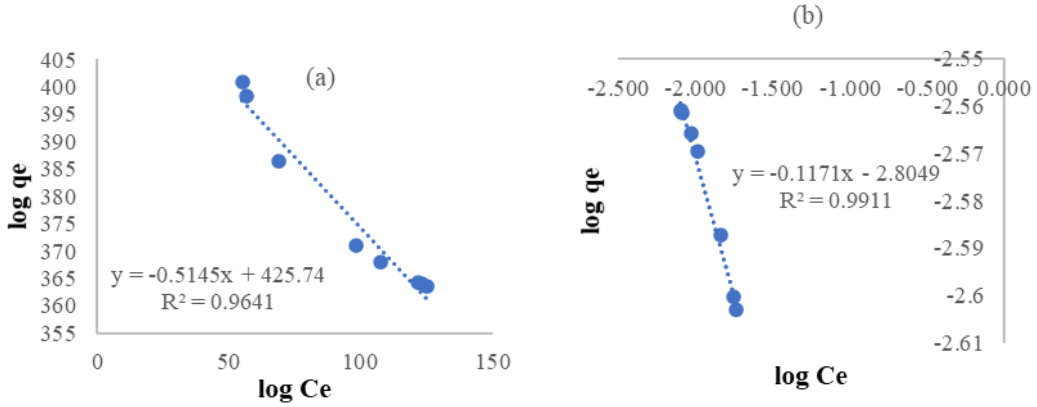
E6: Fitting of isotherm time data for lead on watermelon peel using (a) Langmuir and (b) Freundlich



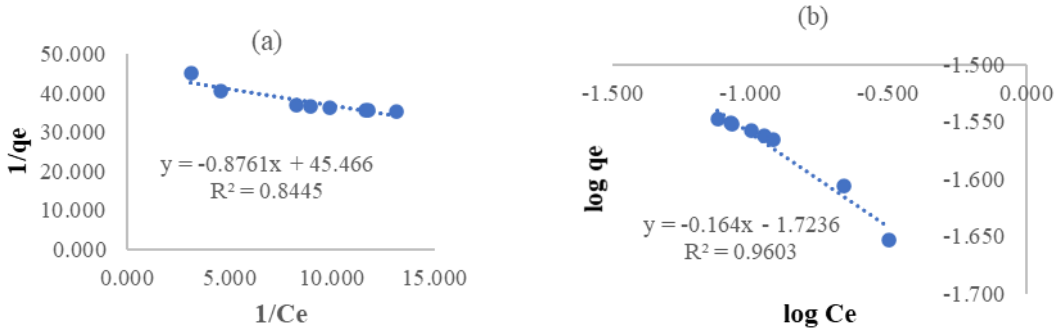
E7: Fitting of isotherm time data for mercury on combination peel using (a) Langmuir and (b) Freundlich



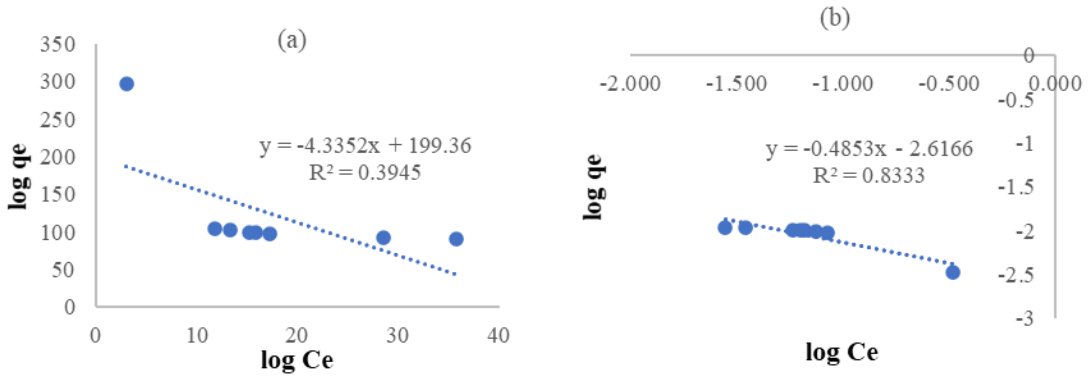
E8: Fitting of isotherm time data for cadmium on combination peel using (a) Langmuir and (b) Freundlich



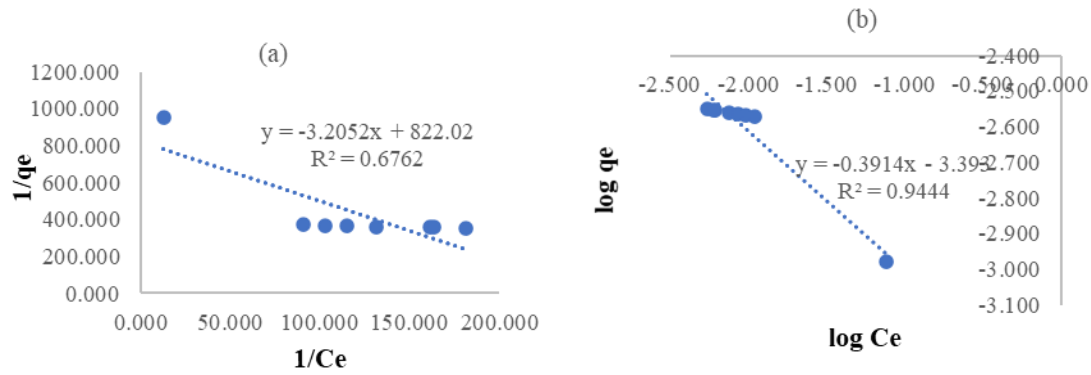
E9: Fitting of isotherm time data for lead on combination peel using (a) Langmuir and (b) Freundlich



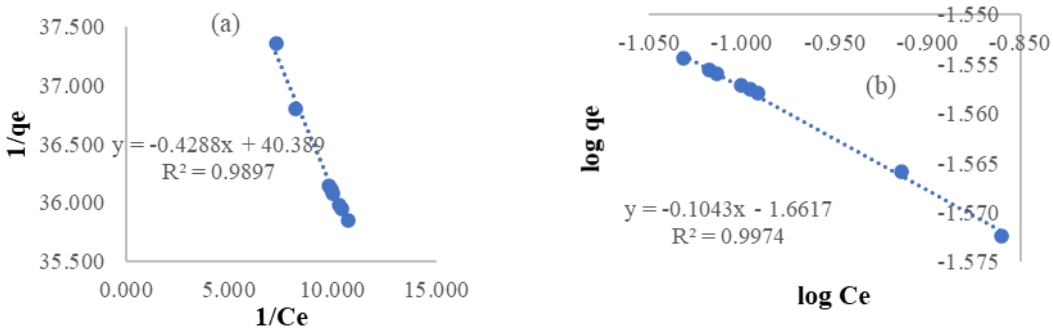
E10: Fitting of isotherm pH data for mercury on orange peel using (a) Langmuir and (b) Freundlich



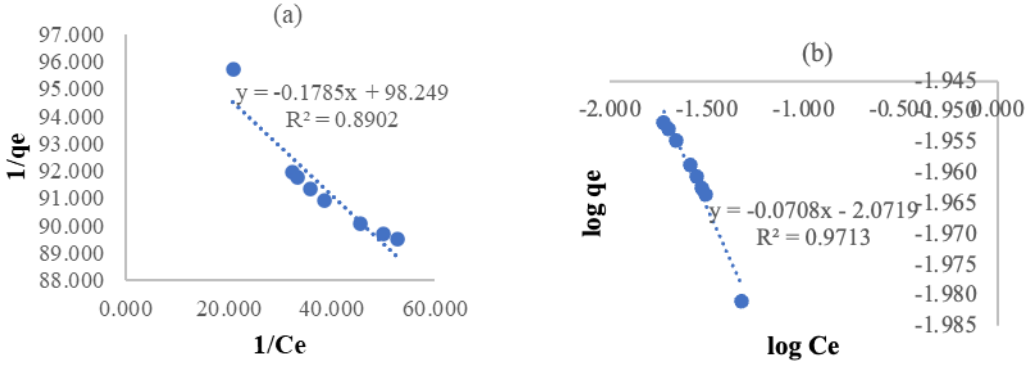
E11: Fitting of isotherm pH data for cadmium on orange peel using (a) Langmuir and (b) Freundlich



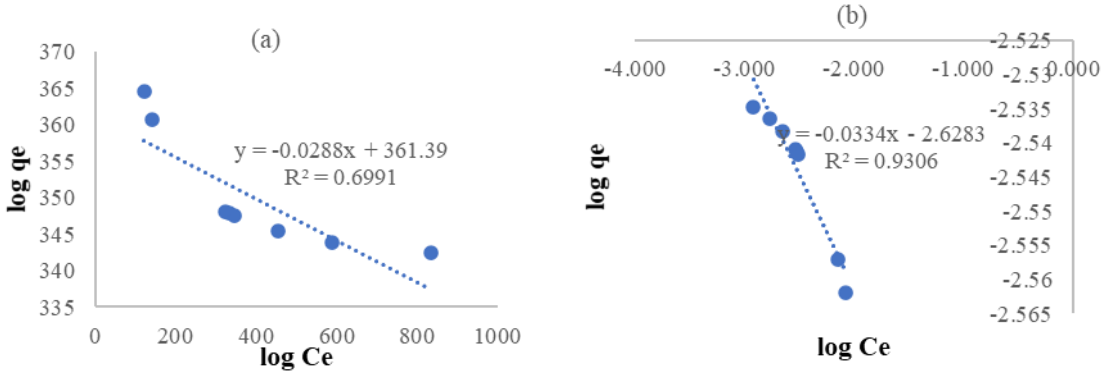
E12: Fitting of isotherm pH data for lead on orange peel using (a) Langmuir and (b) Freundlich



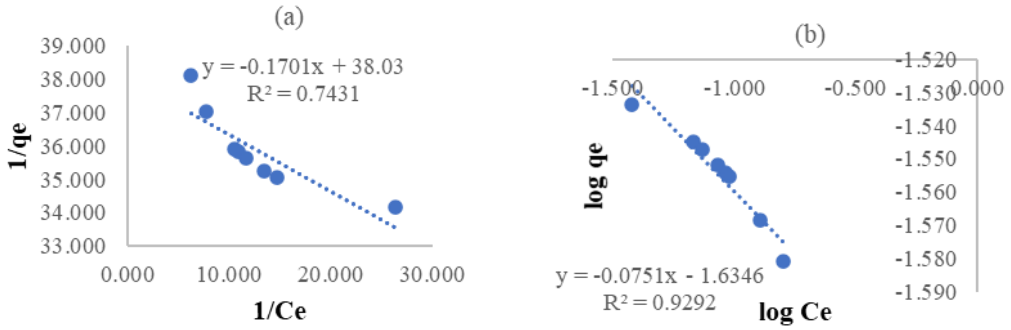
E13: Fitting of isotherm pH data for mercury on watermelon peel using (a) Langmuir and (b) Freundlich



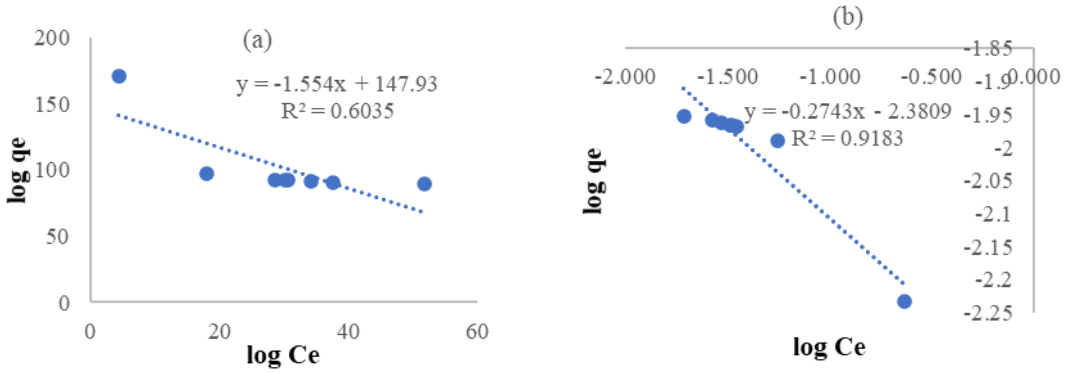
E14: Fitting of isotherm pH data for cadmium on watermelon peel using (a) Langmuir and (b) Freundlich



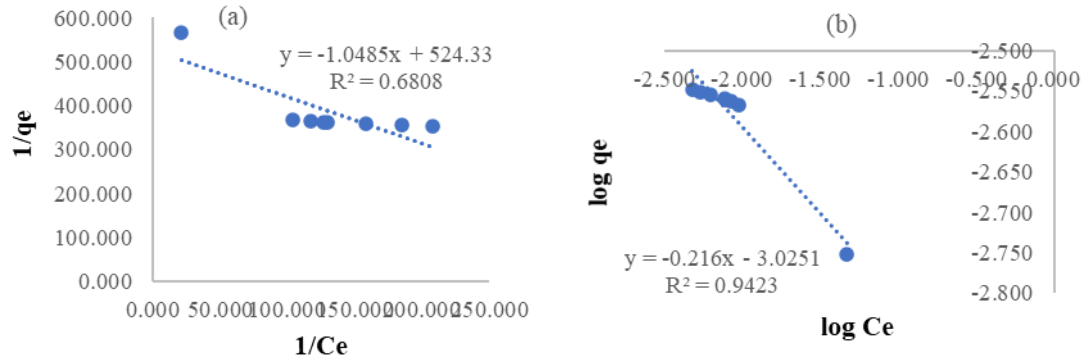
E15: Fitting of isotherm pH data for lead on watermelon peel using (a) Langmuir and (b) Freundlich



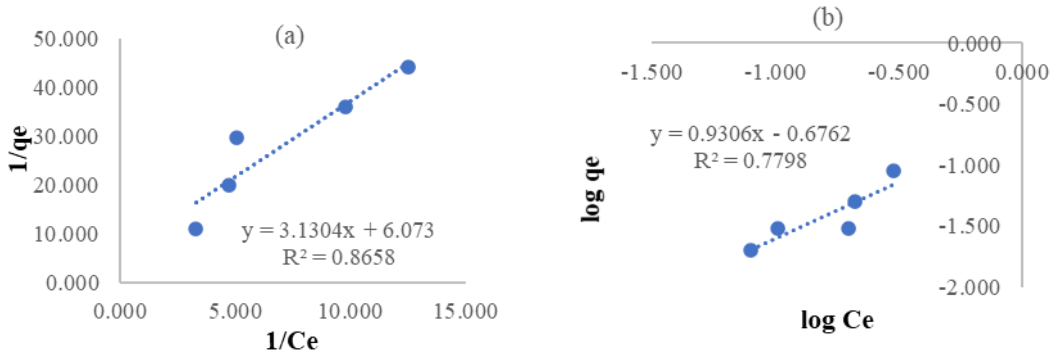
E16: Fitting of isotherm pH data for mercury on combination peel using (a) Langmuir and (b) Freundlich



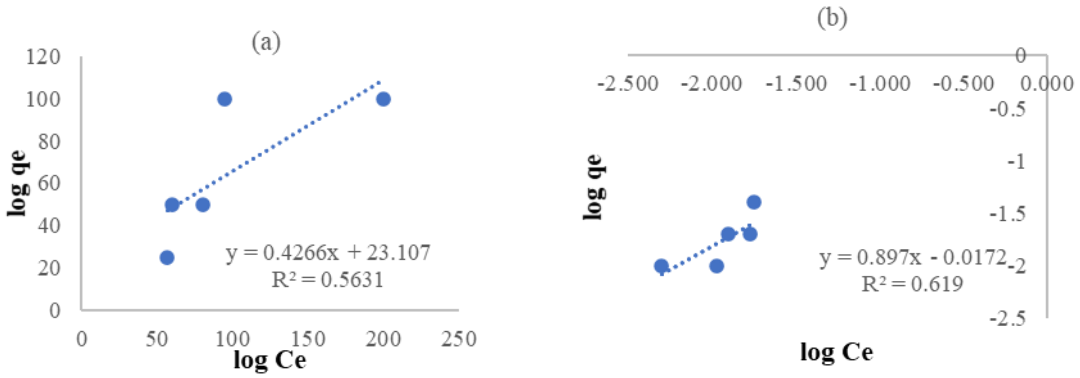
E17: Fitting of isotherm pH data for cadmium on combination peel using (a) Langmuir and (b) Freundlich



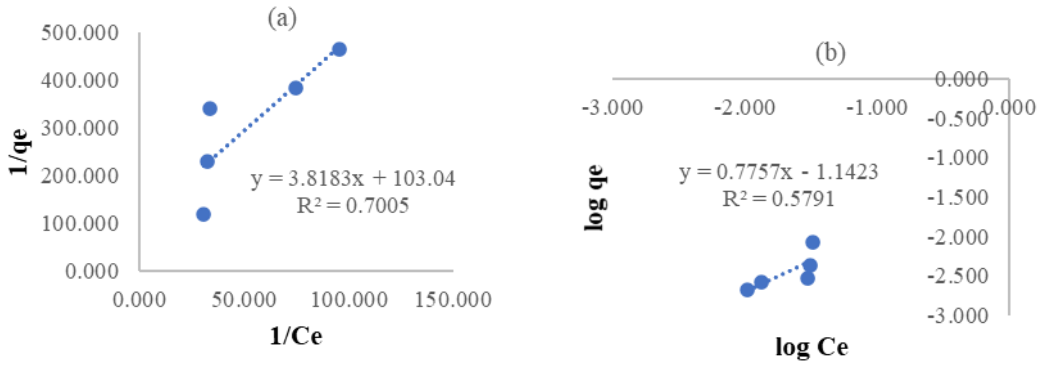
E18: Fitting of isotherm pH data for lead on combination peel using (a) Langmuir and (b) Freundlich



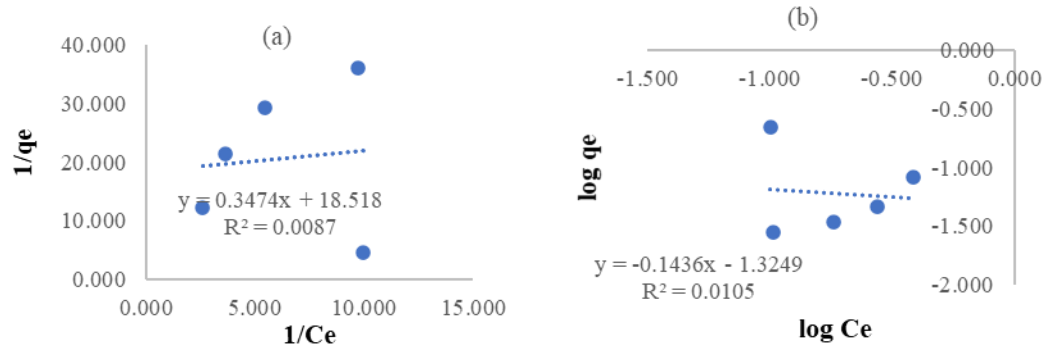
E19: Fitting of isotherm dosage data for mercury on orange peel using (a) Langmuir and (b) Freundlich



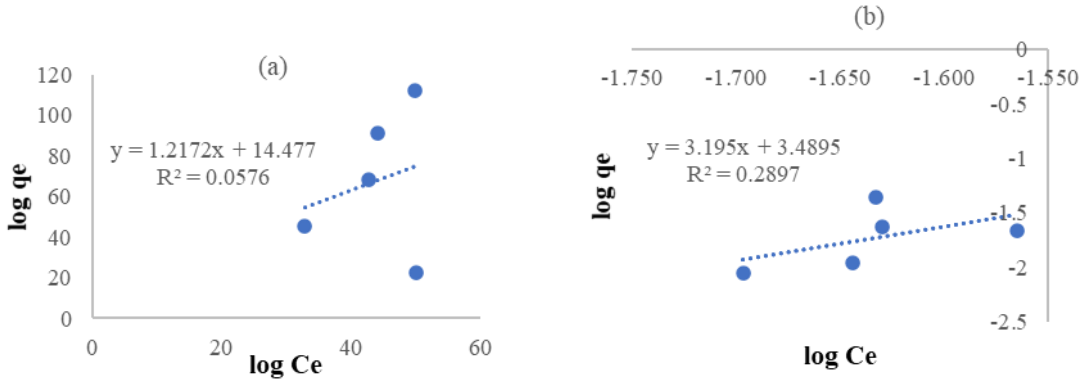
E20: Fitting of isotherm dosage data for cadmium on orange peel using (a) Langmuir and (b) Freundlich



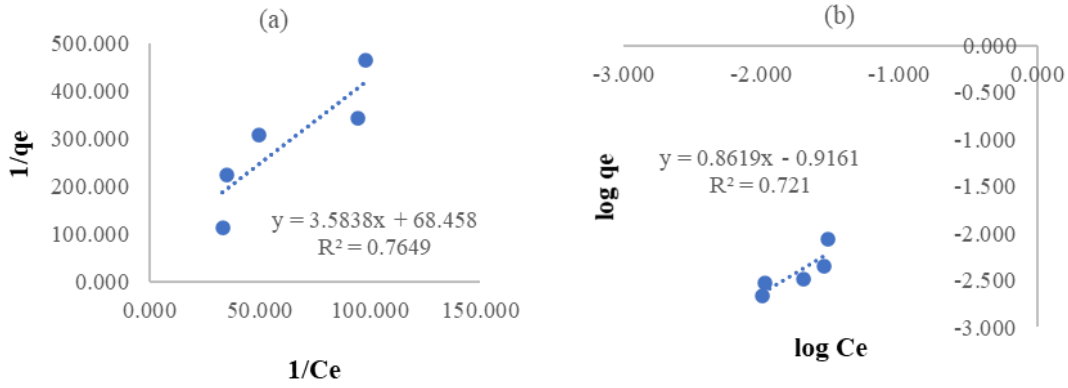
E21: Fitting of isotherm dosage data for lead on orange peel using (a) Langmuir and (b) Freundlich



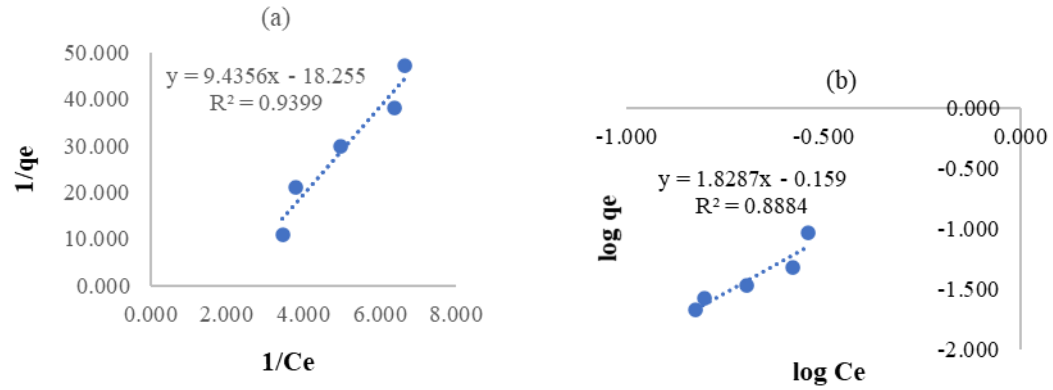
E22: Fitting of isotherm dosage data for lead on watermelon peel using (a) Langmuir and (b) Freundlich



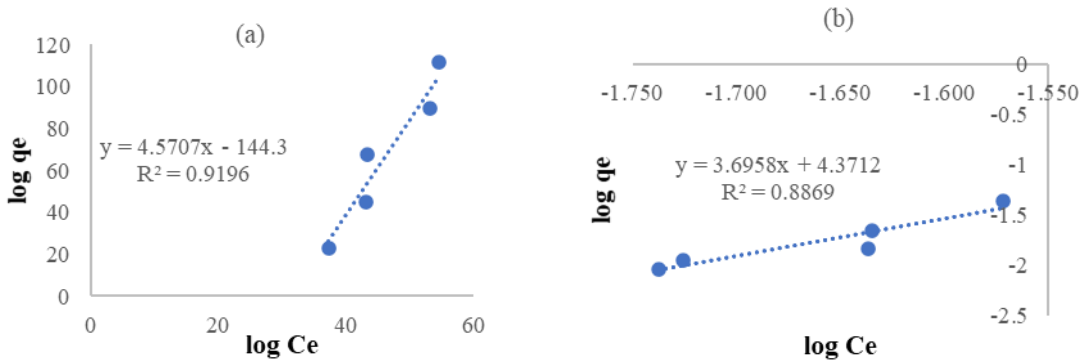
E23: Fitting of isotherm dosage data for cadmium on watermelon peel using (a) Langmuir and (b) Freundlich



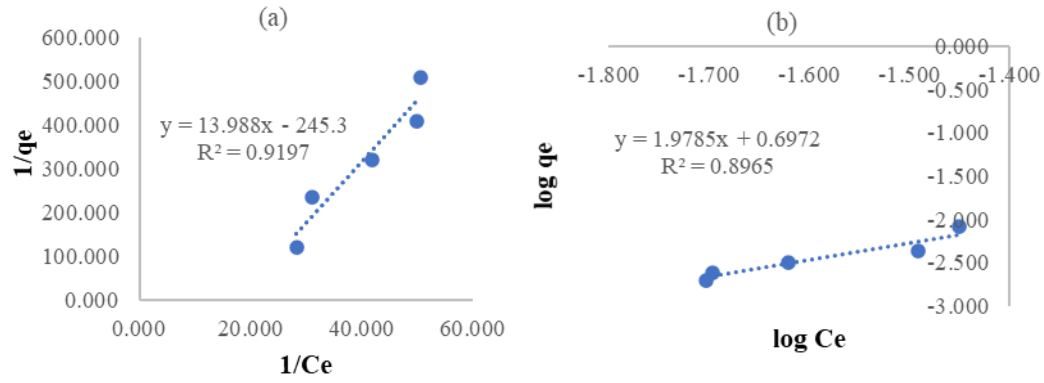
E24: Fitting of isotherm dosage data for lead on watermelon peel using (a) Langmuir and (b) Freundlich



E25: Fitting of isotherm dosage data for mercury on combination peel using (a) Langmuir and (b) Freundlich



E26: Fitting of isotherm dosage data for cadmium on combination peel using (a) Langmuir and (b) Freundlich



E27: Fitting of isotherm dosage data for lead on combination peel using (a) Langmuir and (b) Freundlich