

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**INVESTIGATING THE REMOVAL OF HEAVY
METAL IONS FROM WASTES USING TRIPLE
SUPER PHOSPHATE (TSP)**



by
Mahamane Chapiou SOULEY GARBA

July, 2022
İZMİR

INVESTIGATING THE REMOVAL OF HEAVY METAL IONS FROM WASTES USING TRIPLE SUPER PHOSPHATE (TSP)

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Graduate School of Natural and Applied Sciences of Dokuz Eylül University
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**by
Mahamane Chapiou SOULEY GARBA**

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Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **“Investigating the Removal of Heavy Metal Ions from Wastes Using Triple Super Phosphate (TSP)”** completed by **MAHAMANE CHAPIOU SOULEY GARBA** under supervision of **PROF. DR. EROL KAYA** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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INVESTIGATING THE REMOVAL OF HEAVY METAL IONS FROM WASTES USING TRIPLE SUPER PHOSPHATE (TSP)

ABSTRACT

Heavy metal pollution is one of the global problem due to the increase of industrial and mining activities (power plants, mineral processing, metallurgical extraction, petrochemical, etc.). To solve this heavy metal pollution problem, triple superphosphate (TSP) was investigated thoroughly in this thesis for the removal of heavy metal ions from wastes. TSP was selected amongst various phosphate-based materials and fertilizers to act as the source of orthophosphate (PO_4^{3-}) which is a powerful tool for metal fixation in soil and water.

The objective of this study was to investigate the stability conditions of metal ions in an aqueous system and the treatment of contaminated wastes with triple superphosphate, an alternative to lime. TSP or monocalcium phosphate monohydrate with a chemical formula of $[\text{Ca}(\text{H}_2\text{PO}_4)_2\text{H}_2\text{O}]$ is widely used as fertilizer in the agriculture area. In this investigation, firstly, stability diagrams (Eh-pH diagrams) were constructed with HSC chemistry software to establish the predominance areas of the different species and solid/solution equilibrium in the TSP solution. Later, precipitation tests were carried out with pure metals and real wastes in TSP solutions to verify the obtained metal phosphate at the conditions determined from the stability area diagrams and confirm them through the XRD analyses of precipitated samples.

The experimental results demonstrated that TSP effectively removes heavy metals of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn from aqueous solution and real wastes. The performance of the TSP process is influenced by reaction times, metal ions and TSP concentrations. The results of XRD analysis also revealed the formation of insoluble metal phosphates $[\text{Cd}_3(\text{PO}_4)_2, \text{Co}_3(\text{PO}_4)_2, \text{Cu}_2(\text{PO}_4)\text{OH}, \text{Fe}_3(\text{PO}_4)_2, \text{FePO}_4 \cdot 2\text{H}_2\text{O}, \text{Mn}_3(\text{PO}_4)_2, \text{Pb}_3(\text{PO}_4)_2, \text{ZnHPO}_4 \text{ and } \text{Zn}_3(\text{PO}_4)_2]$ in the precipitated and describe the mechanism of TSP on heavy metal removal which includes the dissolution of TSP and precipitation of metal ions.

Keywords: Triple superphosphate, TSP (monocalcium phosphate monohydrate), heavy metal, environmental pollution, stability diagram, waste, precipitation.



AĞIR METAL İÇEREN ATIKLARIN TRİPLE SÜPER FOSFAT (TSP) İLE STABİLİZASYONU

ÖZ

Ağır metal kirliliği, endüstriyel ve madencilik faaliyetlerinin (elektrik santralleri, cevher hazırlama, metalurjik ekstraksiyon, petrokimya vb.) artması nedeniyle küresel sorunlardan biridir. Bu ağır metal kirliliği sorununu çözmek için, ağır metal iyonlarının atıklardan çöktürülmesi amacıyla bu tezde triple süperfosfat (TSP) kapsamlı bir şekilde araştırılmıştır. TSP, Toprakta ve suda metal fiksasyonu için güçlü bir araç olan ortofosfat (PO_4^{3-}) kaynağı olarak etkimek üzere çeşitli fosfat bazlı malzemeler ve gübreler arasından seçilmiştir.

Bu çalışmanın amacı, sulu çözeltisi bir sistemdeki metal iyonlarının stabilite koşullarını ve kirlenmiş atıkların kirecin alternatifi olan triple süper fosfat ile muamele edilmesini araştırmaktır. $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ kimyasal formülüne sahip TSP veya monokalsiyum fosfat monohidrat, özellikle Türkiye’de tarım alanında gübre olarak yaygın kullanılmaktadır. Bu araştırmada, ilk olarak, TSP çözeltisinde farklı türlerin baskınlık alanlarını ve katı/çözelti dengesini oluşturmak için HSC kimya programı ile stabilite diyagramları (Eh-pH diyagramları) oluşturulmuştur. Daha sonra elde edilen metal fosfatın stabilite alanı diyagramlarından belirlenen koşullarda doğrulanması ve çökeltile numunelerin XRD analizleri ile doğrulanması için TSP çözeltilerinde saf metaller ve gerçek atıklar ile çöktürme testleri gerçekleştirilmiştir.

DeneySEL sonuçlar, TSP’nin Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr ve Zn’nin ağır metallerini sulu çözeltiden ve gerçek atıklardan etkili bir şekilde çöktürdüğünü göstermiştir. TSP prosesinin performansı reaksiyon sürelerinden, metal iyonlarından ve TSP derişimlerinden etkilenmektedir. XRD analizinin sonuçları ayırca çözünmeyen metal fosfatların $[\text{Cd}_3(\text{PO}_4)_2, \text{Co}_3(\text{PO}_4)_2, \text{Cu}_2(\text{PO}_4)\text{OH}, \text{Fe}_3(\text{PO}_4)_2, \text{FePO}_4 \cdot 2\text{H}_2\text{O}, \text{Mn}_3(\text{PO}_4)_2, \text{Pb}_3(\text{PO}_4)_2, \text{ZnHPO}_4 \text{ and } \text{Zn}_3(\text{PO}_4)_2]$ çökeltide oluşumunu ortaya koymuş ve TSP’nin ağır metal giderimi üzerine TSP’nin mekanizmasını tanımlamıştır.

Anahtar Kelimeler: Triple süper fosfat, TSP (monokalsiyum monohidrat monofosfat), ağır metal, çevre kirliliği, stabilite diyagram, atık, çöktürme.



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ABBREVIATIONS

AA: Atomic absorption

ΔG : Gibbs energy

Eh: Potential redox

HCl: Hydrochloric acid

HF: Hydrofluoric acid

ICP: Inductively coupled plasma

K: Constant equilibrium

LOD: Limit of detection

Log: Logarithm

LOQ: Limit of quantification

M: Molar

MCP: Maximum concentration permissible

Me: Metal

MCPM: Monocalcium phosphate monohydrate

NC: Not calculate

Nd: Not detected

NA: Not available

Ox: Oxidant

PSD: Particle size distribution

RE: Removal efficiency

Red: Reductant

T: Temperature

TSP: Triple superphosphate

XRD: X-ray diffraction

XRF: X-ray fluorescence

CHAPTER ONE

INTRODUCTION

1.1 Background Information

For thousands of years, many countries have established plants and factories in order to satisfy their needs for economic development or to become industrialized countries. However, those industries especially mining, mineral processing plant, metallurgical extraction, and other industries (pesticides, automobiles, chemicals) produce a large quantity of waste during their activities. Similarly, the defy of increasing the production and dealing with low-grade ore that the mining companies are facing currently results in generating a huge amount of waste. According to Lottermoser (2010) “Mining, beneficiation and extraction of metallic ores with the average grade approximatively 0.5% produce 10,000 million tons (Mt) of wastes whereas 1230 Mt of wastes were produced from the production of 2460 t of gold with average grade approximatively 2 ppm”.

Generally, wastes are considered as non-valuable minerals material and classified as solid, liquid, or gaseous by-products of mining, mineral processing, and metallurgical extraction (Ndlovu et al., 2017). Depending upon the sources, the wastes have a different designation (Figure 1.1). For example, the beneficiation of ore usually provides two products: (1) concentrate containing valuable minerals and (2) waste called tailings through comminution (i.e., crushing, grinding, classification) and separation techniques. In the mining operation, the wastes produced by drilling and fragmentation are referred to the mining wastes. These tailings and mining wastes with different particles size transferred into the storage areas constitute a threat to the environment because they contain metals that are potentially leached in the surface or groundwater (Baba & Tayfur, 2011; Bian et al., 2009; Helios Rybicka, 1996; Yolcubal et al., 2016). In addition, the interaction of the effluents with sulfide tailing impoundment led to oxidation and generate acid mining drainage (AMD) water (Ritcey, 2005). In this situation, these industries are constrained to treat contaminated

wastes and wastewater in order to minimize the risk of contamination and meet the environmental regulations prescribed by the government.

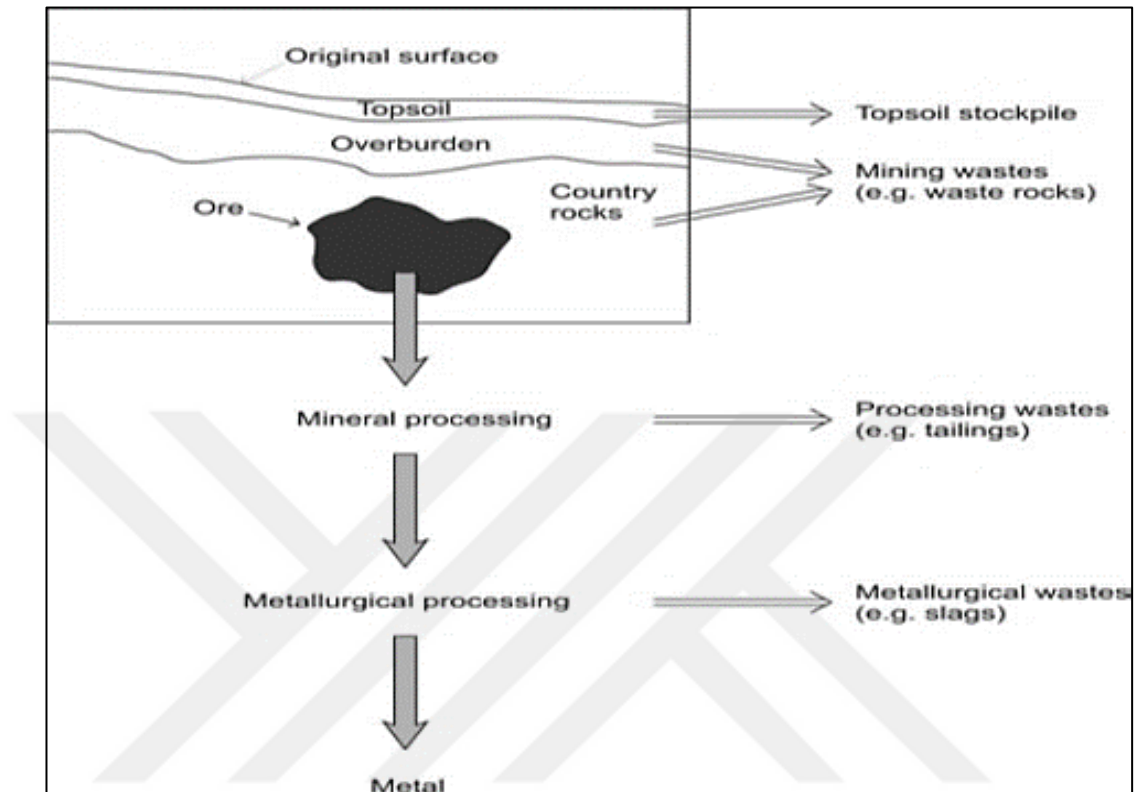


Figure 1.1 Different types of wastes generated from mining, mineral and metallurgical processing (Lottermoser, 2010)

1.2 Problem Statements

The disposal of wastes from metal mining or industrial activities to the environment causes several contaminations in the soils and water due to the presence of heavy metals from these wastes. Furthermore, most of the heavy metals discharged directly or indirectly into the environment are not biodegradable and the dangers of their bioaccumulation in the food chain represent one of the major environmental and health problems of our modern society. To satisfy the discharge regulations and eradicate any possible negative impacts on human health, the heavy metals should be removed. For many years, several technologies have been developed and extensive research has been done on heavy metal remediation (Gong et al., 2018). These remediation technologies involves adsorption, precipitation, membrane filtration, electrochemical oxidation, ion

exchange, coagulation, flotation (Bashir et al., 2019; Greenlee et al., 2009; Hwang et al., 2007). However those methods have limitations in terms of high operational and maintenance cost, and generation of waste (Fu & Wang, 2011). Therefore, there has been substantial research recently in the area of treatment technologies to find low-cost materials that have metal-binding capabilities. The application of phosphate-based for in situ heavy metal immobilization has been shown in numerous studies to be a practical and beneficial remediation technique (Cao et al., 2009; Ma et al., 1993). In addition, heavy metals in water and soil can be successfully immobilized by phosphate minerals such as hydroxyapatite (HA) and phosphate rock (PR) (Boisson et al., 1999; Cao et al., 2004; S. Chen et al., 2007a; Corami et al., 2007, 2008b, 2008a; Marchat et al., 2007).

In this study, triple superphosphate (TSP) was chosen to serve as the source of phosphate ions (PO_4^{3-}) which is a prominent reagent for heavy metal immobilization in contaminated waste and water. TSP fertilizer is the most commonly used in the agriculture area and its chemical name is monocalcium phosphate monohydrate with a chemical formula of $[\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}]$.

1.3 Thesis Objectives

The main objectives of this research were to investigate an alternative chemical called TSP for toxic metal removal capabilities in wastewater and wastes. To reach the above-mentioned aim, the following specific objectives were outlined:

1. Characterization of TSP (Solubility test, moisture content, chemical and mineralogical analysis).
2. Sampling and sample preparation for physicochemical analyses (standard stock solution of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn pure metals; real wastes).
3. Constructing the stability area diagrams of TSP and metals system by using the HSC chemistry program [Eh-pH, log $\{\text{C}_{\text{Metal}}\}$ -pH and $\{\text{C}_{\text{Ligand Complex}}\}$ -pH].
4. Performing experimental tests: precipitation tests of TSP with the standard of metals ions; treatment of real waste containing metals ions by TSP).

5. Analyzing the liquid samples collected from the precipitation test by atomic absorption (AA) and inductively coupled plasma (ICP).
6. Determining the mineralogical composition of precipitates and residues by x-ray diffraction (XRD).
7. Elucidating TSP mechanism for the stability of metals ion and heavy removal from real contaminated wastes.

1.4 Structure of the Thesis

This thesis structured in seven (7) chapters, has four main parts namely, review of heavy metal removal methods and previous studies conducted on the utilization of triple superphosphate (TSP) in the removal of heavy metals, characterization of TSP for its application as precipitating agent, solution chemistry of metal removal by TSP, and heavy metal removal from contaminated wastes and laboratory wastewater using TSP. These chapters are presented as follows:

Chapter one presents an overview of wastes and their disposal impacts into the environment. The problem statement is given, followed by the thesis objective and significance of the research.

Chapter two emphasizes the sources of heavy metals, their toxicities to human exposure and their regulations. Thus, the conventional removal methods for heavy metals are discussed in detail followed by a summary of their disadvantages.

Chapter three outlines the properties of TSP and its application area, and reviews the use of TSP for the remediation of wastes containing leachable metal ions.

Chapter four describes firstly the characterization of TSP which includes tests of solubility, moisture content and chemical analysis of TSP, and determination of the mineralogical composition of raw and insoluble TSP employing an x-ray diffractometer. Secondary precipitations of pure metal ions are performed with TSP

and lime $\text{Ca}(\text{OH})_2$ separately, and show the reason of selecting TSP in this study rather than lime through the comparison of the efficiency of both precipitating agents.

Chapter five elucidates the materials utilized in this thesis, the process applied for constructing the stability speciation (Eh-pH) diagrams HSC 6 chemistry program, the characterization methods for determination of physicochemical properties of waste samples and the precipitation procedures for heavy metals ion removal in aqueous solution and real wastes (industrial and mining).

Chapter six highlights the results and discusses the obtained findings from thermochemical modelling and the precipitation experiments of metals ions in an aqueous solutions and waste contained leachable metal ions.

Chapter seven gives a summary of the significant results (findings) and proposes some recommendations for future research especially the application of TSP to stabilize heavy metals at industrial scale.

1.5 Significance of the Thesis

This thesis shows the importance of using TSP for heavy metal removal rather than the application of calcium hydroxide ($\text{Ca}(\text{OH})_2$). The outcomes of this thesis enhance the preceding studies on the treatment of wastewater or contaminated wastes by TSP. The investigation of TSP solution chemistry for metal removal using stability speciation diagrams (Eh-pH diagram) as well as performing precipitation experiment and x-ray diffraction analysis of precipitate (obtained after metal precipitation with TSP) is the contribution of environmental chemistry because this method permits to identify which metal phosphate compounds and species are stables, to verify and validate the hypothesis. In other words, these results represent a novelty of this thesis and consolidate the TSP mechanism which involves its solubility and insoluble phosphate compound via the precipitation process. For the experimental tests of real wastes (industrial and mining wastes) with TSP, the findings demonstrate the benefit

and the performance of TSP in the stabilization of single and multi-metal ions at the same pH.



CHAPTER TWO

HEAVY METALS, SOURCES AND TOXICITIES, REMOVAL METHODS

This second chapter deals with heavy metal sources and their removal methods. Subtitle 2.1 explains the impact that heavy metals can cause on the environment and their toxic effects on human life. Thus, subtitle 2.2 enumerates the different removal methods and their efficiencies in the decontamination of soil or wastewater.

2.1 Heavy Metals Sources and Toxicities

The term “heavy metals” as defined by (Thornton, 1995) are metals that have a density greater than 5 g cm^{-3} (i.e., Fe, Cu, Pb, Zn, Sn, Ni, Co, Mo, W, Hg, Cd, etc.). These metals are also toxic and are released into the soil and water through different sources. The two main sources of heavy metals are natural and anthropogenic (G. Liu et al., 2018; Masindi & Muedi, 2018; Sindern et al., 2016). The natural origin of the latter is the consequence of the geogenic process which includes the dissolution of metalliferous rock and igneous eruption (Garbarino et al., 1995; Ali et al., 2019). Whereas the anthropogenic sources that contribute to heavy metal contamination are from various industries such as mining, metal finishing, electroplating, battery manufacture, glass, ceramic, paint, pigment, textile, electronic waste, paper and pulp industries, leather tanning, petrochemicals, etc. (Dudka & Adriano, 1997; G M Hettiarachchi et al., 2001).

Both origins of heavy metals contaminate the environment and represent a danger to human health. For example, the environmental contamination from the mobility of Pb may result in important adverse consequences such as loss of ecosystems, human and animal health problems and economical losses (Bulut, 2006; Pruvot et al., 2010). Regarding iron pollution, iron (II) oxidizes with the pyrite (FeS_2) ion to produce acid mining drainage (AMD) and polluted surface and underground water. The high-level concentration of iron in drinking water induces human health issues such as staining fixtures and laundry and causes an astringent taste (Sarkar & Shekhar, 2018). Figure 2.1 elucidates the effect of certain heavy metal toxicities on human life (García-Niño

& Pedraza-Chaverri, 2014). Although heavy metals harm humans via air exposure, water and foods, some metals like Cu, Fe, Mn and Zn are crucial to the human organism at the permissible level. Based on the report furnished by the WHO (World Health Organization, 2021) the permissible limit concentrations of heavy metals in drinking water are in order mercury (0.001 mg/L), cadmium (0.005 mg/L), arsenic (0.01 mg/L), lead (0.01 mg/L), nickel (0.02 mg/L), chromium (0.05 mg/L), cobalt (0.1 mg/L), iron (0.3 mg/L), manganese (0.5 mg/L), copper (2 mg/L) and zinc (5mg/L).

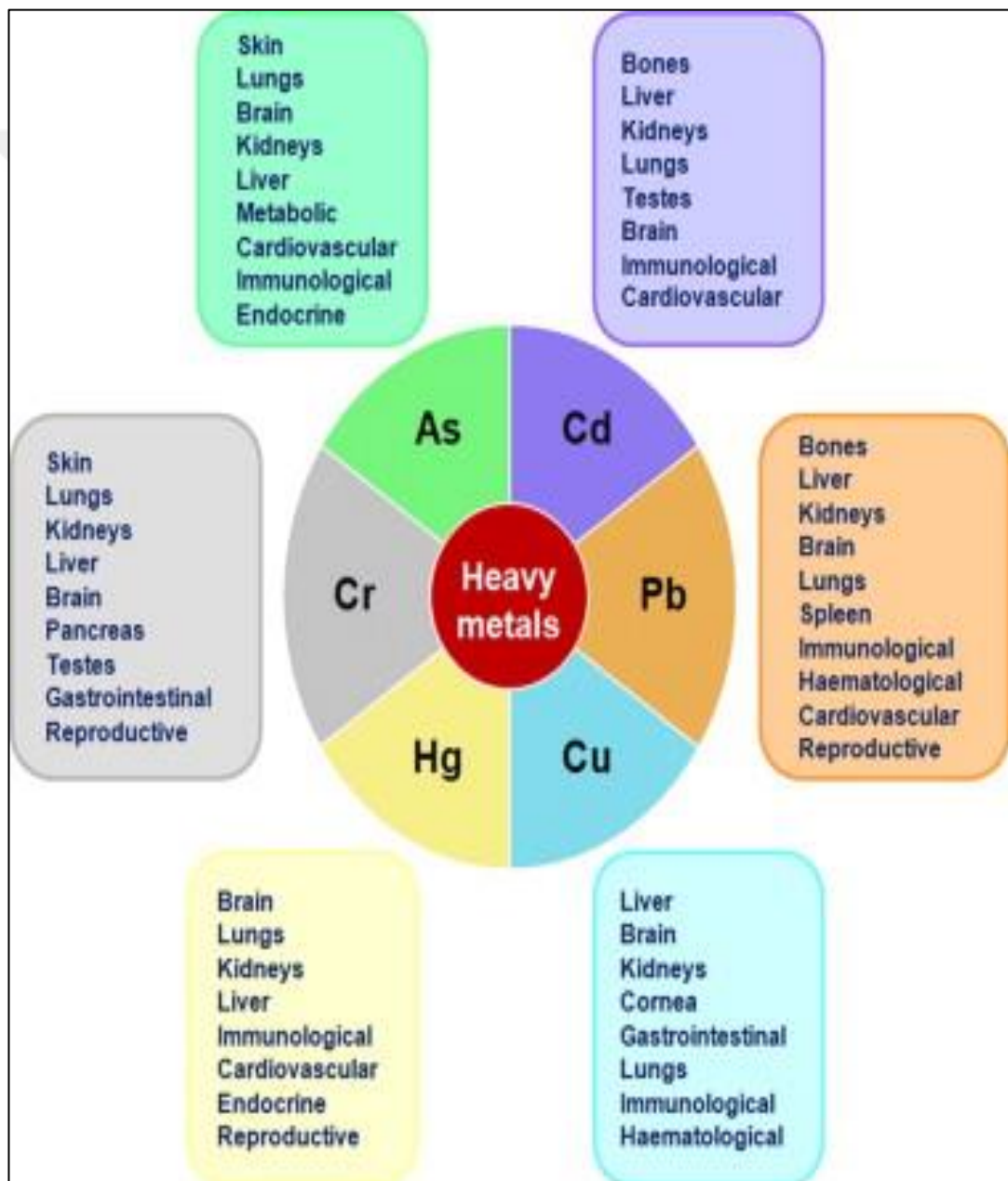


Figure 2.1 Heavy metal toxicity effects on human health (García-Niño & Pedraza-Chaverri, 2014)

2.2 Heavy Metals Removal Methods

2.2.1 Adsorption Method

Adsorption is considered currently an effective and cheap method for removing heavy ions from wastewater (Esmaeili & Foroutan, 2015). This method is performed by the attachment of soluble gas or liquid onto the adsorbent surface. Depending on the bonding types, the adsorption method can be either physisorption or chemisorption. The physisorption is realized when the molecules of adsorbent and adsorbate come together via the forces of van der Waals, whereas the chemisorption, the concerned molecules are bonded to the adsorbent surface through a strong covalent chemical attachment.

Various adsorbents have been utilized in the adsorption method: activated carbon which is the most used for the immobilization of organic pollutants (Jusoh et al., 2007), coal fly ash (Weng & Huang, 2004), biomass (Rezić et al., 2011), natural unwanted product (Saka et al., 2012), etc. The criteria that determine the quality of the adsorbent is its adsorption capacity and is influenced by the surface characteristics of the adsorbent and its dosage. Cui et al. (2015), stated that the results of adsorption test indicate 95.5% of Pb, 94.9% of Hg and 95.7% of Cu concentrations were reduced with low dosage of EDTA adsorbent, while all metals concentrations were practically zero at high dosage.

2.2.2 Chemical Precipitation Method

The precipitation process is widely used by many industries because of its simplicity and low operating cost. Figure 2.2 present a brief explanation of experimental precipitation setup. In this method, the precipitant agent reacts with heavy metals to form a stable compound. The familiar conventional precipitation processes include hydroxides and sulfides precipitations (Fu & Wang, 2011).

Hydroxide precipitation consists of converting heavy metal ions to sparingly soluble metal precipitate by adding alkaline precipitant agents (NaOH , CaO , Ca(OH)_2 and Mg(OH)_2). In the literature, Chen et al. (2009) stated that the achieved removal of Zn^{2+} , Pb^{2+} , Cu^{2+} and Cr^{3+} with 100 mg/L initial concentration by lime ranged from 99.4% to 99.6% at pH 7 and 11 values. Furthermore, the experimental study indicated the removal percentage of Zn^{2+} , Cu^{2+} , and Pb^{2+} were between 76.1% and 99.9% at optimum pH 5.9-11.9 depending on the hydrated lime dosage (Q. Chen et al., 2018a). In some conditions, the mixture of Ca(OH)_2 and NaOH reagents has shown great success on Cu^{2+} and Cr^{3+} ions removal from polluted water (Mirbagheri & Hosseini, 2005). However, the disadvantage of hydroxide precipitation is that optimum pH is required for each metal ion to accomplish high removal efficiency (Brbooti et al., 2011). Also, further heavy metal removal may be needed because of high quantities of sludge generated by hydroxide precipitation (Ain Zainuddin et al., 2019).

The sulfide precipitation has the same basic working principle as hydroxide precipitation. In the precipitation process, sulfide agents like sodium sulfide (Na_2S), sodium hydrosulfide (NaHS), ferrous sulfide (FeS), hydrogen sulfide (H_2S) and calcium sulfide (CaS) transform soluble metal ions into almost insoluble sulfide compounds. Sulfide precipitation as hydroxide precipitation is considered as effective method. For example, hydrogen sulfide precipitates up to 99 % of Cu, 94% of Zn and 92% of Pb from aqueous solutions (Alvarez et al., 2007). Even though the high heavy metal ions removal capacity compared to hydroxide precipitation, the probability of realizing free toxic shows the limitation of the sulfide precipitation (Blais et al., 2008).

In general, both precipitation processes are controlled by solubility products which depend on the pH. Figure 2.3 shows the solubility of metals for hydroxides and sulfides precipitations (EPA, 1980). Besides hydroxide and sulfide precipitant, carbonates and phosphate are also utilized in precipitation. The carbonate (CaCO_3 , Na_2CO_3) precipitation aims to stabilize directly heavy metals by precipitation or transforming hydroxide onto carbonate (Kim et al., 2021; Koutsoukos & Kontoyannis, 1984; Mugwar & Harbottle, 2016). Its efficiency is higher than hydroxide precipitation, especially in cadmium ions (Habte et al., 2020; Patterson et al., 1977). Regarding

phosphate precipitation, Wang et al. (2008) mentioned that in the treatment of polluted waste, this remediation is becoming increasingly common. Further details of phosphate precipitation method will be provided in the next chapter.

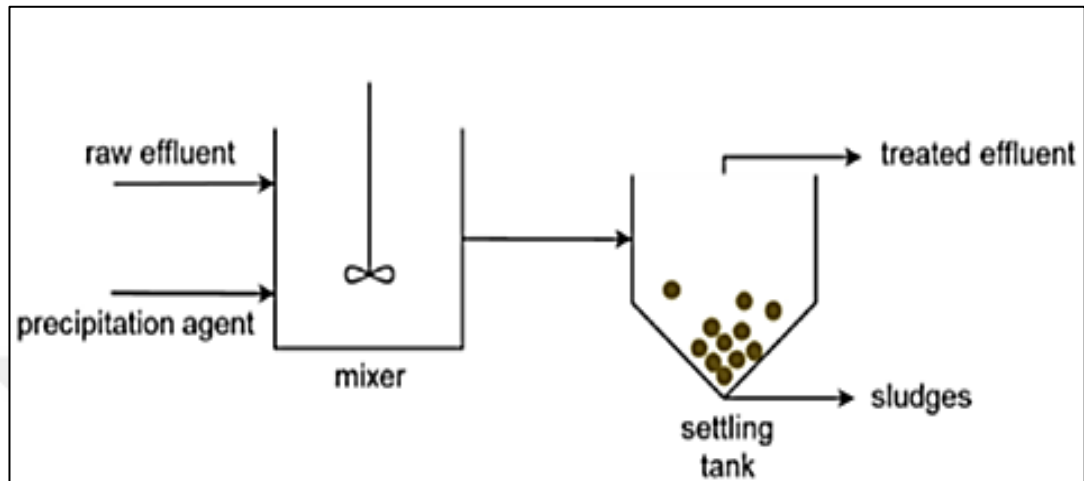


Figure 2.2 A simplified experimental precipitation setup (Vareda et al., 2019)

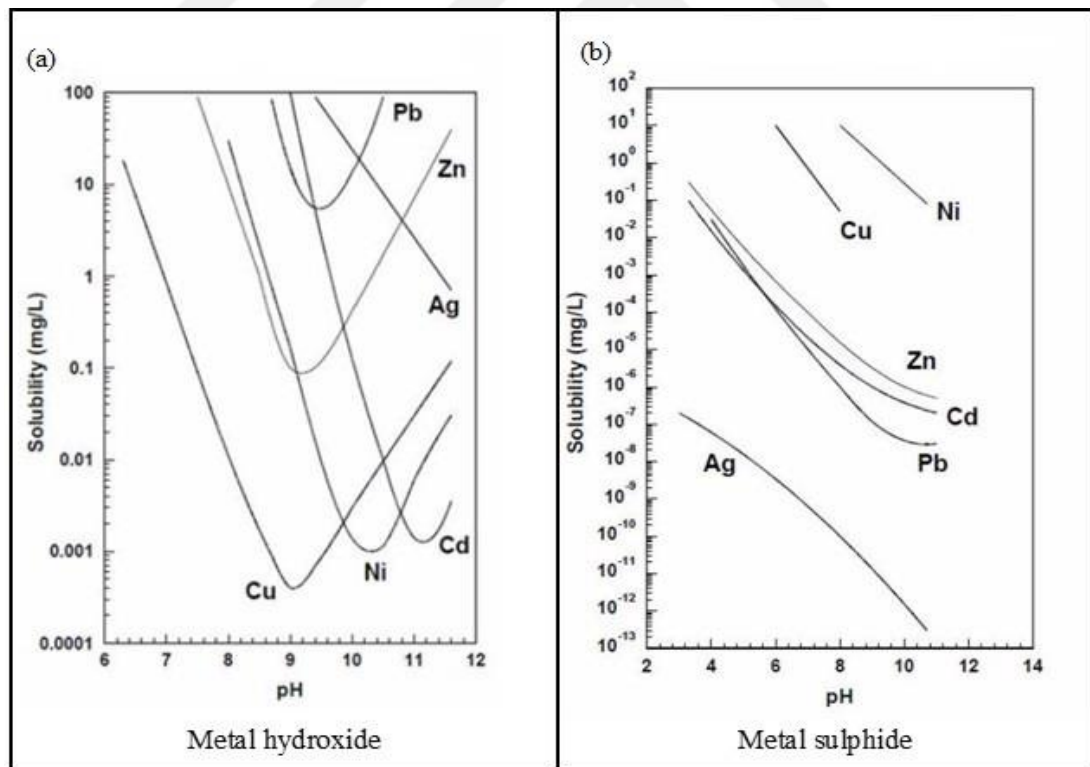


Figure 2.3 Heavy metals solubility curve for precipitation. a. Hydroxide precipitation, b. Sulfide precipitation (EPA, 1980)

2.2.3 Ion-exchange Method

The method of ion exchange is extensively used to treat wastewater containing toxic metal ions because of its great removal efficiency and rapid kinetics. According to Pehlivan & Altun (2007) “the maximum removal of Cu^{2+} , Zn^{2+} , Ni^{2+} and Cd^{2+} ranged from 98 to 99% and 95% for Pb^{2+} using ion-exchange method”. The principle of this technique is exchanging a counter ion of the exchanger resin with the ion in the aqueous solution. The two types of resin are cationic and anionic exchange resin as illustrated in Fig. 2.4 (Singhon, 2014). The ion exchange resin consists of insoluble polymeric matrices containing a functional group and the most common cations exchangers are strongly acidic resins with sulfonic acid groups ($-\text{SO}_3\text{H}$) and weakly acid resins with carboxylic acid groups ($-\text{COOH}$). In addition, the metal ions are replaced by the hydrogen ions when the solution of metal ions enters into the cation columns.

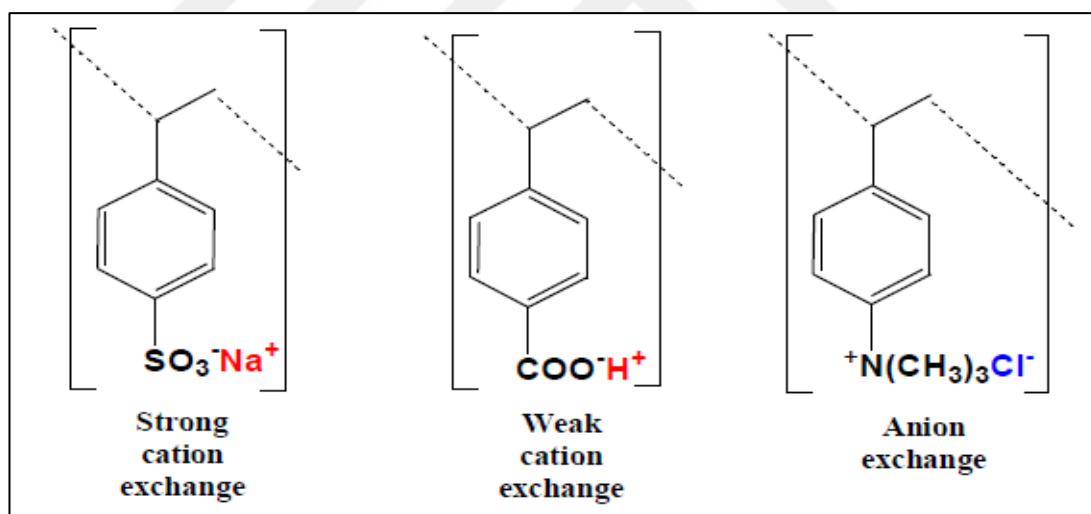


Figure 2.4 Polystyrene cation and anion exchange resins (Singhon, 2014)

2.2.4 Flotation Method

The treatment of hazardous metal ions from wastewater and tailings by the flotation method has been amplified currently. The particularity of this method is the high recovery of metals compared to others. According to Taseidifar et al. (2017) “the flotation technique can remove more than 99% of As, Cd, Cr, Hg and Pb in water”.

The flotation process consists of separating metals from the liquid phase using bubble attachment, which originated in the mineral processing plant. Similarly, the same mechanisms are applied by Rubio et al. (2002) in the decontamination of polluted water. Shammass et al., (2010) reported that the wastewater treatment by flotation can be summarized in three steps as follows:

1. Air-bubble formation/generation/introduction into the system;
2. Contact between solid particles or aggregates and air bubbles (or enclosure of bubbles into aggregates while those are forming);
3. The actual rise of the air bubble–solids complex as it is enhanced or hindered by the continuous flow through the reactor.

2.2.5 Membrane Filtration Method

Membrane filtration technology is defined as a pressure-driven process, flexible and space-saving. The membrane filtrations used to remove metals from wastewater are divided into four categories: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and hyperfiltration or reverse osmosis (RO). The separation process is achieved by MF and UF membranes via mechanical sieving, while capillary flow or solution diffusion is responsible for separation in NF membranes and RO membranes (Carotenuto et al., 2014). The experimental studies indicated high removal efficiencies of Cd^{2+} , Cu^{2+} , Cr^{3+} and Zn^{2+} (93% of Cd, 100% of Cu, 86% Cr and 95% of Zn respectively) were achieved using the membrane filtration method (Juang & Shiau, 2000; Qdais & Moussa, 2004).

2.2.6 Phytoremediation Method

Phytoremediation is a sustainable and environmental technology for the treatment of hazardous (heavy) metals from contaminated environments. The application of plants (algae, or fungi) to recover, stimulate the breakdown of pollutants in soil, or decontamination of hazardous metals has become prominent in phytoremediation method (Meagher, 2000). In phytoremediation, there are five types (phytodegradation,

phytoextraction, phytostabilization and rhizofiltration) and Figure 2.5 describes their mechanisms (Rigoletto et al., 2020). For the treatment of sediment containing heavy metals, phytoremediation studies show an efficient stabilization of Cd, Fe, Mn and Zn (Peng et al., 2009; Suresh & Ravishankar, 2004). Furthermore, Sun et al., (2013) reported that the use of macrophyte plants successfully immobilizes Cr, Cu, Fe and Zn ions from wastewater through the phytoremediation.

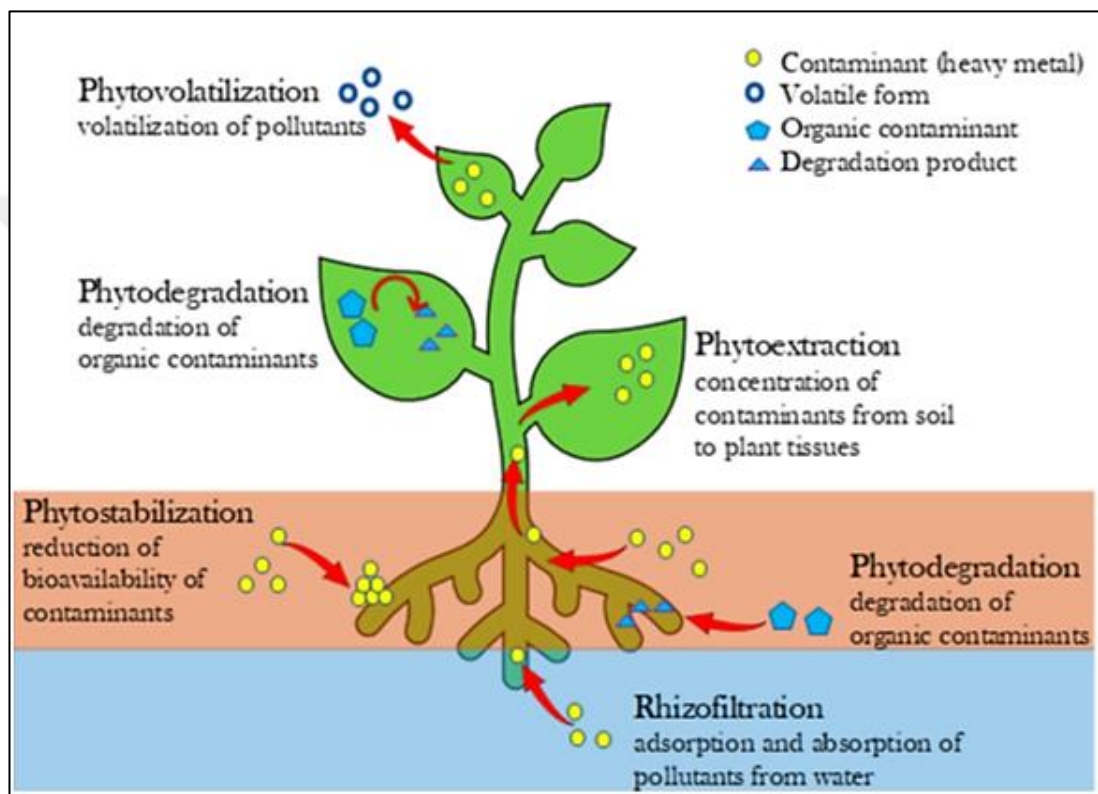


Figure 2.5 Description of different types of phytoremediation (Rigoletto et al., 2020)

2.3 Conclusion

The heavy metals removal methods such as adsorption, ion exchange, chemical precipitation, membrane filtration, flotation and phytoremediation were applied to clean up polluted sites, wastewater and mining wastes. These methods differ from each other according to their principles and operations mode and have some disadvantages. The disadvantage of adsorption method is poor selectivity with the generation of waste products and demands high cost for regeneration. Chemical precipitation produces a large quantity of waste and is ineffective when the heavy metal concentration is low.

For ion exchange, the high cost required by the method and the contamination of bacteria during regeneration. Although Flotation is well known as a highly efficient technology for removing heavy metals, its disadvantage is the requirement of huge initial investment and consumes an important amount of energy. Membrane filtration is simple and removes successfully heavy metals, but it is also too expensive to integrate at the industrial level. On the other hand, the long duration of the process and poor removal efficiency for certain heavy metals limit the application of phytoremediation even though it is an environment-friendly and cheap process.



CHAPTER THREE

TRIPLE SUPERPHOSPHATE: PROPERTIES AND UTILIZATION, REVIEW OF HEAVY METALS REMOVAL BY TRIPLE SUPERPHOSPHATE

3.1 Introduction

The phosphate-based materials such as diammonium phosphate (DAP), hydroxyapatite (HAP), phosphate rock (PR), phosphoric acid (H_3PO_4), triple superphosphate (TSP), tricalcium phosphate (TCP), etc., have been used for the stabilization of heavy metals. Their applications to treat the contaminated environment are effective and are reflected to be environment friendly (Aide et al., 2019; Chen et al., 2007; Chrysochoou et al., 2007; Hong et al., 2010; Li et al., 2021; Liu et al., 2021; Munksgaard et al., 2012; Raicevic et al., 2009; Rizwan et al., 2021; Wang et al., 2008; Wang et al., 2001; Waterlot et al., 2011). In addition, researchers have demonstrated that the use of phosphate-based materials in the metal remediation technology is cost-effective (Hafsteinsdóttir et al., 2015; Raicevic et al., 2005, 2009; Valipour et al., 2016).

The dissolution, precipitation, ion exchange, sorption and adsorption processes are the main mechanism that characterizes the metal phosphate fixation. For example, numerous studies were noted that the removal (stabilization) of toxic metals in solution is achieved by precipitation and formation of stable metal phosphate (Ma et al., 1993; Naeem et al., 2003; Pigaga et al., 2002; Seshadri et al., 2017; Weber et al., 2015). In most cases, the formation of pyromorphite after the application of phosphorous into soil or wastewater is the most successful treatment reported by the previous studies (Basta & McGowen, 2004; Chrysochoou et al., 2007; Cotter-Howells et al., 1994; Nriagu, 1974; Ruby et al., 1994). Despite this statement, researchers argue about the pyromorphite formation. Some findings of experimental tests demonstrated Pb stabilization using phosphate amendment is accomplished by ion exchange method with calcium (Cao et al., 2002; Melamed et al., 2003; Suzuki et al., 1984). While, Dong et al. (2010) and Lei et al. (2015) have mentioned metal phosphates

(pyromorphite) are formed by adsorption of metal cation for calcium divalent in the phosphorous compound. Figure 3.1 recapitulated the mechanism of lead stabilization by phosphate-based materials (Zeng et al., 2017).

On the other hand, the formation of metal complexations can be the result of heavy metal stabilization by phosphate-based materials. In the literature, the test results have shown Cd, Cu, Fe, Pb and Zn are mainly removed by phosphate due to surface complexation rather than the metal phosphate occurrence (Cao et al., 2009; S. Chen et al., 2007b; Ruiti & Thayer, 2015). Similarly, throughout this process, apatite stabilizes approximately the total concentrations of lead, manganese, cobalt, copper, cadmium, magnesium, barium, uranium and thorium from contaminated sludge (Mulligan et al., 2001; Raicevic et al., 2009).

Amongst phosphate-based materials mentioned above, triple superphosphate contains a consequent amount of the orthophosphate ions (PO_4^{3-}) which is an effective reagent for metal ions fixation in soil and aqueous solutions. This present chapter discusses the overview of triple superphosphate proprieties, and the review of triple superphosphate as means to stabilize heavy metals from contaminated wastes and polluted water.

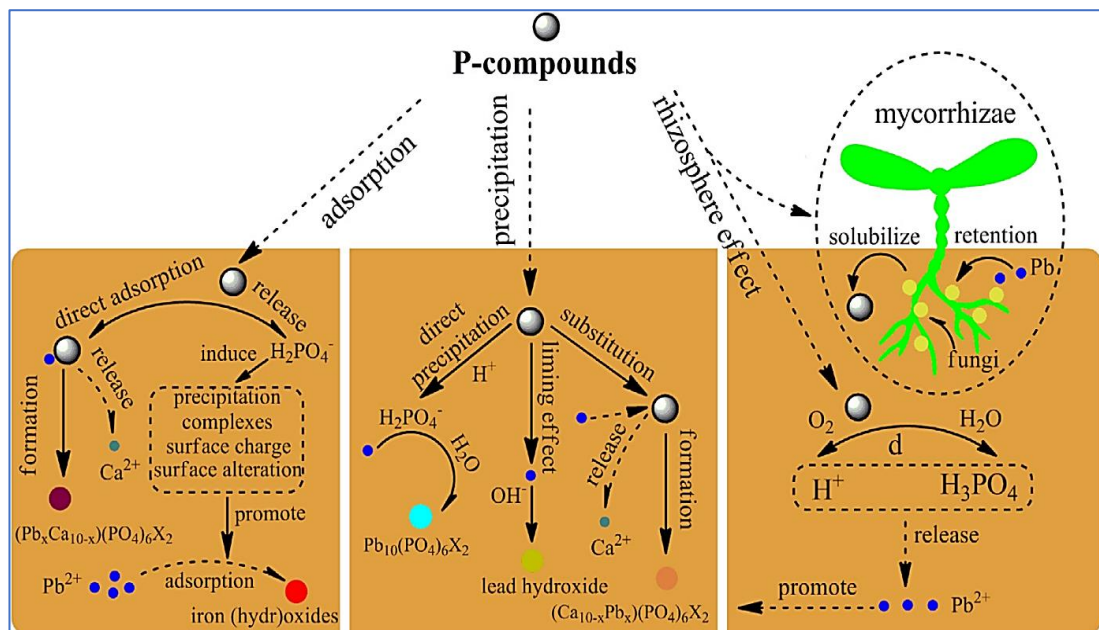
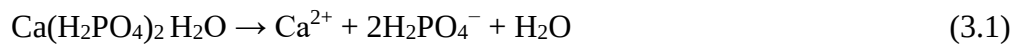


Figure 3.1 Phosphate compound mechanisms for lead removal (Zeng et al., 2017)

3.2 Triple Superphosphate, its Properties and Utilization

Historically, Triple superphosphate (TSP) was the first commonly analyzed phosphorus (P) fertilizer to gain widespread usage in the twentieth century, and it remained a prominent P source in the USA and other nations till the mid-1970s (Russel & Williams, 1977). As commercial fertilizer, TSP is produced by a mixture of ground phosphate rock and phosphoric acid. Figure 3.2 enumerates the different steps in the TSP process. There are two types of triple superphosphate: non-granular and granular. A non-granular TSP is normally made by mixing finely pulverized phosphate rock with liquid phosphoric acid in a mixer. Whereas granular TSP is produced by spraying a ground phosphate rock over the large particles, followed by the reaction of phosphoric acid in a cone-style mixer (Hijran Z. Toama, 2017).

TSP with chemical name as monocalcium monophosphate monohydrate has properties as follows: Chemical formula: $\text{Ca}(\text{H}_2\text{PO}_4)_2\text{H}_2\text{O}$; the proportion of P_2O_5 45%, Ca:13-15%; Water-soluble P: > 81% (Rajan et al., 1994). In an aqueous environment, TSP dissociates as (Varma et al., 1979):



Lindsay (1979) reported the solubility of monocalcium phosphate (TSP) into calcium ion and dihydrogen phosphate ion occurs near pH 4.7, with the formation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ as brushite at pH value near 1.5 and finally the formation of monetite (CaHPO_4) decreasing the pH to near 1.0 (Figure 3.3).

The commercial triple superphosphate is generally employed for the fertilization of soil. In Turkey, TSP is widely used in agricultural areas for plant growth, especially in a greenhouse (Yildiz et al., 2008). Apart from agriculture used; TSP is considered as a precipitant agent for metal ions removal. Its utilization in heavy metal removal will be discussed in the following section 3.2.

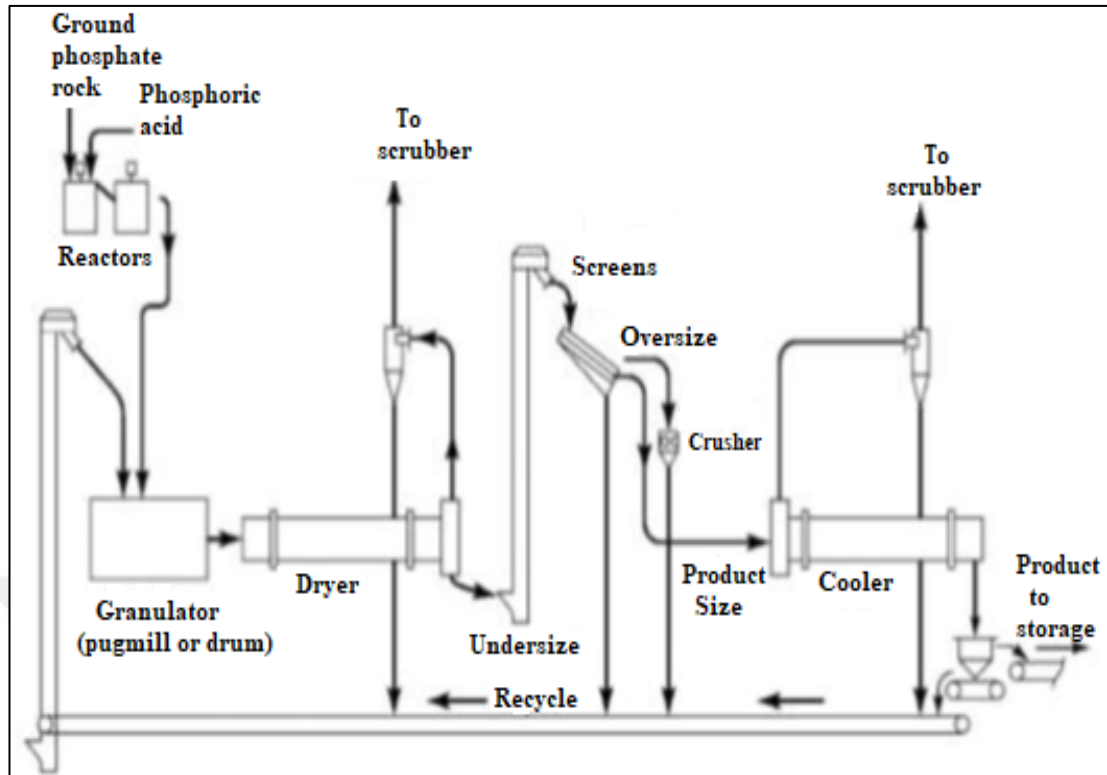


Figure 3.2 Flowsheet for the production of commercial triple superphosphate (Roy, 1976)

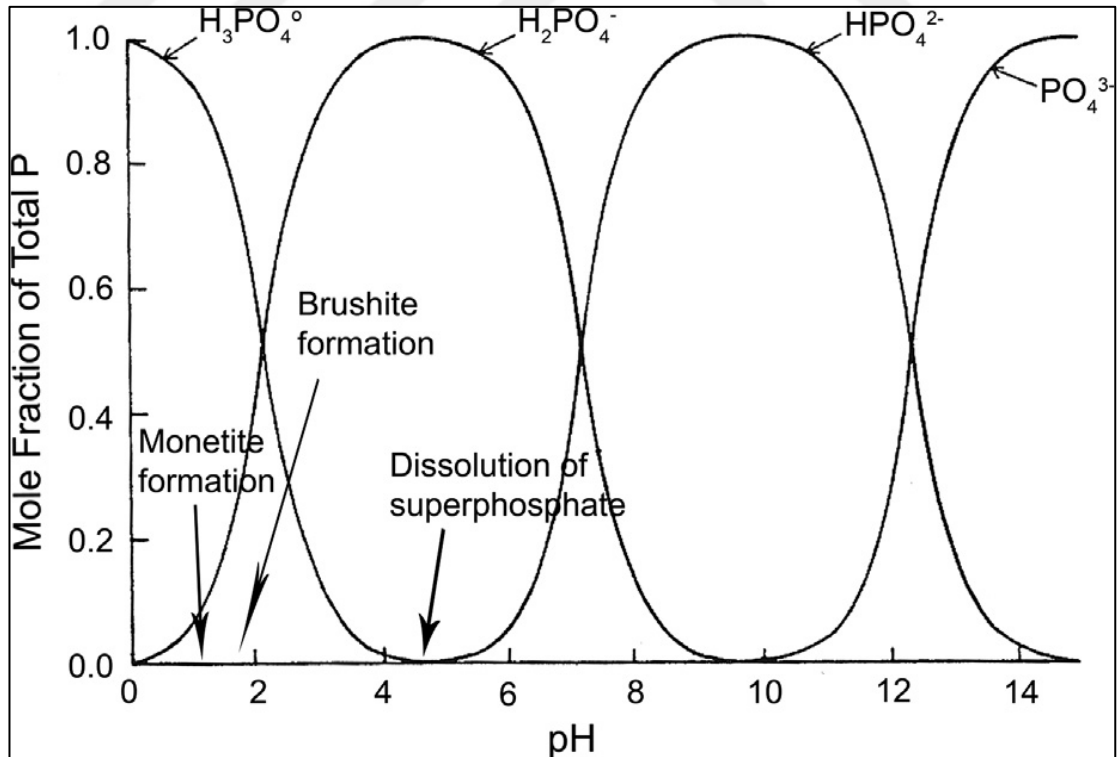


Figure 3.3 Phosphate dissociation depending on pH (Lindsay, 1979)

3.3 Review of Heavy Metals Removal using Triple Superphosphate

Triple superphosphate is classified in P-water soluble group and can be an excellent precipitating reagent for heavy metals treatment because it is an important source of orthophosphate. Wang et al. (2001) reported that the stabilization efficiency of lead, zinc, cadmium and copper ions is better compared to that of dicalcium phosphate dihydrate due to the high content of orthophosphate (76%) in TSP. The following Figure 3.4 enumerates the metals that were stabilized by ion orthophosphate (Hafsteinsdóttir et al., 2015). As stated by Nriagu (1984), the production of mineral phosphate occurred through the interaction of metal with PO_4^{3-} ions.

Scientists in soil science have shown TSP's ability to stabilize heavy metals in wastewater and waste (Aide et al., 2019; Basta & McGowen, 2004; K. Farrell-Poe & Etzel, 1991; Ganga M. Hettiarachchi et al., 2000; Ganga M. Hettiarachchi & Pierzynski, 2002; Labgairi et al., 2020; Liang et al., 2012; Mignardi et al., 2013; Weber, 2014). In terms of effectiveness, TSP performs better for some metals compared to others and according to the experimental methodologies applied. The test results obtained in previous studies indicated that 89 to 99 % of Pb were stabilized by triple superphosphate (Brown et al., 2004; Cao et al., 2002; Stanforth & Qiu, 2001). Similarly, 96% of Cd concentration was reduced by the use of 2 molar TSP (Thawornchaisit & Polprasert, 2009). For the treatment of wastes containing multi-metal ions, triple superphosphate application to Majed Soleiman sludge provides 99% of Pb, 80% of Cd, 70% of Ni and 67% of Cu as stabilization rate (Valipour et al., 2016). In contrast, Maenpaa et al. (2002) showed that triple superphosphate is less effective by removing 70% of Pb, 60% of Zn and 57% of Cd in polluted soil.

Hydrogen H																		Helium He					
Lithium Li	Beryllium Be																	Boron B	Carbon C	Nitrogen N	Oxygen O	Fluorine F	Neon Ne
Sodium Na	Strontium Mg																	Aluminum Al	Silicon Si	Phosphorus P	Sulfur S	Chlorine Cl	Argon Ar
Potassium K	Calcium Ca	Scandium Sc	Titanium Ti	Vanadium V	Chromium Cr	Manganese Mn	Iron Fe	Cobalt Co	Nickel Ni	Copper Cu	Zinc Zn	Gallium Ga	Germanium Ge	Arsenic As	Selenium Se	Bromine Br	Krypton Kr						
Rubidium Rb	Strontium Sr	Yttrium Y	Zirconium Zr	Niobium Nb	Molybdenum Mo	Technetium Tc	Ruthenium Ru	Rhodium Rh	Palladium Pd	Silver Ag	Cadmium Cd	Indium In	Tin Sn	Antimony Sb	Tellurium Te	Iodine I	Xenon Xe						
Cesium Cs	Barium Ba	Lanthanides L	Hafnium Hf	Tantalum Ta	Tungsten W	Rhenium Re	Osmium Os	Iridium Ir	Platinum Pt	Gold Au	Mercury Hg	Thallium Tl	Lead Pb	Bismuth Bi	Polonium Po	Astatine At	Radon Rn						
		Actinides A																					
		L	Lanthanum La	Cerium Ce	Praseodymium Pr	Neodymium Nd	Promethium Pm	Samarium Sm	Europium Eu	Gadolinium Gd	Terbium Tb	Dysprosium Dy	Holmium Ho	Erbium Er	Thulium Tm	Ytterbium Yb	Lutetium Lu						
		A	Actinium Ac	Thorium Th	Protactinium Pa	Uranium U	Neptunium Np	Plutonium Pu	Americium Am	Curium Cm	Berkelium Bk	Californium Cf	Einsteinium Es	Fermium Fm	Mendelevium Md	Nobelium No	Lawrencium Lr						

Figure 3.4 Metals fixation by orthophosphate. Yellow colors refer to the elements that are stabilized by orthophosphate through the formation of metal phosphate. Whereas, blue colors show the feasibility of orthophosphate to precipitate the elements but no clear background (Hafsteinsdóttir et al., 2015)

3.4 Mechanism of TSP on Heavy Metal Removal

The description of TSP mechanism is important to be elucidated for the removal of heavy metals. For instance, the metal phosphate precipitation represents the principal mechanism of heavy metal stabilization (Basta & McGowen, 2004; N. Bolan et al., 2014). In the case of TSP, the prior studies reported that the process of TSP on heavy metals removal involves the dissolution of TSP and the precipitation of heavy metals through the formation of metal phosphate as the insoluble compound (Brown et al., 2005; Contos & Regan Sr, 1995; Kaya et al., 1996; Lindsay et al., 1962; Lindsay & Stephenson, 1959). However, this metal phosphate formation and TSP performance are influenced by certain parameters such as pH, metal concentrations and TSP concentrations.

3.4.1 Effect of pH and Redox Potential

pH and redox potential (Eh) are two important variables that influence the stability and solubility of many compounds as illustrated in Figure 3.5 (Bard & Faulkner, 1980). The pH is an important parameter that controls the dissolution of metal ions. Ma et al. (1993) demonstrated that the solubility of Triple superphosphate (orthophosphate source) and contaminated waste, as well as the production of a stable metal-phosphate mineral are influenced by pH. As mentioned above in section 3.1, TSP is solubilized in aqueous solution at pH acidic. This acidic condition can emphasize the achievement of lead-TSP fixation which provide the formation $Pb_5(PO_4)_2Cl$ (Cao et al., 2008). In addition, the presence of chloropyromorphite was successfully found in low pH (Porter et al., 2004). Alternatively, chloropyromorphite occurred mostly with pH values ranging from 2 to 7 (Zhang & Ryan, 1999b). However, the lead and iron phosphate minerals, and zinc phosphate (hopeite) were found in a wide pH range at equilibrium conditions (Kaya et al., 1996; Lindsay, 1979). The observation made from these results; pH has less influence on the formation of metal phosphate during the application of TSP.

The potential redox (Eh) is also an essential parameter for monitoring the leachability (mobility) of heavy metals. According to Hafsteinsdóttir et al. (2015), some metals can become more soluble and harmful to the environment when their redox changes. In addition to this statement, research was conducted on the change of oxidation sulfide and solubility of metals using a combination of $KMnO_4$ and $Ca(H_2PO_4)_2 \cdot H_2O$ (Harris & Lottermoser, 2006). The results demonstrated a decrease of sulfide oxidation promotes the decrease of Cu, Pb, Sb and Zn solubility and the formation of copper phosphate, lead phosphate and zinc phosphate compounds.

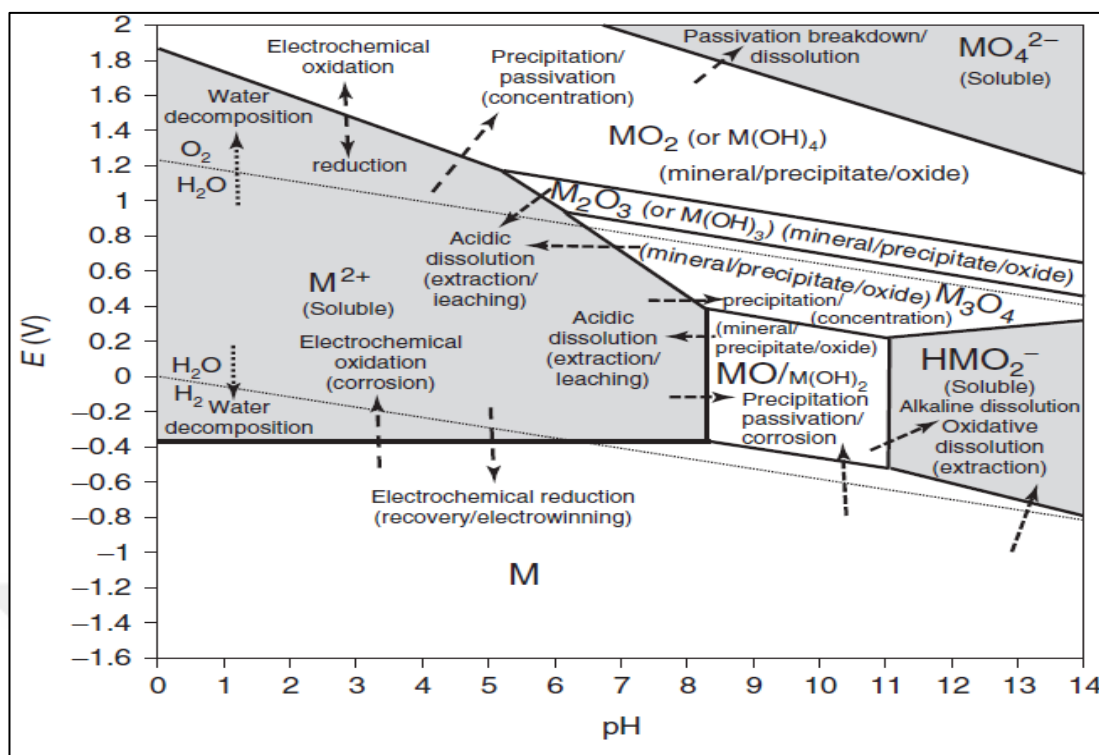


Figure 3.5 Pourbaix (Eh-pH) diagram for a hypothetical metal (M), illustrating predominant phase based on redox potential and pH (Bard & Faulkner, 1980)

3.4.2 Effect of Metal Concentrations

The concentrations of metals can impact the formation of metal phosphate though the use of TSP for heavy metal stabilization. In the presence of high metals concentration, metal precipitation transformation of metal ions in the form of metal phosphates described the mechanism for phosphorus induce stabilization of metals (Bolan et al., 2003). The study performed on the mineralogical determination of lead precipitate by x-ray diffraction demonstrated it is extremely difficult to find the formation of $Pb_5(PO_4)_3(OH, Cl, \dots)$ compounds in the analyzed Pb precipitate with the concentration of lead smaller than 50000 mg/L (Scheckel et al., 2005). Moreover, Baker (2008) mentioned the analyses of the treated sludge (residue collected from in situ remediation by TSP) showed that the presence of pyromorphite and hopeite in high peaks is due to the high concentration of lead and zinc which facilitate those metals to bind with P. On the other hand, Hafsteinsdóttir et al. (2013) noticed that the efficiency of orthophosphate fixation is affected by metal ions concentration even though the formation of Pb, Cu and Zn phosphate minerals such as $Pb_5(PO_4)_3(Cl, OH;$

($\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$); ($\text{Na}_6\text{Zn}_6(\text{PO}_4)_6 \cdot 8\text{H}_2\text{O}$ and $\text{Na}_{12}(\text{Zn}_{12}\text{P}_{12}\text{O}_{48}) \cdot 12\text{H}_2\text{O}$) was detected in the mixed system.

3.4.3 Effect of TSP Concentration

The metal-phosphate bearing is strongly influenced by the availability of phosphate in the solution. Chrysochoou et al. (2007) proposed high concentration or dosage of phosphate is needed in order to obtain a successful metal-phosphate bearing during metal ion stabilization. Similarly, numerous researchers have determined this high amount (excess dosage or concentration of phosphate) based on the theoretical ratio (Hong et al., 2010; Melamed et al., 2003; Stanforth & Qiu, 2001; Zhang & Ryan, 1999b). In thermochemical modeling, a thorough analysis of TSP solution for iron and lead using thermodynamic equilibrium (Pourbaix diagram) indicated the stable iron phosphates ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) and lead phosphates (PbHPO_4 , $\text{Pb}(\text{H}_2\text{PO}_4)_2$, $\text{Pb}_3(\text{PO}_4)_2$, $\text{Pb}_4\text{O}(\text{PO}_4)_2$) cover a large areas of stability speciation diagrams at high TSP concentration (1 mol/L) (Kaya et al., 1996). Meanwhile, few studies describe how relevant to investigate the TSP solution chemistry and its concentration effect for heavy metal removal using thermochemical modeling (stability diagrams). Our study will show the TSP concentration influence as mean to remove heavy metals through the stability speciation diagrams and verification with laboratory tests.

Nonetheless, the requirement of excess P for effective metal stabilization and formation of insoluble compounds (metal phosphate) can be a source of contamination (Atafar et al., 2010; Maenpaa et al., 2002). The results of x-ray analyses in the previous studies reveal that the detected mineral phosphates are produced by the application of optimum TSP or other phosphate source concentrations (Bosso et al., 2008; Corami et al., 2010; Cotter-Howells & Caporn, 1996; Ma et al., 1993; Scheckel et al., 2005). As reported by Baker (2008), more Pb and Zn react with P when optimum TSP amount is added, thus resulting in more Pb and Zn phosphate compounds formation.

CHAPTER FOUR

TRIPLE SUPERPHOSPHATE CHARACTERIZATION FOR REMOVAL OF HEAVY METALS

4.1 Introduction

The triple superphosphate fertilizer is an important phosphorus (P) source and soluble in water. Its properties were given in detail in chapter three. In the presence of aqueous solutions, phosphorus is highly unstable. As a result, it is both a significantly basic element and a potent reducing agent. In addition, P does not occur in its native state in nature. As shown in Figure 4.1, phosphoric acid and its reaction products, H_3PO_4^0 , H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} constitute the aqueous phosphorous species consists of H_2PO_4^- and HPO_4^{2-} are the most common orthophosphate species (Pourbaix, 1966). In other words, this figure describes the phosphorus solubility and stability depending on two parameters such as pH and potential redox (Eh).

This chapter aims to (1) determine the TSP solubility and its moisture content, (2) the chemical analysis of TSP and (3) the mineralogical composition of raw and insoluble TSP samples. Thus, the precipitation tests of pure metal ions are conducted using TSP and slaked lime.

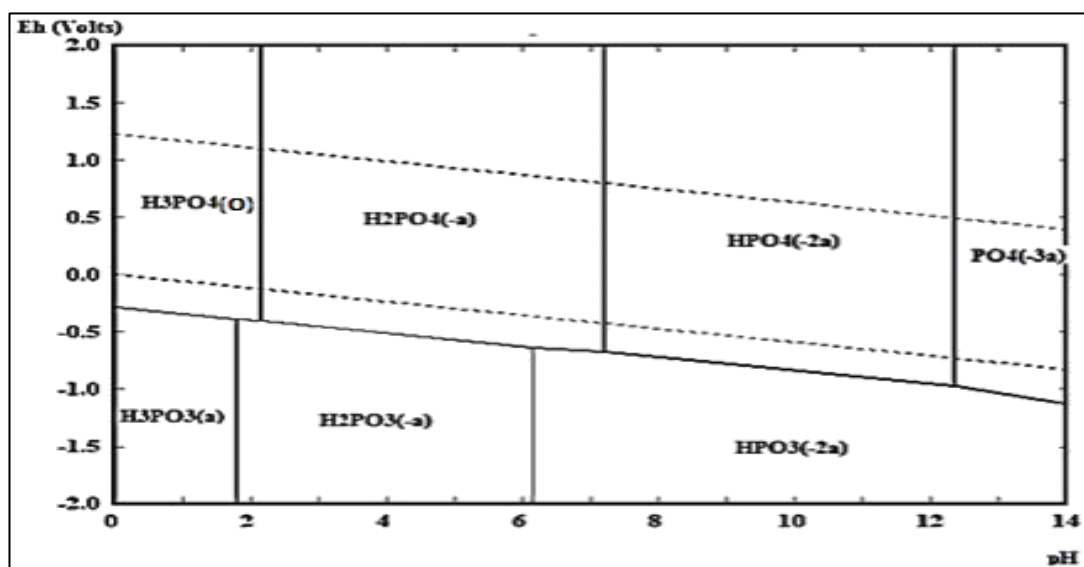


Figure 4.1 Pourbaix diagram of PO_4^{3-} - H_2O system

4.2 Characterization of Triple Superphosphate

4.2.1 Particle Size Distribution and XRD Analyses of TSP sample

The utilized TSP fertilizer was received from the private fertilizer industry Gübretaş in Turkey in a granular form. Firstly, the granular sample was dried and homogenized, then a representative sample was taken through the riffle splitter, then ground using MG100/MG200 mortar grinder and sieved to size under 100µm. The particle size analysis was conducted by the vibratory sieving machine operating with six sieves (aperture of 4.75mm, 2mm, 1.18mm, 600µm, 300µm and 150µm) for the raw TSP while the Horiba LA-950 laser scattering device is employed to determine the ground TSP particle size distribution (Figure 4.2).

The mineralogical composition of raw TSP (particle size <100µm) and the insoluble TSP samples was determined by Rigaku Miniflex X-ray diffraction diffractometer (D/Max 600, Cu K α radiation: 1.54059 Å, 33 KV, 15 m Å). To collect the insoluble TSP for XRD analysis, 20 g of TSP was solubilized in 500 ml distilled water within 30 minutes, then filtrated through a filter paper (Reeve angel- grade: 307; size:125mm), and the solid contents were oven-dried at 105°C for 1 hour and cooled in a desiccator.



Figure 4.2 Grinding and particle size analyses of TSP. (a) TSP as received, (b) Particle size distribution analysis of granular TSP by vibratory sieving machine, (c) Grinding the granular TSP to size below 100µm MG100/MG200 mortar grinder, (d) Particle size analysis of ground TSP by Horiba LA-950 laser scattering device (Personal annal, 2019)

4.2.2 Solubility and Moisture Tests

The solubility tests were performed by weighing different masses of ground triple superphosphate (5.00g, 10.00g, 20.00g, 40.00g, and 80.00g) and transferring in beaker glass containing 500 ml of distilled water. Then, the solution was mixed using magnetic stirring at room temperature (22.05). The pH was measured by a pH meter (Orion 4 Star). After 30 minutes of reaction time, the solution of TSP was filtered through a funnel glass containing filter paper until no water dripped anymore. The sludge obtained was put in an oven maintained at 105° C for 1-hour drying, then the dry solids were cooled in the desiccator and the last step is weighing the remaining solid by a precision balance. As the temperature influence the solubility of TSP in water, the tests were carried out with different temperatures (40, 60, 80, and 100°C).

The moisture tests of TSP were achieved by weighing 5g of TSP granular sample on a crucible, followed by drying in the oven at a temperature above boiling point of water (105°C). After one hour, the crucibles with the TSP sample were cooled in a desiccator and weighed. The percentage of moisture is determined by the following Equation 4.1.

$$\% M = \frac{w_1 - w_2}{w_1} \times 100 \quad (4.1)$$

Where M: moisture; w_1 : net mass weighed before drying and w_2 : mass weighed after drying.

4.2.3 Chemical Analysis Test of Raw TSP Sample

The chemical tests utilized for the fertilizers in different studies were the Association of Official Agricultural Chemists (AOAC) methods. The modified AOAC method was used by dissolving 5 g of TSP in a beaker of 500 ml through the addition of 10 ml of HCl as a reagent. The contents in the beaker were boiled with a hot plate. The boiled contents were vaporized to near the fume hood, and 20 ml from 2 M or mol/L of HCl concentration were added after cooling. A second boiling was conducted, then the contents were filtered through a funnel glass with filter paper after cooling by the addition of 0.1 M HCl. The filtrate solution was put into a 250 ml graduated flask and the residue as slurry was washed with 0.1 M HCl, and the volume was adjusted with the same solution. On the other hand, 63.00g of TSP was dissolved in 500ml distilled water and the solution was transferred to a flask in order to determine the impurity of TSP. The metal concentrations were analyzed by ICP (Inductively Coupled Plasma, Model: Varian 710-ES ICP-OES) and the total heavy metal concentrations are calculated using Equation 4.2.

$$[Me] \left(\frac{mg}{kg} \right) = \frac{ICP \text{ reading} \times df \times V}{\text{mass of sample}} \times 10000 \quad (4.2)$$

Where [Me]: metal concentration in mg/kg, ICP reading: concentration detected by Inductively Coupled Plasma, df: dilution factor, V: volume in L, mass of sample: the weight of sample used in g.

4.3 Precipitation Tests

The chemical and material devices in this preliminary precipitation design are listed in Table 4.1. This laboratory precipitation aims to investigate the feasibility of using TSP for heavy removal in an aqueous solution and present the reason for selecting TSP as precipitant rather than slaked through the comparison between TSP and slaked lime for the removal of Pb in an aqueous solution. To perform the precipitation, the following steps are followed:

1. Weighing 12.6g of TSP (<100 μ m) and dissolving it within 30 minutes;
2. Measure the pH of the solution
3. Adding 10 mg/L of prepared solution (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) from 1000mg/L standard solution;
4. Sampling at 0, 5, 10, 15, 30, 60, 120 and 180 minutes;
5. Determining the metal concentration in the sampled solution by atomic absorption spectrometer.
6. Computing the removal efficiency of TSP.

The following Equation 4.3 that describes the heavy removal efficiencies is as follows:

$$RE (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (4.3)$$

Where: RE is removal efficiency in percentage (%); C_i : initial concentration of heavy metal in solution (mg/l), C_f : final concentration of heavy metal at reaction time in solution (mg/l).

The same procedures were also employed for the removal of Pb by slaked lime (Ca(OH)_2). In this case, the used amount is 3.7g of Ca(OH)_2 which is equivalent to 0.1 M or mol/L (Converting g to mol/L explanation is given in Appendix C).

Table 4.1 Chemical substances and material devices

Sample Names	Quantity	Purposes	Materials	Purposes
TSP (<100 μm)	12.6, 25.2 and 63g	to precipitate metal ions	MG100/MG200 mortar grinder	to grind the granular TSP (size<100 μm)
Slaked lime (Ca(OH)_2)	3.7, 7.4 and 18.6g	to precipitate metal ions	Dry oven	to dry TSP and Slake lime
Nitric acid (HNO_3)	few drops	to decrease the pH	pH meter (model Orion star	to measure the pH of the solution
Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn standard solutions (1000mg/L)	10, 20, 50 mg/L	to prepare a working concentration for the precipitation tests	Magnetic stirrer	to agitate, solubilized TSP to mix the metal and TSP solution
Distilled water	500 ml	to use for dilution	Atomic absorption (AA) spectrometer	to determine metal concentration in the sample collected during precipitation

CHAPTER FIVE

MATERIALS AND METHODS

This part enumerates the samples and materials utilized in this work and provides the background information on the experimental procedures. Section 5.1 explores the solution chemistry of TSP for metals removal in aqueous solutions which includes the explanation of the procedures applied to construct Pourbaix diagrams (Eh-pH diagrams) using HSC 6 software, followed by the laboratory batch precipitations on metal ion concentrations by TSP and the determination of the mineralogical compound of precipitate (obtained after precipitation of metal ions with TSP). As the necessity of sample preparation before starting any test in mineral processing, firstly mechanical preparation of waste samples (i.e., drying, grinding, sieving and homogenizing) is performed and then, the prepared samples (representative samples) are characterized through particle size distribution, chemical composition and mineralogical analyses. Further, the laboratory precipitation tests on heavy metals from industrial and mining wastes are carried out with TSP precipitant. The last step is the analysis of mineralogical composition of residue (collected after the treatment of industrial and mining wastes). The following Figure 5.1 describes the different steps of experimental procedures.

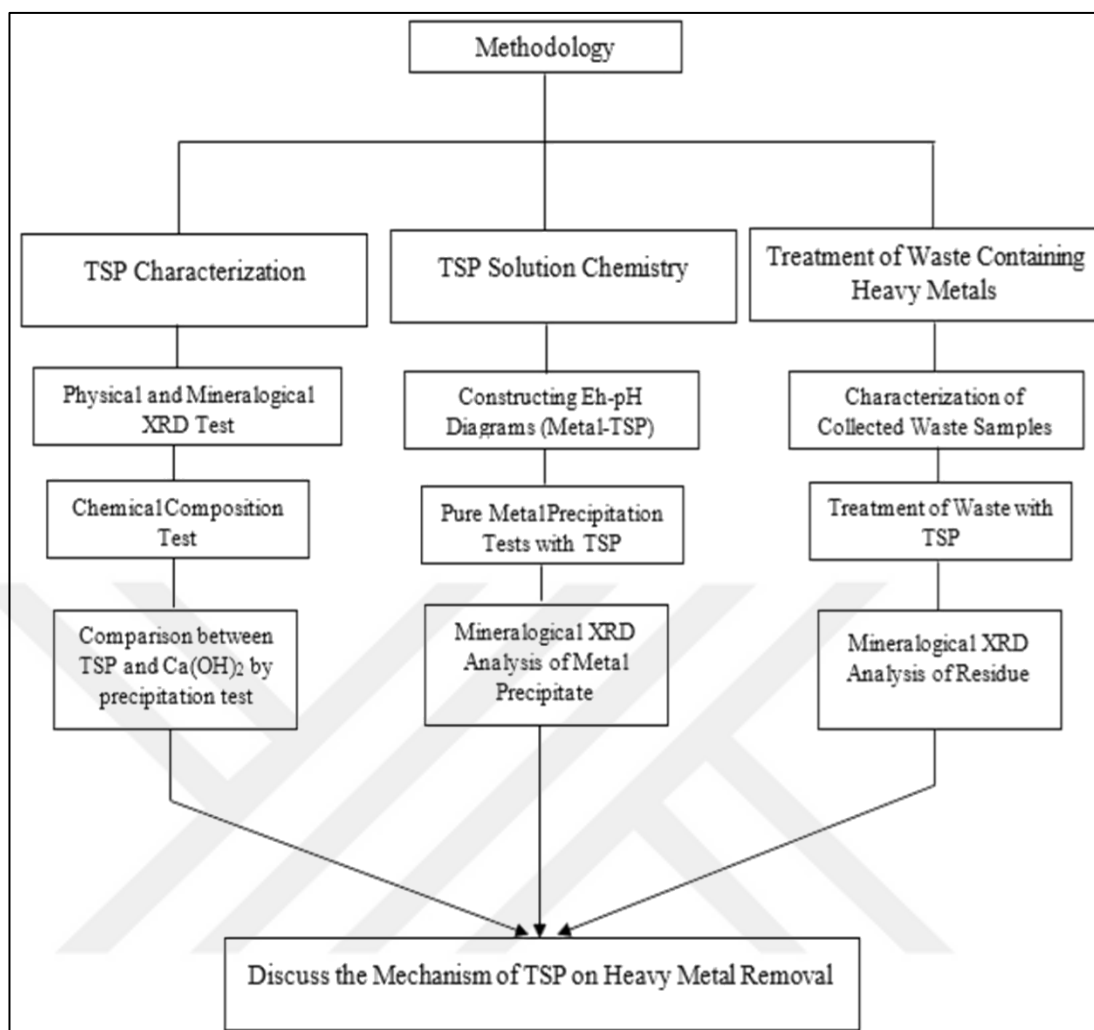


Figure 5.1 Summary of experimental procedures for heavy metal removal by triple superphosphate

5.1 Approach of TSP Solution Chemistry for Pb, Fe, Cd, Cu, and Zn Removal in Aqueous Solutions

As mentioned already in chapter four, the used TSP was received from a Gübretaş company in Turkey with particle size below 0.5 cm, then it is ground to below 100 µm to use in the experiments. The moisture content was 2% as received. The standard solutions of Pb, Fe, Cd, Cu and Zn metal ions containing 1000 mg/L were provided by Merck KGaA company in Germany. A dilution was made from these concentrations to produce working concentrations of 10, 20 and 50 mg/L (Detail of the dilution formula is given in Appendix 1.1).

5.1.1 Precipitation Tests

The laboratory precipitation tests were carried out at room temperature (22.05°C) in compliance with USEPA (1992) procedure. First, TSP weights of 12.6 and 63.0g (equivalent to 0.1 and 0.5 M or Mol/L) were transferred into a glass beaker containing 500 ml of distilled water and agitated with a magnetic bar for 30 minutes at 22.05. Afterward, 10, 20 and 50 mg/l of Cd, Cu, Fe, Pb, and Zn ions prepared from 1000 mg/L of standard stock solution were added to the TSP solution, separately. The pH of the solution decreases to >3 by the addition of the TSP and remains the same during precipitation. At the time intervals of 0, 5, 10, 15, 30, 60, 120 and 180 minutes, 5 ml of samples were taken and filtered by 0.2 μ m filters syringe (Figure 5.2). Thus, the concentrations of the filtrated sample were determined through atomic absorption (AA) spectrometer (Perkin Elmer, model PinAAcle500) operating under certain conditions illustrated in Table 5.1

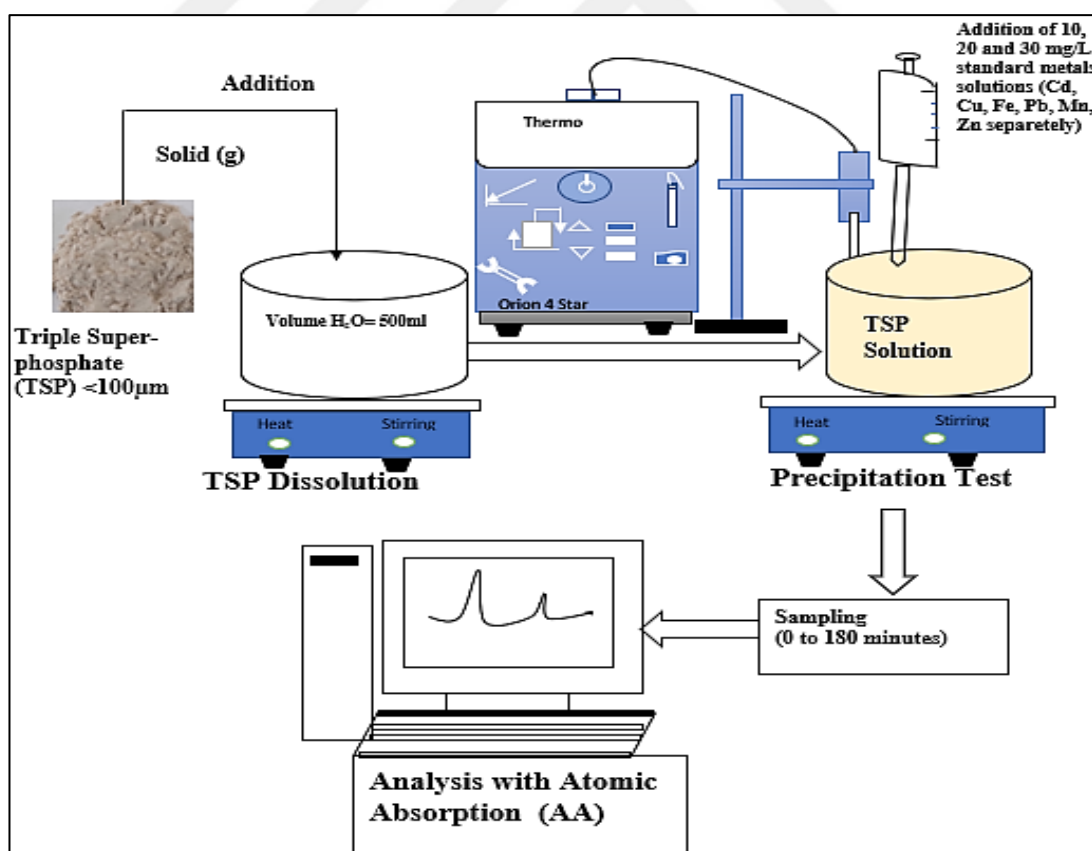


Figure 5.2 Flowsheet of pure metals (Cd, Cu, Fe, Pb and Zn) precipitation experiment by triple superphosphate

Table 5.1 Operating condition of atomic absorption spectrometer

Operating Conditions	Cadmium	Copper	Iron	Lead	Zinc
Wavelength (nm)	228.80	324.74	248.33	283.31	203.86
Slit (nm)	0.70	0.70	0.20	0.70	0.70
Lamp	HCL	HCL	HCL	HCL	HCL
Air Flow (L/min)	8.48	10.00	10.00	9.12	10.00
Acetylene Flow (L/min)	2.06	2.06	2.50	2.50	2.06

HCL: Hollow Cathode Lamp

5.1.1.1 Method Validation

The purpose of the validation method is to provide adequate quality assurance (QA) and quality control (QC) during the sample preparation, digestion, AA spectrometer calibration and measurement. In the validation procedure, we used 10, 20 and 50 mg/L of Cd, Cu, Fe, Pb and Zn to calibrate the spectrometer, as well as in accordance with the experimental procedures defined by Tasgetiren (2014), the measurements are repeated 10 times in order to obtain the accurate limits of detection (LOD) and limits of quantitation (LOQ). The collected data from the analysis are computed by Excel program and reported in Table A2.

5.1.2 X-Ray Diffraction Analyses (XRD) of Pb, Fe, Cd, Cu, and Zn precipitate

The mineralogical analyses of the precipitates aim to determine the type of stable compound and approve the metal phosphate obtained from the stability area diagrams. For this purpose, precipitation tests were conducted by using 50 mg/L metal solutions (Cd, Cu, Fe, Pb and Zn separately) and 0.5 M of TSP precipitating reagent within 180 minutes of reaction periods in order to obtain about 2 grams of precipitate. The collected Cd, Cu, Fe, Pb and Zn precipitates were filtrated using Reeve angel filter paper (Grade: 307; size:125mm), followed by drying at 105°C for 1 hour in a dry oven, cooling in a desiccator, then grinding with a mortar grinder (Model: MG100/MG200). Thus, X-ray diffractometers (Model: Rigaku Miniflex, D/Max 600, Cu K α radiation: 1.54059 Å, 33 KV, 15 m Å) were utilized to analyze the dry precipitate samples.

5.1.3 Analyses of Chemical Content in TSP and Pb Precipitate samples

The X-ray fluorescence (XRF) spectrometer is the common method used to identify the chemical content of samples. In this research, the percentages of chemical content in raw TSP and Pb precipitate samples (particle size below 100 μ m) were determined using XRF spectrometer (Model: Spectro iQ II, Kleve, Germany). The characteristics of spectrometer are the detector of silicon drift 145 eV 10000 pulses for resolution and utilized X-ray tube (25-50 kV) with a highly oriented pyrolytic graphite (HOPG) crystal for the analysis.

5.1.4 Eh-pH Diagrams Design

In this section 5.1.3, the aqueous stability diagrams are employed to analyze the solution chemistry of Cd, Cu, Fe, Pb and Zn with the TSP. Indeed, for a specified chemical element, logarithmic activity-activity diagrams, such as Eh-pH, log {Metal}-pH and log {Ligand}-pH diagrams provide predictions of the equilibrium states of all the possible reactions between the chemical element, its ions and its solid and gaseous compounds in the presence of water (Kaya et al., 1996; Osseo-Asare & Brown, 1979). In addition, these speciation diagrams are directly relevant to aqueous chemical reactions found in the areas of environmental contamination management, corrosion science, geochemistry, ore beneficiation and hydrometallurgy.

HSC Chemistry 6 computer program is the tool used to design the Pourbaix diagram of Cd-H₂O and Cd-PO₄³⁻.H₂O; Cu-H₂O and Cu-PO₄³⁻.H₂O; Fe-H₂O and Fe-PO₄³⁻.H₂O; Pb-H₂O and Pb-PO₄³⁻.H₂O; Zn-H₂O and Zn-PO₄³⁻.H₂O systems. To plot Eh-pH diagram of these metal-water and metal-TSP systems, many reactions occurred during the thermodynamic calculation procedures. Brookins (1989) and van der Perk (2013) have reported that many reactions in nature involve oxidation and reduction, and have described the thermochemical modeling of oxidation-reduction (Equations 5.1 to 5.3) as follows: reduced species = oxidized species + (n) electrons



$$K = \frac{[Cox]^c [Dred]^d}{[A red]^a [B ox]^b} \quad (5.2)$$

$$Eh = E^0 - \frac{RT}{nF} \ln K = E^0 - \frac{RT}{nF} \ln \frac{[Cox]^c [Dred]^d}{[A red]^a [B ox]^b} \quad (5.3)$$

$$Eh = E^0 - \frac{0.0592}{n} \log \frac{[Cox]^c [Dred]^d}{[A red]^a [B ox]^b} \quad (5.4)$$

Where: the symbols ox and red indicate respectively the oxidants and reductants involved in the reaction; n: number of electrons; K: is the equilibrium constant for the activities of A, B and D to their respective powers a, b, c and d.

Eh: redox potential (Volt); E^0 = the standard potential, which is the potential with all substances present at the unit activity at 25 °C and 1-atmosphere pressure (Volt).

As in the Nernst equation, many parameters are constant, the value 0.0592 is determined by using $R = 0.001987 \text{ kcal.deg}^{-1}$, $T = 298.15^\circ$, $F = 23.06 \text{ kcal. volt}^{-1}$ -gram equivalent, and 2.303 to convert the natural log to log base 10. Indeed, all the calculations are automatically computed by HSC 6 program in our study. The used reactions and thermodynamic data were collected from numerous references which are listed in Tables 5.2 to 5.6.

By utilizing the plotted diagrams, the predominant areas of the specific species and the solid/solution equilibrium in the TSP solution can be presented and evaluated properly (Souley Garba et al., 2022).

Table 5.2 Selected equilibrium reactions and constants for Cd-H₂O and Cd-PO₄³⁻.H₂O systems (Sources: Bacon et al., 2014; Iuliano & Porto, 1994; Nriagu, 1984; Pourbaix, 1974; Powell et al., 2011; Smith et al., 1998)

No	Equilibrium Reactions Cadmium	Log K
1	$\text{Cd(c)} \leftrightarrow \text{Cd}^{2+} + 2 \text{e}^-$	3.84
2	$\text{CdOH}^+ + \text{H}^+ \leftrightarrow \text{Cd}^{2+} + \text{H}_2\text{O}$	-10.10
3	$\text{Cd(OH)}_2\text{(c)} + 2\text{H}^+ \leftrightarrow \text{Cd}^{2+} + 2\text{H}_2\text{O}$	13.72
5	$\text{Cd(OH)}_2\text{(aq)} + \text{H}^+ \leftrightarrow \text{Cd}^{2+} + 2\text{H}_2\text{O}$	-20.29
6	$\text{Cd(OH)}_3^- + 3\text{H}^+ \leftrightarrow \text{Cd}^{2+} + 3\text{H}_2\text{O}$	-33.30
8	$\text{Cd(OH)}_4^{2-} + 4\text{H}^+ \leftrightarrow \text{Cd}^{2+} + 4\text{H}_2\text{O}$	-47.29
9	$\text{Cd}_2\text{OH}^{3+} + \text{H}^+ \leftrightarrow 2\text{Cd}^{2+} + \text{H}_2\text{O}$	-9.40
13	$\text{HCdO}_2^- + 3\text{H}^+ \leftrightarrow \text{Cd}^{2+} + 2\text{H}_2\text{O}$	-33.34
	Cadmium-Phosphates	
14	$\text{Cd}_3(\text{PO}_4)_2\text{(c)} + 6\text{H}^+ \leftrightarrow 3\text{Cd}^{2+} + 2\text{H}_3\text{PO}_4^0$	-36.90
15	$\text{Cd}_5(\text{PO}_4)_3\text{OH(c)} + 10\text{H}^+ \leftrightarrow 5\text{Cd}^{2+} + 3\text{H}_3\text{PO}_4^0 + \text{H}_2\text{O}$	-64.62
16	$\text{Cd(H}_2\text{PO}_4)_2\text{(c)} + 2\text{H}^+ \leftrightarrow 2\text{Cd}^{2+} + 2\text{H}_3\text{PO}_4^0$	-2.79
17	$\text{CdHPO}_4\text{(c)} + \text{H}^+ \leftrightarrow \text{Cd}^{2+} + \text{H}_3\text{PO}_4^0$	-2.38
18	$\text{CdH}_2\text{PO}_4^+ + \text{H}^+ \leftrightarrow \text{Cd}^{2+} + \text{H}_3\text{PO}_4^0$	-1.1
19	$\text{CdHPO}_4^0\text{(aq)} + 2\text{H}^+ \leftrightarrow \text{Cd}^{2+} + \text{H}_3\text{PO}_4^0$	-6.9

Table 5.3 Selected equilibrium reactions and constants for Cu-H₂O and Cu-PO₄³⁻·H₂O systems (Ciavatta et al., 1993; Falck, 1992; Free, 2021; Nriagu, 1984a; Powell et al., 2007; Smith et al., 1998)

No	Equilibrium Reactions	Log K
	Copper	
1	$\text{Cu(c)} \leftrightarrow \text{Cu}^{2+} + 2 \text{e}^-$	-25.80
2	$\text{CuOH}^+ + \text{H}^+ \leftrightarrow \text{Cu}^{2+} + \text{H}_2\text{O}$	-7.51
3	$\text{Cu(OH)}_2\text{(c)} + 2\text{H}^+ \leftrightarrow \text{Cu}^{2+} + 2\text{H}_2\text{O}$	9.69
5	$\text{Cu(OH)}_2\text{(aq)} + \text{H}^+ \leftrightarrow \text{Cu}^{2+} + 2\text{H}_2\text{O}$	8.67
6	$\text{Cu(OH)}_3^- + 3\text{H}^+ \leftrightarrow \text{Cu}^{2+} + 3\text{H}_2\text{O}$	-26.9
8	$\text{Cu(OH)}_4^{2-} + 4\text{H}^+ \leftrightarrow \text{Cu}^{2+} + 4\text{H}_2\text{O}$	-39.66
9	$\text{Cu}_2\text{OH}^{3+} + \text{H}^+ \leftrightarrow 2\text{Cu}^{2+} + \text{H}_2\text{O}$	-6.28
10	$\text{HCuO}_2^- + 3\text{H}^+ \leftrightarrow \text{Cu}^{2+} + 2\text{H}_2\text{O}$	26.34
11	$\text{CuO}_2^{2-} + \text{H}^+ \leftrightarrow \text{Cu}^{2+} + 2\text{H}_2\text{O}$	39.46
Copper-Phosphates		
12	$\text{Cu}_3(\text{PO}_4)_2\text{(c)} + 6\text{H}^+ \leftrightarrow 3\text{Cu}^{2+} + 2\text{H}_3\text{PO}_4^0$	-2.21
13	$\text{Cu}_5(\text{PO}_4)_3.\text{OH(c)} + 10\text{H}^+ \leftrightarrow 5\text{Cu}^{2+} + 3\text{H}_3\text{PO}_4^0 + \text{H}_2\text{O}$	-65.6
14	$\text{Cu}(\text{H}_2\text{PO}_4)_2\text{(c)} + 2\text{H}^+ \leftrightarrow 2\text{Cu}^{2+} + 2\text{H}_3\text{PO}_4^0$	41.06
15	$\text{CuHPO}_4\text{(c)} + \text{H}^+ \leftrightarrow \text{Cu}^{2+} + \text{H}_3\text{PO}_4^0$	16.17
16	$\text{CuH}_2\text{PO}_4^+ + \text{H}^+ \leftrightarrow \text{Cu}^{2+} + \text{H}_3\text{PO}_4^0$	20.70
17	$\text{CuHPO}_4^0\text{(aq)} + 2\text{H}^+ \leftrightarrow \text{Cu}^{2+} + \text{H}_3\text{PO}_4^0$	15.65

Table 5.4 Selected equilibrium reactions and constants for Fe-H₂O and Fe-PO₄³⁻·H₂O systems (Lindsay & Stephenson, 1959; Pourbaix, 1974; Vieillard et al., 1979; Vieillard & Tardy, 1984)

No	Equilibrium Reactions	Log K
	Iron	
1	$\text{Fe(c)} \leftrightarrow \text{Fe}^{2+} + 2 \text{e}^-$	15.98
2	$\text{Fe (OH)}_2\text{(c)} + 2\text{H}^+ \leftrightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O}$	12.90
3	$\text{Fe (OH)}_2\text{(c)} + 3\text{H}^+ + \text{e}^- \leftrightarrow \text{Fe}^{2+} + 3\text{H}_2\text{O}$	15.74
4	$\text{Fe}^{3+} + \text{e}^- \leftrightarrow \text{Fe}^{2+}$	13.04
5	$\text{Fe OH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	6.74
6	$\text{Fe (OH)}_2\text{(aq)} + 2\text{H}^+ \leftrightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O}$	16.04
7	$\text{Fe (OH)}_3^- + 3\text{H}^+ \leftrightarrow \text{Fe}^{2+} + 3\text{H}_2\text{O}$	31.99
8	$\text{Fe (OH)}_4^{2-} + 4\text{H}^+ \leftrightarrow \text{Fe}^{2+} + 4\text{H}_2\text{O}$	46.38
9	$\text{Fe}_3\text{(OH)}^{2+} + 4\text{H}^+ \leftrightarrow 3\text{Fe}^{2+} + \text{H}_2\text{O}$	45.39
10	$\text{FeOH}^{2+} + \text{H}^+ + \text{e}^- \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	15.23
11	$\text{Fe}_2\text{(OH)}_4^{4+} + 2\text{H}^+ + 2\text{e}^- \leftrightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O}$	28.98
12	$\text{FeO}_2^{2-} + 4\text{H}^+ \leftrightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O}$	45.17
13	$\text{HFeO}_2^- + 3\text{H}^+ \leftrightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O}$	30.78
Iron-Phosphates		
14	$\text{Fe}_3\text{(PO}_4)_2\text{(c)} + 6\text{H}^+ \leftrightarrow 3\text{Fe}^{2+} + 2\text{H}_3\text{PO}_4^0$	13.50
15	$\text{Fe}_3\text{(PO}_4)_2 \cdot 8 \text{H}_2\text{O(c)} + 6\text{H}^+ \leftrightarrow 3\text{Fe}^{2+} + 2\text{H}_3\text{PO}_4^0 + 8\text{H}_2\text{O}$	7.40
16	$\text{Fe PO}_4\text{(c)} + 3\text{H}^+ + \text{e}^- \leftrightarrow \text{Fe}^{2+} + \text{H}_3\text{PO}_4^0$	12.22
17	$\text{FePO}_4 \cdot 2 \text{H}_2\text{O (c)} + 3\text{H}^+ + \text{e}^- \leftrightarrow \text{Fe}^{2+} + \text{H}_3\text{PO}_4^0 + 2\text{H}_2\text{O}$	9.58
18	$\text{FeH}_2\text{PO}_4^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_3\text{PO}_4^0$	-0.55
19	$\text{FeHPO}_4^0\text{(aq)} + 2\text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_3\text{PO}_4^0$	5.75

Table 5.5 Selected equilibrium reactions and constants for Pb-H₂O and Pb-PO₄³⁻. H₂O system (Sources: Lindsay, 1979; Lindsay & Stephenson, 1959; Vieillard et al., 1979; Vieillard & Tardy, 1984; Wagman et al., 1982)

No	Equilibrium Reactions	Log K
	Lead	
1	$\text{Pb(c)} \leftrightarrow \text{Pb}^{2+} + 2\text{e}$	4.33
2	$\text{PbO(c)} + 2\text{H}^+ \leftrightarrow \text{Pb}^{2+} + \text{H}_2\text{O}$	12.72
3	$\text{Pb}_3\text{O}_4\text{(c)} + 8\text{H}^+ + 2\text{e} \leftrightarrow 3\text{Pb}^{2+} + 4\text{H}_2\text{O}$	73.79
4	$\text{PbO}_2\text{(c)} + 4\text{H}^+ + 2\text{e} \leftrightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$	49.68
5	$\text{PbOH}^+ + \text{H}^+ \leftrightarrow \text{Pb}^{2+} + \text{H}_2\text{O}$	7.70
6	$\text{Pb(OH)}_2^0 + 2\text{H}^+ \leftrightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$	17.75
7	$\text{Pb(OH)}_3^- + 3\text{H}^+ \leftrightarrow \text{Pb}^{2+} + 3\text{H}_2\text{O}$	28.09
8	$\text{Pb(OH)}_4^{2-} + 4\text{H}^+ \leftrightarrow \text{Pb}^{2+} + 4\text{H}_2\text{O}$	39.49
9	$\text{Pb}_2\text{(OH)}_3^{3+} + \text{H}^+ \leftrightarrow 2\text{Pb}^{2+} + \text{H}_2\text{O}$	6.40
10	$\text{Pb}_3\text{(OH)}_4^{2-} + 4\text{H}^+ \leftrightarrow 3\text{Pb}^{2+} + 4\text{H}_2\text{O}$	23.89
11	$\text{Pb}_3\text{(OH)}_4^{4+} + 4\text{H}^+ \leftrightarrow 3\text{Pb}^{2+} + 4\text{H}_2\text{O}$	20.89
12	$\text{Pb}_6\text{(OH)}_8^{4+} + 8\text{H}^+ \leftrightarrow 6\text{Pb}^{2+} + 8\text{H}_2\text{O}$	43.58
13	$\text{HPbO}_2^- + 3\text{H}^+ \leftrightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$	28.07
Lead-Phosphates		
14	$\text{Pb(H}_2\text{PO}_4)_2\text{(c)} + 2\text{H}^+ \leftrightarrow \text{Pb}^{2+} + 2\text{H}_3\text{PO}_4^0$	-5.55
15	$\text{PbHPO}_4\text{(c)} + 2\text{H}^+ \leftrightarrow \text{Pb}^{2+} + \text{H}_3\text{PO}_4^0$	-2.10
16	$\text{Pb}_3\text{(PO}_4)_2\text{(c)} + 6\text{H}^+ \leftrightarrow 3\text{Pb}^{2+} + 2\text{H}_3\text{PO}_4^0$	-0.96
17	$\text{Pb}_4\text{O(PO}_4)_2\text{(c)} + 8\text{H}^+ \leftrightarrow 4\text{Pb}^{2+} + 2\text{H}_3\text{PO}_4^0 + \text{H}_2\text{O}$	6.54
18	$\text{Pb}_5\text{(PO}_4)_3\text{OH(c)} + 10\text{H}^+ \leftrightarrow 5\text{Pb}^{2+} + 3\text{H}_3\text{PO}_4^0 + \text{H}_2\text{O}$	2.31
19	$\text{PbH}_2\text{PO}_4^+ + \text{H}^+ \leftrightarrow \text{Pb}^{2+} + \text{H}_3\text{PO}_4^0$	0.65
20	$\text{PbHPO}_4^0\text{(aq)} + 2\text{H}^+ \leftrightarrow \text{Pb}^{2+} + \text{H}_3\text{PO}_4^0$	6.26

Table 5.6 Selected equilibrium reactions and constants for Zn-H₂O and Zn-PO₄³⁻. H₂O system (Sources: Iuliano & Porto, 1994; Lindsay, 1979; Nriagu, 1984; Powell et al., 2013; Smith et al., 1998)

No	Equilibrium Reactions Zinc	Log K
1	$\text{Zn(c)} \leftrightarrow \text{Zn}^{2+} + 2 \text{e}^-$	-25.80
2	$\text{ZnOH}^+ + \text{H}^+ \leftrightarrow \text{Zn}^{2+} + \text{H}_2\text{O}$	-8.99
3	$\text{Zn(OH)}_2(\text{c}) + 2\text{H}^+ \leftrightarrow \text{Zn}^{2+} + 2\text{H}_2\text{O}$	11.68
5	$\text{Zn(OH)}_2(\text{aq}) + \text{H}^+ \leftrightarrow \text{Zn}^{2+} + 2\text{H}_2\text{O}$	-16.89
6	$\text{Zn(OH)}_3^- + 3\text{H}^+ \leftrightarrow \text{Zn}^{2+} + 3\text{H}_2\text{O}$	-28.39
8	$\text{Zn(OH)}_4^{2-} + 4\text{H}^+ \leftrightarrow \text{Zn}^{2+} + 4\text{H}_2\text{O}$	-41.18
9	$\text{Zn}_2\text{OH}^{3+} + \text{H}^+ \leftrightarrow 2\text{Zn}^{2+} + \text{H}_2\text{O}$	-8.99
10	$\text{HZnO}_2^- + 3\text{H}^+ \leftrightarrow \text{Zn}^{2+} + 2\text{H}_2\text{O}$	28.78
11	$\text{ZnO}_2^{2-} + \text{H}^+ \leftrightarrow \text{Zn}^{2+} + 2\text{H}_2\text{O}$	41.55
Zinc-Phosphates		
12	$\text{Zn}_3(\text{PO}_4)_2(\text{c}) + 6\text{H}^+ \leftrightarrow 3\text{Zn}^{2+} + 2\text{H}_3\text{PO}_4^0$	-35.40
13	$\text{Zn}_5(\text{PO}_4)_3\text{OH(c)} + 10\text{H}^+ \leftrightarrow 5\text{Zn}^{2+} + 3\text{H}_3\text{PO}_4^0 + \text{H}_2\text{O}$	-63.1
14	$\text{Zn(H}_2\text{PO}_4)_2(\text{c}) + 2\text{H}^+ \leftrightarrow 2\text{Zn}^{2+} + 2\text{H}_3\text{PO}_4^0$	-11.37
15	$\text{ZnHPO}_4(\text{c}) + \text{H}^+ \leftrightarrow \text{Zn}^{2+} + \text{H}_3\text{PO}_4^0$	-6.74
16	$\text{ZnH}_2\text{PO}_4^+ + \text{H}^+ \leftrightarrow \text{Zn}^{2+} + \text{H}_3\text{PO}_4^0$	1.2
17	$\text{ZnHPO}_4^0(\text{aq}) + 2\text{H}^+ \leftrightarrow \text{Zn}^{2+} + \text{H}_3\text{PO}_4^0$	2.49

5.2 Characterization of Waste Samples

5.2.1 Samples Preparation

The real waste samples (2Kg) containing leachable heavy metals are collected from mineral processing plants and industrial companies. The coal fly ash was taken from the bottom of the electro filter Yatağan coal-fired power plant located in Mugla western Turkey. The iron-copper tailing was taken from the flotation plant at 2-meter depth using an excavator whereas the copper slag was received from the smelter and electrolyze plant in Turkey. Finally, Pb-Zn mine waste is collected from the abandoned mining company at 100 cm depth. Indeed, we couldn't get authorization from mining

companies, therefore, their companies are not mentioned in this work for iron-copper tailing, copper slag and Pb-Zn mine waste.

The flow sheet of sample preparation for the physicochemical property tests to be performed on the waste samples is shown in Figure 5.1. The waste samples were dried in the oven at 70°C. After drying, the waste samples are ground with an agate mill disc, homogenized and a representative sample was taken through coning and quartering method (Figure 5.3).

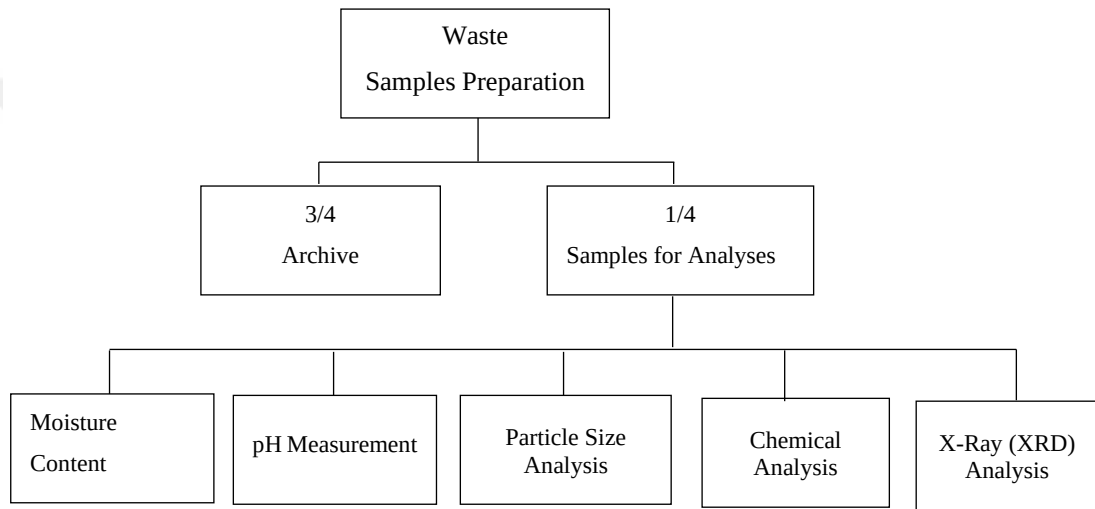


Figure 5.3 Flowsheet of sample preparation

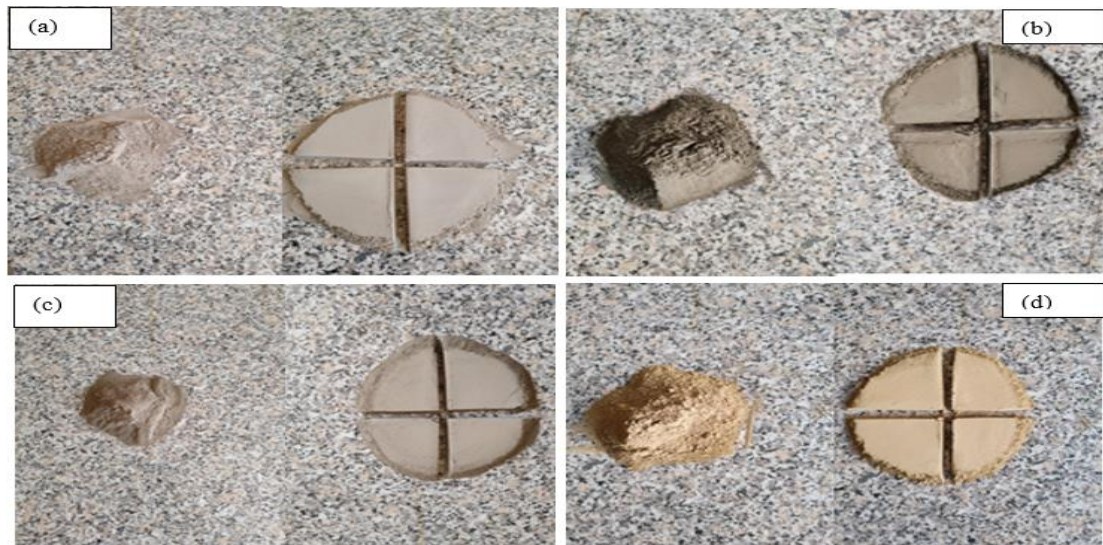


Figure 5.4 Cone quartering method for taking representative samples: (a) Yatağan flay ash, (b) copper slag, (c) iron copper tailing, (d) Pb-Zn mine waste (Personal annal, 2021)

5.2.2 Physicochemical Properties Tests

The physicochemical properties tests of waste samples involve the test of moisture content, pH, analysis of particle size distribution, chemical composition and content test, and the analysis of mineral compounds by x-ray diffraction.

5.2.2.1 Moisture Content, pH and Particle Size Distribution

The test of moisture content was conducted by putting the accurate weight of waste samples in the dry oven at 105°C for 24 h. Afterward, the dry samples were cooled in a desiccator and the content was weighed with the precision balance (model Radwag). The moisture value was obtained by computing the difference between the initial weight (wet) and the dry weight sample.

The pH of the waste samples was obtained in agreement with the USEPA, (2004) procedure for pH measurement of soil and waste. In this study, pH meter (model: Orion 4 Star) was utilized for the measurement.

The determination of particle size distribution of waste samples (fly ash, iron-copper tailing, copper slag and Pb-Zn mine waste) was performed by Horiba LA-950 laser scattering analyzer.

5.2.2.2 Chemical Composition and Content

The waste samples were digested by CEM microwave (Model: Mars 6240/50, power: 400-1800) digestion system (Figure 5.5). This device is currently the most popular digestion system for acid leaching of heavy metal from solid and can heat up to forty samples in one run. To perform the leaching test, 10 ml HNO₃, 5ml HF and 5ml of de-ionized water (2:1.1 ratio) were added to four TFM vessel liners containing 0.2g of waste sample (fly ash, iron-copper tailing, copper slag and Pb-Zn mine waste) separately. Thus, the vessels are closed with the standard cover and are loaded in the CEM microwave. Before running the digestion, the temperature of CEM microwave is adjusted to 200°C within 15 minutes for ramping, and the same temperature (200°C)

is kept at 10 minutes, and 50°C in 15 minutes for cooling. After cooling, the leachate solution was put into a volumetric flask and filled to 250 ml volume using de-ionized water. The final step is the determination of heavy metal concentration in the leachate solution by inductively coupled plasma (ICP, model: Varian 710-ES ICP-OES).

The major element tests were conducted with ground waste samples (fly ash, iron-copper tailing, copper slag and Pb-Zn mine waste with particle sizes $<100\mu\text{m}$). To accomplish that, 0.25 g of each sample were mixed with 3 g of lithium tetracarbonate thoroughly in the platinum crucible. The crucible and the mixture were put in the furnace for melting at 1100°C within one and half hours. After melting, the crucibles containing a mixture of waste sample and lithium tetracarbonate were cooled in a desiccator, and they were transferred to a 400 ml beaker followed by the addition of 10% of 100 mL HCl. The mixture contents were heated until boiling in order to dissolve all elements. Thus, the solutions were poured into a flask and filled up to 250ml through the addition of de-ionized water and the solution was analyzed by atomic absorption spectrometer (Perkin Elmer, model PinAAcle 500)



Figure 5.5 Image of CEM Microwave digestion system. (a) Vessels loading, (b) At the starting of microwave operation (Personal annal, 2021)

5.2.2.3 Mineralogical Composition Analyses (XRD) of Waste Samples

The analysis of XRD is considered the most concise and useful technique for identifying the mineral composition in soil or powder samples (Bish, 1994; Holder & Schaak, 2019). In our work, the mineral component determination of fly ash, iron-copper tailing, copper slag and Pb-Zn mine waste samples is achieved by using X-ray diffractometer Rigaku Miniflex (D/Max 600, Cu K α radiation: 1.54059 Å, 33 KV, 15 m Å) and Philips X'Pert Pro diffractometer (Cu K α radiation: 1.5418 Å, 45 KV, 40 mÅ).

5.3 TSP Application for Treatment of Wastes and Simulated Wastewater

5.3.1 Precipitation Tests of Heavy Metal from Solid Wastes

The precipitation experiments were performed followed the protocols used in prior experimental studies on chemical stabilization using phosphate amendment (Mignardi et al., 2012; Yoon et al., 2007). First, a mixture of 25 waste samples (i.e., fly ash, iron-copper tailing, copper slag and Pb-Zn mine waste) containing leachable metals ions (L/S=20) and different amounts (12.6, 25.2 and 63.0g) of TSP (equivalent to 0.1, 0.2 and 0.5 M or mol/L) were dissolved in glass beakers containing 500ml distilled water at room temperature (22.05°C) and agitated with magnetic stirring bar for 30 minutes. The pH level of the solution was adjusted and maintained at 5 with a small addition of nitric acid or NaOH during testing. After 30 minutes of the solubility test, samples of 5 ml were taken at different time intervals of 0, 5, 10, 15, 30, 60, 120 and 180 minutes and filtered immediately by 0.2 µm filters (Figure 5.6).

The concentration of metals in each sample was determined by ICP (model: Varian 710-ES ICP-OES) the following operating conditions: 1300 watts of RF Power, 15 liters per minute of plasma flow rate, 0.7 liter per minute of Nebulizer flow rate and 0.2 liter per minute of auxiliary flow rate. Calibration of ICP device was conducted before sample injection by using 2.0 mg/L of Cd, 5 mg/L of Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, and Zn standard solutions and repeated 10 times. For the accuracy of collecting

data (Table 5.7), quality assurance and quality control (QA/QC) are performed following the experimental design described by (Tasgetiren, 2014).

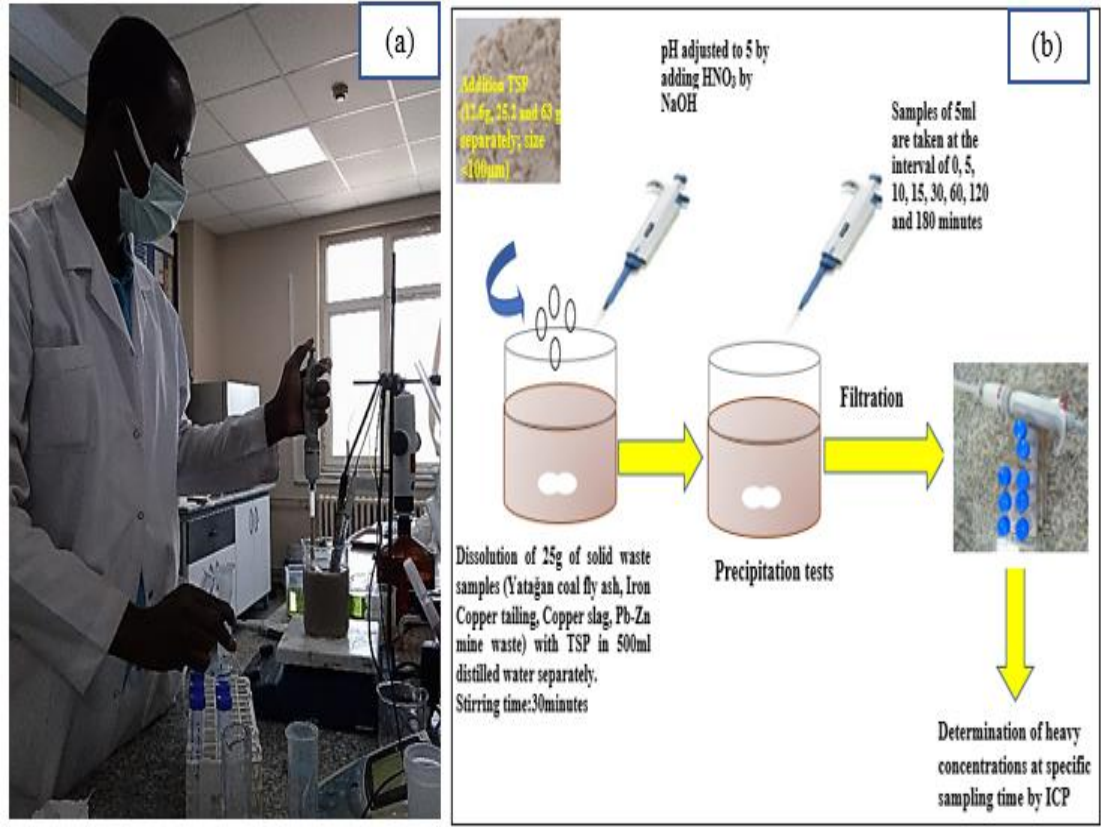


Figure 5.6 Precipitation of heavy metal from mining and industrial wastes. (a) Image of precipitation test. (b) Description of different steps of precipitation test (Personal annal 2021)

Table 5.7 Limits of detection (LOD) and quantification (LOQ) for inductively coupled plasma spectrometer measurements

Metals	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
Initial Concentrations (mg/L)	2	5	5	5	5	5	5	5	5	5
Test Number										
1	2.04	5.02	4.97	5.05	5.07	5.06	5.00	4.98	4.96	5.05
2	2.06	5.05	5.06	5.01	5.03	5.06	5.08	5.03	4.95	5.01
3	2.03	5.05	4.98	5.07	5.04	4.98	5.02	4.99	5.02	5.02
4	1.98	4.95	4.96	4.96	4.98	4.98	4.97	4.99	4.99	4.98
5	2.04	5.08	5.01	5.08	5.06	5.04	5.04	5.04	4.97	5.02
6	2.04	5.07	5.04	5.06	5.07	5.03	5.00	5.01	5.09	5.03
7	2.01	4.97	4.98	5.02	4.97	5.02	4.94	4.98	5.03	5.02
8	2.02	5.04	5.03	5.07	5.03	5.03	5.02	5.05	4.97	5.04
9	2.02	4.99	4.96	5.01	4.99	5.02	4.97	4.95	5.04	5.01
10	1.97	4.98	4.99	4.98	4.97	5.03	4.96	4.97	5.08	5.03
Mean	2.02	5.02	5.00	5.03	5.02	5.02	5.00	5.00	5.01	5.02
SD(±)	0.03	0.05	0.04	0.04	0.04	0.03	0.04	0.03	0.05	0.02
LOD	0.08	0.14	0.11	0.12	0.12	0.09	0.13	0.10	0.15	0.06
LOQ	0.28	0.45	0.35	0.40	0.39	0.29	0.42	0.32	0.52	0.19

5.3.2 Precipitation of Heavy Metal from Wastewater

5.3.2.1 Preparation of Laboratory Wastewater

The simulated wastewaters of Pb-Zn mine waste containing metal ions were prepared by acid leaching. To collect 2 liters, the leaching experiments were conducted by dissolving 50 g of Pb-Zn mine waste sample with 0.5 M HNO₃ at the ratio of solid-liquid 1/10 (w/v) and 40°C in four 500ml beakers following the leaching procedure described by Hussaini et al. (2021). The mixture of Pb-Zn waste and HNO₃ in 500ml distilled water was stirred by a horizontal mixer at 400 rpm within 1 hour. After the leaching test, the suspension (effluent) was separated through a vacuum membrane using filter paper (Reeve angel- grade: 307; size:125mm), then transferred into 2000ml

of flask (Figure 5.7). The dissolved heavy metal concentrations were analyzed by ICP (Model: Varian 710ES ICP-OES).

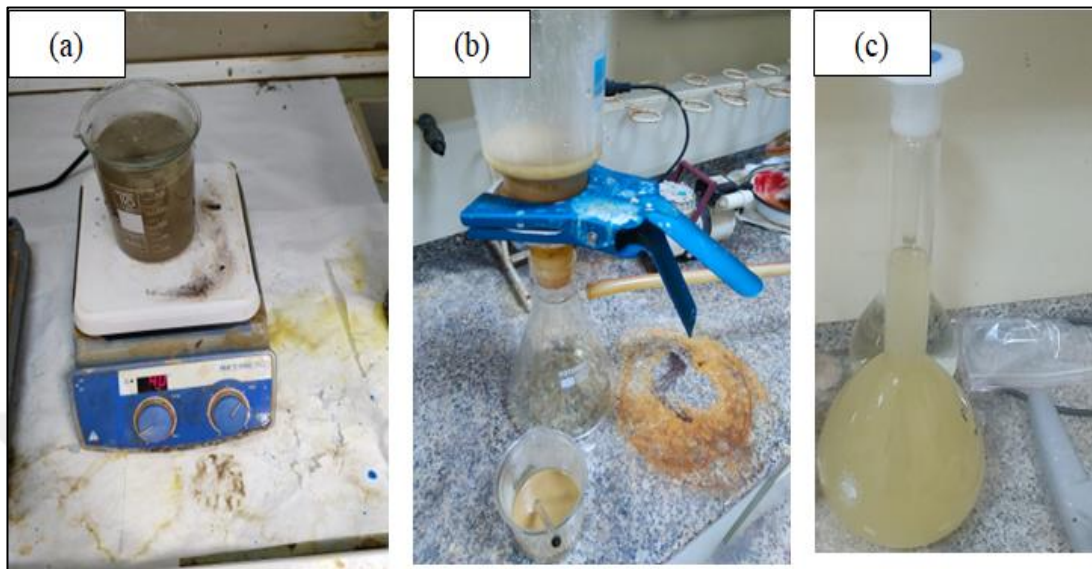


Figure 5.7 Preparation of simulated wastewater. (a) Acid leaching, (b) Solid-liquid separation by vacuum membrane filtration, (c) Simulated wastewater solution in 2000 mL flask (Personal annual, 2022)

5.3.2.2 Precipitation Test of heavy metal from simulated Wastewater

The precipitation tests were performed by adding 0.1, and 0.5 M of TSP concentrations (i.e., 12.6g and 63gTSP) separately in the beaker containing 500ml of Pb-Zn mine simulated wastewater and stirring the solution at a constant speed of 400 rpm for 30 minutes. After the dissolution of TSP, the pH of the solution increased to greater than 3 and remained constant during the precipitation tests. pH and potential redox (Eh) of the solution were measured by pH meter Orion 4 Star and potential electrode. Samples of 5 ml were taken at different period intervals of 0, 5, 15, 30, 60, 120, 180 and 240 minutes and filtered immediately using 0.2 μm syringe filters. Finally, the filtrates were acidified and diluted at 10 dilution factors for the determination of metal concentrations by Inductively Coupled Plasma (Model: Varian 710ES ICP-OES). Figure 5.8 elucidate the different steps of precipitation test.

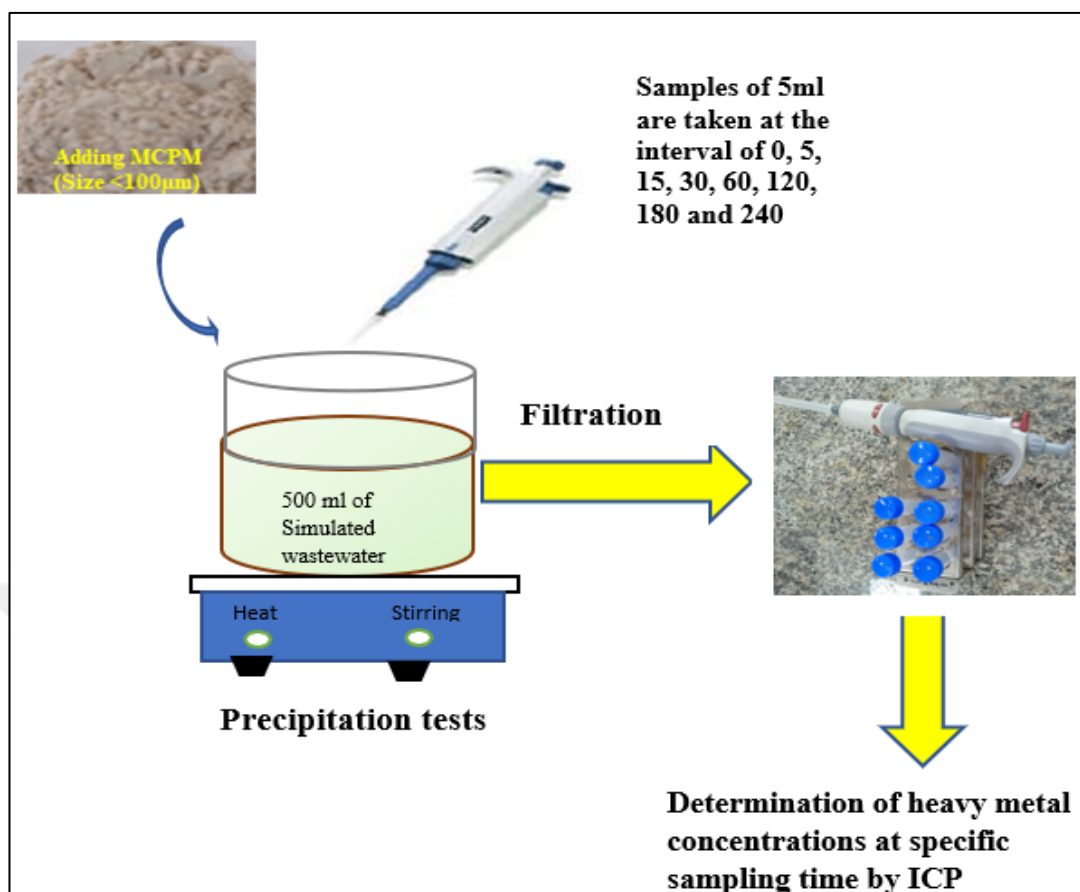


Figure 5.8 Flowsheet of precipitation test for heavy metal removal from simulated wastewater

5.3.3 X-Ray Diffraction Analyses (XRD) of Residue

The collected slurry wastes (precipitate obtained treatment of fly ash, iron-copper tailing, copper slag and Pb-Zn mine waste by TSP) were filtrated through a filter paper (Reeve angel- grade: 307; size:125mm), then, solid contents were oven-dried at 105°C for 1 hour, cooled in a desiccator, and ground to size below 100 µm using agate mill disc. The dry samples were analyzed using X-ray diffractometer Rigaku Miniflex (D/Max 600, Cu K α radiation: 1.54059 Å, 33 KV, 15 m Å) and Philips X'Pert Pro diffractometer (Cu K α radiation: 1.5418 Å, 45 KV, 40 mÅ).

CHAPTER SIX

EXPERIMENTAL RESULTS AND DISCUSSIONS

6.1 Triple Superphosphate Characterization for Removal of Heavy Metals

6.1.1 *Physiochemical Properties of TSP*

6.1.1.1 *Particle Size Distribution and XRD Analyses of TSP Sample*

The result of particle size distribution for raw TSP as received and the ground TSP sample is presented in Table A1 and Figure 6.1. As illustrated in Figure 6.1a, 100% of the particle of the raw TSP sample is under 5 mm and 50% is under 2mm, whereas Figure 6.2b of the ground TSP shows more than 80 % of TSP particles is below 80 μ m sizes and 30% of particles have sizes lower than 18 μ m. The mean particle diameter of the ground TSP sample is approximately 49 μ m.

The performed X-ray diffraction (XRD) analysis indicates the mineralogical composition of both the raw and insoluble TSP samples. As illustrated in Figure 6.2, the XRD peaks indicated that the structure of the fresh TSP sample is crystalline. These results agree with the previous studies which showed the formation of the crystalline form in the raw triple superphosphate (Labgairi et al., 2020; Seesanong et al., 2021). The main compound was monocalcium phosphate monohydrate $[\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}]$, and the formation of minor mineral compounds such as fluorapatite $(\text{Ca}_5(\text{PO}_4)_3\text{F})$ bassanite $(2\text{CaSO}_4\text{H}_2\text{O})$, and quartz (SiO_2) were detected as small peaks (see Figure 6.2). Figure 6.3 shows an amorphous form of TSP insoluble, and the peaks demonstrated the presence of fluorapatite $(\text{Ca}_5(\text{PO}_4)_3\text{F})$, bassanite $(2\text{CaSO}_4\text{H}_2\text{O})$, and quartz (SiO_2) .

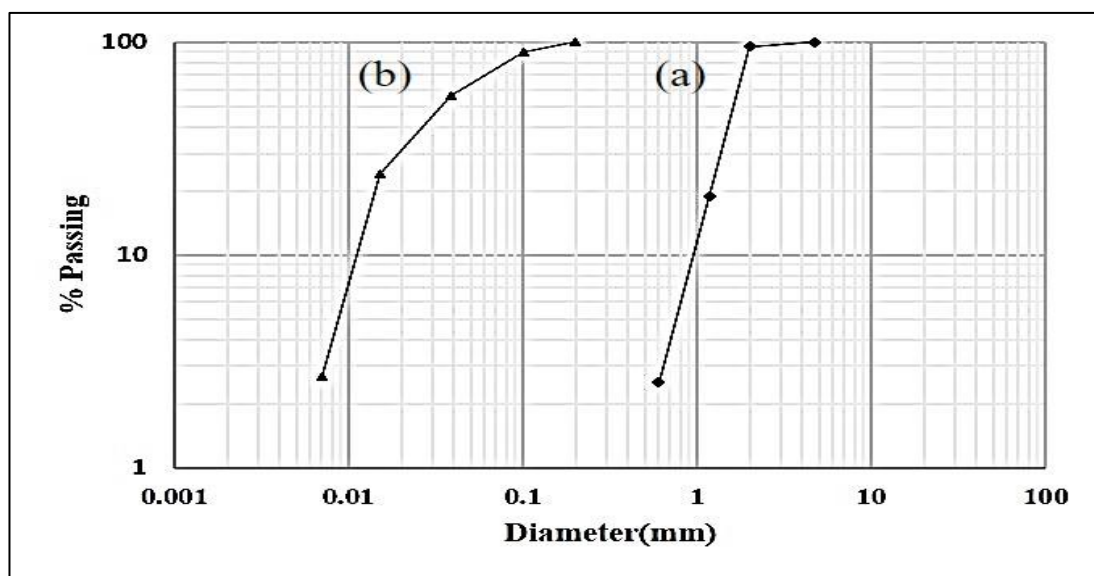


Figure 6.1 Particle size distribution of TSP samples. (a) Raw TSP; (b) Ground TSP (<100µm).

6.1.1.2 TSP Solubility and its Moisture Content TSP

The results presented in Table 6.1 indicate that 85% of TSP is solubilized in the water after mixing 5 g of TSP with 500 ml of distilled water. The pH of the solution was measured as 3.5. No pH adjustment is made. Research has also demonstrated that phosphate-based materials containing 30% of total P in water-soluble, have a solubility rate ranging from 82 to 96 % (Chien et al.; 1990). Although the solubility of TSP is high, a slight decrease in solubility rate is observed when the amount of TSP increases. Regarding the effect of temperatures, the results demonstrated that the solubility percent of TSP increases with increasing temperature (Table 6.2). Similarly, Lo et al., (2009) state that higher temperature promotes optimum solubility of phosphate with a reaction time.

The moisture content of TSP results obtained through the ratio of the difference in the weight of the initial and the dry TSP sample by the initial weight is 2%.

6.1.1.3 Chemical Analysis of Raw TSP

The chemical analyses of the TSP fertilizer sample indicated that TSP contains heavy metals. As reported in the literature, commercial fertilizers produced in several

countries such as India, Italy, Australia, New Zealand, England, and United State contain important concentration values of Cd, Cr, Cu, Ni, Pb, and Zn (Lee & Keeney, 1975). Presence of heavy metals is originated from the phosphate rock, and the characteristics of TSP fertilizers. Except for Cr, Mn and Zn concentrations, all the concentrations of heavy metals in this study exceed the average of heavy metal concentration values in 24 TSP samples analyzed by Charter et al. (1993) as given in Table 6.3. As the TSP fertilizer differs based on its proprieties, the chromium concentration obtained by El-Taher & Althoyaib, (2012) is greater than the Cr concentration in our study. The concentration value of Pb in the TSP sample using AOAC methods is lesser than the maximum permissible concentration (MPC) of soil pollution regulation for Turkey and Europe, while the other concentrations of heavy metals exceed the permissible limit values (Anonim, 2001; Kabata-Pendias, 1995). Referring to the impurities (heavy metals) that 63g of TSP released through the addition of distilled water, the heavy metals concentrations are below the permissible concentration given by Turkey and Germany's environmental regulations except for cadmium concentration.

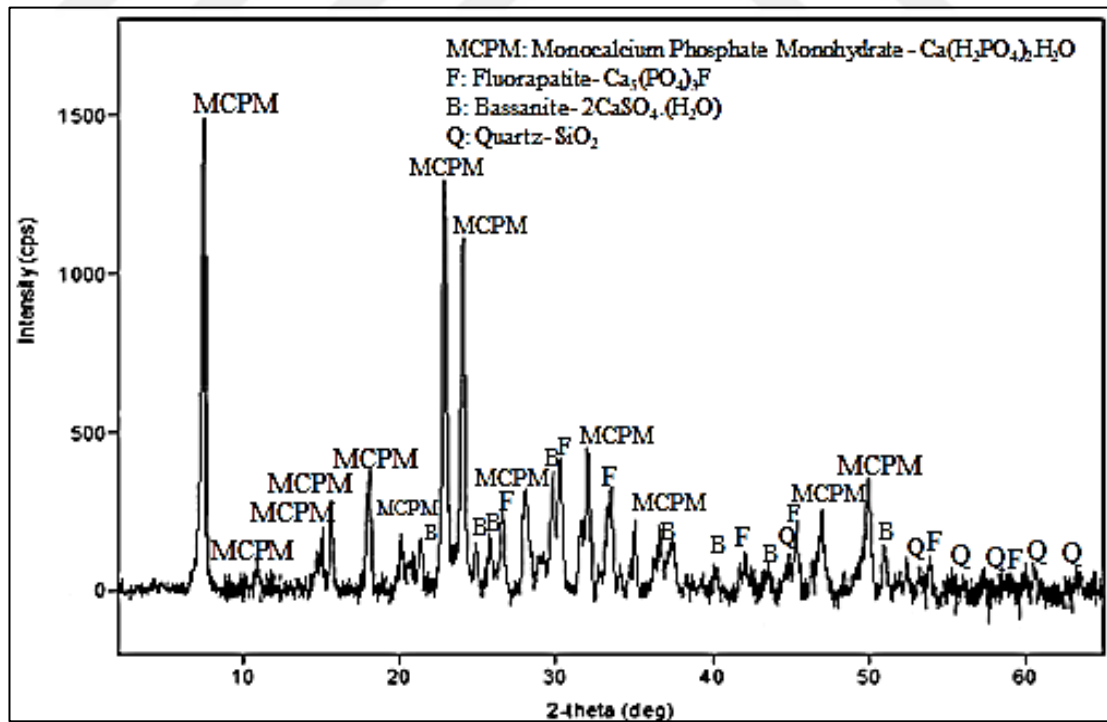


Figure 6.2 XRD pattern of raw TSP sample as received

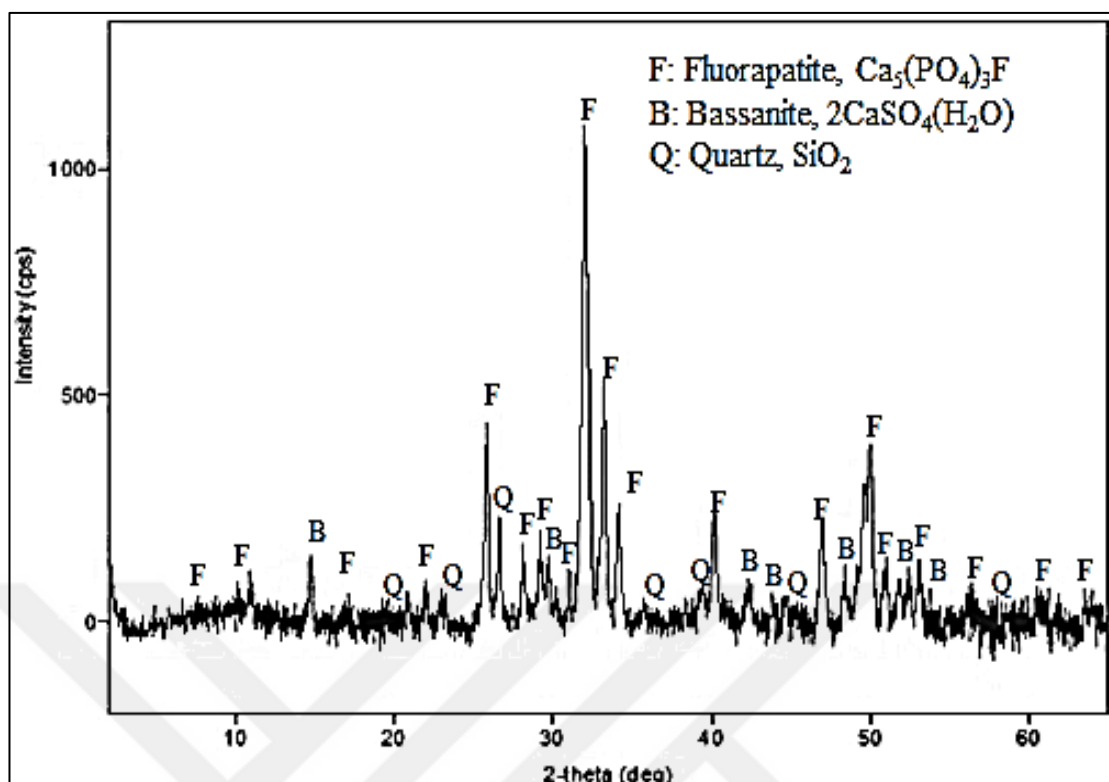


Figure 6.3 XRD pattern of insoluble TSP sample

Table 6.1 Solubility test results with different masses of TSP at 30 n minutes of reaction time

Name of Sample	Mass weighed (g)	Mass of Piece of paper (g)	Net mass weighed (g)	Mass after solubility (g)	Mass of filter paper (g)	Mass of residue (Insoluble) (g)	Net mass of solute (g)	Amount of solute (%)
5g	5.392	0.391	5.001	1.991	1.245	0.746	4.255	85.1
10g	10.418	0.415	10.003	2.915	1.241	1.674	8.329	83.3
20g	20.395	0.409	19.986	4.870	1.246	3.624	16.362	81.9
40g	40.407	0.412	39.995	9.154	1.240	7.914	32.081	80.2
80g	80.405	0.399	80.006	18.590	1.243	17.347	62.659	78.3

Table 6.2 Solubility test for 5g TSP with different temperatures at 30 minutes of reaction time

Mass of TSP weighed (g)	Mass of Piece of paper (g)	Net mass weighed (g)	Mass after solubility (g)	Mass of filter paper (g)	Mass of residue (Insoluble) (g)	Net mass of solute (g)	T °C	Amount of solute (%)
5.362	0.366	4.996	1.901	1.245	0.656	4.34	40	86.9
5.371	0.37	5.001	1.712	1.245	0.467	4.534	60	90.7
5.358	0.359	4.999	1.503	1.245	0.258	4.741	80	94.8
5.371	0.368	5.003	1.294	1.245	0.049	4.954	100	99.0

Table 6.3 Chemical analysis showing impurities of triple superphosphate sample

Heavy metals	Concentrations (mg/kg)					
	TSP used in this study		TSP samples used in the previous study (Concentration ranged)		*(MPC) Turkey	**(MPC) Germany
	Using distilled water	Using HCl acid leaching	Charter (1993)	El-Taher & Althoyaib (2012)		
Cd	5.95	38.50	6.80-47.00	33.00-36.30	3.00	2.00
Co	0.00	37.00	9.00-15.00	20.00-22.00	20.00	NA
Cr	20.16	343.90	63.00-548.00	390.00-410.00	100.00	200.00
Cu	18.17	43.60	2.10-13.00	NA	14.00	50.00
Fe	117.46	1960.00	300.00-1000.00	NA	NA	NA
Mn	12.30	79.60	14.00-352.00	NA	NA	NA
Ni	16.75	120.60	14.00-40.00	67.70-79.80	75.00	100.00
Pb	0.00	50.00	9.00-16.00	32.00-32.40	300.00	500.00
Sr	129.84	1301.80	363.00-1016.00	NA	NA	NA
Zn	193.25	500.20	77.00-696.00	NA	300.00	300.00

MPC: Maximum permissible concentration of soil pollutant; NA: Not available

* Official Gazzette (2001)

** Kabata-Pendias, (1995)

6.1.2 Heavy Metals Removal by TSP in Aqueous Solutions

The experimental results on 10 mg/L of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn removal by 0.1 M of TSP indicate that TSP can successfully precipitate heavy metals such as Cd, Fe, and Pb while Co, Cr, Cu, Mn, Ni, and Zn were less removed by TSP in the aqueous solution (Table 6.4). As the precipitation time increases, the percentage of removal increases in all heavy metals. In addition, it was found that the presence of Cd, Cr, Fe, Cu, Mn, Ni and Zn in TSP blank.

TSP precipitation test with Cd has demonstrated that 60.0% of Cd concentration (10mg/L) was removed at 5-minute of contact time, then increased to 85.1% (Figure 6.4a). For instance, TSP can be used as a phosphate amendment to remove Cd in aqueous solution and the previous experimental study has reported more than 90.0%

of Cd is removed by MCPM through the in-situ method (Thawornchaisit & Polprasert, 2009).

Regarding the removal of Co, TSP precipitating removes Co with a removal percent of 73.4% (Figure 6.4b). The application of apatite to immobilize Co by in-situ remediation indicates high removal of Co (79.9%) within 7 days compared to our findings (Knox et al., 2003)

Figure 6.4c indicate the percentage of Cr removal increases from 18.7 to 69.6 % at 5 and 180 minutes of precipitation test. El Kaim Billah et al. (2019) also mentioned that 67.4% of Cr was immobilized using fluorapatite as natural phosphate. Our results show a better removal of Cr in aqueous solution by 0.1 M of TSP concentration

Precipitation tests of Cu pure metal show that TSP is less effective with Cu provides poor removal efficiency Cu was removed and the maximum removal is 47.7% (Figure 6.4d). Previous study has reported a poor stabilization of Cu over four weeks in contaminated topsoil following the application of triple superphosphate (Bes & Mench, 2008).

For Iron pure metal removal, the results in Figure 6.5a show the concentration of iron decreased by 83.2% at 180 minutes of reaction times. The percentage of iron removal increased with varying times. Similarly, the increase in iron removal efficiency of iron was observed by phosphate amendment (hydroxyapatite) with time (Ruiti & Thayer, 2015).

The removal of Mn pure metal by TSP, and as observed in Figure 6.5b, the concentration decreased with variation time. The stabilization (removal) rate obtained in this study is less than 66.7% by using 12.6g of TSP (i.e., 0.1M of TSP). In contrast, a study performed on Mn removal by phosphate amendment has reported the use of apatite immobilizes 96 % of Mn concentration from the aqueous solution (Oliva et al., 2010).

TSP is ineffective for nickel removal and the maximum rate is 62.7% (Figure 6.5c). Similarly, Seaman et al. (2001) reported the use of hydroxyapatite fails to stabilize Ni successfully. In contrast, hydroxyapatite which is a phosphate-based material stabilizes up to 80% of contaminated soil (Hafsteinsdóttir et al., 2015).

The result of the TSP test with lead pure metal indicates that TSP solution precipitates Pb pure metal successfully (Figure 6.5.d). It shows that 89.9% of Pb is precipitate within 180 minutes of reaction times and pH acidic. The prior study demonstrated that the Pb removal by phosphate amendment was performed in the acid medium (S. Chen et al., 2007b) In this study, the measured pH of the solution during lead precipitation with triple superphosphate was 3.4 which is acidic.

Triple superphosphate is ineffective for the removal of zinc ions and contains an important concentration. According to François et al. (2009) “the amount of Zn in the fertilizers ranges from less than 50 to more than 1500 mg/L. Figure 6.5e indicates that 57.8% of 10mg/L Zn was removed in 180 minutes of reaction period. By contrast, studies have demonstrated that hydroxyapatite reduces Zn concentration effectively through the ion exchange method (Suzuki et al., 1982).

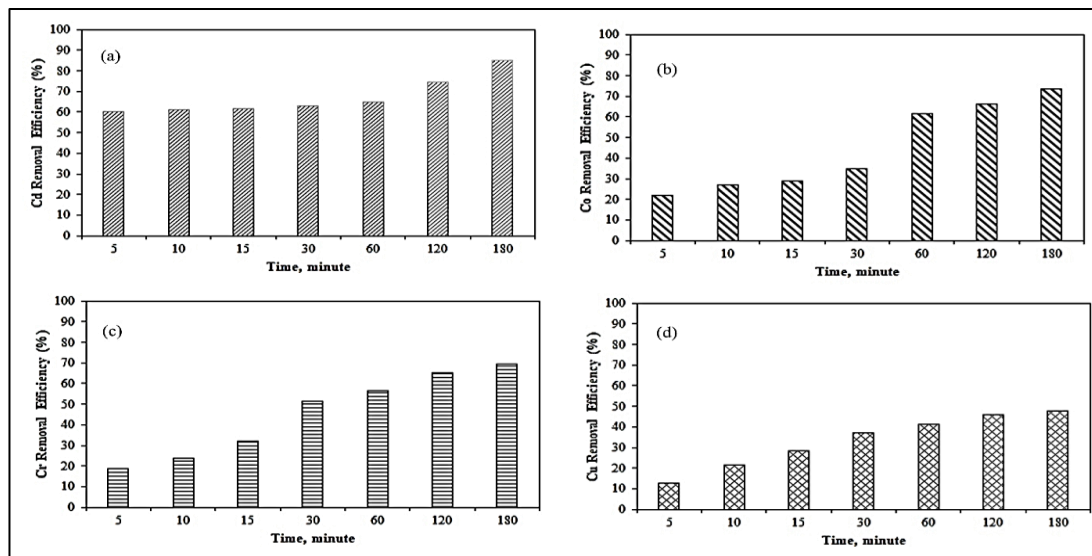


Figure 6.4 Histogram for heavy metal removal by 0.1M TSP at room temperature (22.05). (a) Cd removal, (b) Co removal, (c) Cr removal, (d) Cu removal. The initial concentration of each metal: 10mg/L

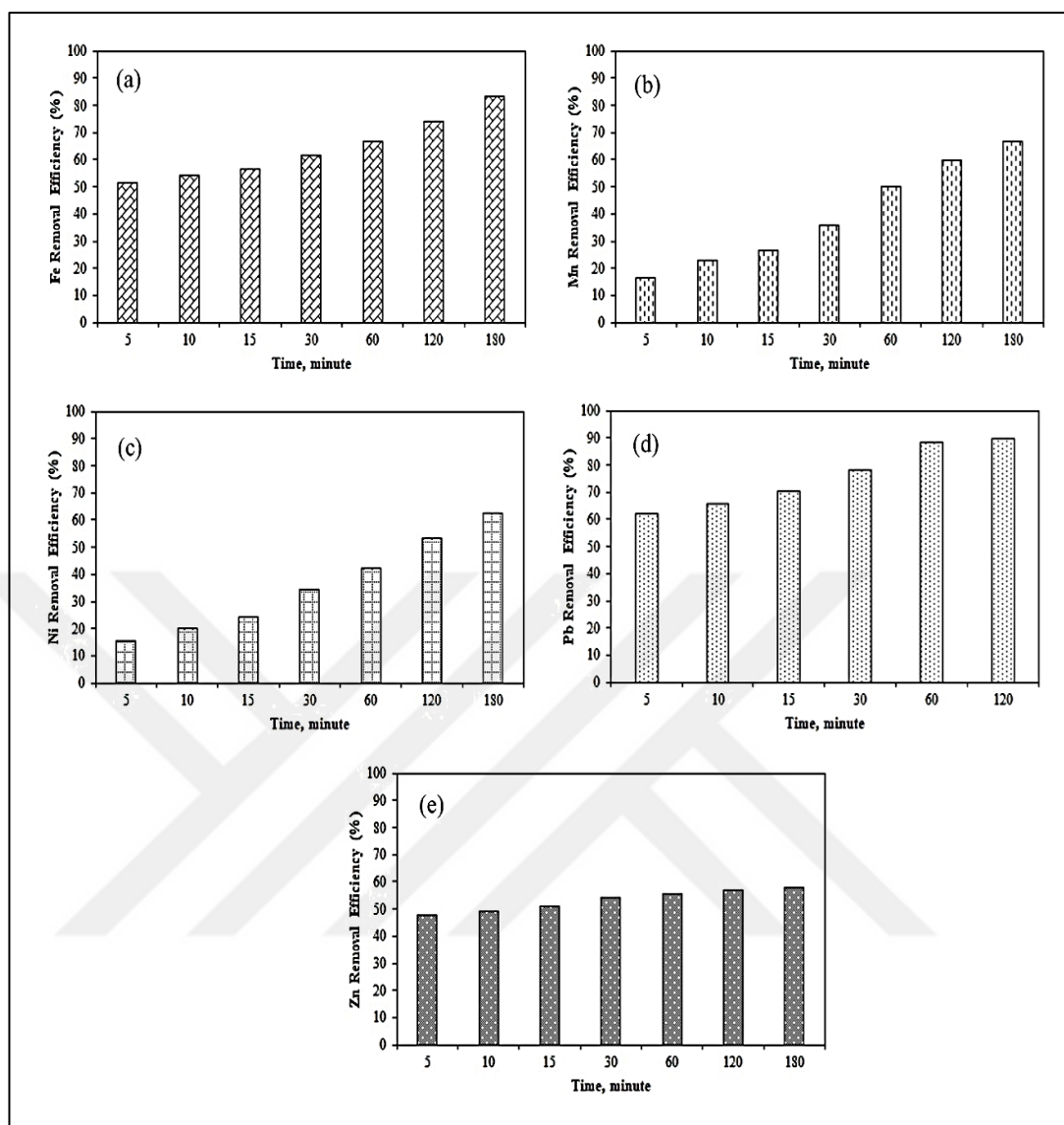


Figure 6.5 Histogram for the heavy metal removal by 0.1M TSP at room temperature (22.05°C). (a) Fe removal, (b) Mn removal, (c) Ni removal, (d) Pb removal, (e) Zn removal. The initial concentration of each metal: 10mg/L

Table 6.4 Result of heavy metals removal using 0.1 M TSP in 500ml of distilled water. (TSP dissolution time:30min.; after addition of TSP pH for Cd=3.4; pH for Co=3.39; pH for Cr=3.42; pH for Cu=3.3; pH for Fe=3.43; pH for Mn=3.37; pH for Ni=3.42; pH for Pb=3.40 and pH for Zn=3.38; initial concentration of each metal=10mg/l).

Times (minutes)	Effluent concentrations with different times (mg/L)								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
TSP Blank	7.45	0.00	0.81	0.58	6.97	0.19	0.97	0.00	8.78
0	17.47	10.0	10.81	10.58	16.97	10.19	10.97	10.0	18.78
5	7.01	7.82	8.79	9.26	6.97	8.5	9.27	4.78	9.79
10	6.85	7.31	8.25	8.28	6.56	7.88	8.74	3.79	9.57
15	6.7	7.11	7.34	7.58	6.25	7.47	8.29	3.44	9.17
30	6.47	6.51	5.26	6.66	5.53	6.53	7.19	2.95	8.6
60	6.17	3.84	4.68	6.19	4.77	5.09	6.34	2.17	8.31
120	4.47	3.39	3.73	5.72	3.75	4.11	5.14	1.15	8.08
180	2.61	2.66	3.28	5.53	2.41	3.39	4.09	1.02	7.92
Times	Removal Efficiency (%)								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
0	0.0	0.0	0.0	0.0	0	0.0	0.0	0.0	0.0
5	60.0	21.8	18.7	12.5	51.3	16.6	15.4	52.2	47.9
10	60.9	26.9	23.6	21.7	54.2	22.7	20.3	62.1	49
15	61.7	28.9	32.1	28.3	56.3	26.7	24.3	65.6	51.2
30	63.0	34.9	51.3	37.1	61.4	36.0	34.4	70.5	54.2
60	64.8	61.7	56.7	41.5	66.6	50.1	42.2	78.3	55.8
120	74.5	66.1	65.5	45.9	73.8	59.7	53.1	88.5	57
180	85.1	73.4	69.6	47.7	83.2	66.7	62.7	89.9	57.8

6.1.3 Lead Removal by Slaked Lime in Aqueous Solution

The results of the precipitation test of lead by slaked lime ($\text{Ca}(\text{OH})_2$) are presented in Table 6.5 and Figure 4.8. As illustrated in Figure 6.6, 0.1M of slaked lime precipitates (removes) 50.2% of 10 mg/L Pb and 84.6% of 10mg/L Pb in aqueous solution at 5 and 180 minutes respectively. The measured pH after 30 minutes of slaked solubility is 12.58. The results of prior studies show a great achievement of lead precipitation by $\text{Ca}(\text{OH})_2$ compared to our findings (Chen et al., 2018; Kavak, 2013; Wirojanagud et al., 2004; Yun & Yu, 2015). According to Fu & Wang (2011) “the low initial concentration of metal constitutes affect strongly the efficiency of lime”. Apart from the influence of initial concentration, the performance of lime is influenced by

the parameters such as pH and Ca(OH)_2 amount. These parameters are discussed in section 6.1.4.

Table 6.5 Result of lead removal using 0.1 M Ca(OH)_2 in 500ml of distilled water. (Ca(OH)_2 solubility time:30min.; pH=11.58 after addition of Ca(OH)_2 , the initial lead concentration:10 mg/L

Time (minutes)	Effluent concentrations (mg/L)	Removal Efficiency (%)
Ca(OH)_2 Blank	0.0	0.0
0	10.00	0.0
5	4.98	50.2
10	3.35	66.5
15	2.86	71.4
30	2.38	76.2
60	1.91	80.9
120	1.63	83.7
180	1.54	84.6

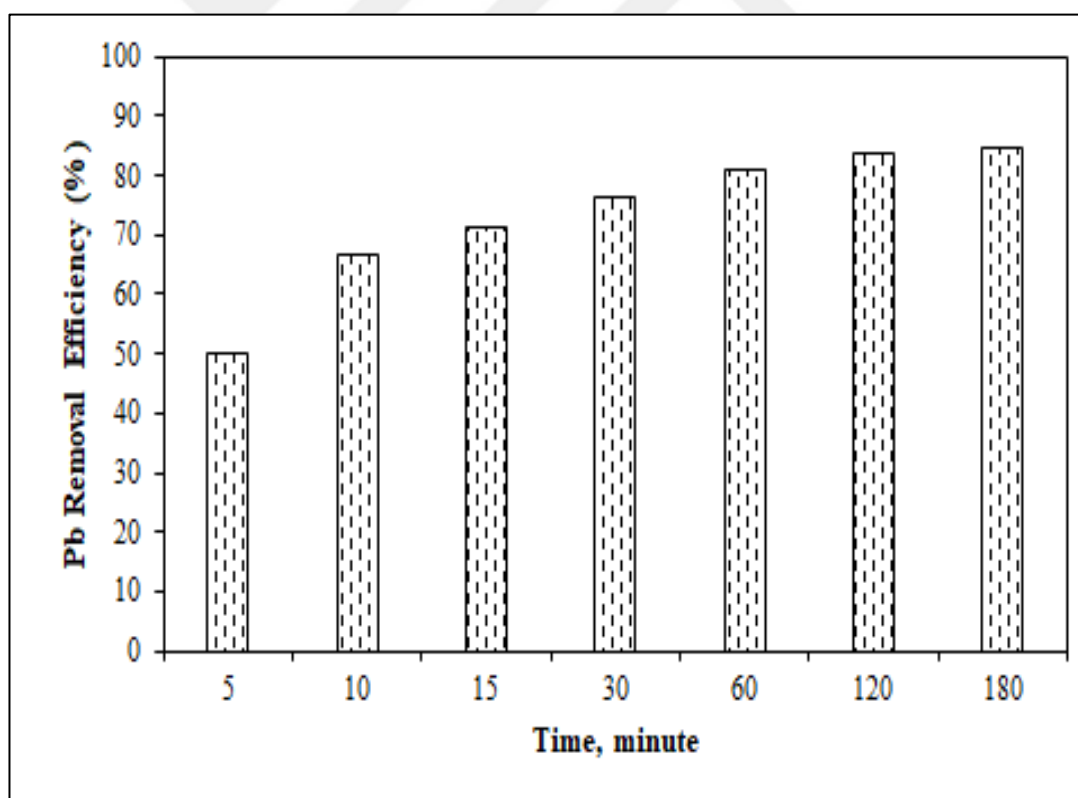


Figure 6.6 Histogram of lead removal by 0.1M slaked lime at room temperature (22.05). The initial lead concentration: 10 mg/L

6.1.4 Comparison between TSP and Slaked Lime for Lead Removal in Aqueous Solutions

The comparison between TSP and slaked lime precipitant on lead removal in aqueous solutions was explored to evaluate the influence of initial lead concentration, TSP and slaked lime concentration and pH on their efficiencies.

6.1.4.1 Influence of Pb Initial Concentration

Precipitation tests on three lead initial concentrations (10, 20 and 50mg/L) were performed in 500 ml distilled water using 0.1M TSP and 0.1 M Ca(OH)_2 within 180 minutes. As shown in Table 6.6, the percentage of lead removal through the use of 0.1 M TSP decrease slightly as the initial concentration increase whereas it shows the opposite behavior by using 0.1M of Ca(OH)_2 . The percentage of lead removal by 0.1M TSP are 89.9%, 88.4% and 80.1 for 10 mg/L, 20 mg/L and 50 mg/L of lead respectively. In contrast, 0.1M Ca(OH)_2 precipitate 84.6%, 87.6% and 90.7% of 10mg/L, 20mg/L and 50 mg/L of lead concentrations.

Table 6.6 Influence of lead initial concentration (10, 20 and 50 mg/L) on lead removal by 0.1M TSP and 0.1M Ca(OH)_2 at 180 minutes

Lead initial concentrations (mg/L)	Effluent concentrations (mg/L)		Removal Efficiency (%)	
	TSP	Ca(OH)_2	TSP	Ca(OH)_2
10	1.02	1.54	89.9	84.6
20	2.32	2.62	88.4	87.9
50	9.94	4.95	80.1	90.1

6.1.4.2 Influence of TSP and Slaked Lime concentrations

The influence of TSP and slaked lime dosages (concentrations) on 10 mg/l of lead removal were investigated at 0.1, 0.2 and 0.5M of each precipitant. The obtained experimental results in Table 6.7 show that the more TSP dosages are added in the solution, the better lead removal efficiencies are and its rates are 89.9%, 95.4% and

99.9% for 0.1, 0.2 and 0.5M of TSP respectively. For Ca(OH)_2 precipitating agent, it was found that a decrease and an increase in the percentage of lead removal which are 87.3% at 0.2M TSP and 82.9% for 0.5M of Ca(OH)_2 . The observation made in this work, low lead initial concentration can affect also the dosage of slaked lime. (F. H. Wang et al., 2015) Wang et al.; (2015) reported that controlling the dosage of lime represents a challenge to predict and enhance the heavy metals removal in wastewater.

Table 6.7 Influence of TSP and Ca(OH)_2 on 10 mg/L of lead removal at 180 minutes

Effluent concentration (mg/L)	TSP concentration (M)			Ca(OH)_2 concentration (M)		
	0.1	0.2	0.5	0.1	0.2	0.5
	1.02	0.53	0.01	1.54	1.27	1.71
Removal Efficiency (%)	89.9	94.7	99.9	84.6	87.3	82.9

6.1.4.3 Influence of pH

The pH effects on lead removal by 0.1M TSP and 0.1M Ca(OH)_2 separately were carried out through the small addition of HNO_3 in order to drop the pH into 1, 2 and 3. As shown in Table 6.8, the change in pH decreased slightly the percentage of lead removal at 0.1M of TSP at 180 minutes and the precipitation rates are 89.9%, 87.7% and 86.2% for pH 3, 2 and 1. For pH 3 on the removal of lead by TSP, no addition of HNO_3 was made because the solution pH is already 3.4 after adding 0.1M of TSP. However, a significant diminution of precipitation efficiency was observed for the removal of lead by 0.1M of Ca(OH)_2 as the pH decreased. At pH 1, 2 and 3 the lead precipitation efficiencies using 0.1M of Ca(OH)_2 are 16.4%, 40.3% and 48.6. In environmental science, experimental results demonstrated that the pH is strongly the efficiency of lead removal (Karimi, 2017). In addition, Gong et al. (2018) noticed continuous pH monitoring is essential after using lime in order to prevent metal dissolution again. For instance, the use of TSP can solve this problem because the obtained experimental results show pH has less effect on the lead removal efficiency.

Table 6.8 Influence of pH (1, 2 and 3) on 10 mg/L lead removal by 0.1M TSP and 0.1M Ca(OH)₂ at 180 minutes

pH of the solution after adding HNO ₃	Effluent concentrations (mg/L)		Removal Efficiency (%)	
	TSP	Ca(OH) ₂	TSP	Ca(OH) ₂
1	1.38	8.36	86.2	16.4
2	1.23	6.97	87.7	40.3
3	1.02	5.14	88.9	48.6

6.2 TSP Solution Chemistry for Pb, Fe, Cd, Cu and Zn Removal in Aqueous Solutions

The investigation of TSP solution chemistry for the removal of Pb, Fe, Cd, Cu and Zn ions was done in accordance with our previous study on lead removal by TSP from aqueous solutions (Souley Garba et al., 2022). The study demonstrated the determination of lead phosphate forms through Pourbaix diagrams (stability area diagrams) was verified by precipitation test and was approved by XRD analysis of Pb precipitate.

6.2.1 Pourbaix (Eh-pH) and Speciation Diagrams

6.2.1.1 Pourbaix Diagram of Pb-H₂O and Pb-PO₄³⁻.H₂O

Figure 6.7 illustrates the Pourbaix diagram of Pb-H₂O system with [Pb]=10⁻³ Kmol/m³. The lead concentration [Pb] indicates the amount of total dissolved metal ions in the system. The water stability is shown by the upper and lower dotted lines. As shown in Figure 6.7, Pb(+2a) and Pb₆(OH)₈(+4a) are the two main species at pH below 9.5 while at pH value superior to 12.4, Pb(OH)₄(-2a) is the main soluble lead complex. Between pH 9.5 and 12.4, lead can stabilize (precipitate) as lead oxide (PbO). The Pourbaix diagrams of Pb-PO₄³⁻-H₂O system with different concentrations of TSP and Pb are presented in Figures 6.8 and 6.9. When the total lead concentration is constant at 10⁻³M, the nature and stability zones are affected by the concentrations of TSP (Figure 6.7). As shown in Figure 6.7a, Pb(+2a) interact with phosphate to produce

the insoluble lead phosphate compounds $[\text{Pb}(\text{H}_2\text{PO}_4)_2(\text{c})$ and $\text{PbHPO}_4(\text{c})$] at almost TSP concentrations ($[\text{H}_3\text{PO}_4^0] = 1\text{M}$).

Furthermore, $\text{Pb}_6(\text{OH})_8(+4\text{a})$ reacts with H_3PO_4^0 to produce $\text{Pb}_3(\text{PO}_4)_2(\text{c})$. Under these conditions, lead (Pb) can be removed (precipitated) as lead phosphates at acid ($\text{pH}=4$) and basic ($\text{pH}=12.8$) medium. At pH value up to 12.8, lead forms soluble species of $\text{Pb}(\text{OH})_4(-2\text{a})$. As the concentration of TSP decreases, the stability zone of $\text{Pb}(\text{H}_2\text{PO}_4)_2(\text{c})$ and $\text{PbHPO}_4(\text{c})$ compounds become smaller, then completely disappeared (Figures 6.8b and 6.8c). In contrast, the stability zone of $\text{Pb}_3(\text{PO}_4)_2(\text{c})$ and $\text{Pb}_4\text{O}(\text{PO}_4)_2(\text{c})$ compounds increase and remains stable when the concentration of TSP decreases.

At constant TSP concentrations, Figures 6.9 indicates high and low lead concentrations. In the presence of TSP, lead phosphates occupy the large zone of the Eh-pH diagram. Also, Figures 6.9a and 6.9b show that in the presence of TSP, no lead oxide production occurs apart from a narrow zone of $\text{Pb}_3(\text{PO}_4)_2(\text{c})$ and $\text{Pb}_4\text{O}(\text{PO}_4)_2(\text{c})$. Thus, even at high value of pH, lead phosphates do not dissociate. In other words, TSP reacts with lead and produces a stable precipitate.

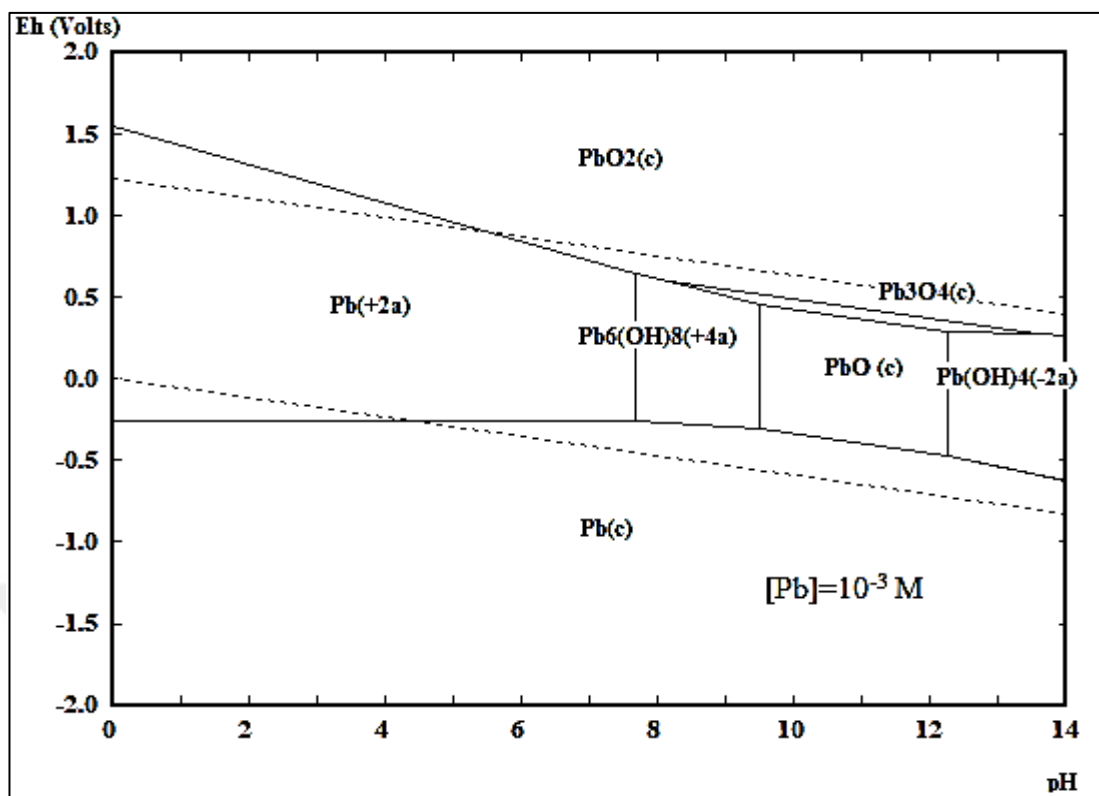


Figure 6.7 Pourbaix diagram of Pb-H₂O system, $[Pb] = 10^{-3} \text{ Kmol/m}^3$

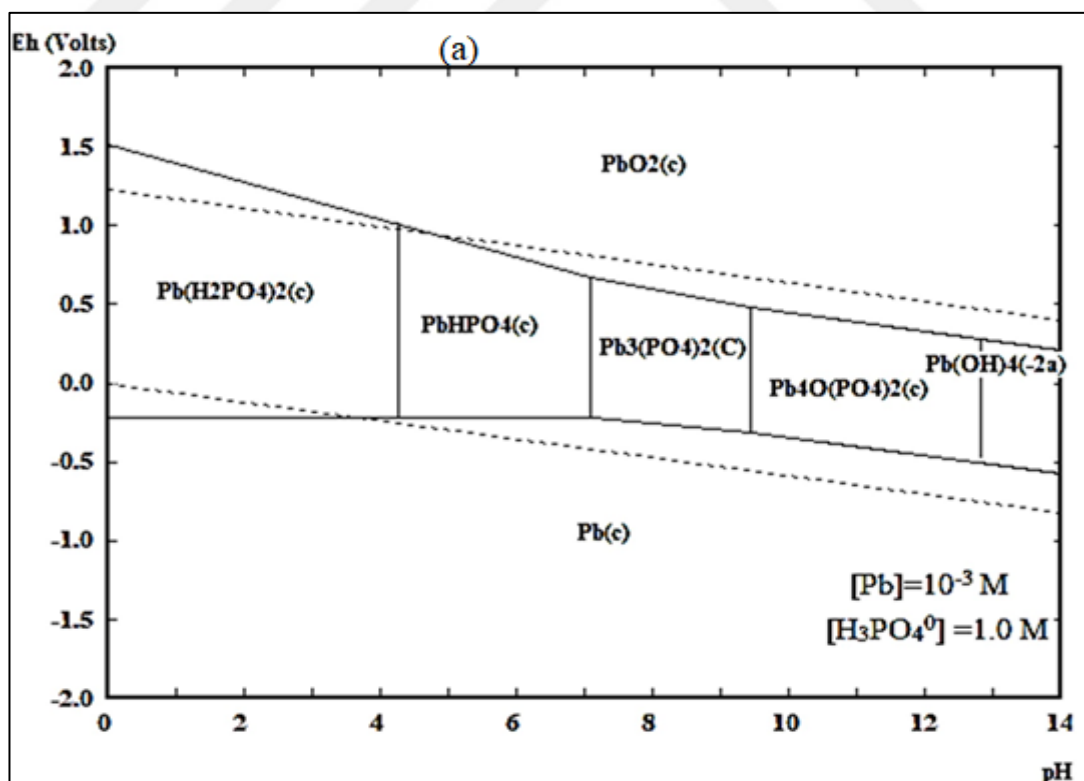


Figure 6.8 Pourbaix diagram of Pb-PO₄³⁻-H₂O system, $[Pb] = 10^{-3} \text{ Kmol/m}^3$. (a) $[H_3PO_4^0] = 1 \text{ Kmol.m}^3$.
(b) $[H_3PO_4^0] = 10^{-3} \text{ Kmol/m}^3$; (c) $[H_3PO_4^0] = 10^{-6} \text{ Kmol/m}^3$

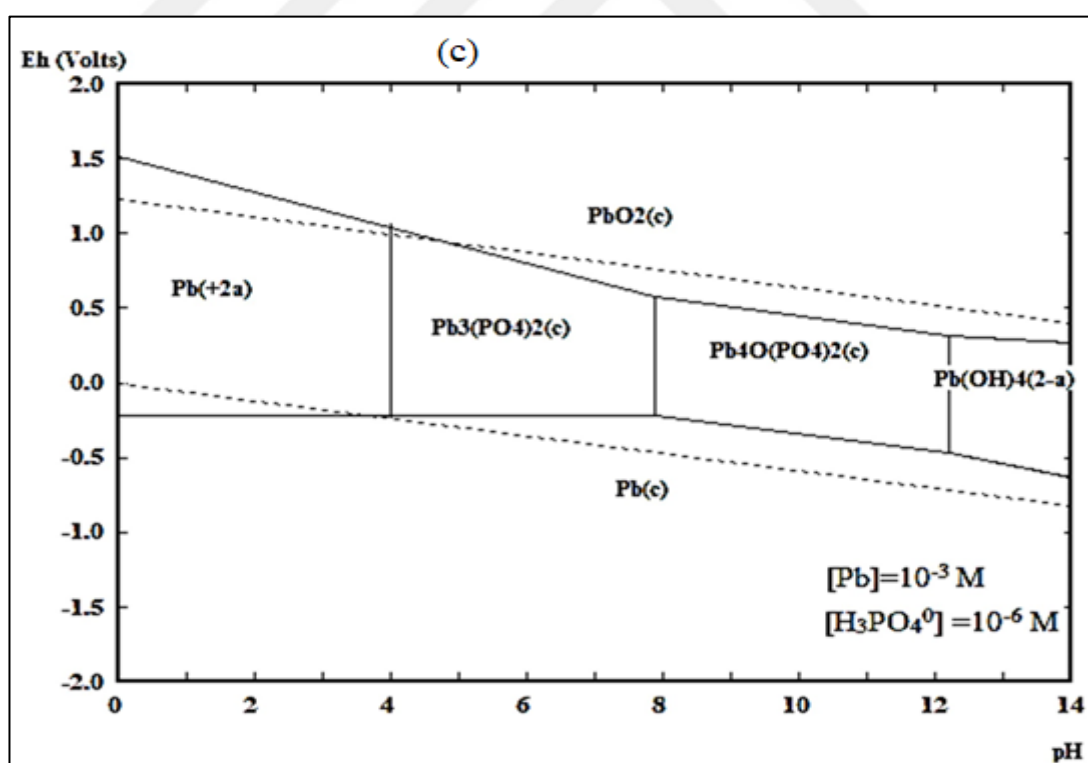
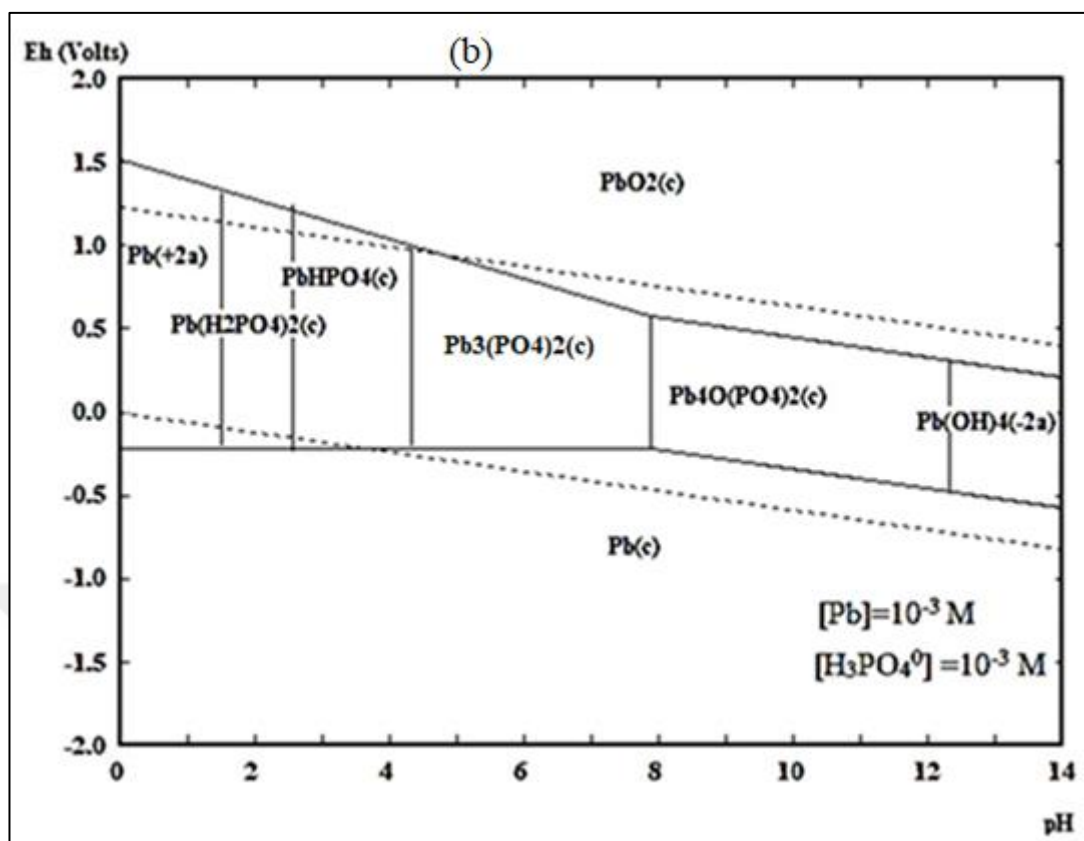


Figure 6.8 Continues

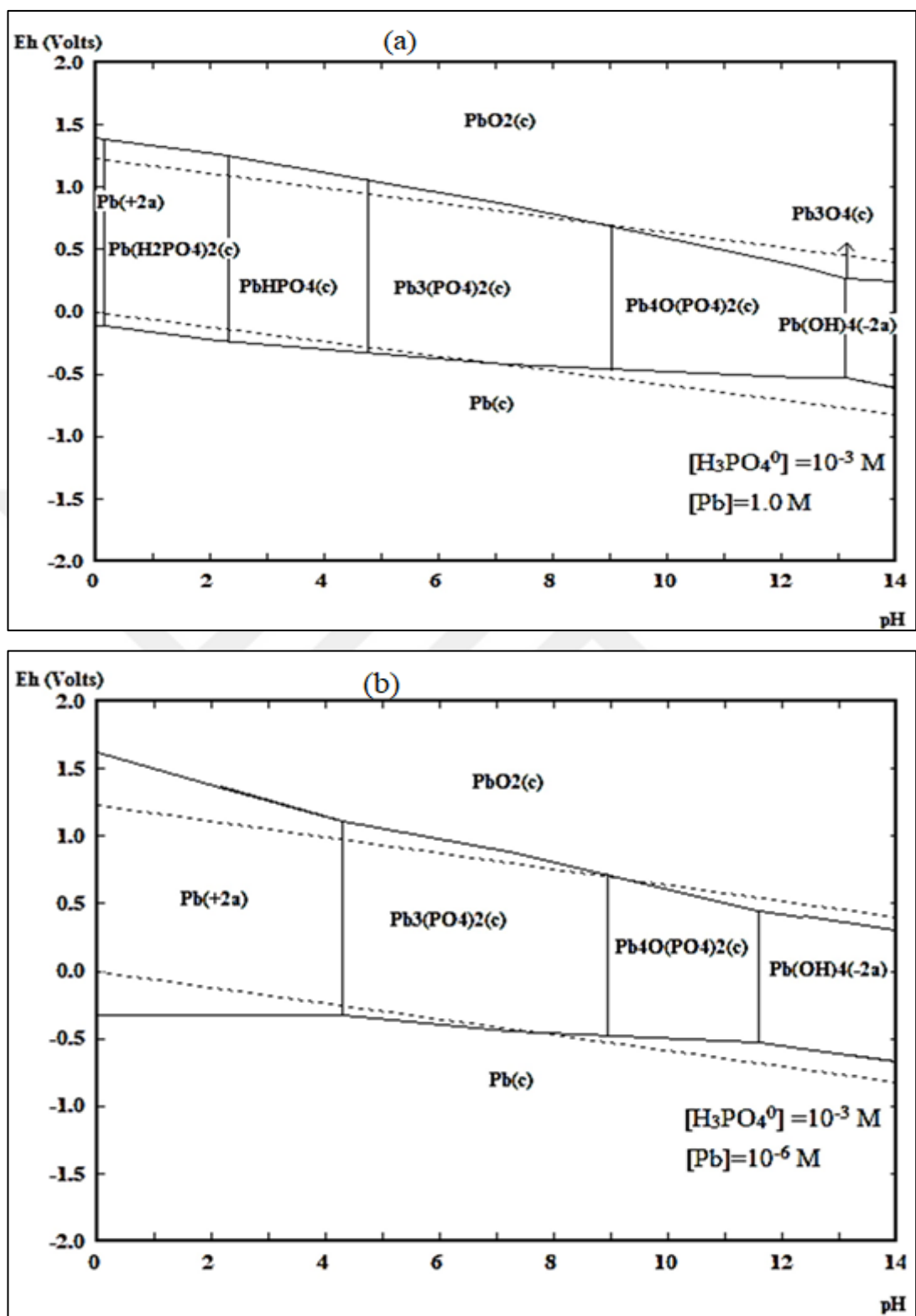


Figure 6.9 Pourbaix diagram of Pb-PO₄³⁻·H₂O system. [H₃PO₄⁰] = 10⁻³ Kmol/m³. (a) [Pb] = 1 Kmol/m³. (b) [Pb] = 10⁻⁶ Kmol/m³

6.2.1.2 Pourbaix Diagram of Fe-H₂O and Fe-PO₄³⁻.H₂O

Figure 6.10 depicts a Pourbaix diagram of Fe-H₂O system with [Fe]=10⁻³ Kmol/m³. As illustrated in Figure 6.10 Fe (+2a) divalent ion and Fe(OH)_{3(c)} cover a maximum area as the stable species. Iron can be transformed to insoluble forms of Fe(OH)_{3(c)} at pH above 1.2 and high potential, whereas Fe(OH)_{2(c)} at pH 10 and low potential.

The plotted Pourbaix diagrams for Fe-PO₄³⁻.H₂O system at different concentrations of TSP and Fe are shown in Figures 6.11 and 6.12. Figure 6.8 indicate that the concentrations of TSP influence the structure of metal phosphate and stability area when the total concentration of iron is fixed. At high TSP concentrations, (i.e., [H₃PO₄⁰]=1 Kmol/m³), the insoluble (stable) compounds [FePO₄.2H₂O(c) and Fe₃(PO₄)₂.8H₂O(c)] covered a large area in acidic and basic medium (Figure 6.11a). For instance, ferric iron Fe(+3a) and iron hydroxide [Fe(OH)_{3(c)}] interact with phosphate to produce FePO₄.2H₂O(c) compound at pH 8. Whereas, the reaction of ferrous iron Fe(+2a) with phosphate produces the soluble form of FeH₂PO₄(+a) below pH 6. Above pH 6, Fe(+2a) reacts with phosphate to form precipitate [Fe₃(PO₄)₂.8H₂O(c)]. However, it was observed that FeH₂PO₄(+a) is replaced by Fe(+2a) and the stability region of iron compounds [FePO₄.2H₂O(c) and Fe₃(PO₄)₂.8H₂O(c)] decreases by reducing TSP concentration (Figure 6.11b and 6.11c).

The effect of iron concentration is shown in Figure 6.12 at constant TSP concentration. As seen, at high concentrations of iron, the iron phosphate of FePO₄.2H₂O(c) forms below pH 6 and above pH 2.3 Fe₃(PO₄)₂.8H₂O(c) occurs as precipitates. Figure 6.12a shows that the stability area for Fe₃(PO₄)₂.8H₂O(c) is relatively predominant at [Fe]=1 Kmol/m³. As the concentration of iron decreases, the stability region of iron phosphate compounds decreases (Figure 6.12b).

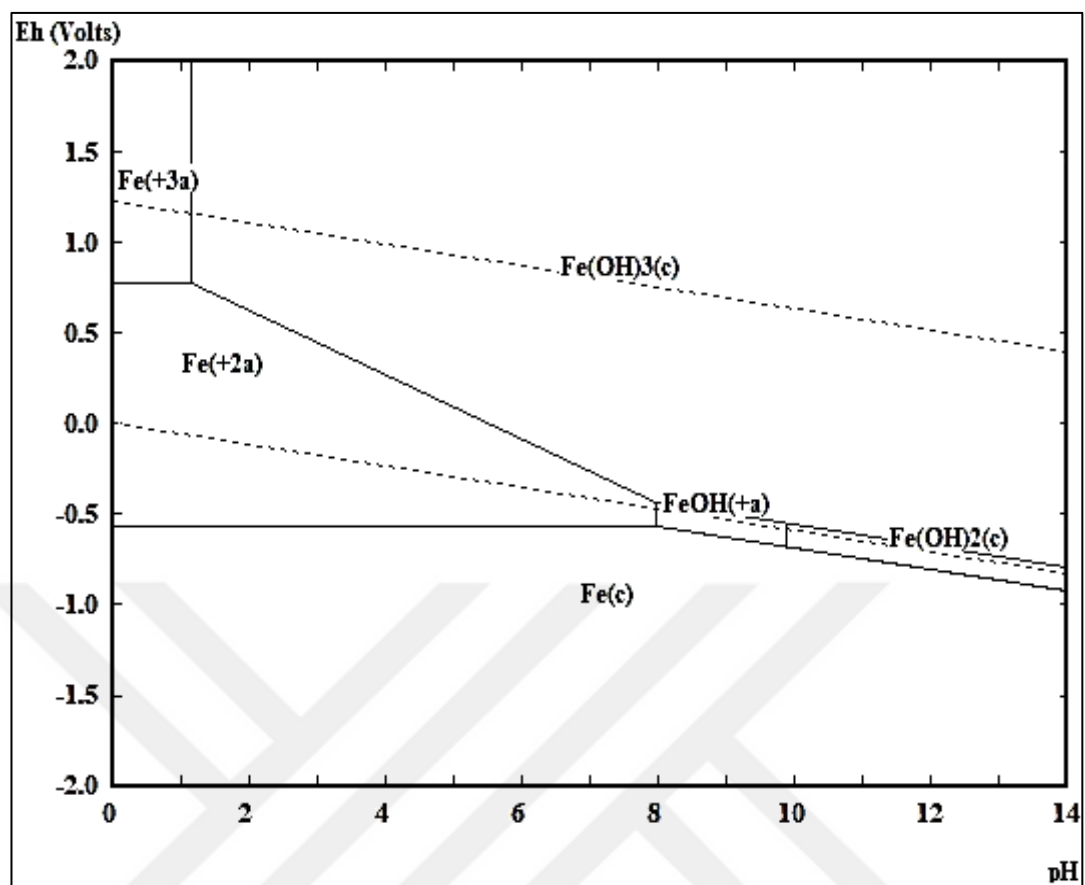


Figure 6.10 Pourbaix diagram of Fe-H₂O system. [Fe]=10⁻³ Kmol/m³

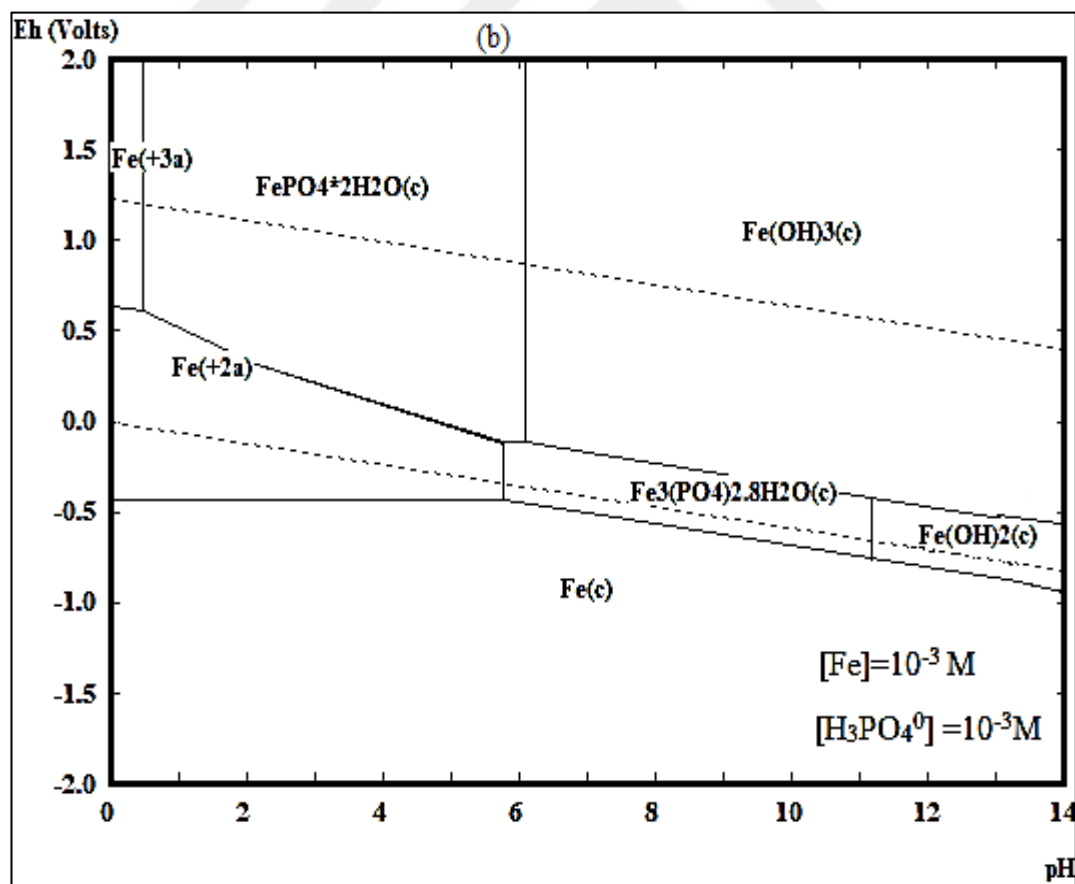
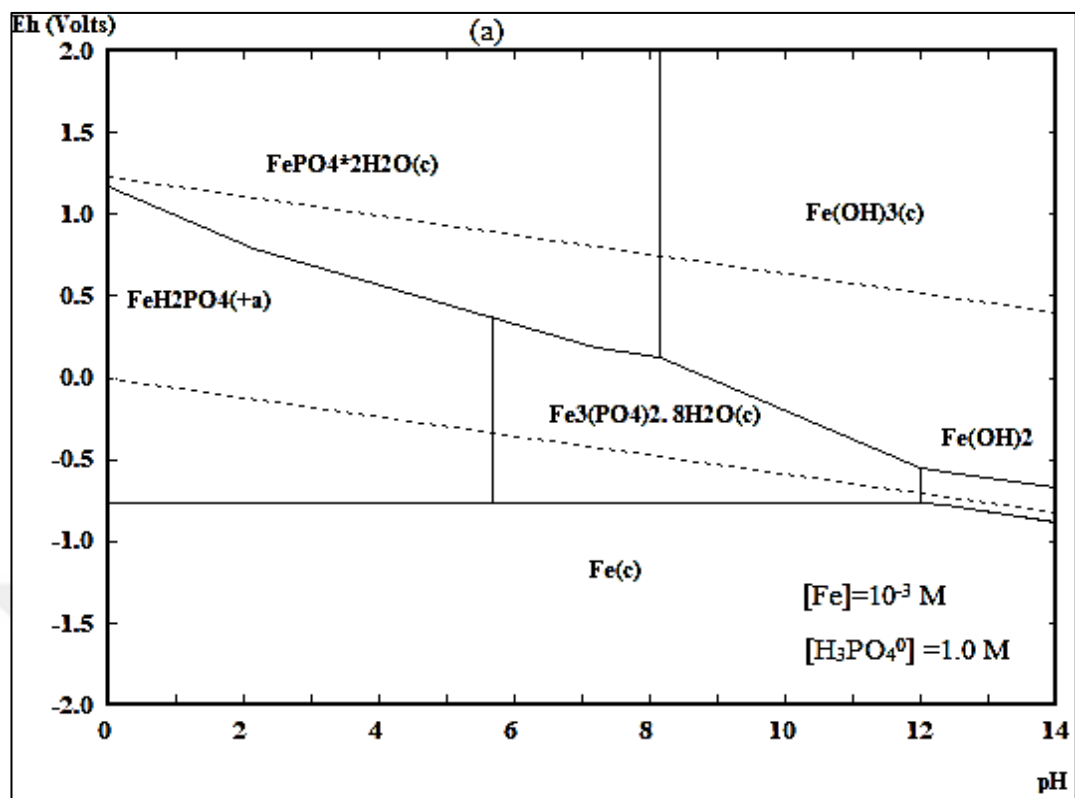


Figure 6.11 Pourbaix diagram of the Fe-PO₄³⁻.H₂O system. [Fe]=10⁻³ Kmol/m³. (a) [H₃PO₄⁰] = 1 Kmol.m³. (b) [H₃PO₄⁰] = 10⁻³ Kmol/m³. (c) [H₃PO₄⁰] = 10⁻⁶ Kmol/m³

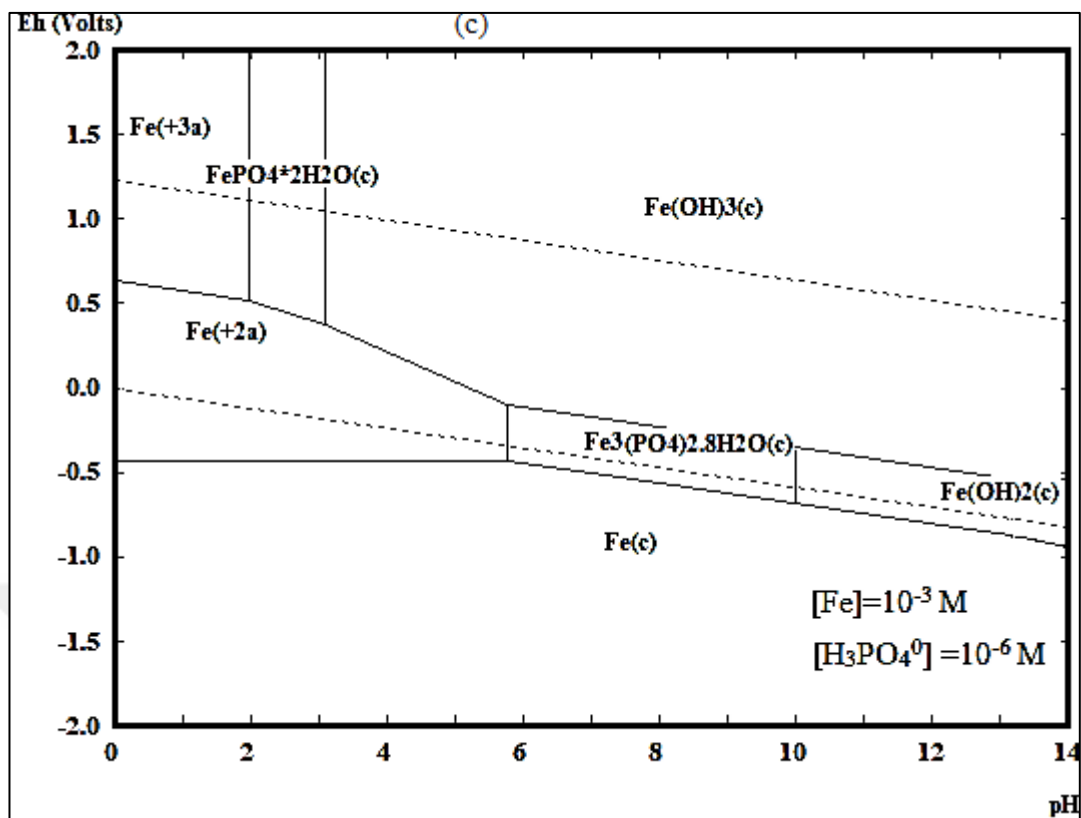


Figure 6.11 Continues

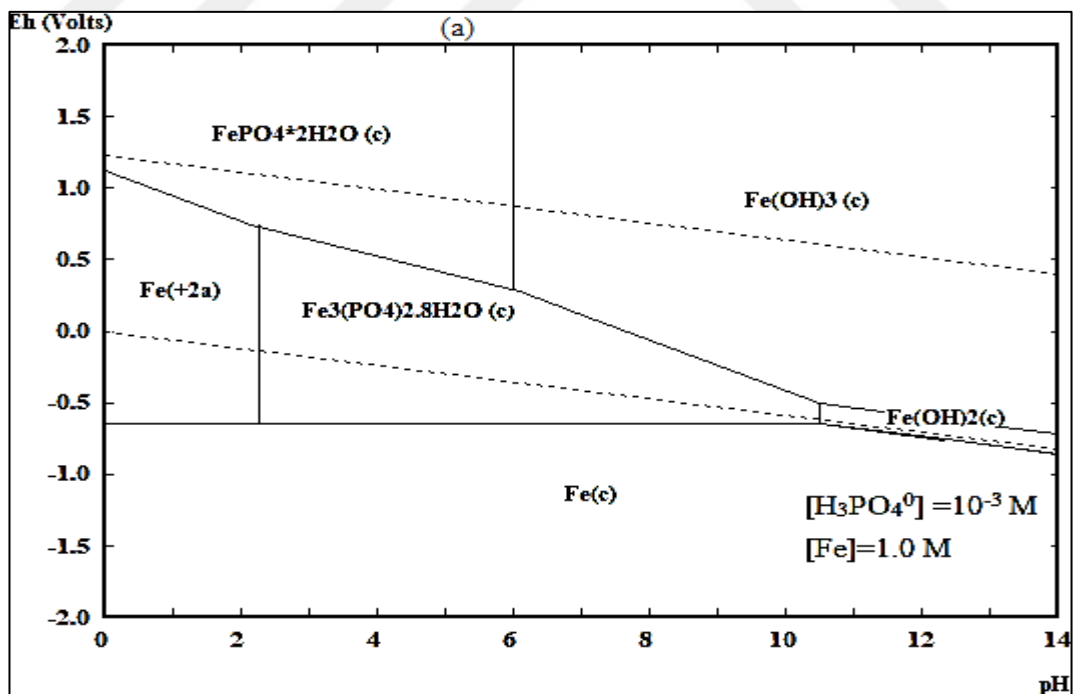


Figure 6.12 Pourbaix diagram of Fe-PO₄³⁻·H₂O system. [H₃PO₄⁰] = 10⁻³ Kmol/m³. (a) [Fe] = 1 Kmol/m³.
(b) [Fe] = 10⁻⁶ Kmol/m³

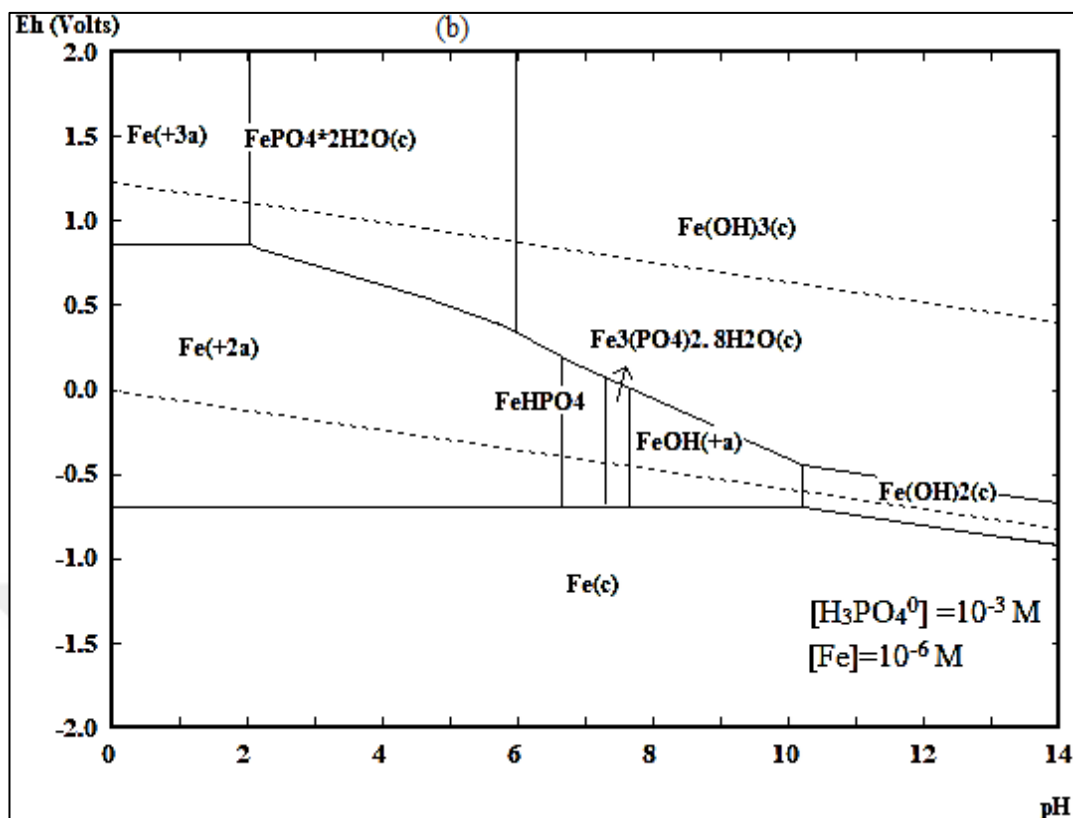


Figure 6.12 Continues

6.2.1.3 Pourbaix Diagram of Cd-H₂O and Cd-PO₄³⁻·H₂O

The Pourbaix diagram of the cadmium water system (Cd-H₂O system) is represented in Figure 6.13. From this figure it can be seen that Cd(+2a) occupies the dominant zone of stability at pH=8.4 and the soluble species Cd(OH)₄(-2a), CdOH(+a) and HCdO₂(-a) are predominant between pH superior to 8.4 and inferior to 12.04.

Figures 6.14 and 6.15 illustrate the Pourbaix diagram of Cd-PO₄³⁻·H₂O constructed with three concentrations of TSP and Cd. Figure 6.14 indicates the dimensions of stability region for cadmium phosphate minerals rely on the concentration of TSP in the solution. The divalent cadmium binds with phosphate to provide the stable compounds of Cd(H₂PO₄)₂(c) and CdHPO₄(c) as precipitates at 3.43<pH<7.03 in the presence of high TSP concentration ([H₃PO₄⁰]=1.0M) and constant Cd concentrations (see Figure 6.14a). Furthermore, Cd(OH)₄(-2a) and CdOH(+a) soluble species are replaced by Cd₃(PO₄)₂(c) and Cd₅(PO₄)₂OH(c) compounds sparingly soluble in water at pH between 9.78 and 12.86. When the concentrations of TSP are 10⁻³M and 10⁻⁶, it

was observed the stability zones of cadmium phosphates compounds ($\text{Cd}_3(\text{PO}_4)_2(\text{c})$ and $\text{Cd}_5(\text{PO}_4)_2\text{OH}(\text{c})$) reduce, thus dissipate. As shown in Figures 6.14b and 6.14c, the stability zone of $\text{Cd}_3(\text{PO}_4)_2(\text{c})$ and $\text{Cd}_5(\text{PO}_4)_2\text{OH}(\text{c})$ compounds increases with a decrease in TSP concentrations.

As can be seen from Figures 6.15a and 6.15b the stability zone $\text{Cd}_3(\text{PO}_4)_2(\text{c})$ and $\text{Cd}_5(\text{PO}_4)_2\text{OH}(\text{c})$ is dominant at high concentration of Cd ($[\text{Cd}]=1.0\text{M}$), and increases with low concentration of Cd ($[\text{Cd}]=10^{-3}\text{M}$) at 10^{-3} M of TSP constant.

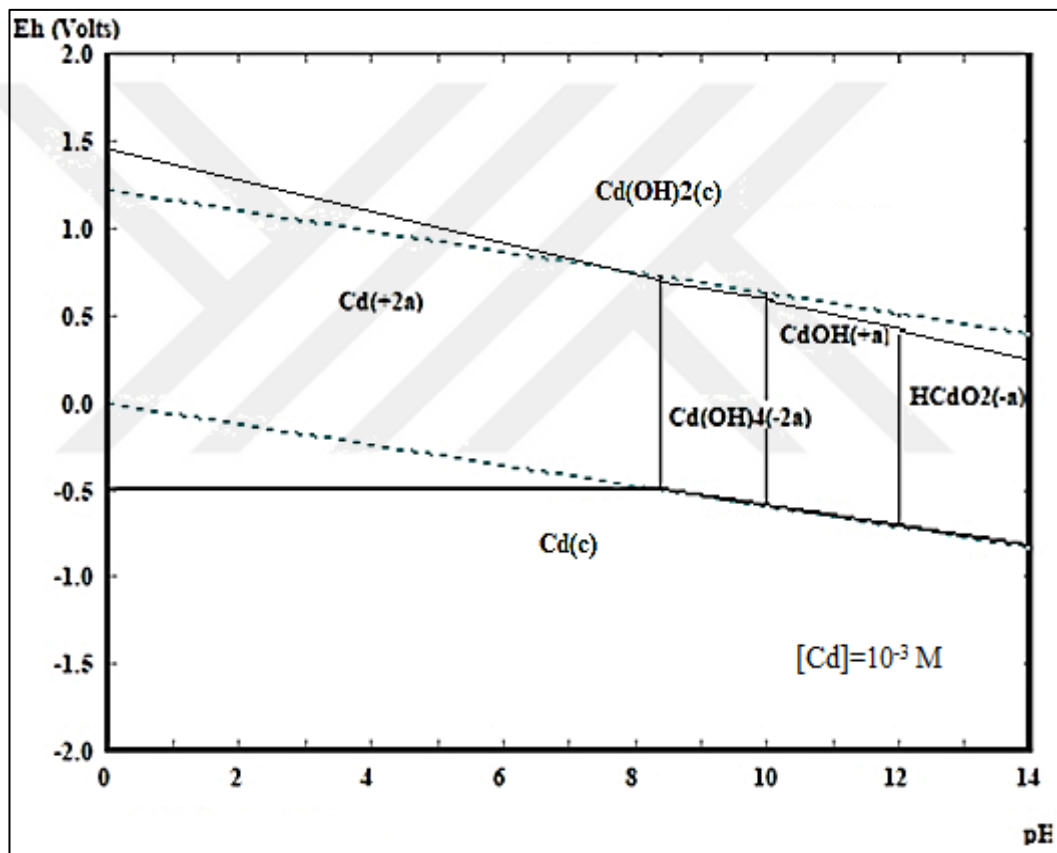


Figure 6.13 Pourbaix diagram of Cd-H₂O system. $[\text{Cd}]=10^{-3}\text{ Kmol/m}^3$

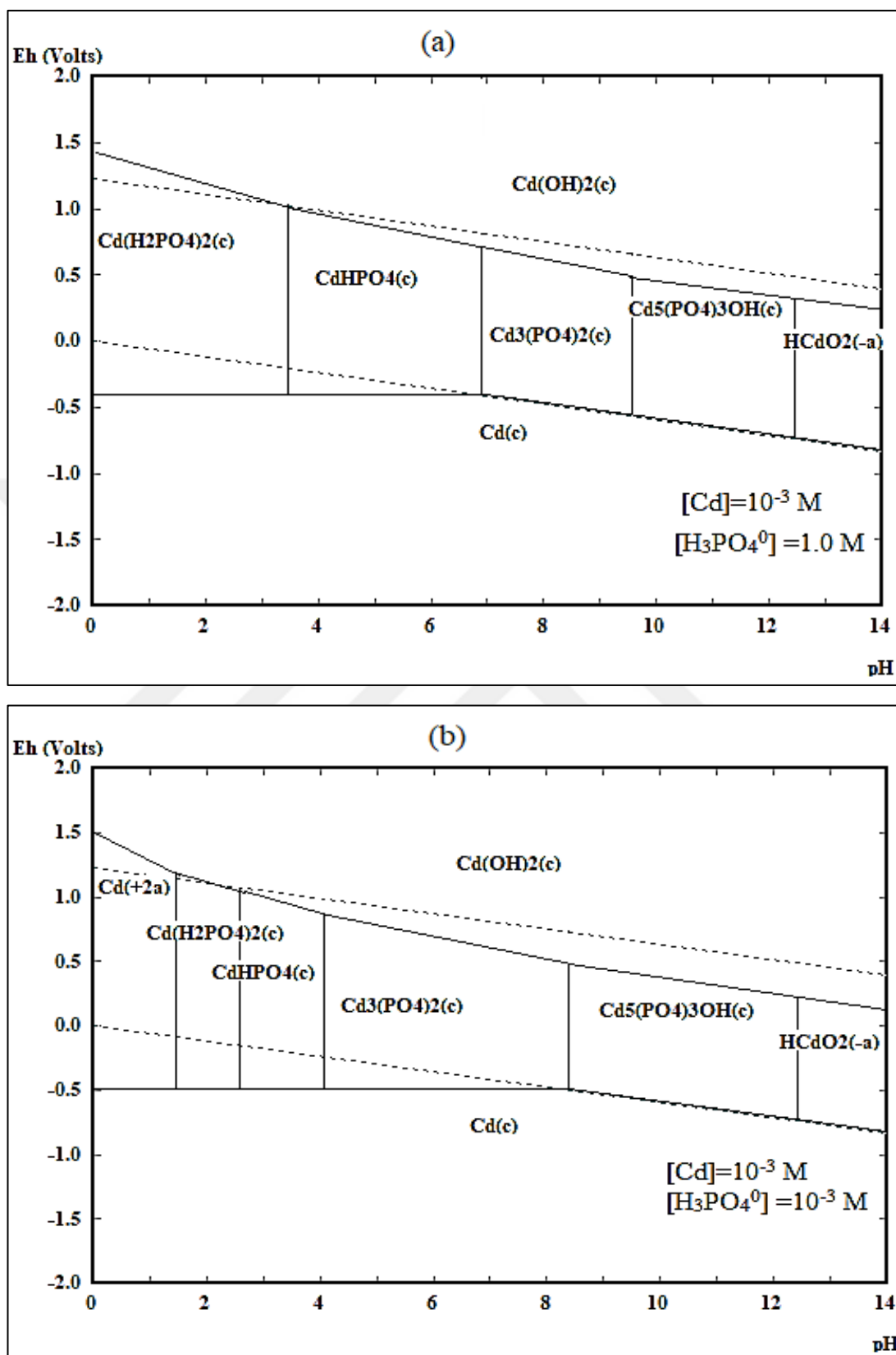


Figure 6.14 Pourbaix diagram of $\text{Cd-PO}_4^{3-}\cdot\text{H}_2\text{O}$ system. $[\text{Cd}] = 10^{-3} \text{ Kmol/m}^3$. (a) $[\text{H}_3\text{PO}_4^0] = 1 \text{ Kmol.m}^3$. (b) $[\text{H}_3\text{PO}_4^0] = 10^{-3} \text{ Kmol/m}^3$. (c) $[\text{H}_3\text{PO}_4^0] = 10^{-6} \text{ Kmol/m}^3$

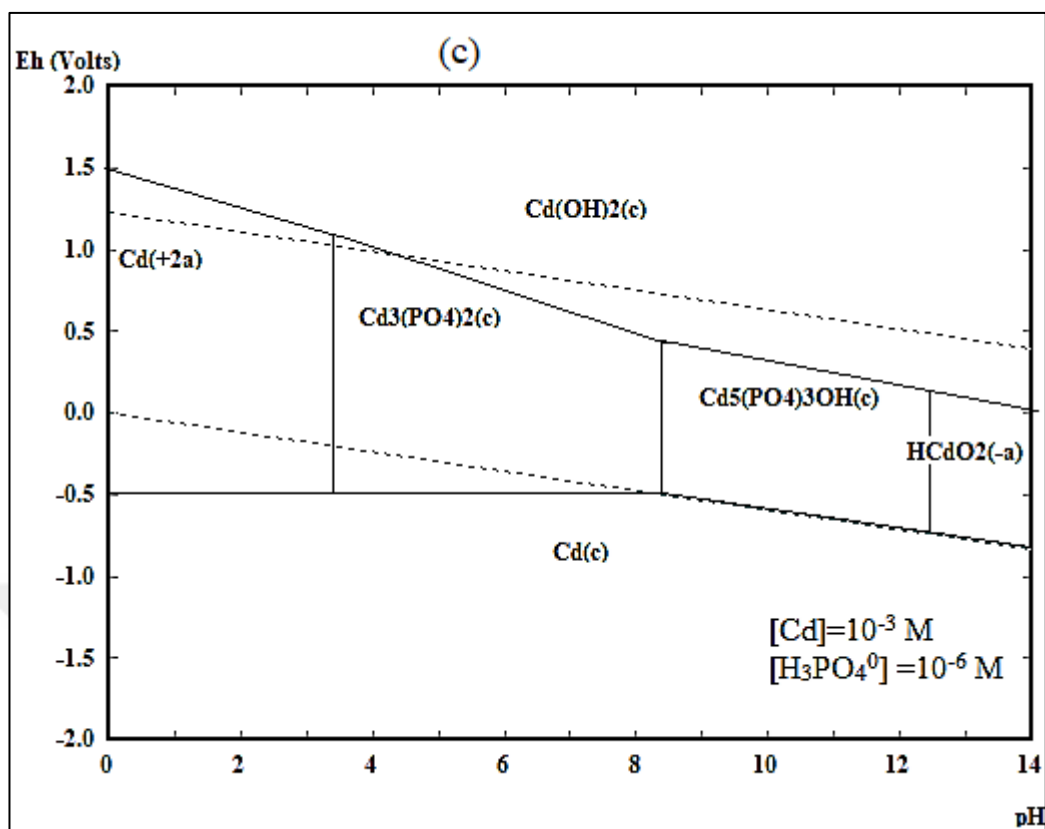


Figure 6.14 Continues

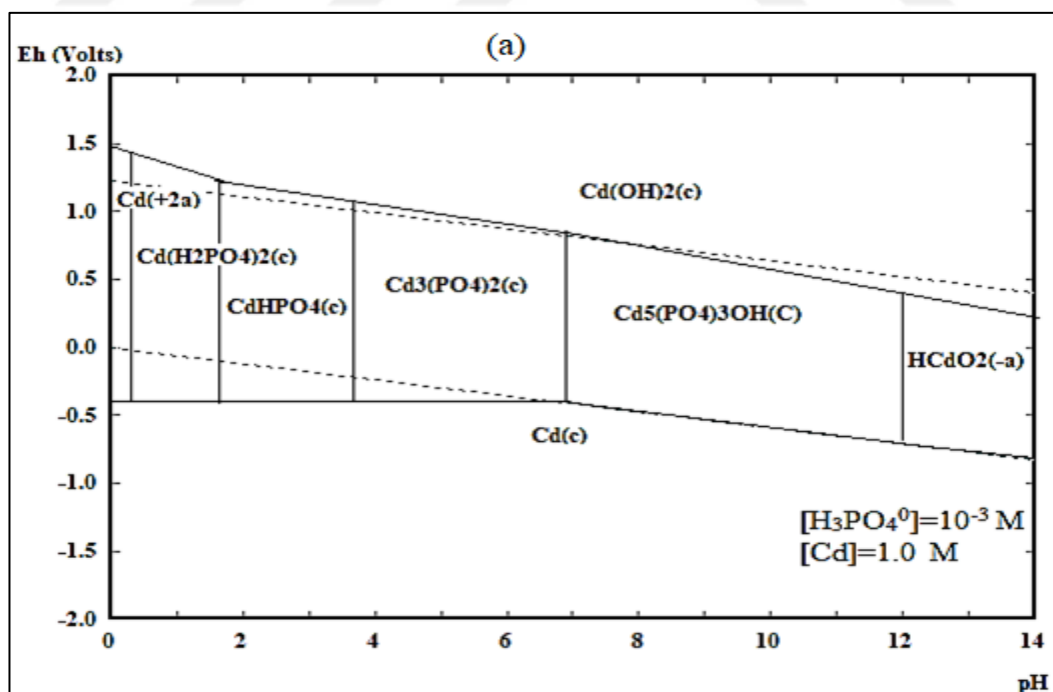


Figure 6.15 Pourbaix diagram of $\text{Cd-PO}_4^{3-} \cdot \text{H}_2\text{O}$ system. $[\text{H}_3\text{PO}_4^0] = 10^{-3} \text{ Kmol/m}^3$. (a) $[\text{Cd}] = 1 \text{ Kmol/m}^3$.
 (b) $[\text{Cd}] = 10^{-6} \text{ Kmol/m}^3$

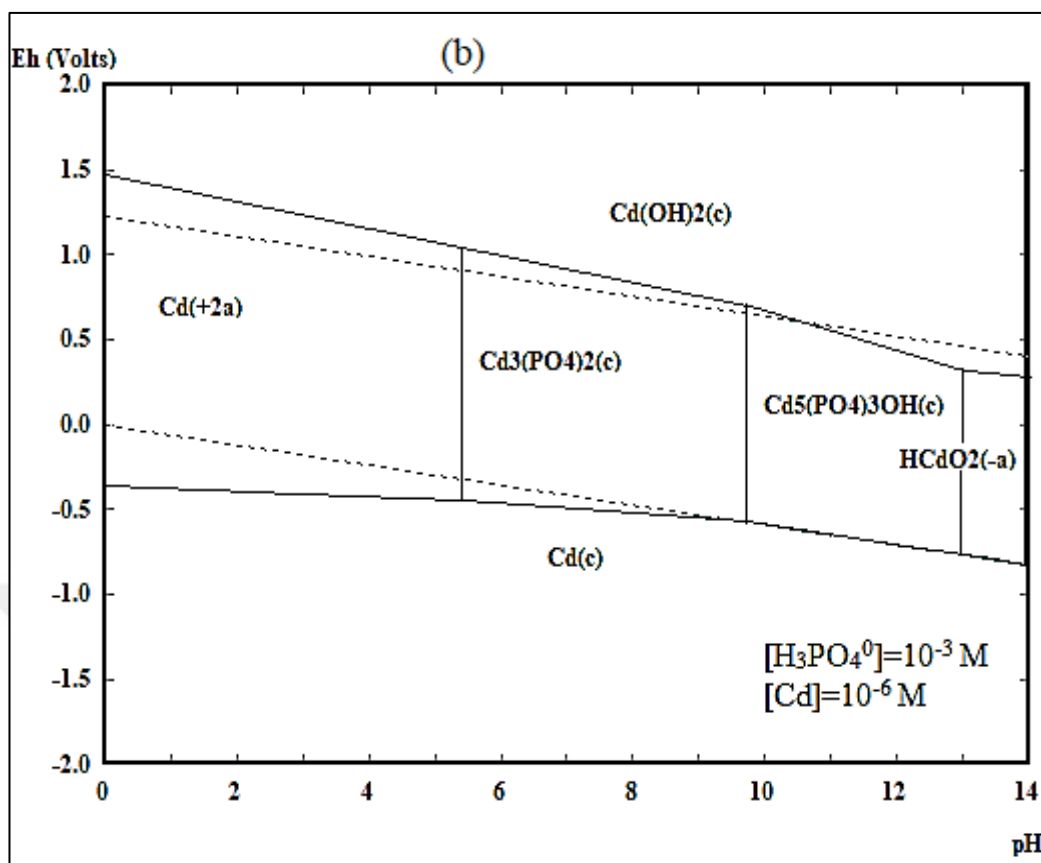


Figure 6.15 Continues

6.2.1.4 Pourbaix Diagram of Cu-H₂O and Cu-PO₄³⁻·H₂O

The copper concentration dissolving in water is given in Figure 6.16. From this figure, the copper ion Cu(+2a) appears in the large zone of stability diagram at pH below 7. Above this pH, the insoluble compound of CuO₂(c) and Cu(OH)₂(c) are significant and the soluble ion complex of Cu₂(-2a) is formed at pH above 13.

Figures 6.17 and 6.18 show the Pourbaix diagrams of Cu-PO₄³⁻·H₂O according to the variation of TSP and Cu concentrations. As illustrated in Figure 6.17, the concentration of TSP addition influences the formation of copper phosphates and their stability zone. At high concentration of TSP and constant Cu concentration, Cu(H₂PO)₂(c) and CuHPO₄(c) compounds are produced by the reaction of Cu(+2a) and phosphates and they have significant stability zone at pH values of 5 and 7.20 respectively (Figure 6.17a). In addition, Copper dioxide and copper hydroxide are substituted into Cu₃(PO₄)₂(c) and Cu₅(PO₄)₂OH(c) compounds. However, a

diminution of TSP concentration narrowed the stability zone of $\text{Cu}(\text{H}_2\text{PO}_4)_2(\text{c})$ and $\text{CuHPO}_4(\text{c})$ and those compounds disappear at 10^{-6} M of TSP as depicted in Figures 6.17b and 6.17c.

The stability zones of $\text{Cu}_3(\text{PO}_4)_2(\text{c})$ and $\text{Cu}_5(\text{PO}_4)_2\text{OH}(\text{c})$ seem to be significant compared to $\text{Cu}(\text{H}_2\text{PO}_4)_2(\text{c})$ and $\text{CuHPO}_4(\text{c})$ at high Cu concentration as presented in Figure 6.18a and no presence $\text{Cu}(\text{H}_2\text{PO}_4)_2(\text{c})$ and $\text{CuHPO}_4(\text{c})$ compounds were observed at lowest Cu concentration (Figure 6.18b).

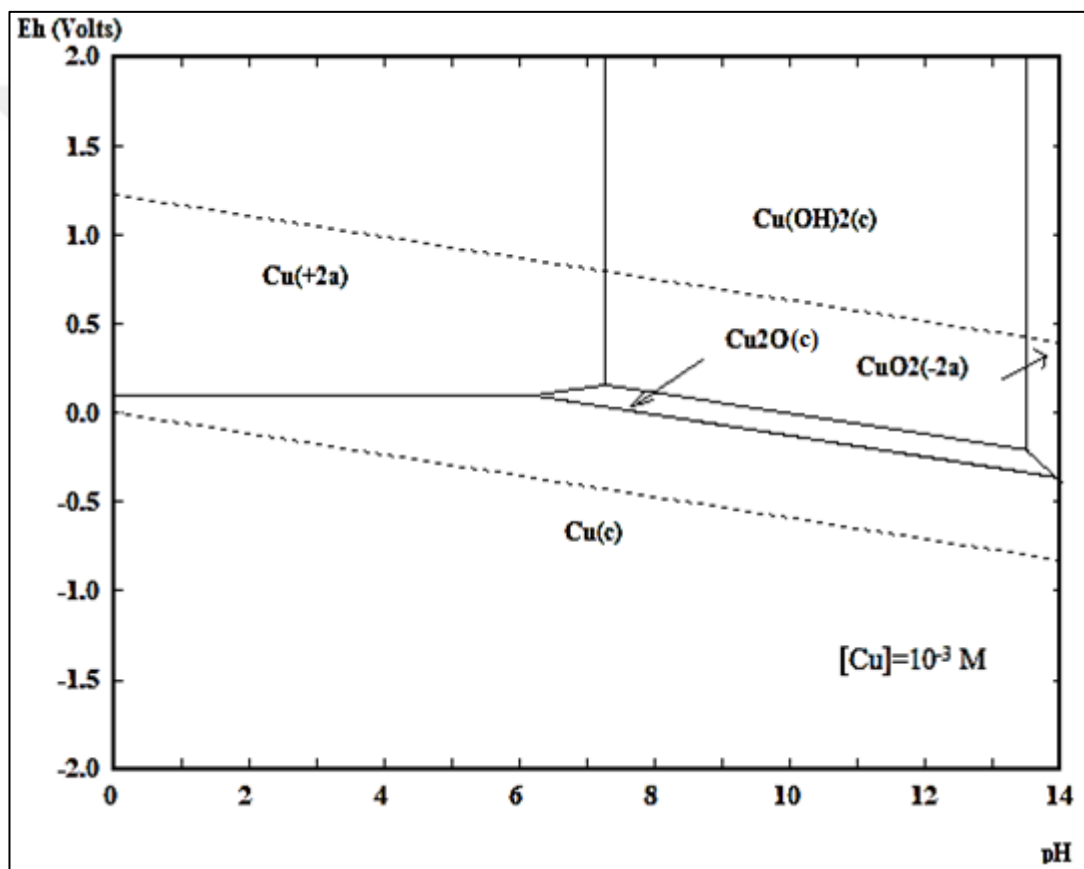


Figure 6.16 Pourbaix diagram of Cu-H₂O system. $[\text{Cu}] = 10^{-3} \text{ Kmol/m}^3$

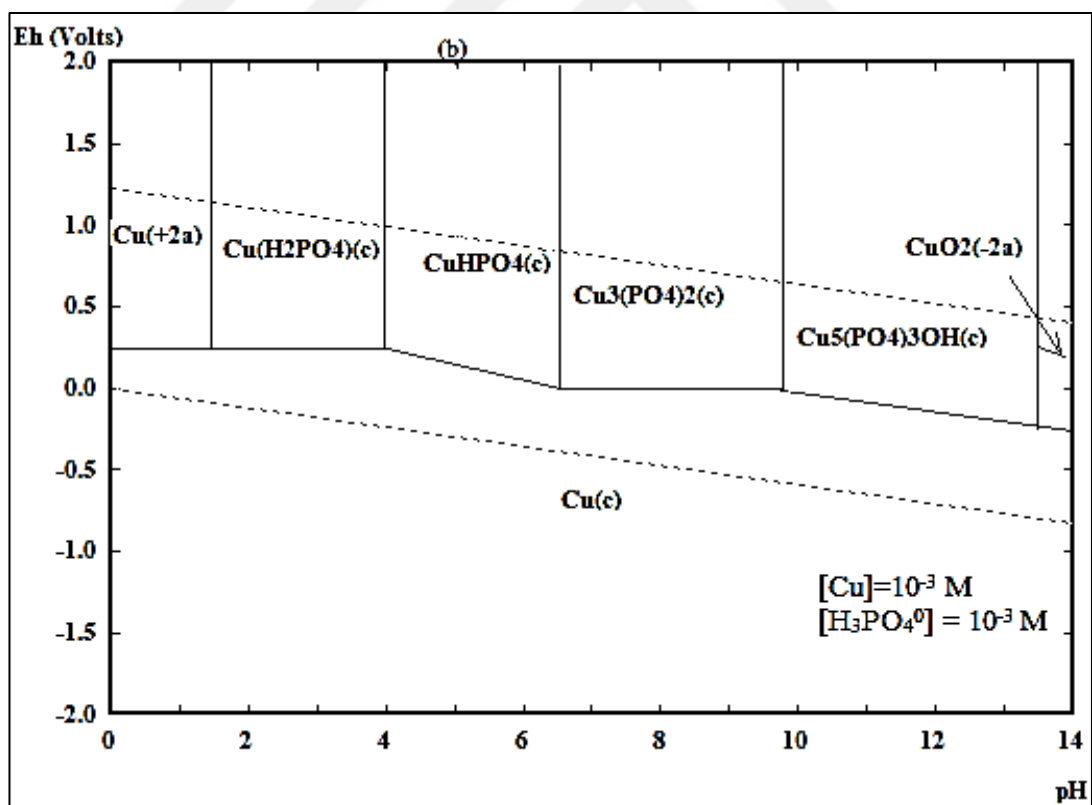
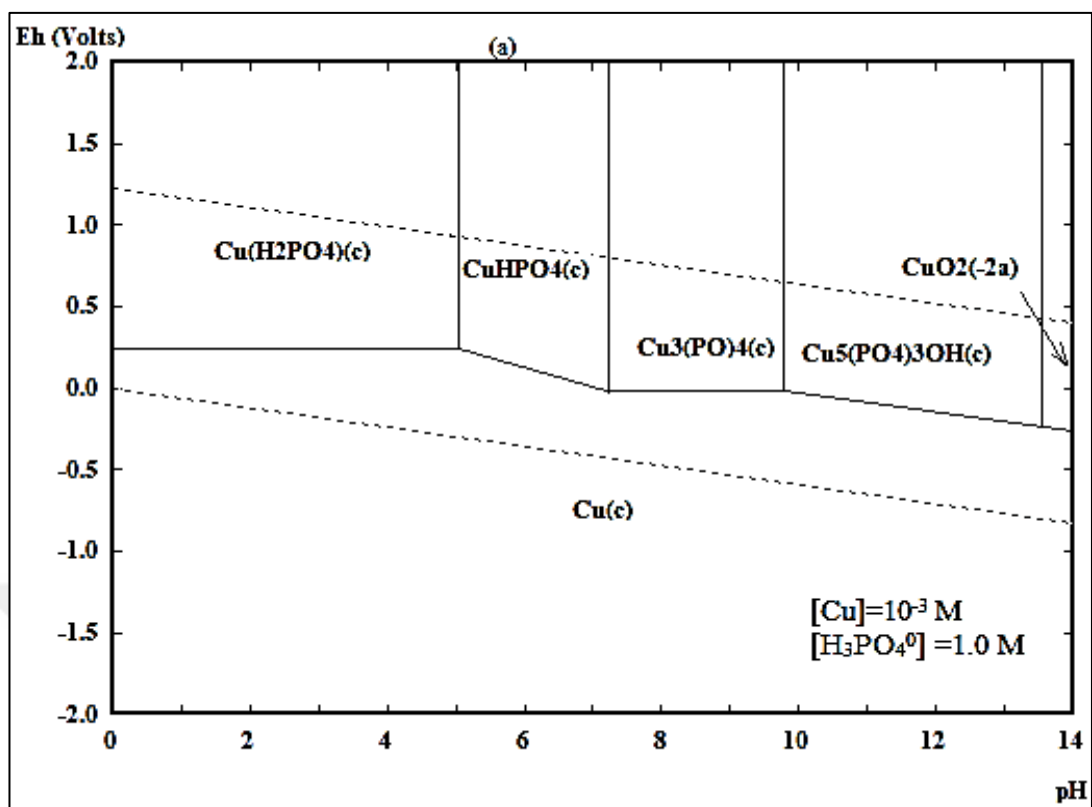


Figure 6.17 Pourbaix diagram of Cu-PO₄³⁻.H₂O system. [Cu] = 10⁻³ Kmol/m³. (a) [H₃PO₄⁰] = 1 Kmol.m³. (b) [H₃PO₄⁰] = 10⁻³ Kmol/m³. (c) [H₃PO₄⁰] = 10⁻⁶ Kmol/m³

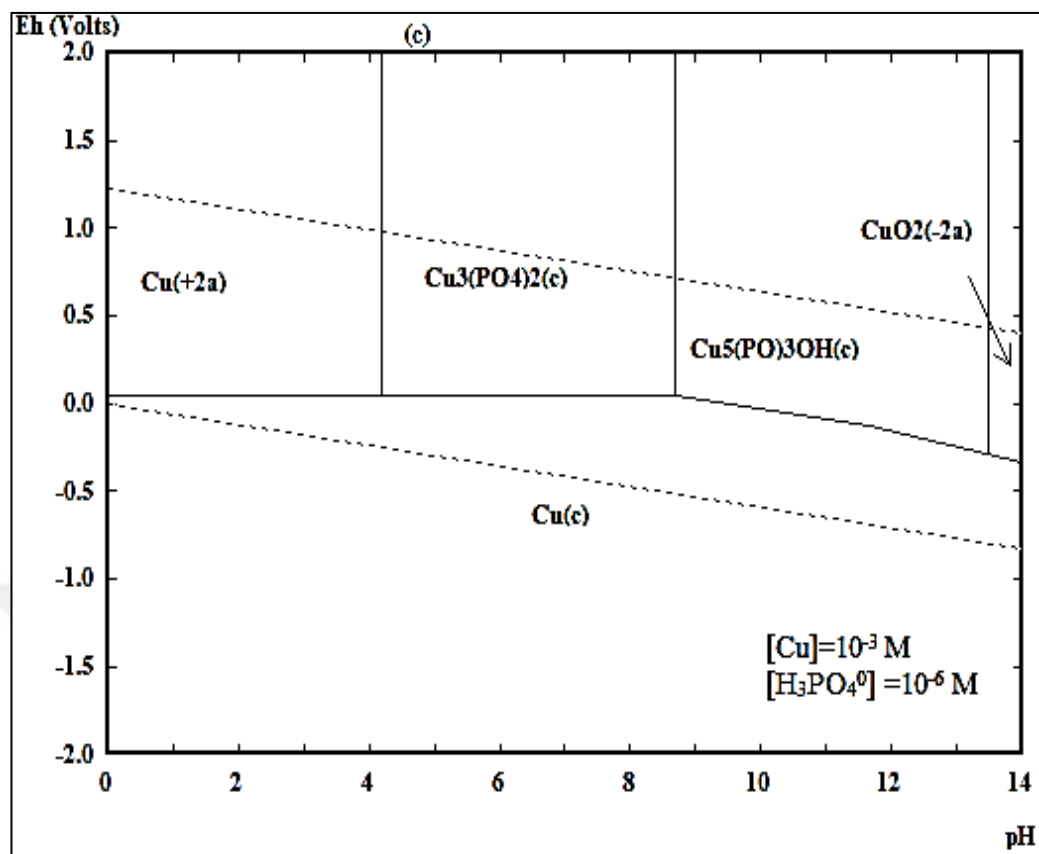


Figure 6.17 Continues

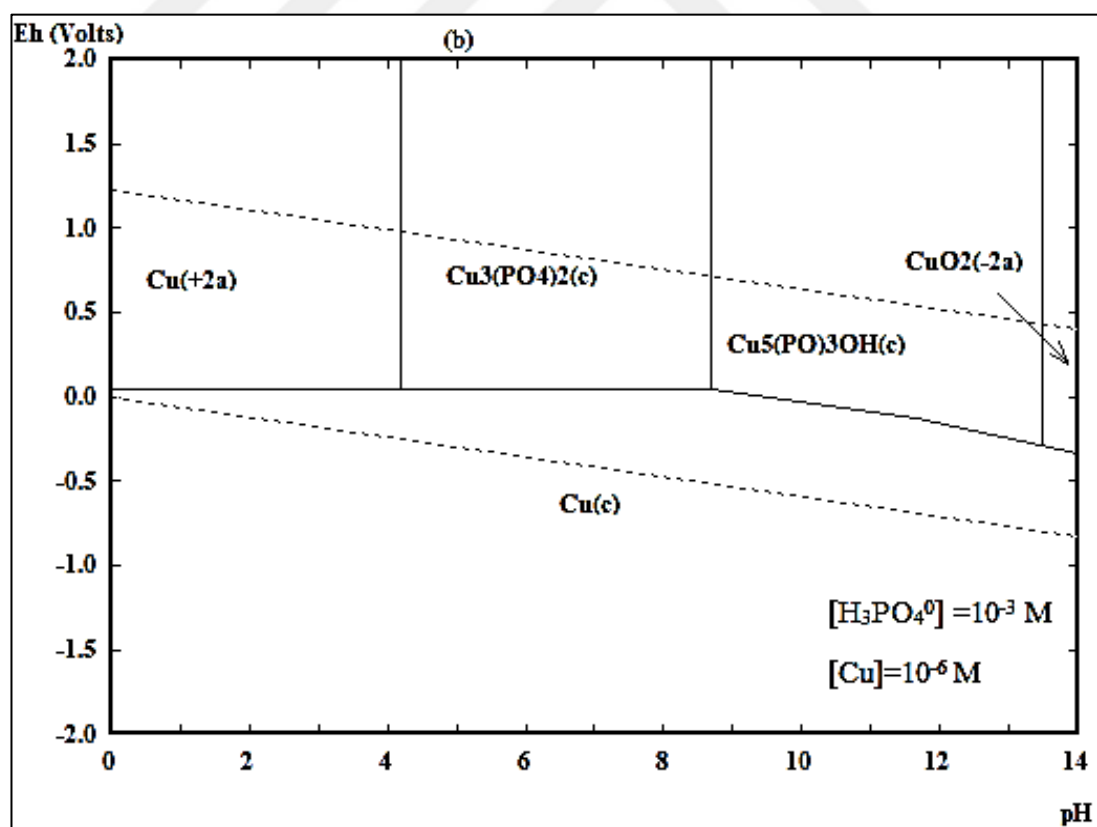
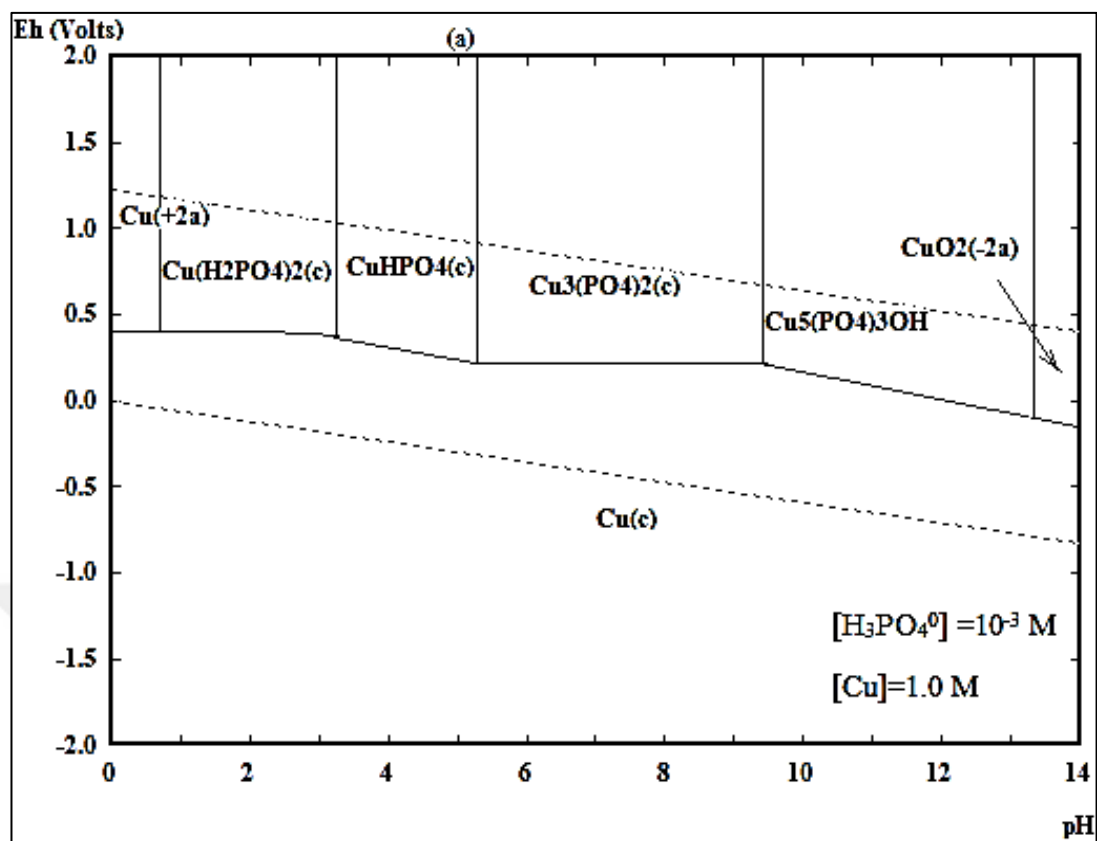


Figure 6.18 Pourbaix diagram of Cu-PO₄³⁻·H₂O system. [H₃PO₄⁰] = 10⁻³ Kmol/m³. (a) [Cu] = 1 Kmol/m³. (b) [Cu] = 10⁻⁶ Kmol/m³

6.2.1.5 Pourbaix Diagram of Zn-H₂O and Zn-PO₄³⁻.H₂O

Pourbaix diagram of Zn-H₂O system indicates the total dissolved zinc in water (Figure 6.19). As shown in this figure, Zn (+2a) is dominant at pH 7.05 and the stability zone of ZnO(c) is significant at pH ranging from 7.05 to 13. The complex soluble specie of ZnO₂(-2a) appears at pH value of 13. The TSP concentration effects are given in Figure 6.20. When TSP concentration is high 1.0M and Zn concentration is constant, the formation of zinc phosphates Zn(H₂PO₄)₂(c) and ZnHPO₄(c) was observed at 3.4 and 6.35 respectively while the precipitates of Zn₃(PO₄)₂(c) and Zn₅(PO₄)₂OH(c) are formed at 10 ≤ pH ≤ 13 (Figure 6.20a). By applying 10⁻³ M and 10⁻⁶ M of TSP, the stability zones of Zn₃(PO₄)₂(c) and Zn₅(PO₄)₂OH(c) increase while those of Zn(H₂PO₄)₂(c) and ZnHPO₄(c) compounds decrease (Figure 6.20b and 6.20c).

Figure 6.21 presents Pourbaix diagram of Zn-PO₄³⁻.H₂O with different Zn concentrations and constant H₃PO₄⁰ (10⁻³M of TSP). At 1.0M of Zn concentration, the stability zones of zinc phosphates such as Zn(H₂PO₄)₂(c) and ZnHPO₄(c) decrease, while the stability zones of Zn₃(PO₄)₂(c) and Zn₅(PO₄)₂OH(c) are significant (Figure 6.21a). On the other hand, it was found that Zn(H₂PO₄)₂(c) and ZnHPO₄(c) precipitates disappear with a further decrease of Zn concentrations and remain only the precipitate of Zn₃(PO₄)₂(c) and Zn₅(PO₄)₂OH(c) (see Figure 6.21b).

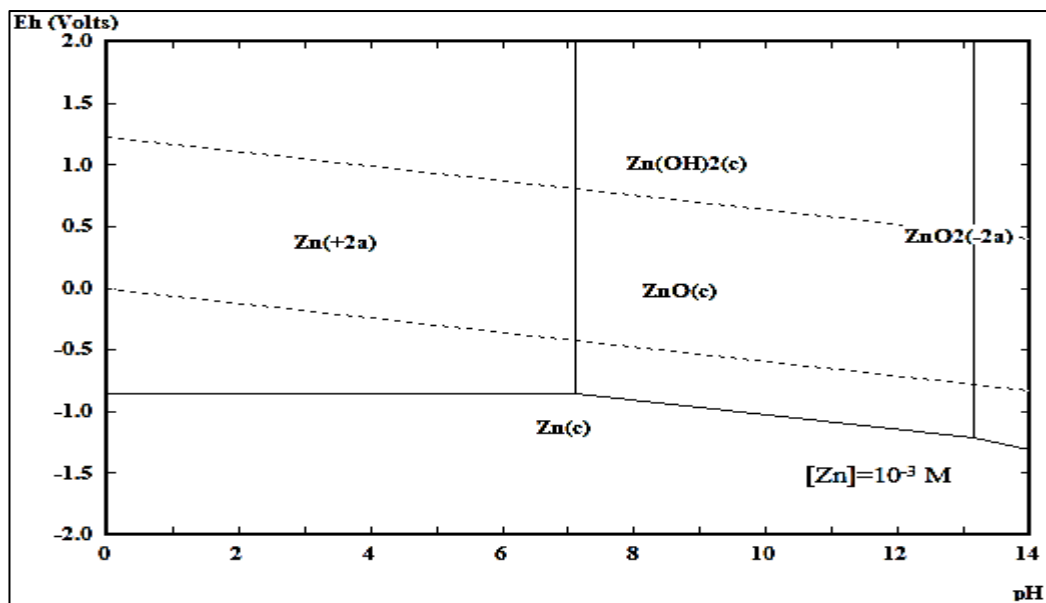


Figure 6.19 Pourbaix diagram of Zn-H₂O system. [Zn]=10⁻³ Kmol/m³

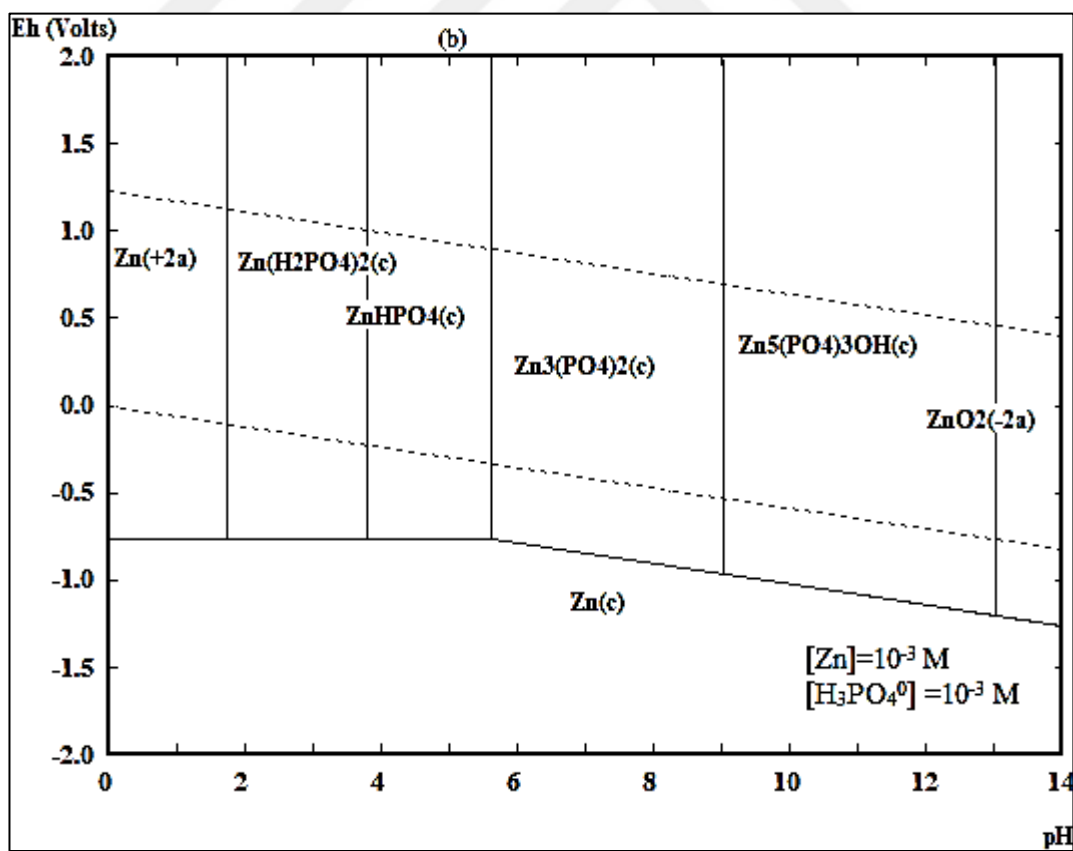
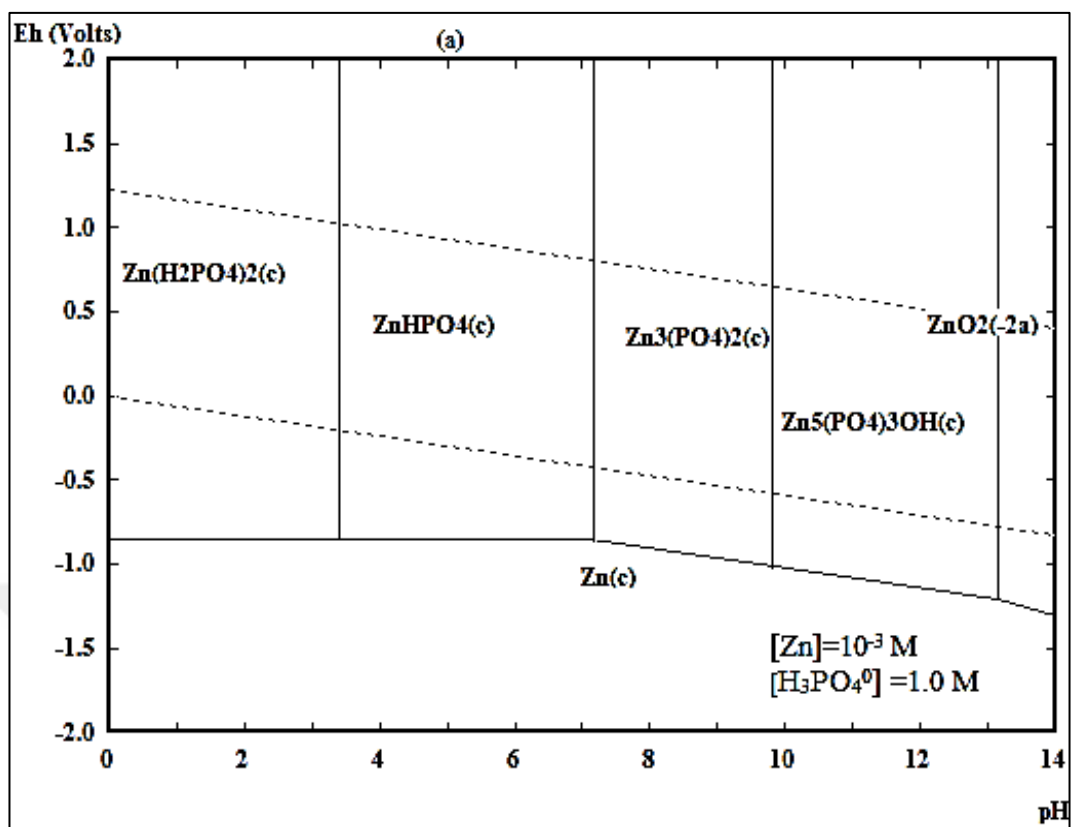


Figure 6.20 Pourbaix diagram of Zn-PO₄³⁻.H₂O system. [Zn]=10⁻³ Kmol/m³. (a) [H₃PO₄⁰] = 1 Kmol.m³. (b) [H₃PO₄⁰] = 10⁻³ Kmol/m³; (c) [H₃PO₄⁰] = 10⁻⁶ Kmol/m³

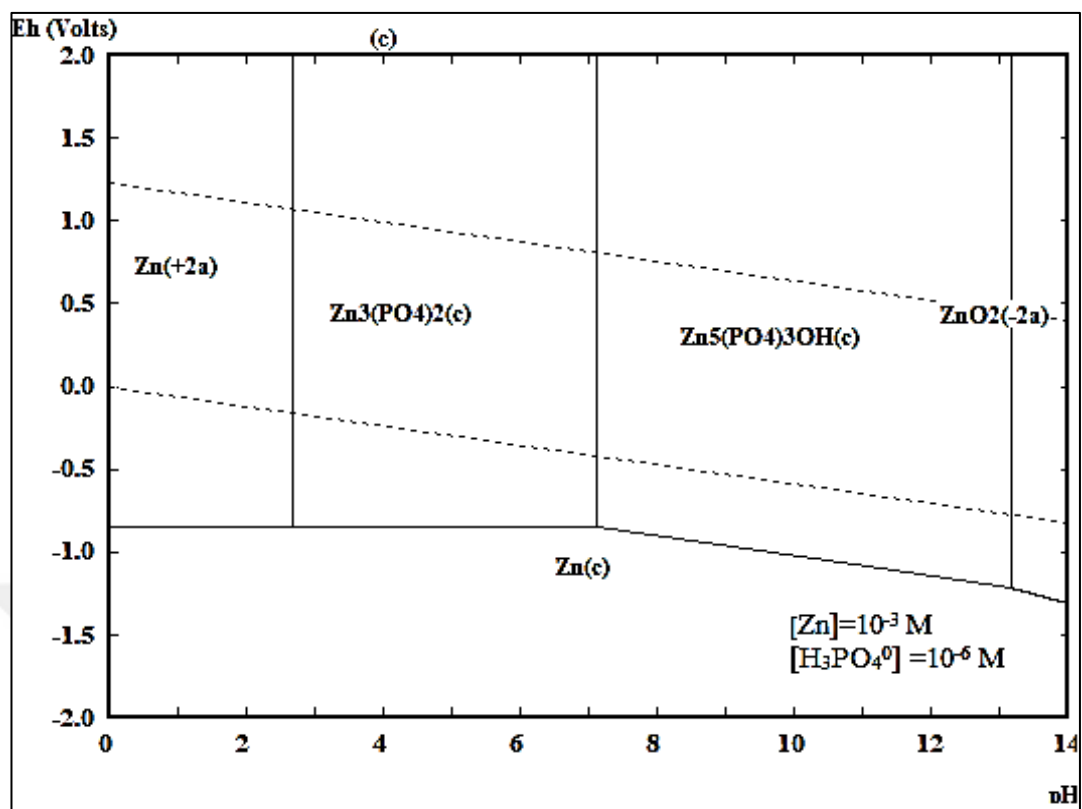


Figure 6.20 Continues

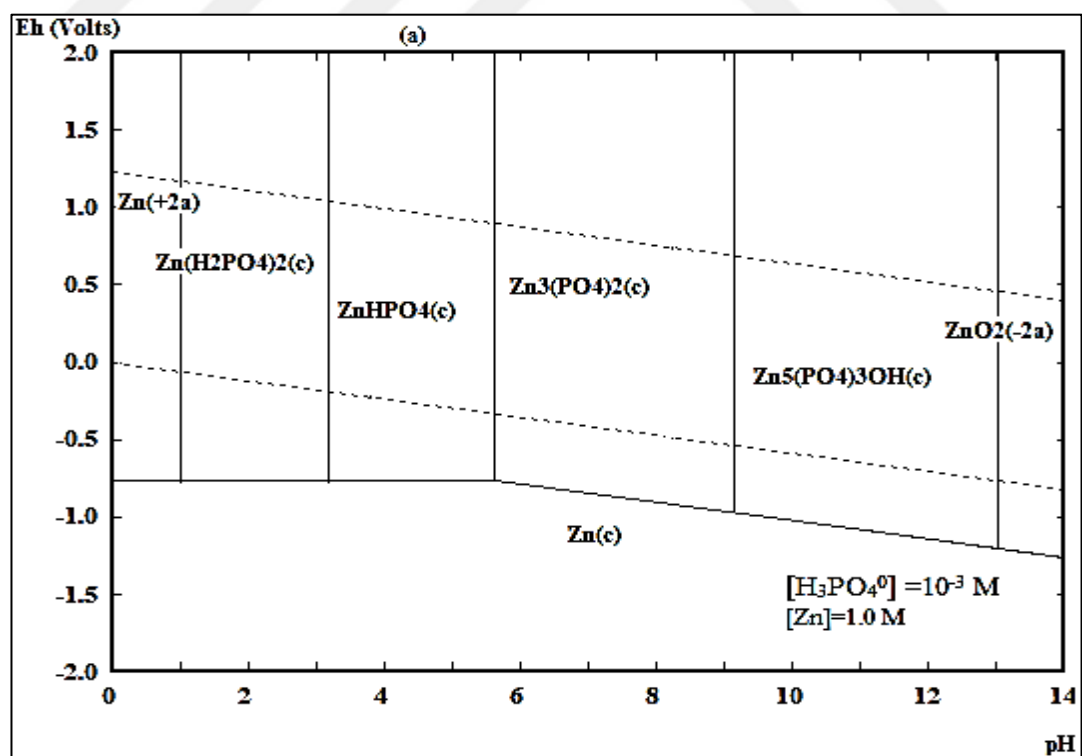


Figure 6.21 Pourbaix diagram of Zn-PO₄³⁻.H₂O system. [H₃PO₄⁰] = 10⁻³ Kmol/m³. (a) [Zn] = 1 Kmol/m³.
(b) [Zn] = 10⁻⁶ Kmol/m³

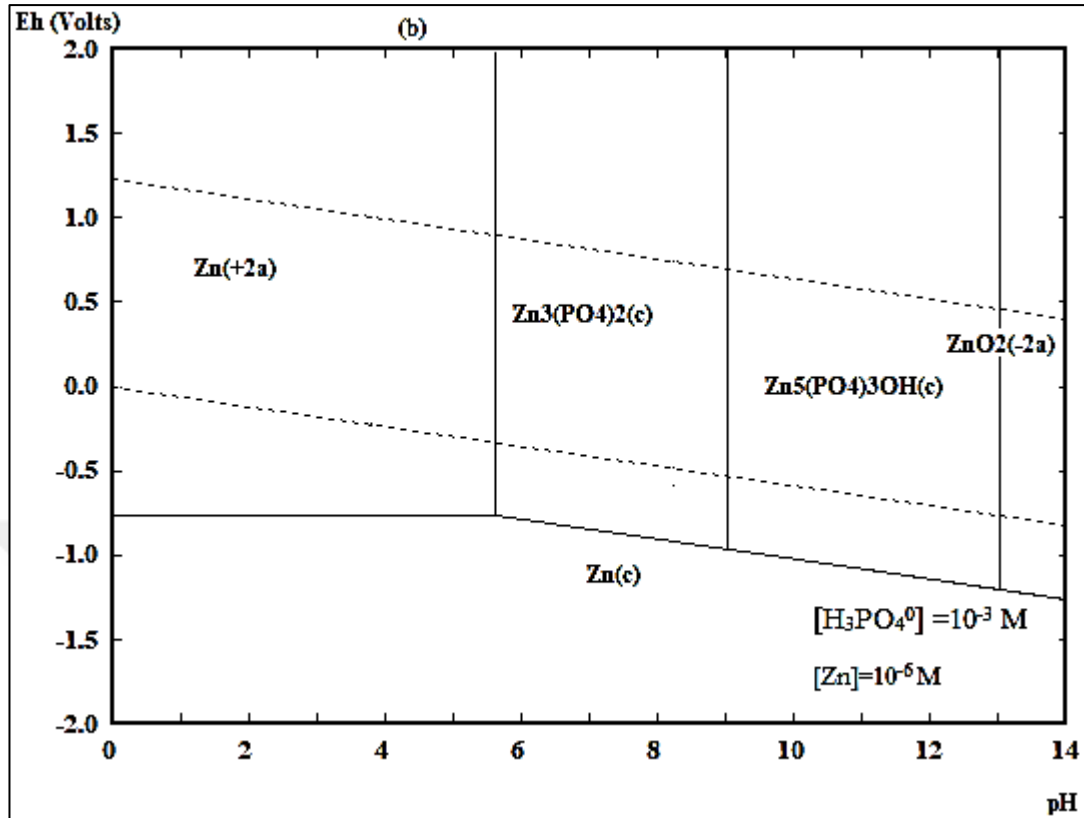


Figure 6.21 Continues

6.2.2 Removal of Pb, Fe, Cd, Cu and Zn in Aqueous Solutions using TSP

The metals ions (Pb, Fe, Cd, Cu and Zn) precipitation results are calculated through Equation 4.3 and reported in Tables A3 to A6. At three Pb, Fe, Cd, Cu and Zn concentrations (10, 20, and 50 mg/L), the effects of two TSP concentrations (0.1 and 0.5 M) on metal ions removal were investigated.

6.2.2.1 Removal of Pb in Aqueous Solutions

The results, as shown in Figure 6.22, indicate that Pb removal effectiveness is affected by the concentrations of Pb and TSP in the solution. With higher TSP concentrations, the performance of Pb removal improved. For the aqueous solution containing 50 mg/L of Pb, the removal percentage of lead was 80.1% using 0.1 M TSP concentration and 98.0% using 0.5 M TSP concentration. With low TSP and high Pb

concentrations, the percentage of lead removal decreases. By using 0.1M of TSP, it was shown that 89.9 % of 10 mg/L Pb, 88.4% of 20 mg/L Pb and 80.1% of 50 mg/L Pb were precipitated within 180 minutes of reaction periods. For the addition of 0.5M TSP, the precipitations of three lead concentrations were successfully achieved and the percentages of Pb precipitation were 99.9 % of 10 mg/L Pb, 99.4% of 20 mg/L Pb and 98.0% of 50 mg/L Pb were precipitated within 180 minutes of reaction periods. The measured pH was 3.4 after adding TSP and stayed the same with the addition of TSP and variation of reaction times.

The precipitations results match with the plotted Pourbaix diagrams in Figure 6.8 that indicate the formation of lead-phosphate compounds under the same pH levels. In the literature, Stanforth & Qiu (2001) reported similar results, demonstrating the influence of phosphate dosage on lead stabilization in acidic conditions, and (S. Chen et al., 2007b) explained a decrease in soil pH by adding soluble phosphoric amendments, a decrease in solubility in the solution, and a fast formation of pyromorphite as lead-phosphate minerals.

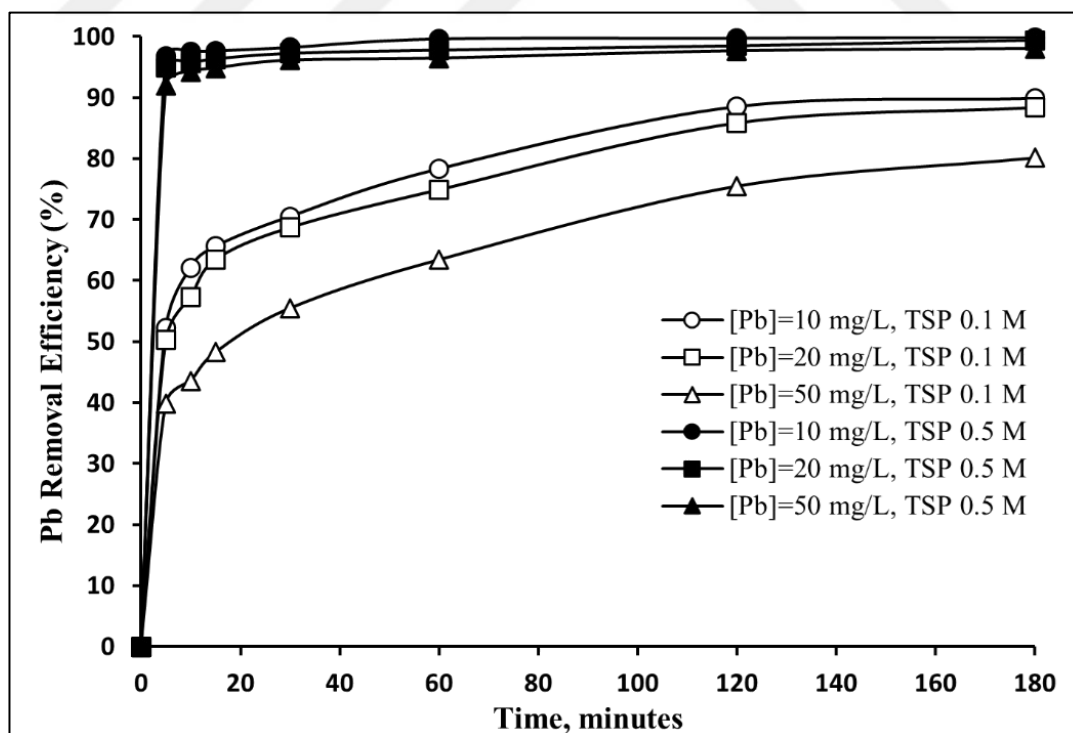


Figure 6.22 Effect of TSP concentrations (0.1, 0.5 M) on lead removal at three concentrations of Pb (10, 20, 50 mg/L) in 500ml distilled water. TSP dissolution time: 30 minutes. After adding TSP, pH=3.4

6.2.2.2 Removal of Fe in Aqueous Solutions

The findings, as shown in Figure 6.23, demonstrate that iron removal is influenced by the concentrations of TSP and Fe in the solution. With higher TSP concentrations, Fe removal becomes more efficient. For 0.1 M TSP and 0.5 M TSP, the removal effectiveness of the iron-containing solution was 63.6% and 93.4% for 10mg/L of Fe. The use of 0.1 M TSP stabilizes (precipitates) 83.2 %, 78.9% and 63.6% of 10, 20 and 50 mg/L Fe respectively, within 180 minutes of contact times. Similarly, Elnasr et al. (2017) have reported that the percentage of iron removal decreases with increasing Fe concentration using phosphate base materials. Alternatively, 0.5 M TSP precipitates 93.4%, 89.0% and 86.6% of 10, 20 and 50 mg/L Fe respectively. The measured solution pH was 3.43 in the presence of TSP under these conditions, and it did not decrease with the addition of Fe and variation of reaction periods. These findings are in good agreement with Pourbaix diagram of $\text{Fe-PO}_4^{-3}\cdot\text{H}_2\text{O}$ system that is plotted in Figure 6.11.

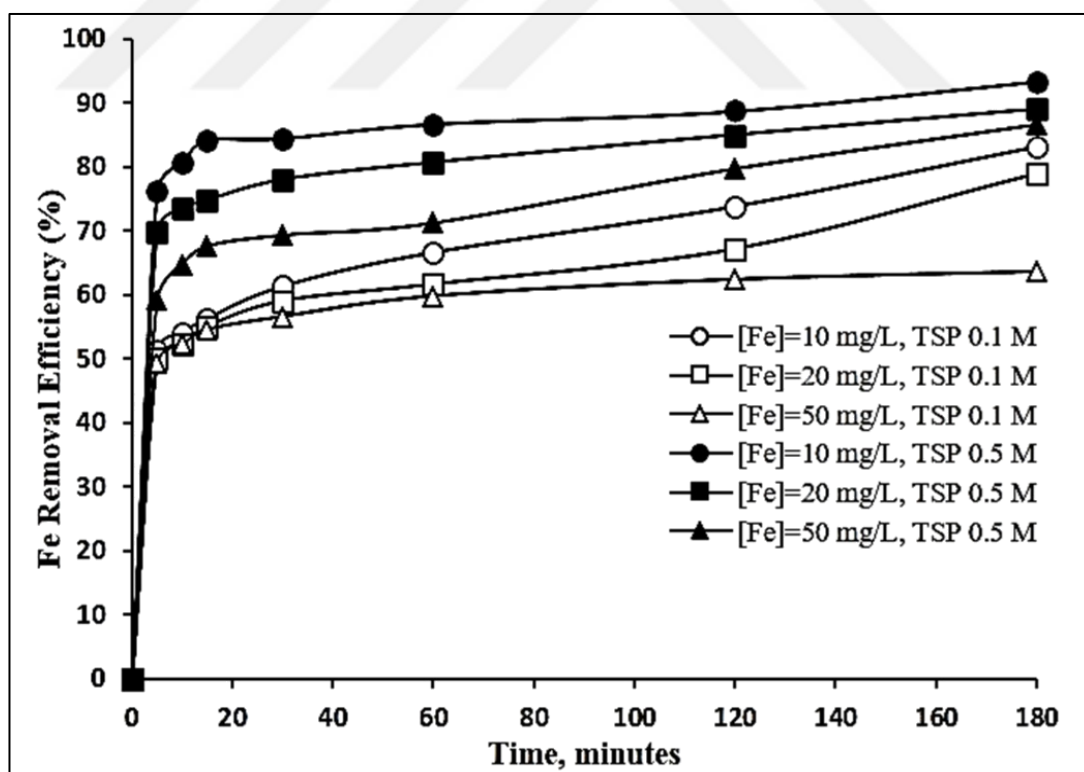


Figure 6.23 Effect of TSP concentrations (0.1, 0.5 M) on iron removal at three concentrations of Fe (10, 20, 50 mg/L) in 500ml distilled water. TSP dissolution time: 30 minutes. After adding TSP, pH=3.43

6.2.2.3 Removal of Cd in Aqueous Solutions

The results of Cd precipitation experiment are given in Figure 6.24 and indicate that the Cd removal depends on the Cd and TSP concentrations in the solution. The percentage of Cd removal increased with the rise of TSP concentrations. Cadmium removal decreases with low TSP and high Cd concentrations. As shown in Figure 6.24, the removal efficiencies at 0.1M of TSP were 85.1 % at 10 mg/L of Cd, 79.1 % at 20 mg/L of Cd and 66.5 % at 50 mg/L of Cd within 180 minutes of reaction time. At 0.5 M of TSP concentration, the percentages of Cd removal were 95.4 %, 91.8 % and 87.8 % for 10, 20 and 50 mg/L of Cd concentrations respectively. At these conditions, the measured pH was measured 3.41 with the TSP additions and stayed the same with Cd additions and throughout the precipitation reaction times. These results are compatible with the plotted Pourbaix diagram (see Figure 6.14) indicating the formation of stable cadmium phosphate in acid medium.

On the other hand, the observation made is that maximum TSP concentration is required to remove Cd metal ions from the aqueous solution efficiently. Similar fundings have mentioned the high concentration of phosphate-based materials (natural phosphate, TSP, K_2PO_4) promoted the removal of Cd from wastewater and polluted soils (Andrunik et al., 2020; Ruangcharus et al., 2020; Ruiti & Thayer, 2015).

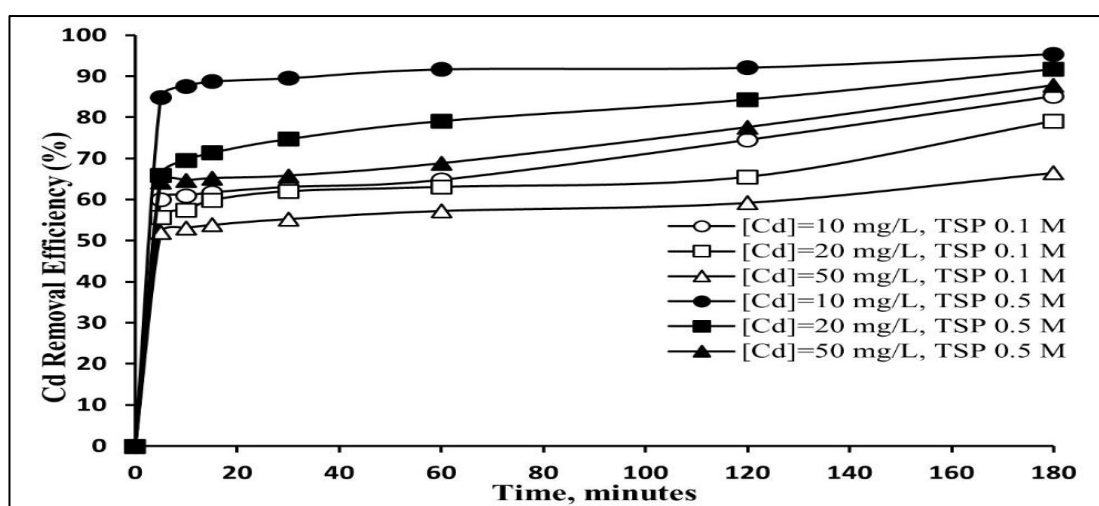


Figure 6.24 Effect of TSP concentrations (0.1, 0.5 M) on cadmium removal at three concentrations of Cd (10, 20, 50 mg/L) in 500ml distilled water. TSP dissolution time: 30 minutes. After adding TSP, pH=3.41

6.2.2.4 Removal of Cu in Aqueous Solutions

Copper (Cu) precipitation tests by TSP show an inefficient precipitation process. As can be seen from Figure 6.25, the TSP addition at 0.1M to the solution containing 10, 20, and 50 mg/L of Cu precipitate (remove) 47.7%, 42.0% and 33.2% of 10, 20 and 50 mg/L of Cu respectively. Whereas 0.5 M of TSP precipitates 58.8% of 10 mg/L Cu, 51.8% of 20 mg/L Cu and 39.4% of 50mg/L Cu. In addition, it was found that the precipitation percentage decreases at high concentrations of Cu and low concentrations of TSP. The solution pH was 3.36 after adding TSP and no big change was observed even during the test. This finding was quite unexpected compared to the obtained result of thermodynamic and speciation diagram of $\text{Cu-PO}_4^{3-} \cdot \text{H}_2\text{O}$ system.

The most likely explanation of the inefficient Cu removal may be the parameter reaction time. The prior study shows a high Cu removal (90%) using phosphate based-material up to 5 months of treatment (Qian et al., 2009).

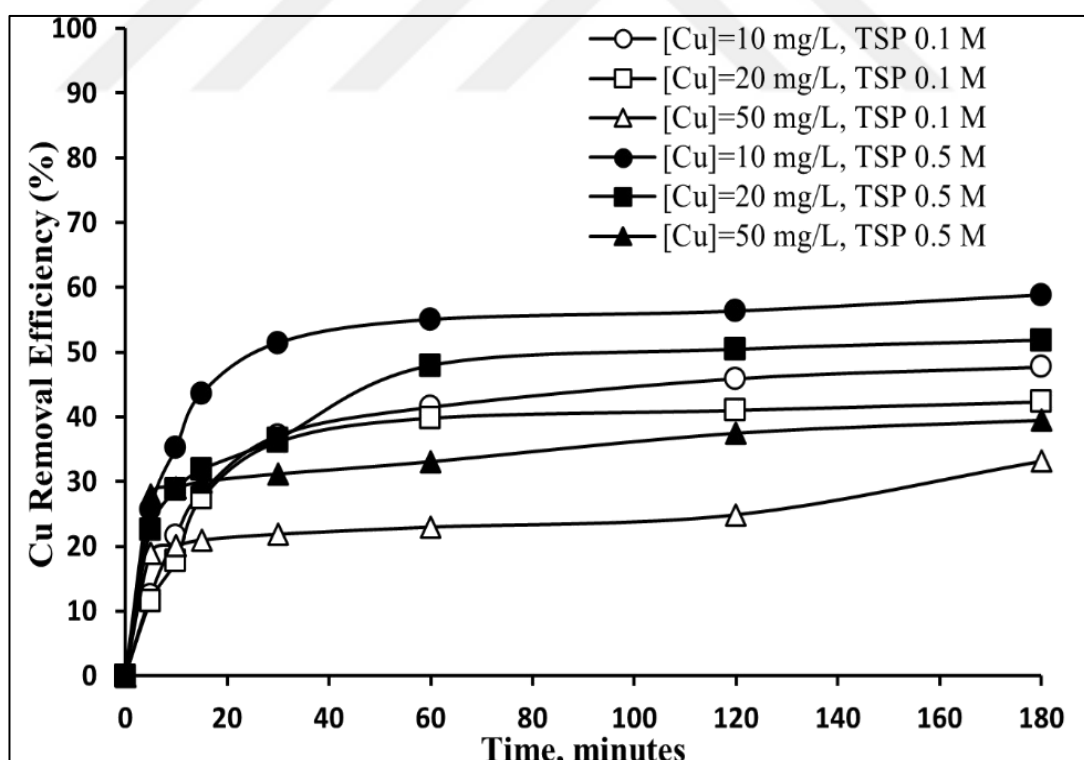


Figure 6.25 Effect of TSP concentrations (0.1, 0.5 M) on copper removal at three concentrations of Cu (10, 20, 50 mg/L) in 500ml distilled water. TSP dissolution time: 30 minutes. After adding TSP, pH=3.36

6.2.2.5 Removal of Zn in Aqueous Solutions

Figure 6.26 present the concentration effect of TSP on the removal of zinc in aqueous solutions. From this figure it can be seen that the increase of zinc removal efficiency with contact time variation and its decrease in the presence of high zinc concentration and small concentration of TSP. It was also observed percentage of zinc precipitation were zinc removal efficiency increases with low concentration of zinc and addition of high TSP concentration. For the application of low TSP concentration (0.1M), 57.8% of 10 mg/L Zn, 53.7% of 20 mg/L Zn and 44.7% of 50 mg/L were precipitated within 180 minutes of contact time. At 0.5M of TSP the zinc removal percentage were 68.7%, 64.1% and 49.9% for 10, 20 and 50 mg/L respectively. The measured pH was 3.38 during 180 minutes of zinc precipitation time. The result of zinc precipitation at pH value 3.38 match with the stability diagrams drawn in Figure 6.20.

In the past, Farrell-Poe (1990) studied the removal of zinc by TSP in aqueous solution and showed that TSP precipitating agent is able to stabilize 44.4% of Zn. Our findings are better than his results, but the experimental procedures are different.

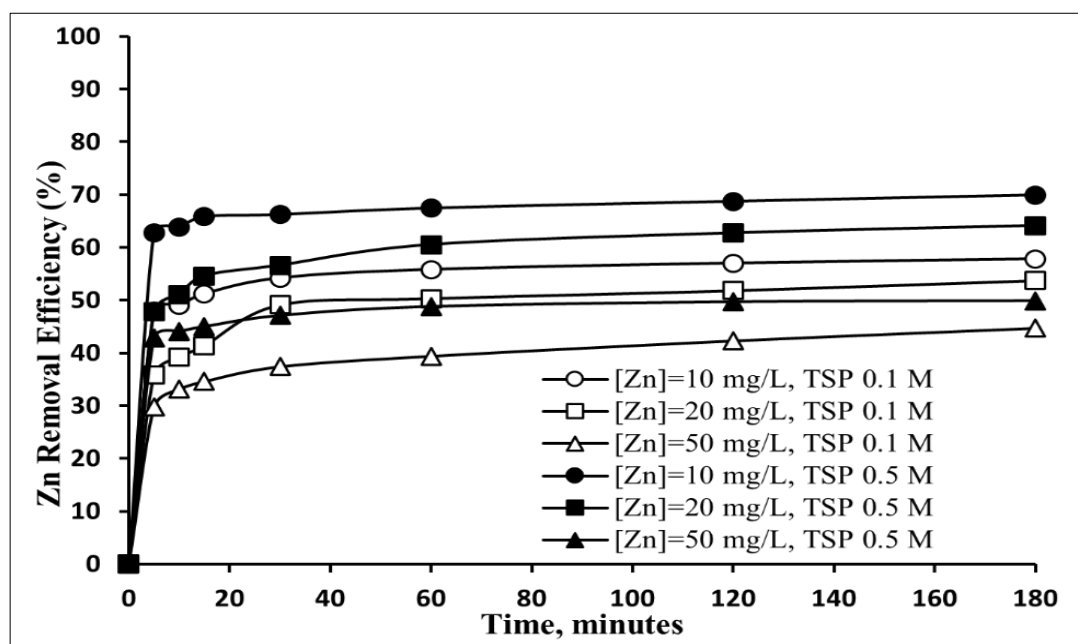
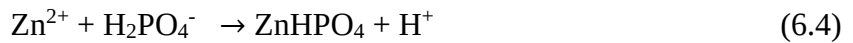
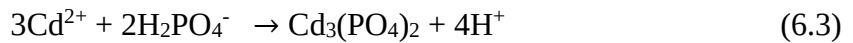
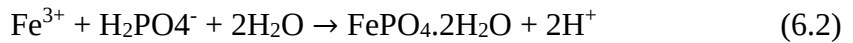


Figure 6.26 Effect of TSP concentrations (0.1, 0.5 M) on zinc removal at three concentrations of Zn (10, 20, 50mg/L) in 500ml distilled water. TSP dissolution time: 30 minutes. After adding TSP, pH=3.38

6.2.3 TSP Mechanism on Pb, Fe, Cd, Cu, and Zn Removal

XRD analyses of metals (Pb, Fe, Cd, Cu, and Zn) precipitated (removed from solution) were performed to approve the detected metals phosphate compounds obtained from stability diagrams. The major compounds detected in Pb, Fe, Cd, Cu and Zn precipitate samples were fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$, Quartz (SiO_2) and bassanite ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$) which are originated from TSP raw sample. Figure 6.2 provides a clarification of this statement. As shown in Figure 6.27, some XRD patterns reveal the presence of lead phosphate and lead oxide compounds in the analyzed lead precipitate. In the Fe precipitate, the formation of ferric phosphate ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) compounds was observed in low peaks (Figure 6.28). Figure 6.29 shows the formation of cadmium phosphate [$\text{Cd}_3(\text{PO}_4)_2$] in certain peaks. The analysis of Cu precipitate by XRD was not enabled us to determine copper phosphate (see Figure 6.30). For Zn precipitate, the identification zinc hydrogen phosphate was found in Figure 6.31. From these findings, we conclude that the mechanism of TSP on metal ions removal in aqueous solutions by can be described by its dissolution (Equation 3.1) and precipitation reaction (Equations 6.1 to 6.4):



In the literature, the results offered by Sugiyama et al. (2002) reveal that the stabilization of Pb using MCPM (monocalcium monophosphate monohydrate) was accomplished by of dissolution and precipitation process. Additionally, Pb stabilization with hydroxyapatite phosphate material and production of hydroxylpyromorphite compounds were reported by Cao et al. (2002, 2004) and Zhang & Ryan (1999) and the use of phosphate amendment to stabilize heavy metals were mentioned by Masambi et al. (2016) and (Munksgaard et al., 2012). By contrast, some findings have shown that insoluble metal phosphate was not detected in soil residue

but the removal of heavy metals by phosphate amendment is mainly due to surface complexation (Cao et al., 2009; S. Chen et al., 2007b; Ruiti & Thayer, 2015).

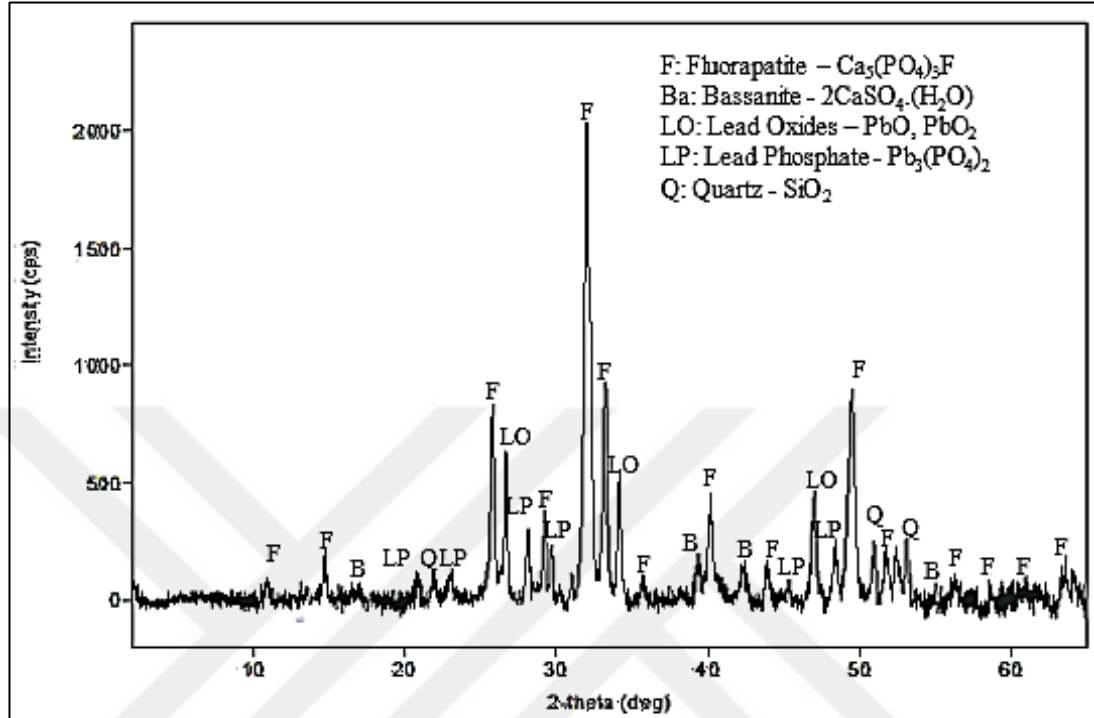


Figure 6.27 XRD pattern of lead precipitated (removed from the solution)

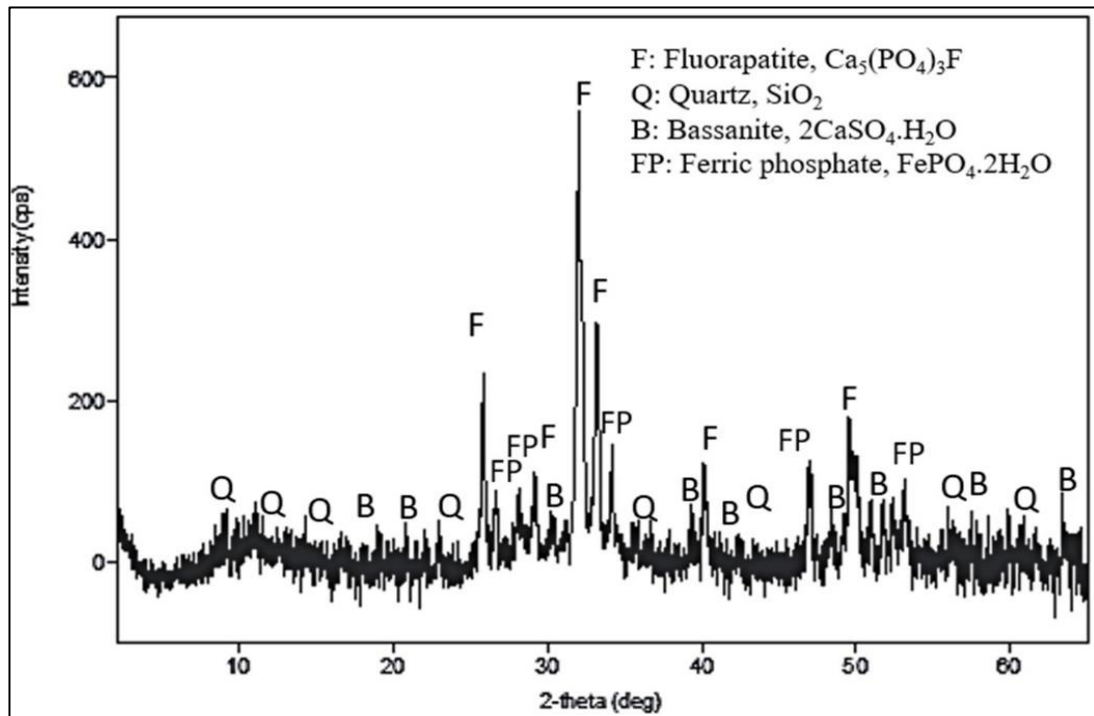


Figure 6.28 XRD pattern of iron precipitated (removed from the solution)

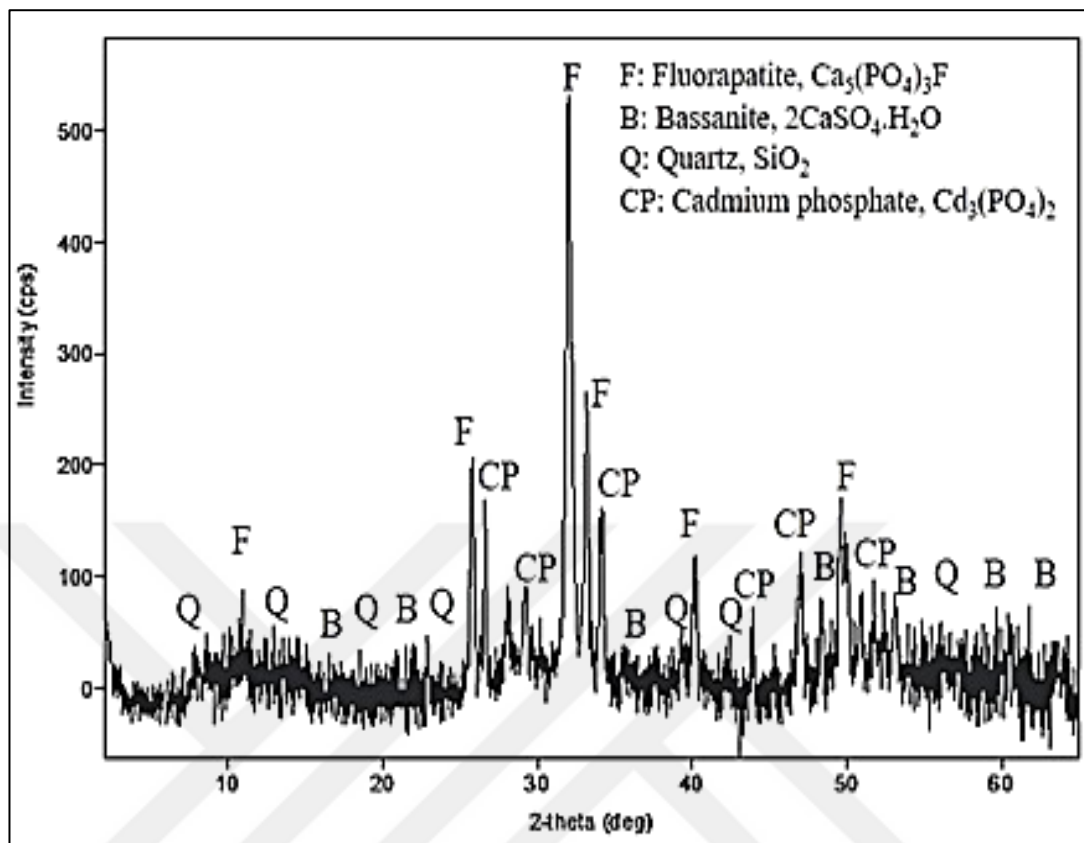


Figure 6.29 XRD pattern of cadmium precipitated (removed from the solution) by TSP

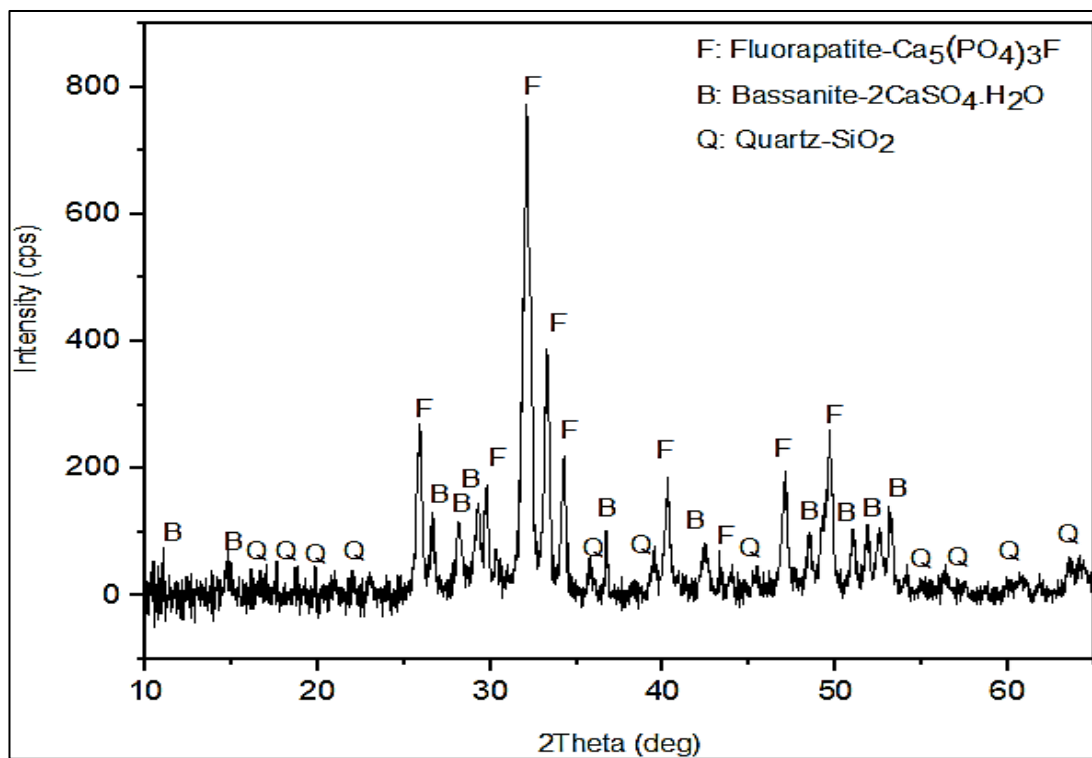


Figure 6.30 XRD pattern of copper precipitated (removed from the solution) by TSP

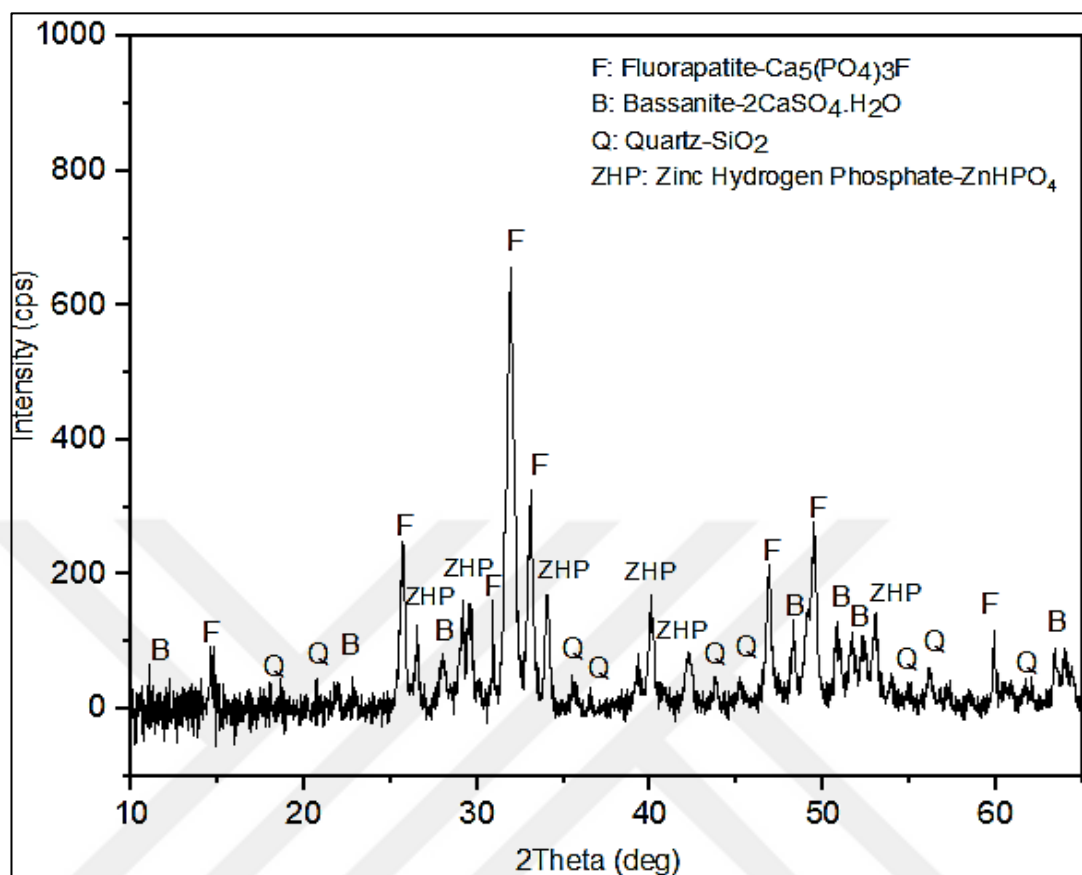


Figure 6.31 XRD pattern of zinc precipitated (removed from the solution) by TSP

6.2.4 Chemical Content in TSP and Pb Precipitate samples

The XRF analysis of TSP and Pb precipitate samples shows the presence of various chemical components. The investigated elements are grouped into two categories, as indicated in Table 6.9: major chemical oxides (Na_2O , P_2O_5 , MgO , CaO) and minor chemical oxides (Al_2O_3 , SiO_2 , K_2O , Fe_2O_3 , MnO , ZnO , SrO , TiO_2 and PbO). According to Chauhan et al. (2013) fertilizers contain 15 chemical components as impurities, based on their source. In our study, the same number of elements are found in the raw TSP sample. Except for calcium oxide, the main components in the precipitate of Pb sample decreased in concentration, and a new oxide (PbO) was formed. Such process may be illustrated by the interaction of oxide components produced by TSP with Pb to obtain the compound of lead oxide.

Table 6.9 Result of chemical content in TSP and Pb precipitate samples identified by XRF

Chemical content (%)	TSP raw	Pb precipitate
Na₂O	47.55	40.16
MgO	7.03	5.26
Al₂O₃	3.42	4.51
SiO₂	<0.0011	<0.0011
P₂O₅	27.23	19.27
SO₃	0.52	1.23
Cl	0.044	0.012
K₂O	<0.0012	<0.0012
Fe₂O₃	0.11	0.63
ZnO	0.013	0.008
Br	0.0001	<0.00003
CaO	14.04	28.61
MnO	0.001	<0.014
SrO	0.06	0.039
TiO₂	<0.0008	<0.0008
PbO	<0.0002	0.097

6.3 Treatment of Waste Containing Leachable Metal Ions and Simulated Wastewater by TSP

6.3.1 Physicochemical Properties Waste Samples

6.3.1.1 Moisture Content, pH and Particle Size Distribution

The waste samples used in our study contain a moisture content ranging from 3.5 to 22% and pH from 6.7 to 12.17. As presented in Table 6.10, the obtained results indicate that fly ash has the lowest and highest pH whereas the pH of Pb-Zn mine waste in the water is 6.7.

Table 6.10 Results of moisture content and pH for the collected waste samples

Characteristics	Fly ash	Fe-Cu tailing	Cu Slag	Pb-Zn waste
Moisture (%)	3.5	21.9	10	9.09
pH	12.17	8.03	8.6	6.7

The particle size distributions of the real waste samples (fly ash, iron-copper tailing, copper slag and Pb-Zn mine waste) were shown in Figure 6.32. As seen, more than 80 % of the particle sizes of Yatagan fly ash samples are below 81.55 μ m and more than 30% of particles have a size under 16.82 μ m. The median particle diameter is approximately 30 μ m (Figure 6.32a.). For iron copper tailing, 80% of particles are under 97.61 μ m, 30% of particles are below 16 μ m and the median is 36.13 μ m (Figure 6.32b). The plotted size distribution of copper slag indicates that 80% of ground copper slag particles are under 82.4 μ m, 30% of particles are below 17.7 μ m and the mean of the particle size is 52.40 μ m (Figure 6.32c.). 99.81% of the particle size of ground Pb-Zn mine waste is under 100 μ m and 50% of particles are 17 μ m (Figure 6.32d.).

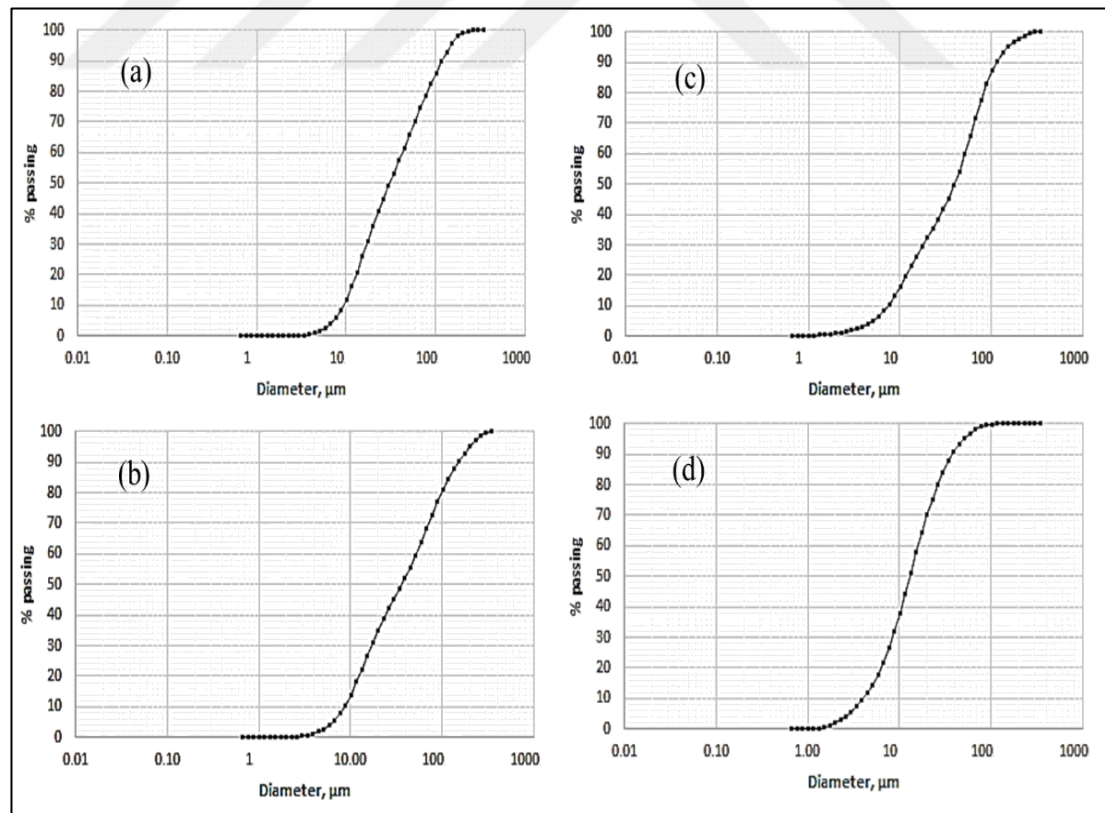


Figure 6.32 Particle size distribution of waste samples. (a) Fly ash. (b) Iron copper tailing. (c) Copper slag. (d) Pb-Zn mine waste

6.3.1.2 Chemical Composition and Content in Waste Sample

Table 6.11 presents the concentrations of heavy metals (i.e., hazardous metals) and major elements. From this table, it was found that the waste samples (fly ash, iron-copper tailing, copper slag and Pb-Zn mine waste) contain hazardous metals such as Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, and Zn. For instance, iron copper, copper slag and Pb-Zn waste samples are classified as a threat to the environment due to the presence of high concentrations that exceed by far the government regulation.

The analyses of major elements demonstrated that the percentage of SiO₂ (52.74%) and Al₂O₃ (18.34%) were found more in fly ash sample while copper slag contains high chemical oxides contents of Fe₂O₃ (56.57%) followed by iron copper tailing and Pb-Zn waste. Those results obtained in our work are consistent with the previous studies (Baba et al., 2003; Kursun et al., 2017; Turan & Ergun, 2009; Yilmaz, 2015).

Table 6.11 Chemical composition of the tested waste samples (Fly ash, iron copper (Fe-Cu) tailing, copper slag (Cu-slag) and Pb-Zn mine waste)

Major elements (%)	Sample Names				Heavy metals mg/Kg	Sample Names			
	Fly ash	Fe-Cu tailing	Cu slag	Pb-Zn mine waste		Fly ash	Fe-Cu tailing	Cu slag	Pb-Zn mine waste
SiO ₂	52.74	45.83	36.14	37.71	Cd	2.9	Nd	20.0	388.8
Al ₂ O ₃	18.34	8.95	2.97	9.60	Co	Nd	Nd	1040.0	317.1
Fe ₂ O ₃	6.19	16.99	56.57	14.50	Cr	137.3	Nd	320.0	282.1
CaO	13.26	11.90	1.30	24.12	Cu	73.0	1100.0	5460.0	2656.0
MgO	2.24	5.77	0.67	3.60	Fe	116.8	119000.0	39600.0	32970.0
Na ₂ O	0.62	1.46	0.46	0.15	Mn	321.4	1100.0	240.0	2531.0
K ₂ O	2.35	2.86	0.52	3.12	Ni	82.78	Nd	30.0	231.60
MnO	0.05	0.19	0.03	0.26	Pb	Nd	<2	2910.0	1174.0
TiO ₂	0.77	0.25	0.13	0.43	Sr	297.0	387.7	110.0	296.4
SO ₃	2.38	0.43	1.24	7.75	Zn	98.4	1000.0	31900.0	4360.0

6.3.1.3 Mineralogical Composition Analyses (XRD) of Waste samples

The mineralogical composition of raw fly ash is presented in Figure 6.33 showing the presence of quartz (SiO_2), albite ($\text{NaAlSi}_3\text{O}_8$), anhydrite (CaSO_4), gehlenite ($\text{Ca}_2\text{Al}[\text{AlSiO}_7]$), lime (CaO), and hematite (Fe_2O_3). From this figure, it can be seen that the main compound is quartz and the secondary minerals are albite, anhydrite, and gehlenite which are the sources of calcium in fly ash. Figure 6.34 shows that iron copper tailing contains chalcopyrite, and magnetite as primary sulfide minerals and secondary sulfides are digenite. For copper slag, it was seen the identification of the main mineral compounds such as fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4) and quartz (SiO_2) in some peaks (Figure 6.35). As shown in Figure 6.36, galena (PbS), chlorite magnetite (Fe_3O_4) and pyrite (FeS_2) in the Pb-Zn mine waste sample.

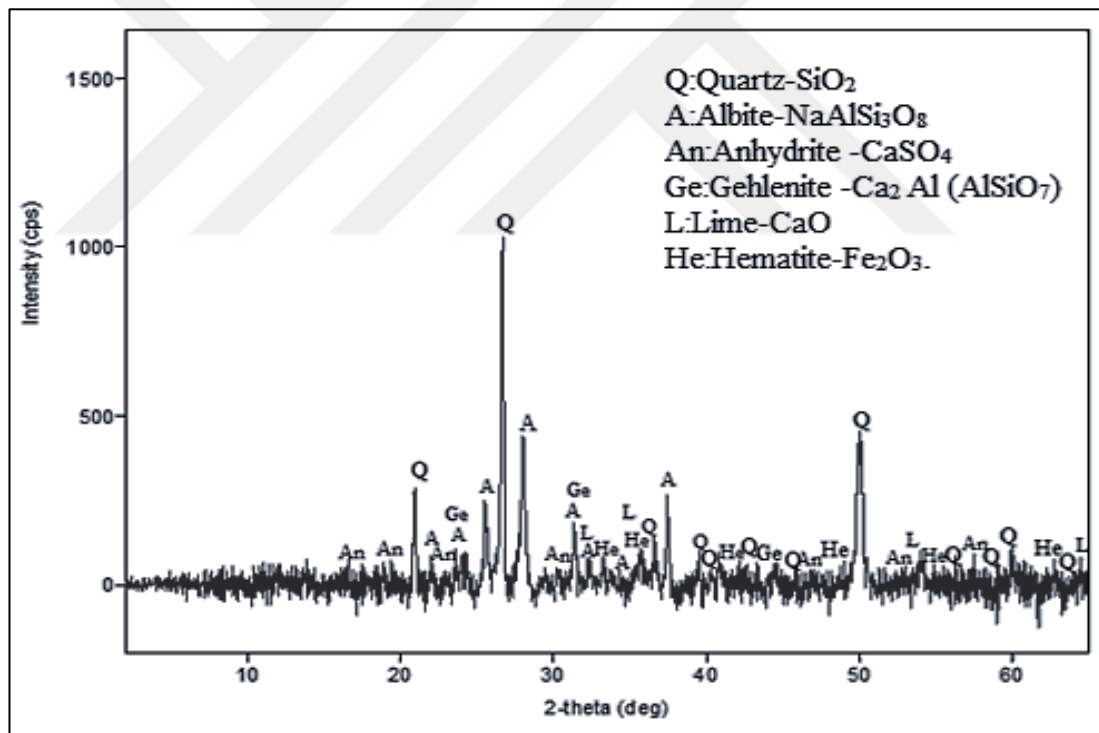


Figure 6.33 XRD pattern of fly ash sample

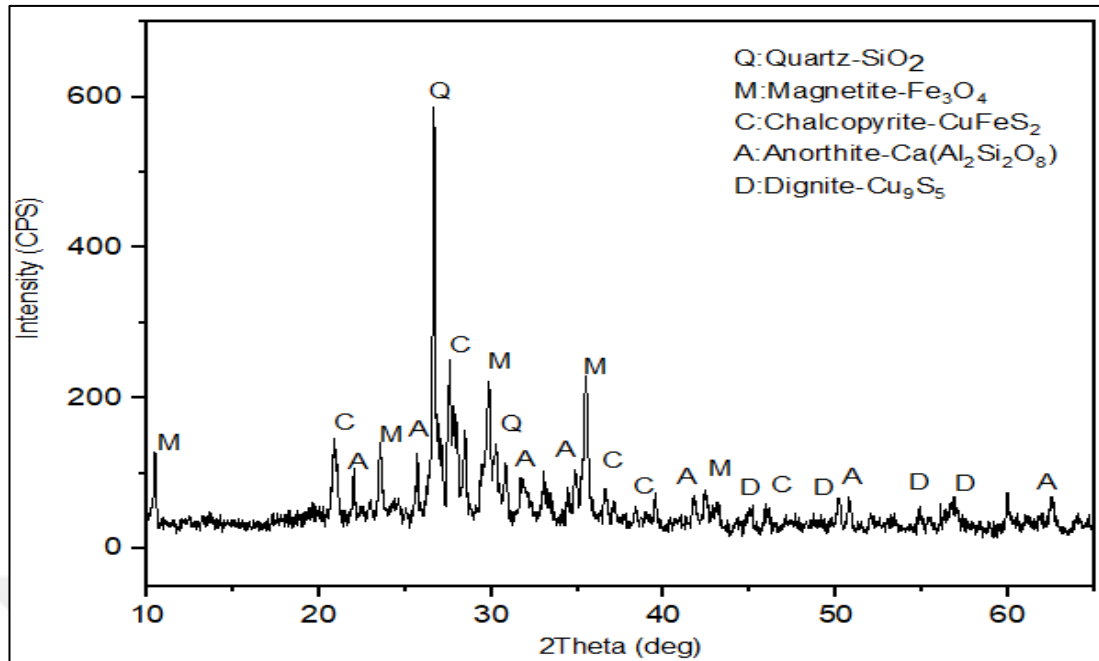


Figure 6.34 XRD pattern of iron copper tailing sample

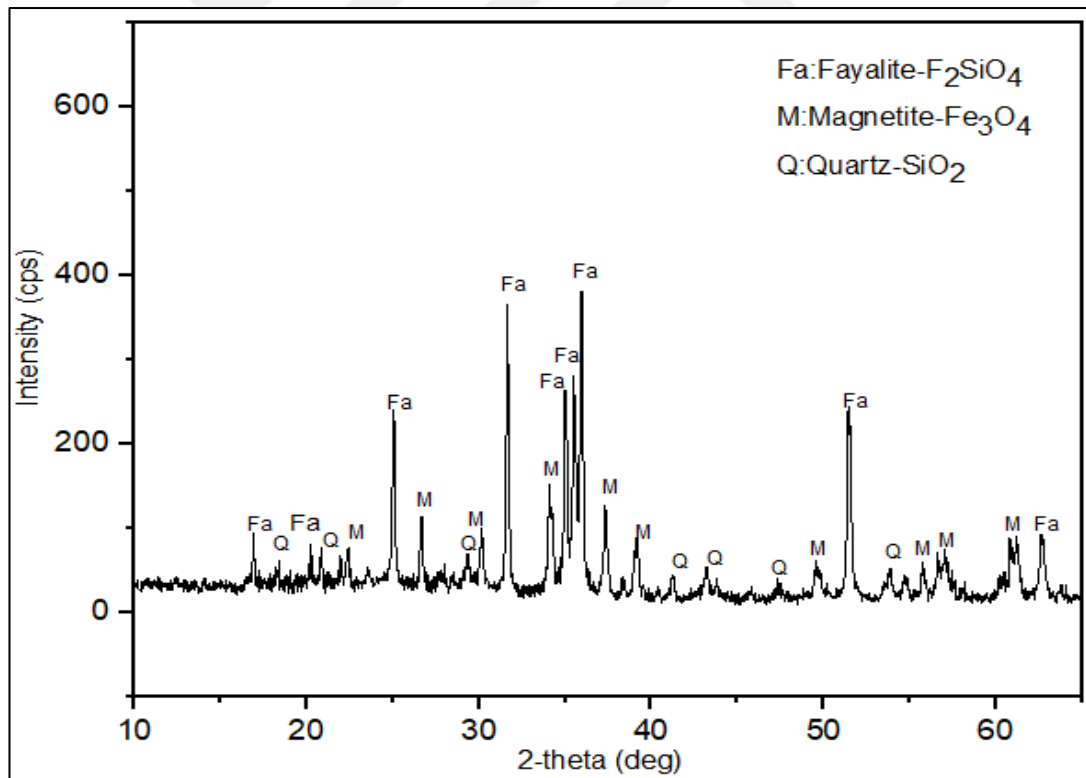


Figure 6.35 XRD pattern of copper slag sample

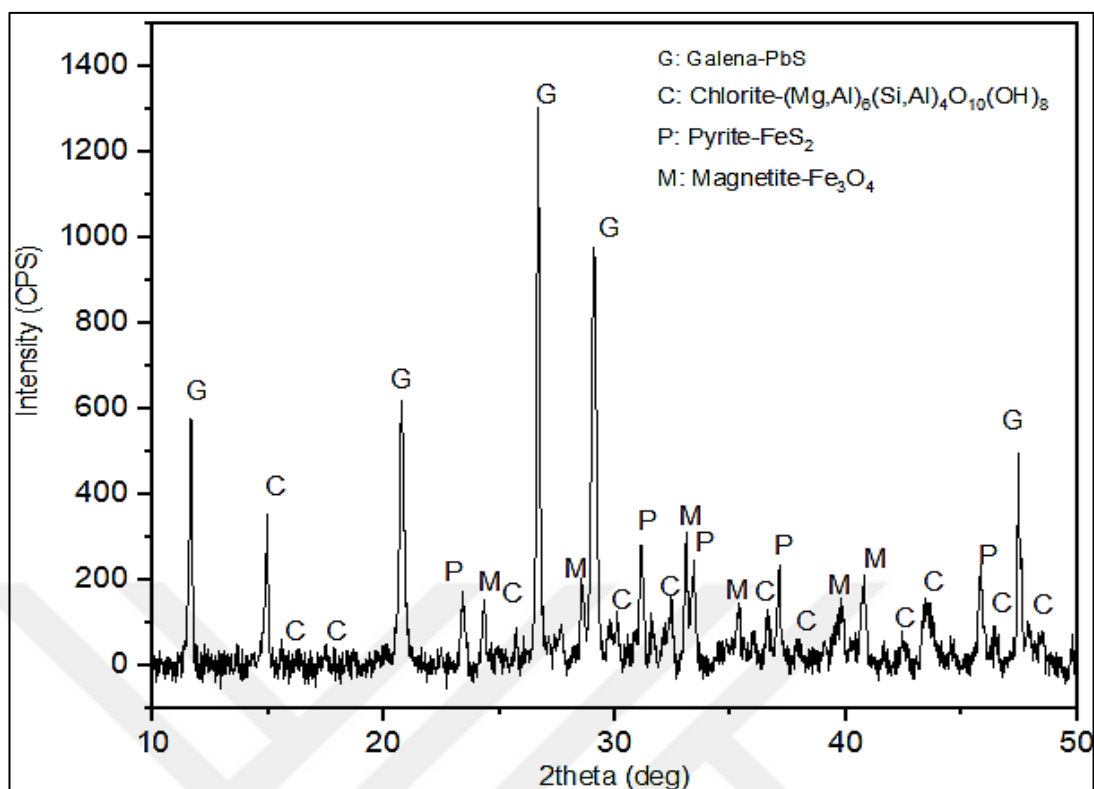


Figure 6.36 XRD pattern of Pb-Zn mine waste sample

6.3.2 Treatment of Waste Containing Leachable Metal Ions by TSP

The use of TSP to treat waste samples (fly ash, iron-copper tailing, copper slag and Pb-Zn mine waste) under different conditions (liquid/solid ratio: 20, pH:5, reaction times and different TSP concentrations) shows that TSP removes heavy metals efficiently (Tables A.8 to A.11). The effects of reaction times and TSP concentrations on the removal (stabilization) efficiency of heavy metals by TSP were discussed below.

6.3.2.1 Effect of Reaction Times

The reaction time effect on the removal of heavy metals ions from fly ash was conducted between 5 to 180 minutes using 0.1 M of TSP. Figure 6.37 also demonstrates that the variation of reaction time increases the removal efficiency of Cd, Cr, Fe, Mn, Sr and Zn metal ions at constant TSP concentration. 0.1 M stabilize more Cd and Fe (78.4 and 68.2%) compared to Cu (37%), Cr (59.7%), Mn (54.7%), Ni

(58.5%), Sr (52.9%) and Zn (41.7%) at 180 minutes. This is an unexpected finding that shows the inefficiency of TSP at low metal concentrations. We assume that the high addition of HNO_3 due to the high pH of fly ash (12.17) may be responsible for this decrease.

The precipitation results of Cu, Fe, Mn, Sr and Zn ions in iron copper tailing show that 29 to 51% of Cu, 62.8 to 78.2% of Fe, 33.9 to 57.2% of Mn, 39.6 to 69.4% of Sr and 30.7 to 53% of Zn are stabilized by 0.1M of TSP at 5 and 180 minutes (See Figure 6.38).

As shown in Figure 6.39, the reaction time increases the removal efficiency of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn metal ions. Similar findings were reported that the reaction time plays an important role in the stabilization of heavy metals by phosphate amendment (Mignardi et al., 2013). The removal efficiency of heavy metals by TSP ranged from 41.1% to 78.8% for Cd, 24.8% to 54.1% for Co, 24.6% to 52.4% for Cr, 12.4% to 42.2% for Cu, 32.1% to 77.5% for Fe, 30.0% to 53.3% for Mn, 19.6% to 52.7% for Ni, 56.7% to 98.9% for Pb, 37.8% to 72.7% for Sr and 18.6% to 50.4% for Zn at 5 and 180 minutes of reaction times respectively. However, except for Pb, Cd, Fe and Sr, low removal efficiency was observed for other metals at 180 minutes of precipitation times. It was also observed that TSP was able to precipitate up to 97% of Pb at only 30 minutes due to the high affinity of TSP to bind with lead.

For the treatment of Pb-Zn mine waste containing heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn), it was found that 99.4% of Pb was removed by 0.1M TSP at just 5 minutes of precipitation time as presented in Figure 6.40. On the other hand, the removal percentage for other heavy metals increases as the reaction period increases.

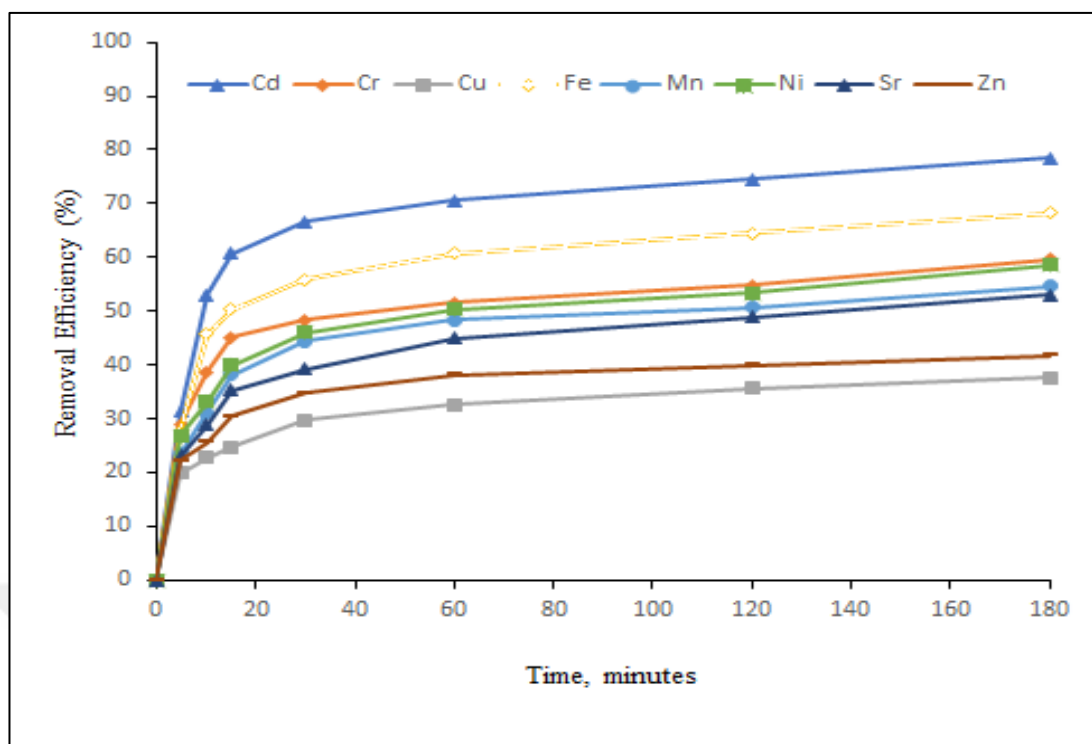


Figure 6.37 Effect of reaction time on removal of heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Sr and Zn) from fly ash by 0.1M TSP at pH=5. Dissolution time of fly ash and TSP :30 minutes. pH adjustment by HNO_3 or NaOH

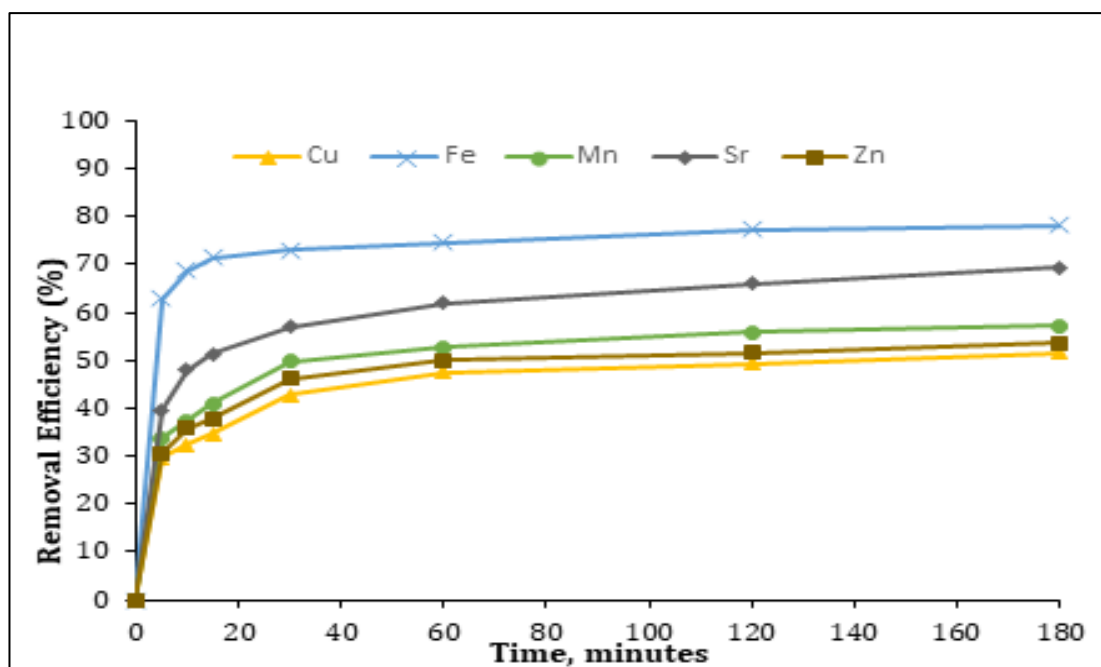


Figure 6.38 Effect of reaction time on removal of heavy metals (Cu, Fe, Mn, Sr and Zn) from iron copper tailing by TSP at pH=5. Dissolution time of iron copper tailing and TSP:30 minutes. pH adjustment by HNO_3 or NaOH

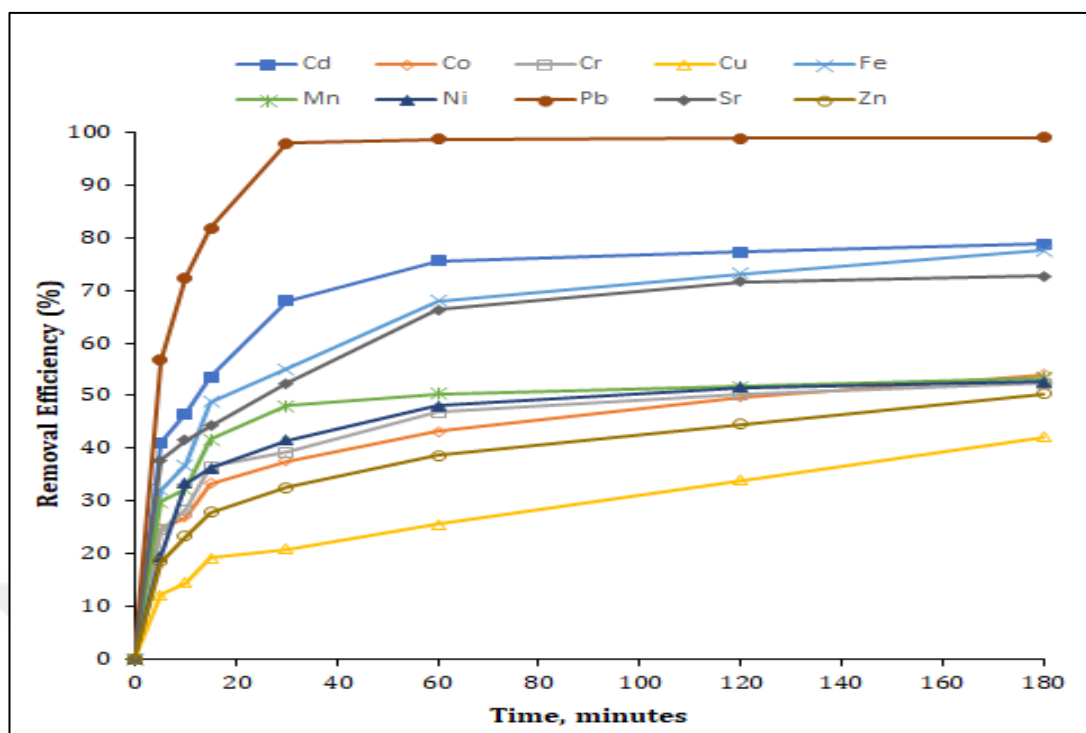


Figure 6.39 Effect of reaction time on removal of heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn) from copper slag by TSP at pH=5. Dissolution time of copper slag and TSP :30 minutes. pH adjustment by HNO_3 or NaOH

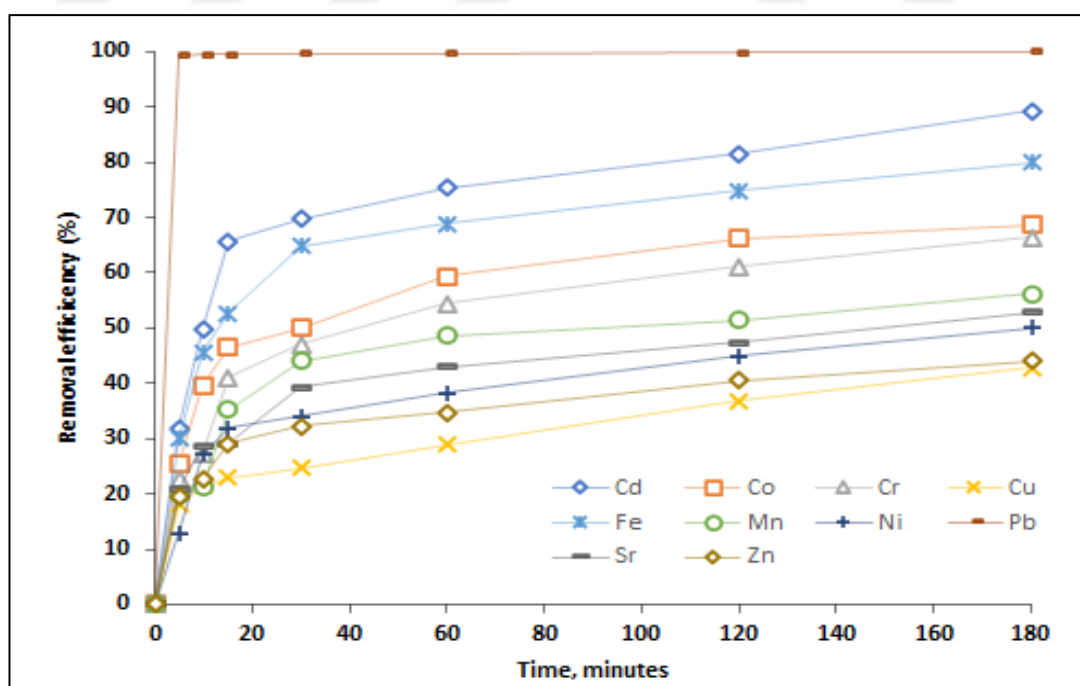


Figure 6.40 Effect of reaction time on removal of heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn) from Pb-Zn mine waste by TSP at pH=5. Dissolution time of Pb-Zn mine waste and TSP:30 minutes. pH adjustment by HNO_3 or NaOH

6.3.2.2 Effect of TSP Concentrations

The effect of TSP concentrations of heavy metal ions from wastes containing leachable metal ions was investigated at 0.1, 0.2 and 0.5 M of TSP. Table 6.12 demonstrated the total cadmium concentration (100%) in the fly ash were stabilized by 0.5M of TSP. Whereas more than 90% of Cr, Fe, Mn, Sr and Zn were reduced at 180 minutes reaction, except for Cu (89%).

Table 6.13 show the concentration of TSP effect on heavy metal removal. By adding 0.1M TSP, the precipitation efficiency of Cu, Fe, Mn, Sr and Zn metal ions in iron copper tailing is low. At the addition of 0.2M and 0.5M of TSP concentration, the percentage of precipitation ranged from 55.3 to 91.2% for Cu, 97.7 to 99.0% for Fe, 90.8 to 96.7% for Mn and 87.5 to 94.24% for Zinc.

Table 6.14 demonstrates that the removal efficiency for all metals increased with increasing TSP concentrations. At 180 minutes of reaction time, it was observed that 0.1 M of TSP remove 78.8% of Cd, 54.1% of Co, 52.4% of Cr, 42.2% of Cu, 77.5% of Fe, 53.3% of Mn, 52.7% of Ni, 98.9% of Pb, 72.7% of Sr and 50.4% of Zn concentrations, while 93.2% of Cd, 79.3% of Co, 71.6% of Cr, 61.2% of Cu, 91.1% of Fe, 70.4% of Mn, 68.4% of Ni, 99.0% of Pb, 84.5% of Sr and 67.9% of Zn concentrations were removed from copper slag by 0.2 M of TSP. On the other hand, the high removal efficiency was achieved by 0.5 M of TSP in which all metal concentrations were reduced by more than 90% except for Cu (83.7%) and Zn (86.6%).

As reported in Table 6.15, the lowest removal efficiency was found in Cu (87.8%) and Zn precipitation from Pb-Zn mine waste using 0.5M of TSP at 180 minutes. For the other heavy metals, their removal efficiency is up to 93.0%. The addition of more TSP concentration is suitable for Cu and in order to accomplish high removal efficiency. Feng et al. (2010) and Weber et al. (2015) also stated that the use of excess phosphate-based materials including monocalcium phosphate monohydrate (MCPM), diammonium phosphate (DAP), hydroxyapatite (HA) is required to immobilize toxic elements such as Pb, Cd, Fe from the soil, water, and sludge.

The obtained results for the removal of metal ions in fly ash using 0.5 M of TSP indicate the concentrations of the metals are under the limit concentrations of heavy metals given by Turkish soil pollution regulation (Gazette, 2001). In other words, the residue of fly ash can be stored or used in agriculture area. For the iron copper tailing and copper slag, it was observed that the concentrations of all metals in the residue by using 0.5M TSP are under the permissible concentrations except for Cu. In this case a further addition of TSP concentration is necessary in order to satisfy the environmental regulation. On the other hand, as TSP precipitating agent is less effective to Cu and Zn, special attention should be taken by decreasing the concentration of Cu and Zn before storing the residue to the environmental land.

Table 6.12 Effect of TSP concentrations (0.1, 0.2 and 0.5 M TSP) on heavy metals removal from 25g fly ash (Dissolution time of fly ash and TSP: 30 minutes; initial pH=12.17; pH adjusted to 5 by HNO₃ or NaOH)

Metals	Effluent Concentration (mg/Kg)						Removal Efficiency (%)			
	Fly Ash TSP	0.1M TSP	Fly Ash TSP	0.2M TSP	Fly Ash TSP	0.5M TSP	TSP concentration			
							0.0	0.1M	0.2M	0.5M
Cd	10.1	2.2	10.8	1.4	17.5	0.0	0.0	78.4	87.3	100.0
Cr	12.3	5.0	12.8	2.9	16.5	0.8	0.0	59.7	77.0	95.2
Cu	20.0	12.47	24.8	7.1	36.5	3.7	0.0	37.6	71.5	89.8
Fe	93.5	29.7	97.4	16.1	118.0	0.6	0.0	68.2	83.5	99.5
Mn	63.4	28.7	66.8	19.2	80.0	2.7	0.0	54.7	80.0	96.6
Ni	38.2	15.2	42.8	10.2	63.5	1.4	0.0	58.5	76.2	97.8
Sr	218.8	103.0	221.0	67.0	221.0	10.6	0.0	52.9	69.7	95.2
Zn	138.8	81.0	150.2	45.1	199.3	14.5	0.0	41.7	70.0	92.7

Table 6.13 Effect of TSP concentrations (0.1, 0.2 and 0.5 M TSP) on heavy metals removal from 25g iron copper (Fe-Cu) tailing (Dissolution time of Fe-Cu and TSP: 30 minutes; initial pH=8.03; pH adjusted to 5 by HNO₃ or NaOH)

Metals	Effluent Concentration (mg/Kg)						Removal Efficiency (%)			
	Fe-Cu TSP	0.1M TSP	Fe-Cu TSP	0.2M TSP	Fe-Cu TSP	0.5M TSP	TSP concentration			
							0.0	0.1M	0.2M	0.5M
Cu	1780	861.4	1782.6	796.7	1802.4	157.2	0.0	51.6	55.3	91.3
Fe	4144	905.1	4149.2	96.4	4184.4	44.10	0.0	78.2	97.7	99.0
Mn	905	387.3	905.8	82.9	921.0	30.38	0.0	57.2	90.8	96.7
Sr	499	152.9	501.4	34.1	522.40	10.98	0.0	69.4	93.2	97.9
Zn	822	380.8	862.4	108.2	926.20	53.31	0.0	53.7	87.5	94.2

Table 6.14 Effect of TSP concentrations (0.1, 0.2 and 0.5 M TSP) on heavy metals removal from 25g Cu-slag (Dissolution time of Cu slag and TSP: 30 minutes.; initial pH=8.6; pH adjusted to 5 by HNO₃ or NaOH)

Metals	Effluent Concentration (mg/Kg)						Removal Efficiency (%)			
	Cu slag TSP	0.1M TSP	Cu slag TSP	0.2M TSP	Cu slag TSP	0.5M TSP	TSP concentration			
							0.0	0.1M	0.2M	0.5M
Cd	31.6	6.7	31.7	2.2	32.4	0.4	0.0	78.8	93.2	98.8
Co	470.8	216.2	471.4	97.6	472.0	29.8	0.0	54.1	79.3	93.7
Cr	352.4	167.7	353.4	100.2	354.2	23.7	0.0	52.4	71.6	93.3
Cu	933.0	539.7	933.4	361.6	952.2	151.9	0.0	42.2	61.2	83.7
Fe	1106.4	248.9	1108.4	98.8	1128.2	23.7	0.0	77.5	91.1	97.9
Mn	282.4	131.8	283.4	83.5	285.6	20.6	0.0	53.4	70.4	92.7
Ni	37.8	11.2	38	12.0	40.2	3.5	0.0	52.7	68.4	90.7
Pb	386.4	4.3	387.2	3.9	393.4	0.0	0.0	98.9	99.0	100.0
Sr	137.8	37.7	138.0	21.4	139.9	11.4	0.0	72.7	84.5	91.8
Zn	940.6	466.8	942.0	302.2	984.2	125.6	0.0	50.4	67.9	86.6

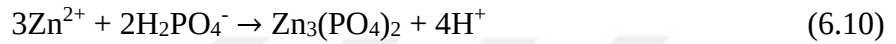
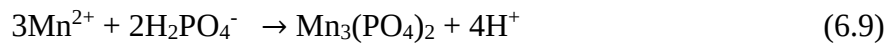
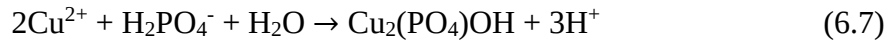
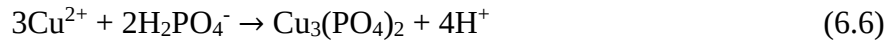
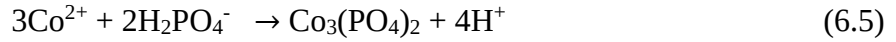
Table 6.15 Effect of TSP concentrations (0.1, 0.2 and 0.5 M TSP) on heavy metals removal from 25g Pb-Zn mine waste (Dissolution time of Pb-Zn mine waste and TSP: 30min.; initial pH=6.7; pH adjusted to 5 by HNO₃)

Metals	Effluent Concentration (mg/Kg)						Removal Efficiency (%)			
	Pb-Zn waste TSP	0.1M TSP	Pb-Zn waste TSP	0.2M TSP	Pb-Zn waste TSP	0.5M TSP	TSP concentration			
							0.0	0.1M	0.2M	0.5M
Cd	202.0	21.8	202.2	8.8	202.6	0.6	0.0	89.2	95.7	99.7
Co	243.6	76.2	243.62	22.8	244.2	5.4	0.0	68.7	90.6	97.8
Cr	184	61.8	184.8	21.4	185.2	8.8	0.0	66.4	88.4	95.2
Cu	702.4	401.4	702.8	176.8	704.2	85.6	0.0	42.9	74.8	87.8
Fe	2852	570.0	2853.4	184.8	2912.4	30.6	0.0	80	93.5	98.9
Mn	2180	956.4	2182	299.6	2182	70.8	0.0	56.1	86.3	96.8
Ni	148	77.0	148.6	25.8	148.6	8.8	0.0	50	82.6	94.1
Pb	498.2	0.4	498.8	0.0	503.0	0.0	0.0	99.9	100.0	100.0
Sr	324.2	152.8	324.4	50.8	329.0	18.4	0.0	52.9	84.3	94.4
Zn	3109.2	1742.4	3109.4	641.4	3121.6	351.6	0.0	44.0	79.4	88.7

6.3.3 X-Ray Diffraction Analyses (XRD) of Residue

The mineralogical composition was detected by X-ray diffraction. Based on XRD analysis, the most probable minerals were identified (Figures 6.41 to 6.44). Except for Figure 6.41, the presence of fluorapatite in other XRD pattern of residue samples is originated from raw TSP sample (see Figure 6.2). Figure 6.41 indicate the formation of metal phosphates (Cd₃(PO₄)₂, Cu₃(PO₄)₂, Fe₃(PO₄)₂, Mn₃(PO₄)₂, and Zn₃(PO₄)₂) at low intensity of XRD pattern. As illustrated in Figure 6.42, copper phosphate [Cu₃(PO₄)₂], iron phosphate [Fe₃(PO₄)₂], manganese phosphate [Mn₃(PO₄)₂] and Zinc phosphate [Zn₃(PO₄)₂] were found in certain peaks. From Figure 6.43, the formation of new compounds such as cadmium phosphate [Cd₃(PO₄)₂], libethenite [Cu₂(PO₄)OH], iron phosphate [Fe₃(PO₄)₂], manganese phosphate [Mn₃(PO₄)₂], lead phosphate [Pb₃(PO₄)₂] and zinc phosphate [Zn₃(PO₄)₂] were found in low peaks. Figure 6.44 indicates Cd₃(PO₄)₂, Co₃(PO₄)₂, Fe₃(PO₄)₂, Mn₃(PO₄)₂, and Zn₃(PO₄)₂ compound are formed in the residue of Pb-Zn mine waste.

Those metal phosphate compounds in the residue samples are sparingly soluble in water (insoluble) and their formation is elucidated by TSP mechanism on heavy metals: Equation 3.1 describing TSP dissolution, Equation 6.1 and Equations 6.5 to 6.10 indicate metal precipitation reaction:



The results from XRD analysis seem to be in correlation with the previous study (Y. Sun et al., 2011). Similarly, Crannell et al., (2000) and Eighmy et al., (1997) have reported that phosphate-containing minerals (i.e., $\text{Zn}_3(\text{PO}_4)_2$, $\text{Zn}(\text{PO}_4)_3\text{Cl}$, $\text{Mn}_2\text{Zn}(\text{PO}_4)_2$, $\text{ZnHPO}_4 \cdot \text{H}_2\text{O}$), and $\text{Zn}_5(\text{PO}_4)_3\text{OH}$ are formed during phosphate stabilization process.

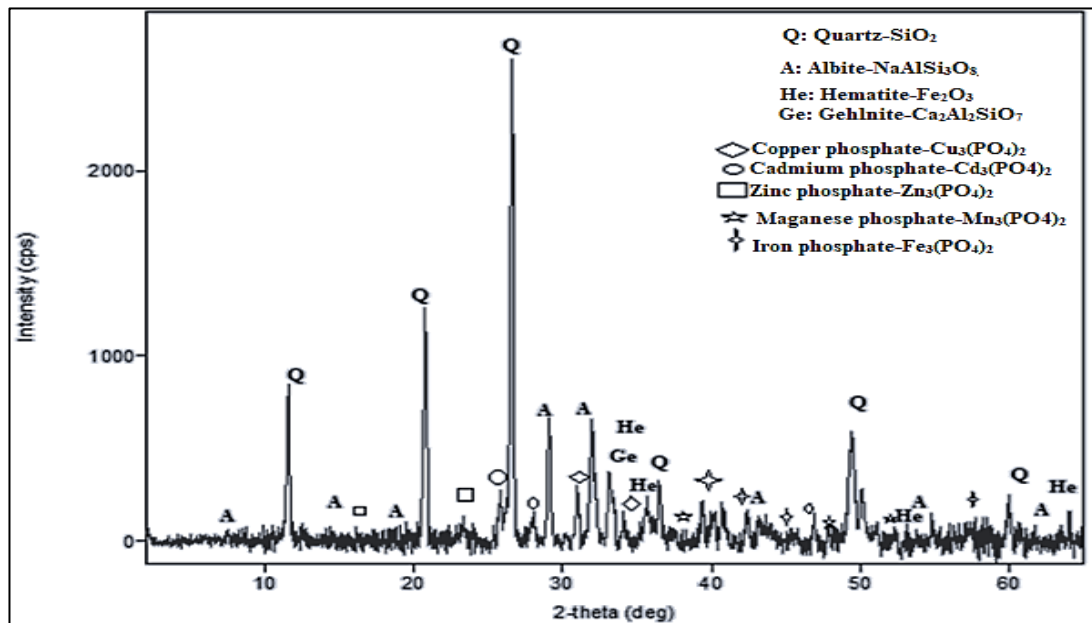


Figure 6.41 XRD pattern of coal fly ash residue (obtained after precipitation with TSP)

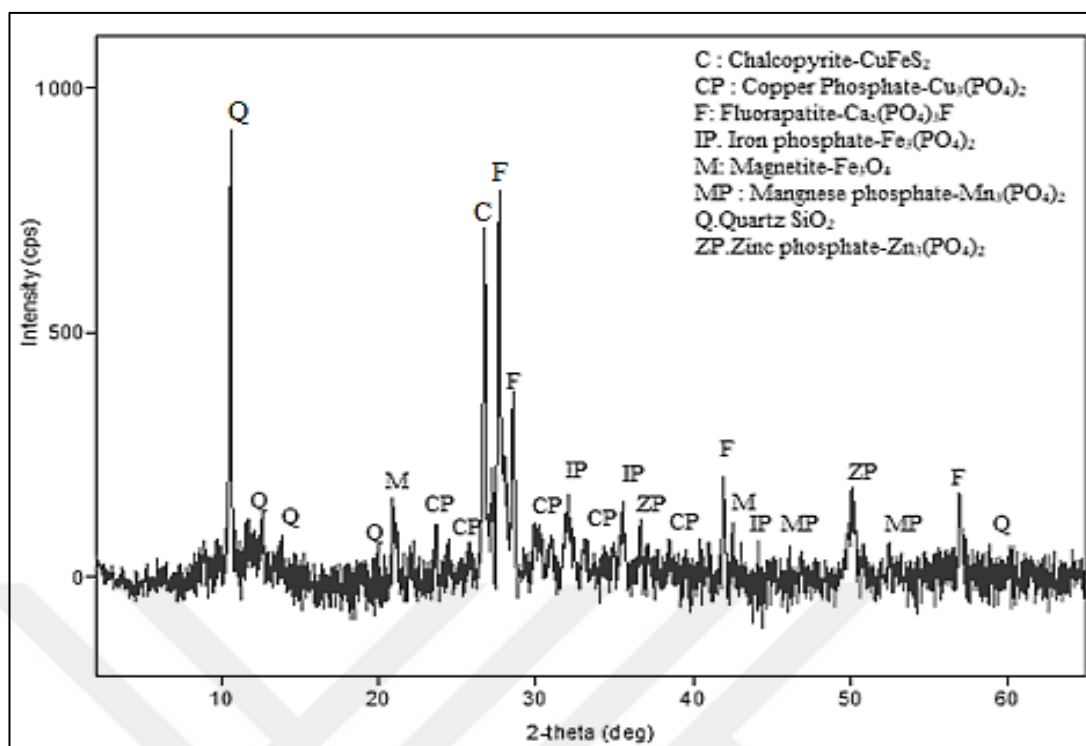


Figure 6.42 XRD pattern of iron copper residue (obtained after precipitation with TSP)

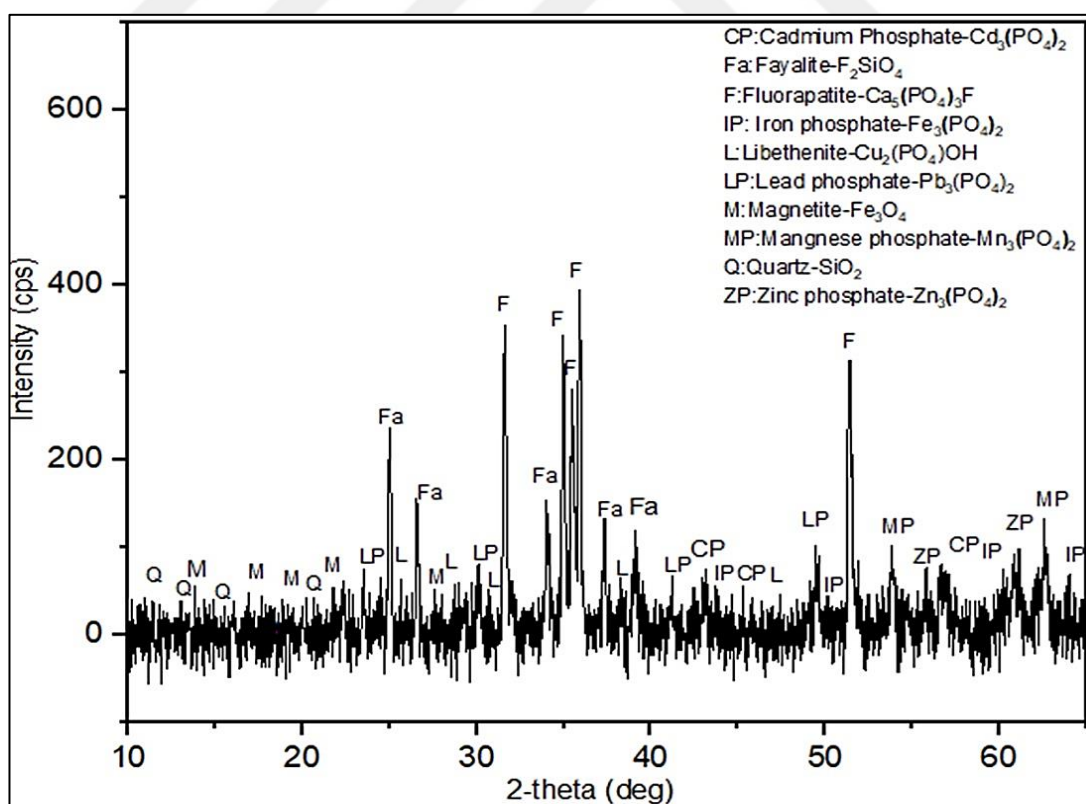


Figure 6.43 XRD pattern of copper slag residue (obtained after precipitation with TSP)

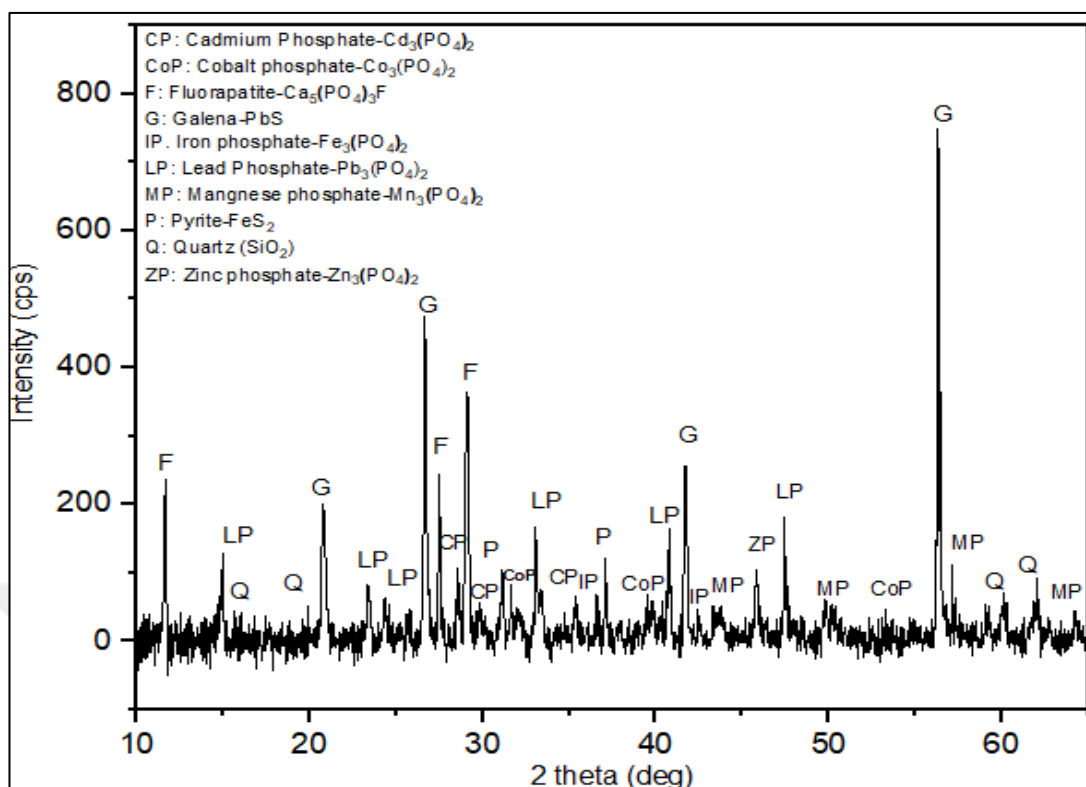


Figure 6.44 XRD pattern of Pb-Zn residue (obtained after precipitation with TSP)

6.3.4 Treatment of Simulated Wastewater by TSP

Table 6.16 shows the concentrations of hazardous metals (i.e., heavy metals). The results from wet analysis indicate the presence of several hazardous metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, and Zn) in industrial and mining samples with high concentrations. The results are in agreement of the heavy metals reported in the chemical analyses of the collected samples.

The precipitation experiments were conducted on simulated wastewater of Pb-Zn wastes using two concentrations of TSP reagent (0.1 and 0.5 M) to determine the behavior and efficiency of TSP. The results in Table A12 and A13 have shown that the heavy metals from simulated wastewater such as Cd, Co, Cr, Cu, Fe, Mn, Ni, and Zn were stabilized efficiently by TSP in an acidic medium through the precipitation method. Research has reported that the hydrometallurgical process owing to its simplicity and cost-effectiveness is utilized for detoxification of wastes containing toxic metals (Alorro et al.; 2008). The triple superphosphate considers as fertilizer and

classified in water-soluble phosphate-based materials is capable to stabilize heavy metals with the variation of time. For instance, 0.1 M of TSP precipitates 66.8 to 87.7% of Cd, 54.8 to 81.6% of Co, 51.0 to 79.2 % of Cr, 19.1 to 60.4% of Cu, 63.8 to 86.6% of Fe, 45.1 to 78.5% of Mn, 44.6 to 72.4% of Ni, 99.6 to 99.9% of Pb, 53.6 to 74.2% of Sr and 22.2 to 63.9% of Zn concentrations at 5 to 240 minutes of contact periods (See Figure 6.45).

As shown in Figure 6.46, the increase of TSP (0.5) increases the removal of all metal increased and the percentage of removal are: 99.4% for cadmium, 96.4% for cobalt, 85.2% for chromium, 87.5% for copper, 98.3% for iron, 93.3% for manganese, 89.4% for nickel, 100.0% for lead, 90.6% for strontium and 88.8% for zinc.

It was observed that high TSP concentration is required to remove zinc ions from the wastewater efficiently. Similar findings have mentioned the high concentration of phosphate-based materials (natural phosphate, TSP, K_2PO_4) promotes the removal of metal from wastewater and polluted soils (Andrunik et al., 2020; Ruangcharus et al., 2020; Ruiti & Thayer, 2015).

The laboratory experimental results have shown the capability of TSP agent to precipitate metal ions in wastewater as discussed in the previous paragraph. For instance, a flowsheet that describes the TSP precipitation process for metal ions removal from wastewater is given in Figure 6.47. Also, this flowsheet design can be used in industrial wastewater treatment.

Table 6.16 Heavy metal concentrations dissolved in 2000 ml using nitric acid. (L/S ratio=10, 50g of Pb-Zn waste are dissolved by 0.5M HNO_3 in 500ml distilled water at $T=40^\circ C$, leaching time: 60 minutes)

Metals	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
Concentration (mg/L)	351.0	271.8	202.0	523.2	26760.0	1912.0	154.0	429.4	292.1	3754.6

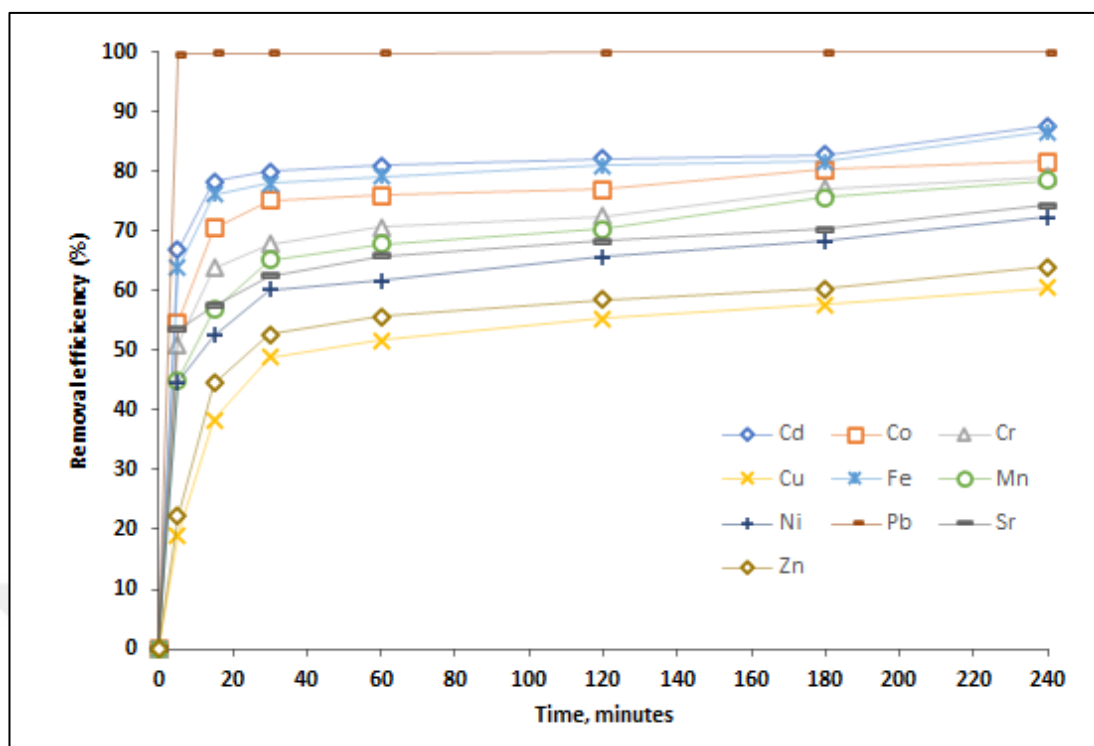


Figure 6.45 Heavy metals removal from 500 ml of Pb-Zn simulated wastewater using 0.1 M of TSP (S/L=1/10, TSP dissolution time: 30minutes).

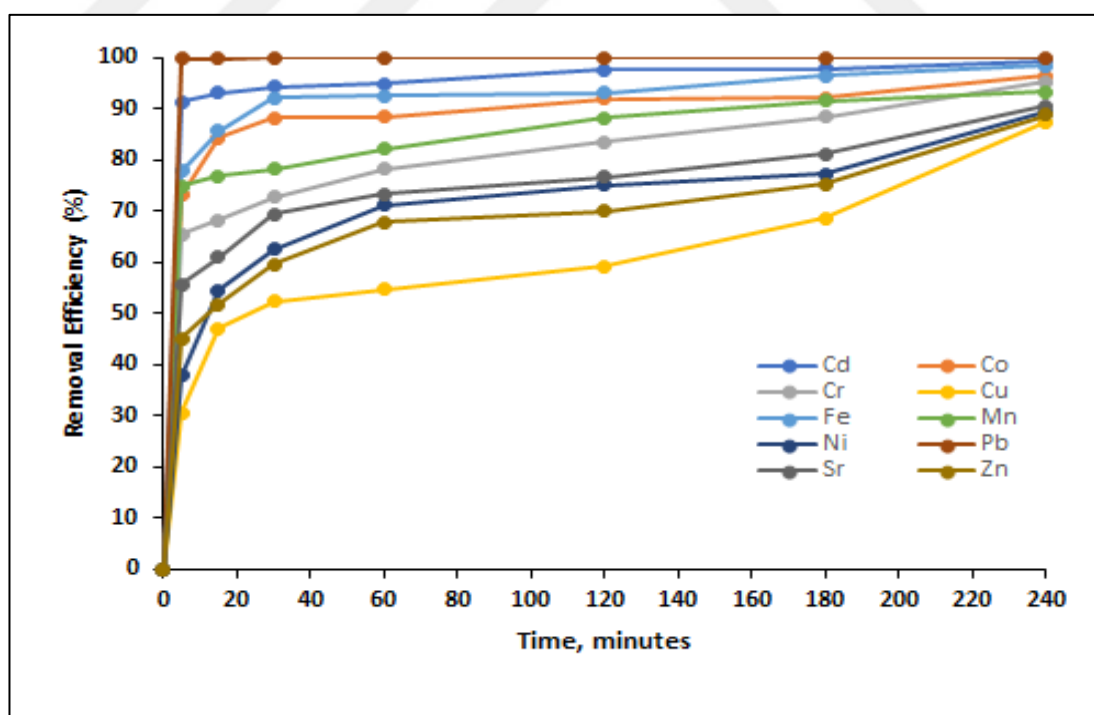


Figure 6.46 Heavy metals removal from 500 ml of Pb-Zn simulated wastewater using 0.5 M of TSP (S/L=1/10, TSP dissolution time: 30minutes)

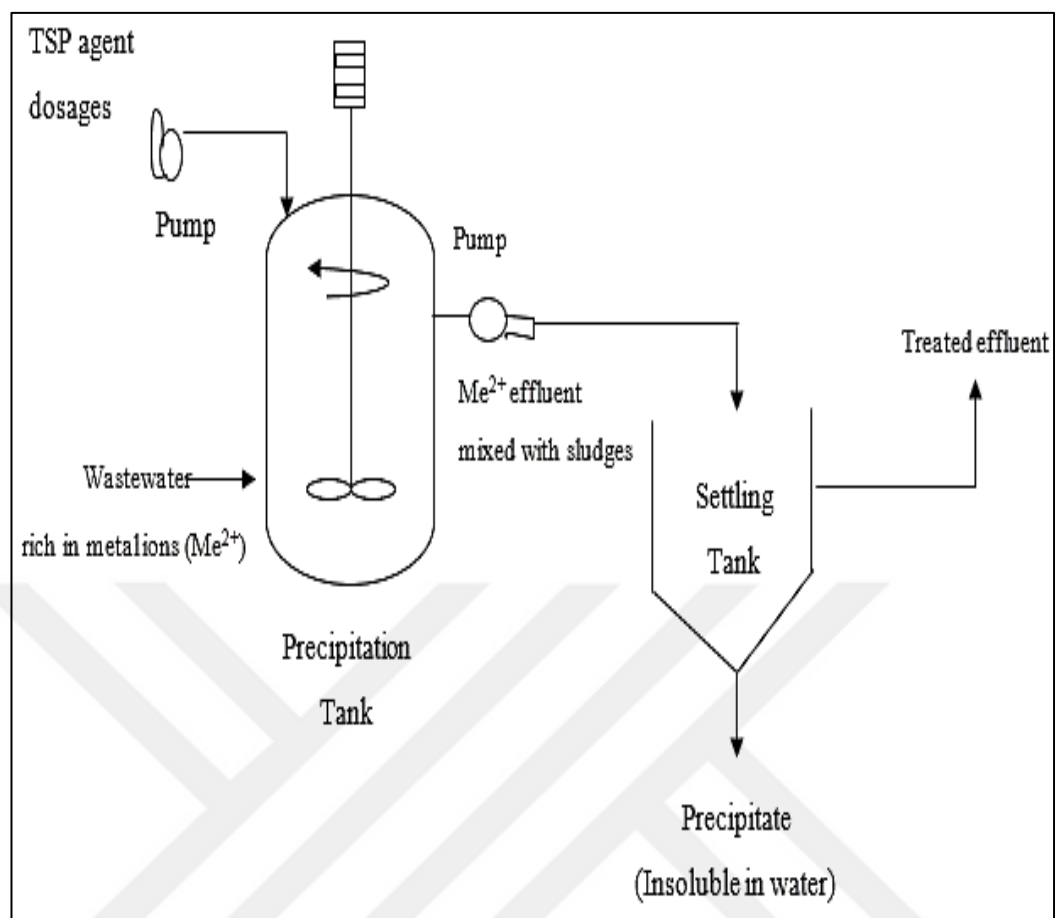


Figure 6.47 Flowsheet of TSP precipitation process for removal of metal ions in wastewater

CHAPTER SEVEN

CONCLUSIONS AND RECOMMANDATIONS

7.1 Conclusions

In this work, the investigation of heavy metal ions removal using triple superphosphate indicates the feasibility of TSP to stabilize metal ions from aqueous solutions, wastes containing leachable metal ions and simulated wastewater. Based on the obtained results, the following findings can be summarized:

- Triple superphosphate (TSP) is phosphorus (P) water-soluble (85%) at measured solution pH of 3.5 and its granular form as received has about 2% moisture. The chemical analysis results indicated that triple superphosphate contains heavy metals such as Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn as impurities. XRD analyses revealed that Raw TSP has crystalline forms and contains monocalcium phosphate monohydrate $[\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}]$ as the main compound and minor mineral compounds of fluorapatite $(\text{Ca}_5(\text{PO}_4)_3\text{F})$ bassanite $(2\text{CaSO}_4\text{H}_2\text{O})$, and quartz (SiO_2) .
- Through the aid of computer program HSC 6.0 and a thorough analysis of speciation diagrams [Eh-pH, of Pb-H₂O and Pb-PO₄³⁻·H₂O; Fe-H₂O and Fe-PO₄³⁻·H₂O; Cd-H₂O and Cd-PO₄³⁻·H₂O; Cu-H₂O and Cu-PO₄³⁻·H₂O; Zn-H₂O and Zn-PO₄³⁻·H₂O], the investigated TSP solution chemistry for Pb, Fe, Cd, Cu and Zn metal ions removal in aqueous solutions demonstrate that TSP may stabilize (precipitate) lead, iron, cadmium, copper and Zinc in the solutions via the formation of insoluble metal phosphates $[\text{PbHPO}_4(\text{c})$, $\text{Pb}(\text{H}_2\text{PO}_4)_2(\text{c})$, $\text{Pb}_3(\text{PO}_4)_2(\text{c})$, $\text{Pb}_4\text{O}(\text{PO}_4)_2(\text{c})$, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}(\text{c})$ and $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}(\text{c})$ $\text{Cd}(\text{H}_2\text{PO}_4)_2(\text{c})$, $\text{CdHPO}_4(\text{c})$, $\text{Cd}_3(\text{PO}_4)_2(\text{c})$, $\text{Cd}_5(\text{PO}_4)_3\text{OH}(\text{c})$; $\text{Cu}(\text{H}_2\text{PO}_4)_2(\text{c})$, $\text{CuHPO}_4(\text{c})$, $\text{Cu}_3(\text{PO}_4)_2(\text{c})$, $\text{Cu}_5(\text{PO}_4)_3\text{OH}(\text{c})$; $\text{Zn}(\text{H}_2\text{PO}_4)_2(\text{c})$, $\text{ZnHPO}_4(\text{c})$, $\text{Zn}_3(\text{PO}_4)_2(\text{c})$, $\text{Zn}_5(\text{PO}_4)_3\text{OH}(\text{c})$;] in both acid and basic mediums as identified through the stability diagrams. The laboratory precipitation tests show that TSP is able to precipitate up to 99.9% of Pb, 95.4% of Cd, 93.4% of Fe, 68.7% of Zn and 58.8% of Cu according to the solution conditions. On the other hand,

the percent of removal effectiveness decrease with low TSP and high concentrations of Pb, Fe, Cd, Cu and Zn. The detections of lead phosphate, iron phosphate, cadmium phosphate and zinc hydrogen phosphate by x-ray analyses of precipitates support the hypothesis that stated TSP dissolution and formation of metal compounds sparingly soluble (insoluble) by precipitation are the main TSP mechanism in heavy metal removal.

- The experimental results of real wastes (Yatağan coal fly ash, iron copper tailing, copper slag and Pb-Zn mine waste) indicate that the reaction times and concentrations of TSP parameters affect the removal efficiency of heavy metals during the precipitation process. Increasing reaction times and concentrations of TSP promote a high removal of heavy metals at pH value 5 and the percentage of removal efficiencies were:
- For Yatağan coal fly ash, 0.5M TSP stabilized 100% of Cd, 95.2% of Cr, 89.8% of Cu, 99.5% of Fe, 96.6% of Mn, 97.8% of Ni, 95.2% Sr and 92.7% of Zn at 180 minutes of reaction time.
The concentration of 0.5M TSP precipitates 91.2% of Cu, 99% of Fe, 96.7% of Mn, 97.7% of Sr and 92.7% of Zn iron-copper tailings.
The addition of 0.5M TSP removes 98.8% of Cd, 93.7% of Co, 93.3% of Cr, 83.7% of Cu, 97.9% of Fe, 92.7% of Mn, 90.7% of Ni, 100% of Pb, 91.8% Sr and 86.6% of Zn from copper slag at 180 minutes of reaction time.
- The results of precipitation of metal ions from Pb-Zn mine waste are 99.7% of Cd, 97.8% of Co, 95.2% of Cr, 87.8% of Cu, 98.9% of Fe, 96.8% of Mn, 94.1% of Ni, 100% of Pb, 94.4% Sr and 88.7% of Zn using 0.5M of TSP.
- The XRD analyses of residues obtained after precipitation (treated Yatağan coal fly ash, iron copper tailing, copper slag and Pb-Zn mine waste) by TSP indicate the formation of new compounds: cadmium phosphate $[\text{Cd}_3(\text{PO}_4)_2]$, cobalt phosphate $[\text{Co}_3(\text{PO}_4)_2]$, copper phosphate $[\text{Cu}_3(\text{PO}_4)_2]$, libethenite $[\text{Cu}_2(\text{PO}_4)\text{OH}]$, iron phosphate $[\text{Fe}_3(\text{PO}_4)_2]$, lead phosphate $[\text{Pb}_3(\text{PO}_4)_2]$, manganese phosphate $[\text{Mn}_3(\text{PO}_4)_2]$ and zinc phosphate $[\text{Zn}_3(\text{PO}_4)_2]$ as insoluble metal phosphate.

- The results of heavy metals from simulated wastewater show that 0.5 M of TSP stabilize efficiently heavy metal, but the concentration of Cu, Fe and Zn are above the limit concentration given by environmental regulation.
- Under acid conditions and the same pH, TSP precipitates heavy metal from contaminated waste or aqueous solution with a high removal efficiency of metal ions. Indeed, the results of our work show that TSP is a prominent precipitant for heavy metals immobilization and its use can also solve the problem of continuous monitoring of pH changes that lead to metal dissolution in aqueous environments.

7.2 Recommendations for Future Work

As mentioned in this study, the efficiency of TSP for the removal of metal ions is affected by reaction times, TSP and metal concentrations, work should be performed on the effect of fine particle size (nanoparticle) of TSP and temperature to improve the process. The surface area of particle determines the dissolution rate of phosphorous (P) and the presence of P for metal precipitation. Optimum temperature can be important in accelerating the reaction rate and may promote the formation of crystal metal phosphate sparingly soluble in water.

Research on the immobilization of metal ions from real wastewater should be carried out using TSP in order to determine the benefit of TSP in environmental sustainability as well as to understand the complexity of the triple superphosphate reactivity. Furthermore, the TSP reagent can be employed for the recovery of valuable minerals via the obtention of metal phosphate as an intermediary product. The reason is that TSP has two specific roles which are leaching and precipitation for metal recovery.

The economical evaluation of TSP amendment is recommended for future work in order to know exactly the operating cost for its application on the industrial scale. This will be a supporting material to decide whether it is cost-effective or not.

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APPENDICES

Appendix 1.1 TSP and Slaked Lime Dosages and Standard Pure Metal Concentration Dilution Calculations

TSP molar mass= $\text{Ca}(\text{H}_2\text{PO}_4)_2\text{H}_2\text{O}$ = $40.078 + [2 \times (2 + 31 + 4 \times 16)] + (2 + 16) = 252 \text{ g/mol}$

Ca=40.078 g/mol

H=1.000794 g/mol

P=30.9737616 g/mol

O=15.99994 g/mol

1 M or mol/L=252 g

The volume used in the experiment 500 mL

1 M= 126g

0.5 M=63 g

0.2 M=25.2 g

0.1 M=12.6 g

Slaked lime molar mass=40+34=74 g/mol

1 M=74 g

By using 500 mL

1M=37 g

0.5M=18.5 g

0.2M=7.4 g

0.1M=3.7 g

Preparation of 10, 20 and 50 mg/L of Pb, Fe, Cd, Cu and Zn from 1000mg/L of stock solutions

$$C_1V_1=C_2V_2; V_1=\frac{C_2V_2}{C_1}$$

C_1, V_1 : concentration and volume of stock solutions

C_2, V_2 : concentration and volume of diluted solutions

The volume taken from stock solution

$$10\text{mg/L}=\frac{10 \times 500}{1000}=5\text{mL}$$

$$20\text{mg/L}=\frac{20 \times 500}{1000}=10\text{mL}$$

$$50\text{mg/L} = \frac{50 \times 500}{1000} = 25\text{mL}$$



Appendix 1.2 Supplementary Materials

Table A.1 Result of particle size distribution of raw TSP sample

Diameter (mm)	weight of retained (g)	% Retained	Σ % Retained	% Passing
4.75	13.71	4.55	4.55	100.00
2.0	230.63	76.61	81.16	95.45
1.18	49.13	16.32	97.48	18.84
0.6	6.35	2.11	99.59	2.52
0.3	0.14	0.05	99.64	0.41
0.15	0.8	0.27	99.90	0.36
0	0.28	0.09	100.00	0.10
Total	301.04		100.00	

Table A.2 Limits of detection (LOD) and quantification (LOQ) for atomic absorption spectrometer measurements

Test	[Pb] (mg/L)			[Fe] (mg/L)			[Cd] (mg/L)			[Cu] (mg/L)			[Zn] (mg/L)		
Numbers	10.00	20.00	50.00	10.00	20.00	50.00	10.00	20.00	50.00	10.00	20.00	50.00	10.00	20.00	50.00
1	10.07	20.14	50.09	9.88	20.15	49.99	10.05	19.99	50.1	10.02	19.96	49.94	9.92	19.9	50.06
2	10.14	20	50.08	10.14	20.16	49.98	9.95	19.96	50.07	9.94	20.07	50.07	10.03	20	50.05
3	10.14	19.96	50.01	10.12	20.07	49.92	10.07	19.93	49.97	10	20.02	49.94	9.9	20.04	49.95
4	10.07	19.9	49.89	10.08	19.88	50.09	10.05	19.97	50.06	9.95	19.91	49.93	9.94	19.95	50.07
5	10.1	20.01	49.98	10.12	19.97	50.13	9.99	19.95	50.05	10.02	20.01	49.97	9.94	20.05	50.07
6	10.04	19.95	50.07	9.98	20.08	49.91	9.93	19.9	50.05	9.93	20.03	50.02	9.97	19.91	49.98
7	10.03	20.02	50.11	10.07	20.17	49.97	9.96	20.1	50.02	10.06	19.93	50.01	10.08	19.97	49.92
8	10.13	20.08	49.95	10.08	19.93	50.1	9.97	20.03	50.02	9.98	19.9	50.05	10.01	19.98	49.94
9	10.01	20.04	50.04	10.07	19.94	49.94	10.03	20.04	49.97	9.97	19.9	50.01	10	19.93	50
10	10.04	20.06	50.02	9.98	20.13	49.88	10.06	20.05	50.04	9.94	19.93	49.91	10.07	19.94	49.91
Means	10.08	20.02	50.02	10.05	20.05	49.99	10	19.99	50.03	9.98	19.97	49.98	9.99	19.97	50
SD(±)	0.0481	0.0693	0.069	0.0811	0.1085	0.087	0.0516	0.0615	0.0413	0.043	0.0606	0.0552	0.063	0.051	0.0639
LOD	0.1443	0.2079	0.207	0.2432	0.3255	0.2609	0.1548	0.1845	0.1239	0.1289	0.1819	0.1656	0.189	0.1529	0.1917
LOQ	0.4809	0.6931	0.6899	0.8108	1.085	0.8698	0.516	0.6149	0.413	0.4297	0.6064	0.5519	0.63	0.5095	0.6389

Table A.3 Effect of TSP concentrations (0.1, 0.5 M) on lead removal at different Pb concentrations (10, 20, 50 mg/L). TSP dissolution time: 30 minutes, pH after adding TSP=3.4, [TSP Blank]=0.00 mg/L

Times	Effluent Concentrations (mg/L)						Pb removal efficiency (%)					
	0.1M TSP	0.5 MTSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP
0	10.00	10.00	20.00	20.00	50.00	50.00	0.0	0.0	0.0	0.0	0.0	0.0
5	4.78	0.32	9.96	1.01	30.08	4.05	52.2	96.8	50.2	95	39.8	91.9
10	3.79	0.25	8.54	0.87	28.22	2.85	62.1	97.5	57.3	95.7	43.6	94.3
15	3.44	0.24	7.31	0.74	25.88	2.55	65.6	97.6	63.5	96.3	48.3	94.9
30	2.95	0.18	6.26	0.56	22.26	1.95	70.5	98.2	68.7	97.2	55.5	96.1
60	2.17	0.04	5.02	0.45	18.29	1.75	78.3	99.6	74.9	97.8	63.4	96.5
120	1.15	0.03	2.83	0.31	12.26	1.15	88.5	99.7	85.9	98.5	75.5	97.7
180	1.02	0.01	2.32	0.12	9.94	0.98	89.9	99.9	88.4	99.4	80.1	98.0

Table A.4 Effect of TSP concentrations (0.1, 0.5 M) on iron removal at different Fe concentrations (10, 20, 50 mg/L). TSP dissolution time: 30 minutes, pH after adding TSP=3.43

Times	Effluent concentrations (mg/L)						Fe removal efficiency (%)					
	0.1M TSP	0.5 MTSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP
TSP Blank	4.3	18.81	4.32	18.5	3.83	18.61	NC	NC	NC	NC	NC	NC
0	14.3	28.81	24.32	38.5	53.83	68.61	0.0	0.0	0.0	0.0	0.0	0.0
5	6.97	6.82	12.16	11.58	27.24	27.93	51.3	76.3	50.0	69.9	49.4	59.3
10	6.56	5.53	11.61	10.17	25.72	24.19	54.2	80.8	52.3	73.6	52.2	64.8
15	6.25	4.55	10.94	9.70	24.44	22.22	56.3	84.2	55.0	74.8	54.6	67.6
30	5.53	4.47	9.97	8.47	23.35	21.04	61.4	84.5	59.0	78.0	56.6	69.3
60	4.77	3.82	9.33	7.43	21.63	19.75	66.6	86.7	61.6	80.7	59.8	71.2
120	3.75	3.24	8.00	5.78	20.23	13.94	73.8	88.8	67.1	85.0	62.4	79.7
180	2.41	1.91	5.14	4.23	19.59	9.20	83.2	93.4	78.9	89.0	63.6	86.6

Table A.5 Effect of TSP concentrations (0.1, 0.5 M) on cadmium removal at different Cd concentrations (10, 20, 50 mg/L). TSP dissolution time: 30 minutes, pH after adding TSP=3.41

Times	Effluent concentrations (mg/L)						Cd removal efficiency (%)					
	0.1M TSP	0.5 MTSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP
TSP Blank	7.45	13.05	7.33	13.09	7.48	13.09	NC	NC	NC	NC	NC	NC
0	17.45	23.05	27.33	33.09	57.48	63.09	0.0	0.0	0.0	0.0	0.0	0.0
5	7.01	3.49	9.03	7.89	27.59	22.55	60.0	84.9	55.6	65.8	52.0	64.3
10	6.85	2.87	8.67	7.03	26.96	22.33	60.9	87.5	57.3	69.5	53.1	64.6
15	6.70	2.60	8.17	6.61	26.53	21.96	61.7	88.7	59.8	71.4	53.8	65.2
30	6.47	2.42	7.72	5.84	25.72	21.58	63.0	89.5	62.0	74.7	55.3	65.8
60	6.17	1.93	7.51	4.83	24.58	19.71	64.8	91.6	63.1	79.1	57.2	68.8
120	4.47	1.83	7.01	3.62	23.45	14.15	74.5	92.0	65.5	84.3	59.2	77.6
180	2.61	1.07	4.25	1.90	19.27	7.72	85.1	95.4	79.1	91.8	66.5	87.8

Table A.6 Effect of TSP concentrations (0.1, 0.5 M) on copper removal at different Cu concentrations (10, 20, 50 mg/L). TSP dissolution time: 30 minutes, pH after adding TSP=3.36

Times	Effluent concentrations (mg/L)						Cu removal efficiency (%)					
	0.1M TSP	0.5 MTSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP
TSP Blank	0.58	2.55	0.54	2.57	0.58	2.55	NC	NC	NC	NC	NC	NC
0	10.58	12.55	20.54	22.57	50.58	52.55	0.0	0.0	0.0	0.0	0.0	0.0
5	9.26	9.35	18.17	17.47	40.97	37.89	12.5	25.7	11.5	22.6	19.0	27.9
10	8.28	8.16	16.89	16.08	40.43	37.34	21.7	35.2	17.8	28.7	20.1	29.0
15	7.58	7.09	14.92	15.40	39.96	36.77	28.3	43.6	27.4	31.8	21.0	30.0
30	6.66	6.11	13.13	14.32	39.49	36.18	37.1	51.4	36.1	36.6	21.9	31.2
60	6.19	5.66	12.36	11.76	38.93	35.14	41.5	55.0	39.8	47.9	23.0	33.1
120	5.72	5.50	12.13	11.19	37.99	32.84	45.9	56.3	41.0	50.4	24.9	37.5
180	5.53	5.19	11.85	10.87	33.76	31.82	47.7	58.8	42.3	51.8	33.2	39.4

Table A.7 Effect of TSP concentrations (0.1, 0.5 M) on zinc removal at different Zn concentrations (10, 20, 50 mg/L). TSP dissolution time: 30 minutes, pH after adding TSP=3.38

Times	Effluent concentrations (mg/L)						Zn removal Efficiency (%)					
	0.1M TSP	0.5 MTSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP	0.1M TSP	0.5M TSP
TSP Blank	8.78	16.14	8.76	16.13	8.77	16.11	NC	NC	NC	NC	NC	NC
0	18.78	26.14	18.76	36.13	58.76	66.11	0.0	0.0	0.0	0.0	0.0	0.0
5	9.79	9.72	18.47	18.87	44.15	47.03	47.9	0.00	35.8	0.00	29.8	42.9
10	9.57	9.46	17.50	17.69	41.23	37.74	49.0	62.8	39.2	47.8	33.1	44.1
15	9.17	8.95	16.85	16.40	39.32	36.93	51.2	63.8	41.4	51.0	34.6	45.0
30	8.60	8.84	14.65	15.69	38.42	36.34	54.2	65.8	49.1	54.6	37.4	47.1
60	8.31	8.53	14.30	14.26	36.81	34.95	55.8	66.2	50.3	56.6	39.4	48.8
120	8.08	8.19	13.87	13.49	35.60	33.86	57.0	67.4	51.8	60.5	42.3	49.7
180	7.92	7.87	13.31	12.97	33.90	33.27	57.8	68.7	53.7	62.7	44.7	49.9

Table A.8 Effect of reaction time on removal of heavy metals (Cd, Cr, Cu, Fe, Mn Ni, Sr and Zn) from fly ash by 0.1M TSP at pH=5. Fly ash and TSP dissolution time:30 minutes. pH adjustment by adding HNO₃ or NaOH

Effluent concentrations (mg/kg)									Removal Efficiency (%)							
Times min.	Cd	Cu	Cr	Fe	Mn	Ni	Sr	Zn	Cd	Cr	Cu	Fe	Mn	Ni	Sr	Zn
0	10.10	20.00	12.28	93.46	63.36	38.21	218.79	138.80	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5	6.93	16.04	8.71	67.32	48.51	27.92	168.30	107.91	31.4	29.0	19.8	28.0	23.4	26.9	23.1	22.3
10	4.75	15.44	7.52	50.69	43.56	25.54	155.63	103.36	52.9	38.7	22.8	45.8	31.3	33.2	28.9	25.5
15	3.96	15.05	6.73	46.33	39.20	22.97	141.57	96.43	60.8	45.2	24.8	50.4	38.1	39.9	35.3	30.5
30	3.37	14.06	6.34	41.18	35.24	20.59	133.06	90.68	66.7	48.4	29.7	55.9	44.4	46.1	39.2	34.7
60	2.97	13.46	5.94	36.63	32.67	19.01	120.58	85.93	70.6	51.6	32.7	60.8	48.4	50.3	44.9	38.1
120	2.57	12.87	5.54	33.26	31.28	17.82	111.87	83.36	74.5	54.8	35.6	64.4	50.6	53.4	48.9	39.9
180	2.2	12.47	5.0	29.7	28.7	15.8	103.0	81.0	78.4	59.7	37.6	68.2	54.7	58.5	52.9	41.7

Table A.9 Effect of reaction time on removal of heavy metals (Cu, Fe, Mn, Sr and Zn) from iron copper tailing by TSP at pH=5. Fe-Cu and TSP dissolution time:30 minutes. pH adjustment by adding HNO₃ or NaOH

Times min.	Effluent concentrations (mg/kg)					Removal Efficiency (%)				
	Cu	Fe	Mn	Sr	Zn	Cu	Fe	Mn	Sr	Zn
0	1780.0	4144.0	905.0	499.0	822.0	0.0	0.0	0.0	0.0	0.0
5	1251.7	1542.7	598.6	301.3	570.0	29.7	62.8	33.9	39.6	30.7
10	1201.9	1296.4	567.2	259.6	528.0	32.5	68.7	37.3	48.0	35.8
15	1164.7	1183.5	534.9	242.3	510.4	34.6	71.4	40.9	51.4	37.9
30	1019.9	1115.6	453.6	214.4	441.8	42.7	73.1	49.9	57.0	46.3
60	936.2	1056.1	428.0	189.5	411.3	47.4	74.5	52.7	62.0	50.0
120	901.3	940.7	400.4	169.7	397.9	49.4	77.3	55.8	66.0	51.6
180	861.4	905.1	387.3	152.9	380.8	51.6	78.2	57.2	69.4	53.7

Table A.10 Effect of reaction time on removal of heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn) from copper slag by TSP at pH=5. Copper slag and TSP dissolution time:30 minutes. pH adjustment by adding HNO₃ or NaOH

Times min.	Effluent concentrations (mg/kg)										Removal Efficiency (%)									
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
0	31.6	470.8	352.4	933.0	1106.4	282.4	37.8	386.4	137.8	940.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5	18.6	354.2	265.8	817.7	751.1	197.8	30.4	167.4	85.7	766.0	41.1	24.8	24.6	12.4	32.1	30.0	19.6	56.7	37.8	18.6
10	16.9	343.5	252.5	797.6	698.5	191.0	25.2	106.9	80.4	720.8	46.5	27.0	28.4	14.5	36.9	32.4	33.5	72.3	41.6	23.4
15	14.7	313.4	223.5	753.3	565.1	164.5	24.1	70.5	76.7	677.9	53.6	33.4	36.6	19.3	48.9	41.7	36.3	81.8	44.3	27.9
30	10.1	293.5	214.0	737.1	497.4	146.5	22.1	8.3	65.7	633.1	68.0	37.7	39.3	21.0	55.0	48.1	41.6	97.9	52.3	32.7
60	7.7	267.1	187.2	694.1	354.1	140.0	19.6	5.6	46.4	577.1	75.5	43.3	46.9	25.6	68.0	50.4	48.1	98.6	66.3	38.6
120	7.2	236.7	175.5	616.4	296.9	136.4	18.3	4.9	39.1	521.1	77.2	49.7	50.2	33.9	73.2	51.7	51.6	98.7	71.6	44.6
180	6.7	216.2	167.7	539.7	248.9	131.8	17.9	4.3	37.7	466.8	78.8	54.1	52.4	42.2	77.5	53.3	52.7	98.9	72.7	50.4

Table A.11 Effect of reaction time on removal of heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn) from Pb-Zn mine waste by TSP at pH=5. Pb-Zn mine waste and TSP dissolution time:30 minutes. pH adjustment by adding HNO₃ or NaOH

Times min.	Effluent concentrations (mg/kg)										Removal efficiency (%)									
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
0	202.0	243.6	184.0	702.4	2852.0	2180.0	148.0	498.2	324.2	3109.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5	137.4	181.6	142.0	576.0	1995.8	1744.0	134.0	3.2	256.8	2504.2	32.0	25.5	22.8	18.0	30.0	20.0	13.0	99.4	20.8	19.5
10	101.4	147.2	133.8	551.6	1552.0	1719.0	112.2	3.0	230.8	2404.0	49.8	39.6	27.3	21.5	45.6	21.1	27.1	99.4	28.8	22.7
15	69.2	130.4	108.4	541.0	1348.0	1409.8	104.8	2.4	229.6	2206.0	65.7	46.5	41.1	23.0	52.7	35.3	31.9	99.5	29.2	29.0
30	61.0	121.6	97.6	529.2	1006.0	1219.0	101.6	2.0	197.0	2104.0	69.8	50.1	47.0	24.7	64.7	44.1	34.0	99.6	39.2	32.3
60	49.6	99.0	83.8	499.4	890.0	1119.0	95.0	1.4	185.0	2028.2	75.4	59.4	54.5	28.9	68.8	48.7	38.3	99.7	42.9	34.8
120	37.4	82.2	71.4	444.0	716.0	1057.2	84.8	0.8	170.8	1850.8	81.5	66.3	61.2	36.8	74.9	51.5	44.9	99.8	47.3	40.5
180	21.8	76.2	61.8	401.4	570.0	956.4	77.0	0.4	152.8	1742.4	89.2	68.7	66.4	42.9	80.0	56.1	50.0	99.9	52.9	44.0

Table A.12 Concentration and percentage of Heavy metals removal from 500 ml of Pb-Zn simulated wastewater using 0.1 M of TSP (S/L=1/10, TSP dissolution time: 30minutes, Initial pH=1.36, pH=3.18 after adding TSP and remained constant, Eh=587.18 mv)

Times min.	Effluent concentrations (mg/kg)										Removal Efficiency (%)									
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
0	351.0	271.8	202.0	523.2	26760.0	1912.0	154.0	429.4	292.1	3754.6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	116.6	123.0	99.0	423.1	9699.9	1050.6	85.3	1.6	135.6	2920.4	66.8	54.6	51.00	19.1	63.6	45.1	44.6	99.6	53.6	22.2
15	76.5	80.3	73.2	322.4	6409.0	825.1	73.1	1.4	123.9	2085.1	78.2	70.5	63.7	38.4	76.1	56.9	52.6	99.7	57.6	44.5
30	70.1	67.7	65.0	267.9	5916.4	666.4	61.3	1.1	109.5	1779.4	80.0	75.1	67.8	48.8	77.9	65.2	60.2	99.7	62.5	52.6
60	66.6	65.3	59.4	252.6	5587.2	615.9	59.2	0.9	99.8	1667.0	81.0	76.0	70.5	51.7	79.1	67.8	61.6	99.8	65.8	55.6
120	62.8	62.6	55.7	233.7	5116.5	566.6	52.9	0.6	92.8	1556.1	82.1	77.0	72.4	55.3	80.9	70.4	65.6	99.9	68.2	58.6
180	60.5	53.8	46.3	221.8	4908.6	465.2	48.8	0.4	86.9	1489.9	82.9	80.2	77.1	57.6	81.7	75.7	68.3	99.9	70.2	60.3
240	43.3	50.0	42.1	207.0	3599.1	411.3	42.6	0.2	75.3	1355.4	87.7	81.6	79.2	60.4	86.6	78.5	72.4	100.0	74.2	63.9

Table A.13 Concentration and percentage of Heavy metals removal from 500ml of Pb-Zn simulated wastewater using 0.5 M of TSP (S/L=1/10, TSP dissolution time: 30minutes, Initial pH=1.42, pH=3.38 after adding TSP and remained constant, Eh=642.60 mv)

Time min.	Effluent concentrations (mg/kg)										Removal Efficiency (%)									
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
0	351.0	271.8	202.0	523.2	26760.0	1912.0	154.0	429.4	292.1	3754.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5	30.5	73.3	69.9	363.1	5953.9	481.1	95.8	1.2	129.8	2059.5	91.3	73.0	65.4	30.6	77.8	74.8	37.8	99.7	55.6	45.1
15	24.2	42.9	64.1	277.0	3857.3	442.1	70.0	0.8	114.1	1811.5	93.1	84.2	68.3	47.1	85.6	76.9	54.6	99.8	60.9	51.8
30	19.8	32.3	55.0	249.4	2116.9	415.1	57.8	0.3	89.3	1514.3	94.3	88.1	72.8	52.3	92.1	78.3	62.5	99.9	69.4	59.7
60	18.2	31.6	44.1	237.3	1984.0	342.2	44.4	0.0	77.7	1209.3	94.8	88.4	78.2	54.7	92.6	82.1	71.1	100.0	73.4	67.8
120	8.7	21.9	33.4	213.4	1838.1	224.6	38.4	0.0	68.3	1129.5	97.5	92.0	83.5	59.2	93.1	88.3	75.0	100.0	76.6	69.9
180	8.0	21.3	23.3	164.1	964.9	160.5	35.0	0.0	55.4	926.0	97.7	92.2	88.5	68.6	96.4	91.6	77.3	100.0	81.1	75.3
240	2.1	9.8	9.6	65.5	451.8	129.0	16.3	0.0	27.3	420.0	99.4	96.4	95.2	87.5	98.3	93.3	89.4	100.0	90.6	88.8