Investigation on the Recovery of Used Engine Oil Using a Single Contactor and South African Clays

This dissertation is submitted in the fulfilment of the requirements for the degree of Master of Engineering: Chemical Engineering in the Faculty of Engineering and the Built Environment at Durban University of Technology

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DECLARATION

I Sithembiso Fortune Makhathini hereby declare that the content presented in this thesis entitled **"Investigation on the Recovery of Used Engine Oil Using a Single Contactor and South African Clays"** is a record of my research work conducted to obtain the Masters in Engineering in Chemical Engineering degree at Durban University of Technology (DUT). The content of this research work has not been previously published or written by another person for the award of any other degree at DUT or any other educational institution. Moreover, I declare that the content presented in the thesis does not violate any copyrights as all the work of others has been indicated accordingly through in-text referencing as well as a comprehensive list of references listed at the end of the thesis.

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DEDICATION

To my mother, the most special person in my life, the support she gave to me through my entire life until the gates of heaven opened and took her. Her sacrifices, love, and care made my life worthwhile.

To my family and friends, you people have been the pillar of my strength. I knew I had your support when I was encouraged to study further. Words of encouragement when I felt like giving up, financial support when required to go further. Words cannot express my gratitude towards the whole family for standing by me through the good and the bad. I salute you people.

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ABSTRACT

In this study, used engine oil has undergone treatment by means of adsorption using three different naturally occurring South African clays. These were activated using sulphuric acid to enhance the removal of heavy metals. Adsorption is an effective and economic method for removing heavy metal constituents from used engine oils. Different types of low-cost adsorbents have been developed and tested to remove heavy metal ions. However, the adsorption efficiency is dependent on the type of adsorbents. Clay porous structure and the high surface area provide benefits in the treatment of liquids such as used oil and the adsorption of heavy metals. The effect of various parameters affecting adsorption behavior, *i.e.* contact time, pH, clay dosage, and initial metal ion concentration have been investigated. The three types of clays have been characterized by X-ray diffraction (XRD) to determine crystalline structure, the components in the clay material using X-ray fluorescence (XRF), and the thermal analysis to detect the structural changes that are accompanied by the thermal treatment. The metallic components found in the oil were determined using an atomic emission spectrometer (AES). Furthermore, the experimental adsorption data have been modelled by means of Langmuir and Freundlich's isotherms. In addition, adsorption kinetics psuedo first and second order used to describe the mechanism of zinc and lead adsorption. Physio-chemical analysis of the treated and untreated used oil showed the presence of iron (Fe), lead (Pb), zinc (Zn), and copper (Cu), in the investigated clays. In conclusion, the Attapulgite clay has the most removal efficiency when compared to the Bentonite and Kaolin clay. Hence, this is observed for both the elemental analysis and the fluid properties before and after treatment.

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CHAPTER 1

INTRODUCTION

1. INTRODUCTION

According to recent studies, mismanagement of used oil is one of the highest contributing factors associated with environmental issues related to land contamination (Isah *et al.* 2013). This results in various negative effects on land and water. In addition, heavy metals in used oil have a high concentration of heavy metal impurities caused by the waring of engine parts. Discarding of used oil inappropriately results contamination of essential elements that play key roles in the existence of nature and humans (Kashif *et al.* 2018). Heavy metals in used oil are not entirely toxic some are natural nutrients below the allowable threshold; hence the greater the concentration increases the toxicity level. Hence, the handling and removal of used oil and heavy metals is one the leading research topics targeted (Atsar *et al.* 2013b).

One of the challenges the automotive industry is currently facing is the disposal or management of used motor oil, due to high contents of heavy metals contained by waste oil. Research shows that many methods are used for the treatment of heavy metal ions from aqueous streams (Raghuvir *et al.* 2018). Conventional techniques for removal of these metals have disadvantages such as poor removal efficiency, high cost, and generation of secondary pollutants (Boadu *et al.* 2019). In addition, conventional methods work remarkably and most effectively in waste containing high metal concentrations due to inherent issues of handling sludge (Diphare *et al.* 2013).

This research will evaluate the performance or absoption efficiency of three kinds of locally sourced natural clays, using a turbulent single stage contactor process. The overall effectiveness of the local clays will be determined by assessing the mass transfer performance (physical and chemical), pre and post processing requirements, cost implications and impact of energy efficiency.

Traditionally, waste oil recycling has focused on neutralization with limestone or similar adsorbent materials that filter metallic elements such as iron and gypsum (Nkonyane, Ntuli and Muzenda 2012). Used oil recovery using limestone significantly increases the pH from 6 to 8, allowing most of the heavy metals to be removed from the solution by means of precipitation (Emam and Shoaib 2012). However, this treatment process of limestone produces large amounts of gypsum sludge that contains heavy metal elements, making disposal and reuse a problematic (El-Maghrabi and Mikhail 2014).

Clays are said to be hydrous aluminosilicates (Goldani, Moro and Maia 2013). Clays mainly consist of quartz, metal oxides and carbonates. Clays are considered pollutant magnets because they adsorb cations and anions through the process of ion exchange, adsorption, or both (Virgen *et al.* 2018b). Clays are excellent adsorbent materials mainly due to large specific surface area, chemical and mechanical stability, high cation exchange capacity (CEC) and layered structure (Kumari and Mohan 2021). The advantages of using clays, cheap and readily available adsorbents. Clays are also excellent materials for adsorbing metal due to their Bronsted and Lewis acidity (Kumari and Mohan 2021). Over the years many techniques were developed for recycling and reusing of used oils, adsorption has shown to be the preferred method for removing heavy metals. Recent studies show that bentonite clay can remove up to 75% metallic elements such as Mn, Fe, Cu, Ni and Co from used oils (Coetzee *et al.* 2003).

1.1 Aim of the study

This main objective of this study is to evaluate the performance or adsorption efficiency of three kinds of locally sourced natural clays, using a turbulent single stage contactor process.

- Identify efficient activating agents for the local clays
- To generate the clay's adsorption thermodynamics and kinetics data in a turbulent contact process.
- Correlate the data to established models to determine the relevant model parameters
- Benchmark the South African clay's against currently used industrial adsorbents
- To gather relevant performance data in a turbulent single stage absorber for upscaling parameters

1.2 The significance of the study

The main goal of the study conducted is based on environmental protection, prevention further degradation of land pollution through recycling resources or processes. In achieving the goal, waste management techniques are to be deployed in the country to curb the amount of used motor oil being discarded inappropriately to land.

In addition, the success of this project or study will demonstrate how waste management organizations and the automobile industry (the main source of polluted oil) can benefit or learn from recycling waste oil from the existing processes employed. This could effectively prompt start a separate processing plant based on local technologies, leading to opportunities in the market.

In addition, the study aims to contribute significantly in the national research industry in combating land pollution and other environmental issues challenging living and non-living organisms.

1.3 Outline of the thesis

This dissertation is outlined as follows:

Chapter One	Introduction of the study.
Chapter Two	A detailed literature review; on the background of heavy metals, use and fresh engine oil properties, clay as adsorbents, previous work done by other researchers, methods or techniques of removing heavy metals on used oils.
Chapter Three	Outlines the materials and methods used to carry out the experiment in this current study.
Chapter Four	Discussion of the results obtained from analysis of the used oils with different types of clays used as adsorbents. Graphs and tables are used to better describe the trends.
Chapter Five	Conclusions on the obtained data if the locally sourced clays were able to remove heavy metals from used oils. Recommendations on how to achieve a greater yield and selectivity on the process chosen.
Chapter Six	Appendix section containing additional information gathered during the research study.

CHAPTER 2

LITERATURE REVIEW

2 CHAPTER 2: LITERATURE REVIEW

2.1 Background

Engine oil refers to the smallest proportion of crude petroleum that exceedingly stable, non-volatile, and non-flammable. Petroleum products such as lubricating oil mostly made up of hydrocarbons, which have between 20 and 70 carbon atoms per molecule (Isah *et al.* 2013).

The three major types of lubricating oil molecules are paraffinic, naphthenic, and aromatic. Paraffinic molecules primarily made up of straight chains, waxy physical appearance, above average in terms of; pour point, viscosity, and temperature stability compared to other types of molecules (Sánchez-Alvarracín *et al.* 2021a). Furthermore, configuration made up of no longer, than five regarded as straight chains, while six membered rings make up naphthenic molecules (Sánchez-Alvarracín *et al.* 2021a). They also have a low pour point, making them ideal for use as refrigeration oils. A fraction of them employed in motor oil production due to their carcinogenic qualities. Aromatics are six-membered ring benzene chains that are straight. In addition, less knowledge is available to these multiple classifications due to a variety of mixtures containing different types of hydrocarbons (Sánchez-Alvarracín *et al.* 2021a).

Engine, gear, hydraulic, turbine, and other lubricating oils are used to reduce friction between moving surfaces, particularly metal parts (Isah *et al.* 2013). Furthermore, lubricating oils prevent corrosion, provide protective layer on exposed metal surfaces, and remove heat generated by moving surfaces from working elements in machinery (Gresham and Totten 2008). In improving the efficiency of machines, lubricating oils also used in various applications namely to glue small ridges and valleys between metal surfaces. Furthermore, lubricating oil are used in the automotive industry as a cleaning detergent to remove impurities attached to various parts of metal surfaces that operate in high tolerance such as bearing (Gresham and Totten 2008).

Extensive use of lubricating oils results in a decrease in efficiency, due to the mixing with foreign matter such as other oils as additives, metallic particles, as well as fillings make lubricating oil age and deteriorate (Szyszlak-Bargłowicz, Zając and Wolak 2021b). Oxidization of lubricating oil results in colour change (darker colour is observed during the process), formation of a precipitate, a thick oil sludge, an increase in acidity as well as hard varnish (Molinari, Gallo and Argurio 2004). These elements affect the overall productivity of machine or engine significantly due to the exposed surface that inherit impurities. Lubricating oil need to be changed regularly to maintain a high level of efficiency (Gresham and Totten 2008).

Human health and the environment are threatened by used oil contaminants if discarded inappropriately; these heavy metal impurities have negative effects on both living and non-living organisms (Martin and Griswold 2009). This is due to a high level of toxicity in waste oils compared to the toxicity level in virgin base oil, which does no harm to both the environment and humans because of the absence of degraded additives, and various by-products (Mekonnen *et al.* 2014). Improper handling or mismanagement can also result in contamination of streams and coastal waters because of disposal into storm water and sewages systems (Yang *et al.* 2008).

Due to a variety of land treatment activities, heavy metals can easily migrate into ground and surface waters if dumped on loose soil or be sent to landfill (Apostoli 2006). Furthermore, unrestricted use of oils poses a harm to plant and animal life, crippling the economy in the fishery and recreation sector. Heavy metal contents in oil increase due to combustion taking place and a collection of a variety of pollutants (Abdulkareem *et al.* 2014).

Inadequate use or treatment of waste oils results in a variety of environmental and human health consequences. Traditional applications of altered oil and sunlight exposure impede dissolved oxygen replenishment, resulting in aquatic plant and animal death (Apostoli 2006). A considerable amount of oil in the wastewater ranging between 50 to 100 ppm can trip the treatment facility operations when used oil is washed into the drains and makes its way to the sewage treatment facility. According to reports, used oil in drains contributes to an estimate of 40% of the total pollution in drainage systems in various rivers in America (Hsu and Liu 2011). Most states are allowed to be dispose in municipal landfills since they do not classify used oil filters as hazardous trash. Residual oil from the filters due to leaks, results in serious issues on the ground by contaminating groundwater supplies that surround the dumps (Singh *et al.* 2011). Proper used oil management and recycling methods is necessary in combating municipal solid waste (Hsu and Liu 2011).

2.2 Previous work on Engine oil Treatment

Acid-clay treatment method is one of the widely used process for recycling used oils (Kukwa and Wuana 2013). The primary raw materials used in this process include sulphuric acid, and clay material to treat waste oil (Emam and Shoaib 2012). Sulphuric acid is a sulphonating and an oxidizing agent since it is a poly functional mineral acid. This treatment process yields degraded products due to sulphonation and oxidation of unsaturated hydrocarbons taking place in the presence of sulphuric acid (Emam and Shoaib 2012). This process however does not change the colour or the odour of the oil after treatment. Further refining with treated clay and additives is required to enhance the colour change (external appearance of the oil) and improve the oil odour. Large amounts of acid-sludge, which contaminated with petroleum, are accumulated during the treatment process hence it is the main disadvantage of using the process. Based on the disadvantage’s acid-clay process has, it is regarded as economically non-effective due to managing the residues (El-Maghrabi and Mikhail 2014).

2.2.1 History of used oil treatment

Used oil was previously categorised as a hazardous waste by the EPA due to various regulatory standards. However, in 1992 September used oils were declassified from the list as hazardous waste by a court ruling.

Further work on the process indicates working under controlled parameters and variables, results in an efficient process that yields minimal amount of acid-sludge (primary disadvantage) (Virgen *et al.* 2018b). Settling of impurities including heavy metals and filtration of used oil are steps in acid-clay process (Szyszlak-Bargłowicz, Zając and Wolak 2021a). Further processing involves re-fining stage that removes all the water content contained through a distillation process. The distillation unit is set at 200 degrees Celsius and fractioned in vacuum pressure of 5 mmHg to remove the key hydrocarbons in used oil (Kukwa and Wuana 2013). Furthermore, an increase in temperature to 350 degrees Celsius forms the residual fraction as well as the saturated oil (feed oil) which then taken and transferred to the stage of the process. The stoichiometric proportions in the acid treatment are 4:1 between the feed oil and sulphuric acid (98% concentration). The mixture then undergoes stirring for one hour at 50 degrees Celsius to maintain a homogenous solution and thus reducing oil viscosity in the process. After stirring, the mixture is cooled naturally by ambient air and kept uninterrupted for a period of 24 hours. This is done to allow settling of unwanted solids and acid sludge from the treated oil. The next step of acid treatment is clay percolation, this allows the adsorption process to manifest which takes place in a continuous process. In this process, a double jacket long glass column filled with activated clay used as an adsorbent to contact with the treated oil. Thereafter, analysis takes place using ASTM standards to determine the physical and chemical properties of the treated oil after treatment is complete (Atsar *et al.* 2013a).

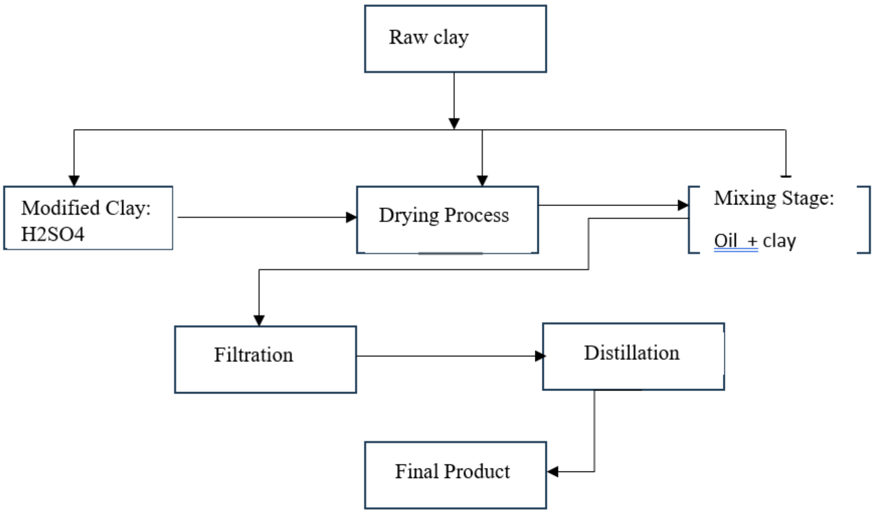


Figure 2-1: Process of raw clay treatment.

In removing heavy metals from waste lubricating oil using clay as an adsorbent taken straight/directly from nature decreases the adsorption process efficiency (Elmehbad 2017). However, improving the efficiency of adsorption requires the clay to be inoculated with 1M, 1.5M, 2M sulphuric acid or heating the clay at temperatures 300, 450, and 600 degrees Celsius to allow calcination (Abdulkareem *et al.* 2014). After activation, the clay will display an increase of 68% in surface area per gram of its original characteristics thus speeding up the adsorption rate of heavy metals and removing metals in shorter time (Talaat *et al.* 2011). Therefore, to achieve the optimum adsorption conditions, relies on the use of activated and calcinated clay in a shorter contact time (Szyszlak-Bargłowicz, Zając and Wolak 2021b).

Optimization of adsorption efficiency requires a series of steps and preparation including heating the clay between 260 to 300 degrees Celsius to remove moisture content, unwanted, and excess materials from clay taken directly from nature (Zając *et al.* 2015). The next step is to sieve and refine to a particle size of microns. After this step, both modes of clay activation take place firstly chemically, which is achieved by the addition of sulphuric acid (H2SO4) using a variety of concentrations of 1M, 1,5M, and 2M. The acid was mixed with 5mL for every gram of clay into a beaker glass. Furthermore, the mixture was stirred at 200 rpm for 60 minutes. After stirring the sulphuric acid is removed and the clay is washed until the acid solution is gone. Filtration takes place to separate the water from clay using agitation by means of filtration; the solid residue clay is then submerged into an oven where it is heated to a temperature of 105 degrees Celsius to remove any excess water remaining. The solid clay is then cooled to a temperature below 25 degrees Celsius, crushed and refined micron a 200-micro sieve (Saad, Cukrowska and Tutu 2015).

A period of four hours is required to calcinate clay at temperatures 30, 45 and 60 degrees Celsius to achieve the physical activation, therefore, ion-exchange therefore takes place after both modes of clay activations are complete, thus using a centrifuge 4500 rpm to the stir and separate the oil from any clay particles (Sánchez-Alvarracín *et al.* 2021a). Decantation of the oil from the precipitate takes place right after the adsorption, this stage normally takes 24 hours. Part of the investigated parameters is contact time, which is observed during the settling phase and thus should be shorter than any normal adsorption contact time (Emam 2018).

2.2.2 Lubricating Oil Properties

Lube oil is primarily used to reduce friction and wear in between metal parts. The main purpose consequently concern the lubricant's performance, i.e., its impact on a system's friction and wear characteristics (Sánchez-Alvarracín *et al.* 2021b). The oil grade or standard, which displays its ability to oppose degradation in use, is the most significant factor. Because the lifetime of oil is as important as its initial level of performance, bulk of the contemporary oil research is devoted to the study, avoidance, and tracking of oil deterioration (Udonne 2011).

Oil degradation is not an issue in and of itself in service, as it can damage functioning machinery and because of corrosion of touching surfaces (Kukwa and Wuana 2013). The physical and chemical properties are the factors used to influence the level of performance and grade of lubricating oil. These include viscosity temperature dependence, viscosity index, pour point, flash point, volatility, oxidation stability, thermal stability, etc.,. During the oil application period, these properties may be lost or degraded (Mekonnen *et al.* 2014).

2.2.2.1 Oil Viscosity

Oil viscosity is a crucial factor in lubrication. Oils have varying viscosities due to the various qualities contained in them. Furthermore, oil viscosity is affected by temperature variations. The amount of pressure, shear, as well as the heaviness of the oil film produced are considered equivalent to oil viscosity (Amro et al., 2019). The oil viscosity is frequently chosen in engineering applications to provide the best performance at the necessary temperature (Asaolu *et al.* 2020).

Lubricating oil viscosity is particularly sensitive to operating temperatures. As a result, the viscosity of oils decreases fast as the temperature rises (Talaat *et al.* 2011). An increase in in temperature by 25 degrees Celsius allows the oil viscosity to drop approximately by up to 80% in extreme situations. From an engineering standpoint, it is important to have a parameter that can accurately represent the viscosity and temperature correlation features of oils. Hence a measure that gives a comparison between the viscosities of two reference the oils and kinematic costly of an oil with significantly viscosity-temperature sensitivity is called viscosity index (Kashif *et al.* 2018).

The viscosity of the lubricant is discovered to be directly proportional to pressure. The viscosity of the lubricant is also affected by increased pressure. When the pressure is far above atmospheric, however, this impact is far more powerful than the effects of temperature or shear for most lubricants (Kashif *et al.* 2018).

2.2.2.2 Density and Specific Gravity

In engineering calculations, the density of a lube oil is a major aspect, and it used to identify lubricants. The density or specific gravity of crude oils is frequently used to identify their properties. It gives an estimate of how much petroleum characteristics such as kerosene and gasoline are in the oil. The density of oil, on the other hand, is frequently confused with specific gravity (Rajendran *et al.* 2022).

The mass of an equal volume of pure water at temperature 't2' refers to the proportion of the mass of a certain amount of oil at temperature 't1' relative to the mass of an equal volume of water at temperature 't2’ (Goldoni *et al.* 2006). Density is the measure of mass in a particular volume of oil with units [kg/m3]. Mineral oil has a typical density of about 850 [kg/m3] at room temperature and, since the density of water is approximately 1000 [kg/m3], the specific gravity of mineral oils is typically 0.85 (Goldoni *et al.* 2006).

2.2.2.3 Pour Point and Cloud Point

Pour point is the lowest temperature at which oil will simply flow when cooled. The lubrication of systems that are subjected to low temperatures, such as automotive engines, construction equipment, military, and space applications, depends on this oil property (Kimbonguila *et al.* 2019).

The cloud point is the temperature at which substances like paraffin wax start to precipitate. The wax precipitation causes characteristic cloudiness or haze to appear at the bottom of the jar. Because the forming wax could obstruct oil flow in capillary or wick-fed systems, the phenomenon has certain practical implications. Measurement is only possible with transparent fluids because it only relies on observation (Kimbonguila *et al.* 2019).

2.3.1 Flash and Fire Point

The flash point of oil refers to the temperature at which its vapour ignites. The flash point of an oil is the temperature at which enough vapour is produced to allow further combustion after ignition. Flash and fire points are very important for safety reasons as they are the only factors that determine the fire hazard of a lubricant (Abdulkareem *et al.* 2014). Additionally, an oil's flashpoint and fire-point rise with its molecular weight. The typical flash point and fire point of lubricating oil are both about 210°C and 230°C, respectively (Saad 2013).

2.3.2 Volatility and Evaporation

Since evaporation can be severe, it is often the main cause of lubricating oil loss in many applications (Rajendran *et al.* 2022). The temperature regulates things. Particularly at high temperatures, evaporation can cause oils to become more viscous and eventually dry up (Kukwa and Wuana 2013). The loss of volatile lubricant components owing to evaporation may result in a significant rise in viscosity, subsequent temperature rises from increased friction, and more oil losses from evaporation. A direct measure of evaporation losses is through the volatility of lubricating oil (Kukwa and Wuana 2013).

2.4 Impacts of used oil

Improper disposal of used oil poses a threat to living and non-living organisms. Contaminants have adverse effect on human health as well as the environment due to the toxic impurities generated from degraded additives. When compared with fresh lubricating or virgin oil. Improper handling or dumping into storm drains and sewers contaminate streams and coastal waters (Molinari, Gallo and Argurio 2004). This however migrates into ground and surface water contamination resulting into landfill caused by a variety of land treatment activities. Furthermore, unrestricted use of oils poses a harm to plant and animal life (Singh *et al.* 2011). The impact is greatly felt in the economy sector as well the fishery department. A range of pollutants generated or collected during combustion in the car engine, thus increasing the impurities in oil (Molinari, Gallo and Argurio 2004).

Another factor that contributes to environmental degradation and health hazards is a result of misuse of waste oil for many purposes. Furthermore, the effect is imminent targeting essential elements that living and non-living organisms depend on such photosynthesis as well as dissolved oxygen (Yang *et al.* 2002). Lack of direct photosynthesis and obstruction of the replenishment of dissolved oxygen, results in death of aquatic plants and animals respectively. The design of the drainage system is built to allow the flow of liquids towards the sewerage system for recycling; hence dumping of used oil on land ends up in the drains thus going to a sewage treatment facility. However, due to the amount of oil detected in wastewater approximately 100 ppm results into equipment failure or malfunctioning (Molinari, Gallo and Argurio 2004). American waterways reported that up to 40% of the total oil pollution is a result of used oil contamination in the drainage. In addition, most states in America allow hazardous waste to be disposed in municipal landfills since used oil filters are not regulated. Residual oils from the ground, causing serious difficulties for the groundwater supplies surrounding the dumps. As a result, proper management and handling of used oil is a key step in reducing solid waste in municipalities (Hsu and Liu 2011).

Table 2-1 represents the typical levels of contamination found in used oils. However, it is categorised by three aspects namely compounds, chlorinated hydrocarbons and organic compounds. Each aspect has a range of accumulated heavy metal concentration ranging from its minimum and maximum concentration that can be accumulated.

In addition to creating issues when released into the environment, improper treatment of these pollutants can also prevent old oils from being recycled. Because of these contaminants' typical concentration in waste streams from reprocessing or re-refining activities, there may be additional disposal problems (Yang *et al.* 2002).

Table 2-1:Typical levels of contaminants in used oils (Singh et al. 2011)

Category	Compounds	Automotive Used Oil Concentrations [ppm]	Industrial Used oil Concentrations [ppm]
	Metals		
	Cadmium	5 – 25	-
	Chromium	50 – 100	-
	Arsenic	2	-
	Barium	3 – 30	-
	Lead	100 – 1200	-
	Zinc	100 – 1200	-
	Chlorinated Hydrocarbons		
	Dichlorodifluoromethane	1000 – 4000	-
	Trichlorotrifluoroethane		-
	Tetrachloroethylene		-
	1,1,1Trichloroethane		
	Trichloroethene		
	Total Chlorine	1000 – 4000	1000 – 6000
	Organic Compounds		
	Benzene	100 – 300	100 – 300
	Toluene	500 – 5000	500 – 5000
	Xylene	500 – 5000	500 – 5000
	Benzo(a)anthracene	10 – 50	-

Benzo(a)pyrene	5 – 20	-
Naphthalene	100 – 1400	-
PCB’s	20	100 - 1000

2.5 Toxicological aspects of heavy metals

The toxicity of heavy metals is determined through a series of factors, which include various types of exposure, either small or chronic, the total amount consumed as well as the chemical form of the metal. The toxicity of heavy metals varies a lot depending on their oxidation state, by means of complex formation, and through the elemental species biotransformation (Yang *et al.* 2008). Exposure of heavy metals can result in a variety of physiological components issues, systems, and organs, including the blood and circulatory system, all internal organs that play a vital role in human existence. In addition, the exposure of heavy metals to human beings has neurological effects and all other systems such enzymes, urine etc. The conclusion is that heavy metal exposure is a health hazard that can result into major health concern if inhaled (Amoako *et al.* 2019).

Inhalation of heavy metals jeopardizes nearly every component of animal and human immune system function. One of the most serious side effects of heavy metals is that they raise blood acidity, producing systemic skeletal disorder referred to as osteoporosis. This results in the hardening of artery walls with gradual blockage of arteries causing inflammation in arteries. This however leads to large amounts of calcium withdrawn as a buffer (Raghuvir *et al.* 2018).

The upside is that heavy metals have lengthy biological half-lives, so they easily cross the placenta and end up in breast milk, inflicting negative effects on children’s behavior, intelligence, and growing neurological system due to breastfeeding naturally. In general, minor amounts of heavy metals detected are damaging to one’s health since they can accumulate over time and reach dangerous levels (Raghuvir *et al.* 2018).

The risk of heavy metal pollution in the water is divided into two categories. Heavy metals, for starters, its longevity in the natural habit or ecosystem. Secondly, the constant buildup of sequential stages of the food chain, results in rapid and gradual illnesses (Boadu *et al.* 2019). Heavy metals, in general, disrupt metabolic function in two ways: first, they collect and disrupt the functionality of the critical organs and glands in humans. These organs include the heart, brain, liver, and kidneys (Martin and Griswold 2009). Lastly, the dislocation of essential nutrients from their original location obstructs or changes their biological function. Table 2 displays a few examples of some of the most dangerous elements human impacts, as well as their origins and acceptable quantities (Martin and Griswold 2009).

The automotive industry in South Africa plays an important role in boosting the economy but also yields a considerable amount of negative environmental issues. This industry is the driving force towards South Africa’s progression. Furthermore, such behavior should be channeled as a tool of motivation in combating and finding appropriate waste management alternatives that are both technologically sound (efficient, applicable, and feasible) and economically sound (cost effective) (Jadia and Fulekar 2009). Above all, long-term economic development plan becomes unadvisable without considering the environmental implications of effective waste management. Awareness of environmental issues to the public and thus causing the environmental law to become more rigorous (Saad, Cukrowska and Tutu 2013). South Africa needs to come up with solutions that are cost ineffective to recycle used oil to create an environment conducive to healthy, social and economic well-being. However, until waste used oil management is documented and regulated the demand for vehicles in South Africa declines drastically (Kukwa and Wuana 2013).

Table 2-2 represents the heavy metal toxicity, sources and permissible levels generated in the automobile. This table allows the reader to get insight of the dangers of each metallic ion present in used oils when exposed to the environment as well as humans. This table gives precautionary measures to handlers of used oils to avoid adverse effects and possible life-threatening illnesses.

Even though the car industry has considerable negative environmental consequences, it also contributes significantly to economic growth. It has been the real driving force behind South Africa's progress. This significant contribution to South Africa's economy and development should be used as motivation to find appropriate waste management alternatives that are both technologically sound (efficiency, applicability, and feasibility) and economically sound (cost-effective) (Pinter et al., 1995). Above all, sustainable economic development cannot be achieved without considering the environmental implications of effective waste management, especially as public awareness of environmental issues grows, and environmental law becomes more rigorous. South Africa needs to come up with solutions that are cost ineffective to recycle used oil to create an environment conducive to healthy, social, and economic well-being. However, South Africa`s growing demands for vehicles cannot be met unless used oil management is revolutionized (Atsar et al., 2013).

Table 2-2: Examples for heavy metals toxicity, sources and permissible levels (Diphare *et al.* 2013)

Metal	Sources	Toxicity	Permissible Level Mg/L
Mercury	Processes involving dust particles and combination of recycled materials namely mining used oil refining, fertilizers, paints, pulp and paper.	Damages the body command that is the nervous system, lead to mental impairment, and have genetic flaws that interfere with cell division and break chromosomes, as well as causing chest pain and dyspnoea.	0.002
Uranium	Mining	Causes damage to major to kidneys (nephrotoxicity), prevention of key cells from transmitting and sending signals in the brain and other parts of the nervous system, causing cell mutation due to the damaged genetic information leading to cancer.	0.03
Arsenic	Agricultural and industrial sectors (Pesticides, fungicides, algaecides, and herbicides), production of wood preservatives.	Carcinogenic, teratogenic (affects foetuses), and mutagenic (induces chromosomal abnormalities), nasal septum, skin changes, peripheral neuritis.	0.05
Selenium	metal industries, glass industry, pesticides and fertilizers	Cancer, cardiovascular illness, cognitive decline, thyroid disease, neurological damage, cirrhosis of the liver, and death.	0.05

Cadium	Welding, Cd and Ni battery electroplating, nuclear power plants, paints and plastics, and fertilizers.	Renal impairment, lung cancer, and issues with reproduction (which affect sperm and lower birth weight).	0.06
Lead	Pint, pesticides, automobile, burning coal.	Brain damage, anaemia, reduced learning abilities, liver and kidney damage, infertility, cardio toxic, high blood pressure, congenital paralysis.	0.015
Zinc	Brass manufacture metal plating plumbing.	Cause damage to nervous membrane.	15.0
Copper	Mining, pesticide production, metal piping.	Anaemia, hypertension, liver and kidney damage, uraemia.	0.05
Iron	Acid mine drainage, landfill leachate sewage or engineering industries.	Cause tissues damage.	0.1
Chromium	Steel and textile industry	Immune system weakened kidney and liver damage, lung cancer, genetic material altered, respiratory issues, irritations and nosebleeds, and skin rash.	0.05

2.6 Used Oil Recycling and Reuse

Sizeable amounts of used oil can be reprocessed and recovered in various forms, directly or after undergoing a series of treatment methods and purification (Diphare *et al.* 2013). The initial step is to preserve the oils qualities, thus allowing for direct reuse according to the waste management hierarchy. Recovery of its heating value and/or the usage in various small level applications are two options. Limited types of waste used oils have the possibility to recovered and reused directly through recycling. Used waste oils often used as a base ingredient comparable to refined virgin base oil or as a clean burning fuel after treatment (Donald. T Kukwa *et al.* 2013).

The concept of recycling used oil is not a new thing, proposed in 1930. For the past four decades, used oils have been reprocessed (Hsu and Liu 2011). Burning and re-blending used oils to generate energy is among a series of treatment stages required to treat used oil desirable outputs. The relevance of waste oil recycling has expanded significantly because of the growing need for environmental protection and increasingly strict environmental legislation, and its disposal has become critical (Talaat *et al.* 2011). Incineration, reprocessing, and re-fining are the three ways of achieving the desired outcome in waste oil.

Figure 2-1 describes the waste oil treatment hierarchy, this illustration highlights the key steps followed to preserve and treat used oils. This is a sliding scale type of illustration describing which steps are taken to recycle waste oils collected in various industries. The process starts at the base of the hierarchy with dumping of used oils and ends with the last part which is refining stage.

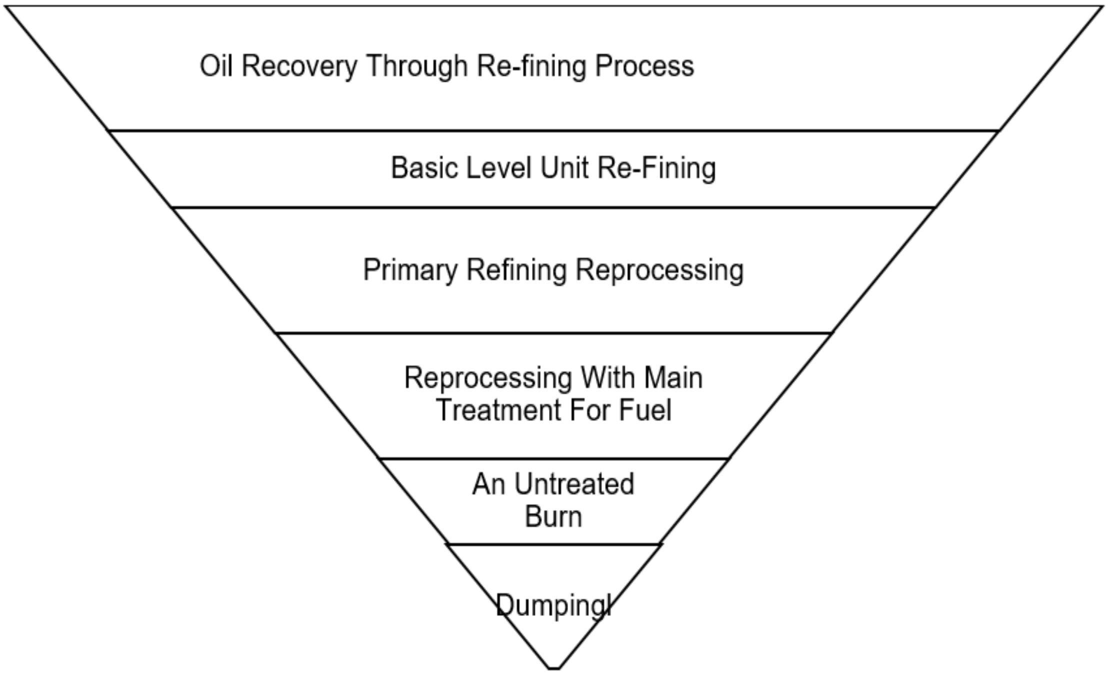


Figure 2-2: Waste oil treatment hierarchy (Diphare et al. 2013)

Thermal elimination of used oil by means of incineration or combustion increases efficiency. Only a small amount of used oil, burnt due to the economic benefits of recycling it. Used oil that has been combusted, has significant levels of harmful pollutants making the process unachievable and hazardous (Isah *et al.* 2013).

A technique that allows used oil to be treated and burnt in order to recover energy is referred to as reprocessing technology. This procedure, on the other hand, entails the removal of water and particles from spent oil before burned as fuel. After that, fuel used to generate heat or power industrial processes. The main downside of this method of recycling is that the oil can be only reused once, making it a less desirable option. Furthermore, it is one of the most cost-effective means of handling used oil while supplying valuable energy, about equivalent to that delivered by standard heating of oil (Diphare *et al.* 2013).

A quantity of 1 liter of used oil reprocessed into fuel generates 8,000 Kcal of energy, sufficient to light a household light bulb and alternatively power up a heater to a considerable amount of 1000W for a period of two hours (Nwachukwu and colleagues). The primary benefit of recycling used oil using reprocessing technology, improves the burning quality of use oil by removing or reducing some impurities as compared to direct burning (Kimbonguila *et al.* 2019).

Used oil can also be processed and repurposed to make new lubricating oil. As a result, lubricating oil is a luxury product with the potential to be recycled multiple times. In general, ambient or moderate vacuum distillation separates moisture content and dissolved low boiling point organics (Atsar *et al.* 2013b). Various treatment methods or unit operations employed in the recovery of used oil. Plant combustion fuels usually made up of volatile components that considered light end by-products.

Diesel and gas oil fractions, on the other hand, recovered through extensive processing as a high-quality by-product (Saad, Cukrowska and Tutu 2015). Waste product generated in the distillation unit as a product residue alternatively used in the asphalt industry as an asphalt flux (Udonne 2011). The asphalt flux contributes to the making of roofing, paving, and insulating asphalt materials. The main purpose of treating used waste oil, eliminate unwanted particles thus using it as a base ingredient during the re-fining process. The oil resource's life cycle is extended forever through re-fining and recycling. This method of recycling is the widely used technique, hence consumes less energy and less virgin oil during the treatment process thus using the same product material as feed ingredient (Kashif *et al.* 2018).

Table 2-3 outlines the comparison of environmental aspects of treatment technologies available with each process being rated either as a high or low contributor of pollution, ash, harmful chemicals, acidic sludge and residual sludge. The table also provides clear understanding of the impacts treatment technologies have towards the environment and humans.

Table 2-2-2: Comparison of environmental aspect of treatment technologies (Kashif *et al.* 2018)

	Recycling Technologies		
	Re-Refining	**Reprocessing**	**Incineration**
Acidic Sludge	High	Low	-
Residual Sludge	High	Low	-
Harmful Chemicals	Sulphuric acid	-	-
Pollution	Low	Low	High
Ash	-	-	High

Table 2-4 provides rating of energy consumption and various cost related aspects such as equipment demand, operating cost, technology maturity, recovery rate and quality of reclaimed oil. These however allow the operating personnel to make an informed decision in the choice or selection of the three recycling technologies based on performance as well as disadvantages.

Table 2-2-3: Comparison of environmental aspect of treatment technologies (Atsar *et al.* 2013b)

	Recycling Technologies		
	Re-Refining	**Reprocessing**	**Incineration**
Technology Maturity	Plant Scale	Plant scale	-
Energy Demand	High	Low	-
Recovery rate	> 63%	> 74 %	-
Quality of reclaimed oil	Good	Fair	-
Equipment Demand	High	Low	Low
Operating Cost	High	Low	-

Table 2-5 outlines the advantages and disadvantages of used oil recycling and reusing methods. This table clearly indicates how each treatment technology might affect the environment and how much capital investment might be required to sustain the operation. Also, the longevity of each method is outlined to provide a better view of which process is best suitable and cost ineffective at the same time.

Table 2-4: Advantages and disadvantages of used oil recycling and reusing methods (Diphare et al. 2013) Advantages and disadvantages of used oil recycling and reusing methods (Diphare *et al*. 2013)

Methods	**Advantages**	**Disadvantages**
Incineration	• Less capital-intensive than the alternatives • Economically viable at lower processing volumes • Cement mills are eager to purchase waste oil • Concentrates the disposal of waste oil to fewer, more readily regulated and supervised places	• Despite being low, air pollution emissions still need to be addressed • Resistance from governmental and regulatory organizations
Reprocessing	• Limits the harmful consequences of the practice of burning garbage in an uncontrolled manner • The buyer oversees overseeing the recycled fuel oil's quality control	• Requires a sophisticated collection system • Significant capital expenditures • Expensive end waste residue disposal
Re-Refining	• Long-term, environmentally friendly remedy • Creates jobs • Stripped light fuels and diesel provide complete self-sufficiency in fuel for the recycling facility	• Re-refined lubricant oil needs a well-developed market and a well-developed collection mechanism • Re-refining requires a recognized recycling business to ensure the product's marketability, which involves a significant capital commitment • It is also expensive to dispose of end waste residues properly

2.7 The importance of recycling reusing of waste oil

Used oil has proven to be a valuable energy source. Oil does not degrade with time; it simply becomes dirty because of its usage (Virgen *et al.* 2018b). Recycled used oil is primarily used as a base ingredient, further reprocessed into various other products including fuel oil, feedstock in the petroleum-based goods using different techniques (Emam and Shoaib 2012). Correct handling or management of used waste oil listed below. Approximately thirty percent of the total energy required to treat and refine crude oil to the allowable standard quality, hence 10 liters of re-fined used oil yields 2.5 quarts of lubricating oil, compared to 42 000 liters of crude oil. The proper handling of spent oils includes collecting and recycling used oil, which protects our environment from contamination while also conserving a precious non-renewable resource (Virgen *et al.* 2018b).

Recycling used oil effectively saves essential, non-renewable resources in accordance with the energy conservation principle. It takes nearly 70 barrels of crude oil be converted into one barrel of virgin oil. Many funds invested in finding new ways to collect and recycle crude oil to achieve a desirable yield. Time and money can be saved significantly just like how used oil generated by consumers is recycled repeatedly into items with significant value such as fresh lube oil (Szyszlak-Bargłowicz, Zając and Wolak 2021a).

Our natural resources will be preserved, which is even more vital. As a result, the management of spent oil is critical because of the huge numbers produced globally, there is the possibility for direct re-use, reprocessing, as well as negative environmental consequences if they not properly managed, processed, or disposed of. Recycling waste lubricating oils is beneficial to both the environment and the economy (Molinari, Gallo and Argurio 2004).

2.7.1 Used oil treatment methods

Used motor oil frequently contaminates soil, and because of the potential environmental effects, it is a major source of worry in modern society (Emam and Shoaib 2012). Because of chemical processes that take place in engines while the oil is being used, heavy metals and aromatic hydrocarbons can be found in old motor oil, has attracted a lot of interest (Virgen *et al.* 2018a). Waste oil is typically processed via the activated mud process, corrosive earth process, propane de asphalting, vacuum heated de asphalting, dissolvable extraction process, and prop Philips refined method.

While some treatment processes are effective at recycling waste oil and recovering metals, their major disadvantages are that they produce large amounts of hazardous sludge, mostly through chemical precipitation, and their treatment cost of makes them uneconomical to use. Insufficient metal removal (poor efficiency), high reagent and energy requirements, enormous amounts of trash that are challenging to dispose of, as well as the production of poisonous waste products, have all been found to be problems with most of these procedures (Goldani, Moro and Maia 2013).

All these methods have involved the use of a few conventional heavy metal ion removal techniques, some of which have produced successful outcomes while others have not (Evbuomwan *et al.* 2019).

2.7.2 Conventional methods

A variety of traditional methods have been used over the last few decades to fight the removal of heavy metals in used oil and demonstrated effective results since its inception. However, a summary of some of the most popular traditional methods' characteristics, benefits, and drawbacks is provided here.

2.7.2.1 Acid – Clay

In the acid clay process, the waste oil is typically filtered and then heated to remove contaminants, particles, and water. It is then mixed with sulfuric acid, which extracts metal salts, acids, aromatics, asphaltenes and other impurities. This produces acid sludge as a by-product, which settles in the oil. The remaining slightly acidic oil is mixed with activated earth (clay) to remove mercaptans and other impurities and improve color. This process takes about 0.4 pounds of clay per gallon of oil. After the clay has been filtered from the oil, the final step is to neutralize and distill the oil. In the past, acid clay treatment was the dominant technology.

For many years, regenerating spent engine oil has been treated using the acid-clay treatment technique. This procedure, like many others, has several drawbacks, including the production of enormous amounts of contaminants that make it challenging to treat modern multigrade oils and its inability to remove asphaltic impurities (Diphare *et al.* 2013) .

2.7.2.2 Solvent Extraction

The preferred technique for enhancing base oil's oxidative stability and viscosity/temperature properties has replaced acid treatment. The desired saturated components, mainly alkanes, are left as a distinct phase (the raffinate), while the solvent selectively dissolves the undesirable aromatic components (the extract) (Schuetze *et al.* 2008). Methyl ethyl ketone (MEK) and 2-propanol were used to create an extracting substance for recycling old engine lubricants in one study (Goldani, Moro and Maia 2013). The oil produced by this procedure is comparable to that made by the acid-clay method, although it is more expensive. This approach calls for the use of pricey solvents and vacuum distillation (Emam and Shoaib 2012). The solvent propane has recently been employed. Paraffinic or waxy materials can be dissolved by propane, and it can partially dissolve oxygenated materials. Asphaltenes Heavy condensed aromatic compounds, as well as particulate particles, are insoluble in liquid propane. These characteristics make propane perfect for recycling spent engine oil, but there are many additional factors to consider. Because propane is dangerous and combustible, this technique is viewed as hazardous (Lesmana *et al.* 2009). Additionally, solvent losses and extremely expert operating maintenance are a part of the extraction process. Additionally, extraction happens at pressures greater than 10 atm and necessitates high-pressure sealing systems, which adds to the cost of construction and operation of solvent extraction plants and results in a significant number of hazardous by-products (Raghuvir *et al.* 2018).

2.7.2.3 Membrane Technology

Regenerating old lubricating oils using membrane technology is another option. The old engine oils were recycled using this process using three different types of polymer hollow fibre membranes: polyethersulphone (PES), polyvinylidene fluoride (PVDF), and polyacrylonitrile (PAN). The procedure is carried out at 0.1 MPa pressure and 40 °C. The procedure enhances the fluidity and flash point of the recovered engine oil while also removing metal dust and particles from old engine oil (Boadu *et al.* 2019). Despite the benefits outlined above, costly membranes are susceptible to degradation and fouling from big particles (Evbuomwan *et al.* 2019).

2.7.2.4 Vacuum Distillation

Two further processes for recovering old engine oil are vacuum distillation and hydrogenation (Boadu *et al.* 2019). The Kinetics Technology International (KTI) method combines hydro finishing with vacuum distillation. This process eliminates most of the impurities in the waste oil (Abdulkareem *et al.* 2014). To remove water and light hydrocarbons, air distillation is used as the first step in the process. Vacuum distillation at a temperature of 250 °C comes next. To get rid of the sulfur, nitrogen, and oxygenated molecules, the products go through hydrogenation as the last step (El-Maghrabi and Mikhail 2014). Additionally, the oil's color and smell are improved during this stage. The product can meet the quality criteria (Gp.I) and have minimal polluting by-products with a yield of about 82%. The high cost of this approach is a drawback (Isah *et al.* 2013).

2.7.3 Clay

Clay is a soil material, which is naturally occurring fine-grained material rich in minerals (Kumari and Mohan 2021). Because of its physical and chemical properties, clay has various forms of state from being a putty solid to plastic when induced in water due to liquid water present in the clay particles (Saad 2013). In addition, the removal or unavailability of liquid water in clay results in the clay being a hard solid object. Various types and forms of clay known to be white in color or very light-colored soil with a combination of different colors present simultaneously. However, impurities present causing the natural clay to exhibit colors such as brownish or reddish with small amounts of iron oxide (Kumari and Mohan 2021). Cation exchange capacities in clay minerals range from (kaolinite) per 100g. Exchange reactions are quick and affect the chemical composition of subsurface fluids (Gupta and Paul 2015).

Clay is a frequent sedimentary rock component. Shale is the most prevalent sedimentary rock and is primarily composed of clay (Gupta and Paul 2015). Many clay deposits, on the other hand, are impure. Both slits and clays found in many naturally occurring deposits. Differences in size and minerals distinguish clays from other fine-grained soils (Hillebrecht *et al.* 1983). The exclusion of clay minerals in slits results in a bigger particle size than normal clay (Hillebrecht *et al.* 1983). In terms of particle size and other physical attributes, however, there is some overlap. The similarity between slit and clay diminishes on various clays. Soil scientists and geologists state that separation commonly to take place at 2m and beyond (signaling that clay has finer grains compared to slits), sedimentologists and colloid chemists use 4-5m and 1m respectively (Goldani, Moro and Maia 2013).

Due to the ability of absorbing water at a high capacity and expanding simultaneously in a dramatic manner, most clay minerals referred to swelling clay minerals (Goldani, Moro and Maia 2013). Drying process enables them to change the physical appearance instantly to their original size. In clay deposits, this results in different textures such as mud-cracks or "popcorn" texture. Civil engineer's worst nightmare swelling clay minerals, damage roadbeds as well as building foundations these include the famous bentonite soil (Mustapha *et al.* 2019a).

2.7.3.1 Clay Properties

Clay exhibit mechanical properties due to its fluidity ability when wet and its hardness when dried or burnt (Emam 2018). The amount of water content present on the clay is subdivided into regions namely the minimum and maximum, which however determines the plasticity of the clay (Ujile 2014). The two regions referred to as the plasticity limit and liquid limit respectively. In detail, the plasticity limit is the point in which the clay is just moist enough to mold a maximum water content. On the other hand, liquid limit is a point in which the molded clay is dry enough to maintain its shape. Kaolinite clay plastic and liquid limit ranges between 36 to 40 percent and 58 to 72 percent respectively (Kumari and Mohan 2021). The amount of mechanical work required to roll a sample of flat clay demonstrates the toughness of high-quality clay. It has a high degree of internal cohesiveness that explains its toughness.

The high mineral content present in clay results in its plasticity (Kumari and Mohan 2021). The mineral content are hydrous aluminum phyllosilicate minerals made of aluminum and silicon ions bonded together by oxygen and hydroxide ions form tiny, thin plates. Due to the flexibility and robustness, the plates stick together in wet clay (Coetzee *et al.* 2003). The particles that form provide the cohesiveness that make the clay plastic. A layer of the water molecules provides the bonding between the plates in kaolinite clay that hydrogen bond them together (Kumari and Mohan 2021). During the clay formation, the bond strength is weak to allow the plate to slip past one another and sufficiently strong to maintain the plate in position and allow the molded clay to maintain shape (Mustapha *et al.* 2019a).

Most of the water molecules are gone when the clay dries, and the plates hydrogen bond directly to each other, making the dried clay stiff but still delicate (Kumari and Mohan 2021). If the clay is soaked again, it will return to its original plastic state. Excess amount of moisture content from the clay removed by means of dehydration process that occurs by heating clay to earthenware stage (Coetzee *et al.* 2003). This process enables the clay plates too irrevocably to attach to each other by means of covalent bonding, thus strengthening the substance. Moistening clay mineral kaolin transforms it into metakaolin, a non-clay substance that stays rigid and hard (Emam 2018). The metakaolin is recrystallized into even stronger minerals like mullite as it is fired through the stoneware and porcelain processes (Kumari and Mohan 2021).

2.7.3.2 Uses of clay

Clay makes both utilitarian and ornamental ceramics, as well as construction materials such as bricks, walls and floor tiles (Kumari and Mohan 2021). Earthenware, stoneware and porcelain produced from a combination of variety clays of different physical and chemical properties. Prehistoric humans credited for the discovery of clay characteristics (Mustapha *et al.* 2019a). Central Honshu awarded for its pottery shards discovery, located in Japan. Japan is home to some of the earliest pottery shards discovered in the globe. There is a connection with the J’mon civilization, and the oldest deposits discovered that date back to roughly 14,000 BC. Before the baking process takes place, clay is converted to a variety of household utilities such as cooking pots, dishware, smoking and musical instruments which includes pipes and ocarina (Mustapha *et al.* 2019a).

2.7.4 Adsorption

Adsorption is the process of transferring matter from a liquid phase to the solid phase (Dąbrowski 2001). The adsorption-related process is analysed using the complexity history from batch adsorption, one-dimensional, equilibrium column adsorption, and one-dimensional non-equilibrium adsorption (Gabelman 2017). Adsorption is a separation process that separates certain materials; adsorbate is concentrated from a bulk vapour or liquid phase at the surface of a porous solid (adsorbent) (Gabelman 2017). Some common examples of adsorption are silica gel packaging to adsorb moisture from packaged electronic or optical devices, and a carbon "filter" to deodorize drinking water (Mustapha *et al.* 2019b).

2.7.4.1 Adsorption Mechanism:

Adsorbate: A substance that concentrates on the surface is called adsorbate (Kwasi Opoku *et al.* 2020). **Adsorbent**: The material on whose surface the adsorption takes place is called an adsorbent. Activated carbon is mainly used as an adsorbent. Adsorbents are used in the form of rods, castings, spherical pellets, or monoliths with diameters between 0.5 and 10 mm. They are characterized by high abrasion resistance, small pore diameter, and high thermal stability, which leads to a larger exposed surface area and thus a high surface adsorption capacity (Ripin A 2010). Adsorbents should also have a porous structure that allows rapid helps transport of the gaseous vapours (Gupta and Bhattacharyya 2012).

Adsorbents fall into one of three classes: 1. Oxygen-containing compounds are generally hydrophilic and polar, including materials such as silica gel and zeolites. 2. Carbon-based compounds are generally non-polar, and hydrophobic including materials such as activated carbon and graphite. 3. Polymer-based compounds are polar or non-polar functional groups in a porous polymer matrix (Opoku *et al.* 2020).

Preferred concentration of a system component at the interface, where the local concentration differs from that of the bulk phase (Opoku *et al.* 2020). Positive adsorption means that the interfacial concentration of the adsorbed species is higher than that of the raw phase, while the interfacial energy decreases. Negative adsorption means an increase in the interfacial energy of a system. Two aspects that can be considered when observing adsorption processes are the thermodynamics, i.e. the speed at which the adsorption process takes place (Gawande, Belwalkar and Mane 2017). The basic concept of adsorption is the adsorption isotherm. It is an equilibrium relation between the pressure and volume concentration of the liquid phase at constant temperature and the amount of liquid adsorbed. The original Gibbs treatment, appropriate for the fluid interface, considers the real interface as a geometrical plane called the Gibbs dividing surface GDS interface. The Gibbs approach has no model, and the structure of the interface layer requires formality (Mustapha *et al.* 2019b).

The basic principle of carbon adsorption is the mass transfer and adsorption of a molecule from a liquid or gas to the surface of a solid (Toth 2002). Activated carbon is manufactured to create extremely porous carbon particles with a very large internal surface area. This porous structure attracts and holds organic molecules, inorganic molecules, and metals (Ali, Ripin and Ahmad 2010). Adsorption occurs because i) The pollutant has low solubility in the waste ii) The pollutant has greater affinity for the carbon than for waste iii) A combination of both used in the fixed beds and powered activated carbon (Kwasi Opoku *et al.* 2020). The activated carbon adsorption process is one of the most applied technologies for the removal of trace organic compounds from an aqueous solution. Activated carbon ratio should be in the range of 500 to 1000 m2 /g which is a good adsorbent for effective removal of organic compounds (Akpomie *et al.* 2018).

CHAPTER 3

METHODOLOGY

3 METHODOLOGY

3.1 Background to Methodical Approach

In this research study, all experimental runs were conducted in the Chemical Engineering laboratories at Mangosuthu University of Technology (MUT).

Used oil samples were collected from Dilex Chemicals, liquid recycling organization located in New Germany North of Durban Kwa Zulu Natal. Dilex Chemicals receives all types of liquid waste from all corners of the Kwa Zulu Natal. These liquid wastes include used oil from the automotive industry including Toyota service centres. For this research study, used oil disposed by Toyota Motors Durban Kwa Zulu Natal from service department was used. These oils were taken from cars of different mileages and of different car makes.

Literature study revealed that the properties exhibited by clay adsorbent previously shown great removal efficiency when being used as adsorbents. In addition, because of their readily available ability, the three clays were selected to be used as adsorbents for this project. Clay 1 and clay 3 were bought in the local pottery shop in Durban, while clay 2 was collected in a local riverbank in uMkhomaas in the South Coast of Kwa Zulu Natal.

3.2 Materials

3.2.1 Instrumentation

An Orion Star A215 pH/Conductivity meter were used in the activation of clay with Sulphuric Acid. Heavy metal ion contents before and after treatment were determined with Thermo-Scientific atomic absorption spectrophotometer. In addition, the functional groups and surface morphology of the adsorbent were determined with a Joel Scanning electron microscopy (model: JSM 5300) and Perklin Elmer Fourier transform-infrared spectroscopy (Spectrum BX FT-IR). Surface area of the adsorbent was determined with Brunauer-Emmett-Teller (BET).

3.2.2 Raw or untreated clay(s), adsorbent(s)

Clay 1 and clay 3 were bought in the local pottery shop in Durban, while clay 2 was collected in a local riverbank in uMkhomaas in the South Coast of Kwa Zulu Natal.

3.2.3 Used engine oil

Used oil samples were collected from Dilex Chemicals, liquid recycling organization located in New Germany North of Durban Kwa Zulu Natal. Dilex Chemicals receives all types of liquid waste from all corners of the Kwa Zulu Natal. These liquid wastes include used oil from the automotive industry including Toyota service centres. For this research study, used oil disposed by Toyota Motors Durban Kwa Zulu Natal from service department was used. These oils were taken from cars of different mileages and of different car makes.

Table 3-1 highlights the physical and chemical properties of used oil before adsorption treatment by means of acid clay process. The oil sample were collected from Toyota cars after service between various mileages driven by the vehicles. The table shows the metallic content in terms concentration (ppm) as well as typical values at minimum and maximum attained.

Table 3-3-1: Used oil characterization of physical and chemical properties before adsorption treatment (Adewole et al 2019).

Properties	**Used Engine oil from Toyota cars**	**Typical values**
	Selected properties	
Density (g/mL)	1.078	0.98 – 1.13
Kinematic Viscosity at 40 ℃ (Pa.s)	1.27	1.07 – 1.33
Kinematic Viscosity at 100℃(Pa.s)	0.66	0.51 – 0.82
Viscosity Index	1.43	1.01 – 2.07
Ash Content %	0.10	0.10 – 0.18
Water Content %	1.85	0.97 – 1.91
Flash Point℃	177	1.70 – 181
Pour Point℃	93	88 - 97
	Metallic Content (ppm)	
Lead (Pb)	52.67	28.53 – 60.15

Chromium (Cr)	65.10	5.75 – 92.14
Zinc (Zn)	66.36	12.38 – 81.02
Iron (Fe)	70.75	70.75 – 332.75
Nickel (Ni)	50.7	2.17 – 158.30
Copper (Cu)	44.17	4.33 – 143.33

3.2.4 Fresh engine oil

Fresh engine oil was collected at Engen Convenience Centre Amanzimtoti. Engen offers a range of high-performance lubricants that are purposely suited for a spectrum of industries for both petrol and diesel engines and gearboxes, hydraulics, turbines, compressors, machine tools, and a variety of other applications including mineral and synthetic base oil stock. For this study petrol engine oil (20W – 50 multi-grade) was selected in comparison with used engine oil collected at the Toyota service department. The mean values of the heavy metal contents ranged as follows:

Table 3-2 shows the mean values of fresh petrol engine oil sold at Engen filling outlets for comparison with the used engine oil collected at Toyota. The table below outlines the actual concentration found in fresh oil for all metallic contents.

Table 3-3-2: Mean values of fresh petrol engine oil sold at Engen filling outlets

Metals	Mean values (ppm)
Lead (Pb)	7.17 – 9.83
Copper (Cu)	3.58 – 3.83
Chromium (Cr)	1.91 – 20.58
Nickel (Ni)	1.42 – 3.83
Iron (Fe)	46.83 – 108.58
Zinc (Zn)	39.05 – 101.27

3.2.5 Equilibrium Isotherm

The Langmuir and the Freundlich equilibrium will be used to assess the removal of metal components and other impurities found on used oil by activated clay. The Langmuir equation described below will be used to determine if the adsorption process is homogenous where the adsorbate molecules onto the surface have the same activation energy (Ntimbani, et al., 2015),

Equation 1: Linear Langmuir Equilibrium Isotherm Equation

$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{(QmKl)} + \frac{C_{eq}}{Q_m} \text{ ………………………………………………………… } 1$$

Where: Q_{eq} – amount adsorbed at equilibrium per unit of mass (mg g^{-1})

C_{eq} – metal residual or ion concentration in the solution (mg L^{-1})

Q_{max} – maximum adsorption capacity (mg g^{-1})

K_L – constant related to the strength of adsorbent-adsorbate interaction (L mg^{-1})

The Freundlich equation described below will be used to also determine if the adsorption processes are heterogeneous where the adsorption system have different activation energies on the surface of the sorbate (Pete, et al., 2014).

Equation 2: Linear Freundlich Equilibrium Isotherm Equation

$$log\, Q_{eq} = log\, K f + \frac{1}{n \log C_{eq}} \text{ ……………………………………………….. } 2$$

Where: K_f – adsorption capacity (mg g^{-1})

n – indicates the strength of adsorption; lies between 0 and 1

3.2.6 Modified or treated clay(s), adsorbent

5 kg of clay 1 and clay 3 were bought in the local pottery shop in Durban, while clay 2 was collected in a local riverbank of uMkhomazi. In preparation, clay 3 was washed off to remove stones and other solid particles, dried, and crushed into fine powder. While clay 1 and 2 were already refined into fine powder. 1 kg of each clay was inoculated with a sulphuric acid solution (1M, 1.5M, and 2M concentrations)

producing three slurry’s of different properties to allow thorough and concise trend expectancy of the treatment to place and for accuracy and precision purposes. The slurry’s were further dried in an oven at 60 degrees Celsius for 24-hour period. Then crushed and sieved into smaller particles using a sieve shaker machine.

3.3 Experimental Apparatus

Experimental setup consisted of three tripods (magnetic stirrers) figure 1; these were used to heat up the used oil to the desired temperature set point value. A set of glassware consisting of six 250 mL beakers, six 250 mL conical flasks and 10mL measuring cylinder were used during the entire duration of the experiment.

Figure 3-1: Tripod (Magnetic stirrer)

A thermometer was used to measure the temperature. A centrifuge was used to separate the solids from liquids using centrifugal force (figure 3). CE130 Pert industrial drier was also used to remove the moisture content on the clay as shown on figure 2.

Figure 3-2: CE 130 Drier

Figure 3-3-3: Centrifuge

An analytical balance, RADWAG AS 220/C/2 was used to accurately measure to the weight of clay dosage to be used for the experiment (figure 4 and 5 respectively). An Orion Star A215 pH/Conductivity meter was used in the activation of clay with Sulphuric Acid.

Figure 3-3-4: Orion Star

Figure 3-5: RADWAG AS 220/C/2

Sieve trays (1000, 710, 500, 355 and 250m aperture size mesh) was used as shown in (figure 6). These sieve trays were arranged in a descending order, ensuring that only the finely grounded soil penetrates and trapping all the rough and coarse soil.

Figure 3-3-6: Sieve trays

3.4 Methods

3.4.1 Adsorption Process

Three batches of modified or activated clays were used to treat the used oils by means of regulated parameters based on previous studies conducted as guidance.

Adsorption Parameters/working conditions

Contact time (minutes): 10, 50 and 90

Clay dosage/concentration (g/100mL used oil): 10, 25, and 40

Temperature (degrees Celsius): 50, 80, and 110

pH: 5 – 7

3.4.2 Operating procedure

Three 400 mL beakers filled with 100 mL of used oil were placed on top of each tripod (3 magnetic stirrer) to provide adequate heat supply while mixing the oil and the adsorbent (activated clay) to form a homogenous mixture. Contact time during each experimental run was set (10 - 60 minutes). In monitoring the heat required, a thermometer was used to measure the temperature of the mixture. The working temperature range was set between (60 – 90 degrees Celsius). Temperature played a vital role in reducing the viscosity of the oil allowing the activated to be in contact properly with the oil.

No additives were used to enhance the color and the removal of the heavy metals. After each run, samples were cooled off and allowed to settle for of 4 hours due to gravity. Samples were then transferred to 250 mL conical flasks and filtered using a vacuum pump. Each flask produced three samples for accuracy and precision purposes. After filtration, samples were then transferred into 15 mL test tubes and placed into the centrifuge to allow proper separation of solids and liquids. In addition, this was to ensure that no solid particles are present during the analysis using FTIR. The centrifuge was set at 10 minutes interval separation and 4000 rpm rotation. Oil samples are very viscous; therefore, a higher rotational speed is required to achieve optimum results.

All three clays were tested under same working conditions for comparison.

CHAPTER 4

RESULTS AND DISCUSSION

4 RESULTS AND DISCUSSION

4.1 Introduction to the Results and Discussion Section

This section of the report reflects on the results achieved during the experimental studies conducted under fixed working conditions temperature, contact-time and clay dosage. The response is presented in both graphical and tabular format to better explain the effectiveness of each clay used as an adsorbent.

Table 8 below, represents heavy metals percentage removal under three different working parameters clay dosage, temperature and contact time against used oils. The number of experimental runs performed for each parameter were 17. Based on previous studies; the minimum and maximum working conditions for all parameters were set at 10 and 40 grams of clay per 100 mL used oil and 50 to 110 degrees Celsius as well as 10 to 90 minutes contact or residence time, respectively. Hence, the use of Design Expert to predict the optimum working condition. However, all three working parameters set were used simultaneously.

Elemental analysis using 3 South African clays as an adsorbent, Atomic Emission Spectroscopy (AES) and FTIR was used to determine bothe elemental analysis and fluid properties as well as contamination.

Clay analysis results for all three South African clays, SEM, XRF, and FTIR

4.2 Model parameters results

Table 4-1 shows the physical and chemical properties of the attapulgite clay after treatment. The properties include density, water content, flash point, pour point, viscosity index, kinematic viscosity at 40 and 100 degrees.

Table 4-4-1: After treatment using attapulgite clay as an adsorbent

Properties	Used Engine oil	Typical values
Selected properties		
Density (g/mL)	1.01	0.98 – 1.13
Kinematic Viscosity at 40 ℃ (Pa.s)	1.11	1.07 – 1.33
Kinematic Viscosity at 100℃(Pa.s)	0.79	0.51 – 0.82
Viscosity Index	1.50	1.01 – 2.07
Ash Content %	0.12	0.10 – 0.18
Water Content %	1.10	0.97 – 1.91
Flash Point℃	103	1.70 – 181
Pour Point℃	91	88 - 97
Metallic Content (ppm)		
Lead (Pb)	26.89	20.01 – 27.20
Chromium (Cr)	29.45	19.31 – 31.89
Zinc (Zn)	30.28	23.36 – 33.06
Iron (Fe)	37.09	34.11 – 44.07
Nickel (Ni)	22.70	19.47 – 27.30
Copper (Cu)	25.05	22.64 – 26.88

Table 4-2 and Figure 4-1 below shows the percentage removal of heavy metals contained in used oil in both tabular and graphical format, the working parameters investigated are contact time, clay dosage and temperature. The removal percentage after treatment by means of the attapulgite clay.

Table 4-4-2: Percentage removal of heavy metals contained in used oil, the effect temperature, contact time and clay dosage (g/100ml used oil; Attapulgite clay)

Parameters			**Heavy metal percentage removal**			
Temperature (ºC)	Clay dosage (Grams of clay/100ml oil)	Contact time (minutes)	Zn	Fe	Pb	Cu
80.00	25.00	50.00	44,55	43,86	37,52	43,89
80.00	25.00	50.00	44,55	43,86	40,87	43,89
110.00	25.00	90.00	41,31	42,14	31,49	36,19
50.00	25.00	10.00	51,03	66,22	50,25	54,67
50.00	10.00	50.00	62,37	69,66	52,93	57,75
80.00	40.00	10.00	46,98	66,22	54,27	60,83
80.00	10.00	90.00	57,56	50,74	34,84	40,04
80.00	25.00	50.00	45,51	54,18	44,89	53,13
80.00	10.00	10.00	72,09	71,27	55,61	63,91
50.00	25.00	90.00	41,31	40,42	35,51	35,42
80.00	40.00	90.00	46,17	35,26	31,49	32,34
80.00	25.00	50.00	42,93	54,18	40,87	49,28
110.00	10.00	50.00	59,13	61,06	47,57	54,67
110.00	25.00	10.00	60,67	61,06	48,91	59,29
110.00	40.00	50.00	41,31	49,02	32,83	46,97

80.00	25.00	50.00	47,79	53,32	44,89	53,13
50.00	40.00	50.00	39,69	44,69	44,597	44,504

The effect of clay-dosage: The minimum and maximum amount of clay used to absorb the metals found in used oil was set at 10-40 grams/100mL of used oil. The results show that the removal of heavy metals increases with an increase in clay dosage. Hence, this is observed for all metals investigated. Lead (Pb) having the highest removal efficiency with 86.67%, 89.37% and 88.37% for clay dosages of 10, 25 and 40grams, respectively. Cu, Cr and Ni showed great response to the absorption by means of clay 3 reaching 88.82%, 90.32% and 90.08% respectively.

The effect of temperature: The effect of temperature in the absorption of heavy metals by means of acid-clay process is significant. A high temperature is required to allow the extraction of metals to be effective. Hence, reducing the viscosity of the oil exposes the metals to inoculated or activated clay. This increases the attraction of ions. The minimum and maximum working conditions were set at 50-110 degrees based on previous studies conducted by various individuals. Lead (Pb) showed a great reaction response to the process having removed up to 90.07% at maximum conditions. While Cu, Cr, Ni also followed with removal efficiency greater than 75% reaching a high of 90.06%, 80.89% and 86.55% respectively. Zinc (Zn) and iron (Fe) had the least percentage removal compared to other metals.

The effect of contact-time: Contact time is one of the factors that influence adsorption. Determination of contact time aims to yield the best time in process of adsorption of heavy metals in used engine oil by means of activated clay. The optimum contact time occurs at 90 minutes with an uptake capacity of 238.57 mg/g. However, a prolonged contact time can result in low percentage reduction of heavy metals in used oil. Hence, a decrease in adsorption will occur because the site that binds the clay with used oil is saturated. Also, Lead (Pb) and Copper (Cu) have shown great response to the adsorption having reached 84.20%, 87.86% at minimum and 90.44% and 90.84% at maximum conditions, respectively.

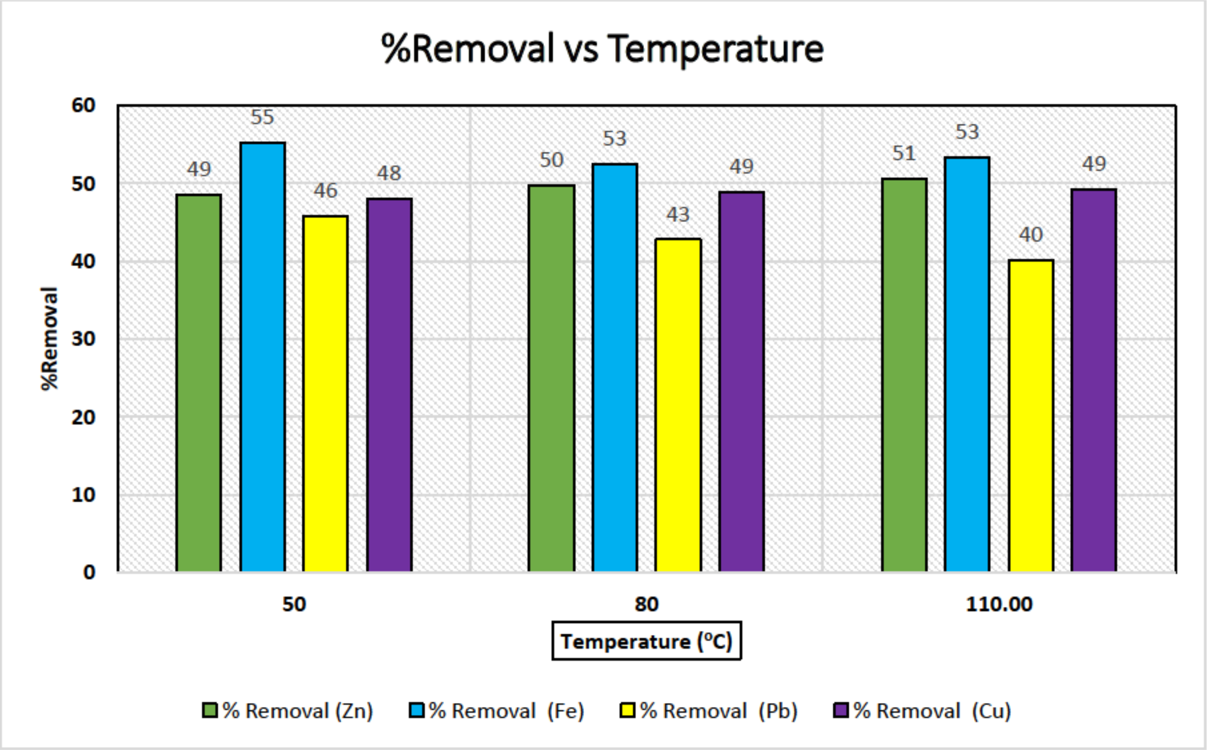


Figure 4-1: The effect of temperature on heavy metal removal in used oil using Attapulgite clay as adsorbent.

The effect of temperature during the adsorption of heavy metals using attapulgite clay is moderately effective. Figure 4-1 shows that temperature-working parameter has a less impact on the extraction of metallic elements obtained in used engine oil. Highest removal percentage obtained being 55% for iron (Fe) at 50 degrees Celsius. The lowest percentage attained is 40% for lead (Pb). Lead however has the least removal efficiency compared to zinc, copper and iron.

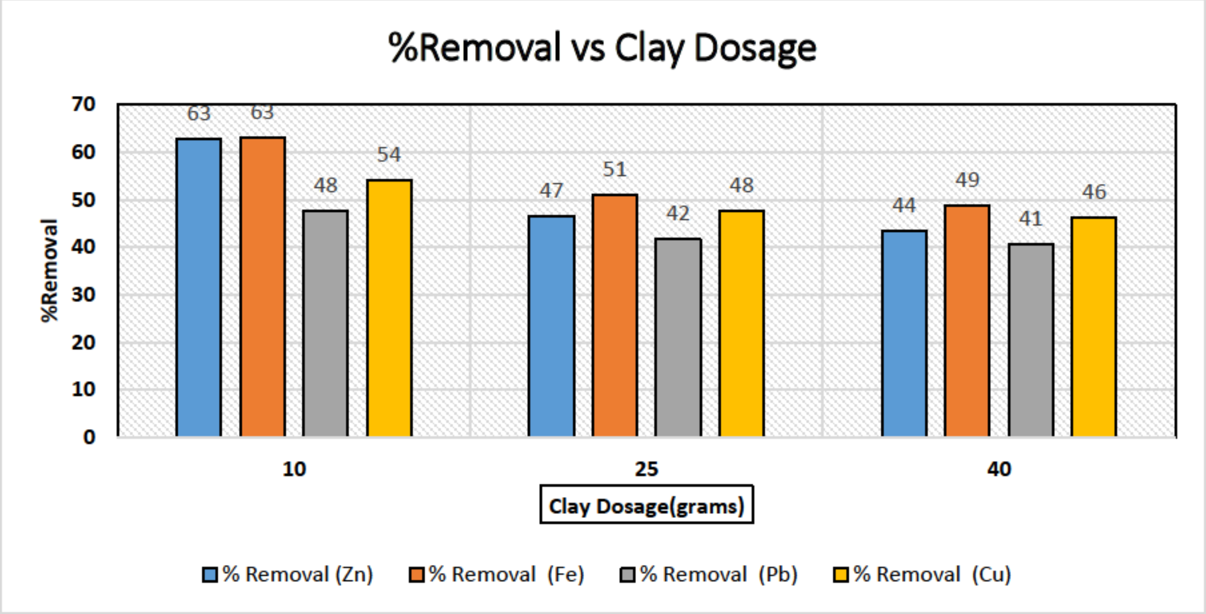


Figure 4-2: The effect clay dosage on heavy metal removal in used oil using Attapulgite clay as an adsorbent

The effect of clay dosage per 100mL used oil, has a positive response for attapulgite clay reaching a high of 63% for both zinc and iron. This could be the bonding structure formed by the clay particles and the sulphuric acid solution after modification. However, the percentage removal drops as the amount of clay dosed into 100mL of used oil. This indicates that the ratio of mixing should be kept at 1:1 to prevent over flooding and coking.

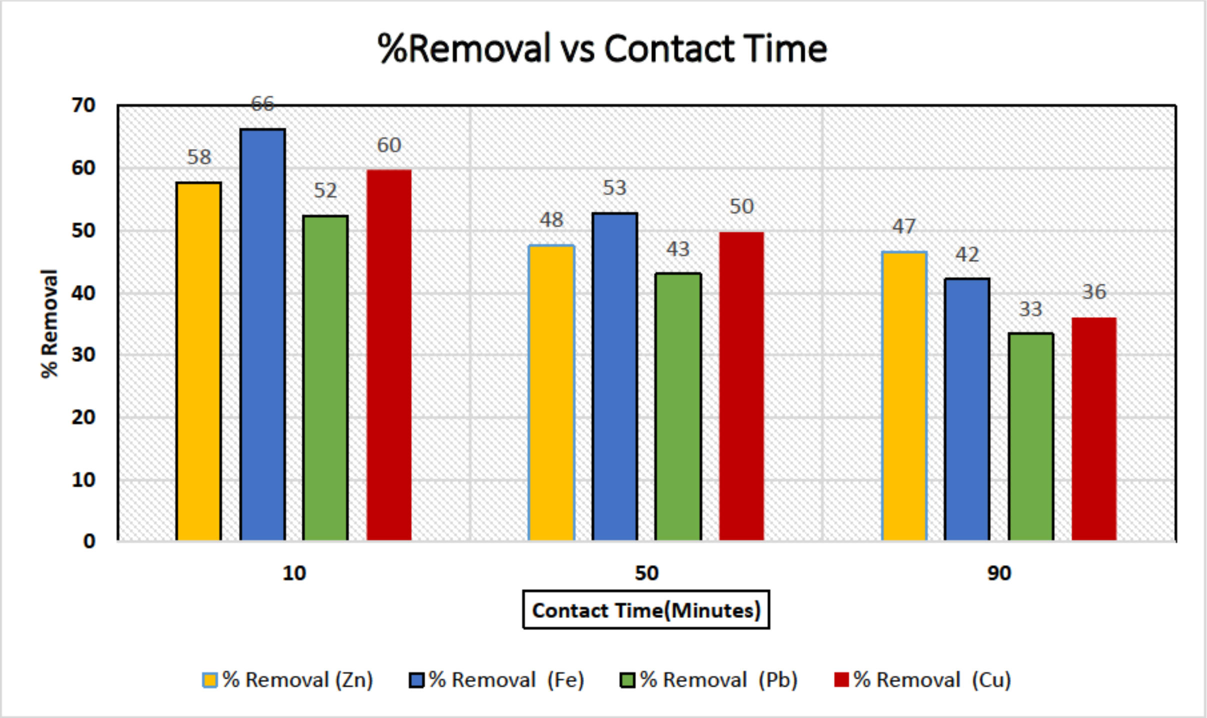


Figure 4-3: The effect of contact time on the removal of heavy metals in used oil using Attapulgite clay as an adsorbent

The effect of contact time on the adsorption of heavy metals in used oil plays a huge role, thus allowing the formation of bond between the oil and adsorbent. Figure 4-3 indicates that the longer the time taken during the adsorption process the less results it will yield. At 10 minutes contact time a high of 66% is attained for iron and a low of 33% is obtained for lead at 90 minutes contact time. This however, is a result of a low viscosity thus the oil is moderately hot allowing a firm bond between the molecular structure of the adsorbent and oil. Table 4-3 and Figure 4-3 shows the tabular and graphical analysis.

Table 4-4-3: After treatment using kaolin clay as an adsorbent

Properties	Used Engine oil	Typical values
	Selected properties	
Density (g/mL)	1.01	0.98 – 1.13
Kinematic Viscosity at 40 ℃ (Pa.s)	1.17	1.07 – 1.33
Kinematic Viscosity at 100℃(Pa.s)	0.59	0.51 – 0.82
Viscosity Index	1.31	1.01 – 2.07
Ash Content %	0.12	0.10 – 0.18
Water Content %	1.27	0.97 – 1.91
Flash Point℃	109	1.70 – 181
Pour Point℃	94	88 - 97
	Metallic Content (ppm)	
Lead (Pb)	24.51	20.01 – 27.20
Chromium (Cr)	23.05	19.31 – 31.89
Zinc (Zn)	23.36	23.36 – 33.06
Iron (Fe)	39.21	34.11 – 44.07
Nickel (Ni)	25.03	19.47 – 27.30
Copper (Cu)	24.52	22.64 – 26.88

Table 4-4-4: Heavy metals removal at various working parameters for bentonite clay

Parameter			Heavy metal percentage removal			
Temperature (ºC)	Clay dosage (Grams of clay/100ml oil)	Contact time (minutes)	Zn	Fe	Pb	Cu
80.00	25.00	50.00	50,60	43,35	40,88	45,60
80.00	25.00	50.00	50,60	43,35	44,53	45,60
110.00	25.00	90.00	46,92	41,65	34,31	37,60
50.00	25.00	10.00	57,96	65,45	54,75	56,80
50.00	10.00	50.00	70,84	68,85	57,67	60.00
80.00	40.00	10.00	53,36	65,45	59,13	63,20
80.00	10.00	90.00	65,38	50,15	37,96	41,60
80.00	25.00	50.00	51,69	53,55	48,91	55,20
80.00	10.00	10.00	81,88	70,44	60,59	66,40
50.00	25.00	90.00	46,92	39,95	38,69	36,80
80.00	40.00	90.00	52,44	34,85	34,31	33,60
80.00	25.00	50.00	48,76	53,55	44,53	51,20
110.00	10.00	50.00	67,16	60,35	51,83	56,80
110.00	25.00	10.00	68,91	60,35	53,29	61,60
110.00	40.00	50.00	46,92	48,45	35,77	48,80
80.00	25.00	50.00	54,28	52,7	48,91	55,20
50.00	40.00	50.00	45,08	45,9	38,69	48,80

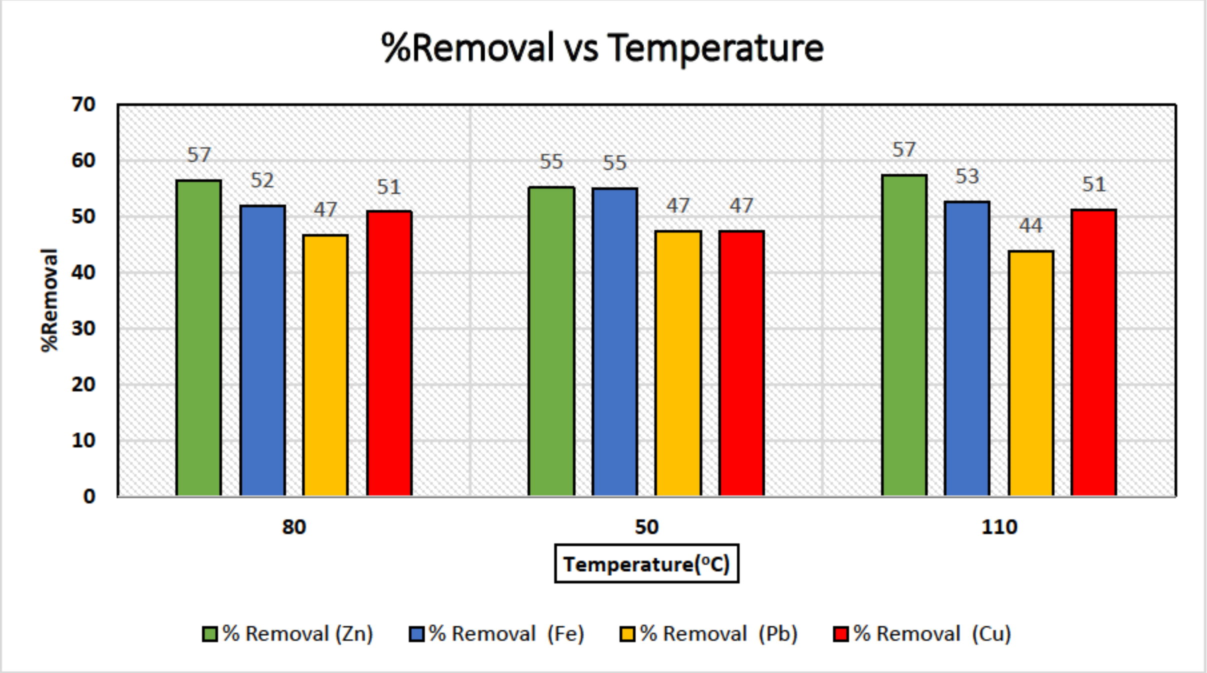


Figure 4-4: The effect of temperature on the heavy metals removal in used oil using Bentonite clay as an adsorbent

The effect of temperature using modified bentonite clay as an adsorbent has average impact on the extraction of metallic elements and other contaminants. Figure 4-4 above reveals that excessive heat is not required to achieve a high removal efficiency. The minimum temperature 50 degrees Celsius does the same as when the temperature is increased to 110 degrees Celsius. A fluctuation is observed from the minimum and maximum temperature.

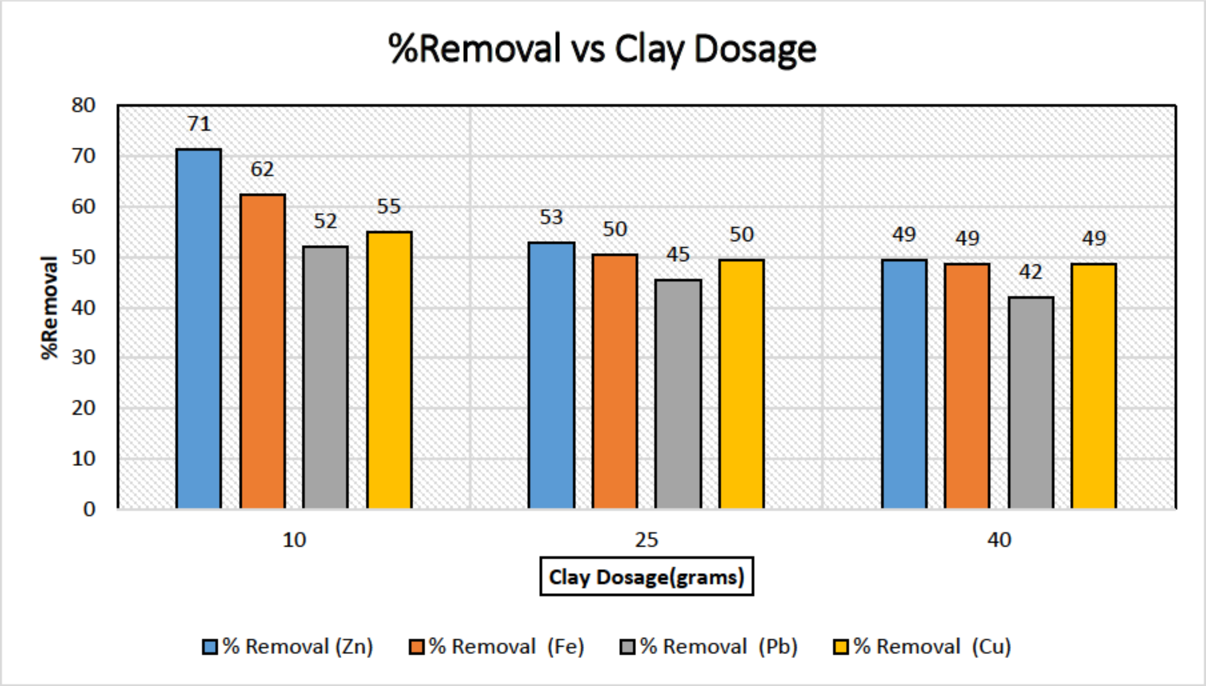


Figure 4-5: The effect of clay dosage on the removal of heavy metals in used oil using Bentonite clay as an adsorbent

The effect of clay dosage per 100mL of used oil plays a vital role in the adsorption process. Figure 4-5 shows a high of 71% is achieve for zinc followed by iron, copper and lead with 62%, 55% and 52% respectively. The amount of zinc removed shows that the bonding structure formed by the modified bentonite clay particles and sulphuric acid solution reduced the grain size of the clay thus allowing a greater adsorption to take place.

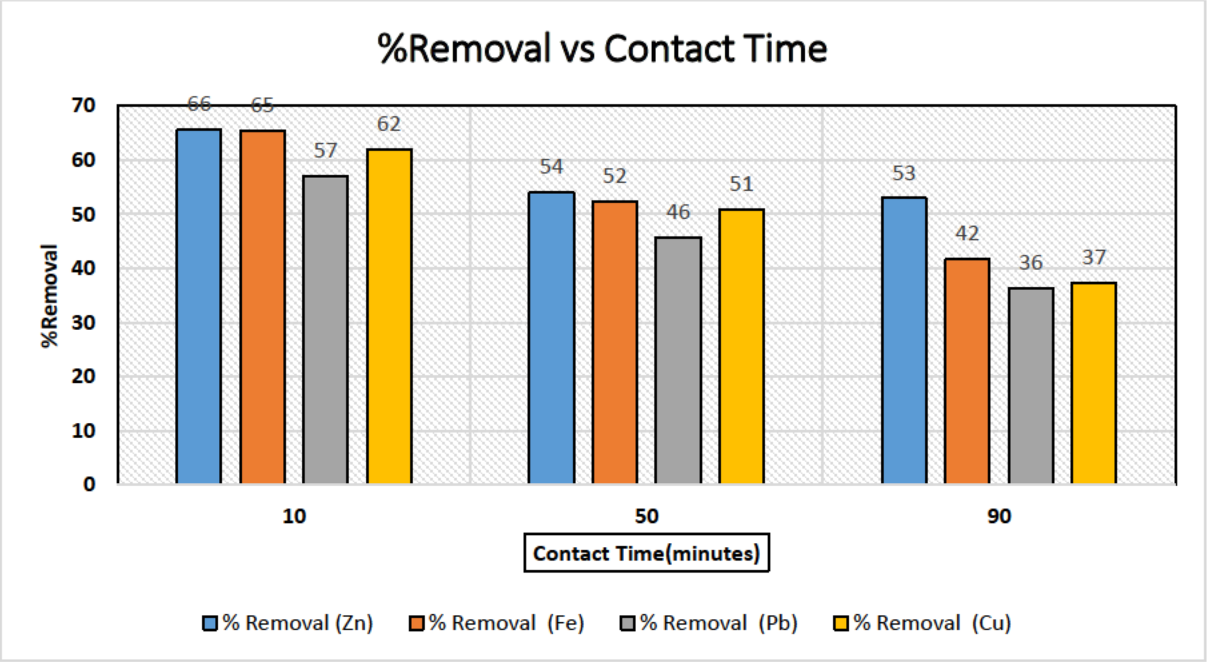


Figure 4-6: The effect of contact time on the removal of heavy metals on used oil using Bentonite clay as an adsorbent

The effect of contact time on adsorption of heavy metals using modified bentonite clay as an adsorbent results in a positive response by surpassing the average mark of 50% by a degree of 10 in the minimum time of 10 minutes. This signals that a prolonged time results in low selectivity and yield. The longer the solution remains on the heated vessel the less metals can be extracted. A drastic drop is noted in the maximum contact time of 90 minutes, saturation of the bonding structure formed between the clay particles and used oil.

Table 4-5: After treatment using kaolin clay as an adsorbent

Properties	Used Engine oil	Typical values
	Selected properties	
Density (g/mL)	1.09	0.98 – 1.13
Kinematic Viscosity at 40 ℃ (Pa.s)	1.11	1.07 – 1.33
Kinematic Viscosity at 100℃(Pa.s)	0.66	0.51 – 0.82
Viscosity Index	1.43	1.01 – 2.07
Ash Content %	0.10	0.10 – 0.18
Water Content %	1.21	0.97 – 1.91
Flash Point℃	101	1.70 – 181
Pour Point℃	91	88 - 97
	Metallic Content (ppm)	
Lead (Pb)	21.30	20.01 – 27.20
Chromium (Cr)	24.77	19.31 – 31.89
Zinc (Zn)	29.05	23.36 – 33.06
Iron (Fe)	35.55	34.11 – 44.07
Nickel (Ni)	19.47	19.47 – 27.30
Copper (Cu)	22.88	22.64 – 26.88

Table 4-4-6: Heavy metals removal at various working parameters for Kaolin clay

Parameter			Heavy metal percentage removal			
Temperature (°C)	Clay dosage (Grams of clay/100ml oil)	Contact time (minutes)	Zn	Fe	Pb	Cu
80.00	25.00	50.00	44,55	43,86	37,52	43,89
80.00	25.00	50.00	44,55	43,86	40,87	43,89
110.00	25.00	90.00	41,31	42,14	31,49	36,19
50.00	25.00	10.00	51,03	66,22	50,25	54,67
50.00	10.00	50.00	62,37	69,66	52,93	57,75
80.00	40.00	10.00	46,98	66,22	54,27	60,83
80.00	10.00	90.00	57,56	50,74	34,84	40,04
80.00	25.00	50.00	45,51	54,18	44,89	53,13
80.00	10.00	10.00	72,09	71,27	55,61	63,91
50.00	25.00	90.00	41,31	40,42	35,51	35,42
80.00	40.00	90.00	46,17	35,26	31,49	32,34
80.00	25.00	50.00	42,93	54,18	40,87	49,28
110.00	10.00	50.00	59,13	61,06	47,57	54,67
110.00	25.00	10.00	60,67	61,06	48,91	59,29
110.00	40.00	50.00	41,31	49,02	32,83	46,97
80.00	25.00	50.00	47,79	53,32	44,89	53,13
50.00	40.00	50.00	39,69	46,44	35,51	46,97

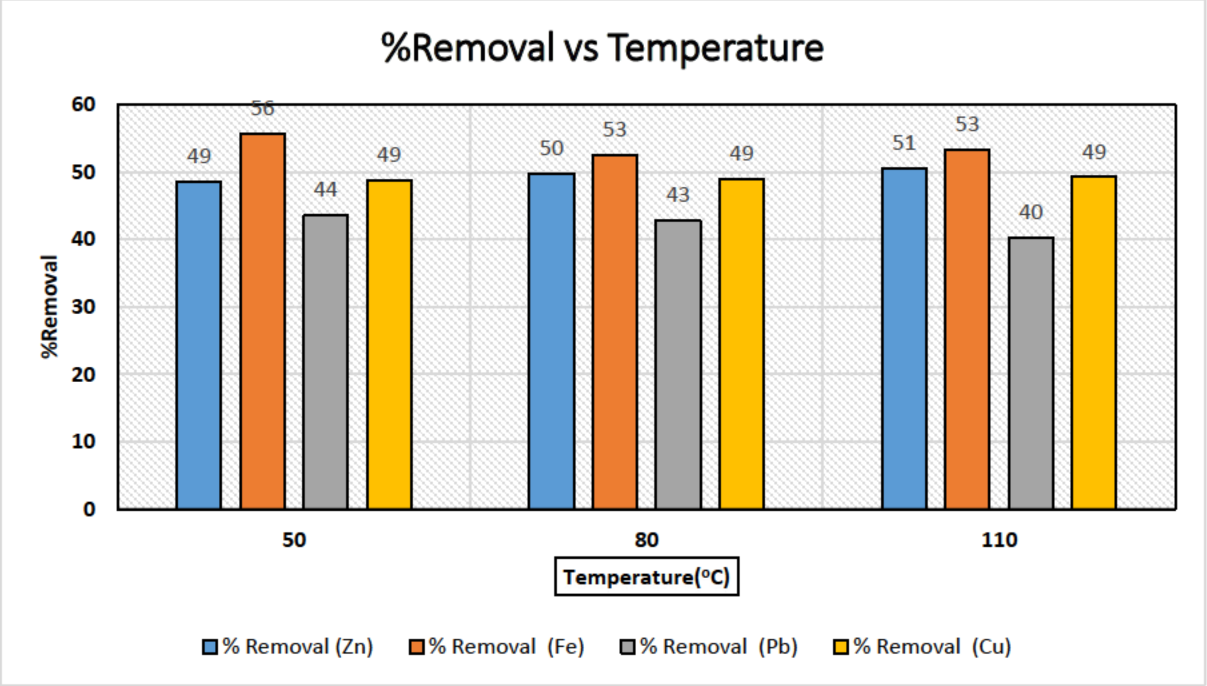


Figure 4-7: The effect of temperature on the removal of heavy metals in used oil using Kaolin clay as an adsorbent

Figure 4-7, best describes the effect or significance temperature has on the adsorption of heavy metals using modified kaolin clay as an adsorbent. However, it must be highlighted that temperature alone cannot have a significant impact on the removal of heavy metals but using all three working or controlled parameters simultaneously will yield the results achieved by other researchers in studies they performed. Iron (Fe) responded very well to the adsorption of metals using modified kaolin clay achieving a high removal percentage of 56% followed by zinc (Zn) closely with 52% while metals like lead (Pb) and copper (Cu) were less responsive to the treatment with 44% and 49% respectively. The declining trend is observed temperatures of 80 and 110 degrees Celsius.

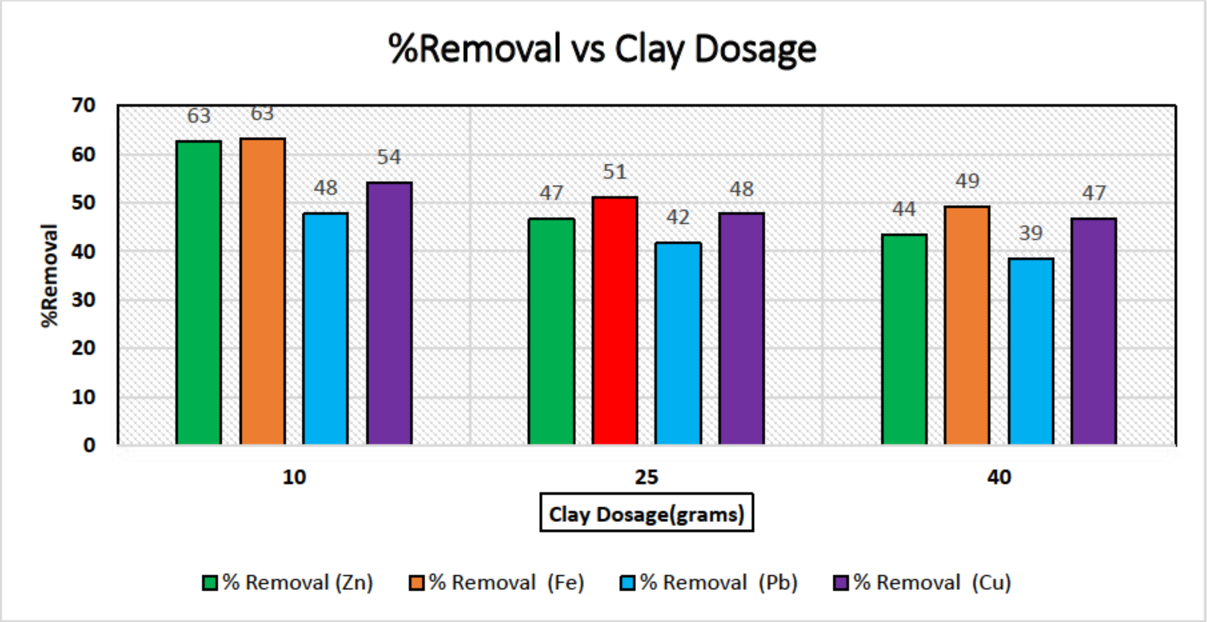


Figure 4-8: The effect of clay dosage on the removal of heavy metals in used oil using Kaolin clay as an adsorbent

Figure 4-8, better explains the outcome of the experiment using fixed clay dosage against two other parameters temperature and contact time. However, the above graphical analysis reflects that modified kaolin clay optimum removal efficiency is at 10 grams of adsorbent per 100mL of used oil. Yielding 63% removal for both zinc (Zn) and iron (Fe) while copper (Cu) and lead (Pb) reached a peak of 54% and 48% respectively.

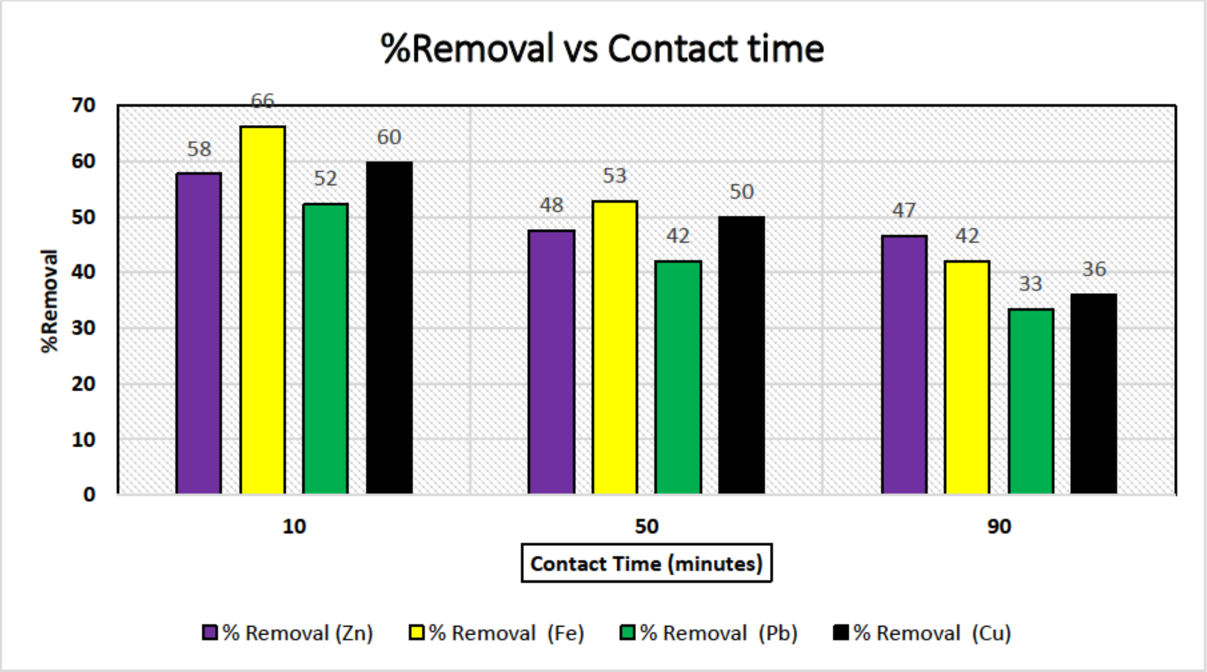


Figure 4-9: The effect of contact time on the removal of heavy metals in used oil using Kaolin clay as an adsorbent

Figure 4-9, best describes the effect of contact-time on the removal or lowering of heavy metals contained by used oils. Contact-time plays a significant role during the process, hence giving allowance to the adsorbent to bind itself to the oil thus attracting any form of metallic components. The graphical analysis reveals that the optimum contact-time to achieve a high yield of metal ions removed is at 10 minutes. This is observed for Fe, Cu and Zn each having 66%, 60% and 54% respectively. Pb, having the lowest removal efficiency in this time each attaining 52%.

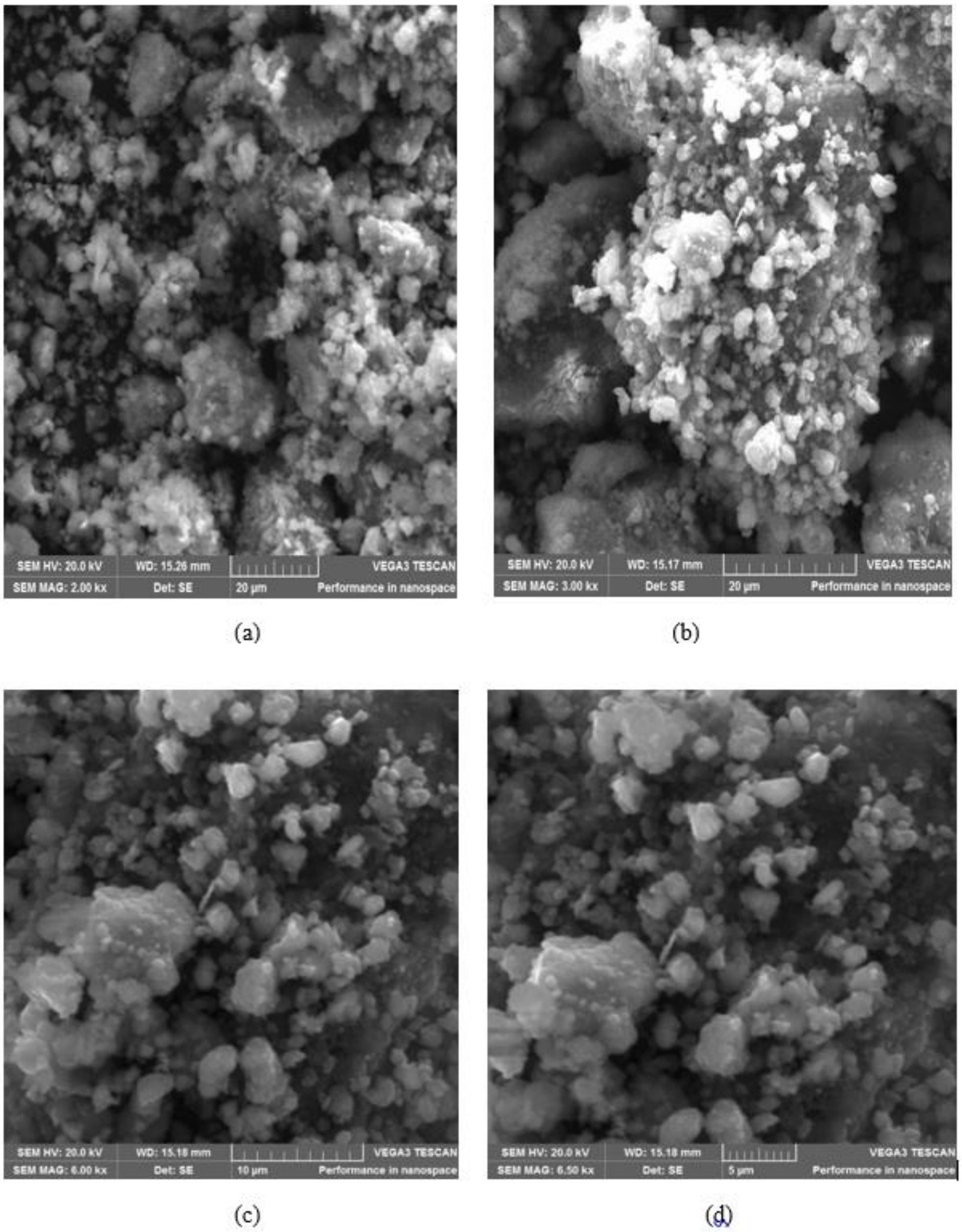
4.3 Clay analysis

In Figure 1 (a-d) shows the scanning electron micrographs of Attapulgite clay of unmodified and modified material are illustrated in Figure 1 (a-d). these micrographs reveal that Figure 1 a and 1b indicate that morphology of attapulgite exhibited to be agglomerate scatted along the surface and it spheric species. However, after modification with H2SO4 the material shows the formation of clusters and agglomeration. Negm et al. (2024) conducted a study on attapulgite clay to enhance the radiation shielding. The author reveal the same properties of surface agglomerated material as obtained which has a tendency of highest adsorption capacity due to the mineral presents in attapulgite clay (Ochieng Ombaka et al,.2016).

Figure 4-11 (a-d) reveals the scanning electron micrographs (SEM) of raw and modified bentonite clay material are illustrated. The micrographs show that Figures 2(a) and 2(b) indicate that morphology of bentonite clay exhibited to be agglomerate scattered along the surface and it spheric species. However, after modification with H2SO4 solution the bentonite clay material shows the formation of clusters and agglomeration. A study conducted by Ochieng Ombaka on clay materials clay related to classification and characterization for potential applications in Rugi Ward, Kenya reveals that using modified clay as an adsorbent to enhance the radiation shielding. The study reveals that the same properties of surface agglomerated material are obtained which have a tendency of highest adsorption capacity due to the mineral presents in bentonite clay (Ochieng Ombaka et al,.2016).

Figure 4-10 (a-d) shows the kaolin clay scanning electron micrographs (SEM) of unmodified and modified clay material are illustrated in Figure 4-10 (a-d). These micrographs reveal that Figures 3(a) and 3(b) indicate that morphology of kaolin exhibited to be agglomerate scattered along the surface and it spheric species. However, after modification with H2SO4 the material shows the formation of clusters and agglomeration. A study conducted on characterization of South African Bentonite and Kaolin clays reveal that after modification of the clay to enhance the radiation shielding, the adsorbent exhibits properties that allow the extraction to be enhanced. The author reveals the same properties of surface agglomerated material as obtained which has a tendency of highest adsorption capacity due to the mineral presents in attapulgite clay (Dipuo P. Kgabi et al. 2023).

Figures 4-10, 4-11 and 4-12 show the grain size of the attapulgite, kaolin, and bentonite clay before and after modification. However, the images show similar properties due to modification with sulphuric acid solution only no additives or enhancers. Furthermore, the SEM analysis aims to show the difference between each clay's mechanical and physical behaviors before and after the modification.



(a) (b)

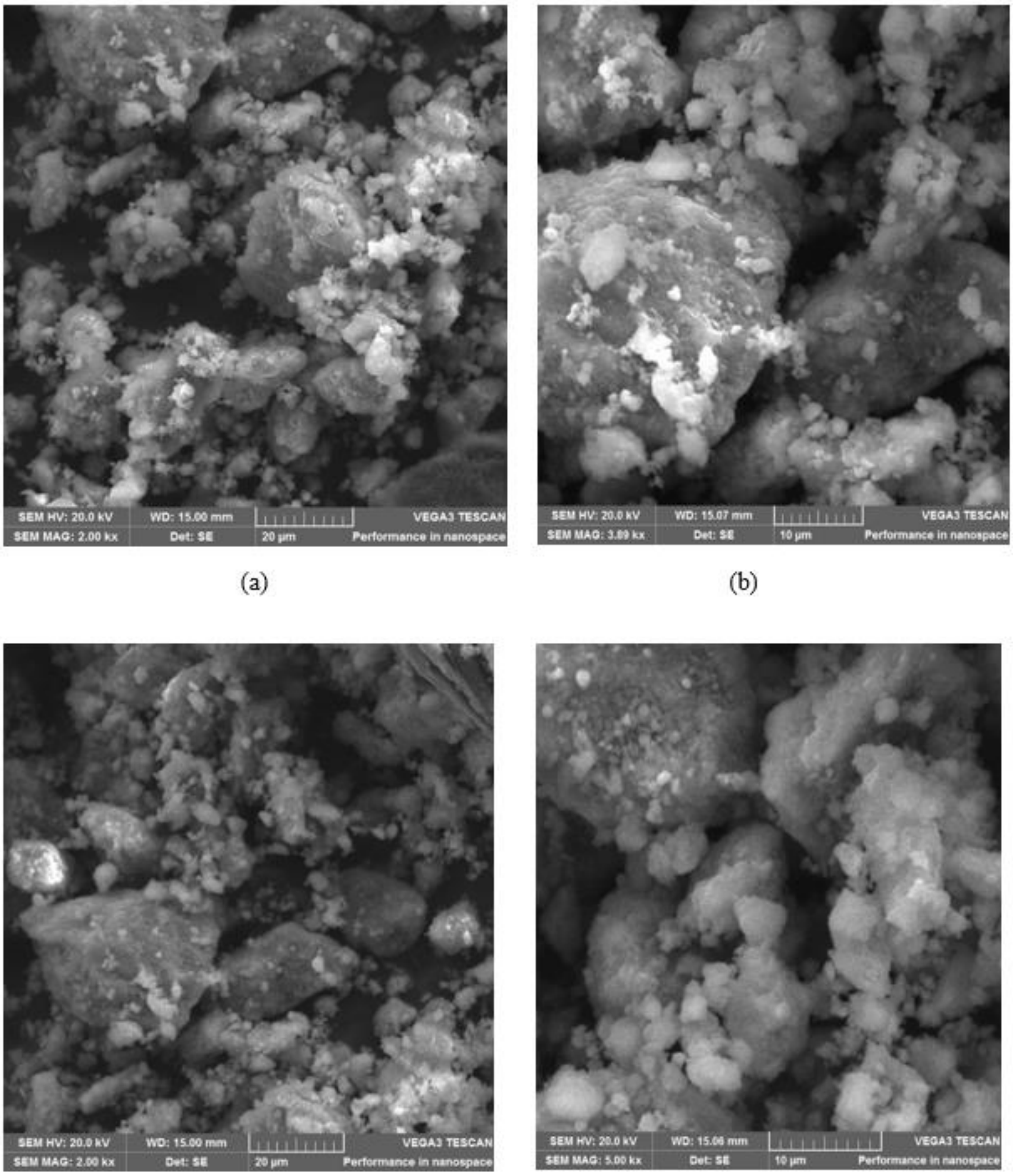
(c) (d)

Figure 4-10: (a) and (b) SEM analysis before, (c) and (d) after modification of attapulgite clay

Figure 4-10 (a) and 1(b) represent the attapulgite clay before modification or improvement with sulphuric acid solution.

Figure 4-10 (c) and 1(d) represent the attapulgite clay after modification or improvement with sulphuric acid solution of 2M. However, the images show that they are no significant impact or changes caused by the inoculation in a sulphuric acid solution. However, they are bonding structures of the additives and clay particles. The grain size has not been impacted.

SEM results: Bentonite clay



(a) (b)

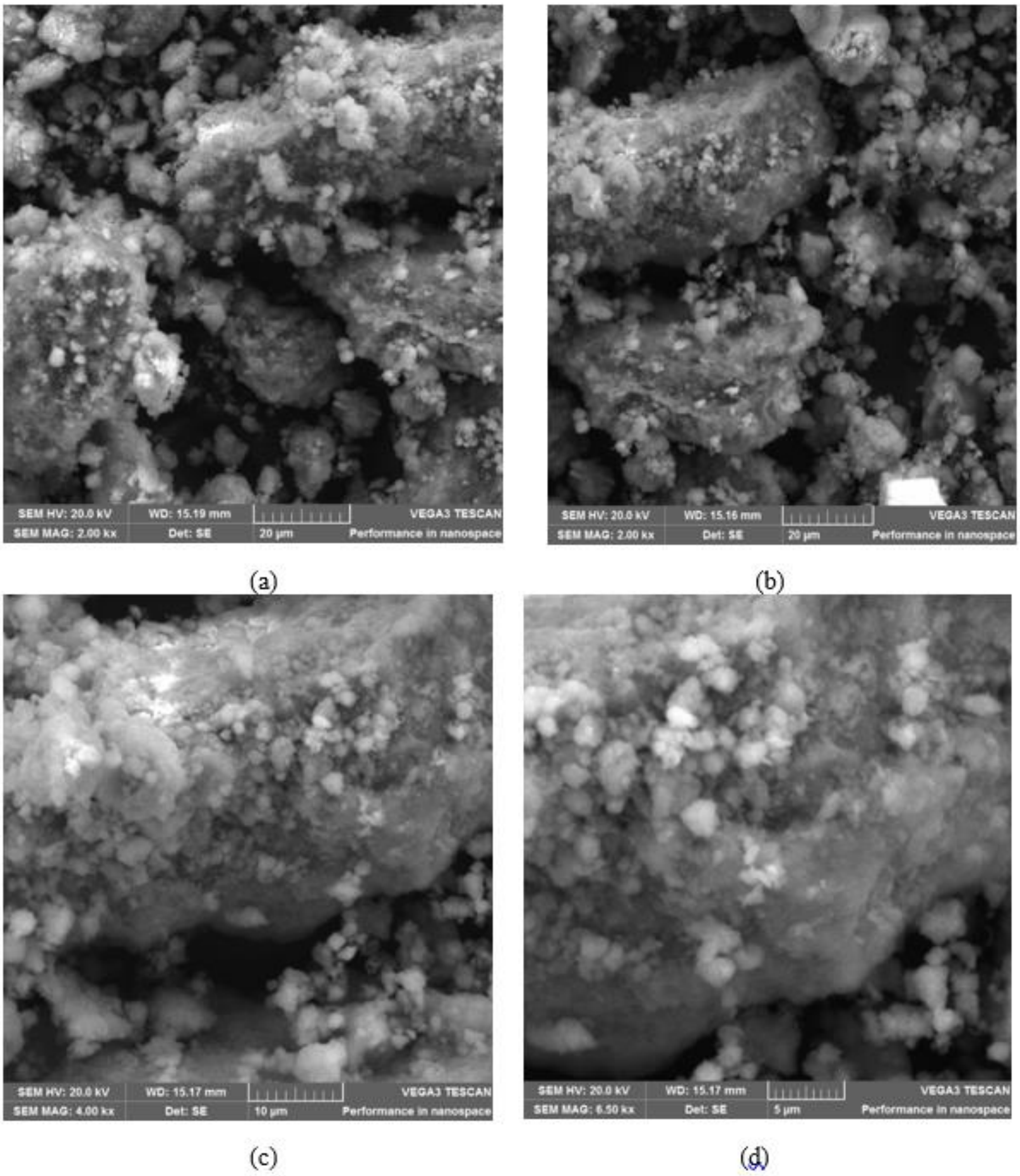
c) (d)

Figure 4-11: SEM analysis before and after modification

Figure 4-11 (a) and (b) represent the bentonite clay before modification with a solution of sulphuric acid, the grainsize greatly exposed.

Figure 4-11 (c) and (d) represent the bentonite clay after treatment or improvement with sulphuric acid solution of 2M. Thus, the physical and mechanical behaviors. The bentonite clay responded moderately to the sulphuric acid solution, this is observed in the images before and after modification. The grain size thus has remained intact with no significant change.

SEM results: Kaolin clay



(a) (b)

(c) (d)

Figure 4-12: SEM analysis before and after modification

Figure 4-12 (a) and (b) represent the kaolin clay scan before modification by means of sulphuric acid solution of 2M.

Figure 4-12 (c) and (d) shows the outcome images of modified clay using a 2M sulphuric acid solution. Figure 1 and 2 show high-resolution images of the kaolin clay before and after the improvement. The kaolin clay’s grain size decreases after treatment with a 2M sulphuric acid solution. This however enables the clay particles and additives to form a solid bond resulting in a reliable and strong adsorbent when used to extract metallic components.

4.4 XRD results: Attapulgite clay

X-ray diffraction is an important tool for material characterization in the field of research. In this study, all clays such as attapulgite, bentonite and kaolin were thoroughly characterized. The peaks were observed at 2θ values of 34, 43 and 71 corresponding to (111), (110) and (211) crystal planes which agreed well with those given in JCPDS card no. 06-0696. Ref…. all though the material shows amorphous with one sharp peak that which is more crystalline. These indicate that the material is agreement went the results from SEM agglomerated and amorphous. Table 4 shows the presence of minerals observed in other studies and with corresponding planes. (Bao et al. 2010)

The method measures the crystal structure by directing a beam of light on the sample shifting at certain angles and intensities. Thus the grain size of clay minerals is less than 2 microns. Therefore, figures 10, 11 and 12 shows the crystal structures of the three clays investigated attapulgite, kaolin and bentonite respectively.

Figure 10 shows the crystal structure of the attapulgite clay which is the layer silicate that belongs to a family or group of phyllosilicates due to its tetrahedral sheets and 2 dimensional structure.

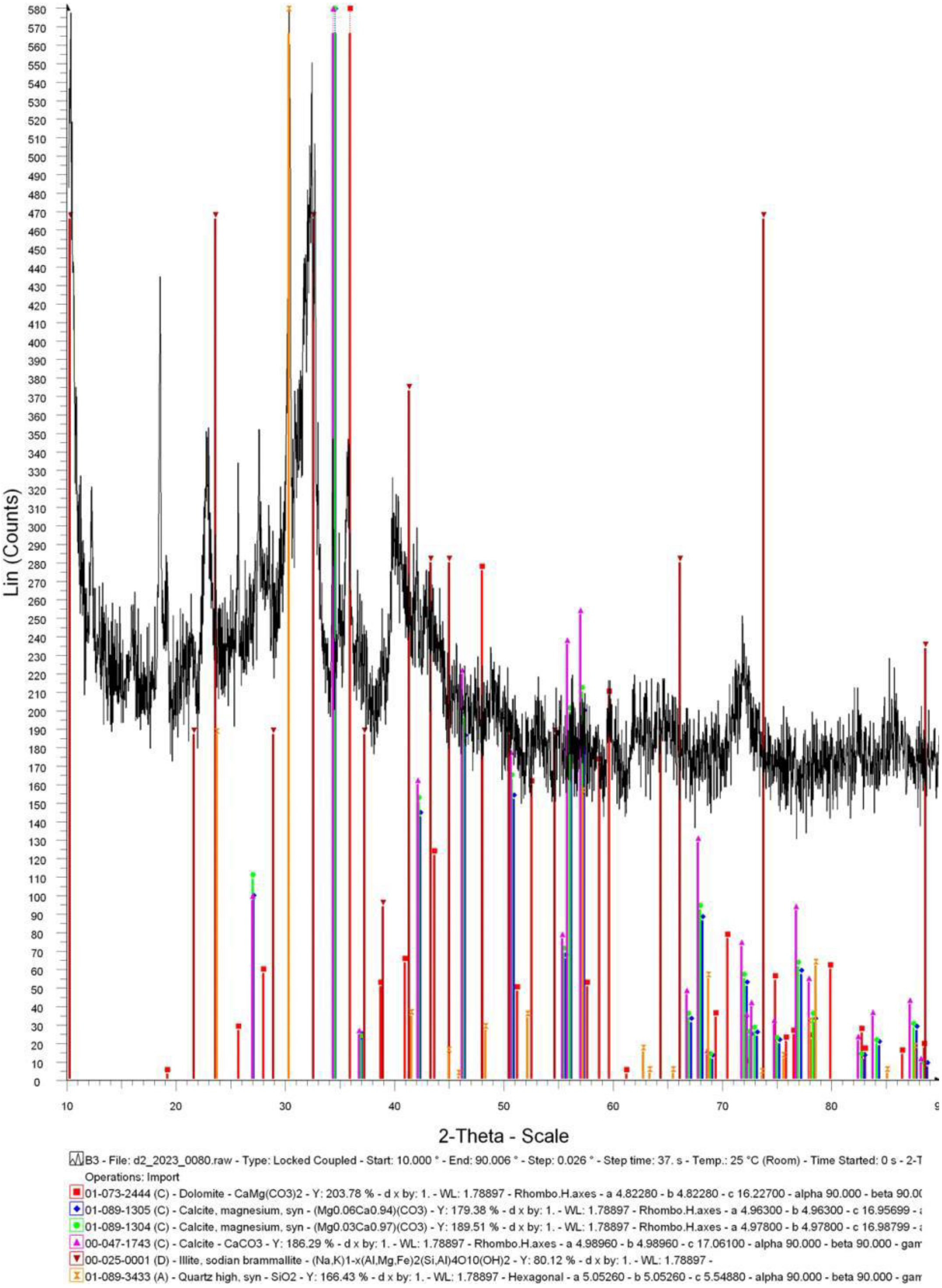


Figure 4-13: XRD results, attapulgite clay

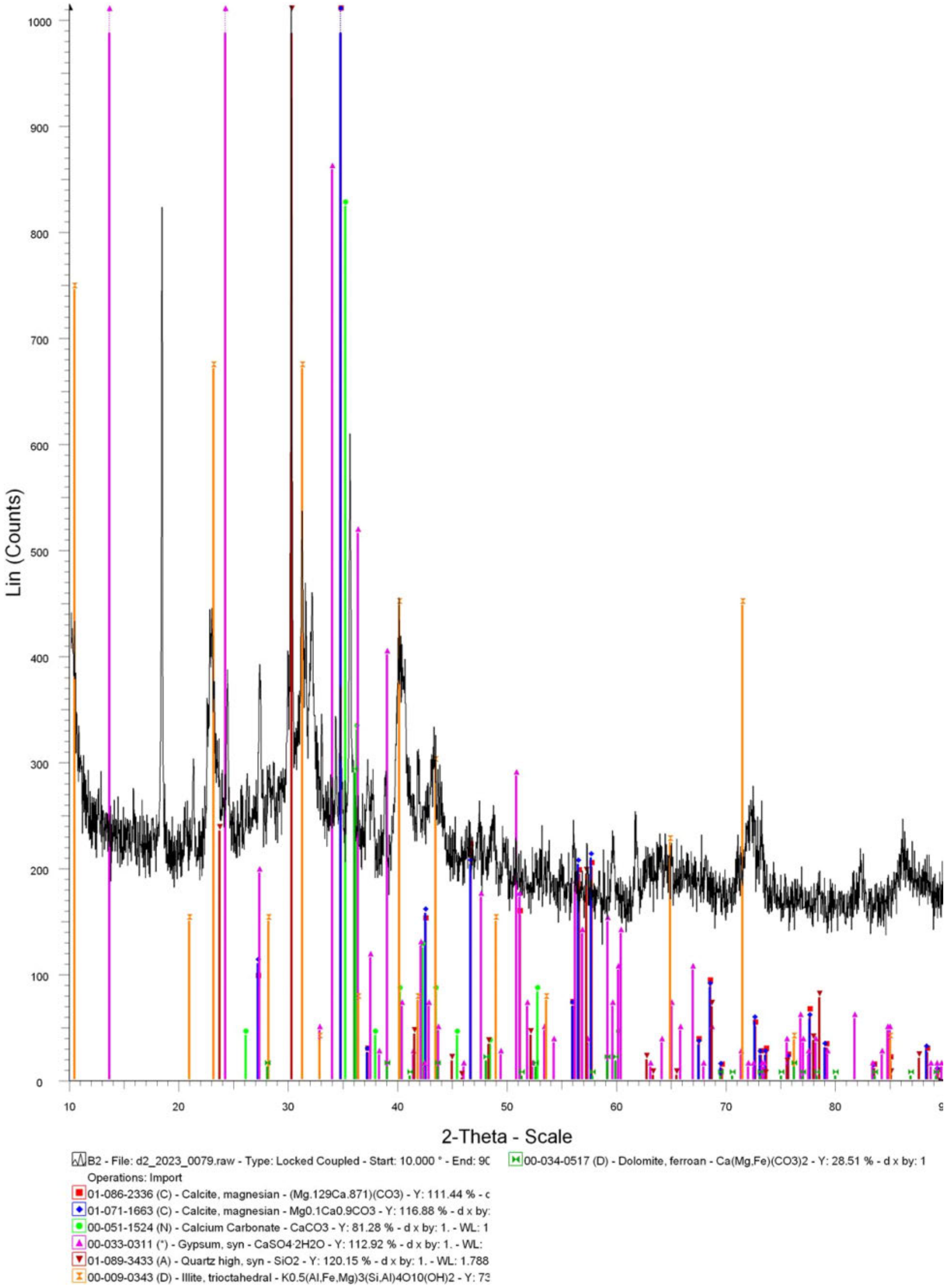


Figure 4-14: XRD results bentonite clay

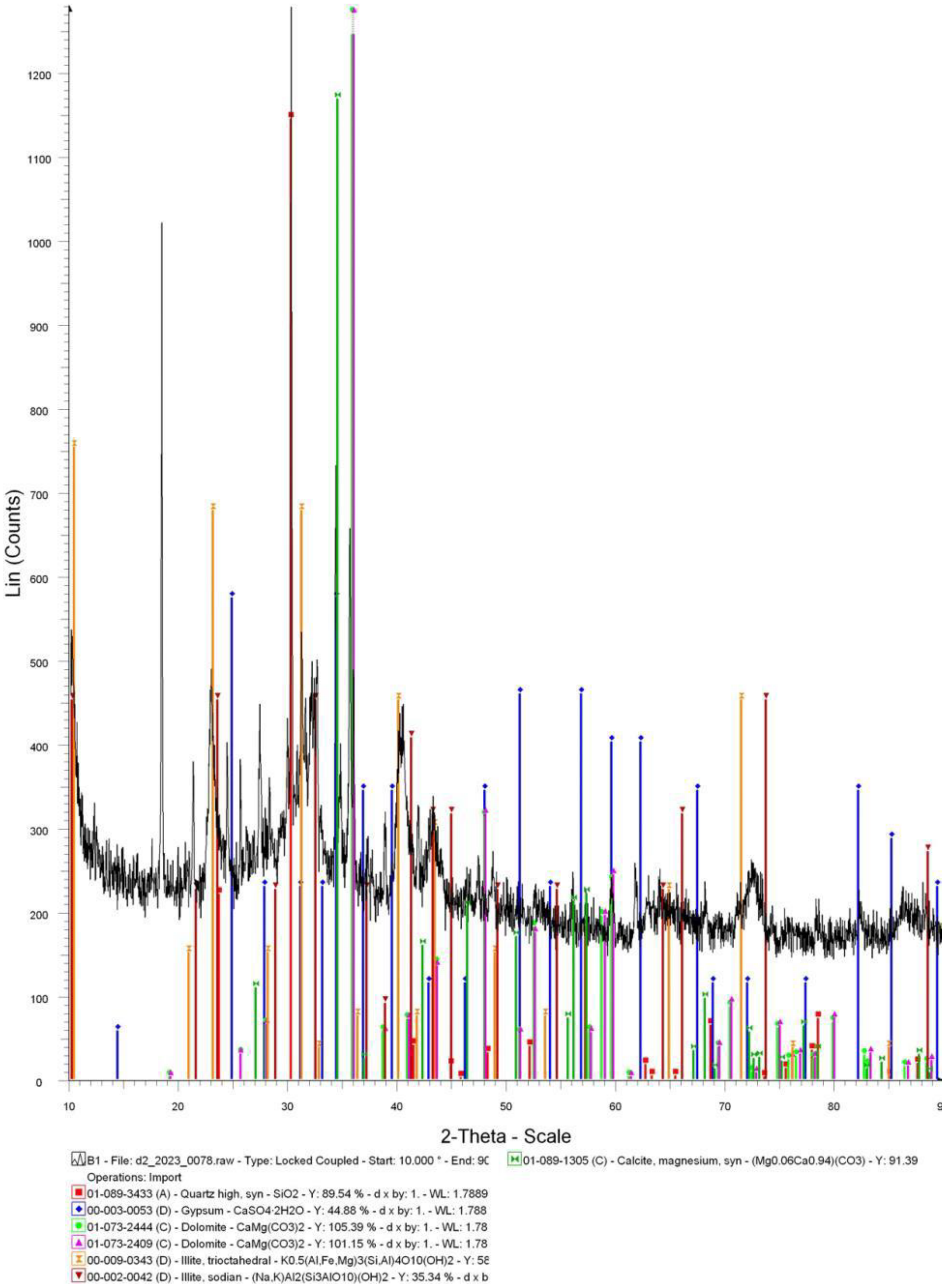


Figure 4-15: XRD results kaolin clay

Table 4-7: XRD results of minerals present attapulgite clay

Component	Unit	Results
SiO_2	Mass %	58.33
Al_2O_3	Mass %	12.66
Fe_2O_3	Mass %	8.99
ZrO_2	Mass %	0.036
MgO	Mass %	6.41
CaO	Mass %	1.97
K_2O	Mass %	6.19
P_2O_5	Mass %	0.34
MnO	Mass %	0.82
TiO_2	Mass %	1.22
CaO	Mass %	1.97
BaO	Mass %	0.029
Rb_2O	Mass %	0.041
ZnO	Mass %	0.015
NiO	Mass %	0.0090
Nb_2O_5	Mass %	0.0067

Table 4-8: XRD results of minerals present in kaolin clay

Component	**Unit**	**Results**
SiO_2	Mass %	56.48
Al_2O_3	Mass %	10.99
Fe_2O_3	Mass %	9.05
ZrO_2	Mass %	0.056
MgO	Mass %	7.56
CaO	Mass %	2.80
K_2O	Mass %	6.35
P_2O_5	Mass %	1.34
MnO	Mass %	0.11
TiO_2	Mass %	1.38
CaO	Mass %	2.80
BaO	Mass %	0.034
Rb_2O	Mass %	0.080
ZnO	Mass %	0.093
NiO	Mass %	0.0086
Nb_2O_5	Mass %	0.011

Table 4-9: XRD results of minerals present in bentonite clay

Component	Unit	Results
SiO_2	Mass %	58.34
Al_2O_3	Mass %	13.77
Fe_2O_3	Mass %	8.99
ZrO_2	Mass %	0.035
MgO	Mass %	6.55
CaO	Mass %	1.89
K_2O	Mass %	6.10
P_2O_5	Mass %	0.36
MnO	Mass %	0.096
TiO_2	Mass %	1.81
CaO	Mass %	1.89
BaO	Mass %	0.024
Rb_2O	Mass %	0.042
ZnO	Mass %	0.015
NiO	Mass %	0.0099
Nb_2O_5	Mass %	0.0067

4.5 FTIR results

Figures 4-13, 4-14 and 4-15 represent the functional groups for all three clays attapulgite, kaolin and bentonite respectively. In addition, the figures help identify the molecular compound for each clay not only distinguishing the functional group they belong to. The method is achieved by measuring the absorbance of the infrared radiation towards the clay sample.

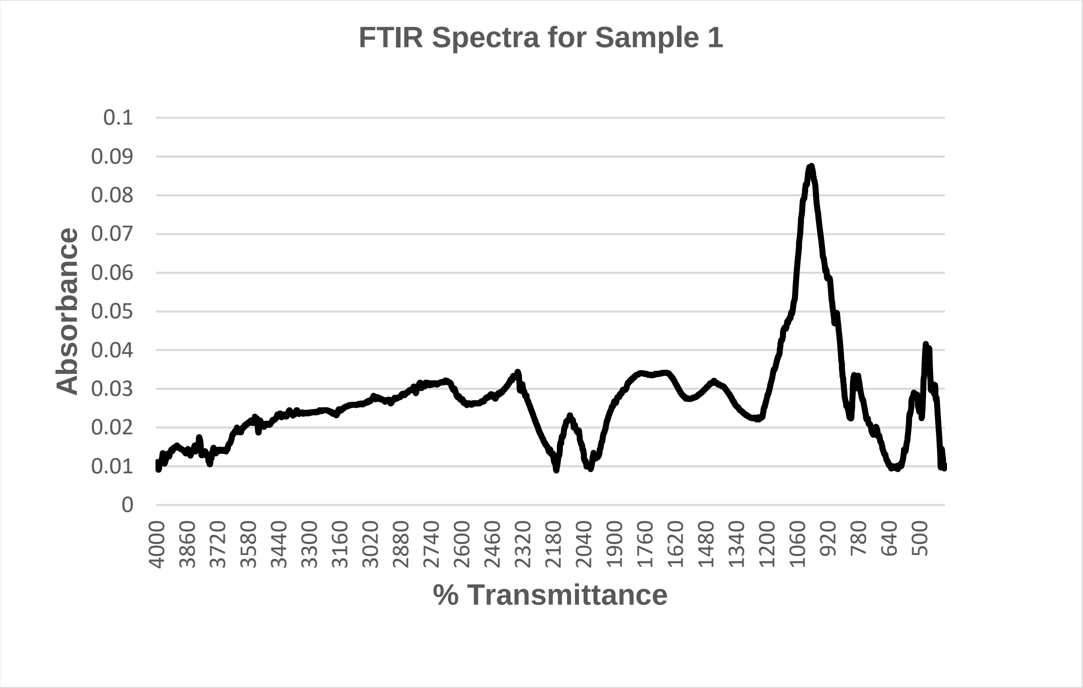


Figure 4-16: FTIR results of attapulgite clay

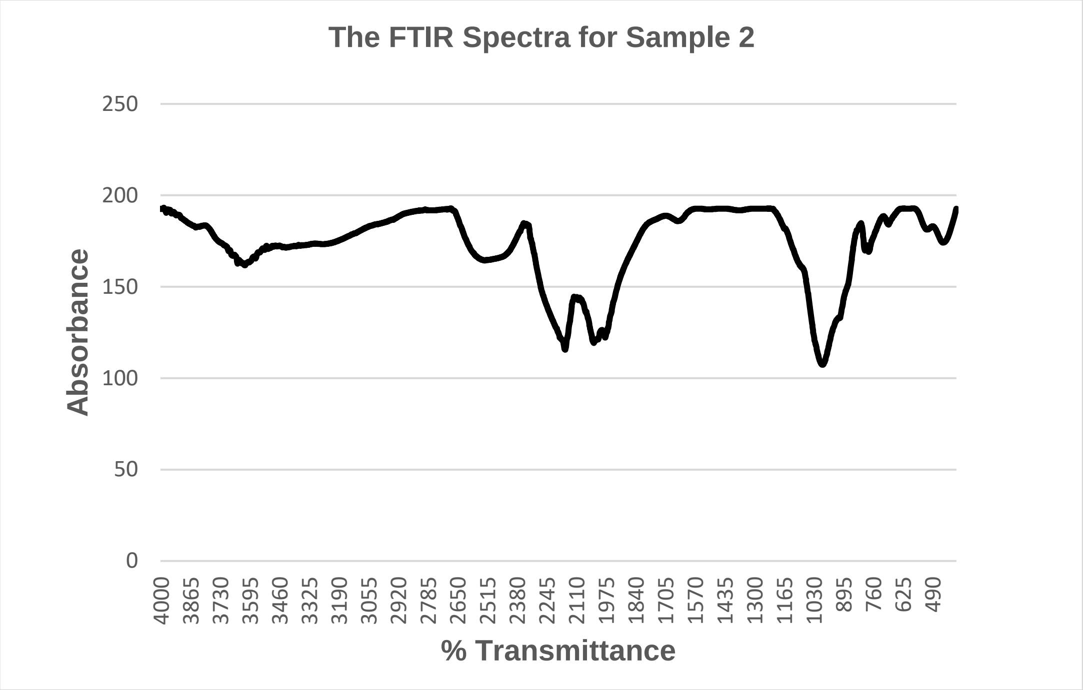


Figure 4-17: FTIR results of kaolin clay

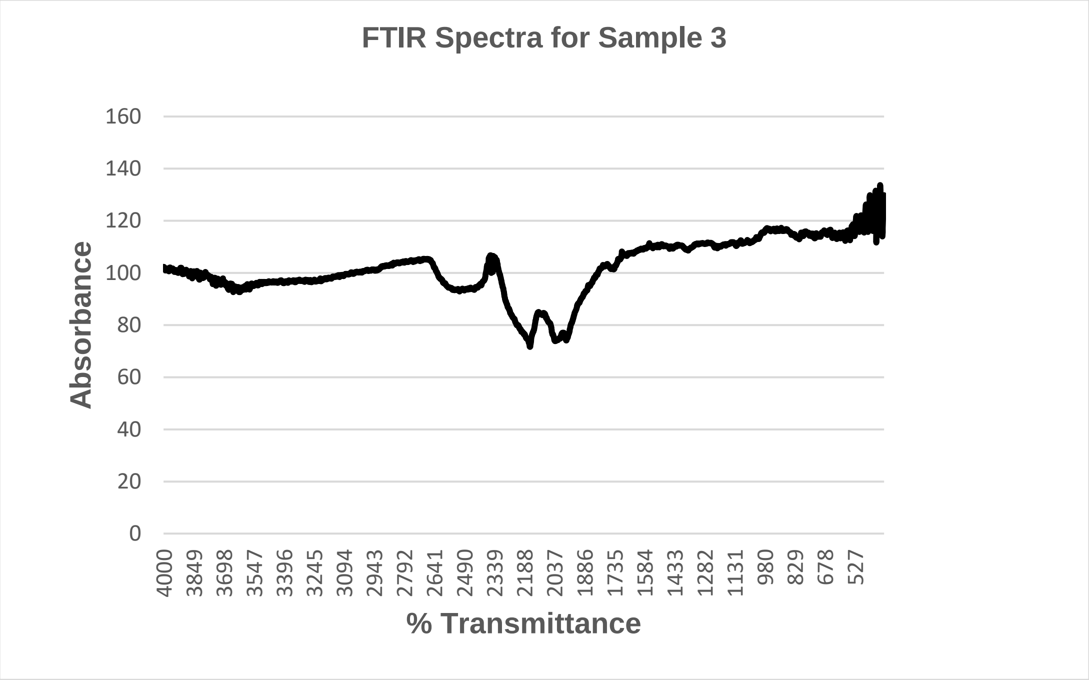


Figure 4-18: FTIR results of bentonite clay

Table 4-10: Adsorption Equilibrium Capacity (Qe), 10g of Attapulgite clay

	Adsorption Equilibrium Capacity (Qe) - Mass 10g					
No. of Runs	Pb (ppm)	Cu (ppm)	Cr (ppm)	Ni (ppm)	Fe (ppm)	Zn (ppm)
1	0,7035	1,0814	0,4966	0,3753	2,9760	1,4976
2	0,7035	1,0814	0,4965	0,3753	2,9760	1,4976
3	0,7818	0,9306	0,5883	0,4089	2,9708	1,5249
4	0,3222	0,7598	0,5638	0,3857	2,8540	1,4169
5	0,4027	0,8801	0,6029	0,4306	2,5853	1,4224
6	0,1866	0,6980	0,5845	0,4430	2,7350	1,3861
7	0,3788	0,9081	0,7509	0,4997	2,4949	1,4802
8	0,6191	1,0303	0,7680	0,5121	2,5867	1,4946
9	0,0312	0,7780	0,6222	0,4608	2,3977	1,4070
10	0,5297	1,2887	0,8054	0,5395	2,9193	1,5245
11	0,5017	1,3324	0,8246	0,5984	3,0212	1,5643
12	0,3581	1,1914	0,7085	0,5438	2,9846	1,5305
13	0,2407	0,9409	0,6950	0,5102	2,5807	1,4166
14	0,1408	0,9201	0,6494	0,4590	2,5512	1,4827
15	0,1106	1,0354	0,7911	0,6323	2,7652	1,5076
16	0,1110	1,1010	0,8149	0,6995	2,5405	1,4999
17	0,0103	1,0762	0,7787	0,6230	2,5986	1,5246

Table 4-10, represents the equilibrium capacity of all heavy metals obtained in used oils for 17 runs performed in response to 10 grams of activated clay 3. Hence, the adsorption equilibrium capacity refers to amount of absorbate extracted per unit mass (or volume) of the adsorbent. Equation 4-1, best describes the concentrations values obtained. From the table 4-4, zinc and iron did not respond as expected. This may be particularly because of the nature of adsorbent used, or the properties exhibited by the adsorbent.

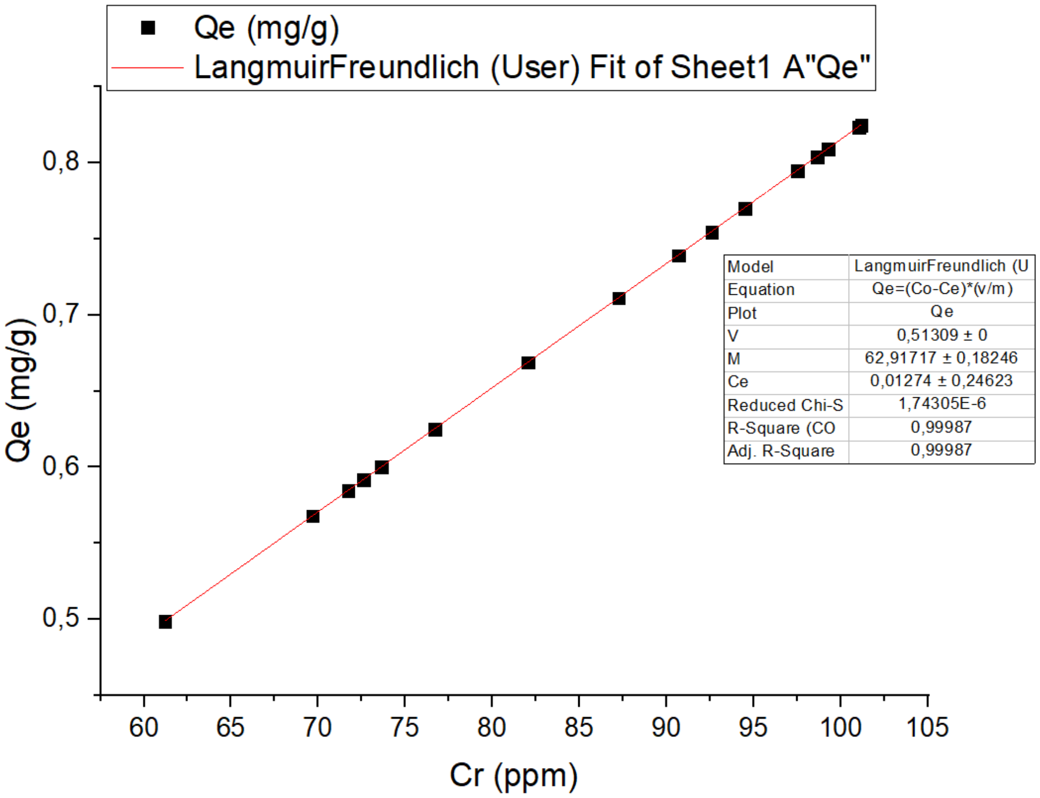


Figure 4-19: Langmuir-Freundlich Isotherm, Chromium fit at 10 grams of Attapulgite clay

Figure 4-19, represents the Langmuir-Freundlich isotherm graphical analysis of metal chromium (Cr) vs the Adsorption Equilibrium Capacity (Qe). The graphical analysis indicates a positive gradient slope, meaning that the altitude or the trend exhibited shows a direct proportionality in concentration vs adsorption capacity. However, the plot alone does not describe the behaviour or response to treatment, other factors should be considered due to the number of iterations performed to achieve the fit.

Table 4-11: Adsorption Equilibrium Capacity (Qe), 25g of Attapulgite clay

	Adsorption Equilibrium Capacity (Qe), 25g Attapulgite clay					
No. of Runs	Pb (ppm)	Cu (ppm)	Cr (ppm)	Ni (ppm)	Fe (ppm)	Zn (ppm)
1	0,2814	0,4326	0,1986	0,1501	1,1904	0,5990
2	0,2814	0,4326	0,1986	0,1501	1,1904	0,5990
3	0,3127	0,3722	0,2353	0,1636	1,1883	0,6100
4	0,1289	0,3039	0,2255	0,1543	1,1416	0,5668
5	0,1611	0,3520	0,2411	0,1722	1,0341	0,5690
6	0,0746	0,2792	0,2338	0,1772	1,0940	0,5545
7	0,1515	0,3632	0,3003	0,1999	0,9980	0,5921
8	0,2476	0,4121	0,3072	0,2049	1,0347	0,5978
9	0,0125	0,3112	0,2489	0,1843	0,9591	0,5628
10	0,2119	0,5155	0,3222	0,2158	1,1677	0,6098
11	0,2007	0,5330	0,3298	0,2394	1,2085	0,6257
12	0,1432	0,4766	0,2834	0,2175	1,1938	0,6122
13	0,0963	0,3764	0,2780	0,2041	1,0323	0,5666
14	0,0563	0,3680	0,2597	0,1836	1,0205	0,5931
15	0,0443	0,4142	0,3165	0,2529	1,1061	0,6030
16	0,0444	0,4404	0,3260	0,2798	1,0162	0,6000
17	0,0041	0,4305	0,3115	0,2492	1,0394	0,6098

Table 4-12: Adsorption Equilibrium Capacity (Qe), 40g of Attapulgite clay

	Adsorption Equilibrium Capacity (Qe), 40g of Attapulgite clay					
No. of Runs	Pb (ppm)	Cu(ppm)	Cr(ppm)	Ni(ppm)	Fe(ppm)	Zn(ppm)
1	0,1759	0,2703	0,1241	0,0938	0,7440	0,3744
2	0,1759	0,2703	0,1241	0,0938	0,7440	0,3744
3	0,1955	0,2327	0,1471	0,1022	0,7427	0,3812
4	0,0805	0,1899	0,1409	0,0964	0,7135	0,3542
5	0,1007	0,2200	0,1507	0,1076	0,6463	0,3556
6	0,0466	0,1745	0,1461	0,1108	0,6837	0,3465
7	0,0947	0,2270	0,1877	0,1249	0,6237	0,3700
8	0,1548	0,2576	0,1920	0,1280	0,6467	0,3737
9	0,0078	0,1945	0,1556	0,1152	0,5994	0,3518
10	0,1324	0,3222	0,2013	0,1349	0,7298	0,3811
11	0,1254	0,3331	0,2061	0,1496	0,7553	0,3911
12	0,0895	0,2979	0,1771	0,1359	0,7461	0,3826
13	0,0602	0,2352	0,1738	0,1275	0,6452	0,3542
14	0,0352	0,2300	0,1623	0,1147	0,6378	0,3707
15	0,0277	0,2589	0,1978	0,1581	0,6913	0,3769
16	0,0278	0,2753	0,2037	0,1749	0,6351	0,3750
17	0,0026	0,2691	0,1947	0,1558	0,6496	0,3811

Table 4-14 and table 4-15 displays the fit summary as well as the sequential model sum of squares respectively which provides or collects the important statistics used to select the correct starting point for the final model. Hence, the suggested model is therefore considered as the suitable starting point for the model fitting. Furthermore, the primary objective of using Design Expert statistical software tool is to optimize the adsorption process by simulating the actual results obtained experimentally.

Table 4-13: Fit Summary analysis for Zinc (Zn) using Design Expert software

Source	**Sequential P-value**	**Lack of Fit P-value**	**Adjusted R2**	**Predicted R2**	**Response**
Linear	0,0007	0,0121	0,6538	0,4947	
2FI	0,5173	0,0093	0,6378	0,1844	
Quadratic	**0,0046**	**0,0944**	**0,9107**	**0,5072**	**Suggested**
Cubic	0,0944		0,9634		Aliased

Table 4-14: Sequential Model Sum of Squares for Zinc (Zn) heavy metal content after adsorption process using Design Expert software to analyse the experimental data collected

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**P-value**	**Outcome**
Mean vs Total	64004,62	1	64004,62			
Linear vs Mean	1517,94	3	505,98	11,07	0,0007	
2FI vs Linear	116,03	3	38,68	0,8089	0,5173	
Quadratic vs 2FI	**395,66**	**3**	**131,89**	**11,19**	**0,0046**	**Suggested**
Cubic vs Quadratic	63,16	3	21,05	4,36	0,0944	Aliased
Residual	19,31	4	4,83			
Total	66116,73	17	3889,22			

Note* Select the highest order polynomial where the additional terms are significant, and the model is not aliased. Hence, the selected or approved polynomial order is Quadratic vs 2FI for Zinc (Zn) as indicated on the table above.

4.6 Analysis of Variance (ANOVA)

Table 4-15 displays the ANOVA estimated results obtained from a simulated model which the Response Surface Method using experimental data collected. According to Ronald Fischer the statistician, the ANOVA is based on the total law of variance, where the observed variance in a particular variable is partitioned into components of various sources of variation. (Analysis of variance, 2020)

Table 4-15: Analysis of variance of Zinc (Zn) heavy metal constituent using modified Attapulgite clay as adsorbing medium and Design Expert software tool

Source	Sum of Squares	df	Mean Square	F-value	P-value	Outcome
Model	2029,63	9	225,51	19,14	0,0004	significant
A-Clay Ratio	1129,55	1	1129,55	95,87	< 0.0001	
B-Temperature	12,33	1	12,33	1,05	0,3405	
C-Contact Time	376,07	1	376,07	31,92	0,0008	
AB	9,00	1	9,00	0,7638	0,4111	
AC	71,57	1	71,57	6,07	0,0432	
BC	35,46	1	35,46	3,01	0,1264	
A^2	257,53	1	257,53	21,86	0,0023	
B^2	3,89	1	3,89	0,3305	0,5833	
C^2	118,42	1	118,42	10,05	0,0157	
Residual	82,48	7	11,78			

Lack of Fit	63,16	3	21,05	4,36	0,0944	not significant
Pure Error	19,31	4	4,83			
Cor Total	2112,11	16				

The Model F-value of 19,14 implies the model is significant. There is only a 0,04% chance that an F-value this large could occur due to noise.

P-values less than 0,0500 indicate model terms are significant. In this case A, C, AC, A², C² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. (ANOVA for Quadratic model | Errors and Residuals | Analysis of Variance, 2020) If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Table 4-16: ANOVA fit statistic response for Zinc (Zn) heavy metal using Attapulgite clay as an adsorbent

Std. Dev.	3,43		R²	0,9609
Mean	61,36		Adjusted R²	0,9107
C.V. %	5,59		Predicted R²	0,5072
			Adeq Precision	16,6589

The Predicted R² of 0,5072 is not as close to the Adjusted R² of 0,9107 as one might normally expect, i.e. the difference is more than 0.2. This may indicate a large block effect or a possible problem with your model and/or data. Things to consider are model reduction, response transformation, outliers, etc. All empirical models should be tested by doing confirmation runs.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 16,659 indicates an adequate signal. This model can be used to navigate the design space.

Equation

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels are specified in the original units for each factor. This equation cannot not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the centre of the design space.

Actual Equation

Zn = {-Clay Ratio + Temperature - Contact Time + (Clay Ratio*Temperature) + (Clay Ratio*Contact Time) – (Temperature*Contact Time) + Clay Ratio^2 – Temperature^2 + Contact Time^2}

Diagnostics

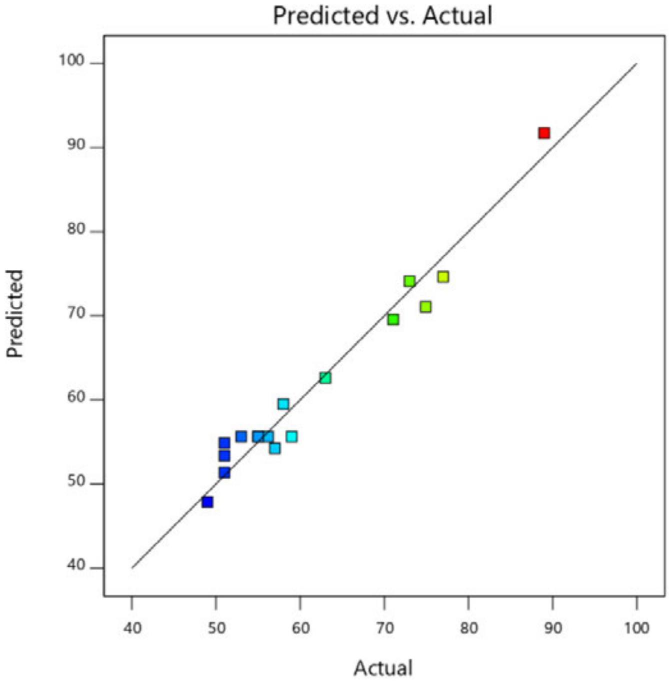


Figure 4-20: Zinc (Zn) Diagnostic graph of Actual vs Predicted percentage removal after adsorption process by means of Attapulgite clay

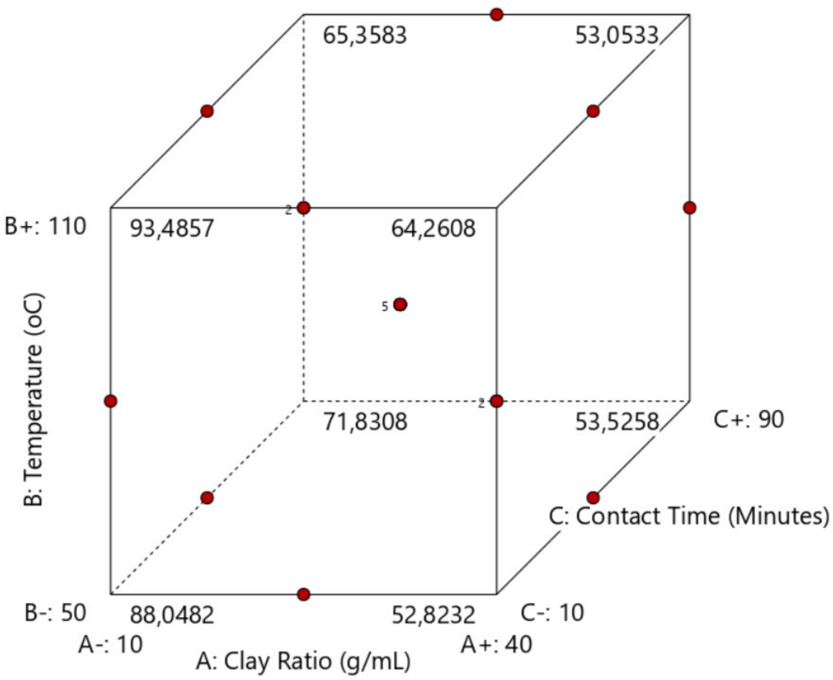


Figure 4-21: Zinc (Zn) model Cube graph of the three working condition using modified Attapulgite clay as an adsorbent

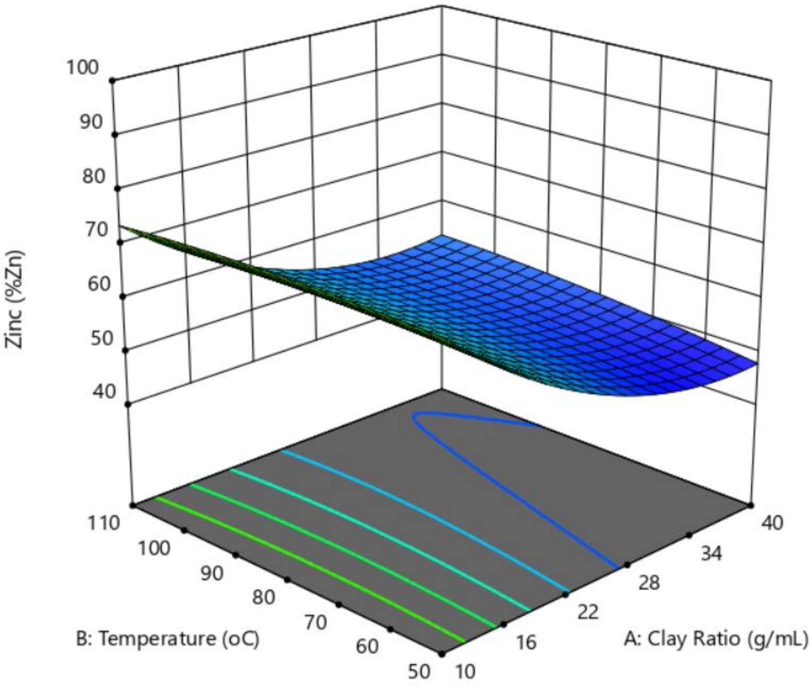


Figure 4-22: 3Dimensional graph of Zinc (Zn) heavy metal after simulating using Design Expert software tool

4.7 Kaolin Clay Results (Design Expert)

Table 4-17: Fit Summary analysis for Zinc (Zn) using Design Expert software

Source	Sequential P-value	Lack of Fit P-value	Adjusted R2	Predicted R2	Response
Linear	**0,0122**	**0,9850**	**0,4534**	**0,3772**	**Suggested**
2FI	0,7880	0,9689	0,3575	0,2120	
Quadratic	0,7453	0,9575	0,2218	0,1339	
Cubic	0,9575		-0,2692		Aliased

Table 4-18: Sequential Model Sum of Squares for Zinc (Zn) heavy metal content after adsorption process using Design Expert software to analyze the experimental data collected using kaolin clay

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Mean vs Total	57981,86	1	57981,86			
Linear vs Mean	**1284,68**	**3**	**428,23**	**5,42**	**0,0122**	**Suggested**
2FI vs Linear	98,28	3	32,76	0,3530	0,7880	
Quadratic vs 2FI	141,19	3	47,06	0,4188	0,7453	
Cubic vs Quadratic	53,48	3	17,83	0,0973	0,9575	Aliased
Residual	733,25	4	183,31			
Total	60292,74	17	3546,63			

Table 4-19: Analysis of variance of Zinc (Zn) heavy metal constituent using kaolin clay as adsorbing medium and Design Expert software tool

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	1284,68	3	428,23	5,42	0,0122	significant
A-Clay Ratio	956,16	1	956,16	12,11	0,0041	
B-Temperature	10,37	1	10,37	0,1314	0,7228	
C-Contact Time	318,15	1	318,15	4,03	0,0659	
Residual	1026,20	13	78,94			
Lack of Fit	292,95	9	32,55	0,1776	0,9850	not significant
Pure Error	733,25	4	183,31			
Cor Total	2310,88	16				

The Model F-value of 5,42 implies the model is significant. There is only a 1,22% chance that an F-value this large could occur due to noise.

P-values less than 0,0500 indicate model terms are significant. In this case A is a significant model term. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The Lack of Fit F-value of 0,18 implies the Lack of Fit is not significant relative to the pure error. There is a 98,50% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4-20: ANOVA fit statistic response for Zinc (Zn) heavy metal using Attapulgite clay as an adsorbent

Std. Dev.	8,88	**R^2**	0,5559
Mean	58,40	**Adjusted R^2**	0,4534
C.V. %	15,21	**Predicted R^2**	0,3772
		Adeq Precision	7,9999

The Predicted R^2 of 0,3772 is in reasonable agreement with the Adjusted R^2 of 0,4534; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 8,000 indicates an adequate signal. This model can be used to navigate the design space.

Equation

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels specified in the original units for each factor. This equation cannot be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the centre of the design space.

Actual Equation

Zn = {-Clay Ratio + Temperature - Contact Time}

Diagnostics

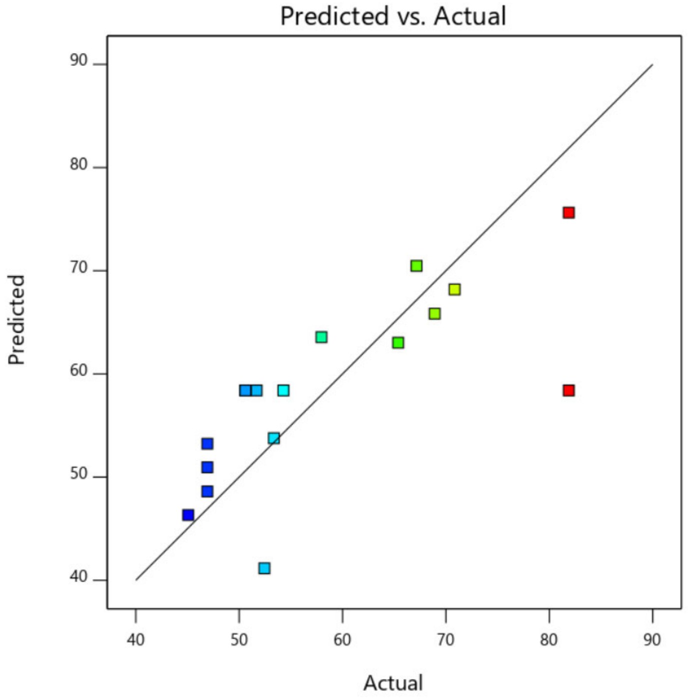


Figure 4-23: Diagnostic graph of the trend of how actual vs predicted results of zinc (Zn) behavior using kaolin clay as an adsorbent

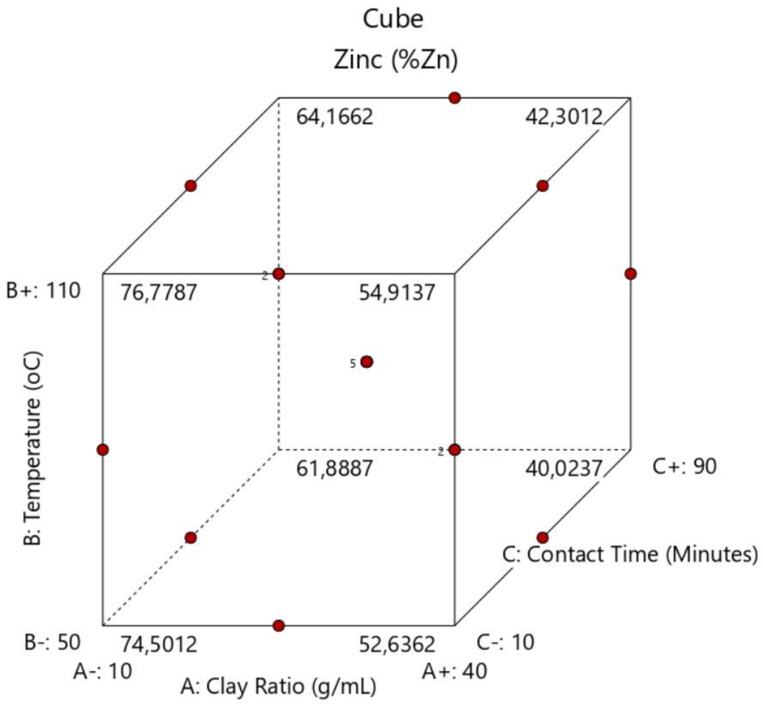


Figure 4-24: Zinc (Zn) model Cube graph of the three-working condition-using kaolin clay as an adsorbent

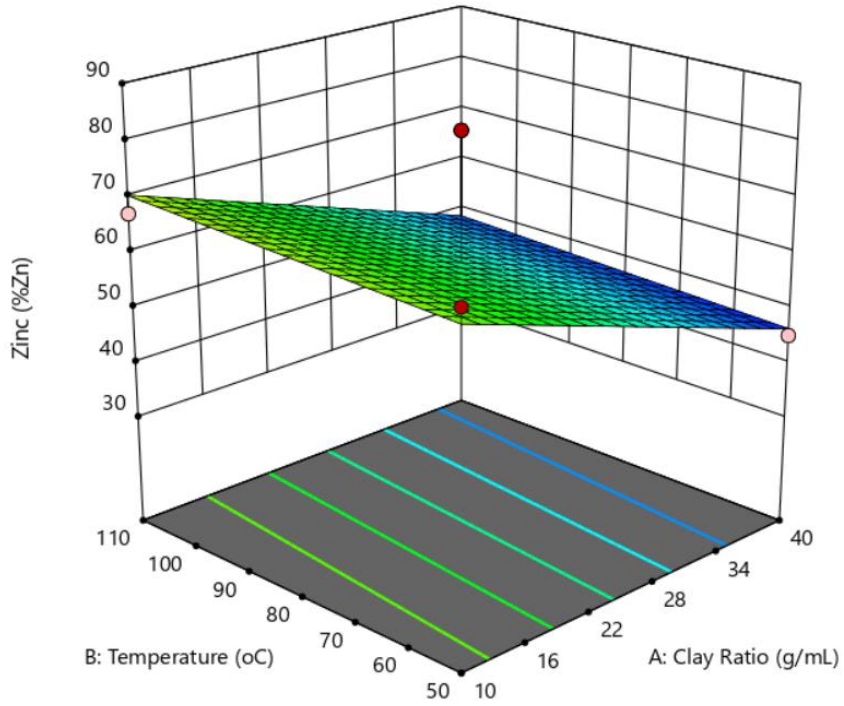


Figure 4-25: 3Dimensional graph of Zinc (Zn) heavy metal after simulating using Design Expert software tool

Table 4-21: Summary between the predicted and adjusted values for all the other metals investigated

Source	Heavy Metal	Sequential P-value	Lack of Fit P-value	Adjusted R2	Predicted R2
Linear	Fe	0,0010	0,9937	0,6360	0,6028
Linear	Pb	0,0005	0,9120	0,6712	0,5939
Linear	Cu	0,0003	0,9821	0,7025	0,6670

Table 4-22: Analysis of variance of iron (Fe) heavy metal constituent using kaolin clay as adsorbing medium and Design Expert software tool

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**P-value**	
Model	1521,24	3	507,08	10,32	0,0010	significant
A-Clay Ratio	380,05	1	380,05	7,73	0,0156	
B-Temperature	10,93	1	10,93	0,2224	0,6451	
C-Contact Time	1130,26	1	1130,26	23,00	0,0003	
Residual	638,84	13	49,14			
Lack of Fit	148,57	9	16,51	0,1347	0,9937	not significant
Pure Error	490,27	4	122,57			
Cor Total	2160,09	16				

The Model F-value of 10,32 implies the model is significant. There is only a 0,10% chance that an F-value this large could occur due to noise.

P-values less than 0,0500 indicate model terms are significant. In this case A, C are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The Lack of Fit F-value of 0,13 implies the Lack of Fit is not significant relative to the pure error. There is a 99,37% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4-23: Analysis of variance of lead (Pb) heavy metal constituent using kaolin clay as adsorbing medium and Design Expert software tool

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	1078,72	3	359,57	11,89	0,0005	significant
A-Clay Ratio	201,50	1	201,50	6,66	0,0228	
B-Temperature	26,64	1	26,64	0,8808	0,3651	
C-Contact Time	8 /850,58	1	850,58	28,12	0,0001	
Residual	393,27	13	30,25			
Lack of Fit	173,29	9	19,25	0,3501	0,9120	not significant
Pure Error	219,98	4	55,00			
Cor Total	1472,00	16				

The Model F-value of 11,89 implies the model is significant. There is only a 0,05% chance that an F-value this large could occur due to noise.

P-values less than 0,0500 indicate model terms are significant. In this case A, C are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The Lack of Fit F-value of 0,35 implies the Lack of Fit is not significant relative to the pure error. There is a 91,20% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4-24: Analysis of variance of copper (Cu) heavy metal constituent using kaolin clay as adsorbing medium and Design Expert software tool

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	1326,56	3	442,19	13,59	0,0003	significant
A-Clay Ratio	115,52	1	115,52	3,55	0,0821	
B-Temperature	0,7200	1	0,7200	0,0221	0,8840	
C-Contact Time	1210,32	1	1210,32	37,21	< 0.0001	
Residual	422,90	13	32,53			
Lack of Fit	125,94	9	13,99	0,1885	0,9821	not significant
Pure Error	296,96	4	74,24			
Cor Total	1749,46	16				

The Model F-value of 13,59 implies the model is significant. There is only a 0,03% chance that an F-value this large could occur due to noise.

P-values less than 0,0500 indicate model terms are significant. In this case C is a significant model term. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The Lack of Fit F-value of 0,19 implies the Lack of Fit is not significant relative to the pure error. There is a 98,21% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

4.8 Equations for other metals

Actual Equation

Fe = {-Clay Ratio – Temperature – Contact Time}

Pb = {-Clay Ratio – Temperature – Contact Time

Cu = {-Clay Ratio + Temperature – Contact Time}

Diagnostics

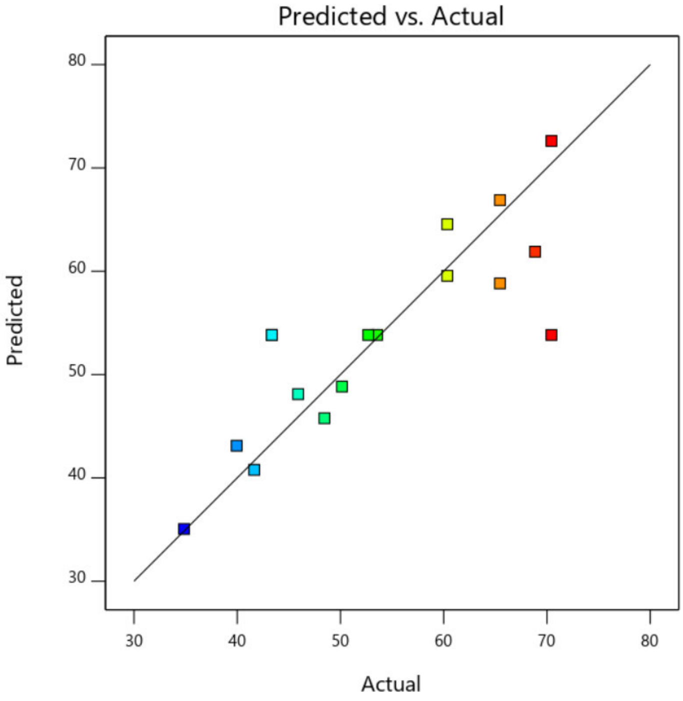


Figure 4-26: Diagnostic graph of the trend of how actual vs predicted results of iron (Fe) behavior using kaolin clay as an adsorbent

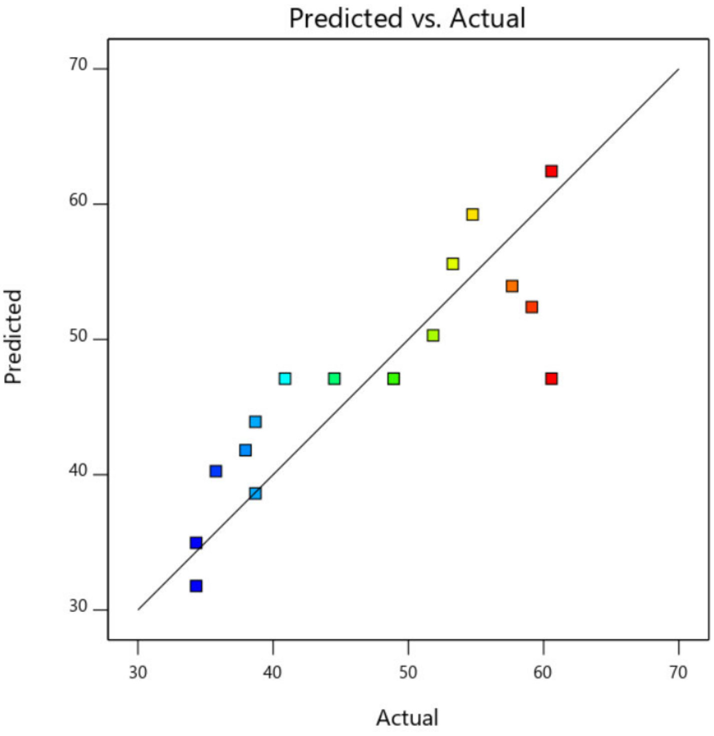


Figure 4-27: Diagnostic graph of the trend of how actual vs predicted results of Lead (Pb) behavior using kaolin clay as an adsorbent

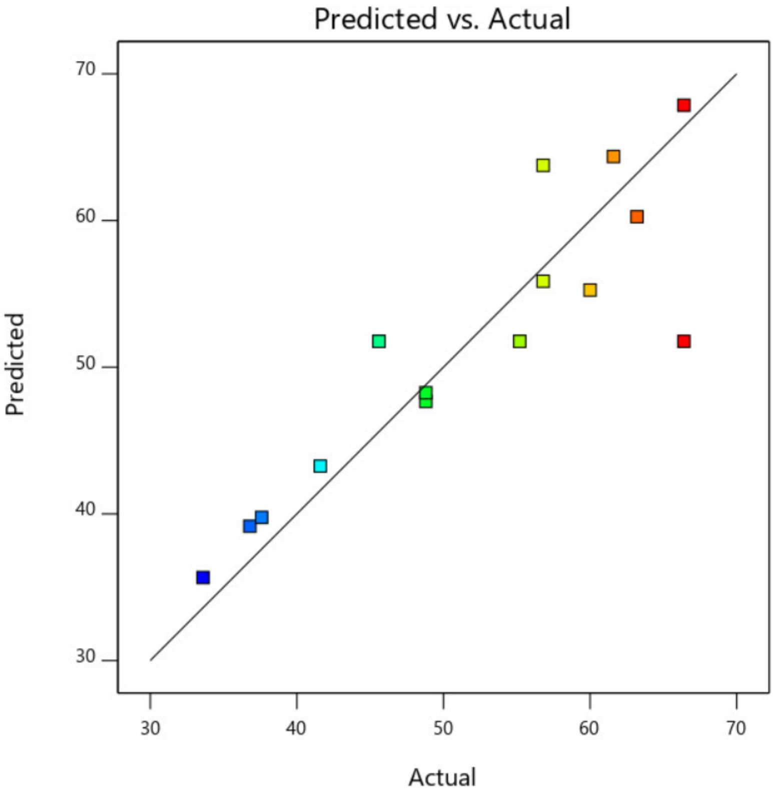


Figure 4-28: Diagnostic graph of the trend of how actual vs predicted results of copper (Cu) behavior using kaolin clay as an adsorbent

4.9 Bentonite Clay Design Expert Results

Table 4-25: Fit Summary analysis for Zinc (Zn) using Bentonite clay as an adsorbent and Design Expert software

Source	Sequential P-value	Lack of Fit P-value	Adjusted R2	Predicted R2	Response
Linear	0,0007	0,0122	0,6535	0,4944	
2FI	0,5173	0,0093	0,6375	0,1838	
Quadratic	**0,0046**	**0,0948**	**0,9107**	**0,5072**	**Suggested**
Cubic	0,0948		0,9633		Aliased

Table 4-26: Sequential Model Sum of Squares for Zinc (Zn) heavy metal content after adsorption process using Design Expert software to analyze the experimental data collected using Bentonite clay

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Mean vs Total	41996,50	1	41996,50			
Linear vs Mean	995,81	3	331,94	11,06	0,0007	
2FI vs Linear	76,20	3	25,40	0,8090	0,5173	
Quadratic vs 2FI	**259,81**	**3**	**86,60**	**11,19**	**0,0046**	**Suggested**
Cubic vs Quadratic	41,45	3	13,82	4,35	0,0948	Aliased
Residual	12,71	4	3,18			
Total	43382,47	17	2551,91			

Table 4-27: Analysis of variance of Zinc (Zn) heavy metal constituent using Bentonite clay as adsorbing medium and Design Expert software tool

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	1331,81	9	147,98	19,13	0,0004	significant
A-Clay Ratio	741,12	1	741,12	95,79	< 0.0001	
B-Temperature	8,04	1	8,04	1,04	0,3419	
C-Contact Time	246,64	1	246,64	31,88	0,0008	
AB	5,90	1	5,90	0,7632	0,4113	
AC	47,06	1	47,06	6,08	0,0431	
BC	23,23	1	23,23	3,00	0,1267	
A^2	169,22	1	169,22	21,87	0,0023	
B^2	2,56	1	2,56	0,3315	0,5828	
C^2	77,65	1	77,65	10,04	0,0158	
Residual	54,16	7	7,74			
Lack of Fit	41,45	3	13,82	4,35	0,0948	not significant
Pure Error	12,71	4	3,18			
Cor Total	1385,97	16				

The Model F-value of 19,13 implies the model is significant. There is only a 0,04% chance that an F-value this large could occur due to noise.

P-values less than 0,0500 indicate model terms are significant. In this case A, C, AC, A^2, C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The Lack of Fit F-value of 4,35 implies there is a 9,48% chance that a Lack of Fit F-value this large could occur due to noise. Lack of fit is bad -- we want the model to fit. This relatively low probability (<10%) is troubling.

Table 4-28: ANOVA fit statistic response for Zinc (Zn) heavy metal using Bentonite clay as an adsorbent

Std. Dev.	2,78	**R^2**	0,9609
Mean	49,70	**Adjusted R^2**	0,9107
C.V. %	5,60	**Predicted R^2**	0,5072
		Adeq Precision	16,6522

The Predicted R^2 of 0,3772 is in reasonable agreement with the Adjusted R^2 of 0,4534; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 8,000 indicates an adequate signal. This model can be used to navigate the design space.

The Predicted R^2 of 0,5072 is not as close to the Adjusted R^2 of 0,9107 as one might normally expect, i.e. the difference is more than 0.2. This may indicate a large block effect or a possible problem with your model and/or data. Things to consider are model reduction, response transformation, outliers, etc. All empirical models were tested by doing confirmation runs.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 16,652 indicates an adequate signal. This model used to navigate the design space.

Equation

The equation in terms of actual factors used to make predictions about the response for given levels of each factor. Here, the levels are specified in the original units for each factor. This equation cannot be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the centre of the design space.

Actual Equation

Zn = {-Clay Ratio + Temperature - Contact Time+ (Clay Ratio*Temperature) + (Clay ratio*Contact Time) + (Clay Ratio)^2 – (Temperature)^2 – (Contact Time)^2}

Diagnostics

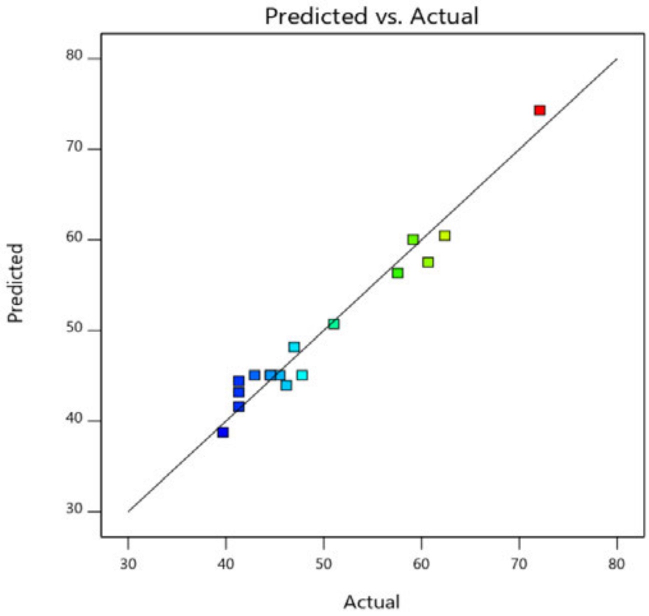


Figure 4-29: Diagnostic graph of the trend of how actual vs predicted results of iron (Fe) behavior using Bentonite clay as an adsorbent

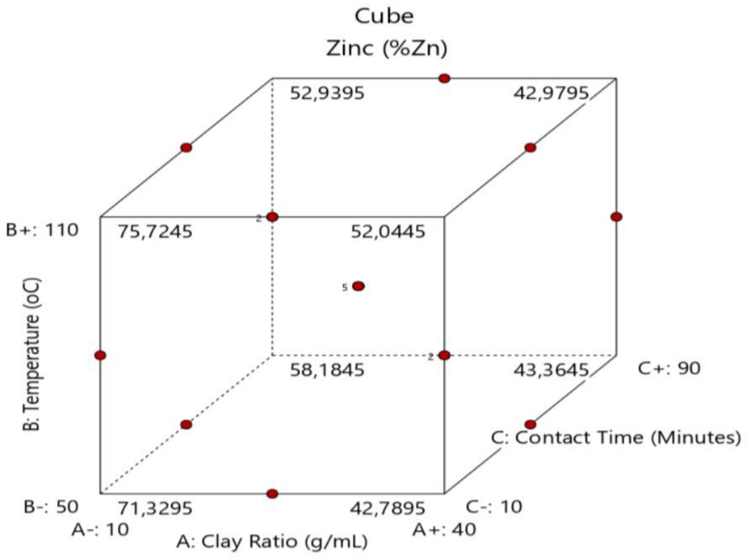


Figure 4-30: Zinc (Zn) model Cube graph of the three-working condition-using Bentonite clay as an adsorbent

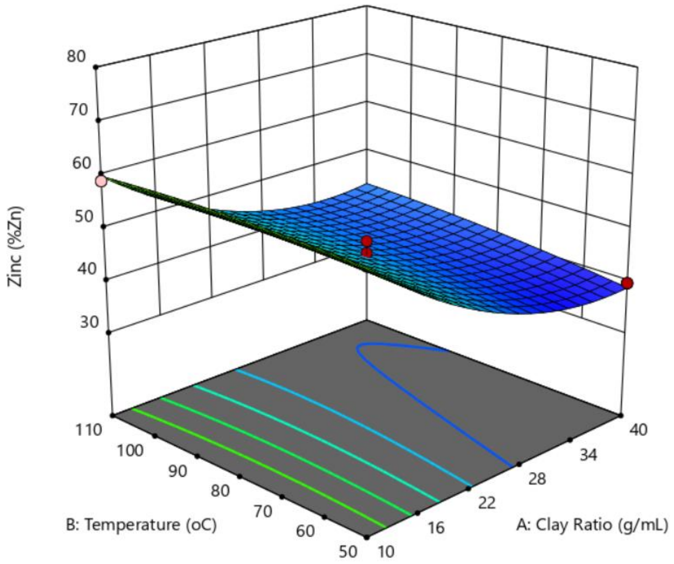


Figure 4-31: 3Dimensional graph of Zinc (Zn) heavy metal after simulating using Design Expert software tool

Table 4-29: Summary between the predicted and adjusted values for all the other metals investigated using clay 3 as adsorbent

Source	Heavy Metal	Sequential P-value	Lack of Fit P-value	Adjusted R2	Predicted R2
Linear	Fe	< 0.0001	0,6139	0,7717	0,7053
Linear	Pb	< 0.0001	0,3700	0,8051	0,7049
Linear	Cu	< 0.0001	0,8263	0,8420	0,7902

Table 4-30: Analysis of variance of Zinc (Zn) heavy metal constituent using Bentonite clay as adsorbing medium and Design Expert software tool

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	1557,30	3	519,10	19,03	< 0.0001	**significant**
A-Clay Ratio	389,07	1	389,07	14,26	0,0023	
B-Temperature	11,19	1	11,19	0,4100	0,5331	
C-Contact Time	1157,05	1	1157,05	42,41	< 0.0001	
Residual	354,69	13	27,28			
Lack of Fit	233,39	9	25,93	0,8552	0,6139	**not significant**
Pure Error	121,29	4	30,32			
Cor Total	1911,98	16				

The Model F-value of 19,03 implies the model is significant. There is only a 0,01% chance that an F-value this large could occur due to noise.

P-values less than 0,0500 indicate model terms are significant. In this case A, C are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The Lack of Fit F-value of 0,86 implies the Lack of Fit is not significant relative to the pure error. There is a 61,39% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4-31: Analysis of variance of Zinc (Zn) heavy metal constituent using Bentonite clay as adsorbing medium and Design Expert software tool

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	908,69	3	302,90	23,03	< 0.0001	significant
A-Clay Ratio	169,74	1	169,74	12,91	0,0033	
B-Temperature	22,45	1	22,45	1,71	0,2140	
C-Contact Time	716,50	1	716,50	54,49	< 0.0001	
Residual	170,95	13	13,15			
Lack of Fit	131,80	9	14,64	1,50	0,3700	not significant
Pure Error	39,14	4	9,79			
Cor Total	1079,63	16				

The Model F-value of 23,03 implies the model is significant. There is only a 0,01% chance that an F-value this large could occur due to noise.

P-values less than 0,0500 indicate model terms are significant. In this case A, C are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The Lack of Fit F-value of 1,50 implies the Lack of Fit is not significant relative to the pure error. There is a 37,00% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4-32: Analysis of variance of Zinc (Zn) heavy metal constituent using Bentonite clay as adsorbing medium and Design Expert software tool

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	1228,93	3	409,64	29,41	< 0.0001	significant
A-Clay Ratio	107,02	1	107,02	7,68	0,0159	
B-Temperature	0,6670	1	0,6670	0,0479	0,8302	
C-Contact Time	1121,25	1	1121,25	80,51	< 0.0001	
Residual	181,05	13	13,93			
Lack of Fit	95,20	9	10,58	0,4928	0,8263	not significant
Pure Error	85,85	4	21,46			
Cor Total	1409,99	16				

The Model F-value of 29,41 implies the model is significant. There is only a 0,01% chance that an F-value this large could occur due to noise.

P-values less than 0,0500 indicate model terms are significant. In this case A, C are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The Lack of Fit F-value of 0,49 implies the Lack of Fit is not significant relative to the pure error. There is a 82,63% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

4.10 Equations for other metals

Actual Equation

Fe = {-Clay Ratio – Temperature – Contact Time}

Pb = {-Clay Ratio – Temperature – Contact Time

Cu = {-Clay Ratio + Temperature – Contact Time}

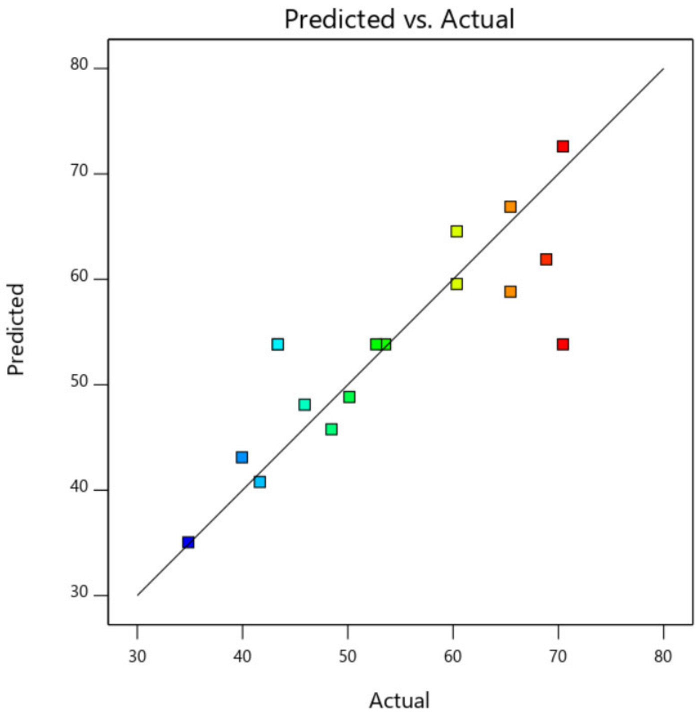


Figure 4-32: Diagnostic graph of the trend of how actual vs predicted results of iron (Fe) behavior using Bentonite clay as an adsorbent

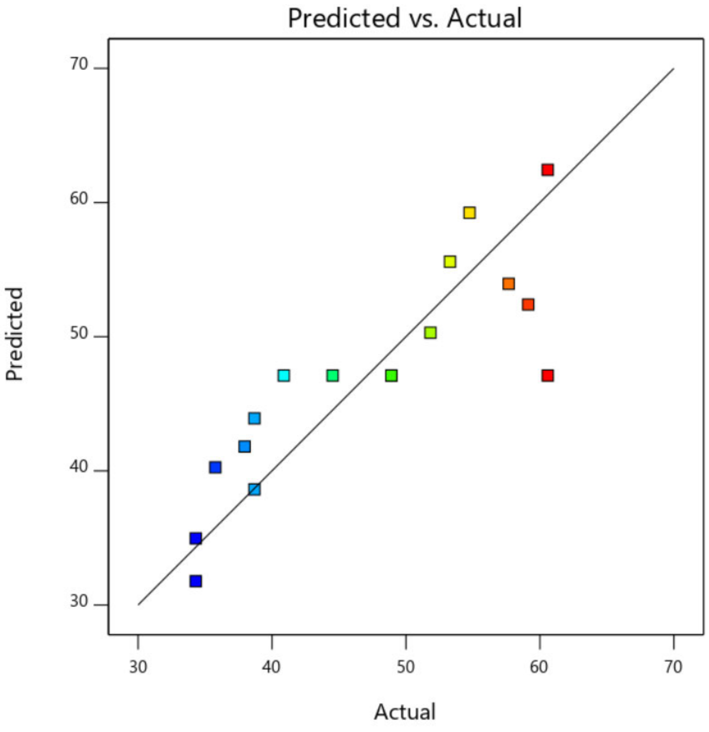


Figure 4-33: Diagnostic graph of the trend of how actual vs predicted results of lead (Pb) behavior using Bentonite clay as an adsorbent

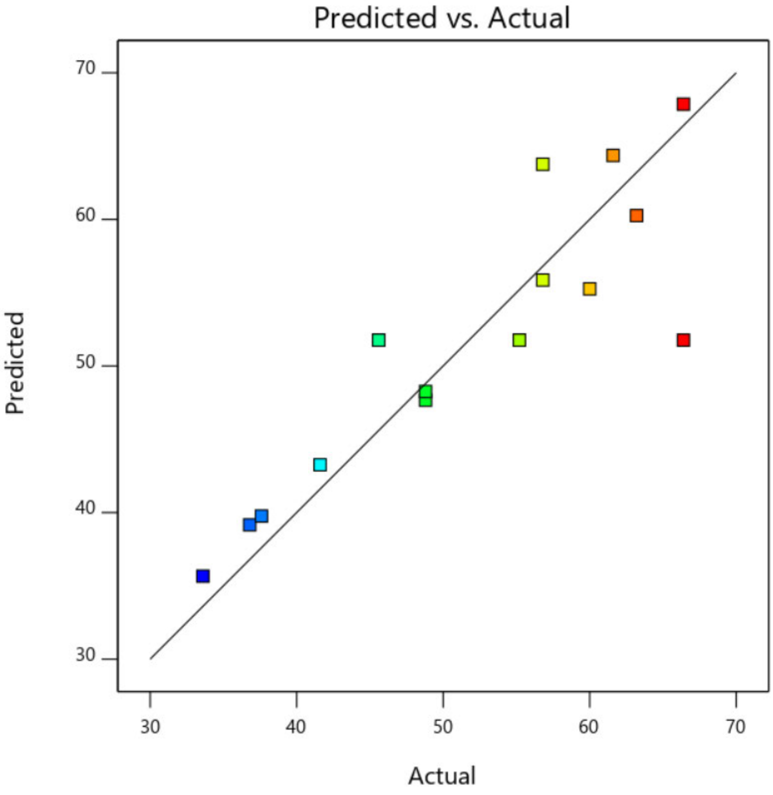


Figure 4-34: Diagnostic graph of the trend of how actual vs predicted results of copper (Cu) behavior using Bentonite clay as an adsorbent

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Batch adsorption experiments were conducted using three different clays as adsorbents to remove or lower the concentration of heavy metals contained in used oils. The focus metal ions included lead (Pb), copper (Cu), iron (Fe) and zinc (Zn). The controlled parameters in achieving this goal included the effect of temperature, the effect of contact time and the effect of clay dosage was studied simultaneously. In addition, Design Expert statistical tool software was used to determine experimental runs required to obtain the optimum; contact time, temperature and clay dosage ratio to achieve a high yield of heavy metals removal.

In conclusion, the Attapulgite clay has the most removal efficiency when compared to the Bentonite and Kaolin clay. Hence, this is observed for both the elemental analysis and the fluid properties before and after treatment. The clay properties it exhibits have a huge impact on the positive response in the removal of heavy metals in used oils. Properties such as the clay fineness and amorphousity thus also having a limited cation exchange capabilities (CEC) and moderate hydration, expansion and plasticity. Furthermore the Attapulgite clay consists of octahedral and Si tetrahedral layers which allows a retention of cation metals. SEM, XRF, XRD, and BET results show that the clay porousness and surface area.

SEM

Figure 2 (a-d) reveals the scanning electron micrographs (SEM) of raw and modified bentonite clay material are illustrated. The micrographs show that Figures 2(a) and 2(b) indicate that morphology of bentonite clay exhibited to be agglomerate scattered along the surface and it spheric species. However, after modification with H2SO4 solution the bentonite clay material shows the formation of clusters and agglomeration. A study conducted by Ochieng Ombaka on clay materials clay related to classification and characterization for potential applications in Rugi Ward, Kenya reveals that using modified clay as an adsorbent to enhance the radiation shielding. The study reveals that the same properties of surface agglomerated material are obtained which have a tendency of highest adsorption capacity due to the mineral presents in bentonite clay (Ochieng Ombaka et al,.2016).

XRD

X-ray diffraction is an important tool for material characterization in the field of research. In this study, all clays such as attapulgite, bentonite and kaolin were thoroughly characterized. The peaks were observed at 2θ values of 34, 43 and 71 corresponding to (111), (110) and (211) crystal planes which agreed well with those given in JCPDS card no. 06-0696. Ref…. all though the material shows amorphous with one sharp peak that which is more crystalline. These indicate that the material is agreement went the results from SEM agglomerated and amorphous. Table 4 shows the presence of minerals observed in other studies and with corresponding planes. (Bao et al. 2010)

In addition, pseudo-first order best fitted the kinetics of the adsorption process. Surface area, surface acidity, and cation exchange capacity change as the severity of acid treatment is increased for three clays when treated or activated with sulphuric acid. Hence, the surface area is an important element based on theoretical considerations because adsorption and catalysis increases with the Increasing surface area. In conclusion, clay activation by means of sulphuric acid results in an increase for both surface area and surface acidity to increase to maxima while cation exchange capacity (number of sites) decreases with increasing severity of treatment.

South African clays have a huge potential of competing with used adsorbents to remove or lower the number of heavy metals accumulated by engine oil through its usage. Hence, they are readily available and economically viable. By comparison, Attapulgite clay showed the highest removal efficiency followed by Bentonite and kaolin clay with the least removal efficiency. This is witnessed by comparing Table 10, 11 and 12 as well as Figures 8, 9 and 10.

The optimum working conditions for the highest removal efficiency in all metallic ions in contrast are found to be at: 50 degrees Celsius, 25 grams and 10 minutes. The combination yields a high reduction of heavy metals accumulated by engine oil for all three clays.

This study has proven that improper handling and disposal of used oil can result in unlimited liability. However, for a complete compliance a brief overview of the regulations has been included to provide basic concept and understanding to the related person/organization. Improper handling of used oil may result in groundwater and soil contamination.

5.2 Recommendations

Extensive work to be carried to ensure a removal efficiency greater than 75% for all heavy metals found in used oils not particularly lead and copper. In addition, a comparative study of recycling used oil using a distillation instead of a single contact might yield a higher percentage removal of metal ions. The composition of heavy metals in used oil reach minimal allowable limit to be contained in used oil, hence this indicates that used oil can be treated or recycled using locally found clays as adsorbent materials.

Combine or mix all three clays to form one adsorbent, this might enhance the removal efficiency. All three clays exhibit different grain sizes according to SEM analysis and respond differently towards the sulphuric acid solution. Furthermore, increase the sulphuric acid solutions by 1M, thus this can create the bonding structure between the clay particles and enhancer used.

CHAPTER 6

REFERENCES

6 REFERENCES

Abdulkareem, O. A., Al Bakri, A. M., Kamarudin, H., Nizar, I. K. and Ala'eddin, A. S. 2014. Effects of elevated temperatures on the thermal behavior and mechanical performance of fly ash geopolymer paste, mortar and lightweight concrete. *Construction and building materials*, 50: 377-387.

Akpomie, K. G., Ezeofor, C. C., Olikagu, C. S., Odewole, O. A. and Ezeorah, C. J. 2018. Abstraction and regeneration potential of temperature-enhanced rice husk montmorillonite combo for oil spill. *Environmental Science and Pollution Research*, 25: 34711-34719.

Ali, S., Ripin, A. and Ahmad, A. 2010. Adsorption of heavy metal from recovered base oil using zeolite. *Journal of Applied Sciences(Faisalabad)*, 10 (21): 2688-2692.

Amoako, Y. A., Awuah, B., Larsen-Reindorf, R., Awittor, F. K., Kyem, G., Ofori-Boadu, K., Osei-Bonsu, E. and Laryea, D. O. 2019. Malignant tumours in urban Ghana: evidence from the city of Kumasi. *BMC cancer*, 19: 1-12.

Apostoli, P. 2006. *Elemental speciation in human health risk assessment*. World Health Organization.

Asaolu, S., Adefemi, S., Ibigbamif, O., Adekeye, D. and Olagboye, S. 2020. Kinetics, isotherm and thermodynamic properties of the basement complex of clay deposit in Ire-Ekiti Southwestern Nigeria for heavy metals removal. *Nature Environment and Pollution Technology*, 19 (3): 897-907.

Atsar, F., Kukwa, D., Tyohemba, R., A, E. and Wuana, R. A. 2013a. Cleaning of heavy metals from Spent Lubrication Oil (SLO) by adsorption process using acid modified clay. *Chemical Science and Technology Journal* 3(4): 71-75.

Atsar, F., Kukwa, D., Tyohemba, R., Ekpo, A. and Wuana, R. 2013b. Cleaning of heavy metals from spent lubrication oil (SLO) by adsorption process using acid modified clay. *International Journal of Chemical Science and Technology*, 3 (4): 71-75.

Boadu, K., Joel, O., Essumang, D. and Evbuomwan, B. 2019. A review of methods for removal of contaminants in used lubricating oil. Article ID.

Coetzee, P., Coetzee, L., Puka, R. and Mubenga, S. 2003. Characterisation of selected South African clays for defluoridation of natural waters. *Water Sa*, 29 (3): 331-338.

Dąbrowski, A. 2001. Adsorption—from theory to practice. *Advances in colloid and interface science*, 93 (1-3): 135-224.

Diphare, M. J., Muzenda, E., Pilusa, T. J. and Mollagee, M. 2013. A comparison of waste lubricating oil treatment techniques. Article ID.

Donald. T Kukwa, Tyohemba, R. L., A, E. and Wuana, R. A. 2013. Cleaning of heavy metals from Spent Lubrication Oil (SLO) by adsorption process using acid modified clay. *Chemical Science and Technology Journal* Article ID.

El-Maghrabi, H. H. and Mikhail, S. 2014. Removal of heavy metals via adsorption using natural clay material. *Journal of Environment and Earth Science*, 4 (19): 38-46.

Elmehbad, D. N. 2017. Enhancement Adsorption of Heavy Metal from Recovered Base Oil using Zeolite and kaolinite by Phase Transfer Catalyst and anionic surfactants-Part 2. *International Journal of Advanced Engineering Research and Science*, 4 (2): 124-128.

Emam, E. A. 2018. Clay adsorption perspective on petroleum refining industry. *Industrial Engineering*, 2 (1): 19-25.

Emam, E. A. and Shoaib, A. M. 2012. Re-refining of used lube oil, II-by solvent/clay and acid/clay-percolation processes. *ARPN Journal of Science and Technology*, 2 (11): 1034-1041.

Evbuomwan, B. O., Essumang, D. K., Joel, O. F. and Boadu, K. O. 2019. A Review of Methods for Removal of Contaminants in Used Lubricating Oil. *Chemical Science International Journal*, Article ID: 1-11.

Gabelman, A. 2017. Adsorption basics: part 1. *Chemical Engineering Progress*, 113 (7): 48-53.

Gawande, S. M., Belwalkar, N. S. and Mane, A. A. 2017. Adsorption and its isotherm–theory. *International Journal of Engineering Research*, 6 (6): 312-316.

Goldani, E., Moro, C. C. and Maia, S. M. 2013. A study employing differents clays for Fe and Mn removal in the treatment of acid mine drainage. *Water, Air, & Soil Pollution*, 224: 1-11.

Goldoni, M., Caglieri, A., Poli, D., Vettori, M. V., Corradi, M., Apostoli, P. and Mutti, A. 2006. Determination of hexavalent chromium in exhaled breath condensate and environmental air among chrome plating workers. *Analytica chimica acta*, 562 (2): 229-235.

Gresham, R. M. and Totten, G. E. 2008. *Lubrication and Maintenance of Industrial Machinery: Best Practices and Reliability*. CRC Press.

Gupta, A. K. and Paul, B. 2015. Ecorestoration of coal mine overburden dump to prevent environmental degradation: A review. *Research Journal of Environmental Sciences*, 9 (7): 307.

Gupta, S. S. and Bhattacharyya, K. G. 2012. Adsorption of heavy metals on kaolinite and montmorillonite: a review. *Physical Chemistry Chemical Physics*, 14 (19): 6698-6723.

Hillebrecht, F. U., Fuggle, J. C., Bennett, P. A., Zołnierek, Z. and Freiburg, C. 1983. Electronic structure of Ni and Pd alloys. II. X-ray photoelectron core-level spectra. *Physical Review B*, 27 (4): 2179.

Hsu, Y.-L. and Liu, C.-C. 2011. Evaluation and selection of regeneration of waste lubricating oil technology. *Environmental monitoring and assessment*, 176: 197-212.

Isah, A., Abdulkadir, M., Onifade, K., Musa, U., Umar, G., Bawa, A. and Sani, Y. 2013. Regeneration of used engine oil. In: Proceedings of. Lecture Notes in Engineering and Computer Science, World Congress on …,

Jadia, C. D. and Fulekar, M. 2009. Phytoremediation of heavy metals: recent techniques. *African journal of biotechnology*, 8 (6).

Kashif, S.-u.-R., Zaheer, A., Arooj, F. and Farooq, Z. 2018. Comparison of heavy metals in fresh and used engine oil. *Petroleum Science and Technology*, 36 (18): 1478-1481.

Kimbonguila, A., Matos, L., Petit, J., Scher, J. and Nzikou, J. 2019. Effect of physical treatment on the physicochemical, rheological and functional properties of yam meal of the cultivar “Ngumvu” from Dioscorea alata L. of Congo. *International Journal of Recent Scientific Research*, 8: 16457-16461.

Kukwa, D. and Wuana, R. A. 2013. Cleaning of heavy metals from Spent Lubrication Oil (SLO) by adsorption process using acid modified clay. *Chemical Science International Journal*, 3 (4): 71-75.

Kumari, N. and Mohan, C. 2021. Basics of clay minerals and their characteristic properties. *Clay Clay Miner*, 24: 1-29.

Kwasi Opoku, B., Ogbonna Friday, J., David Kofi, E. and Benson Osa, E. 2020. Adsorption of Heavy Metals Contaminants in Used Lubricating Oil Using Palm Kernel and Coconut Shells Activated Carbons. *American Journal of Chemical Engineering*, 8 (1).

Lesmana, S. O., Febriana, N., Soetaredjo, F. E., Sunarso, J. and Ismadji, S. 2009. Studies on potential applications of biomass for the separation of heavy metals from water and wastewater. *Biochemical Engineering Journal*, 44 (1): 19-41.

Martin, S. and Griswold, W. 2009. Human health effects of heavy metals. *Environmental Science and Technology briefs for citizens*, 15: 1-6.

Mekonnen, K. N., Ambushe, A. A., Chandravanshi, B. S., Redi-Abshiro, M. and McCrindle, R. I. 2014. Assessment of potentially toxic elements in Swiss chard and sediments of Akaki River, Ethiopia. *Toxicological & Environmental Chemistry*, 96 (10): 1501-1515.

Molinari, R., Gallo, S. and Argurio, P. 2004. Metal ions removal from wastewater or washing water from contaminated soil by ultrafiltration–complexation. *Water research*, 38 (3): 593-600.

Mustapha, S., Ndamitso, M. M., Abdulkareem, A. S., Tijani, J. O., Mohammed, A. K. and Shuaib, D. T. 2019a. Potential of using kaolin as a natural adsorbent for the removal of pollutants from tannery wastewater. *Heliyon*, 5 (11): e02923.

Mustapha, S., Shuaib, D., Ndamitso, M., Etsuyankpa, M., Sumaila, A., Mohammed, U. and Nasirudeen, M. 2019b. Adsorption isotherm, kinetic and thermodynamic studies for the removal of Pb (II), Cd (II), Zn (II) and Cu (II) ions from aqueous solutions using Albizia lebbeck pods. *Applied water science*, 9: 1-11.

Nkonyane, T., Ntuli, F. and Muzenda, E. 2012. Treatment of acid mine drainage using un-activated bentonite and limestone. *Int J Chem Mol Nucl Mat Metall Eng*, 6: 661-666.

Opoku, B. K., Friday, J. O., Essumang, D. K. and Osa, E. B. 2020. Adsorption of heavy metals contaminants in used lubricating oil using palm kernel and coconut shells activated carbons. Article ID.

Raghuvir, P. B., Prabhu, P. P., Prabhu, B. and Mathew, T. M. 2018. A Review on Removal of Heavy Metal Ions from Waste Water using Natural/ Modified Bentonite. *MATEC Web of Conferences*, 144.

Rajendran, S., Priya, T., Khoo, K. S., Hoang, T. K., Ng, H.-S., Munawaroh, H. S. H., Karaman, C., Orooji, Y. and Show, P. L. 2022. A critical review on various remediation approaches for heavy metal contaminants removal from contaminated soils. *Chemosphere*, 287: 132369.

Ripin A, A. S. M. W., Ahmad A 2010. Adsorption of heavy metals from recovered base oil using Zeolite. *Applied Sciences Journal*, 10 (21): 2688-2692.

Saad, D. 2013. Development and application of functionalized polymeric materials for heavy metal ions recovery from industrial and mining wastewaters. Article IDUniversity of the Witwatersrand, Faculty of Science, School of Chemistry.

Saad, D. M., Cukrowska, E. and Tutu, H. 2015. Column adsorption studies for the removal of U by phosphonated cross-linked polyethylenimine: modelling and optimization. *Applied Water Science*, 5: 57-63.

Saad, D. M., Cukrowska, E. M. and Tutu, H. 2013. Selective removal of mercury from aqueous solutions using thiolated cross-linked polyethylenimine. *Applied Water Science*, 3: 527-534.

Sánchez-Alvarracín, C., Criollo-Bravo, J., Albuja-Arias, D., García-Ávila, F. and Pelaez-Samaniego, M. 2021a. Characterization of Used Lubricant Oil in a Latin-American Medium-Size City and Analysis of Options for Its Regeneration. *Recycling*, 6 (1).

Sánchez-Alvarracín, C., Criollo-Bravo, J., Albuja-Arias, D., García-Ávila, F. and Pelaez-Samaniego, M. R. 2021b. Characterization of used lubricant oil in a latin-american medium-size city and analysis of options for its regeneration. *Recycling*, 6 (1): 10.

Schuetze, H. H., Yu, C.-H., Velipasaoglu, O. E. and Stukov, S. 2008. *System and method for processing semi-structured business data using selected template designs*: Google Patents.

Singh, R., Gautam, N., Mishra, A. and Gupta, R. 2011. Heavy metals and living systems: An overview. *Indian journal of pharmacology*, 43 (3): 246.

Szyszlak-Bargłowicz, J., Zając, G. and Wolak, A. 2021a. Heavy metal content in used engine oils depending on engine type and oil change interval. *Archives of Environmental Protection*, 47 (2).

Szyszlak-Bargłowicz, J., Zając, G. and Wolak, A. 2021b. <Heavy_metal_content_in_used_engine_.pdf>. *Heavy metal content in used engine oils depending on engine type and oil change interval*, 47 (2): 81-89.

Talaat, H., El Defrawy, N., Abulnour, A., Hani, H. and Tawfik, A. 2011. Evaluation of heavy metals removal using some Egyptian clays. *International Proceedings of Chemical, Biological and Environmental Engineering*, 6: 37-42.

Toth, J. 2002. *Adsorption*. CRC Press.

Udonne, J. D. 2011. A comparative study of recycling of used lubrication oils using distillation, acid and activated charcoal with clay methods. *Journal of Petroleum and Gas Engineering,* 2 (2): 12-19.

Ujile, A. A. 2014. Chemical engineering unit operations, synthesis and basic design calculations. *Bomn Prints, Ibadan, Nigeria*, Article ID: 61-84.

Virgen, M., Vázquez, O. F. G., Montoya, V. H. and Gómez, R. T. 2018a. Removal of heavy metals using adsorption processes subject to an external magnetic field. *Heavy Metals*, 253.

Virgen, M. d. R. M., Vázquez, O. F. G., Montoya, V. H. and Gómez, R. T. 2018b. Removal of Heavy Metals Using Adsorption Processes Subject to an External Magnetic Field. In: *Heavy Metals*.

Yang, Q.-Z., Wu, L.-Z., Wu, Z.-X., Zhang, L.-P. and Tung, C.-H. 2002. Long-lived emission from platinum (II) terpyridyl acetylide complexes. *Inorganic chemistry*, 41 (22): 5653-5655.

Yang, S.-T., Wang, X., Jia, G., Gu, Y., Wang, T., Nie, H., Ge, C., Wang, H. and Liu, Y. 2008. Long-term accumulation and low toxicity of single-walled carbon nanotubes in intravenously exposed mice. *Toxicology letters*, 181 (3): 182-189.

Zając, G., Szyszlak-Bargłowicz, J., Słowik, T., Kuranc, A. and Kamińska, A. 2015. Designation of Chosen Heavy Metals in Used Engine Oils Using the XRF Method. *Polish Journal of Environmental Studies*, 24: 2277-2283.

7 APPENDICES

Table 7-1: Summary between the predicted and adjusted values for all the other metals investigated

Source	Heavy Metal	Sequential P-value	Lack of Fit P-value	Adjusted R2	Predicted R2
Linear	Fe	< 0.0001	0,6141	0,7716	0,7052
Linear	Pb	< 0.0001	0,3703	0,8050	0,7047
Linear	Cu	< 0.0001	0,8258	0,8421	0,7903
Linear	Cr	<0.0001	0.6208	0.1171	0.8101
Linear	Zn	<0.0001	0.4005	0.3050	0.7077
Linear	Ni	<0.0001	0.5712	0.8112	0.6905

Table 7-2: Analysis of variance of iron (Fe) heavy metal constituent using Design Expert software tool

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	2105,50	3	701,83	19,02	< 0.0001	significant
A-Clay Ratio	526,01	1	526,01	14,25	0,0023	
B-Temperature	15,13	1	15,13	0,4098	0,5332	
C-Contact Time	1564,36	1	1564,36	42,39	< 0.0001	
Residual	479,79	13	36,91			

Lack of Fit	315,65	9	35,07	0,8547	0,6141	not significant
Pure Error	164,14	4	41,04			
Cor Total	2585,30	16				

The Model F-value of 19,02 implies the model is significant. There is only a 0,01% chance that an F-value this large could occur due to noise.

P-values less than 0,0500 indicate model terms are significant. In this case A, C are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. The Lack of Fit F-value of 0,85 implies the Lack of Fit is not significant relative to the pure error. There is a 61,41% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 7-3: Analysis of variance of lead (Pb) heavy metal constituent using Design Expert software tool

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**P-value**	
Model	2024,06	3	674,69	23,01	< 0.0001	significant
A-Clay Ratio	377,99	1	377,99	12,89	0,0033	
B-Temperature	49,95	1	49,95	1,70	0,2144	
C-Contact Time	1596,12	1	1596,12	54,44	< 0.0001	
Residual	381,15	13	29,32			
Lack of Fit	293,83	9	32,65	1,50	0,3703	not significant
Pure Error	87,33	4	21,83			
Cor Total	2405,22	16				

The Model F-value of 23,01 implies the model is significant. There is only a 0,01% chance that an F-value this large could occur due to noise.

P-values less than 0,0500 indicate model terms are significant. In this case A, C are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The Lack of Fit F-value of 1,50 implies the Lack of Fit is not significant relative to the pure error. There is a 37,03% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 7-4: Analysis of variance of copper (Cu) heavy metal constituent using Design Expert software tool

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**P-value**	
Model	2024,06	3	674,69	23,01	< 0.0001	significant
A-Clay Ratio	377,99	1	377,99	12,89	0,0033	
B-Temperature	49,95	1	49,95	1,70	0,2144	
C-Contact Time	1596,12	1	1596,12	54,44	< 0.0001	
Residual	381,15	13	29,32			
Lack of Fit	293,83	9	32,65	1,50	0,3703	not significant
Pure Error	87,33	4	21,83			
Cor Total	2405,22	16				

The Model F-value of 29,44 implies the model is significant. There is only a 0,01% chance that an F-value this large could occur due to noise.

P-values less than 0,0500 indicate model terms are significant. In this case A, C are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The Lack of Fit F-value of 0,49 implies the Lack of Fit is not significant relative to the pure error. There is 82,58% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Equations for other metals

Actual Equation

Fe = {-Clay Ratio – Temperature – Contact Time}

Pb = {-Clay Ratio – Temperature – Contact Time

Cu = {-Clay Ratio + Temperature – Contact Time}

Diagnostics

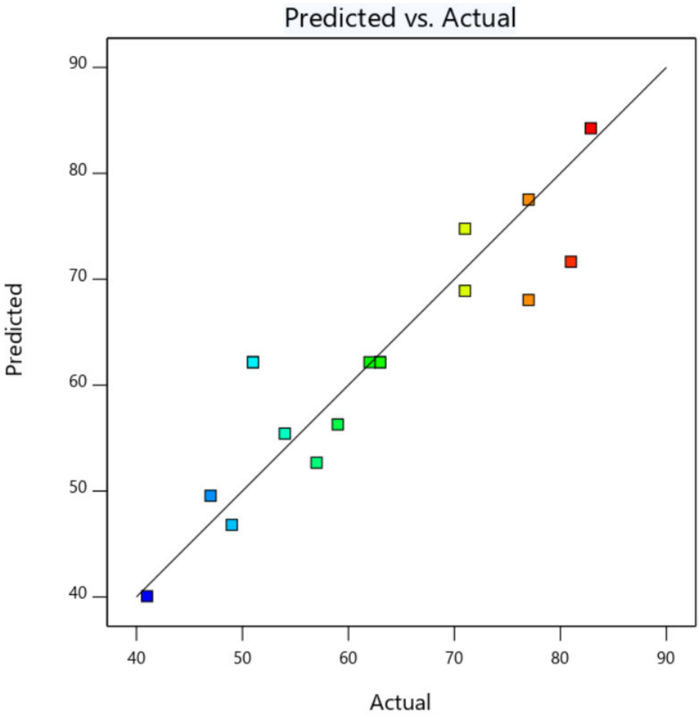


Figure 7-1: Diagnostic graph of the trend of how actual vs predicted results of zinc (Zn) behave

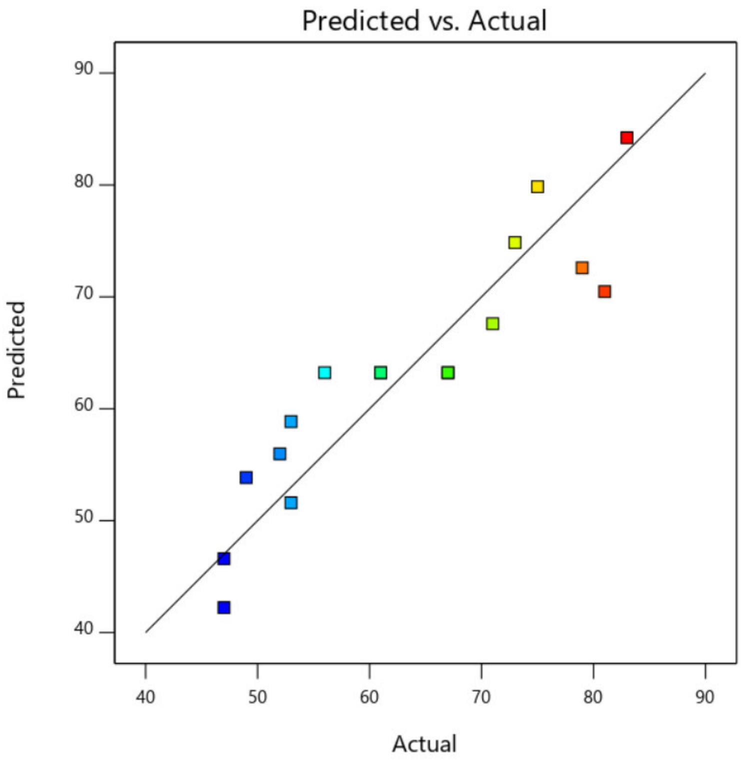


Figure 7-2: Diagnostic graph of the trend of how actual vs predicted results of lead behavior

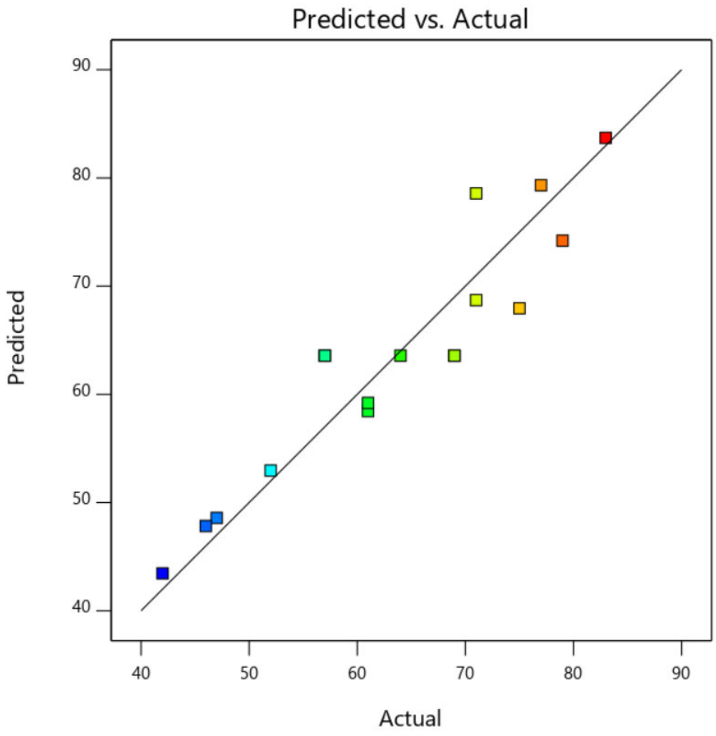


Figure 7-3: Diagnostic graph of the trend of how actual vs predicted results of copper (Cu) behavior