

# **A Composite of Bentonite/CoFe<sub>2</sub>O<sub>4</sub>/Hydroxyapatite for Lead Adsorption from Wastewater**

**Yiene Molla Desalegn**



**A Thesis Submitted to**

**The Department of Materials Science and Engineering**

**School of Chemical, Mechanical and Materials Engineering**

**Presented in Partial Fulfillment of MSc Degree in Materials Science and  
Engineering**

**Office of Graduate Studies**

**Adama Science and Technology University**

**Adama**

**July 2020**

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**Advisor: Temesgen Debelo (Ph.D.)**

**Co-advisor: Dinsefa Mensur (Ph.D.)**



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We, the undersigned, members of the Board Examiners of the final open defense by Yiene Molla have read and evaluated his thesis entitled “**A composite of Bentonite/CoFe<sub>2</sub>O<sub>4</sub>/Hydroxyapatite for Lead Adsorption from Wastewater**” and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirement of Degree of Master’s in Materials and Engineering.

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### **Declaration**

I hereby declare that this MSc Thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been duly acknowledged.

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Signature

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This MSc Thesis has been submitted for examination with my approval as thesis Advisor

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Dr. Temesgen Debelo

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## NOMENCLATURE

|                |                                                                                        |
|----------------|----------------------------------------------------------------------------------------|
| D              | Crystalline size (nm)                                                                  |
| C <sub>0</sub> | Initial concentration (mg/L)                                                           |
| C <sub>e</sub> | Equilibrium concentration (mg/L)                                                       |
| q <sub>e</sub> | Adsorption capacity at equilibrium (mg/g)                                              |
| q <sub>m</sub> | Maximum adsorption capacity (mg/g)                                                     |
| η              | Removal efficiency (%)                                                                 |
| K <sub>F</sub> | Freundlich constant                                                                    |
| n              | Intensity of adsorption                                                                |
| b              | Langmuir constant                                                                      |
| R              | Correlation coefficient                                                                |
| R <sub>L</sub> | Separation factor                                                                      |
| K <sub>1</sub> | Rate constant of Pseudo-first-order kinetics (min <sup>-1</sup> )                      |
| K <sub>2</sub> | Rate constant of pseudo-second-order kinetics (g.mg <sup>-1</sup> .min <sup>-1</sup> ) |

## ABSTRACT

Heavy and toxic metals from various chemical processing industries cause environmental pollutions and damage healthy life of the societies. Among these toxic metals is lead, which causes severe threats to human health, as well as a major contributor to environmental pollutions as it can be easily incorporated into ecosystems and therefore to the food-chains. Thus, it is essential to remove lead from wastewater before reaching to the atmosphere. In this work, a composite of bentonite/ $\text{CoFe}_2\text{O}_4$  (B/CF) and bentonite/ $\text{CoFe}_2\text{O}_4$ /Hydroxyapatite (B/CF/HAP) were synthesized via chemical coprecipitation methods. Herein, a composite of B/CF was first synthesized:  $(100-x)\text{B}/(x)\text{CF}$  where  $x = 5, 15, 25$  weight percent of  $\text{CoFe}_2\text{O}_4$  in the bentonite matrix. The sample with composition of 85%B/15%CF was the optimal amount in its adsorption capacity (19.9 mg/g) towards  $\text{Pb}^{2+}$ . Ternary composites were prepared with different weight ratios of HAP, i.e., 25%HAP/75%(85%B/15%CF), 35%HAP/65%(85%B/15%CF) and 45%HAP/55%(85%B/15%CF). Among these ternary composites, the sample of 35%HAP/65%(85%B/15%CF) revealed best adsorption capacity, which was then selected for further study. The synthesized materials were characterized via X-ray powder diffraction (XRD) for phase purity, Scanning electron microscopy with energy-dispersive X-ray (SEM-EDX) for microstructure and morphology studies, Fourier transform infrared spectroscopy (FTIR) to determine functional groups, and Thermogravimetric analysis-differential thermogravimetry (TGA-DTA) to investigate thermal stability of the materials. Atomic absorption spectrometry (AAS) was also utilized to determine the adsorption capacity of the samples. The adsorption capacity of B/CF/HAP was investigated at different contact time (30-120 min) and initial concentration of lead ion (50-200 ppm). The maximum adsorption capacity of B/CF/HAP towards  $\text{Pb}^{2+}$  was 67.1 mg/g. Adsorption isotherm data best fitted with Freundlich isotherm model and kinetic behavior adopted pseudo-second order adsorption mechanism. The result of this study pinpoints that B/CF/HAP composite is an alternative method for the removal of lead ion from aqueous sources.

**Keywords:** bentonite/ $\text{CoFe}_2\text{O}_4$ /Hydroxyapatite, Adsorption, lead ion, and wastewater.

# 1. INTRODUCTION

## 1.1. Background of the Study

Environment can be referred to the surroundings within which human exists. It comprises of land, water and atmosphere of the earth. An environment can be polluted or contaminated [1]. Environment is said to be polluted when undesirable change severely affect its component [2]. Water is a very important natural resource for living organisms to live on earth, although, its contamination has become the most worrying environmental issue in recent years. The quality of water sources face challenges related to population growth and globalization [3]. The entry of the enormous amount of pollutants including sediments, surfactants, synthetic dyes, sewages, and heavy metals into water bodies pollute and demolish the quality of water [4]. The presence of heavy metals in aqueous system is considered as a major universal problem related to many harmful causes on the health of humans and other life forms. Now a days, heavy metals pollution has become a severe problem in the environment [5]. Heavy metals are generally considered to be those whose density greater than  $5 \text{ g/cm}^3$  [6]. Lead, chromium, cadmium, arsenic, mercury, copper, zinc, and nickel are the very toxic heavy metals in the environment context [7]. Among heavy metals, lead (Pb) is highly toxic metal present in nature, primarily in inorganic form [8]. It is commonly discharged from industries such as, steel plating facilities, oil processing and in the manufacturing of storage devices, television tubes, photography, paints, dyes, photographic products, matches, etc. [9]. Lead come in contact with humans with countless sources, and may enter the human body through food, water, air or absorption through the skin [10, 11]. According to world health organization (WHO), the maximum tolerable contaminant level of lead in drinking water is  $10 \text{ }\mu\text{g/L}$  [12]. Lead is non-biodegradable and has the ability to accumulate in the living systems. Once it is transported into the body cells and tissues, it bonds to proteins and nucleic acids, change their cellular functions by disrupting metabolism. Furthermore, because of its ability to imitate various metals such as  $\text{Na}^+$ ,  $\text{Ca}^+$  and  $\text{Mg}^{2+}$  which contribute in various biological functioning, it caused several damages in the human body. It can affect the central nervous function leading to mental disorder, headache, and loss of memory [1, 13]. Generally, lead has no biological function in the body, its presence can cause damage by any means [14]. Although all humans have faced lead poisonousness, particularly young children are bump into lead poisoning as compared

to the adult generation. Since their age-appropriate hand-to-mouth behavior, lead-containing or lead-coated objects like toys, paint etc. could be swallowed in to their mouth easily [15]. As we all know; it is important for us to drink lead free water but lead is presented even in tap water to some extent. Lead can easily reach water body after it dissolved and detached from water plumbing container like pipes which contain lead compound and results in high lead dosage in drinking water [16].

As reviewed from [17], wastewater remediation were established to reduce human and environmental exposure to toxic heavy metals. Therefore, waste water can be treated by conventional technologies including ion exchange, electrochemical and adsorption. Among these techniques, adsorption has been used widely regarded for the treatment of wastewater, as it is economically and environmentally advantageous [18-20]. This technology, therefore, is the basis to develop a new type of adsorbent with properties such as higher adsorption efficiency, recyclability and facile separation properties to remove toxic  $Pb^{2+}$  from water.

Bentonite is capable of exchanging its interlayer cation in addition to its greater abundance and inexpensiveness so that it could be a promising material for adsorption of heavy metals such as  $Pb^{2+}$ . However, the adsorption capacity of bentonite needs to be improved using several approaches [21], such as formulations of composite with other novel materials such as nanoparticles and highly porous materials. Currently, composite materials got huge attention from researchers in different fields of studies because of their composite performance (synergistic effect) [22]. In this study, an environmentally friendly and cost-effective adsorbent was synthesized by assimilating the high adsorption capacity of bentonite and HAP with higher magnetic properties of  $CoFe_2O_4$ . The composite of (B/CF/HAP) was synthesized by co-precipitation methods, followed by characterizations using XRD, SEM-EDX, FTIR and TGA-DTA. Atomic absorption spectroscopy (AAS) was used to determine the adsorption performance of B/CF/HAP composite. The adsorption mechanism was discussed using a combination of adsorption isotherm models and kinetics equations.

## **1.2. Statement of Problems**

Currently, researchers have made attempts to use bentonite as an adsorbent to remove lead ions from wastewater. However, the difficulty of separation limits its industrial applications due to expansion of bentonite on hydration, which results a tedious filtration and separation process from

wastewater. For this reason, adding magnetic particles such as  $\text{CoFe}_2\text{O}_4$  to bentonite, *i.e.* a composite of bentonite and  $\text{CoFe}_2\text{O}_4$  could hinder the separation problem due to easy separation of magnetic  $\text{CoFe}_2\text{O}_4$  by magnetic field. However,  $\text{CoFe}_2\text{O}_4$  has a potential to occupy available active sites on the surface of bentonite, leading to lower adsorption performance. This can be surpassed by incorporating Hydroxyapatite (HAP) to the above-mentioned composite, *i.e.*, formulating a composite of B/CF/HAP to enhance adsorption of heavy metals such as lead ion adsorption due to the surface functionalization property of HAP. The functional surface possessing phosphate groups, which exhibit high affinity towards  $\text{Pb}^{2+}$  ion *via* electrostatic interaction and ion exchange between  $\text{Pb}^{2+}$  and  $\text{Ca}^{2+}$  present in the HAP lattice.

### 1.3. General Objective

- ✚ To develop composites from bentonite clay, cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) nanoparticles, and hydroxyapatite (HAP) for adsorption of lead ion from waste water.

### 1.4. Specific Objectives

- ✚ To extract hydroxyapatite from eggshell
- ✚ To synthesis a composite of bentonite clay,  $\text{CoFe}_2\text{O}_4$  and HAP using co-precipitation methods, followed by materials characterizations
- ✚ To evaluate of adsorption efficiency of the composites towards lead ion at different contact time and initial concentrations of lead.
- ✚ To study the adsorption isotherm and adsorption kinetics

### 1.5. Scope of the Study

In this work, a composite of B/CF was synthesized *via* coprecipitation method. Then, HAP was extracted from the eggshell *via* wet chemical method. Afterward, a composite of B/CF/HAP was synthesized *via* coprecipitation method from the as-synthesized B/CF and HAP. Materials characterization were followed by evaluation of its  $\text{Pb}^{2+}$  adsorption capacity at different initial concentrations and contact times. The kinetic and adsorption model of the optimal B/CF/HAP composite were also studied.

## 2. LITRATURE REVIEW

In this chapter, a description, summary, and critical evaluation of research works about treatment techniques of wastewater, adsorption, and the factors affecting the performance of adsorption were discussed. The other portion of this chapter covers the adsorbents which used for the wastewater remediation with their advantage and disadvantage. Among the adsorbent, bentonite,  $\text{CoFe}_2\text{O}_4$ , HAP, and bentonite clay-based composite are included.

### 2.1. Wastewater Treatment Techniques

Several works have been done to remove heavy metal ions from wastewater such as chemical precipitation, ion exchange, bioremediation, membrane filtration, chemical coagulation and flocculation, and adsorption [23]. Fig. 2.1 described several treatment techniques of heavy metals from industrial effluents.

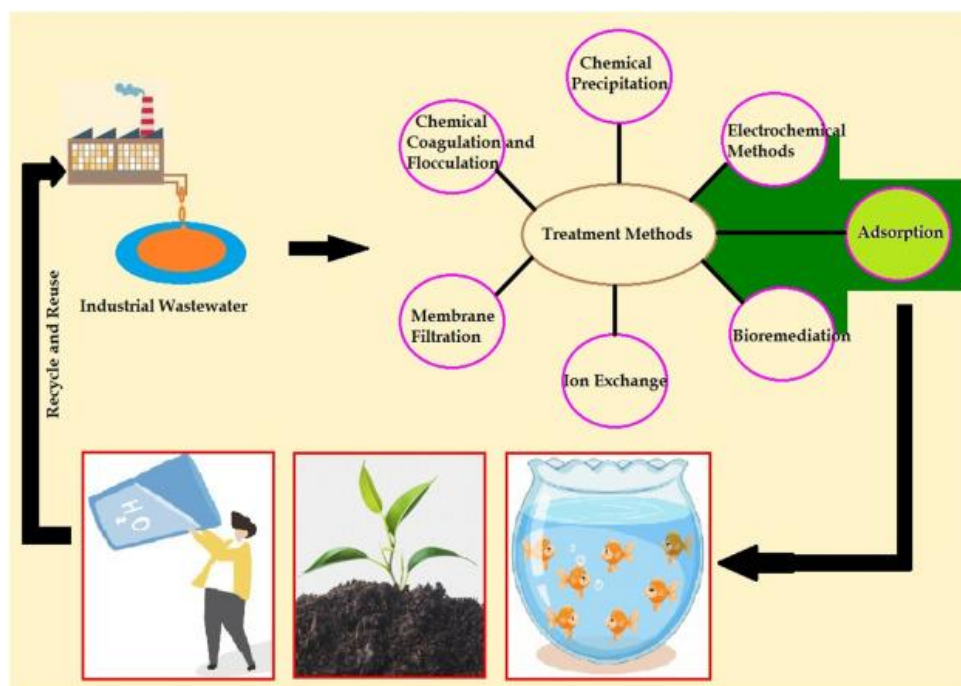


Figure 2.1. Treatment techniques for removal of heavy metal from water [24].

### 2.1.1. Adsorption

Among the treatment methods, the adsorption process is more advantageous for wastewater remediation because of its cost-effectiveness, recyclability, facile handling, high adsorption efficiency and operational simplicity. The other methods have a disadvantage related to their inefficiency and high cost of mechanism [18-20]. Adsorption is related to surface phenomenon when metal ions are adsorbed on solid surface [25]. The Adsorbent is the surface where adsorption is occurred and adsorbate is the metal ion adsorbed on the surface. Desorption is the reverse method in which, adsorbate impurities are detached from the adsorbent surface to the liquid phase [19]. Adsorption has expanded considerably to remove pollutants in wastewater treatment, and its rate is determined by properties such as porosity, specific surface area, pore-volume, cation exchange capacity, interaction time and adsorbent dose [19, 20].

According to A. Sarkar.*et al.*, adsorption can be categorized as chemical adsorption (chemisorption) and physical adsorption (physisorption). Physical adsorption can be reversed and exothermic process with low adsorption heat. Physical adsorption is accompanied by Vander Waals forces, hydrophobicity, static and  $\pi$ -interactions [26]. While, crosslinking of adsorbate and adsorbent *via* strong chemical bond leads chemisorption process [27]. Two types of adsorption process are described in Fig.2.2.

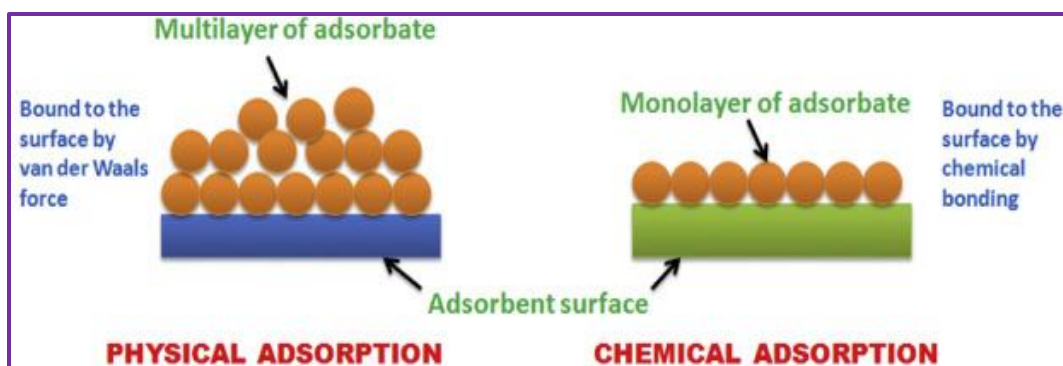


Figure 2.2. Chemical and physical adsorption [26]

Adsorption isotherm models are the root to study adsorption process [28]. Adsorption isotherms are the main cornerstone to define the adsorption or movement of substance. So far, several equilibrium models are utilized to define adsorption process, such as Langmuir, Freundlich, Brunauer-Emmett-Teller, Temkin, Slips, Hill, Flory-Huggins and Radke-Prausnitz isotherm. But,

Langmuir and Freundlich adsorption isotherm are the most commonly applicable models up to now [29]. Langmuir isotherm model assumes that adsorption cannot occur in any of the active sites, it only occurs at a fixed number of adsorption sites, and adsorption sites are equivalent to attract adsorbates, with the absence of crosswise interruption between the adsorbed molecule [30]. Unlike the Langmuir adsorption model, Freundlich isotherm model assumes that adsorption can occur with diverse surface, not fixed to the foundation of monolayer. It described that each localized adsorption sites have their own bond energy; the adsorbed amount is defined by the adsorption on all the sites; the stronger binding sites are occupied first till the end of adsorption process [30]. According to [32], the intensity of adsorption and surface heterogeneity can be defined by the slope of Freundlich isotherm. The slope (1/n) could determine the type of adsorption processes. which is as the value of 1/n below unity implies adsorption is achieved by forming chemical bond. while 1/n greater than unity indicates the adsorption is combination of both chemisorption and physisorption. Mathematical expressions of Freundlich and Langmuir isotherm models are tabulated in Table 2.1

Table 2.1. Equations for Freundlich and Langmuir isotherm models

| Isotherm model | nonlinear formula                       | linear formula                                                                                                                                                                                                             | plot                                                                                                                 | reference |
|----------------|-----------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|-----------|
| Langmuir       | $q_e = \frac{q_{max} b C_e}{1 + b C_e}$ | $\frac{1}{q_e} = \frac{1}{q_{max}} + (\frac{1}{b q_{max}}) \frac{1}{C_e}$<br>$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{C_e}{q_{max}}$<br>$q_e = q_{max} - \frac{q_e}{b C_e}$<br>$\frac{q_e}{C_e} = b q_{max} - b q_e$ | $\frac{1}{q_e} Vs \frac{1}{C_e}$<br>$\frac{C_e}{q_e} Vs C_e$<br>$q_e Vs \frac{q_e}{C_e}$<br>$\frac{q_e}{C_e} Vs q_e$ | [31]      |
| Freundlich     | $q_e = K_f C_e^{\frac{1}{n}}$           | $ln q_e = ln K_f + \frac{1}{n} ln C_e$                                                                                                                                                                                     | $ln q_e Vs ln C_e$                                                                                                   | [32]      |

Where,  $q_e$  (mg/g) is the adsorption capacity at equilibrium time,  $q_{max}$  (mg/g) is the maximum adsorption capacity achieved by the adsorbent,  $b$  (L/mg) is the Langmuir adsorption constant,

$C_e$ (mg/L) is the equilibrium concentration,  $K_f$  is the Freundlich constant  $[(\text{mg/g})(\text{L/g})^{1/n}]$  which represents binding energy of the adsorbents, and  $n$  is the adsorption intensity.

### 2.1.2. Factors Affecting Adsorption

According to [33], interfaces between phases are convenient sites for adsorption to take place. S. Iftikhar *et al.* stated that the increase in the adsorbent dosage leads to increase the capacity of adsorbate to be attached on the adsorbent [34]. In a study by J. Xie *et al.* by increasing the adsorbent dosage it is possible to achieve a greater surface area and a large number of available binding sites [35]. Chella Santhosh *et al.* studied the adsorption capacity of  $\text{CoFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  @ graphene towards  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ . Adsorption capacity was found to increase, as the adsorbent dosage increased from 0.01-0.07 g/L, because of the availability of large number of active sites on the adsorbent surface [36]. In Li Qin *et al.* study, the effect of adsorbent concentration on  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  removal was studied. Because of the presence of large number of active sites on the adsorbent surface the adsorption capacity of both ions was increased as adsorbent concentration increased from 0.1 g/L to 1.2 g/L [23]. Melichova Z *et al.*, studied the adsorption capacity of natural bentonite for removal of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions from aqueous solution. It was stated that the adsorption capacity of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions increased with pH, metal ion concentration, and contact time. As they stated, the adsorption of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  on bentonite were expressed as follows. At low pH values, the aluminol (Al-O-H) and silanol groups (Si-O-H) on the surface of bentonite were shielded by  $\text{H}^+$  and, hence, there would be competition between the cations and  $\text{H}^+$ , resulted in reduced removal of metal ions. At high pH values, highest removal of metal ions was resulted due to inner-sphere complexes through Si-O $^-$  and Al-O $^-$  groups at the clay particle edge [37]. Abdulaziz Ali Alghamdi *et al.* reported a polypyrrole-based activated carbon for removal of  $\text{Pb}^{2+}$  from aqueous solution. Adsorption capacity was rapidly increased in the first stage of their adsorption experiment then slowly increased with time until it reaches constant after 120 min. This is because at the initial step of adsorption there were high availability of unoccupied active site for adsorption. Once the metal ion reached on to the surface of adsorbent it had better chance to form repulsive force, make the remain site inaccessible [38] and therefore resulted in the decrease of the available active sites.

### 2.1.3. Adsorption Characteristics of Bentonite

Currently, adsorbents such as nanoscale iron particles, porous carbon materials, hydroxyapatite, clay, and biochar are commonly used for the treatment of wastewater [39]. Alumina, silicate and water are the components found in most clay minerals. Clays are presented, as dirt in the air, as a component of soil or sedimentary rock wide on earth [40]. Kazakhstani natural zeolite and Ukrainian chamotte clay were used for the adsorption of  $Pb^{2+}$  and it was found 14 mg/g for zeolite and 11 mg/g for clay as described using Langmuir adsorption model. Bentonite consists basically of clay minerals of montmorillonite, and it is easily accessible in bulk quantities, economically effective and environmentally friendly [42]. Their large specific area, chemical stability, and high cation exchange capacity have made bentonite as a well-known adsorbent [40, 43]. Types of Montmorillonite is classified based on the dominant elements present in its structure [44, 45]. As shown in Fig. 2.3 below the structure of sodium montmorillonite is made up of aluminate layer and silicate layer.

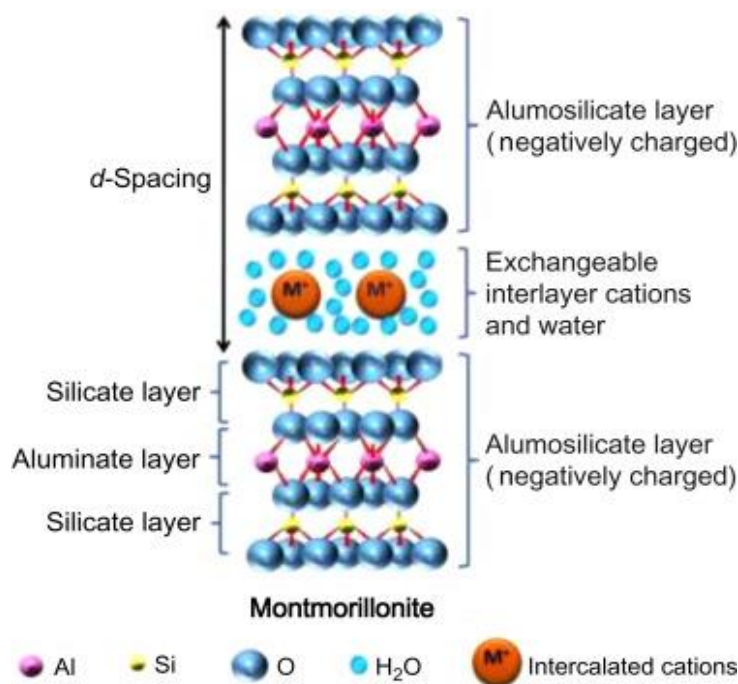


Figure 2.3. Representation of the layer structure present in Na-MMT [45]

Montmorillonite is one of the common types of dioctahedral smectite [46], chemically montmorillonite is explained as  $(Na,Ca)_{0.33}(Al, Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$  where “n” indicates the

varying levels of water in mineral type. Montmorillonite has a 2:1 expanding crystal structure consists of an octahedral alumina layer being squeezed in between two tetrahedral silica sheets [47, 48]. Main components of the clay have been replaced by cation of lesser charge (Isomorphous substitutions) [49] i.e.,  $\text{Mg}^{2+}$  can replace  $\text{Al}^{3+}$  in the octahedral layer and  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral layer when this is the case, a charge deficiency results at the surface of the clay, which is then counterbalanced by the presence of interlayer exchangeable cations such as  $\text{Na}^+$  [50, 51].

#### 2.1.4. $\text{CoFe}_2\text{O}_4$ towards Adsorption

Magnetic materials of ferrite type  $\text{MFe}_2\text{O}_4$  ( $\text{M}=\text{Co}$ ,  $\text{Zn}$ ,  $\text{Mn}$ ,  $\text{Cu}$ ) have cubic spinel structure [52]. Fig.2.4 shows, distribution of cations between the tetrahedral (yellow) and octahedral sites (blue), this materials may exhibit a normal arrangement ( $\text{M}^{2+}$  located at tetrahedral sites,  $\text{Fe}^{3+}$  located at octahedral sites), inverse ( $\text{Fe}^{3+}$  is equally distributed between tetrahedral and octahedral sites, while  $\text{M}^{2+}$  is located in octahedral sites) [53].

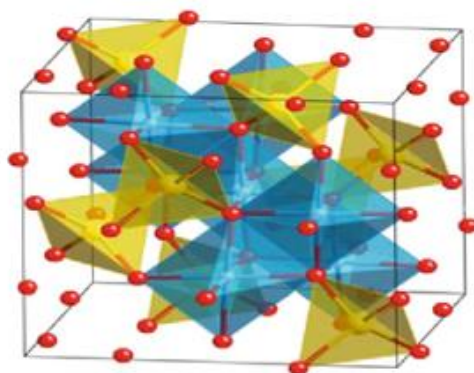


Figure 2.4.  $\text{MFe}_2\text{O}_4$  Structure, oxygen atom are denoted by red [54]

In recent years, research areas like nanoscience and nanotechnology have increasingly regarded spinel ferrite nanoparticles due to their outstanding properties [55], Daniela S. Tavares *et al.* have investigated the magnetic spinel-type ferrite nanoparticles ( $\text{Fe}_3\text{O}_4$ ,  $\text{MnFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ ) for the removal of arsenic from contaminated water samples. It has been reported a good performance of  $\text{CoFe}_2\text{O}_4$  and  $\text{MnFe}_2\text{O}_4$  as compared with the one observed for  $\text{Fe}_3\text{O}_4$ . That was consequence of a surface-mediated process in which the attachment of arsenate species on the nanoparticles is facilitated. As they stated,  $\text{CoFe}_2\text{O}_4$  and  $\text{MnFe}_2\text{O}_4$  exhibited lower chemical stability than  $\text{Fe}_3\text{O}_4$ . Thus, cations ( $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ) could easily release from their respective tetrahedral sites, and they

operate as counter ions. ( $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ) could exchange with arsenic ion to preserve charge neutrality. Which in turn facilitate the adsorption of arsenate species on to the surface of nanoparticles [56].

Among ferrite, cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) is a fascinating material due to its relatively larger coercivity, nanometer size, permeability, reasonable magnetic saturation, chemical stability, mechanical hardness, high electromagnetic and tunable magnetic properties at the atomic level [57, 58]. Z. Ding *et al.* synthesized  $\text{CoFe}_2\text{O}_4$  by facile hydrothermal method, and the adsorption capacity of the as-synthesized ferrite for the organic pollutant (Congo Red), where the maximum adsorption capacity was found to be 190.5 mg/g, and pseudo-second model was used to describe the adsorption kinetic [55]. In S. Zhang *et al.* report, chemical coprecipitation method was used to synthesized  $\text{CoFe}_2\text{O}_4$  for the adsorption of inorganic arsenic species., and the adsorption capacity was found to be 100 mg/g and 74 mg/g for arsenite and arsenate, respectively. It was also stated that the presence of large number of hydroxyl ( $-\text{OH}$ ) species on the surface of  $\text{CoFe}_2\text{O}_4$ , have played a role to improve its adsorption capacity towards arsenite and arsenate than  $\text{Fe}_3\text{O}_4$  [59].

### **2.1.5. Hydroxyapatite towards Adsorption**

Hydroxyapatite (HAP), with a chemical formula of  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , is an inorganic biomaterial with highest calcium phosphates composition and its calcium to phosphate molar ratio is 1.67. The superior feature of this structure is because of its ability to form solid-solution and its ability to exchange with charged species [60, 61]. S. Campisi *et al* stated that HAP has flexible crystal lattice and therefore able to exchange  $\text{Ca}^{2+}$  ions with different metal ions, such as heavy metals [62]. According to Sawittree Rujitanapanich *et al.*, HAP is widely applicable for ecological management, owing to its improved adsorption performance, its acid-base adjustability, its ion exchange capability and its good thermal stability [63]. As indicated in Fig.2.5  $\text{OH}^-$ ,  $\text{PO}_4^{3-}$  and  $\text{Ca}^{2+}$  forms HAP, which is hexagonal in structure.  $\text{Ca}^{2+}$  is found at the wall of the channel, which is flexible and ready for cation exchange.

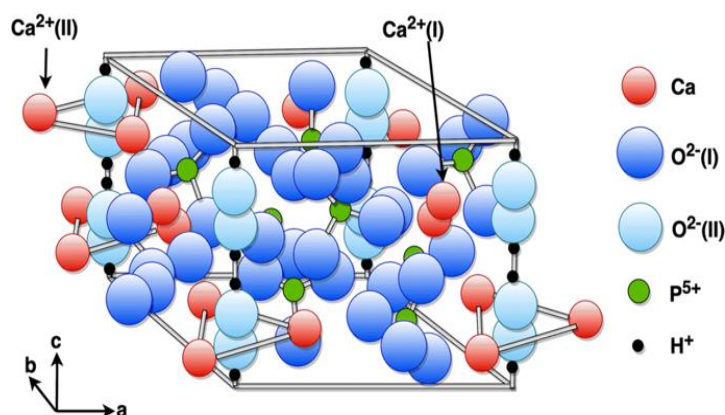
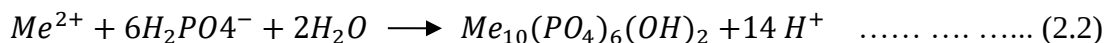
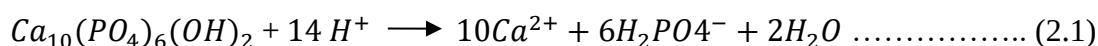


Figure 2.5. Structure of hydroxyapatite (HAP) [63]

M. Ibrahim *et al.*, stated the best known mechanisms of metal adsorption by hydroxyapatite (HAP) through a process represented by the following equations [64].

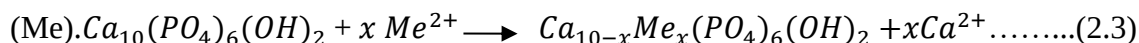
### I. Dissolution- precipitation

⇒ When HAP dissolved in a solvent it forms a solution rich in phosphate ion, which in turn reacted with metal cations (Me)



### II. Ion exchange

⇒ When the calcium ions in the HAP lattice substituted by a divalent metal ions



Young Lei *et al.* [65], fabricated a composite of hydroxyapatite/chitosan (HAP/CS) porous materials for adsorption of lead ( $Pb^{2+}$ ) ions. It was proved that the maximum adsorption capacity of (HAP/CS) was 246.42 mg/g while that of the porous material was only 5.67 mg/g. The better adsorption property of HAP/CS was attributed to the presence of HAP particles that means HAP particles were converted to lead hydroxyapatite ( $Pb_{10}(PO_4)_6(OH)_2$ ) particles via dissolution - precipitation reaction method described as above.

### 2.1.6. Bentonite Clay-based Composites

Many studies have done on utilizing clay based adsorbents such as bentonite [66, 67], kaolin [68, 69] and other types of clay loaded with metal oxide for heavy metal adsorption. C. Irawan, *et al.*

[70] reported a magnetic nanoparticle to adsorb  $Pb^{2+}$  and  $As(V)$  ion. Based on Langmuir adsorption isotherm model a maximum adsorption performance for  $Pb^{2+}$  and  $As(V)$  of 38.15 mg/g and 19.10 mg/g was attained because the surface layer of montmorillonite was functionalize to increase the surface area. Furthermore, electrostatic interaction was also another factor for the adsorption of adsorbates on the adsorbent. L.Jiang *et al.*, synthesized a composite of bentonite- $Fe_3O_4$ - $MnO_2$  using two-step co-precipitation method towards  $Cd^{2+}$  ion. The capacity of the adsorbent towards  $Cd^{2+}$  was affected by pH of the solution. As shown in Fig.2.6, the pH of zero point charge of bentonite- $Fe_3O_4$ - $MnO_2$  was the limiting parameter, which is about 3.36. i.e. when pH is greater than this value the surface could be charged negative. Thus,  $Cd^{2+}$  could be adsorbed on the surface by electrostatic attraction.

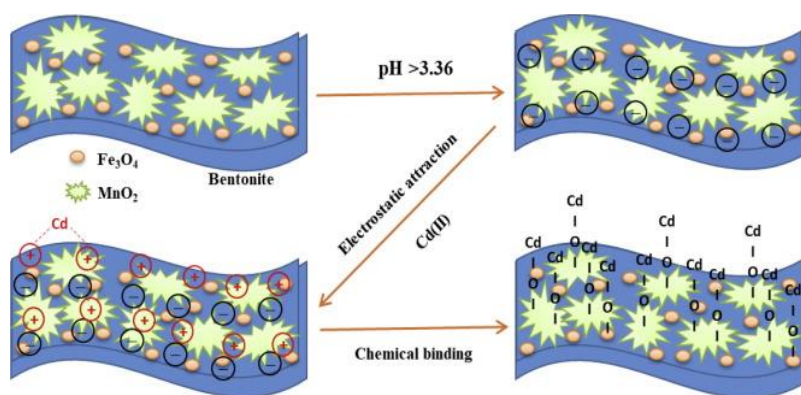


Figure 2.6. Mechanism of  $Cd^{2+}$  adsorption on bentonite- $Fe_3O_4$ - $MnO_2$

It was also stated that bentonite- $Fe_3O_4$ - $MnO_2$  was resulted in higher BET surface area and pore volume relative to the pure bentonite. The presence of  $-OH$  groups on the surface of bentonite- $Fe_3O_4$ - $MnO_2$ , facilitates adsorption of  $Cd^{2+}$  by forming surface complexation as shown in Fig.2.6 [71]. G.zhou *et al* [39] found a composite of bentonite/ $CoFe_2O_4$ - $MnO_2$ - $NH_2$  (BCFMNs), and it was found a maximum adsorption performance of 115.79 mg/g towards  $Cd^{2+}$ . The adsorption isotherm was best described using Langmuir model, which implies the homogeneous adsorption of  $Cd^{2+}$  on bentonite- $CoFe_2O_4$ - $MnO_2$ - $NH_2$ . The presence of amino group improved the surface of the adsorbent. Moreover, Chenglong, *et al.* [72] also prepared a composite of  $Fe_3O_4$  and aluminum-pillared bentonite for the removal of  $Hg^{2+}$  from effluents. The adsorption mechanism was described by Langmuir isotherm, and its adsorption capacity was 26.18mg/L towards  $Hg^{2+}$ , where the kinetic adsorption model was best described by a pseudo-second order model.

Piyali Roy Choudhury [73] introduced a nanocomposite of bentonite-hydroxyapatite for the removal of  $Pb^{2+}$  from aqueous solution. The maximum adsorption performance attained by the composite was about 346 mg/g. Moreover, the correlation coefficient of pseudo-second order kinetic model was greater than the one observed for pseudo-first order implies the adsorption mechanism was chemisorption.

In recent years several works have been done on bentonite clay-based composites for adsorption of lead ion. The comparison between the maximum adsorption capacity of various adsorbents is listed in table 2.2.

Table 2.2. Summary of clay (bentonite)-based adsorbents

| Adsorbent                                    | Heavy metal              | Maximum adsorption capacity(mg/g) | Methods                   | Equilibrium time (h) | Reference    |
|----------------------------------------------|--------------------------|-----------------------------------|---------------------------|----------------------|--------------|
| bentonite- $Fe_3O_4$ - $MnO_2$               | $Cd^{2+}$                | 35.35                             | Co-precipitation          | 0.5                  | [71]         |
| bentonite/ $CoFe_2O_4@MnO_2-NH_2$            | $Cd^{2+}$                | 115.79                            | Solvothermal              | 3                    | [39]         |
| Ag- $MnFe_2O_4$ /bentonite                   | $Pb^{2+}$ ,<br>$Cd^{2+}$ | 129.87, 48.31<br>respectively     | Co-precipitation          | 4                    | [23]         |
| Magnetic nanoparticle coated montmorillonite | $Pb^{2+}$ ,<br>As(V)     | 38.15,19.0                        | Solvothermal              | 8                    | [74]         |
| 4-aminoantipyrine immobilized bentonite      | $Hg^{2+}$ ,<br>$Pb^{2+}$ | 52.9, 55.5<br>respectively        | Hydrothermal              | -                    | [75]         |
| HAP granules                                 | $Pb^{2+}$                | 7.99                              | Sintering                 | -                    | [76]         |
| High-fixation HAP                            | $Hg^{2+}$                | 49                                | Precipitation             | -                    | [77]         |
| Hydroxyapatite/bentonite                     | $Pb^{2+}$                | 346                               | Chemical co-precipitation | 24                   | [73]         |
| Bentonite/ $CoFe_2O_4$ /HAP                  | $Pb^{2+}$                | 67.11                             | Co-precipitation          | 1.5                  | Present work |

### 3. MATERIALS AND METHODS

#### 3.1. Materials

In this work, all reagents were analytical grade. Ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) (99%), cobalt nitrate  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (97%), ortho-phosphoric acid ( $\text{O}-\text{H}_3\text{PO}_4$ ) (85%), sodium hydroxide ( $\text{NaOH}$ ), ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), glutaraldehyde ( $\text{C}_5\text{H}_8\text{O}_2$ ) (25%), lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ) (99%), were used. Bentonite powder was purchased from Alkane chemicals P.L.C (Addis Ababa) while the eggshell was collected from cafeteria of Adama Science and Technology University (ASTU). Distilled water was used to prepare all solutions required in this thesis work.

#### 3.2. Methods

##### 3.2.1. Pre-treatment of Bentonite

Bentonite powder was subjected to pass through a 200-mesh sieve and air-drying to obtain a uniform particle sized powder.

##### 3.2.2. Synthesis of $\text{CoFe}_2\text{O}_4$

To prepare 4 g of  $\text{CoFe}_2\text{O}_4$ , about 4.611 g of ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) and 2.483 g of cobalt nitrate  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were dissolved in 100 mL distilled water for 30 min, forming a homogeneous solution. Then, 2 M of  $\text{NaOH}$  solution was added drop-wise into the obtained aqueous solution under stirring for 30 minutes to adjust the pH to 12. Then, the mixture was stirred for further 3 h at 70 °C in a constant temperature heating water bath. After that, a suspension was formed and the solid precipitate was collected and washed by solvents such as distilled water and ethanol several times until neutral supernatant is found. Finally, the product was dried at 100 °C overnight, followed by calcination at 600 °C for 6 h [78].

##### 3.2.3. Extraction of Hydroxyapatite (HAP) from Eggshell

Eggshell is considered as useless and is found extensively in the environment as waste, can pollute the environment. Eggshell can be used as precursor to synthesis Hydroxyapatite because it is rich in calcium oxide. HAP extracted from eggshell is environmentally friendly and cost effective. HAP was extracted from eggshell by wet chemical precipitation method according to a procedure

reported elsewhere [79]. The following flow diagram is an illustration of the overall extraction process.

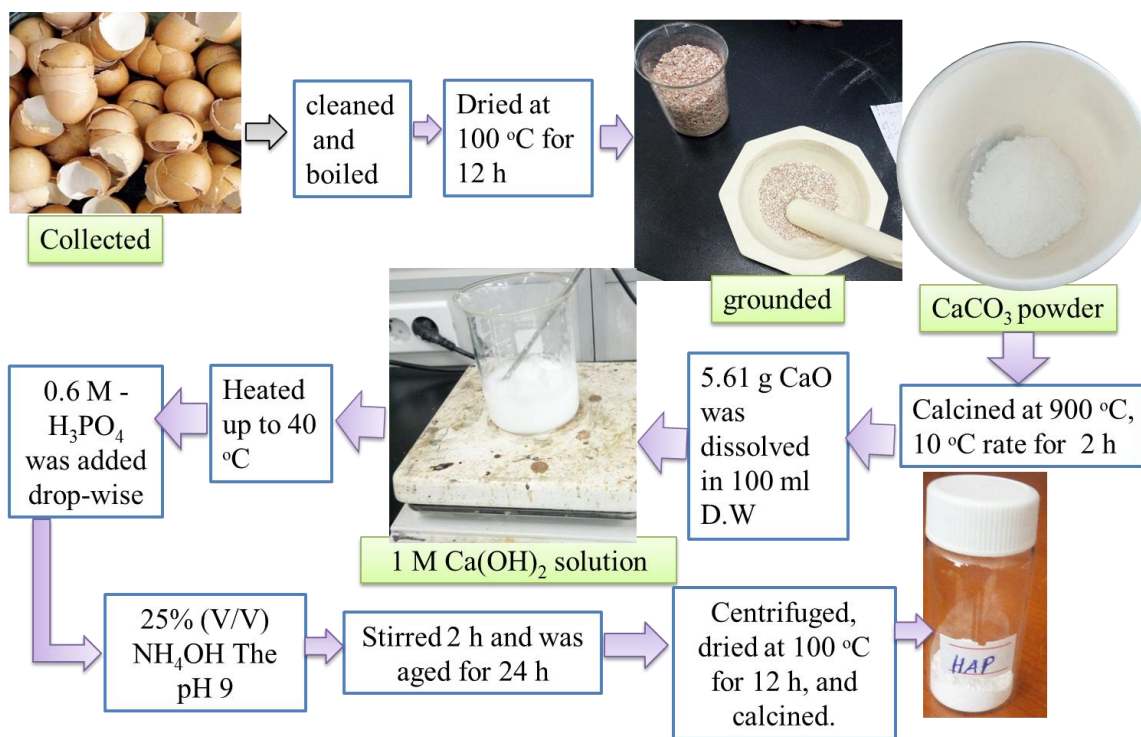
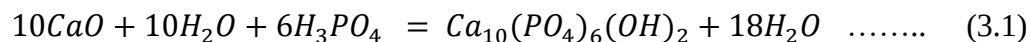


Figure 3.1. flow diagram showing extraction of HAP from eggshell

It should be noted that after synthesis of CaO from CaCO<sub>3</sub> powder at calcination of 900 °C, CaO was dispersed in water to produce Ca(OH)<sub>2</sub>. So, the actual reaction can be seen as in Eq. (3.1) below.



### 3.2.4. Synthesis of Bentonite/CoFe<sub>2</sub>O<sub>4</sub> (B/CF) Composites

The composite of bentonite/CoFe<sub>2</sub>O<sub>4</sub> were synthesized in different weight percentage of CoFe<sub>2</sub>O<sub>4</sub> in the bentonite matrix, which was (100-x)B/(x)CF where x =5, 15, 25 weight percentage of CoFe<sub>2</sub>O<sub>4</sub>. To synthesis 4 g of bentonite/CoFe<sub>2</sub>O<sub>4</sub> composites, measured amounts of Fe<sup>3+</sup> and Co<sup>2+</sup> with a molar ratio of 2: 1 were successively dissolved in 150 mL of distilled water for 30 minutes under constant stirring. Then different amount of bentonite powder was added and stirred for another 2 hours. After forming solutions, 2M of NaOH was added dropwise to adjust the pH to 12,

followed by ultrasonication at 70 °C for 3 h. After that, suspension solution was formed and solid precipitate was collected and washed with distilled water and ethanol several times, followed by drying the product at 100 °C overnight [78].

### **3.2.5. Synthesis of Bentonite/CoFe<sub>2</sub>O<sub>4</sub>/HAP (B/CF/HAP) Composite**

To load the appropriate HAP on the B/CF composite, first the Pb<sup>2+</sup> adsorption capacity of all as-synthesized bentonite/CoFe<sub>2</sub>O<sub>4</sub> composites were analyzed, followed by loading of different HAP contents on the optimum adsorbent. Then, the prepared composites were denoted as 25%HAP/75%(B/CF), 35%HAP/65%(B/CF) and 45%HAP/55%(B/CF). They were prepared as follow: measured amount of as-synthesized B/CF composite and HAP were utilized for B/CF/HAP composite preparation. Both of the solutions (50 mL) were stirred separately in 100 mL beakers overnight. HAP solutions was then poured into the B/CF composite solution with continuous stirring. About 50 mL glutaraldehyde was added drop wise to the mixture as a cross linker. Since glutaraldehyde is dialdehyde with a longer flexible hydrocarbon chain, it can form cross linkage between the hydroxyl groups and the aldehyde group. Then, the pH was adjusted into 3 using 0.1 N HCl solutions. The solution was then keep stirring overnight at room temperature. Then, the obtained precipitate was centrifuged until a neutral supernatant is found. Finally, the prepared B/CF/HAP composites was dried at 60 °C for 12 h [80]. The prepared samples were stored in an ambient air tight sample holder for further use.

### **3.2.6. Characterization**

The phase purity of the synthesized bentonite, CoFe<sub>2</sub>O<sub>4</sub>, HAP, bentonite/CoFe<sub>2</sub>O<sub>4</sub> and bentonite/CoFe<sub>2</sub>O<sub>4</sub>/HAP, composites were examined using X-ray powder diffraction (XRD-700, Shimadzu, South Korea) at copper K $\alpha$  radiation ( $\lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA}$ ), a scan speed of 4.0000 (deg/min), voltage (40 kV), current (30 mA), and scanning range (4-80 °). The surface morphology and elemental composition of the adsorbents were analyzed by Scanning electron microscopy with energy-dispersive X-ray spectrometry (SEM-EDX) using COXIEM-30 (Shimadzu, South Korea). Fourier transform infrared (FTIR) spectra with a wave number range of 500-4000 cm<sup>-1</sup> collected using FTIR spectrophotometer to identify functional groups on the adsorbent surface. Thermogravimetric analysis coupled with its differential analysis (DTG-60H, Shimadzu, South Korea) was used to study the thermal stability of the samples from 20 to 800 °C under an inert

atmosphere maintained by inject N<sub>2</sub> at a flow rate of 50 mL/min. The adsorption capacity of the samples was examined using Analytik jena atomic absorption spectrometer (AAS) model: (ZEEnit 700P #150Z7P1025 Tech: Flame) with detection limit 0.06 ppm, energy =71.5, PMT[V]=298, slit width=1.2nm, lamp current=3mA.

### 3.2.7. Adsorption Experiment

Pb<sup>2+</sup> stock solution (500 mg/L) was prepared by dissolving 799 mg Pb(NO<sub>3</sub>)<sub>2</sub> in distilled water. Afterward, initial solution of varying Pb<sup>2+</sup> concentrations were prepared daily by diluting concentrations from the stock solution.

Then, a series of the adsorption tests were carried out at typical equilibrium conditions for the optimization of adsorbents. For each adsorption test, 30 mL of Pb<sup>2+</sup> solution at a concentration of 50 mg/L was treated with 25 mg of adsorbents. Then, the mixture was stirred for 5 h. And samples were filtered using Whatman filter paper qualitative circles (125nmØ × 100 circles) and analyzed the filtrates by atomic absorption spectrometer (AAS).

Removal efficiency and adsorption capacity of the adsorbents were calculated using equation 3.2 and 3.3 as follows:

$$q_e = \frac{V(C_o - C_e)}{m} \dots\dots\dots(3.2)$$

$$\eta(\%) = \frac{(C_o - C_t)}{C_o} \times 100 \dots\dots\dots (3.3)$$

Where q<sub>e</sub>(mg/g) is the equilibrium adsorption capacity, C<sub>o</sub> is the initial concentration of heavy-metal ion (mg/L), C<sub>e</sub> (mg/L) is the concentration of Pb<sup>2+</sup> ion at equilibrium time, C<sub>t</sub> is the concentration of heavy metal at a given time, V is the volume of reaction solution, m is mass of the adsorbent, η (removal efficiency).

An adsorption isotherm study was conducted with 25 mg adsorbent in 30 ml Pb solution at a contact time of 5 h by varying its initial concentration from 50 to 200 mg/L.

To determine the kinetic performances, 100 mg of adsorbent was added to 100 mL solution containing 50 mg/L initial concentration of Pb<sup>2+</sup>. Then, the mixture was stirred and the samples were taken at different time interval (30-120 min) and analyzed the filtrates by AAS.

## 4. RESULTS AND DISCUSSIONS

### 4.1. XRD Analysis

In this section, the XRD characterization of adsorbents such as bentonite,  $\text{CoFe}_2\text{O}_4$ , HAP, bentonite/ $\text{CoFe}_2\text{O}_4$  and bentonite/ $\text{CoFe}_2\text{O}_4$ /HAP composites were presented and discussed.

Figure 4.1. below is XRD result of bentonite, the diffraction peaks at angles of  $2\theta=6.6^\circ$ ,  $20.1^\circ$ ,  $35.7^\circ$ ,  $54.1^\circ$ ,  $61.8^\circ$ , correspond to the (001), (100), (105), (210), (300) crystallographic plane, indicating existence of Na-Montmorillonite (Na-MMT), a main component of bentonite (JCPDS No. 13-0135) [81]. Apart from these main peaks, several peaks were shown owing to the presence trace impurities such as Feldspar, quartz, and calcite [82].

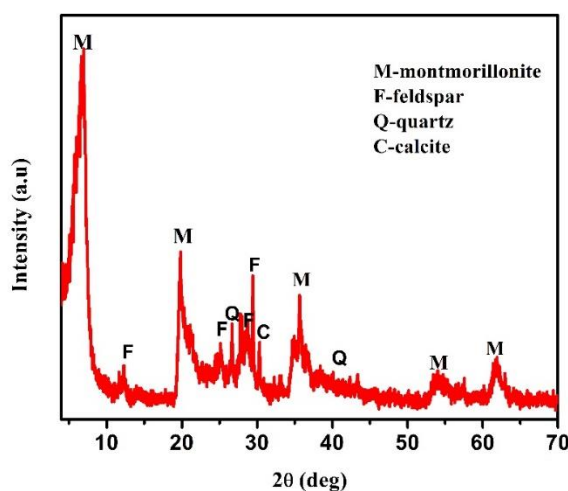


Figure 4.1. XRD pattern of bentonite

Figure 4.2. correspond to XRD result of  $\text{CoFe}_2\text{O}_4$  particles, showing diffraction peaks at  $2\theta$  of  $18.3^\circ$ ,  $30.2^\circ$ ,  $35.5^\circ$ ,  $37.1^\circ$ ,  $43.2^\circ$ ,  $53.6^\circ$ ,  $57.1^\circ$ ,  $62.7^\circ$  indexed to (111), (220), (311), (222), (400), (422), (511) and (400) crystalline structure with a spinel structure. Comparing XRD patterns of synthesized NPs with standard diffraction spectrum (JCPDS card, no.22-1086, cubic symmetry), the synthesized product is crystalline  $\text{CoFe}_2\text{O}_4$  [83]. The effect of ultrasonication during synthesis can contribute for crystalline size reduction of particles and which might in turn improve surface

area [84]. The crystalline size of  $\text{CoFe}_2\text{O}_4$  particles was calculated to be around 18.7 nm using Scherrer formula, according to equation (4.1) below.

$$D = \frac{K\lambda}{\beta \cos \theta} \dots \dots \dots (4.1)$$

Where,  $\lambda=0.15406\text{nm}$  (wavelength of X-ray),  $K=0.9$  (Scherrer constant),  $D=\text{crystalline size (nm)}$ ,  $\beta=\text{FWHM}$ .

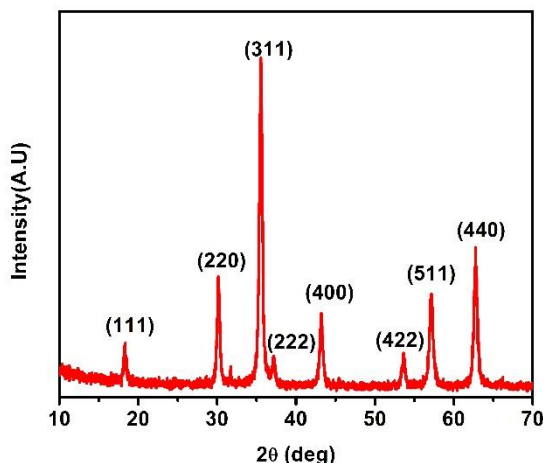


Figure 4.2. XRD pattern of  $\text{CoFe}_2\text{O}_4$

XRD pattern of  $\text{CaO}$  is presented in Figure 4.3. Since  $\text{CaO}$  (the main composition of the calcined eggshell) could be precursor for the synthesis of hydroxyapatite, it is supportive to assure the formation of  $\text{CaO}$  at first. As indicated in Figure 4.3,  $\text{CaO}$  species are located at  $2\theta$  of  $32.3^\circ$ ,  $37.4^\circ$ ,  $53.9^\circ$ ,  $64.2^\circ$ ,  $67.4^\circ$  and is indexed to (111), (200), (220), (311), (222) crystallographic planes, respectively.  $\text{Ca(OH)}_2$  was found as a minor species (impurity) that could be related to the exposure of sample to humidity in the air [85].

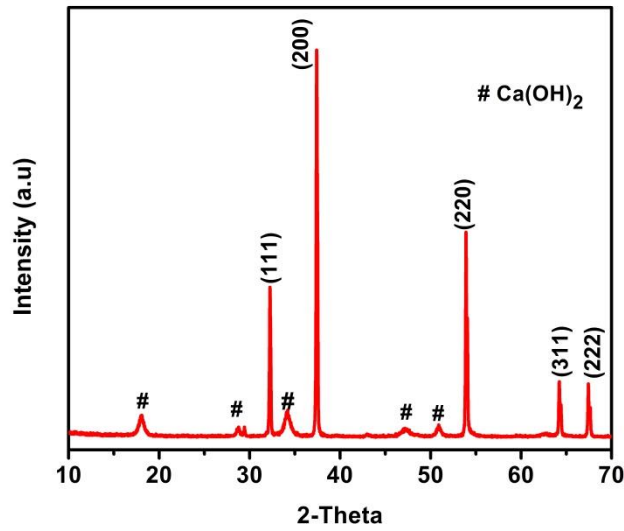


Figure 4.3. XRD pattern of CaO

The XRD result of the synthesized HAP is presented in Figure 4.4. with all the peaks matching to the (JCPDS pattern 09-0432) for hydroxyapatite, confirming that pure HAP was synthesized [86].

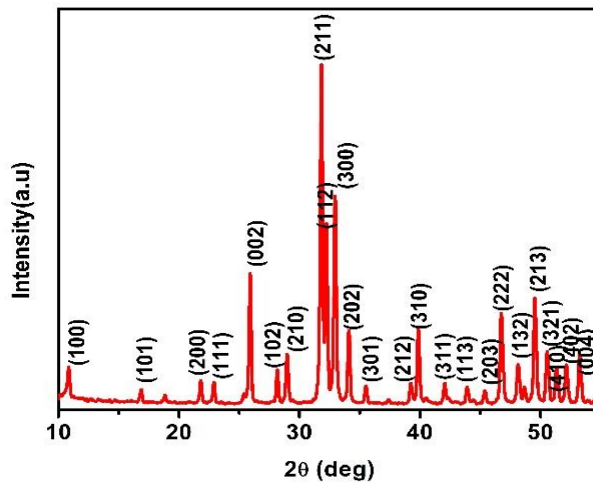


Figure 4.4. XRD pattern of HAP

Figure 4.5. shows XRD pattern of bentonite,  $\text{CoFe}_2\text{O}_4$ , and bentonite/ $\text{CoFe}_2\text{O}_4$  composites with varying percentages of cobalt ferrite such as 5, 15, 25, 50 weight percentages. The diffraction peaks are occurred at  $2\theta$  of  $6.6^\circ$ ,  $20.1^\circ$ ,  $35.7^\circ$ ,  $54.1^\circ$ , and  $61.8^\circ$ , which correspond to the (001), (100),

(105), (210), (300) crystallographic planes, respectively, with the (JCPDS No.12-0204). This indicates the existence of the hexagonal phase of Na-montmorillonite [87]. The diffraction peaks related to  $\text{CoFe}_2\text{O}_4$  samples are at  $2\theta$  of  $18.3^\circ$ ,  $35.5^\circ$ ,  $37.1^\circ$ ,  $43.2^\circ$ ,  $53.6^\circ$ ,  $57.1^\circ$ , corresponding to the (111), (311), (222), (400), (422), (511) crystallographic plane of cubic  $\text{CoFe}_2\text{O}_4$  (JCPD No.22-1086) [88]. All samples exhibited the presence of Na-MMT and  $\text{CoFe}_2\text{O}_4$ . The characteristics peaks of  $\text{CoFe}_2\text{O}_4$  and MMT are shown in the pattern of  $\text{CoFe}_2\text{O}_4/\text{MMT}$  composites, suggesting that the crystal structure of  $\text{CoFe}_2\text{O}_4$  and MMT do not change noticeably. The (001) plane intensity of the  $\text{CoFe}_2\text{O}_4/\text{MMT}$  composites decreased means that the layer structure was altered to some extent, which can be attributed to the intercalation of  $\text{CoFe}_2\text{O}_4$  or adsorbed on the surface [89, 90]. The d-spacing of bentonite after interaction with  $\text{CoFe}_2\text{O}_4$  shows negligible shift and this implies that  $\text{CoFe}_2\text{O}_4$  could be attached on the surface of bentonite [91]. Particularly, the (001) plane disappeared for 50%  $\text{CoFe}_2\text{O}_4$  loading which indicates the layer of the composite is disordered and exfoliated. Thus,  $\text{CoFe}_2\text{O}_4$  predominately appeared at the external surface of bentonite [92]. For 5%, 15%, 25%  $\text{CoFe}_2\text{O}_4$ , the (001) peaks of Na-MMT is higher than that of  $\text{CoFe}_2\text{O}_4$  in the bentonite/ $\text{CoFe}_2\text{O}_4$  composite pattern, meaning that Na-MMT has a higher proportion in the composite [93].

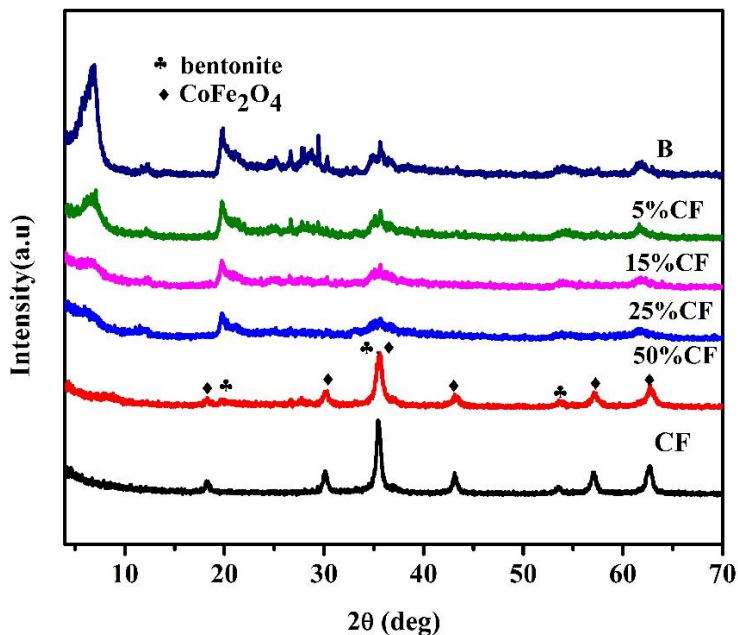


Figure 4.5. XRD pattern of bentonite,  $\text{CoFe}_2\text{O}_4$ , and bentonite/ $\text{CoFe}_2\text{O}_4$  composites

Finally, the XRD result of bentonite/CoFe<sub>2</sub>O<sub>4</sub>/HAP composites are shown in Figure 4.6. below. The sharp and major peaks related to bentonite are observed at 2 $\theta$  of 6.6°, 20.1°, 35.7°, 54.1°, 61.8° indicates the existence of Na-Montmorillonite (Na-MMT) based on (JCPDS No. 13-0135) [82], in an agreement with Figure 4.1. CoFe<sub>2</sub>O<sub>4</sub> particles with a spinel structure showed diffraction peaks at 35.5°, 43.2°, 53.6°, 57.1°, 62.7° indexed to (311), (400), (422), (511) and (400) crystallographic planes, respectively (JCPDS, no.22-1086, cubic symmetry) [84]. Moreover, the peaks index to crystallographic planes of (100), (101), (200), (111), (201), (002), (102), (210), (211), (112), (300), (202), (301), (212), (310), (221), (311), (113), (400), (203), (222), (312), (320), (213), (321), (410), (402), (004), (104), (322), (313), (501), (420), (331), (214), (502), and (510) confirming the presence of HAP in the composite. The position and d-value matched well with spectrum. The crystalline size was estimated from Scherrer equation, which was 42.03 nm. Therefore, the formation of B/CF/HAP composite was confirmed by XRD analysis.

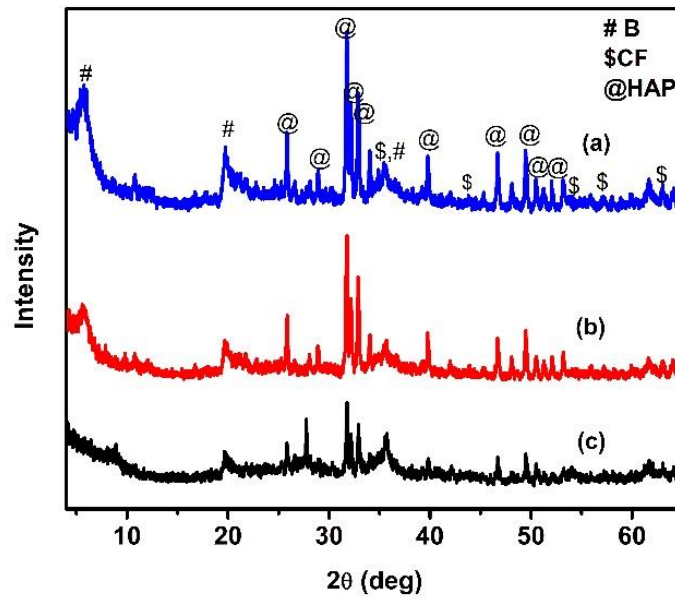
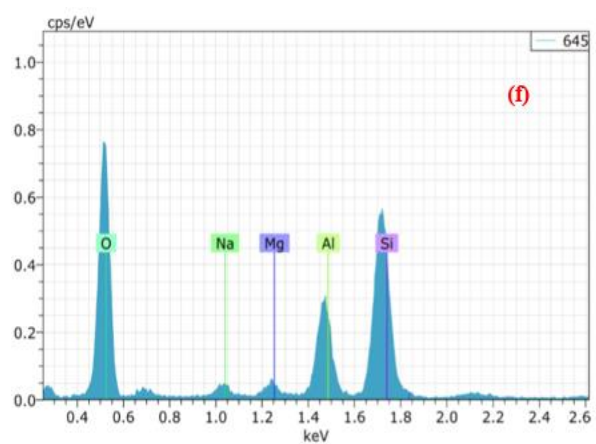
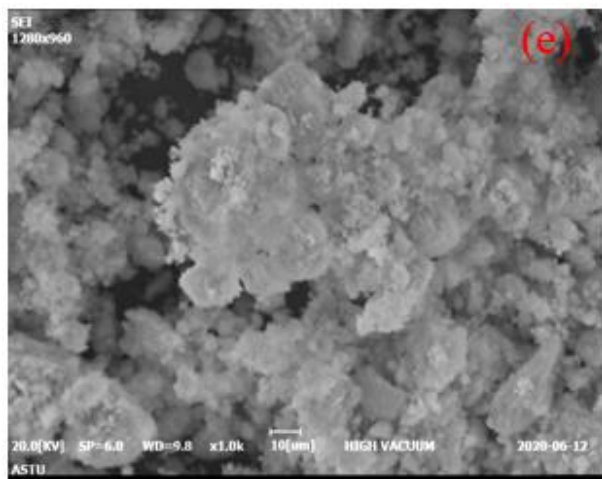
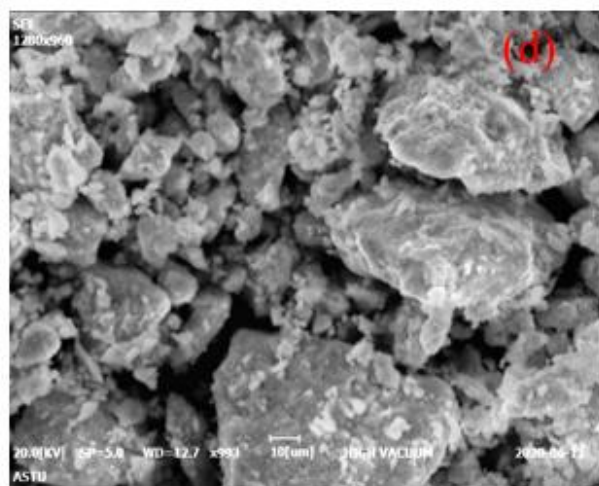
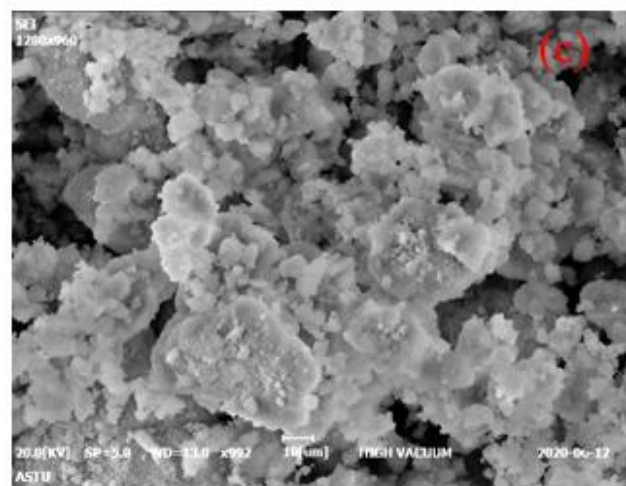
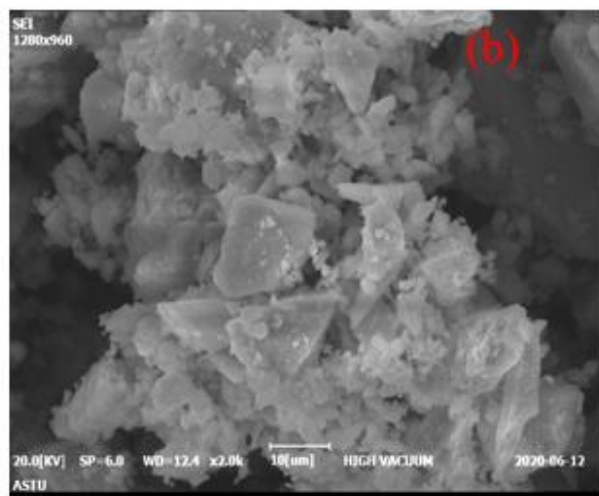
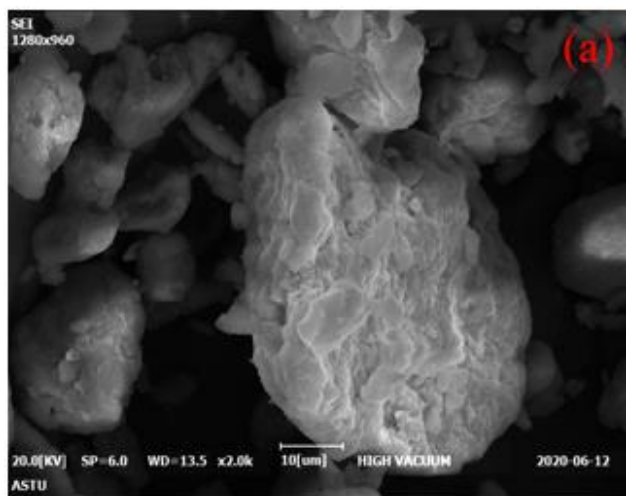


Figure 4.6. XRD pattern of (a) 25% HAP, (b) 35% HAP (c) 45% HAP loaded on (85%B/15%CF)

## 4.2. SEM-EDX Analysis

The surface morphology and microstructure of bentonite,  $\text{CoFe}_2\text{O}_4$ , HAP, bentonite/ $\text{CoFe}_2\text{O}_4$ , bentonite/ $\text{CoFe}_2\text{O}_4$ /HAP are presented in Figure 4.7 (a-e). In Fig.4.7 (a), bentonite exhibited a smooth block like microstructure, with scattered and different size of particles. Analyzing each particle, there is a layered structure stacked on top of each other. Fig.4.7 (b) is the morphology of  $\text{CoFe}_2\text{O}_4$  revealed irregular aggregates with platelets like structures, which could be related to either the magnetic dipole interactions among the  $\text{CoFe}_2\text{O}_4$  nanoparticles or their instability because of their high surface energy; surfactant could return their stability [94]. In Fig.4.7 (d) the surface of bentonite/ $\text{CoFe}_2\text{O}_4$  is relatively rougher as compared with the surface of bentonite alone suggesting that bentonite/ $\text{CoFe}_2\text{O}_4$  has a large surface area that could lead to higher adsorption capacity [78]. Figure 4.7 (c) revealed spherical scattered flake structure of HAP, which is highly porous, as expected. Figure 4.7 (e) is the microstructure of the ternary composite, i.e., 35%HAP/65%(85%B/15%CF), showing large number of particles covered or enveloped with bentonite/ $\text{CoFe}_2\text{O}_4$ /HAP surface which could be ascribed to the loading of HAP particles. Moreover,  $\text{CoFe}_2\text{O}_4$  particles were randomly assembled on the surface of bentonite.

Furthermore, to investigate the presence and distribution of elements in each sample, i.e., in B, B/CF, and B/CF/HAP samples, an energy dispersive X-ray (EDX) analysis was performed and the corresponding result is presented in Figure 4.7 (f-h). The EDX analysis of bentonite in Figure 4.7 (f) confirmed the presence of sodium, aluminum, magnesium, silicon and oxygen in the Na-bentonite sample. The result of EDX elemental analysis for the bentonite/ $\text{CoFe}_2\text{O}_4$  composite is presented in Figure 4.7 (g) showing the corresponding elements expected in the composite sample. Figure 4.7 (h) exhibits the EDX spectrum of composite of B/CF/HA, with further confirmation of the presence of elements such as sodium, aluminum, magnesium, silicon, cobalt, iron and oxygen in the composite sample.



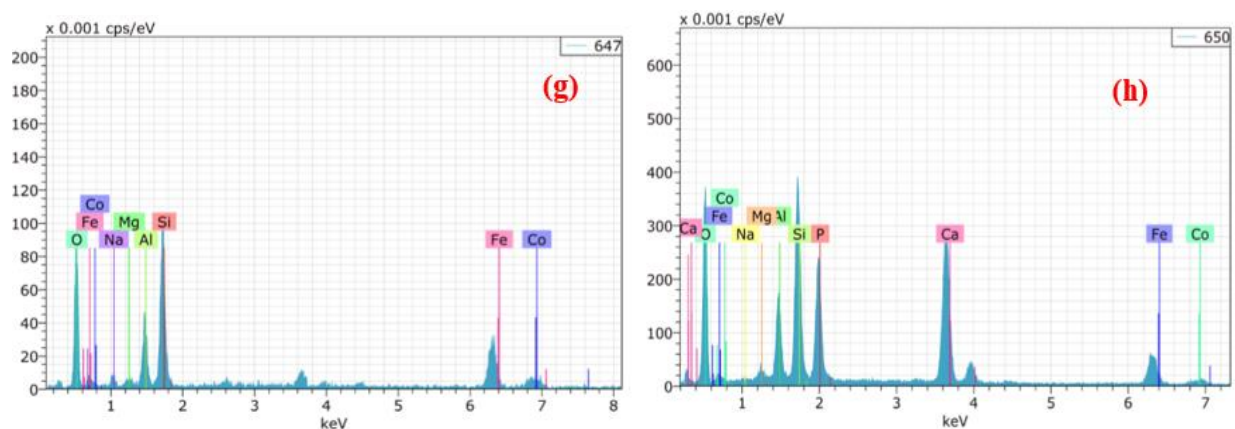


Figure 4.7. SEM image of (a) bentonite, (b)  $\text{CoFe}_2\text{O}_4$ , (c) HAP, (d) B/CF(85%B/15%CF), (e) B/CF/HAP (35%HAP/65%(85%B/15%CF)) and EDX spectra of (f) bentonite, (g) bentonite/ $\text{CoFe}_2\text{O}_4$ , bentonite/ $\text{CoFe}_2\text{O}_4$ /HAP (h)

### 4.3. FTIR Analysis

The presence of chemical functional groups on the adsorbent was determined by FTIR spectra in the wave number range of  $4000\text{--}500\text{ cm}^{-1}$ . Figure 4.8 exhibits FTIR spectra of B/CF/HAP, B/CF, B, and HAP composite samples. Initially, the band around  $1640\text{ cm}^{-1}$  and  $3440\text{ cm}^{-1}$  were attributed to the bending vibrations of water molecule of O-H and H-OH stretch vibrations in all samples. The sharpness of the peaks could determine the amount of water ( $\text{H}_2\text{O}$ ) molecule attached on to the surface of the composite [39]. Relatively, the sharpness of the band was reduced for bentonite/ $\text{CoFe}_2\text{O}_4$  composite, which implies the composite has fewer bonded  $\text{H}_2\text{O}$  molecules. This might be due to effects of stirring and sonication at  $70\text{ }^\circ\text{C}$  during synthesis. However, increasing of the peaks of the band for bentonite/ $\text{CoFe}_2\text{O}_4$ /HAP composite was observed, which is credited to the presence of more water on the surface and the O-H groups because of HAP. Fortunately, the presence of large number of O-H groups on bentonite/ $\text{CoFe}_2\text{O}_4$ /HAP composite suggests that the composite is favorable for adsorption of lead ion. The occurrence of  $\text{PO}_4^{3-}$  was indicated by the appearance of a band at  $1037\text{ cm}^{-1}$  confirming the successful loading of HAP on the bentonite surface. The characteristic peak at absorption peaks for phosphate group of HAP are observed at  $561\text{ cm}^{-1}$  and  $602\text{ cm}^{-1}$  P-O bending vibration. The bentonite displayed typical Si-O-Si stretching around  $1037\text{ cm}^{-1}$ ; it was larger for bentonite/ $\text{CoFe}_2\text{O}_4$ /HAP composite. The apparent peaks at  $565\text{ cm}^{-1}$  and  $472\text{ cm}^{-1}$  shows the vibration of Co-O and Fe-O peaks [39]. Typical bentonite peak at  $570\text{ cm}^{-1}$ , represent the Al-O-Si deformation vibration [95].

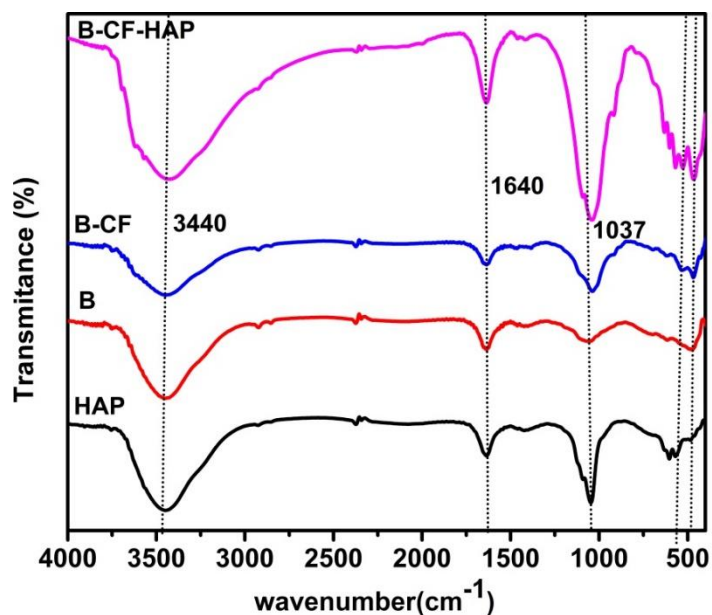


Figure 4.8. FTIR spectra of the bentonite, B/CF (85%B/15%CF), B/CF/HAP (35%HAP/65%(85%B/15%CF)) and HAP samples

#### 4.4. Thermal Property Analysis

The thermal stability of bentonite, bentonite/CoFe<sub>2</sub>O<sub>4</sub> (85%B/15%CF), bentonite/CoFe<sub>2</sub>O<sub>4</sub>/HAP (35%HAP/65% (85%/15%CF)) were assessed from the TGA and DTA curves as shown in Figure 4.9. (a-c) from room temperature to 800 °C. For all samples, the weight loss exhibited three stages. The first stage of weight loss, which is 8.816%, 9.618%, 7.869 % for bentonite, bentonite/CoFe<sub>2</sub>O<sub>4</sub> and bentonite/CoFe<sub>2</sub>O<sub>4</sub>/HAP, respectively. It was because of endothermic signal attributed to the inner exchangeable cations and to the weekly attached water. This also suggests the presence of Na<sup>+</sup>, as exchangeable cation in interlayer space. The second endothermic showing a few weight losses of 1.668%, 3.475%, 2.275% for bentonite, bentonite/CoFe<sub>2</sub>O<sub>4</sub>, bentonite/CoFe<sub>2</sub>O<sub>4</sub>/HAP, respectively. As bentonite exposed to thermal treatment it might have decreased its pore volume and surface area, give rise to distortion of the crystal lattice in some extent *i.e.*, dihydroxylation of bentonite could happen which is unexpected or abnormal event [96, 97]. The third weight loss was also about 3.35%, 2.668%, 0.899%, for bentonite, bentonite/CoFe<sub>2</sub>O<sub>4</sub> and bentonite/CoFe<sub>2</sub>O<sub>4</sub>/HAP samples. Generally, the total amount of weight loss of the samples follows the order bentonite/CoFe<sub>2</sub>O<sub>4</sub>/HAP (11.043%) < bentonite (13.846%) < bentonite/CoFe<sub>2</sub>O<sub>4</sub>(15.761%), which indicates that all samples were stable up to 800 °C which is much higher than that of the

temperature used in the present adsorption process, *i.e.*, room temperature. Based on the slight weight loss by the samples, bentonite/CoFe<sub>2</sub>O<sub>4</sub>/HAP was highly thermally stable than bentonite and bentonite/CoFe<sub>2</sub>O<sub>4</sub>. The presence of bentonite matrix in all samples could attributed to the higher thermal stability [98]. Moreover, the presence of HAP in the composite of bentonite/CoFe<sub>2</sub>O<sub>4</sub>/HAP improved its thermal stability [99].

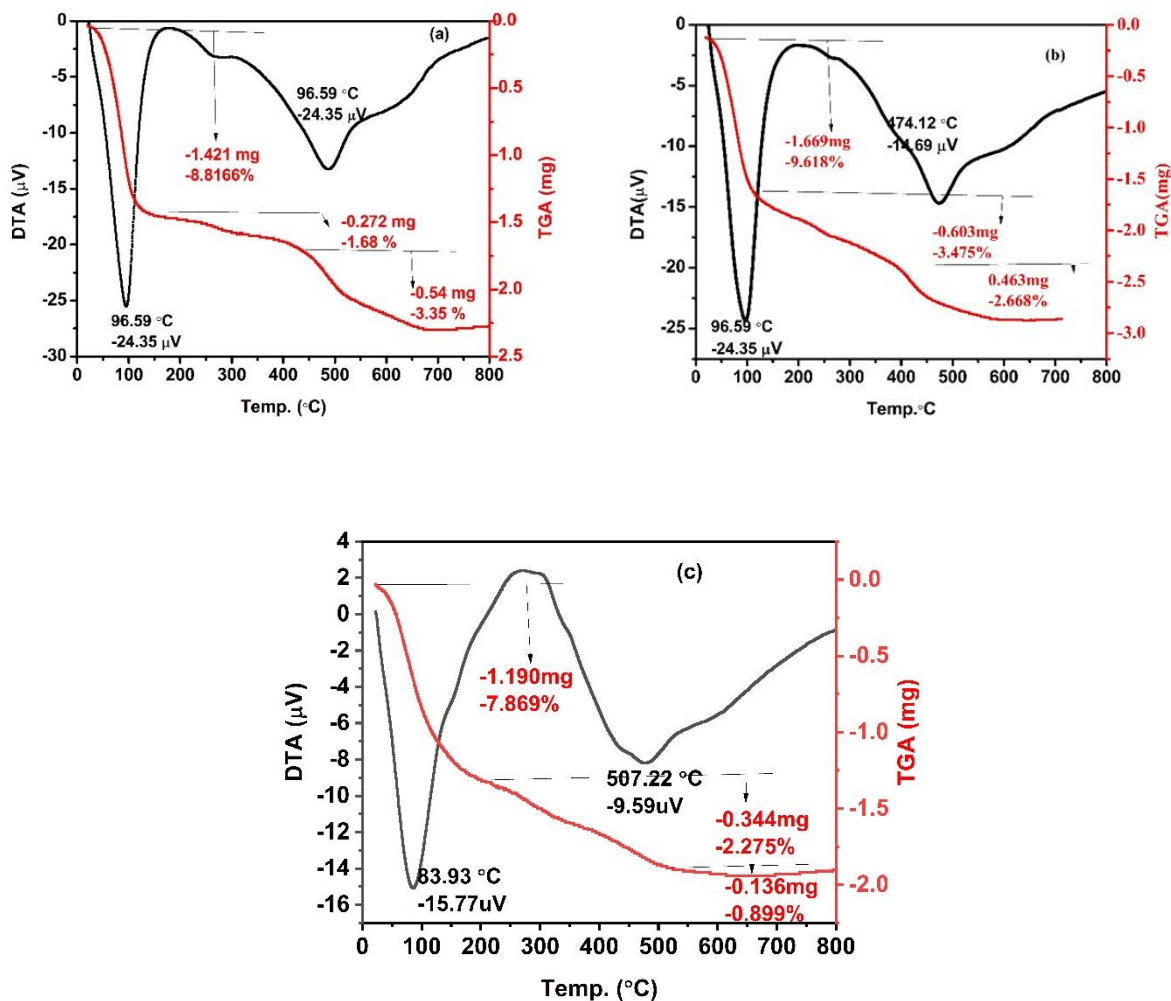


Figure 4.9. TGA-DTG analysis of (a) bentonite, (b) B/CF(85%B/15%CF), (c) B/CF/HAP (35%HAP/65%(85%B/15%CF)).

#### 4.5. Adsorption performance study

A series of adsorption tests have been carried out at a typical equilibrium conditions ( $C_0=49.96$  mg/L, adsorbent dosage=25 mg,  $V=30$  mL, contact time=5h, pH=5.5) for the optimization of

adsorbents. Initially, an equilibrium adsorption capacity ( $q_e$ ) of the adsorbents with compositions of (100- $x$ )B/( $x$ )CF ( $x=0, 5, 15, 25$ , weight in percent of CF) towards adsorption of lead ion was calculated using equation 3.2.  $q_e$  of the adsorbents was found to be 16.6 mg/g, 19.6 mg/g, 19.9 mg/g, and 17 mg/g for raw bentonite, 95%B/5%CF, 85%/15%CF, 75%/25%CF composites, respectively. The effect of bentonite with different CoFe<sub>2</sub>O<sub>4</sub> loadings on the Pb<sup>2+</sup> uptake capacity was depicted in Fig.4.10. In typical the equilibrium concentration ( $C_e$ ) which used in this calculation was depicted in Appendix A, table A (2).

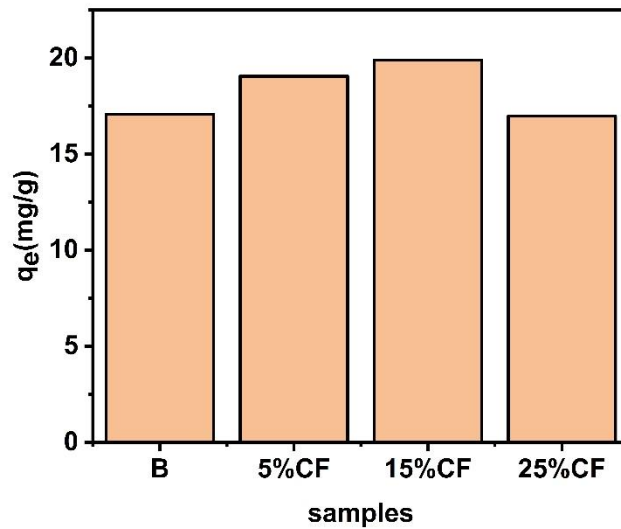


Figure 4.10. Equilibrium adsorption capacity ( $q_e$ ) of B/CF composites with different CF loading

Based on Fig.4.10, the Pb<sup>2+</sup> adsorption capacity increased with the increase in CoFe<sub>2</sub>O<sub>4</sub> content, almost reaching a peak when the CoFe<sub>2</sub>O<sub>4</sub> is 15%. Further increase in the CoFe<sub>2</sub>O<sub>4</sub> resulted in lower adsorption capacity. This could be attributed to the fact that with increasing CoFe<sub>2</sub>O<sub>4</sub> composition increased in the bentonite matrix, CoFe<sub>2</sub>O<sub>4</sub> could occupied some of the active sites on the bentonite surface [71] and thereby decreases the adsorption efficiency of the composite sample. Thus, based on these experimental results the adsorption performance towards Pb<sup>2+</sup>, 85%B/15%CF composite was selected for subsequent experiment.

Then, three different ternary composites were prepared from 85%B/15%CF and different amount of HAP, denoted as, 25%HAP/75%(85%B/15%CF), 35%HAP/65%(85%B/15%CF) and 45%HAP/55%(85%B/15%CF). As shown in Figure 4.11, the equilibrium adsorption capacity ( $q_e$ )

of the ternary composites was 28.88 mg/g for 25%HAP/75(85%B/15%CF), 35.90 mg/g for 35%HAP/65%(85%B/15%CF), and 32.34 mg/g for 45%HAP/55%(85%B/15%CF). This suggests that the composite sample with a composition of 35%HAP/65%(85%B/15%CF), shows the optimal composition.

The designations B/CF/HAP represents 35%HAP/65%(85%B/15%CF) for the next discussions. For further information see Appendix A table A (2).

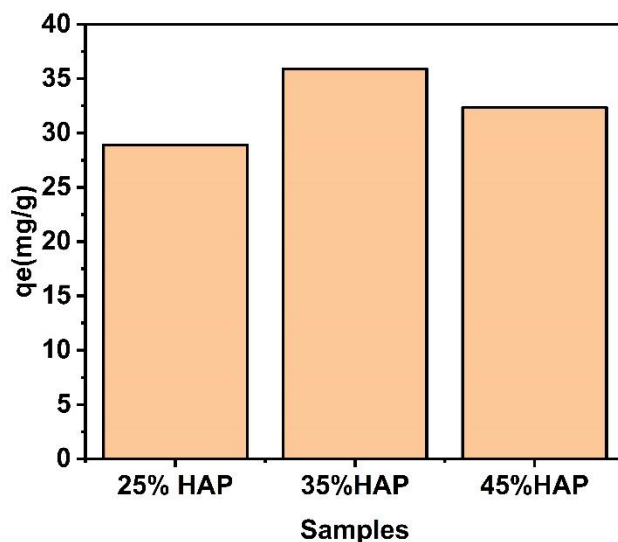


Figure 4.11. Equilibrium adsorption capacity ( $q_e$ ) of B/CF/HAP composite by loading 25%, 35% and 45% HAP on 85%B/15%CF composite

Generally, the performance of adsorbents towards  $Pb^{2+}$  is determined by the properties of adsorbents such as surface area, surface charge, structure, and functional groups present on the adsorbents. Based on the adsorption capacity of the adsorbents, the ternary composites of B/CF/HAP exhibited the highest adsorption capacity, ( $q_e$ ) as compared to bentonite and bentonite- $CoFe_2O_4$  composites. This is because, as displayed in the FTIR spectrum, large amount of -OH functional groups were presented on the surface of B/CF/HAP, which could fasten the adsorption of  $Pb^{2+}$  by forming surface complexation [71]. Moreover, the presented  $Ca^{2+}$  sites on B/CF/HAP being preferentially occupied by  $Pb^{2+}$  as  $Pb^{2+}$  has bigger ionic radius and electronegativity than  $Ca^{2+}$ . Furthermore, as described in the SEM analysis, loading of CF on bentonite showed relatively rough surface which in turn enhances its adsorption capacity to take advantage over bentonite.

Then, based on the  $Pb^{2+}$  adsorption capacity as shown in fig. 4.11, 35%HAP/65%(85%B/15%CF) was selected for further study.

#### 4.5.1. Effect of Contact Time

The adsorption of  $Pb^{2+}$  by bentonite, bentonite/ $CoFe_2O_4$ , bentonite/ $CoFe_2O_4$ /Hydroxyapatite (B/CF/HAP) at  $T=25\text{ }^{\circ}C$ , initial lead concentration of 50 mg/L, and adsorbent dosage of 1g/L were performed to study the effect of contact time (30 – 120 min) and to compare the capacities of the adsorbents. The adsorption of  $Pb^{2+}$  was very fast in the first 30 min for all samples, because of the availability of large number of vacant active-sites on the surface of the adsorbents, followed by a slight increase and eventually reached equilibrium, as shown in Figure 4.12. The presence of large number of active sites on the surface (surface diffusion) and pores resulted in rapid adsorption process. For example; 73 % of the adsorption capacity of B/CF/HAP was completed in the first 30 min followed by gradual occupation of sites with  $Pb^{2+}$  ion. Adsorption reached equilibrium within 90 min. For further information see Appendix A, table A (2).

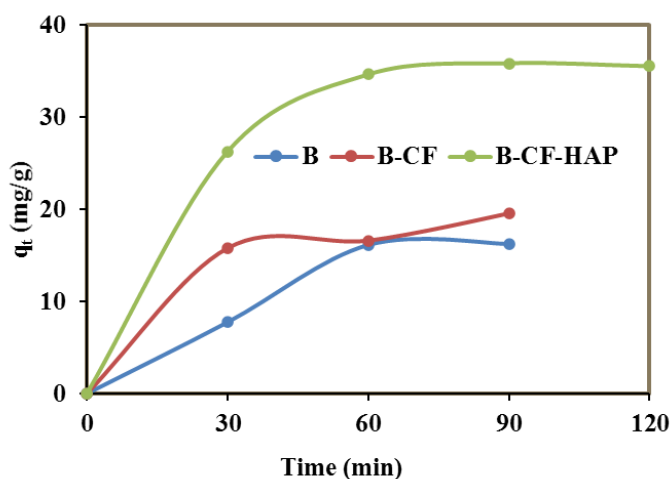


Figure 4.12. Effect of contact time on adsorption capacity of B, B/CF and B/CF/HAP

#### 4.5.2. Effect of Initial Concentrations

The percentage removal of lead ion by the composite samples decreased as the concentrations of lead ion increases from 50 – 200 mg/L. This is due to the fact that at low initial concentration of the lead ion, the availability of adsorption site was relatively high compared the amount of the

species to be adsorbed. While, at high initial concentration, the total available adsorption site of the adsorbents with limited dosage may be insufficient (saturation of adsorption site) resulted in a decrease in the adsorption efficiency [100]. As shown in Figure 4.13, when the initial concentration of  $Pb^{2+}$  increased from (50 – 200 mg/L), it had a positive influence on adsorption capacity. It can be speculated that the availability of adsorption sites could be relatively high for 50 mg/L of  $Pb^{2+}$  ion, as the adsorption capacity increased quickly. As the concentrations of  $Pb^{2+}$  ion increased, the adsorption capacity increased slightly and showed a tendency of being constant with further increment of lead ion concentration. For further information referee Appendix A, table A (2).

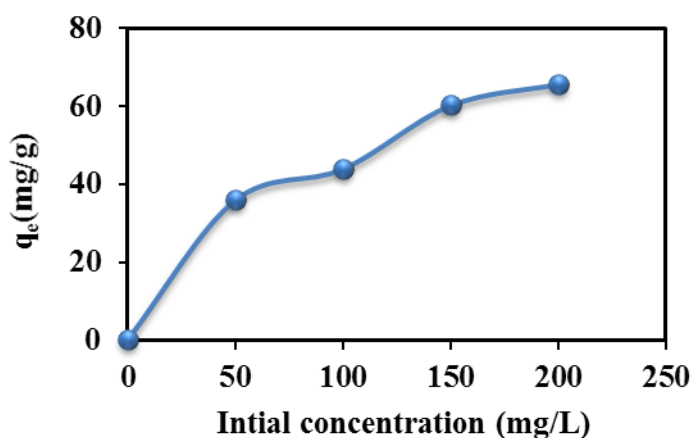


Figure 4.13. Effect of initial concentration on adsorption capacity of 35%HAP/65%(85%B/15%CF) composite

#### 4.5.3. Adsorption Isotherm Study

An adsorption isotherm defines the relation between the amount of adsorbate adsorbed per unit mass of adsorbent and its remaining equilibrium concentration [101]. Adsorption isotherm are useful to state surface properties, and adsorption mechanisms. Based on the data given in Table 4.1. the equilibrium data for adsorbed  $Pb^{2+}$  ions onto B/CF/HAP was expressed using two isotherm models i.e., Freundlich and Langmuir adsorption isotherm. The equilibrium concentration ( $C_e$ ) is depicted in Appendix A, table A (2)

Table 4.1. Parameters for plotting Freundlich and Langmuir adsorption isotherm of Pb<sup>2+</sup> on B/CF/HAP composite

| Initial con.<br>(ppm) | $C_e$ (mg/g) | $q_e$ (mg/g) | $1/C_e$ | $1/q_e$ | $\ln C_e$ | $\ln q_e$ |
|-----------------------|--------------|--------------|---------|---------|-----------|-----------|
| 50                    | 20.04        | 35.904       | 0.0499  | 0.0278  | 3.00      | 3.58      |
| 100                   | 63.4         | 43.92        | 0.016   | 0.0228  | 4.15      | 3.78      |
| 150                   | 99.72        | 60.28        | 0.010   | 0.0166  | 4.6       | 4.10      |
| 200                   | 145.2        | 65.76        | 0.007   | 0.015   | 4.98      | 4.19      |

### Freundlich Isotherm Model

Freundlich isotherm model assumes that the adsorption could happen via heterogeneous surfaces (multiple layers), such that there is no overload loading at high concentration [32]. The equation describing this model can be given as follows:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \dots \dots (4.2)$$

Where,  $K_f$  is the Freundlich constant  $[(\text{mg/g})(\text{L/g})^{1/n}]$ ,  $C_e$  is the equilibrium concentration, and  $n$  is index of heterogeneity. A plot of  $\ln q_e$  against  $\ln C_e$  would yield a straight line according to Freundlich isotherm model. The slope of the line and the intercept, provides  $n$  and  $K_f$ , respectively, the calculated values are reported in Table 4.2.

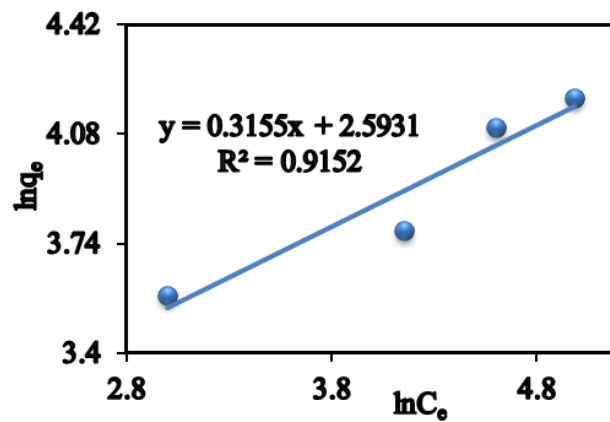


Figure 4.14. Freundlich isotherm model

## Langmuir Isotherm model

Langmuir isotherm on solid surface assumes that adsorption is homogeneous (monolayer adsorption) [29]. The Langmuir isotherm model can be described according to equation 4.3 to determine adsorption isotherm.

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{bq_{max}}\right) \frac{1}{C_e} \dots\dots\dots(4.3)$$

where  $q_e$  = the equilibrium amount of adsorbate adsorbed per unit mass of adsorbent (mg/g),  $b$  = Langmuir adsorption constant(1/mg),  $q_{max}$  = the maximum adsorption capacity of the adsorbent (mg/g),  $C_e$  = equilibrium solution concentration of the adsorbate (mg/L).

A plot of  $1/q_e$  against  $1/C_e$  is presented in Figure 4.15 and its slope yields  $1/bq_{max}$  while the intercept can provide  $1/q_{max}$ .

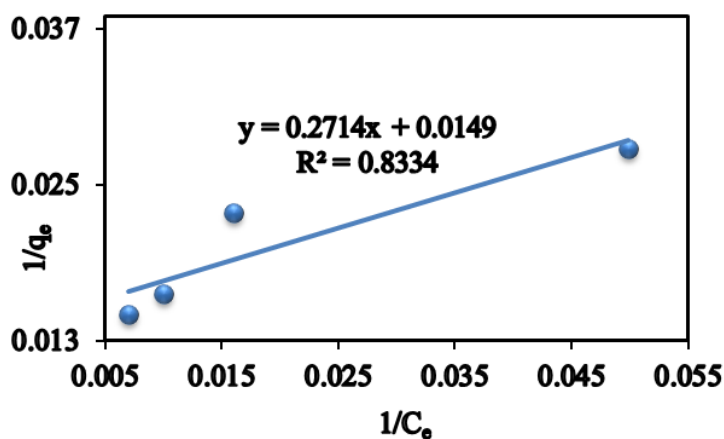


Figure 4.15. Langmuir adsorption isotherm

Table 4.2. Table showing the parameters extracted from isotherm models

| Samples                                         | Isotherm models       |       |        |                     |        |        |
|-------------------------------------------------|-----------------------|-------|--------|---------------------|--------|--------|
|                                                 | Freundlich parameters |       |        | Langmuir parameters |        |        |
|                                                 | $n$                   | $K_F$ | $R^2$  | $q_{max}(mg/g)$     | $b$    | $R^2$  |
| Bentonite/CoFe <sub>2</sub> O <sub>4</sub> /HAP | 3.169                 | 13.37 | 0.9152 | 67.114              | 0.0549 | 0.8334 |

Therefore, based on the results in table, the adsorption data conformed to both the Langmuir and Freundlich isotherm. However, Freundlich isotherm was apparently best fitted model with a correlation coefficient ( $R^2$ ) around 0.9152, thus, proving the multilayer adsorption of Pb<sup>2+</sup> on heterogeneous surface of B/CF/HAP and porous nature of the adsorbent [102, 103]. Furthermore, the dimensionless Freundlich constant  $n > 1$ , which implies adsorption was favorable on heterogeneous surface [104]. Generally, the value  $1/n < 0.5$  implies easy adsorption, and  $1/n > 2$  implies difficult adsorption [71]. In this work, the adsorption intensity  $(1/n) = 0.3155$  implied that the adsorption of Pb<sup>2+</sup> on the surface of bentonite/CoFe<sub>2</sub>O<sub>4</sub>/HAP was favorable. However, Freundlich isotherm model could not predict the maximum adsorption capacity on the surface, it only describes the nature of adsorption on the surface of adsorbents [105]. Thus, the maximum adsorption capacity of the B/CF/HAP towards Pb<sup>2+</sup> was 67.114 mg/g as determined using Langmuir equation. The favorability of Langmuir isotherm was determined by the value of separation factor ( $R_L = 1/(1 + K_L C_0)$ ) where,  $K_L$  is the Langmuir rate constant,  $C_0$  represent the highest initial concentration [23]. Herein, the value of  $R_L$  was found to be  $0 < 0.0834 < 1$ , which indicates the favorability of adsorption.

#### 4.5.4. Adsorption Kinetics

Adsorption kinetics study is critical in remediation of effluents since significant information on performance of the process, reaction ways and the mechanism of adsorption reactions are provided. Adsorption process are mostly described using the pseudo-first-order and pseudo-second-order kinetic models based on chemical reactions kinetics [106]. Based on the given data in table 4.3, pseudo-first-order and pseudo-second-order kinetic models are discussed. For further information see Appendix A, table A (2).

Table 4.3. Parameters for plotting adsorption kinetics

| Time (min) | $q_e$ (mg/g) | $q_t$ (mg/g) | $q_e - q_t$ | $\log(q_e - q_t)$ | $t/q_t$ |
|------------|--------------|--------------|-------------|-------------------|---------|
| B30        | 16.16        | 7.76         | 8.4         | 0.9243            | 3.866   |
| B60        | 16.16        | 16.16        | 0.0         | -                 | 3.713   |
| B90        | 16.16        | 16.26        | -           | -                 | 5.535   |
| B-CF30     | 15.76        | 15.76        | 0.0         | -                 | 1.904   |
| B-CF60     | 15.76        | 16.58        | -           | -                 | 3.619   |
| B-CF90     | 15.76        | 19.52        | -           | -                 | 4.611   |
| T30        | 35.86        | 26.26        | 9.6         | 0.9822            | 1.142   |
| T60        | 35.86        | 34.64        | 1.22        | 0.086             | 1.732   |
| T90        | 35.86        | 35.86        | 0.0         | -                 | 2.510   |
| T120       | 35.86        | 35.54        | 0.32        | -0.495            | 3.376   |

In table 4.3 above, the designations such as B30, B60 and B90 represents bentonite, B-CF30, B-CF60 and B-CF90 represents bentonite/CoFe<sub>2</sub>O<sub>4</sub> and T30, T60 and T120 represent bentonite/CoFe<sub>2</sub>O<sub>4</sub>/HAP (B/CF/HAP).

### Pseudo-First Order

The pseudo-first order kinetic model for B/CF/HAP composite is calculated using equation 4. 4.

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \dots \dots \dots (4.4)$$

Where,  $q_e$  (mg/g) and  $q_t$  (mg/g) is the equilibrium adsorption capacity,  $K_1$ (min<sup>-1</sup>) is pseudo-first order kinetic model.

A graph is constructed using  $\log(q_e - q_t)$  Vs  $t$  to illustrate the pseudo-first-order kinetic model for B/CF/HAP composite. The calculated value of the parameters is found in table 4.4.

### Pseudo-second Order

The pseudo-second order kinetic model states that the rate limiting step may be chemical sorption involving valence forces through sharing or exchanging of electrons between heavy metal ions and adsorbent [107].

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \dots \dots \dots (4.5)$$

Where  $q_t$  and  $q_e$ (mg/g) are the amount of  $Pb^{2+}$  adsorbed per mass of adsorbent (g) at time  $t$  (min) and at equilibrium, respectively,  $K_2$  (g.mg<sup>-1</sup>.min<sup>-1</sup>) is the rate constants of pseudo-second order models, respectively. Fig.4.16 (a, b) described the pseudo-first and pseudo-second order model of B/CF/HAP accompanied with  $R^2$  value.

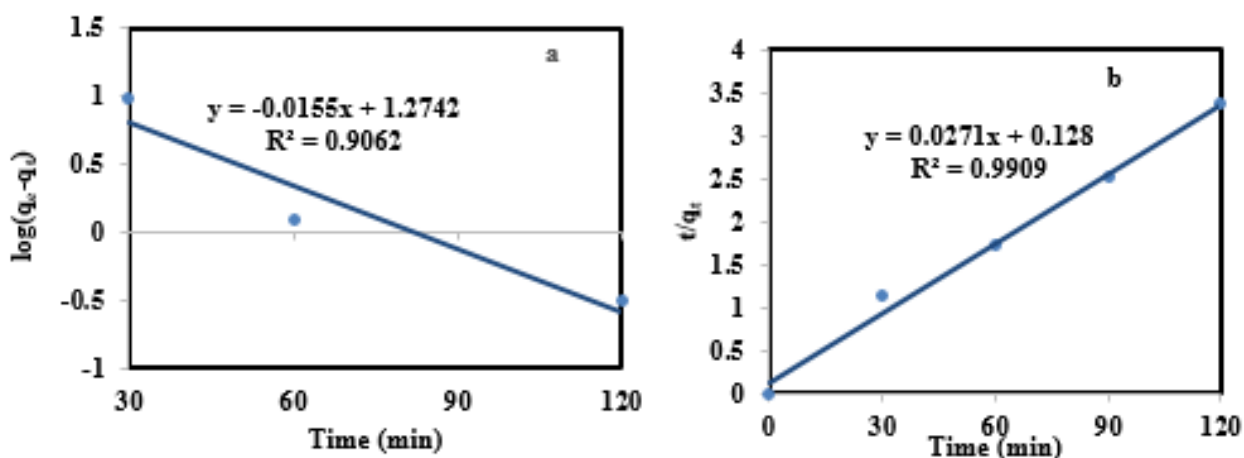


Figure 4.16. Pseudo-first-order (a) and Pseudo-second-order kinetic model for B/CF/HAP composite

The calculated parameters from two kinetic models for bentonite/CoFe<sub>2</sub>O<sub>4</sub>/HAP are listed in Table 4.4

Table 4.4. Pseudo-first and second-order kinetic models for B/CF/HAP

|           |                       | Pseudo-first-order    |                            |        | Pseudo-second-order   |                            |        |
|-----------|-----------------------|-----------------------|----------------------------|--------|-----------------------|----------------------------|--------|
| adsorbent | $q_{e,exp}$<br>(mg/g) | $q_{e,cal}$<br>(mg/g) | $K_1$ (min <sup>-1</sup> ) | $R^2$  | $q_{e,cal}$<br>(mg/g) | $K_2$ (min <sup>-1</sup> ) | $R^2$  |
| B/CF/HAP  | 35.86                 | 18.80                 | 0.0345                     | 0.9062 | 36.9                  | 0.00574                    | 0.9909 |

As listed in the table 4.4, the large difference between  $q_{e,exp}$  and  $q_{e,cal}$  from Pseudo-first-order kinetic models indicate that the adsorption of  $Pb^{2+}$  onto B/CF/HAP doesn't obey pseudo-first-order kinetics. However, the  $q_{e,cal}$  value obtained through pseudo-second-order model is almost closer to the experimental  $q_{e,exp}$  values. Moreover, pseudo-second order kinetics model showed a good fit with experimental data, with higher correlation coefficient ( $R^2$ ) = 0.9909 as compared to that obtained by pseudo-first-model ( $R^2$ ) = 0.9062 for B/CF/HAP composite.

Furthermore, the pseudo-second-order kinetic model for bentonite and bentonite/ $CoFe_2O_4$  was also studied, as shown in Figure 4.17.

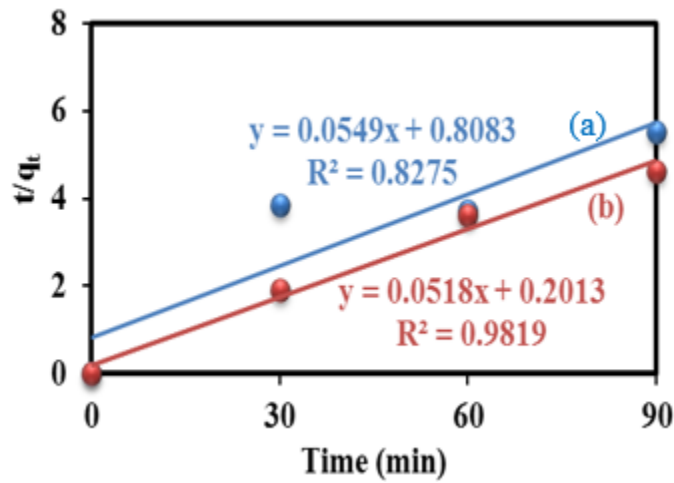


Figure 4.17. Pseudo-second order kinetics model for B (a) and B/CF (b)

Table 4.5. indicated the necessary parameters to state pseudo-second-order model of B and B/CF, in which the ( $R^2$ ) value for bentonite and bentonite/ $CoFe_2O_4$  was found to be 0.8275, 0.9819, respectively. Further their  $q_{e,cal}$  value obtained through pseudo-second-order model is in good agreement with the experimental  $q_{e,exp}$  values. This could be good indication to confirm pseudo-second-order is best fitted model for the samples.

Table 4.5. Table showing the Pseudo-second-order kinetic model for B and B/CF

| pseudo-second-order |                    |                    |                                                |        |
|---------------------|--------------------|--------------------|------------------------------------------------|--------|
| Adsorbent           | $q_{e,exp}$ (mg/g) | $q_{e,cal}$ (mg/g) | $K_2$ (g.mg <sup>-1</sup> .min <sup>-1</sup> ) | $R^2$  |
| B                   | 16.26              | 18.215             | 0.00373                                        | 0.8275 |
| B/CF                | 19.52              | 19.3               | 0.01333                                        | 0.9819 |

## 5. CONCLUSIONS

In this study, a composite of B/CF and B/CF/HAP was synthesized from bentonite, CF and HAP via coprecipitation methods. i.e., B/CF is synthesized by loading different weight percentage of  $\text{CoFe}_2\text{O}_4$  by keeping bentonite as matrix. Based on the adsorption capacity towards lead ion, as the percentage of CF increased up to 15%, it improved the adsorption capacity of bentonite from 16.6 mg/g to 19.9 mg/g towards  $\text{Pb}^{2+}$ , but further increasing the percentage of the CF reduces the performance. The possible reason could be that an increased amount of CF can result in the disappearance of bentonite layers as confirmed in the XRD spectrum, and thus decreased the adsorption capacity. Because eggshell is considered as useless and is found extensively in the environment as waste (can pollute the environment), it can be recycled since it is rich in calcium oxide (CaO) so that it can be used as precursor to synthesis Hydroxyapatite (HAP), which was then loaded to the optimal B-CF composite to obtain a ternary composite. Then three composite types of B/CF/HAP were synthesized in different amounts of HAP and 35%HAP/65%(85%B/15%CF) was found to be the optimal concentration based on adsorption capacity towards  $\text{Pb}^{2+}$ . The composite was characterized via XRD, SEM-EDX, FTIR, TGA-DTG. The synthesized B/CF/HAP composite showed adsorption capacity for  $\text{Pb}^{2+}$  (67.1 mg/g), which was attributed to the complexation of  $\text{Pb}^{2+}$  with -OH groups. The  $\text{Pb}^{2+}$  ion can also exchange with the mobile  $\text{Ca}^{2+}$  component of HAP and could lead to a formation of lead-hydroxyapatite complexes. It was presumed from Freundlich isotherm model that the adsorption process was multilayer and the adsorption sites on the surface of B/CF/HAP distributed heterogeneously while the adsorption kinetics was best fitted with pseudo-second-order kinetic model, which indicated chemisorption. In summary, the experimental results suggest that B/CF/HAP which is cost effective and environmentally friendly, could be a potential adsorbent of lead ion from wastewater.

## 6. RECOMMENDATIONS

Heavy metals and toxic species removal from industrial effluents should be given special emphasis to secure the environmental and societal health. In this study, we investigated the adsorption capacity of B/CF/HAP ternary composites towards lead ion removal from aqueous solution. We further recommend the investigation of the removal capacity of these ternary composites towards other heavy and toxic metals such as mercury, arsenide, cobalt and so on as these are toxic and carcinogenic to human health. These elements can be found in industrial effluents such as leather and textile industries.

The materials synthesis route also plays an important role in engineering the surface morphology. The active surfaces of the adsorbent can be further engineered in such a way that the specific surface area of the particles can be increased. In this work, we used coprecipitation method to synthesis the powders, which has its own drawbacks such as particles aggregations which leads to a decrease in the specific surface area. Therefore, we recommend that if these samples are prepared in a controlled synthesis technology such as hydrothermal and solvothermal methods, the surface morphologies can be enhanced, which could improve the adsorption capacity of the composite materials towards the above mentioned toxic and heavy metals.

Surface area and porosity of the adsorbent basically affect the adsorption performance of the synthesized materials. Therefore, we recommended the determination of specific surface area and porosity using BET.

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## APPENDIX A: AAS ANALYSIS RESULTS OF SAMPLES TOWARDS $Pb^{2+}$

Calibration curve was made to determine the concentration of  $Pb^{2+}$  in the samples by comparing it to a set of standard samples of 1, 2, 3, 4 ppm lead ion concentration.

Table A.1. Calibration data of  $Pb^{2+}$  and Working parameters of AAS.

| <p>አዲስ አበባ ዩኒቨርሲቲ<br/>የተፈጥሮና ኮምፒውተራዊ ሳይንስ<br/>ኮሌጅ<br/>የኬሚስትሪ ትምህርት ኮሎኒ<br/>አዲስ አበባ፣ ኢትዮጵያ</p>                                                                                                                                                                                                                                           |        | <p>Addis Ababa University<br/>College of Natural and Computational<br/>Sciences<br/>Department of Chemistry<br/>Addis Ababa, Ethiopia</p> |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------|---|---|---------|---|---|---------|---|---|---------|---|---|---------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|---------------|------|---|---|---------|---|---|---------|---|---|---------|---|---|---------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|---------------|------|---|---|---------|---|---|---------|---|---|---------|---|---|---------|
| <p>Date : June 19, 2020</p>                                                                                                                                                                                                                                                                                                             |                                                                                         |                                                                                                                                           |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| <p>AAS Analysis Result of Samples</p>                                                                                                                                                                                                                                                                                                   |                                                                                         |                                                                                                                                           |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| <p>Pb<br/>Calibration data</p>                                                                                                                                                                                                                                                                                                          |                                                                                         |                                                                                                                                           |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| <table border="1"> <thead> <tr> <th>Standard</th> <th>Conc. ( ppm )</th> <th>Abs.</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>1</td> <td>0.00284</td> </tr> <tr> <td>2</td> <td>2</td> <td>0.00494</td> </tr> <tr> <td>3</td> <td>3</td> <td>0.00776</td> </tr> <tr> <td>4</td> <td>4</td> <td>0.01018</td> </tr> </tbody> </table> | Standard                                                                                | Conc. ( ppm )                                                                                                                             | Abs.                                             | 1 | 1 | 0.00284 | 2 | 2 | 0.00494 | 3 | 3 | 0.00776 | 4 | 4 | 0.01018 | <table border="1"> <thead> <tr> <th>Standard</th> <th>Conc. ( ppm )</th> <th>Abs.</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>1</td> <td>0.00284</td> </tr> <tr> <td>2</td> <td>2</td> <td>0.00494</td> </tr> <tr> <td>3</td> <td>3</td> <td>0.00776</td> </tr> <tr> <td>4</td> <td>4</td> <td>0.01018</td> </tr> </tbody> </table> | Standard | Conc. ( ppm ) | Abs. | 1 | 1 | 0.00284 | 2 | 2 | 0.00494 | 3 | 3 | 0.00776 | 4 | 4 | 0.01018 | <table border="1"> <thead> <tr> <th>Standard</th> <th>Conc. ( ppm )</th> <th>Abs.</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>1</td> <td>0.00284</td> </tr> <tr> <td>2</td> <td>2</td> <td>0.00494</td> </tr> <tr> <td>3</td> <td>3</td> <td>0.00776</td> </tr> <tr> <td>4</td> <td>4</td> <td>0.01018</td> </tr> </tbody> </table> | Standard | Conc. ( ppm ) | Abs. | 1 | 1 | 0.00284 | 2 | 2 | 0.00494 | 3 | 3 | 0.00776 | 4 | 4 | 0.01018 |
| Standard                                                                                                                                                                                                                                                                                                                                | Conc. ( ppm )                                                                           | Abs.                                                                                                                                      |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| 1                                                                                                                                                                                                                                                                                                                                       | 1                                                                                       | 0.00284                                                                                                                                   |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| 2                                                                                                                                                                                                                                                                                                                                       | 2                                                                                       | 0.00494                                                                                                                                   |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| 3                                                                                                                                                                                                                                                                                                                                       | 3                                                                                       | 0.00776                                                                                                                                   |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| 4                                                                                                                                                                                                                                                                                                                                       | 4                                                                                       | 0.01018                                                                                                                                   |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| Standard                                                                                                                                                                                                                                                                                                                                | Conc. ( ppm )                                                                           | Abs.                                                                                                                                      |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| 1                                                                                                                                                                                                                                                                                                                                       | 1                                                                                       | 0.00284                                                                                                                                   |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| 2                                                                                                                                                                                                                                                                                                                                       | 2                                                                                       | 0.00494                                                                                                                                   |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| 3                                                                                                                                                                                                                                                                                                                                       | 3                                                                                       | 0.00776                                                                                                                                   |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| 4                                                                                                                                                                                                                                                                                                                                       | 4                                                                                       | 0.01018                                                                                                                                   |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| Standard                                                                                                                                                                                                                                                                                                                                | Conc. ( ppm )                                                                           | Abs.                                                                                                                                      |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| 1                                                                                                                                                                                                                                                                                                                                       | 1                                                                                       | 0.00284                                                                                                                                   |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| 2                                                                                                                                                                                                                                                                                                                                       | 2                                                                                       | 0.00494                                                                                                                                   |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| 3                                                                                                                                                                                                                                                                                                                                       | 3                                                                                       | 0.00776                                                                                                                                   |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| 4                                                                                                                                                                                                                                                                                                                                       | 4                                                                                       | 0.01018                                                                                                                                   |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| <p>Energy= 71.5<br/>Lamp current= 3mA</p>                                                                                                                                                                                                                                                                                               | <p>PMT [V] = 298<br/>Detection limit = 0.06 ppm</p>                                     | <p>λ=283.3nm<br/>Slit width= 1.2nm</p>                                                                                                    |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| <p>Instrument: Analytikjena Atomic Absorption Spectrophotometer<br/>Model: ZEE nit 700P #150Z7P1025 Tech: Flame<br/>SW-Version: Aspects LS 1.3.1.0RC1</p>                                                                                                                                                                               |                                                                                         |                                                                                                                                           |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| <p>Sample Analyzed by:</p>                                                                                                                                                                                                                                                                                                              | <p>Approved by:</p>                                                                     |                                                                                                                                           |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| <p>Name <u>Henok Mekonnen</u><br/>Signature <u>[Signature]</u><br/>Date <u>19/06/20</u></p>                                                                                                                                                                                                                                             | <p>Name <u>Dr. Negash</u><br/>Signature <u>[Signature]</u><br/>Date <u>19/06/20</u></p> |                                                       |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| <p>ቁጽ<br/>Tel: +251-011-4239466</p>                                                                                                                                                                                                                                                                                                     | <p>ፖ.ሰ.ቦ<br/>P.O.Box 33658</p>                                                          | <p>ፋክስ<br/>Fax: +251-011-4239470</p>                                                                                                      | <p>ኢ.ሜል<br/>E-mail: chemistry_CNS@aau.edu.et</p> |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |
| <p>ጥበብን እጅግ የሚረጅምልን፣ እውነትን እናገኛለን-Seek Wisdom, elevate your intellect and serve humanity</p>                                                                                                                                                                                                                                            |                                                                                         |                                                                                                                                           |                                                  |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |                                                                                                                                                                                                                                                                                                                                         |          |               |      |   |   |         |   |   |         |   |   |         |   |   |         |

Those parameters indicated in figures (4.10-4.13) and tables (4.1-4.3) are determined based on the data depicted in Appendix A (table A.2).

In section 4.2 (figure 4.10), the designations such as std, ben, 5%CF, 15%CF, and 25%CF implied standard initial concentration, bentonite, 95%B/5%CF, 85%B/15%CF, 75%B/25%CF. The respective equilibrium  $Pb^{2+}$  concentrations were represented in table A.2 from N $\underline{o}$  1-5 respectively.

In section 4.2 (figure 4.11), 25%HAP, 35%HAP, 45%HAP implied the ternary composites 25%HAP/75%(85%B/15%CF), 35%HAP/65%(85B/15%CF), 45%HAP/55%(85%B/15%CF). The respective equilibrium  $Pb^{2+}$  concentrations of the samples were represented in table A.2 from N $\underline{o}$  6-8, respectively.

In section 4.2.1 (figure 4.12) and section 4.2.4 table (4.3), B30, B60 and B90 implied bentonite; B-CF30, B-CF60, B-CF90 stands for 85%B/15%CF (B/CF) and T30, T60, T90, T120 implied 35%HAP/65%(85B/15%CF) (B/CF/HAP). The concentrations of samples at a contact time of 30, 60, 90, 120min were represented in table A.2 from N $\underline{o}$  9-18, respectively.

In typical study of adsorption isotherms (table 4.1), the designation C100, C150, C200 stands for initial concentrations of  $Pb^{2+}$ , and its equilibrium concentrations were represented in table A.2 from N $\underline{o}$  19-21.

Table A.2. The concentration of  $Pb^{2+}$  ion in the samples

| <p>አዲስ አበባ ዩኒቨርሲቲ<br/>የተፈጥሮና ኮምፒውተር ሳይንስ<br/>ኮሌጅ<br/>የኬሚስትሪ ትምህርት ክፍል<br/>አዲስ አበባ፣ ኢትዮጵያ</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |  | <p>Addis Ababa University<br/>College of Natural and Computational<br/>Sciences<br/>Department of Chemistry<br/>Addis Ababa, Ethiopia</p>                                                                                                                          |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------|----------------------|------------------------------|------------------------------------------|---|-----|-------|---|-------|-------|---|-------|-------|---|-------|-------|---|-------|-------|---|-------|-------|---|-------|-------|---|-----|-------|----|-----|-------|----|-----|-------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|--------|--------------|----|--------|-------|----|--------|-------|----|--------|-------|----|-----|-------|----|-----|-------|----|-----|-------|----|------|-------|----|------|------|----|------|-------|----|------|-------|
| <b>Date : June 19, 2020</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                   |                                                                                                                                                                                                                                                                    |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| <p><b>Sample</b></p> <table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <thead> <tr> <th>No.</th> <th>Sample</th> <th>Conc. in ppm</th> </tr> </thead> <tbody> <tr><td>1</td><td>Std</td><td>49.96</td></tr> <tr><td>2</td><td>ben</td><td>35.74</td></tr> <tr><td>3</td><td>5 %CF</td><td>34.08</td></tr> <tr><td>4</td><td>15%CF</td><td>33.38</td></tr> <tr><td>5</td><td>25%CF</td><td>35.80</td></tr> <tr><td>6</td><td>25HAP</td><td>25.89</td></tr> <tr><td>7</td><td>35HAP</td><td>20.04</td></tr> <tr><td>8</td><td>45HAP</td><td>23.01</td></tr> <tr><td>9</td><td>B30</td><td>42.20</td></tr> <tr><td>10</td><td>B60</td><td>33.80</td></tr> <tr><td>11</td><td>B90</td><td>33.70</td></tr> </tbody> </table> | No.                                                                               | Sample                                                                                                                                                                                                                                                             | Conc. in ppm                             | 1                    | Std                          | 49.96                                    | 2 | ben | 35.74 | 3 | 5 %CF | 34.08 | 4 | 15%CF | 33.38 | 5 | 25%CF | 35.80 | 6 | 25HAP | 25.89 | 7 | 35HAP | 20.04 | 8 | 45HAP | 23.01 | 9 | B30 | 42.20 | 10 | B60 | 33.80 | 11 | B90 | 33.70 | <p><b>data</b></p> <table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <thead> <tr> <th>No.</th> <th>Sample</th> <th>Conc. in ppm</th> </tr> </thead> <tbody> <tr><td>12</td><td>B-CF30</td><td>34.20</td></tr> <tr><td>13</td><td>B-CF60</td><td>33.38</td></tr> <tr><td>14</td><td>B-CF90</td><td>30.44</td></tr> <tr><td>15</td><td>T30</td><td>23.70</td></tr> <tr><td>16</td><td>T60</td><td>15.32</td></tr> <tr><td>17</td><td>T90</td><td>14.10</td></tr> <tr><td>18</td><td>T120</td><td>14.42</td></tr> <tr><td>19</td><td>C100</td><td>63.4</td></tr> <tr><td>20</td><td>C150</td><td>99.72</td></tr> <tr><td>21</td><td>C200</td><td>145.2</td></tr> </tbody> </table> | No. | Sample | Conc. in ppm | 12 | B-CF30 | 34.20 | 13 | B-CF60 | 33.38 | 14 | B-CF90 | 30.44 | 15 | T30 | 23.70 | 16 | T60 | 15.32 | 17 | T90 | 14.10 | 18 | T120 | 14.42 | 19 | C100 | 63.4 | 20 | C150 | 99.72 | 21 | C200 | 145.2 |
| No.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | Sample                                                                            | Conc. in ppm                                                                                                                                                                                                                                                       |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | Std                                                                               | 49.96                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 2                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | ben                                                                               | 35.74                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 3                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 5 %CF                                                                             | 34.08                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 4                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 15%CF                                                                             | 33.38                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 5                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 25%CF                                                                             | 35.80                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 6                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 25HAP                                                                             | 25.89                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 7                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 35HAP                                                                             | 20.04                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 8                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 45HAP                                                                             | 23.01                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 9                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | B30                                                                               | 42.20                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 10                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | B60                                                                               | 33.80                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 11                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | B90                                                                               | 33.70                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| No.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | Sample                                                                            | Conc. in ppm                                                                                                                                                                                                                                                       |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 12                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | B-CF30                                                                            | 34.20                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 13                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | B-CF60                                                                            | 33.38                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 14                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | B-CF90                                                                            | 30.44                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 15                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | T30                                                                               | 23.70                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 16                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | T60                                                                               | 15.32                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 17                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | T90                                                                               | 14.10                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 18                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | T120                                                                              | 14.42                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 19                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | C100                                                                              | 63.4                                                                                                                                                                                                                                                               |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 20                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | C150                                                                              | 99.72                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| 21                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | C200                                                                              | 145.2                                                                                                                                                                                                                                                              |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| <p><b>Sample Analyzed by:</b></p> <p>Name <u>Henok Mekonnen</u><br/>         Signature <u>[Signature]</u><br/>         Date <u>19/06/20</u></p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                   | <p><b>Approved by:</b></p> <p>Name <u>Dr. Negash</u><br/>         Signature <u>[Signature]</u><br/>         Date <u>19/06/20</u></p> <div style="text-align: center;">  </div> |                                          |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| <table border="0" style="width: 100%;"> <tr> <td style="width: 25%;">ቴሌ<br/>Tel: +251-011-4239466</td> <td style="width: 25%;">ፖስታ<br/>P.O.Box 33658</td> <td style="width: 25%;">ፋክስ<br/>Fax: +251-011-4239470</td> <td style="width: 25%;">ኢ.ሜል<br/>E-mail: chemistry_CNS@aau.edu.et</td> </tr> </table> <p style="text-align: center; font-size: small;">"የዘብን እሾ የእእምራችንን ልልልና አበላሽጥ/Seek Wisdom, elevate your intellect and serve humanity"</p>                                                                                                                                                                                                                                                                                                         |                                                                                   |                                                                                                                                                                                                                                                                    | ቴሌ<br>Tel: +251-011-4239466              | ፖስታ<br>P.O.Box 33658 | ፋክስ<br>Fax: +251-011-4239470 | ኢ.ሜል<br>E-mail: chemistry_CNS@aau.edu.et |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |
| ቴሌ<br>Tel: +251-011-4239466                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | ፖስታ<br>P.O.Box 33658                                                              | ፋክስ<br>Fax: +251-011-4239470                                                                                                                                                                                                                                       | ኢ.ሜል<br>E-mail: chemistry_CNS@aau.edu.et |                      |                              |                                          |   |     |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |       |       |   |     |       |    |     |       |    |     |       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |        |              |    |        |       |    |        |       |    |        |       |    |     |       |    |     |       |    |     |       |    |      |       |    |      |      |    |      |       |    |      |       |