ADSORPTION CHARACTERISTICS OF LEAD FROM AQUEOUS SOLUTION BY PYROLYSED USED BLEACHING CLAY

NORAZURA BINTI ABD JALIL

UNIVERSITI MALAYSIA PAHANG

UNIVERSITI MALAYSIA PAHANG

BORANG PENGESAHAN STATUS TESIS

JUDUL   :   **ADSORPTION CHARACTERISTICS OF LEAD FROM AQUEOUS SOLUTION BY PYROLYSED USED BLEACHING CLAY**

SESI PENGAJIAN   : <u>**2008/2009**</u>

Saya   **NORAZURA BINTI ABD JALIL**

(HURUF BESAR)

mengaku membenarkan tesis Projek Sarjana Muda ini disimpan di Perpustakaan Universiti Malaysia Pahang dengan syarat-syarat kegunaan seperti berikut :

1.   Tesis adalah hakmilik Universiti Malaysia Pahang.
2.   Perpustakaan Universiti Malaysia Pahang dibenarkan membuat salinan untuk tujuan pengajian sahaja.
3.   Perpustakaan dibenarkan membuat salinan tesis ini sebagai bahan pertukaran antara institusi pengajian tinggi.
4.   **Sila tandakan (√)

    ☐ SULIT   (Mengandungi maklumat yang berdarjah keselamatan   atau kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA RASMI 1972)

    ☐ TERHAD   (Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)

    ☑ TIDAK TERHAD

Disahkan oleh

_____   _____
    (TANDATANGAN PENULIS)   (TANDATANGAN PENYELIA)

No 1 Kg Keriang Pulau,   **Prof. Dr Mohd Ridzuan bin Nordin**
Km 3 Lebuhraya Sultan Abdul Halim,   Nama Penyelia
05400, Alor Star,
Kedah Darul Aman.

Tarikh: _____   Tarikh: _____

CATATAN :   *   Potong yang tidak berkenaan.
              **   Jika tesis ini **SULIT** atau **TERHAD**, sila lampirkan surat daripada pihak berkuasa/organisasiberkenaan dengan menyatakan sekali sebab dan tempoh tesis ini perlu dikelaskan sebagai **SULIT** atau **TERHAD**.
              ♦   Tesis dimaksudkan sebagai tesis bagi Ijazah Doktor Falsafah dan Sarjana secara penyelidikan, atau disertasi bagi pengajian secara kerja kursus dan penyelidikan, atau Laporan Projek Sarjana Muda (PSM).

"I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of the degree in Bachelor of Chemical Engineering"

Signature   : ....

Name of Supervisor   : Prof. Dr Mohd Ridzuan Bin Nordin

Date   : ....

ADSORPTION CHARACTERISTICS OF LEAD FROM AQUEOUS SOLUTION BY
PYROLYSED USED BLEACHING CLAY

NORAZURA BINTI ABD JALIL

A thesis submitted in fulfillment of the requirements for the award
of the degree in Bachelor of Chemical Engineering

FACULTY OF CHEMICAL AND NATURAL RESOURCES ENGINEERING
UNIVERSITY MALAYSIA PAHANG

APRIL 2009

I declare that this thesis entitled " Adsorption Characteristics of Lead from Aqueous Solution by Pyrolysed Used Bleaching Clay" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature   : ....

Name of Candidate   : Norazura binti Abd Jalil

Date   : ....

To my beloved father, mother and family

ACKNOWLEDGEMENT

Bismillahirrahmanirrahim…

ABSTRACT

This study was conducted to investigate the adsorption characteristics of lead (Pb) from aqueous solution by pyrolysed used bleaching clay. Used bleaching clay, a waste from an edible oil refinery has been treated by pyrolysis in a furnace. The used bleaching clay was pyrolysed at four temperatures which is 500°C, 600°C, 700°C and 800°C. The pyrolysed samples were characterized using Thermogravimetric Analysis (TGA) to find the carbon content. The parameter involves in this experiment are contact time, pH of solution, initial concentration and carbonization temperature. The Langmuir sorption isotherm was plotted to describe the equilibrium adsorption and the maximum sorption capacities of the bleaching clay towards Pb. From the adsorption kinetics experiment, it was clearly observed that the concentration of Pb decrease as time increased until it reaches the equilibrium time while the uptake capacity increase as time and initial concentration increased. For the effect of pH of adsorption solution, the highest maximum sorption capacity was determined at pH 6 and the carbonization temperature that yields highest sorption capacity is 600°C. This experiment was repeated for another adsorbent which is the untreated clay and the natural bleaching clay for comparison.

ABSTRAK

Kajian ini dijalankan adalah untuk mengkaji sifat-sifat penyerapan daripada larutan plumbum (Pb) oleh tanah liat yg sudah digunakan. Tanah liat ini ialah bahan buangan daripada kilang pemprosesan kelapa sawit dan dirawat terlebih dahulu dengan membakarnya di dalam alat pembakaran. Tanah liat yang sudah digunakan ini dibakar pada suhu yg berlainan iaitu 500°C, 600°C, 700°C dan 800°C. Tanah yang telah dibakar ini dikaji menggunakan Thermogravimetric Analysis (TGA) untuk mengetahui kandungan karbon didalamnya. Pembolehubah yang terlibat dalam eksperimen ini ialah masa, pH larutan, kepekatan awal dan suhu karbonisasi. Model Langmuir dilakar untuk menerangkan penyerapan yang seimbang dan maksimum kapasiti serapan oleh tanah liat ini terhadap plumbum. Daripada eksperimen penyerapan kinetik, jelas menunjukkan bahawa kepekatan plumbum berkurang apabila masa meningkat sehingga ianya mencapai masa yang seimbang. Selain itu kadar ambilan plumbum meningkat apabila kepekatan awal meningkat. Untuk kesan pH terhadap kadar resapan larutan, kapasiti resapan paling tinggi adalah pada pH 6 dan suhu karbonisasi yang menghasilkan kapasiti serapan paling tinggi ialah pada 600°C. Eksperimen ini diulang untuk sampel yang lain iaitu tanah liat yang belum dirawat dan tanah liat semulajadi untuk tujuan perbandingan.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

C_0 - Equilibrium Pb concentration (mg/L)

C_e - Initial Pb concentration (mg/L)

K_L - Langmuir constant (L/mg)

M   - Concentration of used bleaching clay in the reaction mixture (g/L)

q_e - Amounts of adsorbed Cu onto used bleaching clay at equilibrium (mg/g)

Q_{max} - Maximum adsorption capacity (mg/g)

t   - Contact time (min)

R^2 - Least-squares correlation coefficient

CHAPTER 1

INTRODUCTION

1.0   Background of study

The research that is conducted is on adsorption characteristics of Lead(II) from aqueous solution by pyrolysed used bleaching clay. In palm oil refining process, the main steps in the refining of edible oils are degumming, neutralization, bleaching and deodorization. Bleaching of edible oils is performed using imported natural or acid activated clays.

The bleaching clay is used to remove colourings, soap, gums, metals and oxidizing compounds and the clay consist mainly of bentonites or montmorillonites, which are finely crystalline silicate of aluminum with various amounts of alkali metals and transition metals.

Used bleaching clay, mainly generated by the edible oil processing is an industrial waste. It is noted that used bleaching clay can present a fire hazard for example spontaneous combustion, because it usually contains 20–35 wt% oil by weight. Only a few studies, however, are found in the literature regarding oil recovery and regeneration of used clay in edible oil refining. Solvent extraction processes for recovery of oil from used bleaching clay have been suggested. This is because they give a high yield and an acceptable quality of oil than other methods which is recovery of the

entrapped oil by washing with non polar solvents followed by steam treatment or washing with a solution of anionic detergent and a solution of sodium triphenylphosphate and secondly is regeneration by burning. The regeneration of used clay by solvent extraction can be done using acids, ethers and ketones. A low molecular weight ketone was found to be the most effective solvent.

In this research, the first step involve in preparing of the adsorbent is the treatments on the used bleaching clay that is pyrolysed at different temperature which are 500°C, 600°C, 700°C and 800°C. The function of pyrolysis or carbonization process is to turn the used bleaching clay into carbon-containing residue. Commonly, carbon containing materials especially the activated carbon, were used as adsorbent for the removal of both trace organic contaminants and heavy metals due to its high adsorption capacity. The main disadvantages of using activated carbon as adsorbent are its high cost, problems of regeneration, and difficulties of separating powdered activated carbon from wastewater for regeneration. For comparison, the adsorption of lead by used bleaching clay and natural bleaching clay were also determined.

All the three adsorbent involves have different properties of clay which is:
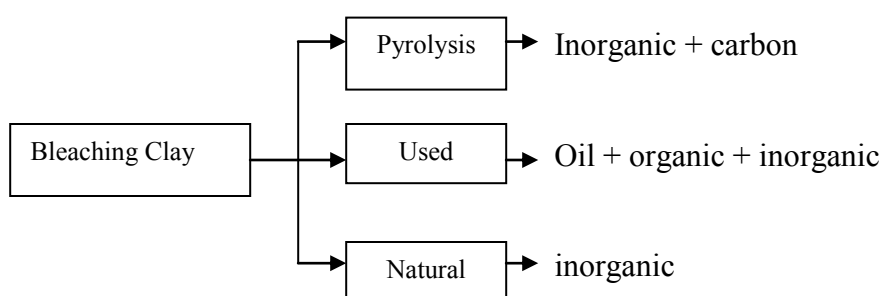
Figure 1.1: Properties of the adsorbent

The pyrolysed used bleaching clay was mixed with lead aqueous solutions. The suspensions were stirred during different time intervals (10-240min) then centrifuged.

Finally, the experimental analysis was conducted to study the performance of pyrolysis, used and natural bleaching clay. The equilibrium lead concentrations in the supernatants were determined using flame atomic absorption spectroscopy (AAS). The sorption properties of the treated material were studied for lead removal from aqueous solutions. Lead is one of the most toxic elements and is present in industrial wastewaters from battery manufacturing, metallurgy, metal finishing, and chemical industry. The uptakes capacities of the materials were calculated from the difference between the initial and final concentrations.

The parameters that were focused in this experiment are the equilibrium time for the contact time, then the pH and initial concentration of aqueous solution and finally is carbonization temperature that will affect the adsorption capacity of the adsorbent.

1.1 Problem Statement

Used bleaching clay was usually dumped in landfills without treatment causing serious environmental problems such as pollution. The environmental problems related to the used clay disposal could be largely solved by removing the oil and colouring materials adsorbed on the clay. The used bleaching clay which contains about 20±35% (w/w) of residual oil will rapidly oxidizes to the spontaneous auto-ignition point, and also produces unpleasant odors. In order to minimize the risk of pollution and these environmental problems, this research was conducted to study the adsorption characteristics of lead from aqueous solution with this treated used bleaching clay.

1.2 Objectives

Objectives of this research are:

   i.   To study effect of contact time on the adsorption capacity.

   ii.   To investigate the difference between the treated clay and clay without treatment that influences the performance of adsorption capacities.

   iii.   To determine carbon content of the clay after doing the pyrolysis or carbonization process with different temperatures.

   iv.   To study the effect of pH and initial concentration of Pb(II) in aqueous solution to the adsorption capacity.

1.3 Scope of Study

The scopes for this research are:

   i.   The study effect of contact time on the adsorption capacity, to find the equilibrium time for each adsorbent.

   ii.   The study also indicates the investigation on the difference between the treated clay which is pyrolysis and clay without treatment that will influence the performance of adsorption.

   iii.   Thermal treatment done from temperature 500-800 °C, to determine carbon content of the used bleaching clay after doing the pyrolysis or carbonization process.

   iv.   Adsorption done from aqueous solution in the pH range 2 to 7 and initial concentration of Pb(II) aqueous solution in the range 100mg/L to 500mg/L.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Investigation on adsorption characteristics of Pb(II) ions from aqueous solution by pyrolysed used bleaching clay is a research that requires a lot of study in adsorption process, environmental study, filtration and clay technology. This study is mainly focused on adsorption process. Adsorption is an alternative technology for metal separation from aqueous solutions. With the selection of a proper adsorbent, the adsorption process can be a promising technique for the removal of certain types of contaminants. Adsorption is used as a tertiary treatment process in a number of wastewater treatment plants to fulfill the requirements of effluent regulations. (Weng *et. al*, 2007).

Clays have been good adsorbents due to the existence of several types of active sites on the surface, which include Bronsted and Lewis acid sites, and ion exchange sites. The edge hydroxyl groups have been particularly active for various types of interactions. In the case of kaolinite for example, although kaolinite has a net zero layer charge, the small negative charge at the broken edges has been responsible for the activity. Montmorillonite, on the other hand, has a net negative charge of 0.8 units per unit cell and this has been responsible for giving superior activity as an adsorbent. The activity however depends on many other environmental factors such as pH and temperature. Modification of clays by pillaring and acid activation has considerable

influence on the structural properties, very often enhancing their adsorption capacities, but the reverse trends are also observed. Clays and modified clays have been found particularly useful for adsorption of heavy metals. Clays have received attention as scavengers of As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Zn in their ionic forms from aqueous medium. The adsorption capacities vary from metal to metal and also depend on the type of clay used. When a comparison is made with other low-cost adsorbents, the clays have been found to be either better or equivalent in adsorption capacity. Environmental factors like pH do have effects on the adsorption capacity as also the case with other adsorbents. The results also show how and why clays can be effectively used as a liner in water treatment plants. (Bhattacharyya and Gupta, 2008)

2.2 Palm oil refining
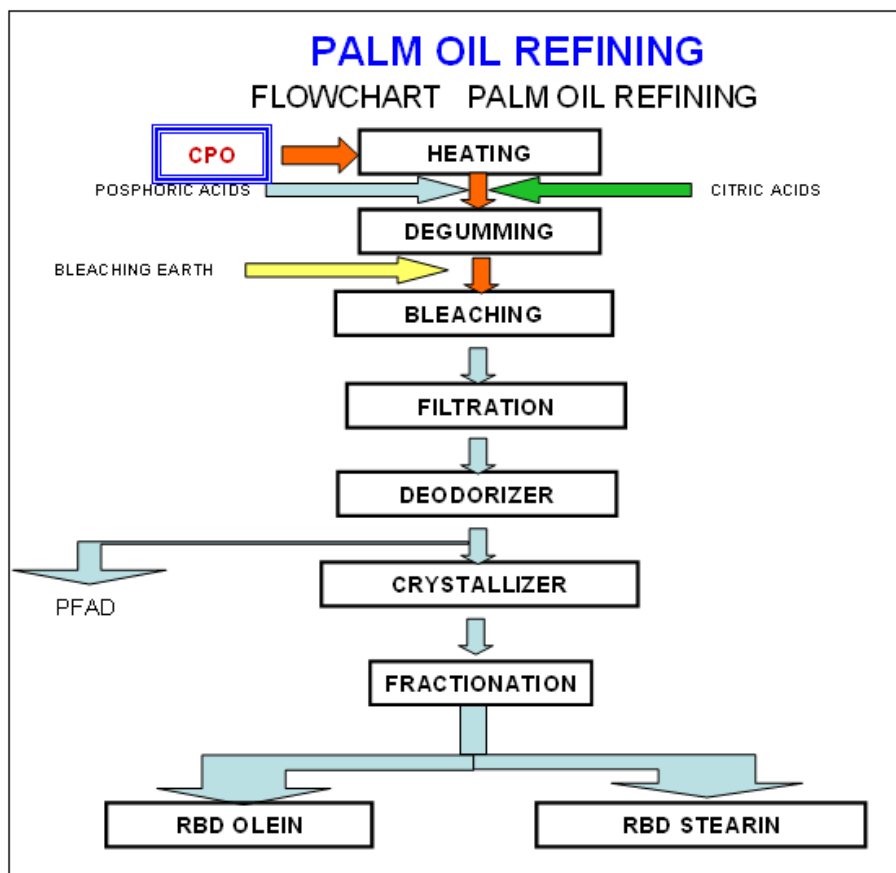
Figure 2.1: Palm oil refining process

Figure 2.1 shows the processes involve in palm oil refining. The main step that is the focus of this research is the bleaching process. The raw material which is used by physical plant is crude palm oil (CPO) from the CPO storage tank. CPO is feed at the flow rate of about 35-60 tons/hour. The initial temperature of CPO is at 40 – 60°C. The feed is pumped through the heat recovery system, that is plate heat exchanger to increase the temperature around 60 – 90°C.

After that is degumming process. Degumming is a process for separating gums and substances made up of phosphatides, proteins, carbohydrates and resin without reducing the amount of free fatty acids in the oil. Gums in vegetable oils must be removed to prevent color and taste changes prior to the next purification stage. Hydratable phosphatides are removed by water. Non-hydratable phosphatides are removed by treatment with citric acid or phosphoric acids in special mixes at 60-85°C. The Pennwalt Process involves mixing phosphoric acid and hot water followed by complete removal of hydrated gums by high speed centrifugation. The process is applicable to most vegetable oils.

Then, there is about 20% of the CPO feed to into the slurry and mix with the bleaching earth (6 – 12kg/ton CPO) to form slurry (CPO + Bleaching earth/ Bleaching clay). The agitator inside the slurry tank will mixed the CPO and bleaching earth completely. Then, the slurry will go into the bleacher.

At the same time, another 80% of the CPO is pumped through another plate heat exchanger (PHE) and steam heater to increase the CPO temperature to 90 – 130°C (it is a desired temperature for the reaction between CPO and phosphoric acid). Then, the CPO feed is pumped to static mixers and the phosphoric acid is dosed at 0.35 – 0.45 kg/ton. Inside there, the intensive mixing is carried out with the crude oil for precipitation up the gums. The precipitation of gums will ease the later filtration process; avoid the scale formation in deodorizer and heating surface. The degumming CPO then will go into bleacher. (Knapp & Johnson, 2008)

The bleaching step involves the addition of bleaching earth to remove any undesirable impurities (all pigments, trace metals, oxidation products) from CPO and this improves the initial taste, final flavor and oxidative stability of product. It also helps to overcome problems in subsequent processing by adsorption of soap traces, pro-oxidant metal ions, decomposition of peroxides, colour reduction and adsorbtion of other minor impurities. The temperature inside the bleacher must be around 100°C – 130°C to get the optimum bleaching process after 30 minutes of bleaching period. Low pressure steam is purged into bleacher to agitate the concentrated slurry for a better bleaching condition.

The slurry containing the oil and bleaching clay is then passed through Niagara filter to give a clean, free from bleaching clay particles oil. The temperature must be maintain at around 80 – 120°C for good filtration process. In edible oil refining, the bleaching treatment is a critical step. The purposes of bleaching are:

i.   To remove undesired colors in the oil where bleaching clay is added to the oil at 90-120°C in agitated vessels followed by filtration.
ii.   An adsorption process, using natural clays (bentonite & montmorrillonite) activated by acid treatment.
iii. In combination with activated carbon to remove organic compounds (pesticide residues, environmental pollutants).
iv.   To remove traces of soap and phospholipids - the oil which has been neutralized, washed and dried still contains some color and soap (< 50 ppm).
v.   Decompose oxidation products.

In the Niagara filter, the slurry passes through the filter leaves and the bleaching clay is trapped on the filter leaves. Actually, the bleaching clay must be clear from Niagara filter after 45minutes in operation to get a good filtration. Bleached palm oil (BPO) from Niagara filter is then pumped into buffer tank as a temporary storage before further processing. (Knapp & Johnson, 2008)

Usually, a second check filter, trap filter is used in series with the Niagara filter to doubly ensure that no bleaching clay slips occur. The presence of bleaching clay fouls deodorizer, reduces the oxidative stability of the product oil and acts as a catalyst for dimerizaition and polymerization activities. So, the "blue test" is carried out for each batch of filtration to ensure the perfect filtration process. This test indicates whether any leakage is occurring in Niagara filter or trap filter. Hence, any corrective actions can be taken intermediately.

The BPO comes out from the filter and passes through another series of heat recovery system. The hot BPO from spiral heat exchanger then proceeds to the next stage where the free fatty acid content and the color are further reduced and more important, it is deodorized to produce a product which is stable and bland in flavor.

In the pre-stripping and deodorizing column, deacidification and deodorization process happen concurently. Deodorization is a high temperature, high vacuum and steam distillation process. A deodorizer operates in the following manner: (1) dearates the oil; (2) heat up the oil, (3) steam strips the oil and (4) cools the oil before it leaves the system. All materials made of stainless steel.

In the column, the oil is generally heated to approximately 240 – 280°C under vacuum. A vacuum of less than 10 torr is usually maintained by the use of ejectors and boosters. Heat bleaching of the oil occurs at this temperature through thermal destruction of the carotenoid pigments. The use of direct steam ensures ready removal of residue free fatty acids, aldehydes and ketones which are responsible for unacceptable odor and flavors. The lower molecular weights of vaporized fatty acids rise up the column and are pulls out by the vacuum system. The fatty acid vapor leaving the deodorizer are condensed and collected in the fatty acid condenser as fatty acid. The fatty acids then is cooled in the fatty acid cooler and discharged to the fatty acid storage tank with temperature around 60 – 80°C as palm fatty acid distillate (PFAD), a by-product from refinery process. (Knapp & Johnson, 2008)

The main product of the pre-stripper and deodorizer is Refined, Bleached, and Deodorized Palm Oil (RBDPO). The hot RBDPO (250 – 280°C) is pumped through Schmidt PHE to transfer its heat to incoming BPO with lower temperature. Then, it passes through another trap filters to have the final oil polishing (120 – 140°C) to prevent the earth traces from reaching the product tank. After that, the RBDPO will pass through the RBDPO cooler and plate heat exchanger to transfer the heat to the CPO feed. The RBDPO then is pumped to the storage with temperature 50 – 80°C. (Knapp & Johnson, 2008)

2.3 Bleaching Clay

Bleaching clays are activated adsorbents which contain hydrated aluminium silicates. Figure 2.2 shows the raw bleaching clay that available in the market. The main task of bleaching clay is to improve the appearance, favor, taste and stability of the final product. They mainly consist of bentonites or montmorillonites, which are finely crystalline silicate of aluminum with various amounts of alkali metals and transition metals.

Figure 2.2: Raw Bleaching Clay

In edible oil refining, either by chemical or physical process, the bleaching treatment is a critical step. The adsorbents used for bleaching can remove pigments and other impurities, such as soaps, trace metals, phospholipids, oxidation products, and polyaromatics (Mag, 1990). The removal of these impurities improves the sensory quality and the oxidative stability of the deodorized oil (Greyt & Kellens, 2000).

The acidity of bleaching clays depends on the degree of activation where the higher the degree of activation, the higher the degree of cation substitution. Neutral clays, which are naturally active, are also used for bleaching. They are excellent metal adsorbents, able to remove soaps and phospholipids and to minimize free fatty acid formation during bleaching (Rossi *et. al*, 2003).

2.4 Used Bleaching Clay

Used bleaching clay is an industrial waste, mainly generated from the edible oil processing. It is noted that used bleaching clay can present a fire hazard because it usually contains 20±35% oil by weight. These oils retained and not removed by filter pressing may possess the pyrogenic nature due to the unsaturation. The waste is commonly disposed to landfill without any pretreatment. From the environmental, safety and regulatory points of view, it is urgent to restrict the landfill practice in the future. Based on the resource conservation and recovery, the utilization of this food processing waste has increased in recent years. Some alternatives to landfill disposal include (Tsai *et. al*, 2002):

  i.   Burning
  ii.   Utilization in cementation furnaces
 iii.   Utilization in brick industry
 iv.   Use as soil improve
  v.   Extraction for oil recovery
 vi.   Regeneration
vii.   Utilization in water treatment plants

Among these alternatives, most researches focused on the oil left in the used clay or the clay reused in other fields. The clay itself is not regenerated to its adsorption

capacity. In recent years, the rising costs of landfill and associated utilization methods have shifted the emphasis from oil reclamation to added-on values of used bleaching clay for environmental applications. There are several methods reported for the treatment of the used bleaching clay that will effect its performances (Tsai *et. al*, 2002). For example:

i. Used bleaching clay was regenerated with the pretreatment of hexane extraction, and then reclaimed by an autoclave with the methods of wet oxidation or of heating in aqueous medium.

ii. Used bleaching clay was de-oiled and thus regenerated by high-pressure extraction with supercritical CO_2.

iii. Used bleaching clay was used as a precursor material for the production of clay-carbon adsorbent under chemical and physical activation methods.

iv. Used bleaching clay was first de-oiled by the solvent (i.e. hexane, methanol, and supercritical CO_2) extraction, and then regenerated by acid and heat treatments.

v. Used bleaching clay was thermally regenerated in a box furnace and thermogravimetric analysis system, respectively.

vi. Used bleaching clay was regenerated by thermal processing followed by washing with a solution of hydrochloric acid.

2.5 Performance of Used Bleaching Clay

There are a lot of factors that affect the performances of the used bleaching clay. One of the researches that have been done is effects of some additives on the performances of the clay in bleaching palm oil (Hymore, 1996). The additives that were used are $FeCl_3$ and $CuSO_4$. Results show the addition of $FeCl_3$ and $CuSO_4$ to the acid-activated clay considerably improved their performance in the bleaching of palm oil. The improvement in the performance from the addition of $FeCl_3$ is higher than that from the addition of $CuSO_4$. The extent of improvement depends on the amount and

type of additive. For the two additives the maximum performance was obtained when the additive content of the acid activated clay was 12% by weight. Clay activated by acid strength of 15% proved most effective.

Besides, there is a research on the role of bleaching clays and synthetic silica in palm oil physical refining (Rossi *et. al*, 2003). The adsorption characteristics of three bleaching clays having different degrees of activation were studied in a palm oil physical refining process. Different clay types and concentrations were used in combination with a fixed amount of synthetic silica. The analytical characteristics of crude, degummed, bleached and steam-refined oils were compared. The isotherms of colour removal vs. clay concentration demonstrated that acid-activated clays were more efficient than natural clay in removing carotene pigments. The phosphorus adsorption capacity of clay seemed also to be positively affected by acid activation. However, no relationship was observed between acid activation and copper, lead or iron adsorption; the adsorption of these metal ions seemed more probably related to the presence of synthetic silica in the bleaching mixes. Although the tested clays had different activities, the analytical characteristics of the corresponding refined palm oil samples were similar. This can be explained by the fact that synthetic silica, due to its synergic action with clays, smoothes the differences between the performances of the various clays.

Another research is on removal of lead from aqueous solutions by treated used bleaching clay (Mana *et. al*, 2008). Used bleaching clay from an edible oil refinery has been treated by impregnation with a normal sodium hydroxide solution followed by mild thermal treatment (100°C). The obtained material, treated used bleaching clay was washed, dried and characterized by X-ray diffraction, FTIR, SEM, BET and thermal analysis. The clay structure was not apparently affected by the treatment and the impregnated organic matter was quantitatively removed. They have investigated the sorption of lead on this material, the used bleaching clay and the virgin bleaching clay. The kinetic results fit the pseudo second-order kinetic model and the Weber & Morris, intraparticle diffusion model. The pH had effect on the sorption efficiency. The sorption isotherms followed the Langmuir model for various sorbent concentrations with good

values of determination coefficient. The comparison between their results and those of the literature shows that the used bleaching clay and the treated used bleaching clay are among the cheaper materials and present very good lead sorption efficiency.

2.6 Langmuir Sorption Isotherms

The equilibrium sorption experimental data obtained in this study were analyzed using the commonly used Langmuir isotherm models. The Langmuir isotherms model is described by the following equation:

$$q_e = \frac{Q_{max} \, K_L \, C_e}{1 + K_L \, C_e}$$

Where q_e (mg/g) is the amount of lead removed per gram of sorbent, Q_{max} (mg/g) is the maximum sorption capacity, C_e (mg/L) is the lead concentration in the equilibrium solution, and K_L (L/g) is the Langmuir constant related to the adsorption energy. The Langmuir equation can be rearranged to linear form for the convenience of plotting and determining the Langmuir constants as below:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} K_L} + \frac{C_e}{Q_{max}}$$

The essential characteristic of Langmuir can be expressed in terms of dimensionless separation factor R_L which is defined by:

$$R_L = \frac{1}{1 + K_L C_o}$$

Where Co is the initial metal concentration (mg/L) and K_L is the langmuir constant. The value between zero and one indicate favourable adsorption. (Mana *et. al*, 2008)

CHAPTER 3

METHODOLOGY

3.1 Materials and Equipments

3.1.1   Used Bleaching Clay

Used bleaching clay is an industrial waste, mainly generated from an edible oil processing and contain about 20±35% oil by weight. Natural bleaching clay and used bleaching clay was obtained from Cargill Palm Oil Sdn. Bhd. at Gebeng, Pahang.

3.1.2   Reagents

Reagent use in this research are analytical grade $Pb(NO_3)_2.7H_2O$, Hydrochloric acid (HCl) and Sodium Hydroxide (NaOH).

3.1.3   Equipments

The major equipments used in this research include the Thermogravimetric Analysis (TGA) and Atomic Adsorption Spectrophotometer (AAS).

3.2 Research design

In this experiment, the process to produce adsorbent from used bleaching clay involves a few stages. The flow of the process involve are as figure 3.1:

```
┌─────────────────────────┐
│  Preparation of adsorbent │
└─────────────────────────┘
            │
┌─────────────────────────┐
│   Preparation of Stock   │
│        Solution          │
└─────────────────────────┘
            │
┌─────────────────────────┐
│  Experimental Procedure   │
└─────────────────────────┘
            │
┌─────────────────────────┐
│   Experimental Analysis   │
└─────────────────────────┘
```
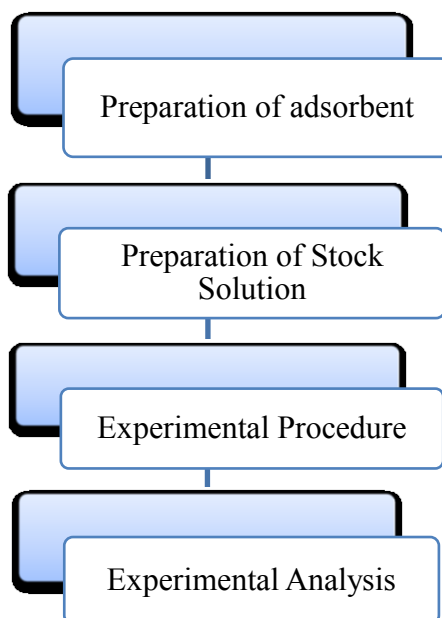
Figure 3.1: Process Flow Design

From figure 3.1, first process is preparation of adsorbent which involves the pre-treatment of the used bleaching clay to remove the remaining oil by pyrolysis process, then, the preparation of stock solution and experimental procedure where the suspensions were stirred during different time intervals and centrifuged. Finally is the experimental analysis.

3.2.1 Preparation of adsorbent

Figure 3.2 shows classification of adsorbent involves in this experiment. There are three samples prepared which is natural bleaching clay, used bleaching clay and pyrolysed bleaching clay.
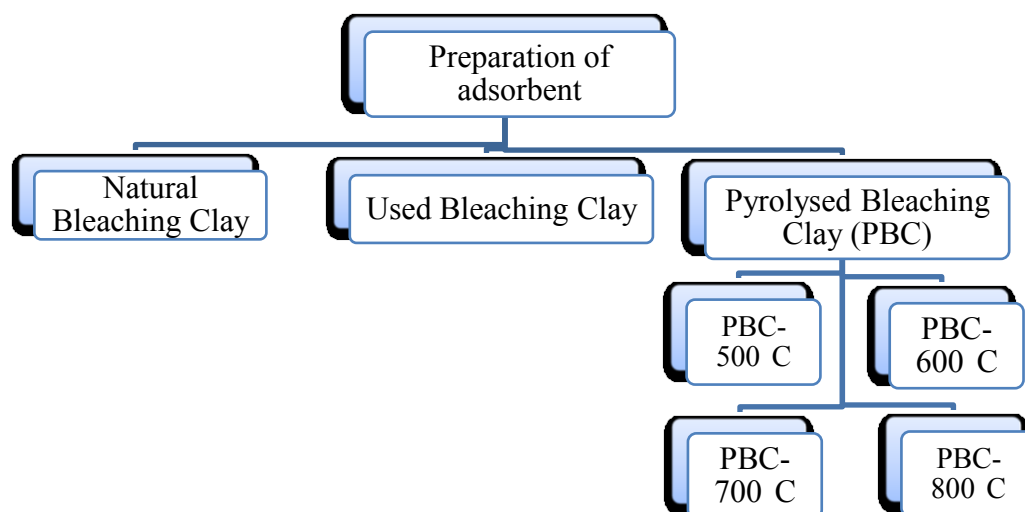
Figure 3.2: Classification of Adsorbent

The used bleaching clay then was divided into two samples. First is the sample without treatment and second is the sample with treatment which is pyrolysis. The steps for pyrolysis process are as illustrated in figure 3.3:

```
┌─────────────────────────────────────┐
│  30 g of used bleaching clay were put in 5  │
│  crucible then were placed in a furnace      │
└─────────────────────────────────────┘
                   ⇩
┌─────────────────────────────────────┐
│  The furnace and Nitrogen valve was          │
│  switched on                                  │
└─────────────────────────────────────┘
                   ⇩
┌─────────────────────────────────────┐
│  Temperature profile was setup for heating.  │
│  First at the temperature 500 C for 1 hour   │
└─────────────────────────────────────┘
                   ⇩
┌─────────────────────────────────────┐
│  After 1 hour the furnace was cooled down    │
│  about 1 hour                                 │
└─────────────────────────────────────┘
                   ⇩
┌─────────────────────────────────────┐
│  All steps above were repeated for           │
│  temperature at 600 C, 700 C and 800 C       │
└─────────────────────────────────────┘
                   ⇩
┌─────────────────────────────────────┐
│  Thermogravimetric Analysis (TGA)            │
└─────────────────────────────────────┘
```
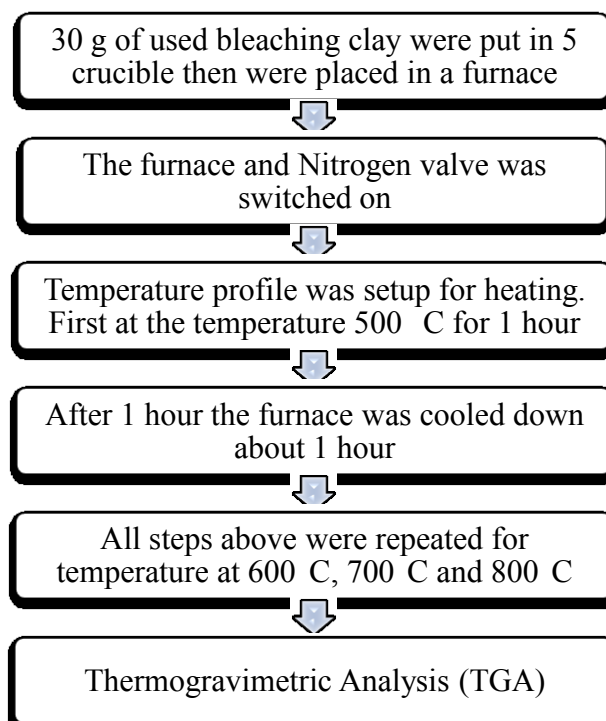
Figure 3.3: Pyrolysis Process

The pyrolysis process in figure 3.3 was done for several times to get desired amount of samples to run the experiment.

3.2.2 Preparation of stock solution

Lead (Pb^{2+}) ions were prepared by dissolving $Pb(NO_3)_2.7H_2O$ in distilled water. 1.6 g of Lead(II) Nitrate, $Pb(NO_3)_2$ are mixed with distilled water in 1L volumetric flask to produce solution with concentration of 1000 mg/L. All working solution obtained by varying the concentration of this stock solution is by dilution using distilled water.

3.2.3 Experimental Procedure

3.2.3.1 Effect of Contact Time and Pyrolysis Temperature

Three conical flasks containing 100 mL of lead solution with initial concentration 100 mg/L was prepared. The three adsorbent which is natural, used and pyrolysed bleaching clay was added to the conical flasks. The amount of adsorbent was fixed at 10 g/L meaning 1 g in 100 ml solution. These different conical flasks were closed/sealed and placed on the orbital shaker for shaking at different time interval. The time range is from 10 min to 240 min for natural and pyrolysed bleaching clay while time interval for used bleaching clay is from 10 min to 360 min. About 1 ml of solution was taken during every interval then centrifuged. After dilution with distilled water, the supernatant was analyzed using Atomic Absorption Spectrophotometer (AAS). The steps was repeated using another concentration which is 200mg/L, 300mg/L, 400mg/L and 500mg/L and for each pyrolysed bleaching clay.

3.2.3.2 Effect of pH

Three conical flasks containing 100 mL of lead solution with initial concentration 100 mg/L was prepared. Using 0.1 M HCl or NaOH, the pH value of the solution was adjusted so each of the conical flasks has the different value of pH 2, 3, 4, 5, 6 and 7. The three adsorbents which is natural, used and pyrolysed bleaching clay was added to the conical flasks. The amount of adsorbent was fixed at 10 g/L meaning 1 g in 100 ml solution. These different conical flasks were closed/sealed and placed on the orbital shaker for shaking at their equilibrium time from contact time experiments then centrifuged. After dilution with distilled water, the supernatant was analyzed using Atomic Absorption Spectrophotometer (AAS). The steps was repeated using another concentration which is 200mg/L, 300mg/L, 400mg/L and 500mg/L and for each pyrolysed bleaching clay

CHAPTER 4

RESULT AND DISCUSSION

4.1 Effect of Contact Time

4.1.1 Natural Bleaching Clay

Natural bleaching clay is raw clay that palm oil mill use in their processing plant. Table 4.1 below shows concentration and uptake capacity of lead for natural bleaching clay.

Table 4.1: Concentration and Uptake Capacity of Lead for Natural Bleaching Clay

Time (min)	Initial Concentration	Concentration before analysis (mg/L)	Concentration after analysis (mg/L)	Uptake Capacity (mg/g)
10	100	99.5	7.9	9.16
20			4.5	9.5
30			4.2	9.53
60			3.8	9.57
120			3.7	9.58
180			3.5	9.6
240			2.9	9.66
300			0.25	9.925
10	200	184.1	10.5	17.36
20			8.6	17.55
30			6.9	17.72
60			5.4	17.87

120			5	17.91
180			4.8	17.93
240			2	18.21
300			0.55	18.355
10	300	281.4	23.7	25.77
20			17.85	26.355
30			13.05	26.835
60			12.45	26.895
120			10.2	27.12
180			9.3	27.21
240			7.8	27.36
300			1	28.04
10	400	386.6	66.2	32.04
20			28.6	35.8
30			24.4	36.22
60			18.8	36.78
120			18.6	36.8
180			12	37.46
240			11.6	37.5
300			1.8	38.48
10	500	485.75	122.75	36.3
20			105	38.075
30			79	40.675
60			49.75	43.6
120			19	46.675
180			14	47.175
240			10	47.575
300			2.7	48.305
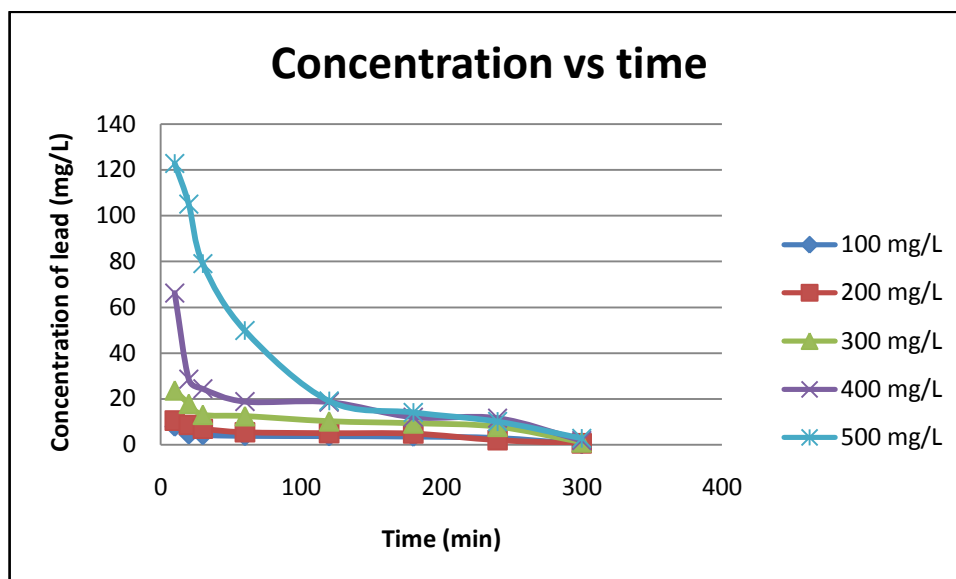
Figure 4.1: Graph Concentration of Lead versus Contact Time for Natural Bleaching Clay

Figure 4.1 shows the concentration of lead for natural bleaching clay versus contact time. The concentration decreased with increasing of time and lead initial concentration. For concentration 100 mg/L, the equilibrium time is at 60 minutes, for 200 mg/L the equilibrium time is 120 minutes, for 300 mg/L the equilibrium time is 180 minutes, for 400 mg/L the equilibrium time is 300 minutes and finally for 500 mg/L the equilibrium time is more than 300 minutes.
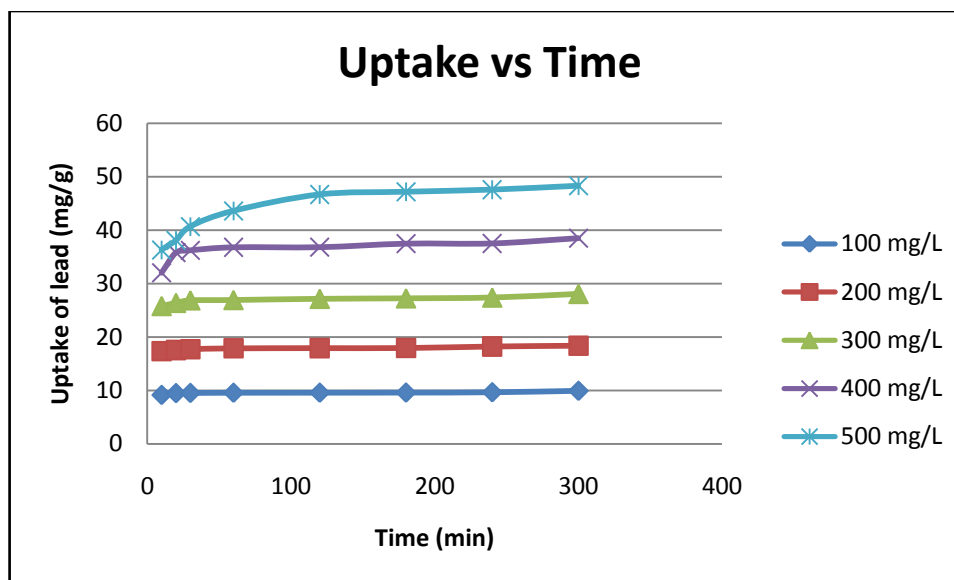
Figure 4.2: Graph Uptake Capacity of Lead versus Contact Time for Natural Bleaching Clay

Figure 4.2 shows the uptake capacity of lead for natural bleaching clay versus contact time. The uptake capacity increase as time increased. At the equilibrium time, the uptake capacity is different for each concentration. The uptake capacity increase when the concentration increased. For concentration 100 mg/L and at its equilibrium time, the capacity uptake is 9.57 mg/g, for 200 mg/L the uptake capacity is 17.91 mg/g, for 300 mg/L the uptake capacity is 27.21 mg/g, for 400 mg/L the uptake capacity is 38.48 mg/g and finally for 500 mg/L the uptake capacity is 48.305 mg/g. An increase in the initial lead concentration led to the increase in the amount of lead adsorbed onto natural bleaching clay. This may be attributed to an increase in the driving force of the concentration gradient with the increase in the initial lead concentration.

Langmuir Isotherm Model

Co	Ce	qe	Ce/qe
100	0.25	9.25	0.02703
200	0.55	18.355	0.02996
300	1	28.04	0.03566
400	1.8	38.48	0.04678
500	2.7	48.305	0.05589

Q_{max}	K_L	R^2
83.3333	0.52174	0.996
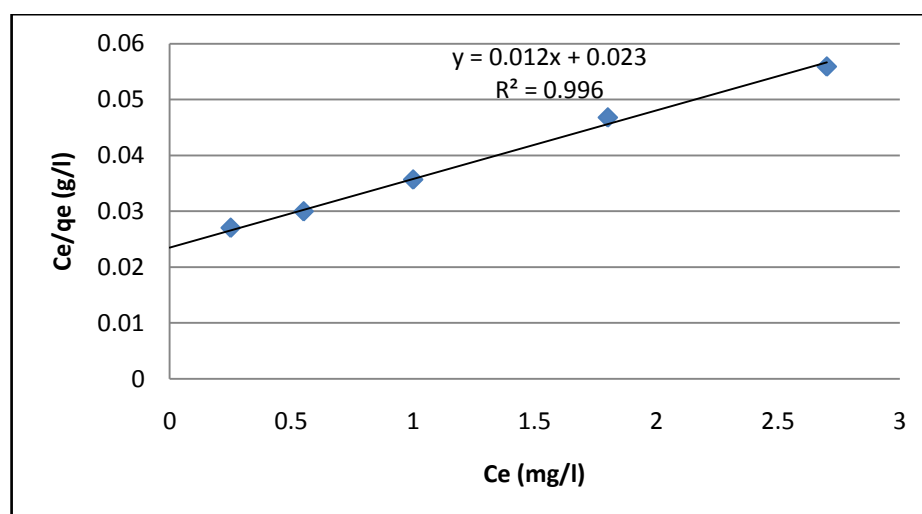
Figure 4.3: Langmuir Isotherm for Natural Bleaching Clay

Figure 4.3 shows Langmuir sorption isotherms for natural bleaching clay. The maximum sorption capacity for this clay is 83.333 mg/g and the Langmuir constant is 0.52174.

4.1.2 Used Bleaching Clay

Used bleaching Clay is a waste from edible oil processing plant that contains 20±35% oil by weight. Table 4.2 shows concentration and uptake capacity of lead of used bleaching clay.

Table 4.2: Concentration and Uptake Capacity of Lead for Used Bleaching Clay

Time (min)	Initial Concentration	Concentration before analysis (mg/L)	Concentration after analysis (mg/L)	Uptake Capacity (mg/g)
10	100	99.5	30.6	6.89
20			18.3	8.12
30			2.8	9.67
60			1.8	9.77
120			0.1	9.94
10	200	166	165.7	0.03
20			124.7	4.13
30			94.9	7.11
60			59.5	10.65
120			20.08	14.592
180			5	16.1
240			2	16.4
300			1.4	16.46
360			0.2	16.58
10	300	259	205.8	5.32
20			187.05	7.195
30			164.1	9.49
60			104.4	15.46
120			75.45	18.355
180			54	20.5
240			34	22.5
300			20	23.9
360			11.5	24.75
10	400	349.6	347	0.26
20			330.2	1.94

30			282.8	6.68
60			245.8	10.38
120			200.4	14.92
180			147	20.26
240			111.6	23.8
300			85.4	26.42
360			50	29.96
10	500	422	417.75	0.425
20			394.5	2.75
30			364.75	5.725
60			282.25	13.975
120			267	15.5
180			225.25	19.675
240			178.75	24.325
300			154.7	26.73
360			98.3	32.37
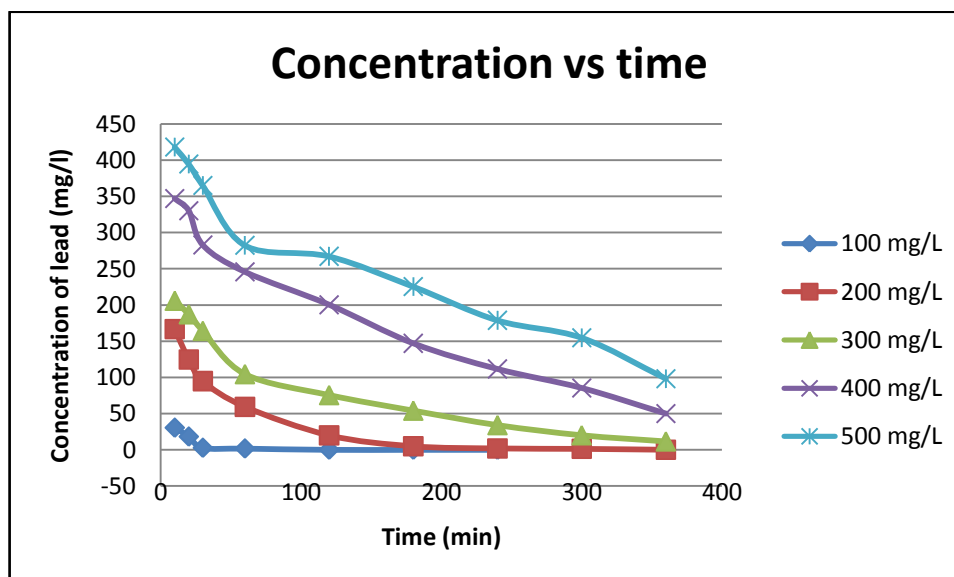
Figure 4.4: Graph Concentration of Lead versus Contact Time for Used Bleaching Clay

Figure 4.4 shows the concentration of lead for used bleaching clay versus contact time for used bleaching clay. The concentration decreased with increasing of time and lead initial concentration. For concentration 100 mg/L, the equilibrium time is at 60 minutes,

for 200 mg/L the equilibrium time is 240 minutes, for 300 mg/L the equilibrium time is 300 minutes and for 400 mg/L and 500 mg/L the time taken to reach the equilibrium is more than 360 minutes.
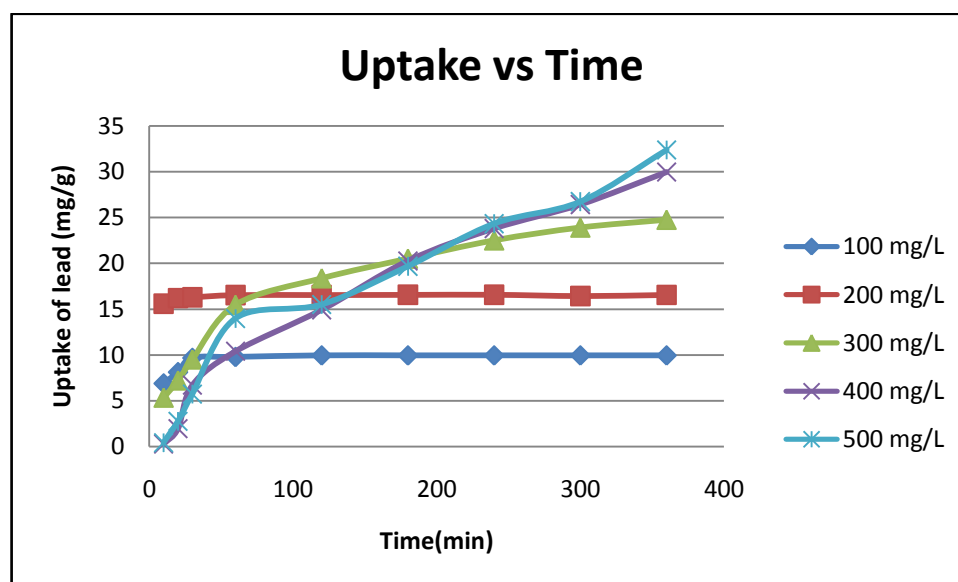
Figure 4.5: Graph Uptake Capacity of Lead versus Contact Time for Used Bleaching Clay

Figure 4.5 shows the capacity uptake of lead for natural bleaching clay versus contact time. The uptake capacity increase as time and initial concentration increased. At the equilibrium time, the uptake capacity is different for each concentration. For concentration 100 mg/L and at its equilibrium time, the uptake capacity is 9.77 mg/g, for 200 mg/L the uptake capacity is 16.4 mg/g, for 300 mg/l the uptake capacity is 23.9 mg/g, for 400 mg/L the uptake capacity is 29.96 mg/g and finally for 500 mg/L the uptake capacity is 32.37 mg/g. The uptake capacity for this clay is much slower than the other clay because the used bleaching clay still contains amount of remnant oil that make the adsorption capacity is lower.

Langmuir Isotherm Model

Co	Ce	qe	Ce/qe
100	0.1	9.94	0.01006
200	0.2	16.55	0.01208
300	11.5	24.75	0.46465
400	30	31.96	0.93867
500	98.3	32.37	3.03676

Q_{max}	K_L	R^2
33.3333	0.85715	0.998
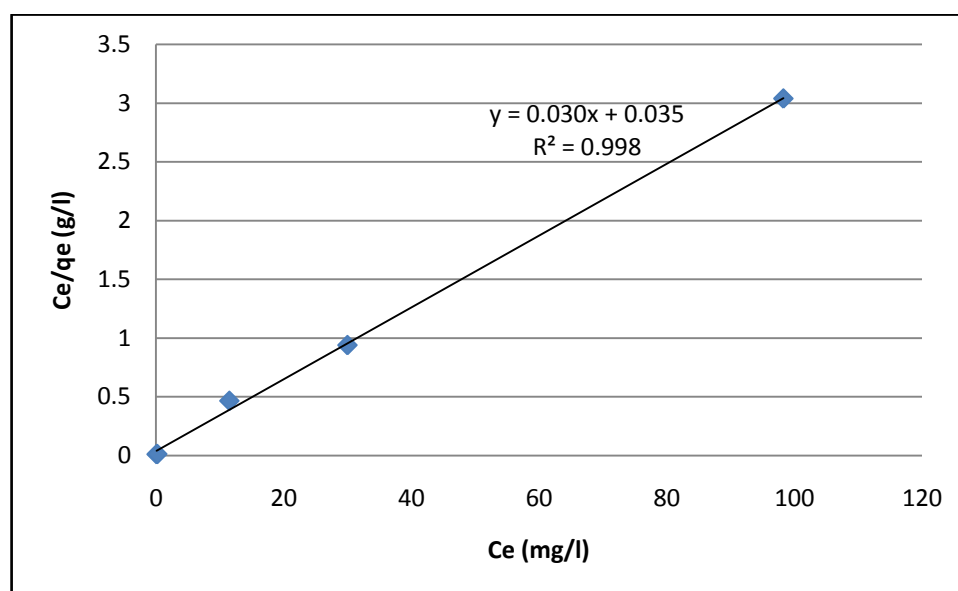
Figure 4.6: Langmuir Isotherm for Used Bleaching Clay

Figure 4.6 shows Langmuir sorption isotherms for used bleaching clay. The maximum sorption capacity for this clay is 33.333 mg/g and the Langmuir constant is 0.85715.

4.1.3 Pyrolysed Bleaching Clay

4.1.3.1 Pyrolysed Bleaching Clay at 500 °C (PBC-500 °C)

Used bleaching clay was pyrolysed at 500 °C using furnace under certain condition. Table 4.3 shows concentration and uptake capacity of used bleaching clay pyrolysed at 500 °C.

Table 4.3: Concentration and Uptake Capacity of Used Bleaching Clay Pyrolysed at 500 °C

Time (min)	Initial Concentration	Concentration before analysis (mg/L)	Concentration after analysis (mg/L)	Uptake Capacity (mg/g)
10	100	99.5	3.5	9.6
20			1.3	9.82
30			1.1	9.84
60			0.9	9.86
120			0.4	9.91
10	200	165.7	32	8.79
20			5.9	14.32
30			4.5	15.04
60			4	16.45
120			3.1	16.45
180			2	16.51
240			0.8	16.49
10	300	263	95.6	16.74
20			54.8	20.82
30			29.9	23.31
60			11.2	25.18
120			1.7	26.13
180			1.7	26.13
240			1.5	26.15
10	400	362.3	165.5	19.68
20			129.6	23.27
30			113.7	24.86
60			64	29.83

120			22.9	33.94
180			4.8	35.75
240			3.2	35.91
10	500	477.7	367.5	11.02
20			103	37.47
30			66	41.17
60			31.5	44.62
120			25	45.27
180			20	45.77
240			4.5	47.32
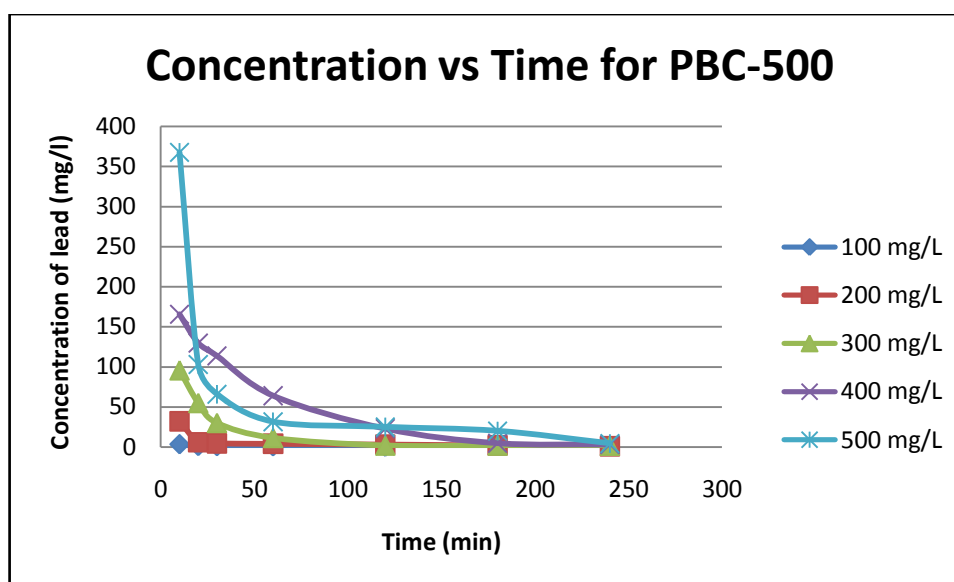
Figure 4.7: Graph Concentration of Lead versus Contact Time for Used Bleaching Clay Pyrolysed at 500 °C

Figure 4.7 shows concentration of lead for used bleaching clay pyrolysed at 500 °C versus contact time. The concentration of lead decrease as time and initial concentration increased. The equilibrium time for PBC-500°C is different for each concentration. At concentration 100 mg/L, the equilibrium time is at 20 minutes, for 200 mg/L the equilibrium time is 30 minutes, for 300 mg/L the equilibrium time is 60 minutes, for 400 mg/L the equilibrium time is 120 minutes and finally for 500 mg/L the equilibrium time is 120 minutes.
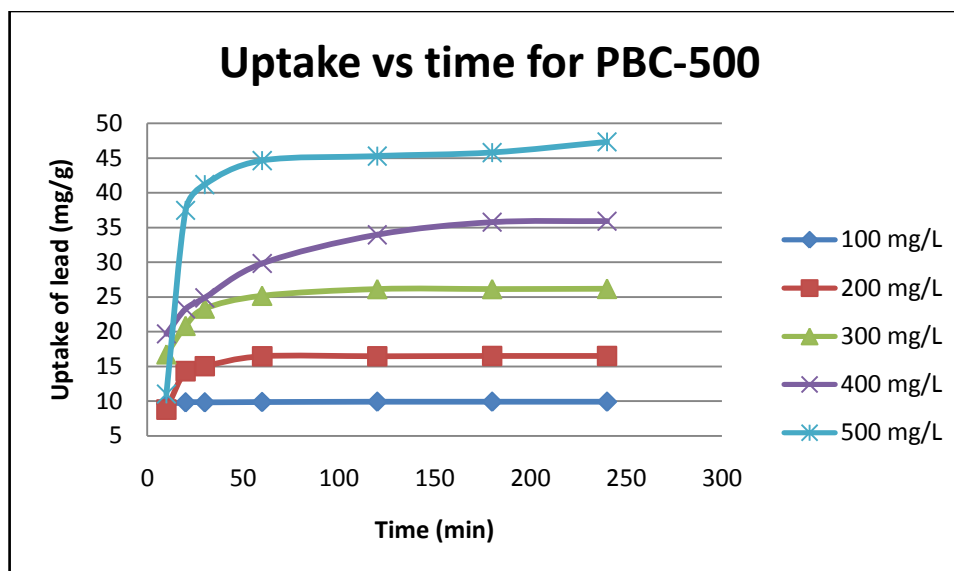
Figure 4.8: Graph Uptake Capacity of Lead versus Contact Time for Used Bleaching Clay Pyrolysed at 500 °C

Figure 4.8 shows uptake capacity of lead for used bleaching clay pyrolysed at 500°C versus contact time. The uptake capacity increase as time and initial concentration increased. At the equilibrium time, the uptake capacity is different for each concentration. At concentration 100 mg/L and at the equilibrium time for PBC-500°C the uptake capacity is about 9.82 mg/g, for 200 mg/L the uptake capacity is about 14.32 mg/g, for 300 mg/L the uptake capacity is about 25.18 mg/g, for 400 mg/L the uptake capacity is 33.94 mg/g and finally for 500 mg/L the uptake capacity is 45.27 mg/g.

Langmuir Isotherm Model

Co	Ce	qe	Ce/qe
100	0.4	9.91	0.04036
200	0.8	16.49	0.04851
300	1.5	26.15	0.05736
400	3.2	36.91	0.0867
500	4.5	47.32	0.0951

Q_{max}	K_L	R^2
76.9231	0.35135	9.77
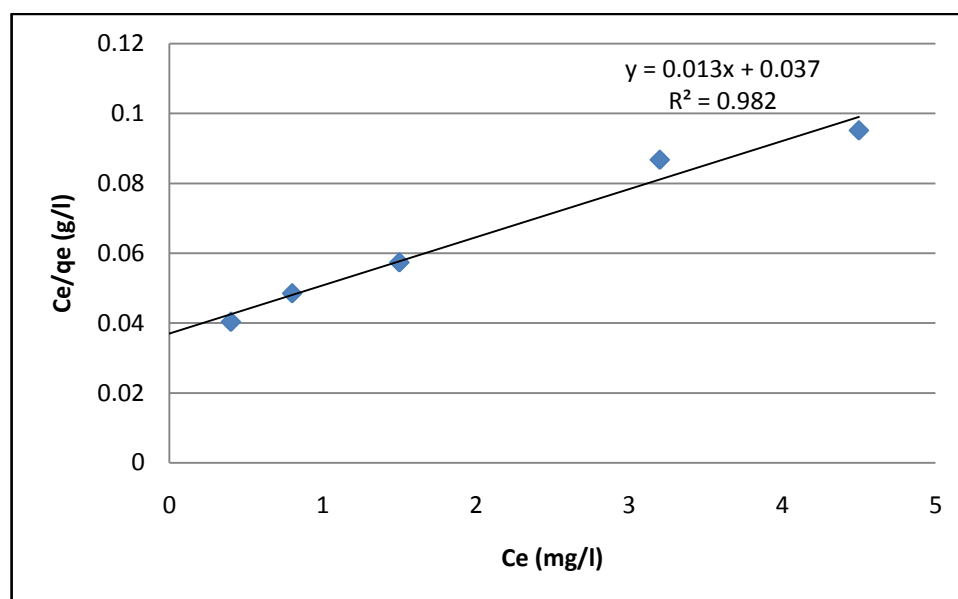
Figure 4.9: Langmuir Isotherm for Used Bleaching Clay Pyrolysed at 500 °C

Figure 4.9 shows Langmuir sorption isotherms for used bleaching clay pyrolysed at 500 °C. The maximum sorption capacity for this clay is 76.9231mg/g and the Langmuir constant is 0.35135.

4.1.3.2 Pyrolysed Bleaching Clay at 600 °C (PBC-600°C)

Used bleaching clay was pyrolysed at 600 °C using furnace under certain condition. Table 4.4 shows concentration and uptake capacity of used bleaching clay pyrolysed at 600 °C.

Table 4.4: Concentration and Capacity Uptake of Used Bleaching Clay Pyrolysed at 600 °C

Time (min)	Initial Concentration	Concentration before analysis (mg/L)	Concentration after analysis (mg/L)	Uptake Capacity (mg/g)
10	100	99.5	1.8	9.77
20			1.6	9.79
30			1.5	9.8
60			1	9.85
120			0.2	9.93
10	200	165.7	26.8	13.89
20			10.5	15.52
30			2.9	16.28
60			2.6	16.31
120			2	16.37
180			1.3	16.39
240			0.4	16.4
10	300	263	83	18
20			41.3	22.17
30			23.8	23.92
60			2.6	26.04
120			1.5	26.15
180			1.2	26.18
240			0.7	26.23
10	400	362.3	175.8	18.65
20			122	24.03
30			87.5	27.48
60			55.6	30.67
120			5.9	35.64
180			1.1	36.12
240			1.1	36.12

10	500	477.7	254.6	22.31
20			208.7	26.9
30			169.5	30.82
60			125.2	35.25
120			48.1	42.96
180			3.8	47.39
240			1.7	47.6
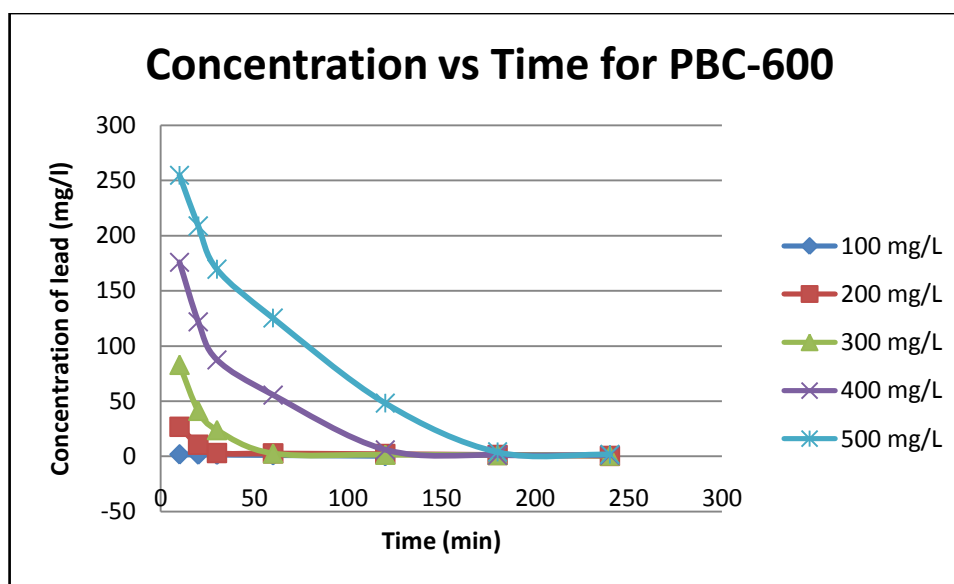
Figure 4.10: Graph Concentration of Lead versus Contact Time for Used Bleaching Clay Pyrolysed at 600 °C

Figure 4.10 shows concentration of lead for used bleaching clay pyrolysed at 600 °C versus contact time. The concentration of lead decrease as time and initial concentration increased. The equilibrium time for PBC-600°C is different for each concentration. At concentration 100 mg/L, the equilibrium time is at 20 minutes, for 200 mg/L the equilibrium time is 30 minutes, for 300 mg/L the equilibrium time is 60 minutes, for 400 mg/L the equilibrium time is 120 minutes and finally for 500 mg/L the equilibrium time is 180 minutes.
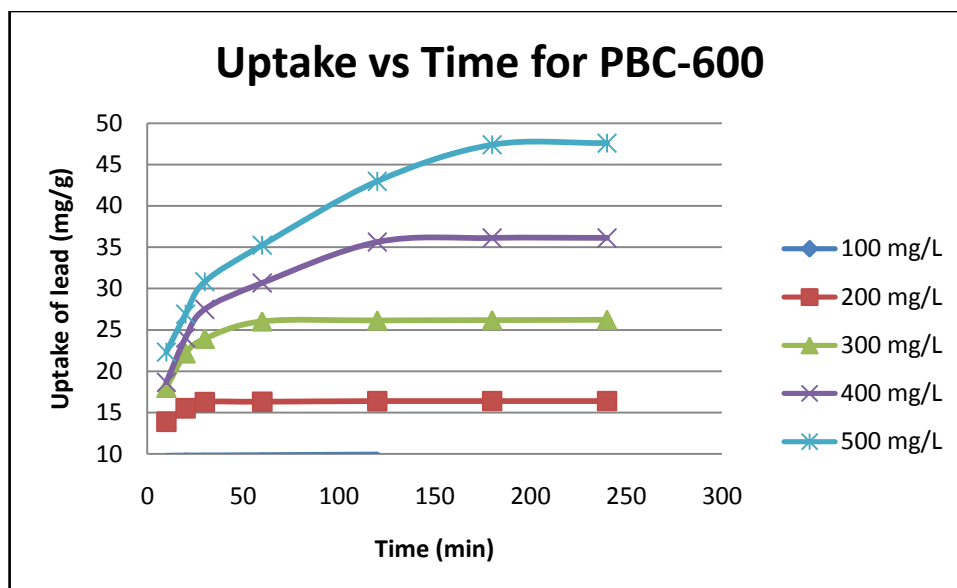
Figure 4.11: Graph Uptake Capacity of Lead versus Contact Time for Used Bleaching Clay Pyrolysed at 600 °C

Figure 4.11 shows uptake capacity of lead for used bleaching clay pyrolysed at 600°C versus contact time. The uptake capacity increase as time and initial concentration increased. At the equilibrium time, the uptake capacity is different for each concentration. At concentration 100 mg/L and at the equilibrium time for PBC-600°C the uptake capacity is about 9.79 mg/g, for 200 mg/L the uptake capacity is about 16.28 mg/g, for 300 mg/L the uptake capacity is about 26.04 mg/g, for 400 mg/L the uptake capacity is 35.64 mg/g and finally for 500 mg/L the uptake capacity is 42.96 mg/g.

Langmuir Isotherm Model

Co	Ce	qe	Ce/qe
200	0.4	16.4	0.02439
300	0.8	26.22	0.03051
400	1.1	36.12	0.03045
500	1.7	47.6	0.03571

Q_{max}	K_L	R^2
111.111	0.47368	0.978
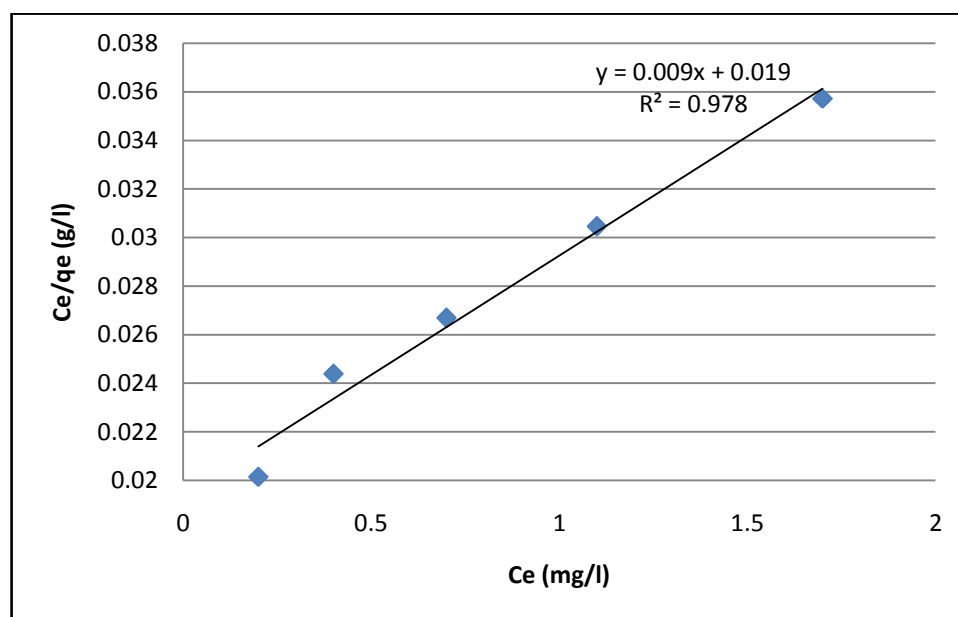
Figure 4.12: Langmuir Isotherm for Used Bleaching Clay Pyrolysed at 600 °C

Figure 4.12 shows Langmuir sorption isotherms for used bleaching clay pyrolysed at 600 °C. The maximum sorption capacity for this clay is 111.111 mg/g and the Langmuir constant is 0.47368.

4.1.3.3 Pyrolysed Bleaching Clay at 700 °C (PBC-700°C)

Used bleaching clay was pyrolysed at 700 °C using furnace under certain condition. Table 4.4 shows concentration and uptake capacity of used bleaching clay pyrolysed at 700 °C.

Table 4.5: Concentration and Uptake Capacity of Used Bleaching Clay Pyrolysed at 700 °C

Time (min)	Initial Concentration	Concentration before analysis (mg/L)	Concentration after analysis (mg/L)	Uptake Capacity (mg/g)
10	100	99.5	2.4	9.71
20			2.1	9.74
30			1.9	9.76
60			1.3	9.82
120			0	9.95
10	200	165.7	9.9	15.58
20			3.8	16.19
30			2.8	16.29
60			0.4	16.53
120			0.3	16.54
180			0.1	16.56
240			0.1	16.56
10	300	263	45.9	21.71
20			12.9	25.01
30			3.9	25.91
60			3.6	25.94
120			2.7	26.03
180			1	26.2
240			0.2	26.28
10	400	347	200.4	14.66
20			158	18.9
30			113.4	23.36
60			57.8	28.92
120			1.6	34.54
180			0.6	34.64
240			0.3	34.67

10	500	477.7	288.5	18.92
20			227.7	25
30			179.8	29.79
60			107.1	37.06
120			1.5	47.62
180			1.5	47.62
240			1	47.67
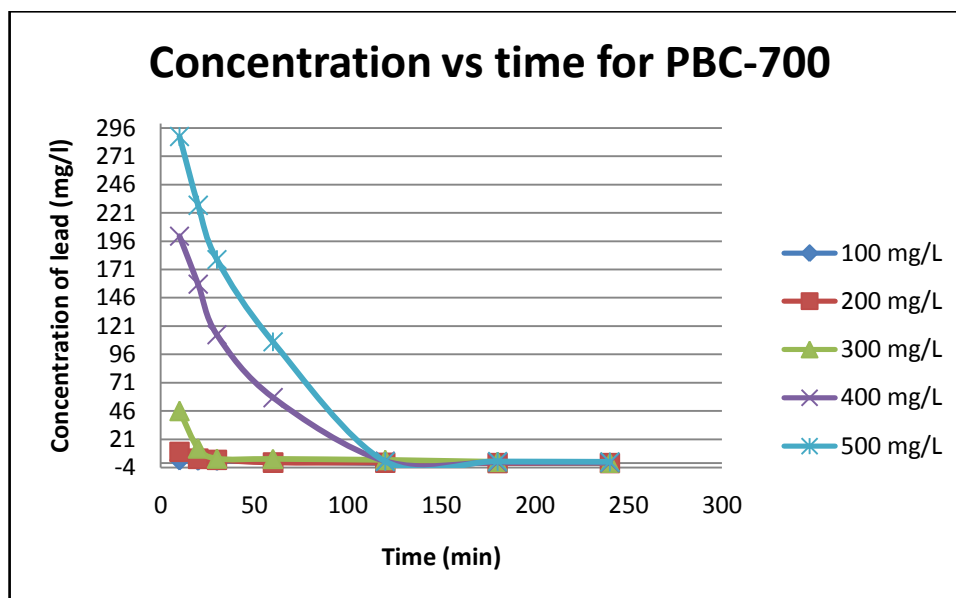
Figure 4.13: Graph Concentration of Lead versus Contact Time for Used Bleaching Clay Pyrolysed at 700 °C

Figure 4.13 shows concentration of lead for used bleaching clay pyrolysed at 600 °C versus contact time. The concentration of lead decrease as time and initial concentration increased. The equilibrium time for PBC-600°C is different for each concentration. At concentration 100 mg/L, the equilibrium time is at 20 minutes, for 200 mg/L the equilibrium time is 30 minutes, for 300 mg/L the equilibrium time is 60 minutes, for 400 mg/L the equilibrium time is 120 minutes and finally for 500 mg/L the equilibrium time is 120 minutes.
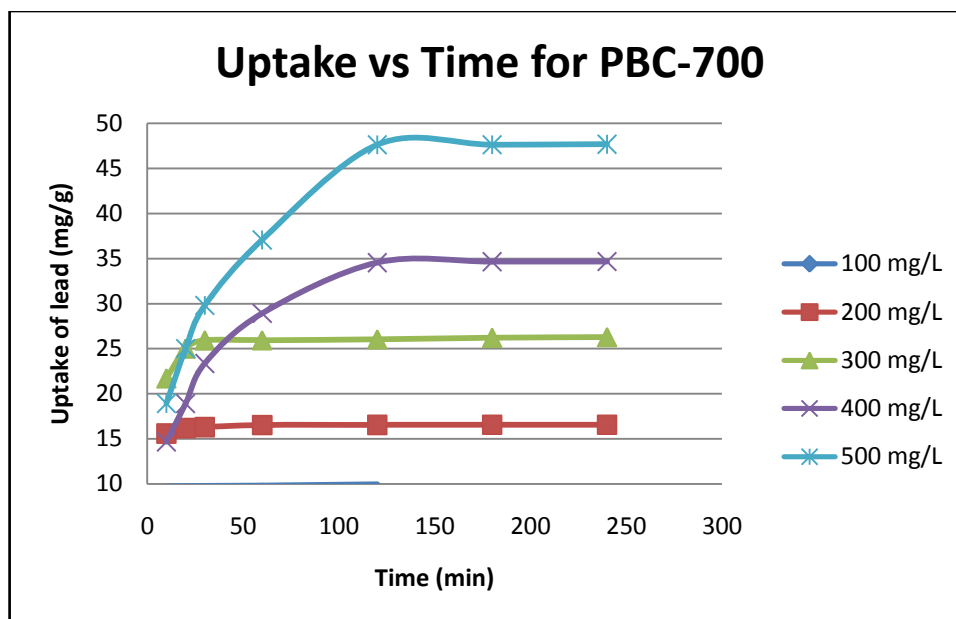
Figure 4.14: Graph Uptake Capacity of Lead versus Contact Time for Used Bleaching Clay Pyrolysed at 700 °C

Figure 4.14 shows uptake capacity of lead for used bleaching clay pyrolysed at 700°C versus contact time. The uptake capacity increase as time and initial concentration increased. At the equilibrium time, the uptake capacity is different for each concentration. At concentration 100 mg/L and at the equilibrium time for PBC-700°C the uptake capacity is about 9.74 mg/g, for 200 mg/L the uptake capacity is about 16.29 mg/g, for 300 mg/L the uptake capacity is about 25.94 mg/g, for 400 mg/L the uptake capacity is 35.54 mg/g and finally for 500 mg/L the uptake capacity is 47.62 mg/g.

Langmuir Isotherm Model

Co	Ce	qe	Ce/qe
100	0	9.95	0
200	0.1	16.56	0.00604
300	0.2	26.28	0.00761
400	0.3	34.67	0.00865
500	1	47.67	0.02098

Q_{max}	K_L	R^2
55.5556	9	0.952
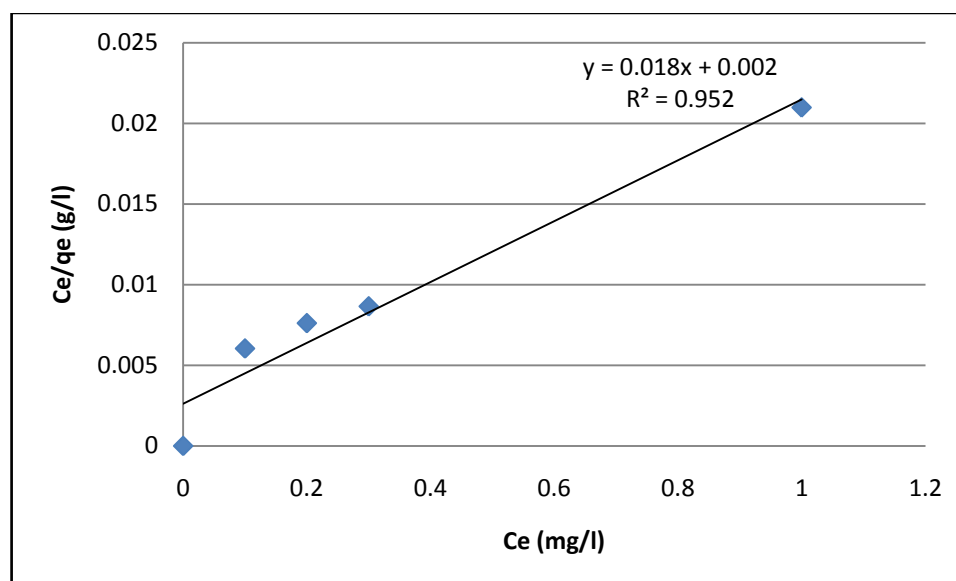
Figure 4.15: Langmuir Isotherm for Used Bleaching Clay Pyrolysed at 700 °C

Figure 4.15 shows Langmuir sorption isotherms for used bleaching clay pyrolysed at 700 °C. The maximum sorption capacity for this clay is 55.5556 mg/g and the Langmuir constant is 9.

4.1.3.4 Pyrolysed Bleaching Clay at 800 °C (PBC-800°C)

Used bleaching clay was pyrolysed at 800 °C using furnace under certain condition. Table 4.4 shows concentration and uptake capacity of used bleaching clay pyrolysed at 800 °C.

Table 4.6: Concentration and Uptake Capacity of Used Bleaching Clay Pyrolysed at 800 °C

Time (min)	Initial Concentration	Concentration before analysis (mg/L)	Concentration after analysis (mg/L)	Uptake Capacity (mg/g)
10	100	99.5	2.4	9.71
20			1.9	9.76
30			1	9.85
60			0.9	9.86
120			0.2	9.93
10	200	165.7	77.8	8.79
20			22.5	14.32
30			15.3	15.04
60			1.2	16.45
120			1.2	16.45
180			0.6	16.51
240			0.4	16.53
10	300	192.6	106.8	8.58
20			53.7	13.89
30			26.7	16.59
60			3.6	18.9
120			3.6	18.9
180			1.8	19.08
240			0.7	19.19
10	400	277.6	164	11.36
20			114	16.36
30			86	19.16
60			22	25.56
120			4	27.36
180			2	27.56
240			1.6	27.6

10	500	422.6	367.5	5.51
20			293.5	12.91
30			227	19.56
60			151.5	27.11
120			65.25	35.735
180			13	40.96
240			4.4	41.82
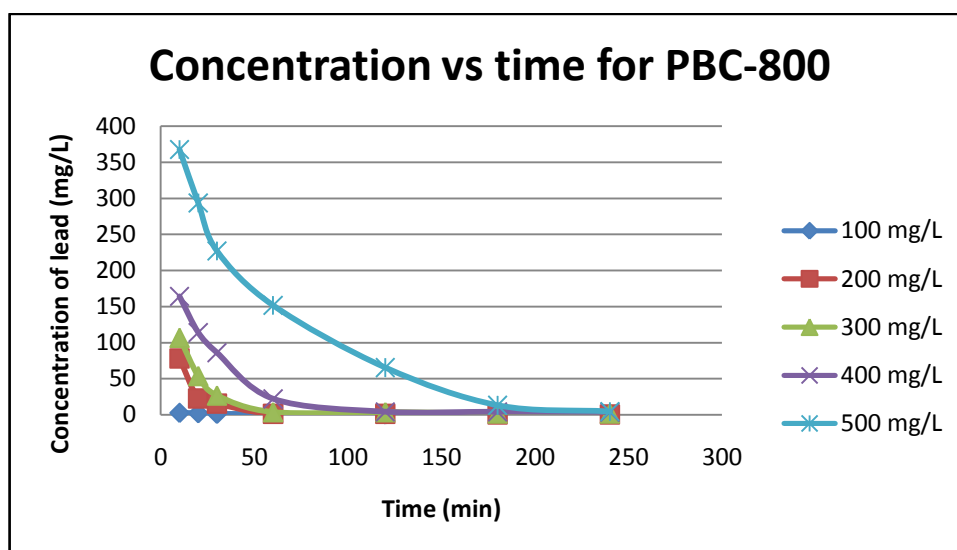
Figure 4.16: Graph Concentration of Lead versus Contact Time for Used Bleaching Clay Pyrolysed at 800 °C

Figure 4.16 shows concentration of lead for used bleaching clay pyrolysed at 800 °C versus contact time. The concentration of lead decrease as time and initial concentration increased. The equilibrium time for PBC-800°C is different for each concentration. At concentration 100 mg/L, the equilibrium time is at 20 minutes, for 200 mg/L the equilibrium time is 30 minutes, for 300 mg/L the equilibrium time is 60 minutes, for 400 mg/L the equilibrium time is 120 minutes and finally for 500 mg/L the equilibrium time is 180 minutes.
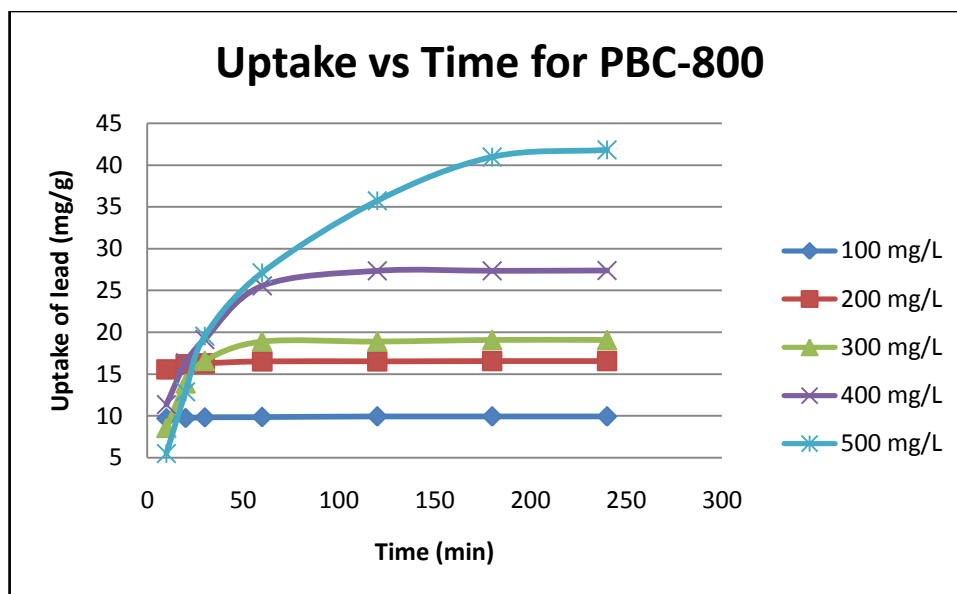
Figure 4.17: Graph Capacity Uptake of Lead versus Time Contact for Used Bleaching Clay Pyrolysed at 800 °C

Figure 4.17 shows uptake capacity of lead for used bleaching clay pyrolysed at 800°C versus contact time. The uptake capacity increase as time and initial concentration increased. At the equilibrium time, the uptake capacity is different for each concentration. At concentration 100 mg/L and at the equilibrium time for PBC-800°C the uptake capacity is about 9.76 mg/g, for 200 mg/L the uptake capacity is about 15.04 mg/g, for 300 mg/L the uptake capacity is about 18.9 mg/g, for 400 mg/L the uptake capacity is 27.36 mg/g and finally for 500 mg/L the uptake capacity is 40.96 mg/g.

Langmuir Isotherm Model

Co	Ce	qe	Ce/qe
200	0.4	16.57	0.02414
300	1.8	19.08	0.09434
400	3.6	27.4	0.13139
500	4.4	41.82	0.10521

Q_{max}	K_L	R^2
50	1.05263	0.983
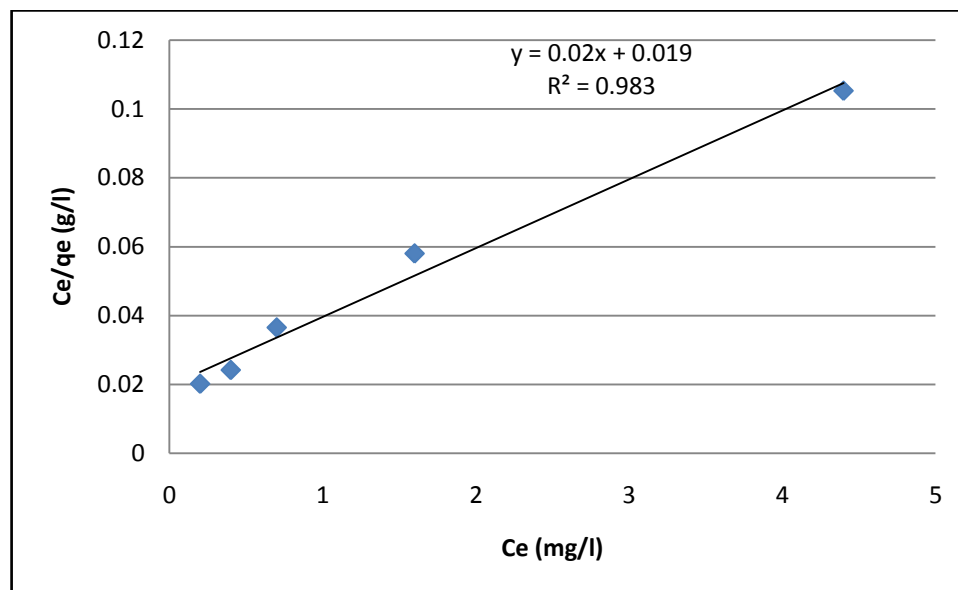
Figure 4.18: Langmuir Isotherm for Used Bleaching Clay Pyrolysed at 800 °C

Figure 4.18 shows Langmuir sorption isotherms for used bleaching clay pyrolysed at 800 °C. The maximum sorption capacity for this clay is 50 mg/g and the Langmuir constant is 1.05263.

Apparently, the initial lead concentration plays an important role in affecting the adsorption capacity of lead onto pyrolysed bleaching clay. It can be visualized that a faster adsorption rate at the beginning of the adsorption was found for a lower initial lead concentration. The results show that a rapid increase in lead adsorption occurred within 10 min with more than 90% of total lead adsorption completed in all cases.

Table 4.7: Value of Langmuir isotherms for different adsorbents

Adsorbents	Q_{max} (mg/g)	K_L	R^2
Natural Bleaching Clay	83.333	0.521741217	0.996
Used Bleaching Clay	33.3333	0.85715	0.998
Pyrolysis Bleaching Clay-500 °C	76.9231	0.35135	0.982
Pyrolysis Bleaching Clay-600 °C	111.111	0.47368	0.978
Pyrolysis Bleaching Clay-700 °C	55.55556	9	0.952
Pyrolysis Bleaching Clay-800 °C	50	1.05263	0.983

Table 4.7 shows comparison between values of Langmuir isotherms for each adsorbent. By comparing the clay with treatment and the clay without treatment, it shows that the clay with treatment which is pyrolysis bleaching clay give higher maximum sorption capacity than the clay without treatment which is the used bleaching clay. It is because the used bleaching clay is still contain the remnant oil that make the adsorption capacity is lower while the pyrolysis bleaching clay is a carbon containing clay that has high adsorption capacity.

4.2 Effect of Pyrolysis Temperature
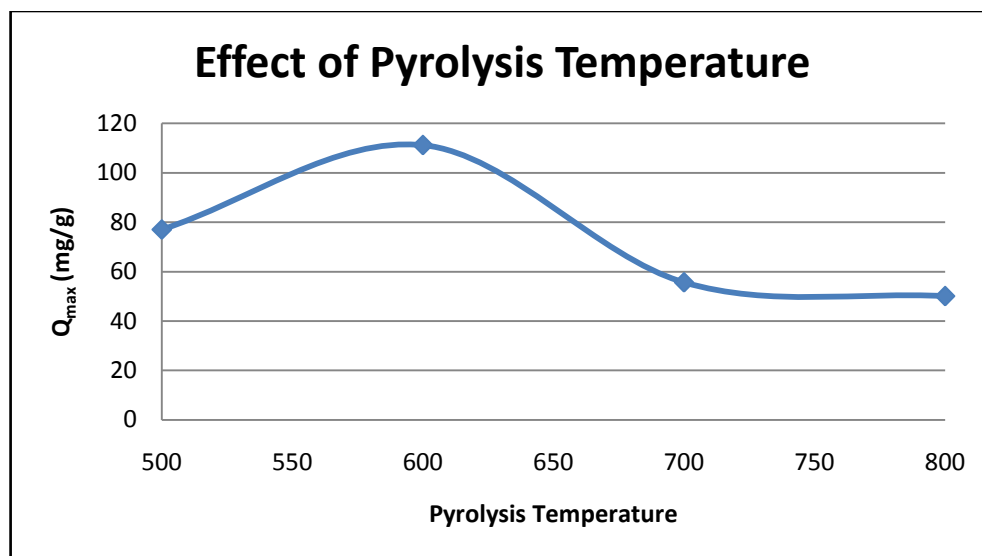
Figure 4.19: Graph maximum sorption capacity of lead versus pyrolysis temperature

Figure 4.19 shows a plot of maximum sorption capacity of lead versus pyrolysis temperature. To examine the effect of the heating temperature on the adsorbents, the temperature was varied from 500 to 800°C. As shown in the figure, the maximum sorption capacity increase for PB-500°C to PBC-600°C and decrease for PBC-700°C and PBC-800°C. The highest maximum sorption capacity is at temperature 600 °C. This indicates that the porosity of the used bleaching clay was developed by burning off part of the carbon to produce new pores and open closed pores at temperatures between 500 and 600°C. Above 600°C, carbon which constructs the walls of each pore was volatilized to widen the pores. The sample treated above temperature 600°C has the lowest carbon content resulting in a decrease of the adsorption energy and capacity.

4.3 Effect of pH

Solution pH played a significant role in determining the adsorption characteristics. Table 4.8 shows Langmuir isotherm value of Pyrolysed Bleaching Clay at 600 °C.

Table 4.8: Langmuir isotherm value of Pyrolysed Bleaching Clay at 600 °C

pH	Co	Ce	qe	Ce/qe	Q_{max}
2	100	4.3	9.53	0.451207	16.9492
	200	33	15.47	2.133161	
	300	102	14.97	6.813627	
	400	156.8	22.72	6.901408	
	500	247.75	15.55	15.93248	
3	100	0.8	9.84	0.081301	30.303
	200	3.3	17.96	0.183742	
	300	14.25	25.02	0.569544	
	400	41.2	34.82	1.183228	
	500	125.5	29.675	4.229149	
4	100	0.3	9	0.033333	33.3333
	200	0.4	17.52	0.022831	
	300	3.3	25.17	0.131108	
	400	36.4	32.48	1.12069	
	500	90.75	32.675	2.777353	
5	100	0.6	8.75	0.068571	33.3333
	200	1.1	16.97	0.06482	
	300	3.15	24.54	0.128362	
	400	1.5	36.63	0.04095	
	500	94.25	32.525	2.897771	
6	100	0.7	7.68	0.091146	35.7143
	200	1.1	16.45	0.066869	
	300	6.15	24.24	0.253713	
	400	3.4	34.5	0.098551	
	500	80	34.125	2.344322	
7	100	0.4	5.61	0.071301	32.2581
	200	0.6	10.6	0.056604	
	300	1.65	19.62	0.084098	
	400	4.2	28.36	0.148096	
	500	14	29.2	0.479452	
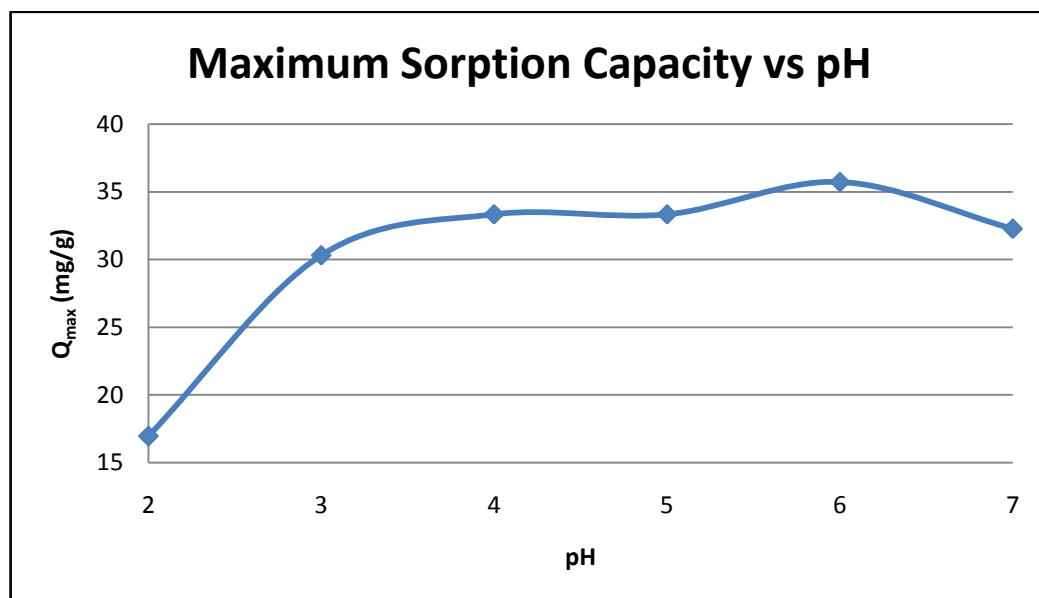
Figure 4.20: Graph maximum sorption capacity of lead for PBC-600 °C versus pH

The pH value of the solution is an important controlling parameter in the adsorption process. Figure 4.20 shows maximum sorption capacity for PBC-600°C versus pH. From this figure, it was clearly observed that the maximum sorption capacity (Q_{max}) of PBC-600 °C increase with increased pH from pH 2 to 6 and decreased at pH 7. The highest maximum sorption capacity was determined at pH 6. In general, metal adsorption is small at low pH value because of the H_3O^+ ions competitions. At pH 7 the solution tend to form precipitation that makes the adsorption capacity is lower.

4.4 Thermogravimetric Analysis (TGA)

Figure 4.21 and shows results from Thermogravimetric analysis (TGA) for each adsorbent. As a preliminary study on finding the operating condition of pyrolysis temperature, the TGA analysis was used to investigate the thermal decomposition of used bleaching clay.
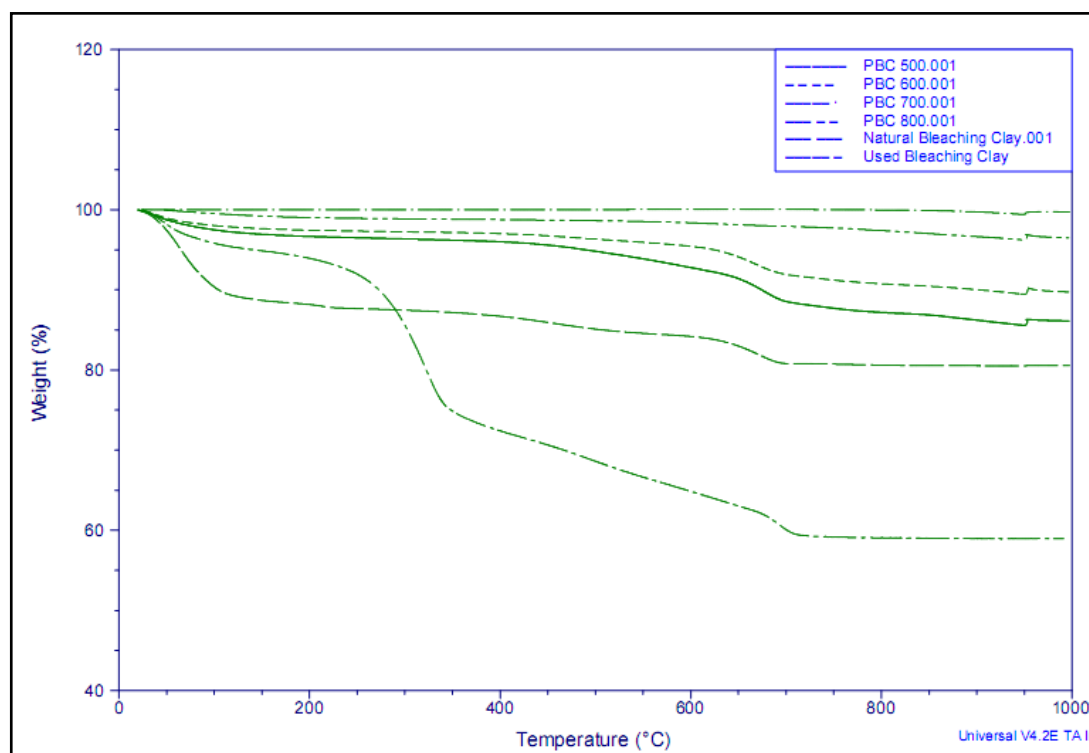
Figure 4.21: Graph of TGA analysis for each adsorbent

Figure 4.21 shows that the thermal decomposition of the bleaching clay reveals a multistage process; that is, the mass loss rates display three peaks at about 200 and 700°C. The mass loss of sample between 100 and 200°C may be mostly due to moisture content of the sample. The second peak after 200 °C is because of evaporation processes, which are associated with the evolution of volatile products or oils from the used bleaching clay sample. On the other hand, the occurrence of the third peak in the temperature range of 650 to 700°C can be attributed to the carbonization of residual

used bleaching clay. After we switch to gas oxygen, we can determine the ash content of the sample. Obviously, the pyrolysis temperature at about 500°C may be used as a minimum operating temperature for thermal regeneration of used bleaching under an inert atmosphere.

TGA Analysis for Each Adsorbent

	Natural Clay	Used clay	PBC-500	PBC-600	PBC-700	PBC-800
Moisture content (%)	11.83	10.32	3.018	2.544	1.322	0.9703
Volatile Matter (%)	7.243	10.867	10.07	7.987	5.278	2.761
Fixed Carbon (%)	0.2856	0.1322	0.7079	0.7883	0.6903	0.6063
Ash Content (%)	80.32	78.54	86.02	88.63	92.46	95.49
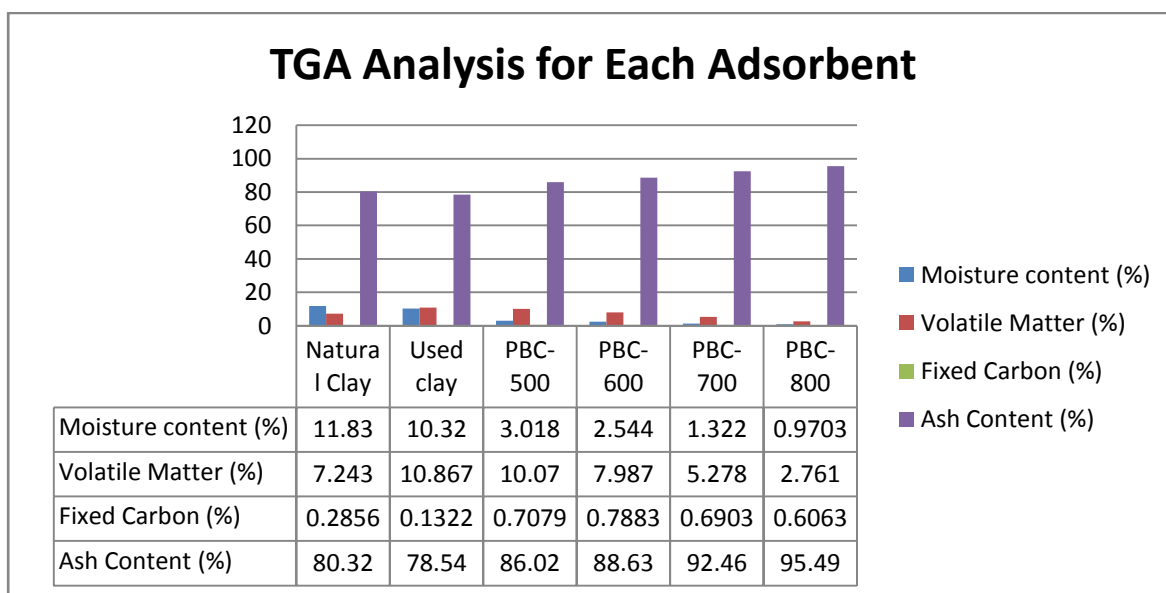
Figure 4.22: Bar Chart of TGA analysis of each adsorbent

Figure 4.22 summarize the data from bar chart on TGA analysis for every sample. The bar chart shows classification of component that degrades during pyrolysis process. The component involves are moisture content, volatile matter, fixed carbon and ash content of the used bleaching clay. The highest amounts of the component in the samples are the ash content. For pyrolysed bleaching clay, the value of ash content increase as the carbonization temperature increased. The amounts of fixed carbon in every sample are the lowest compared to the other component while the moisture content in every samples also is not too high. For adsorption experiment, it is evident that the adsorption depends on the carbon content in the samples. Samples having higher carbon content exhibit a larger adsorption capacity. Therefore, it can be concluded that the adsorption occurred mainly on the surface of the carbon constituent (Zhonghua and Vansant, 1995).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From this research, we can conclude that

i. Pyrolysed used bleaching clay give higher capacity uptake than fresh bleaching clay. It is because the untreated bleaching clay still contains amount of remnant oil that make the adsorption capacity is lower while the treated bleaching clay depends on the carbon content in the samples. Samples having higher carbon content exhibit a larger adsorption capacity. Therefore, it can be concluded that the adsorption occurred mainly on the surface of the carbon constituent.

ii. Used Bleaching Clay Pyrolysed at 600°C gives maximum sorption capacity. The sample treated above temperature 600°C has the lowest carbon content resulting in a decrease of the adsorption energy and capacity.

iii. Highest maximum sorption capacity for PBC-600°C was determined at pH 6 and at pH 7 the adsorption capacity decreased because the solutions tend to form precipitation.

iv. This study has demonstrated that the low-cost adsorbent, PBC, could be efficiently utilized for the removal of Pb(II) from aqueous solutions.

v. It is found that an increase of temperature from 500 to 600°C is an effective operation for the carbonization with N_2.

vi. An increase in the initial lead concentration led to the increase in the amount of lead adsorbed onto the clay. This may be attributed to an increase in the driving force of the concentration gradient with the increase in the initial lead concentration.

5.2 Recommendations

i. Undergo another treatment of used bleaching clay, for example by acid activation. Previous study shows activation using Sodium Hydroxide (NaoH) gives higher adsorption capacity. Activation process has cleared the pore of the used bleaching clay particle therefore increasing its surface area.

ii. Use different heavy metals for example Zinc, Chromium, Copper and others to compare their adsorption performances.

REFERENCES

Al-Zahrani, A.A, Daous, M.A. 2000. Recycling of spent bleaching clay and oil Recovery. *Process Safety and Environmental Protection.* **78**(3): 224-228 .

Belouatek, A, Ouagued, A, Belhakem M, Addou A. 2008. Filtration performance of microporous ceramic supports. *Journal of Biocheical and Biophysical Methods.* **70**(6): 1174-1179.

Bhattacharyya, K.G, Gupta, S.S. 2008. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. *Advances in Colloid and Interface Science.* **140**(2): 114–131.

Causserand, C, Jover, K, Aimar, P, Meireles, M. 1997. Modification of clay cake permeability by adsorption of protein. *Journal of Membrane Science.* **137**(1-2): 31-44.

Greyt, D.W, Kellens, M. 2000. Refining Practice. *Edible Oil Processing.* **78**(5): 79-128

Hymore, F.K. 1996. Effects of some additives on the performance of acid-activated clays in the bleaching of palm oil. *Applied Clay Science.* **10**(5): 379-385.

Knapp, F.L, Johnson, W.R. 2008. Chemical Technology. *Journal of Chemistry.* **1**(3): 387-429

Mag T.K. 1990. Bleaching- Theory and Practice. *Edible Fats and Oil Processing*. **78**(5): 107-116)

Mana, M, Ouali, M.S, Lindheimer, M, Menorval, L.C. 2008. Removal of lead from aqueous solutions with a treated spent bleaching earth. *Journal of Hazardous Materials*. **159**(2-3): 358-364.

Rossi, M, Gianazza, M Alamprese, C, Stanga, F. 2003. The role of bleaching clays and synthetic silica in palm oil physical refining, *Food Chemistry* **82**(2): 291- 296.

Tsai, W.T, Chang, Y.M, Lai, C.W, Lo, C.C. 2005. Adsorption of basic dyes in aqueous solution by clay adsorbent from regenerated bleaching earth. *Applied Clay Science* **29**(2): 149– 154.

Tsai, W.T, Chen, H.P, Hsieh, M.F, Sun, H.F, Chien, S.F. 2002. Regeneration of spent bleaching earth by pyrolysis in a rotary furnace. *Journal of Analytical and Applied Pyrolysi*s. **63**(1): 157–170.

Tsai, W.T, Lai, C.W. 2006. Adsorption of herbicide paraquat by clay mineral regenerated from spent bleaching earth. *Journal of Hazardous Materials*. **134**(1-3): 144–148.

Weng, C.H, Tsai, C.Z, Chu, S.H, Sharma, Y.C. 2007. Adsorption characteristics of copper(II) onto spent activated clay*, Separation and Purification Technology* **54**(2): 187–197.

Zhongihua,H., Vansant, E.F. 1995. Chemical Activation Of Elutrilithe Producing Carbon-Aluminosilicate Composite Adsorbent. *Carbon*. **33**(5). 173-179

APPENDIX A

PREPARATION OF SOLUTION

A.1 Preparation of Stock Solution, $Pb(NO_3)_2$

Molecular weight $Pb(NO_3)_2$ = 331.2 g/mol

Atomic weight Pb   = 207.2 g/mol

1 g $Pb(NO_3)_2$ = Atomic weight Pb/ Molecular weight $Pb(NO_3)_2$

1 g Pb   = 331.2/207.2 $Pb(NO_3)_2$

                = 1.6 g of Pb in 1 L distilled water

A.2 Preparation of Plumbum(Pb) Standard Solution

$$M_1V_1 = M_2V_2$$

$$(1000 \text{ mg/L}) V_1 = (20 \text{ mg/L})(100/1000)$$

$$V_1 = 0.002 \text{ L}$$

= 2 mL of Pb standard solution + 98 mL ultra pure water

Concentration : 2 mg/L

$$M_1V_1 = M_2V_2$$
$$(20 \text{ mg/L}) V_1 = (2 \text{ mg/L})(15/1000)$$
$$V_1 = 0.0015 \text{ L}$$
$$= 1.5 \text{ mL of Pb standard solution} + 13.5 \text{ mL ultra pure water}$$

Concentration : 4 mg/L

$$M_1V_1 = M_2V_2$$
$$(20 \text{ mg/L}) V_1 = (4 \text{ mg/L})(15/1000)$$
$$V_1 = 0.003 \text{ L}$$
$$= 3 \text{ mL of Pb standard solution} + 12 \text{ mL ultra pure water}$$

Concentration : 8 mg/L

$$M_1V_1 = M_2V_2$$
$$(20 \text{ mg/L}) V_1 = (8 \text{ mg/L})(15/1000)$$
$$V_1 = 0.006 \text{ L}$$
$$= 6 \text{ mL of Pb standard solution} + 9 \text{ mL ultra pure water}$$

Concentration : 16 mg/L

$$M_1V_1 = M_2V_2$$
$$(20 \text{ mg/L}) V_1 = (16 \text{ mg/L})(15/1000)$$
$$V_1 = 0.012 \text{ L}$$
$$= 12 \text{ mL of Pb standard solution} + 3 \text{ mL ultra pure water}$$

A.3 Preparation of Natrium Hydroxide (NaOH) solution

$$MV = \frac{Jisim}{JMR}$$

(0.1M)(250/1000) = Jisim/40

Jisim   = 1 g of NaOH pellet in 250 distilled water

A.4 Preparation of Hydrochloric acid (HCl) solution

Sg = 1.19

JMR = 36.46

Purity = 37%

$$M_1 = \frac{sg \times Purity \times 1000}{JMR}$$

$$M_1 = \frac{1.19 \times 0.37 \times 1000}{36.46}$$

$$= 12.08 \text{ mg/L}$$

$$M_1V_1 = M_2V_2$$

(12.08 mg/L) V_1 = (0.1 mg/L)(250/1000)

$$V_1 = 0.00207 \text{ L}$$

$$= 2.1 \text{ mL of HCl} + 250 \text{ mL distilled water}$$

APPENDIX B

PREPARATION OF SAMPLE SOLUTION

B.1 Effect of Contact Time

Metal : Pb

Sample: FBC, UBC, PBC-500°C, PBC-600°C, PBC-700°C, PBC-800°C

Dosage: 10 g/L or 1 g in 100 mL solution

Time   : 10 min, 20 min, 30 min, 1 h, 2 h, 3 h, 4 h

Initial Concentration   : 100 mg/L

$$M_1V_1 = M_2V_2$$

$$(1000 \text{ mg/L}) V_1 = (100 \text{ mg/L})(100/1000)$$

$$V_1 = 0.01 \text{ L}$$

= 10 mL of Pb stock solution + 90 mL distilled water

Initial Concentration   : 200 mg/L

$$M_1V_1 = M_2V_2$$

$$(1000 \text{ mg/L}) V_1 = (200 \text{ mg/L})(100/1000)$$

$$V_1 = 0.02 \text{ L}$$

= 20 mL of Pb stock solution + 80 mL distilled water

Initial Concentration   : 300 mg/L

$$M_1V_1 = M_2V_2$$

$$(1000 \text{ mg/L}) \ V_1 = (300 \text{ mg/L})(100/1000)$$

$$V_1 = 0.03 \text{ L}$$

$$= 30 \text{ mL of Pb stock solution} + 70 \text{ mL distilled water}$$

Initial Concentration   : 400 mg/L

$$M_1V_1 = M_2V_2$$

$$(1000 \text{ mg/L}) \ V_1 = (400 \text{ mg/L})(100/1000)$$

$$V_1 = 0.04 \text{ L}$$

$$= 40 \text{ mL of Pb stock solution} + 60 \text{ mL distilled water}$$

Initial Concentration   : 500 mg/L

$$M_1V_1 = M_2V_2$$

$$(1000 \text{ mg/L}) \ V_1 = (500 \text{ mg/L})(100/1000)$$

$$V_1 = 0.05 \text{ L}$$

$$= 50 \text{ mL of Pb stock solution} + 50 \text{ mL distilled water}$$

Dilution

Initial Concentration   : 100 mg/L

$$M_1V_1 = M_2V_2$$

$$(100 \text{ mg/L}) \ V_1 = (10 \text{ mg/L})(15/1000)$$

$$V_1 = 0.0015 \text{ L}$$

$$= 1.5 \text{ mL solution} + 13.5 \text{ mL distilled water}$$

Initial Concentration   : 200 mg/L

$$M_1V_1 = M_2V_2$$

$$(200 \text{ mg/L}) \ V_1 = (20 \text{ mg/L})(15/1000)$$

$$V_1 = 0.0015 \text{ L}$$

$$= 1.5 \text{ mL solution} + 13.5 \text{ mL distilled water}$$

Initial Concentration   : 300 mg/L

$$M_1V_1 = M_2V_2$$

$$(300 \text{ mg/L}) V_1 = (20 \text{ mg/L})(15/1000)$$

$$V_1 = 0.001 \text{ L}$$

= 1 mL solution + 14 mL distilled water

Initial Concentration   : 400 mg/L

$$M_1V_1 = M_2V_2$$

$$(400 \text{ mg/L}) V_1 = (20 \text{ mg/L})(15/1000)$$

$$V_1 = 0.00075 \text{ L}$$

= 0.75 solution + 14.25 mL distilled water

Initial Concentration   : 500 mg/L

$$M_1V_1 = M_2V_2$$

$$(500 \text{ mg/L}) V_1 = (20 \text{ mg/L})(15/1000)$$

$$V_1 = 0.0006 \text{ L}$$

= 0.6 mL solution + 14.4 mL distilled water

B.2 Effect of pH

Metal : Pb

Sample: PBC-600°C

Dosage: 10 g/L or 1 g in 100 mL solution

Time : 1 h

pH : 2, 3, 4, 5, 6, 7

Initial Concentration : 100 mg/L

$$M_1V_1 = M_2V_2$$
$$(1000 \text{ mg/L}) V_1 = (100 \text{ mg/L})(100 \times 6/1000)$$
$$V_1 = 0.06 \text{ L}$$
$$= 60 \text{ mL of Pb stock solution} + 540 \text{ mL distilled water}$$

Initial Concentration : 200 mg/L

$$M_1V_1 = M_2V_2$$
$$(1000 \text{ mg/L}) V_1 = (200 \text{ mg/L})(100 \times 6/1000)$$
$$V_1 = 0.12 \text{ L}$$
$$= 120 \text{ mL of Pb stock solution} + 480 \text{ mL distilled water}$$

Initial Concentration : 300 mg/L

$$M_1V_1 = M_2V_2$$
$$(1000 \text{ mg/L}) V_1 = (300 \text{ mg/L})(100 \times 6/1000)$$
$$V_1 = 0.18 \text{ L}$$
$$= 180 \text{ mL of Pb stock solution} + 420 \text{ mL distilled water}$$

Initial Concentration : 400 mg/L

$$M_1V_1 = M_2V_2$$
$$(1000 \text{ mg/L}) V_1 = (400 \text{ mg/L})(100 \times 6/1000)$$
$$V_1 = 0.24 \text{ L}$$
$$= 240 \text{ mL of Pb stock solution} + 360 \text{ mL distilled water}$$

Initial Concentration : 500 mg/L

$$M_1V_1 = M_2V_2$$

$$(1000 \text{ mg/L}) V_1 = (500 \text{ mg/L})(100 \times 6/1000)$$

$$V_1 = 0.3 \text{ L}$$

= 300 mL of Pb stock solution + 300 mL distilled water

Dilution

Initial Concentration : 100 mg/L

$$M_1V_1 = M_2V_2$$

$$(100 \text{ mg/L}) V_1 = (10 \text{ mg/L})(15/1000)$$

$$V_1 = 0.0015 \text{ L}$$

= 1.5 mL solution + 13.5 mL distilled water

Initial Concentration : 200 mg/L

$$M_1V_1 = M_2V_2$$

$$(200 \text{ mg/L}) V_1 = (20 \text{ mg/L})(15/1000)$$

$$V_1 = 0.0015 \text{ L}$$

= 1.5 mL solution + 13.5 mL distilled water

Initial Concentration : 300 mg/L

$$M_1V_1 = M_2V_2$$

$$(300 \text{ mg/L}) V_1 = (20 \text{ mg/L})(15/1000)$$

$$V_1 = 0.001 \text{ L}$$

= 1 mL solution + 14 mL distilled water

Initial Concentration   : 400 mg/L

$$M_1V_1 = M_2V_2$$

$$(400 \text{ mg/L}) V_1 = (20 \text{ mg/L})(15/1000)$$

$$V_1 = 0.00075 \text{ L}$$

$$= 0.75 \text{ solution} + 14.25 \text{ mL distilled water}$$

Initial Concentration   : 500 mg/L

$$M_1V_1 = M_2V_2$$

$$(500 \text{ mg/L}) V_1 = (20 \text{ mg/L})(15/1000)$$

$$V_1 = 0.0006 \text{ L}$$

$$= 0.6 \text{ mL solution} + 14.4 \text{ mL distilled water}$$