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Removal of Heavy Metals from Industrial Wastewater in Petroleum Refinery

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Oil and Gas**

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Abstract

This research presents a case study of treatment industrial wastewater in Daure petroleum refinery ,by adsorption process, to removal heavy metals, Cr(III) and Zn(II) ions. The influent wastewater from all process Daure petroleum refinery is equal $850 \text{ m}^3/\text{hr}$,therefore it has high effect on river pollution.

The experiments were carried out in batch adsorption process by using Iraq Kaolinite ($0.45\mu\text{m}$) pore size as an adsorbent agent, the samples is to treated taken from wastewater after API separator and subjected to adsorption process . The sample was adjusted for each run to required level of concentration Zn(II) or Cr(III), by dissolving required amount of metal salts and at constant $\text{pH}=6.5$.

Several working parameters such as kaolinite weight (0.01-2.5)gm, mixing period (10-60)min. initial ion concentration of Cr(III) and Zn(II)

(0.03-1.5)gm , were studied in an attempt to achieve a higher removal capacity .

The results show that the percent removal of metals ions increases with increases in the kaolinite weight, mixing period, it reach up to 90% removal efficiency .

The optimum values of Kaolinite weight ,mixing period were found 1.0 g Kaolinite/ 10 ml solution,40 min. and 1.5 g Kaolinite/ 10 ml solution,30 min. for Cr(III) and Zn(II) respectively .

The initial concentration of these heavy metals were 1.5 and 1.1 gm/lit. for Cr(III) and Zn(II) respectively.

The results show residual concentration of Cr(III) and Zn(II) after the treatment is (0.03,0) ppm respectively, and these values agreement with the allowable limit of standard properties.

Contents

| Contents | Page |
|-----------------|-------------|
| Acknowledgement | i |
| Abstract | ii |
| Nomenclature | iv |
| Contents | viii |

Chapter One Introduction

| | | |
|-----|--|---|
| 1.1 | Introduction | 1 |
| 1.2 | Petroleum Refineries and Heavy Metals | 2 |
| 1.3 | Impact of Refinery Effluent on the Physicochemical | 4 |
| 1.4 | Objective | 5 |
| 1.5 | Case Study | 6 |

Chapter Two Literature Survey

| | | |
|-------|--|----|
| 2.1 | Oil refinery Description | 10 |
| 2.2 | Sources of Water | 11 |
| 2.3 | Water Leaving the Refinery | 13 |
| 2.4 | Wastewater | 13 |
| 2.5 | Major Products | 15 |
| 2.6 | Heavy Metals | 18 |
| 2.7 | Effects of Chromium on the Environment | 20 |
| 2.8 | Water Released from Petroleum Refinery | 21 |
| 2.9 | Treatment Technologies of Heavy Metals Removal | 22 |
| 2.9.1 | Coagulation / Flocculation | 22 |
| 2.9.2 | Activated carbon adsorption | 23 |
| 2.9.3 | Ion exchange | 24 |
| 2.9.4 | Cementation | 25 |

| <i>Contents</i> | <i>Contents</i> |
|-----------------|---|
| 2.9.5 | Foam floatation 25 |
| 2.9.6 | Evaporation / Distillation 26 |
| 2.9.7 | Eelectrodialysis 27 |
| 2.9.8 | Biological treatment 28 |
| 2.9.9 | Insoluble starch xanthate(ISX) 28 |
| 2.9.10 | Electrochemical treatment: 29 |
| 2.10 | Selection of Proper Technique 30 |
| 2.11 | Heavy Metals and pH 30 |
| 2.12 | Background Review 36 |
| 2.13 | Theoretical Models of Adsorption 60 |
| 2.13.1 | Langmuir Isotherm 61 |
| 2.13.2 | BET Isotherm 63 |
| 2.13.3 | Freundlich Isotherm 64 |
| 2.13.4 | Linear Isotherm 65 |
| 2.13.5 | Redlich-Peterson Isotherm 66 |
| 2.13.6 | Combination of Langmuir-Freundlich Model 66 |

Chapter Three **Experimental Work**

| | |
|-------|---|
| 3.1 | Introduction 68 |
| 3.2 | Materials 69 |
| 3.2.1 | Adsorbent 69 |
| 3.2.2 | Adsorbate 70 |
| 3.3 | Equipment 70 |
| 3.4 | Preparation of metal ion solution 71 |
| 3.5 | Batch experiments 72 |
| 3.5.1 | Effect of Kaolinite weight 72 |
| 3.5.2 | Effect of the initial heavy metal weight 73 |
| 3.5.3 | Effect of Time 74 |

Chapter Four **Results and Discussion**

| | |
|-----|-----------------|
| 4.1 | Introduction 76 |
|-----|-----------------|

| <i>Contents</i> | <i>Contents</i> |
|--|---|
| 4.2 | Effect of Different Operation Variables on the the 76 |
| | Removal of Cr(III) and Zn(II): |
| 4.2.1 | Effect of Kaolinite 76 |
| 4.2.2 | Effect of Mixing Period 79 |
| 4.2.3. | Effect of Initial concentration 81 |
| 4.3 | The Best Conditions 83 |
| 4.4 | Equilibrium Isotherm Experiments 83 |
| | |
| Chapter Five | |
| Conclusions and Recommendations | |
| 5.1 | Conclusion 85 |
| 5.2 | Recommendations for future work 87 |
| | |
| References | |
| | |
| Appendices | |
| | |
| Appendix A- | Analytical Technique A-1 |
| Appendix B- | Batch Experiments Results B-1 |

Nomenclature

Abbreviation

| Symbol | Definition |
|-------------------|--|
| ASP | Activated Sludge Process |
| BCS | Basic Chromium Sulphate |
| <i>BET</i> | Brunauer, Emmett and Teller |
| BOD | Biochemical Oxygen Demand |
| DAF | Dissolved Air Flotation |
| EPP | Environmental Pollution Project |
| <i>HM</i> | Heavy metals |
| IPPC | Integrated Pollution Presentation and Control |
| LECA | light expanded clay aggregate |
| O&M | Operation and Maintenance |
| <i>PCD</i> | Photo Catalytic Degradation |
| <i>pH</i> | -Log [H⁺] |
| ppm | Parts per million |
| Rpm | Revolutions per minute |
| SEE | Square error of estimate |
| SS | Suspended Solid |
| VOCs | Volatile Organic Compounds |
| WHO | World Health Organization |
| WWTP | Wastewater Treatment Plant |

| Symbol | Definition | Unit |
|--------|--|-------------------|
| C_e | Equilibrium liquid-phase concentration | (mg/lit.) |
| C_o | Initial liquid-phase concentration | (mg/lit.) |
| P_p | Particle density | Kg/m ³ |
| t | Time | minute |
| T | Temperature | K |
| V | Volume of solution | m ³ |
| W | Weight of adsorbent in batch experiments | (Kg) |

Greek symbols

| Symbol | Definition | Unit |
|-----------------|--------------------------------|-------------------|
| ε_p | Porosity of adsorbent particle | - |
| μ_c | Kinematics viscosity | m ² /s |
| μ_w | Viscosity of water | Kg/m s |
| ρ | Density | Kg/m ³ |
| ρ_w | Density of water | Kg/m ³ |

CHAPTER ONE

Introduction

1.1 Introduction:

The problem of generating hazardous waste has been increasing recently due to the rapid growth of industrialization activities in the world ⁽¹⁾.

All over the industrial world legislation with regard to the discharge of industrial wastewater is being sharpened. Many industries, which have not previously considered wastewater as a big problem, are now being forced to think along new lines, such as, which wastewater treatment methods are available? Is it feasible to change the quality and/or the quantity of the wastewater? Will it be profitable to consider complete or partial recirculation and recovery? Figure (1.1) show wastewater treatment plant in the Daura Refinery⁽²⁾.



Figure 1.1: Wastewater treatment plant in the Daura Refinery on the Tigris River⁽²⁾.

1.2 Petroleum Refineries and Heavy Metals:

From all kind of wastewater such as process water, different heavy metals should be removed⁽³⁾.



Figure 1.2: Daura Refinery⁽⁴⁾.

The process water has different concentration of heavy metals depend on the type of source of the wastewater. The source of wastewater in the present work from unit processes in the Daura Refinery as shown in Fig.1.2 ⁽⁴⁾. The waste heavy metals can be present in the wastewater as shown in Table 1.1.

Table 1.1 shows which heavy metals are mainly present ⁽⁵⁾.

| Cd | Cr | Cu | Hg | Pb | Ni | Sn | Zn |
|----|----|----|----|----|----|----|----|
| ++ | ++ | + | - | ++ | + | - | ++ |

Water as resource for life on earth, has several unique properties that help make it such a necessary part of the environment. For example, the entire essential functions within living cells are maintained by water. Water ecosystems are as varied as their individual sites because they are influenced not only by characteristic local climate, soil, resident communities but also by the surrounding terrestrial ecosystem.

As man advances in technology and industry, large amounts of water are used for industrial activities and consequently significant volumes of wastewaters are generated. Based on the type of industry, various levels of pollutants are deliberately released and discharged into the environment directly. Among these industries that discharge their effluents into the aquatic environments are the petroleum oil refineries. As not all refineries have the same processes, the effluents that are produced will have different chemical compositions depending on the type of treatment they received. Wastewaters released by oil refineries contain large amounts of toxic derivatives such as oil and grease, phenols, sulphides, cyanides, suspended solids, nitrogen compounds as well as heavy metals such as iron, nickel, copper, selenium, zinc, molybdenum, etc⁽⁶⁾. Due to the ineffectiveness of purification systems, wastewaters

from the refineries may become seriously dangerous, leading to the accumulation of toxic products in the receiving water bodies with potentially serious consequences on the ecosystem. Thus the discharge of these effluents containing persistent chemicals into a receiving water body may result in the long term effects to aquatic biota. The toxicity of oil refinery effluents to aquatic organisms has been reported in many literatures. Toxicity of petroleum refinery depends on a number of factors which include quantity, volume and variability of discharge. The different components of the effluents may have varying effects and toxicity. Aruldoss⁽⁷⁾ reported the toxicity of refinery wastewater to luminescent bacteria (*Photobacterium phosphoreum*) using microtox in the bioassay. This is based on monitoring changes in natural light emissions from the organism. Toxicity and end point was measured as the effective concentration of a test sample that can cause 50% decrease in light output (IC50) after 30min of contact time⁽⁸⁾.

1.3 Impact of Refinery Effluent on the Physicochemical Properties of a Water Body:

Wastewaters released by crude oil-processing and petrochemical industries are characterized by the presence of large quantities of crude oil products, polycyclic and aromatic hydrocarbons, phenols, metal derivatives, surface-active substances, sulfides, naphthylenic acids and other chemicals⁽⁹⁾. Due to the ineffectiveness of purification systems, wastewaters may become seriously dangerous, leading to the accumulation of toxic products in the receiving water bodies with potentially serious consequences on the ecosystem.

Various studies have shown positive correlation between pollutions from refinery effluents and the health of aquatic organisms. Previous observations suggested a correlation between contamination of water and sediments with aromatic hydrocarbons from refinery effluents, and compromised fish health ^(10, 11).

Heavy metals have long been recognized as one of the major sources of pollution in the aquatic and terrestrial environment. Heavy metals are natural components of the Earth's crust and cannot be degraded or destroyed. Heavy metals may affect organisms directly by accumulating in their bodies or indirectly by transferring to the food chain. They tend to accumulate in soils, sediments and certain tissues of plants and animals. Despite regulatory measures carried out in many countries, these substances continue to rise in environment. Wastewaters contain heavy metals as Pb, Zn, Hg, Cu, and Ni which are produced by many manufacturing processes and find their way into the environment. These metals can be harmful to human and aquatic life even at very low concentrations. They inhibit photosynthesis in water plants, prevent phytoplankton growth in water, cause to chromosomal and tissue damage in terrestrial plants and induce carcinogenesis in human ⁽¹²⁾.

1.4 Objective:

The aim of the present work is to select the appropriate treatment method by adsorption for the removal of the heavy metal ions from Daura Refinery wastewater in batch process also review different methods of the treatment of wastewater. Also the aim is to reuse the produced water in different process such as in cooling.

1.5 Case Study:

The foregoing discussion has shown the importance of treatment of the industrial wastewater as an environmental challenge, and the need to develop an adequate management scheme to select the proper method or process of treatment related to certain wastewater characteristics and the surrounding conditions.

The wastewater discharged from the Daura Refinery in the rate of (850 m³/hr) and it has the following characteristics as show in Table 1.1:

Table 1.1: The Characteristics of Wastewater Discharge from the Daura Petroleum Refinery.

| Date | Cr in ppm | Cr out ppm | Zn in ppm | Zn out ppm | pH in | pH out | Tur. in ppm | Tur.out ppm |
|-----------|--------------|------------------|--------------|------------------|-------|-----------|----------------|----------------|
| January | 0.721 | 0.035 | 0.815 | 0.19 | 7.72 | 7.91 | 55.74 | 7.99 |
| February | 0.827 | 0.053 | 0.34 | 0.4 | 7.57 | 7.63 | 51.8 | 15 |
| march | 0.727 | 0.021 | 0.18 | 0.17 | 7.6 | 7.8 | 95.1 | 7.1 |
| April | 0.524 | 0.028 | 0.015 | 0.16 | 7.59 | 7.8 | 75.4 | 9.27 |
| may | 0.625 | 0.032 | 0.01 | 0.02 | 7.74 | 7.85 | 68.8 | 9 |
| June | 0.726 | 0.034 | 0.1 | 0.02 | 7.6 | 7.9 | 57.8 | 7.2 |
| July | 0.624 | 0.042 | 0.02 | 0.02 | 7.9 | 7.3 | 77.7 | 20.5 |
| august | 0.623 | 0.031 | 0.26 | 0.1 | 7.7 | 7.8 | 60.77 | 9.99 |
| September | 0.627 | 0.041 | 0.02 | 0.21 | 7.7 | 7.8 | 54 | 11 |
| October | 0.482 | 0.022 | 0.15 | 0.00 5 | 7.8 | 7.9 | 114 | 23 |
| November | 0.629 | 0.033 | 0.03 | 0.01 | 7.4 | 6.9 | 43.2 | 5.6 |
| December | 0.821 | 0.030 | 0.25 | 0.01 | 7.4 | 7.5 | 30 | 3.8 |

And the Characteristics of Wastewater discharge from the Daura Petroleum Refinery can be represented by the following figures:

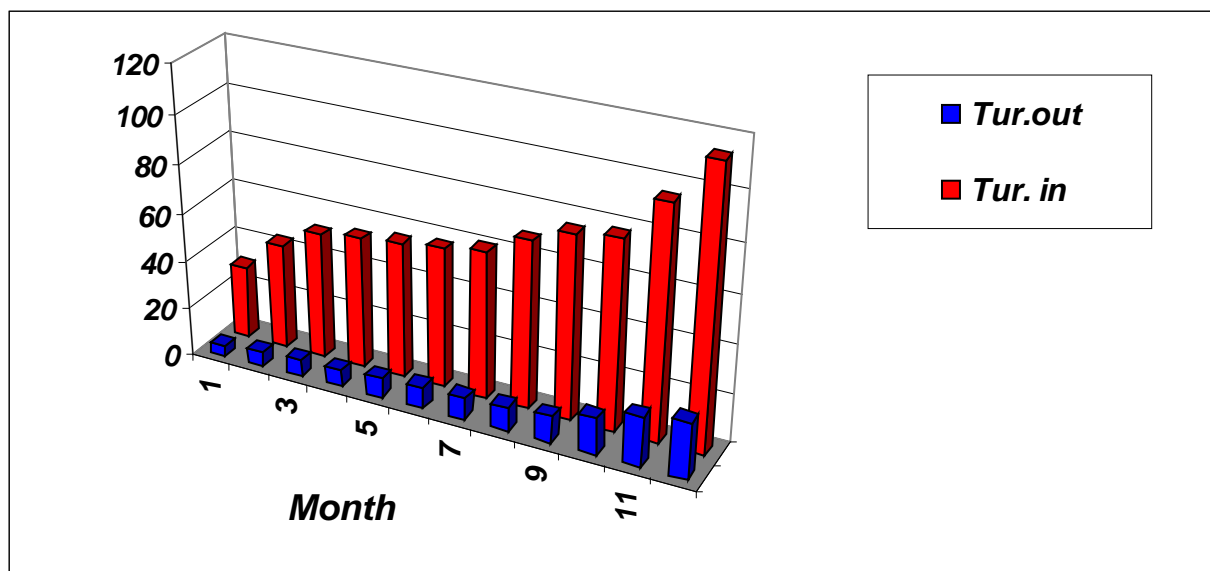


Figure 1.3: The relationship between the inlet and outlet Turbidity from the Daura Petroleum Refinery Treatment unit along one year.

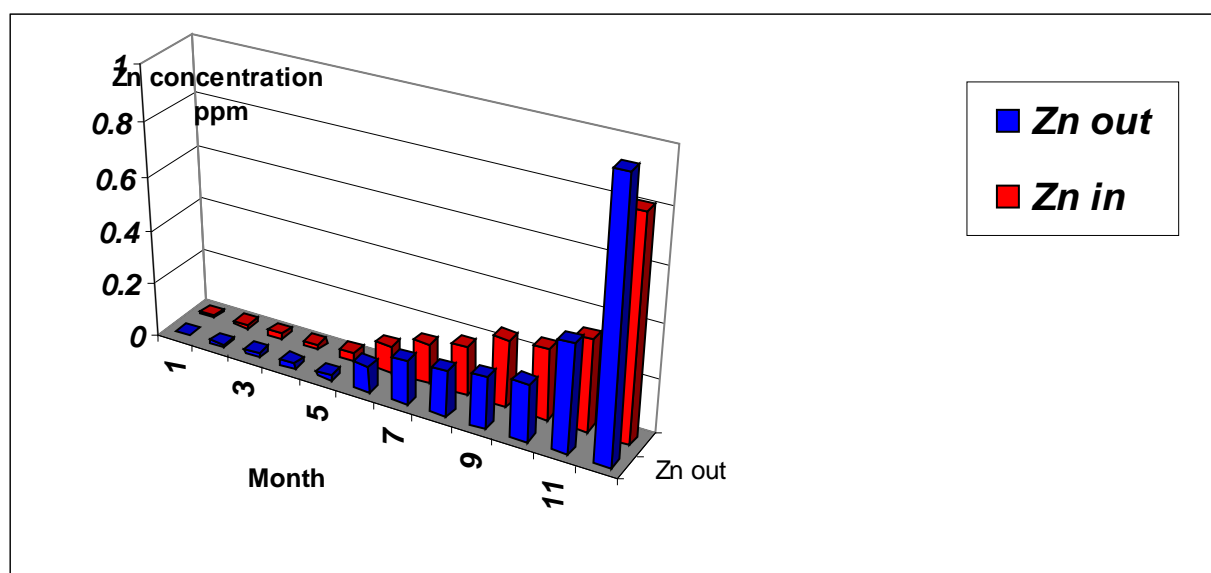


Figure 1.4: The relationship between the inlet and outlet Zn conc. (ppm) from the Daura Petroleum Refinery Treatment unit along one year.

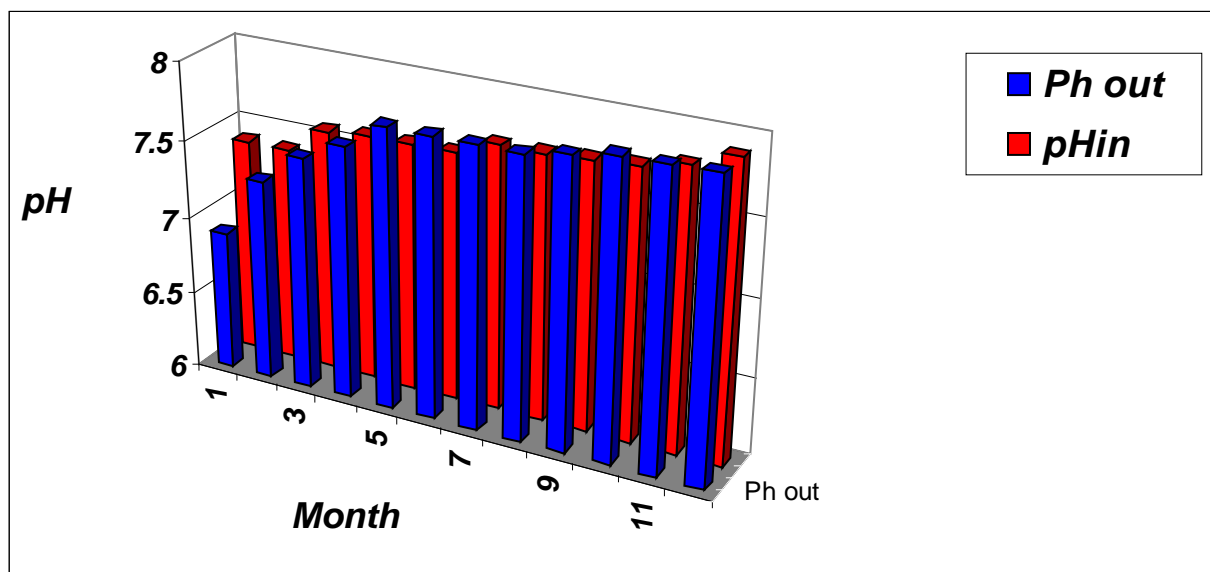


Figure 1.5: The relationship between the inlet and outlet pH from the Daura Petroleum Refinery Treatment unit along one year.

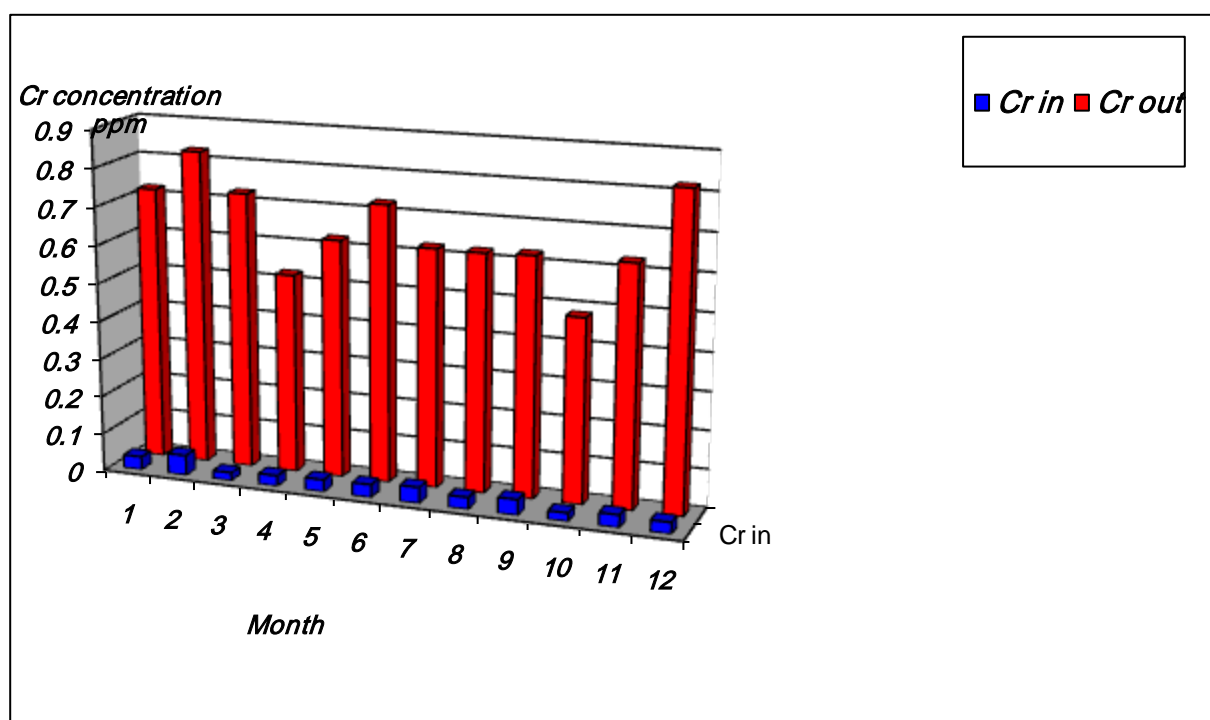


Figure 1.6: The relationship between the inlet and outlet Cr conc. (ppm) from the Daura Petroleum Refinery Treatment unit along one year

The aim of the wastewater treatment plant in the Daura Petroleum Refinery is to treat the industrial wastewater discharged from all operational parts of the refinery and then discharged to the Tigris River under an environmental limitation to avoid killing the living organisms.

CHAPTER TWO

Literature survey

2.1 Oil refinery Description:

Petroleum refineries are complex systems of multiple operations that depend on the type of crude refined and the desired products. For these reasons, no two refineries are alike. Depending on the size, crude, products and complexity of operations, a petroleum refinery can be a large consumer of water, relative to other industries and users in a given region. Within a refinery, the water network is as unique to the refinery as its processes. This section describes the typical sources of water supplied to a refinery and the typical discharges of water from a refinery. It also provides an overview of the types of contaminants contained in the raw water and the methods used to remove these contaminants. Overall refinery water balance shown in figure (1.3) ⁽¹³⁾.

Many of the processes in a petroleum refinery use water, however, not each process needs raw or treated water, and water can be cascaded or reused in many places. A large portion of the water used in a petroleum refinery can be continually recycled within a refinery. There are losses to the atmosphere, including steam losses and cooling tower evaporation and drift.

A smaller amount of water can also leave with the products. Certain processes require a continuous make-up of water to the operation such as

steam generating systems or cooling water systems. Understanding water balance for a refinery is a key step towards optimizing water usage, recycle and reuse as well as optimizing performance of water and wastewater treatment systems⁽¹³⁾.

2.2 Sources of Water:

Surface Water: Water to the refinery can be supplied from various surface-water sources such as rivers or lakes. In some cases it may also be supplied from the sea or from other brackish water sources. Additional supply of water can come from groundwater located in aquifers, if the subsurface water is available and accessible. Typical characteristics of raw water can include varying amounts of solids and/or salts, also referred to as total suspended solids (TSS), total dissolved solids (TDS) and turbidity⁽¹⁴⁾.

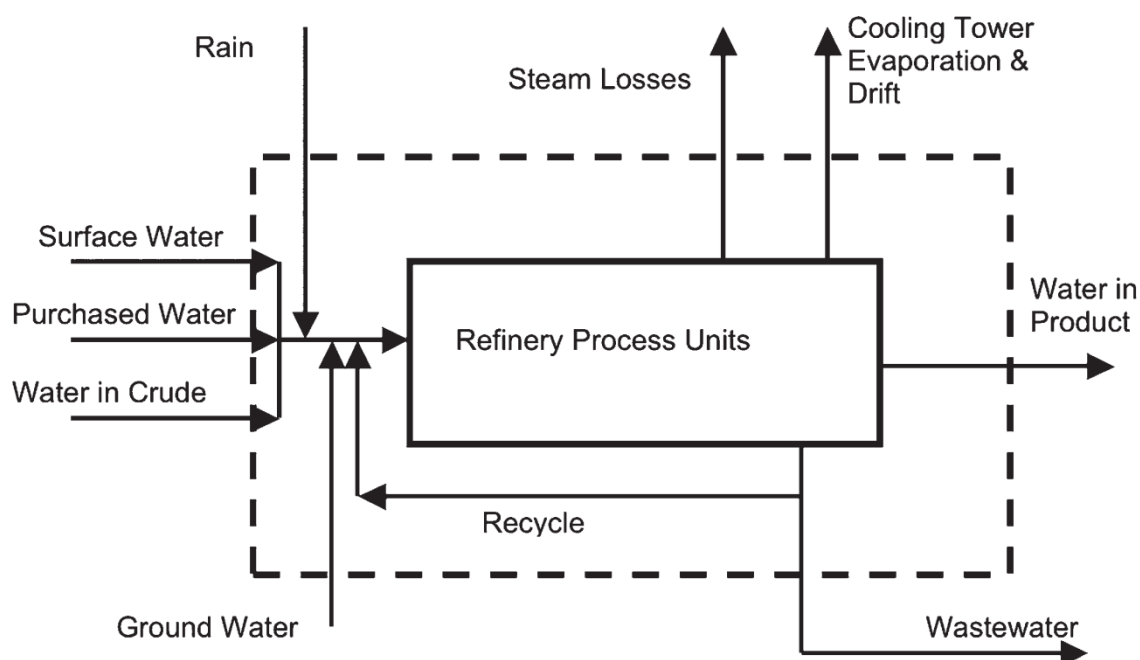


Figure 2.1: Refinery Water Balance⁽¹⁴⁾

Each water body. And aquifer has a unique quality associated with it and may require treatment before use in a refinery.

The level of pretreatment required for source water before it is used in the refinery is dependent on the uses of the water in the refinery and what level of solids and salts is compatible with the process. Table 2.1 shows the types of water sources and typical characteristics of the water from each source ⁽¹⁵⁾.

Table 2.1 Typical sources of water ⁽¹⁵⁾:

| Source | Typical characteristics |
|---------------------|--|
| Lake | Suspended solids, dissolved solids (metals), turbidity |
| River | Suspended solids (with seasonal variation), dissolved solids (metals), turbidity |
| Groundwater (wells) | Suspended solids, dissolved solids (metals), dissolved organics |
| Sea water | Suspended solids, dissolved solids (metals, chlorides) |

Purchased Water: Water can also be supplied from a municipality. Municipalities generally can offer potable water (drinking water) but may also be able to offer a treated effluent for industrial use or reuse. Potable water (drinking water and sanitary water) required by a refinery is frequently purchased from a local municipality. If available, potable water may also come from groundwater aquifers or alternative sources ⁽¹⁵⁾.

Water in crude: When crude arrives at a refinery, it often carries entrained water that remains from the oil well extraction process and/or pickup during transshipment. The water is typically removed as storage

tank bottom sediment and water (BS&W) or in the de Salter which is part of the crude unit in the refinery, and is typically sent to wastewater treatment⁽¹⁵⁾.

Rain: Another source of water for a refinery is rain. Rain that falls within the refinery battery limits is typically treated before discharge. Rain that falls in non industrial areas of a refinery, e.g. parking lots, green areas or administrative housing, may be discharged without treatment depending on local regulations.

Storm water harvesting can be a technique that is employed to capture uncontaminated storm water. With proper storage and or treatment(if needed) this storm water can be used for certain processes such as equipment washing⁽¹⁵⁾.

2.3 Water Leaving the Refinery:

The water that leaves refineries is indicated in Figure 2.1 and described briefly below⁽¹⁴⁾.

2.4 Wastewater:

Refineries can generate a significant amount of wastewater that has been in contact with hydrocarbons. Wastewater can also include water rejected from boiler feed water pretreatment processes (or generated during regenerations). Wastewater can also refer to cooling tower blow downstream, or even once-through cooling water that leaves the refinery.

Once-through cooling water typically does not receive any treatment before discharge. Cooling tower blow down water and wastewater from raw water treating may or may not receive treatment at the wastewater treatment plant (WWTP) before discharge. Contaminated wastewater is typically sent to either a wastewater treatment plant that is located at the facility, or it can be pretreated and sent to the local publicly owned treatment works or third-party treatment facility for further treatment.

Water that has not been in direct contact with hydrocarbons or which has only minimal contamination can be a source for reuse. Wastewater can sometimes also be reused after passing through the wastewater treatment plant, sometimes requiring additional treatment to remove suspended solids and other contaminants. A typical refinery wastewater treatment system is shown in Figure 2.2⁽¹⁵⁾.

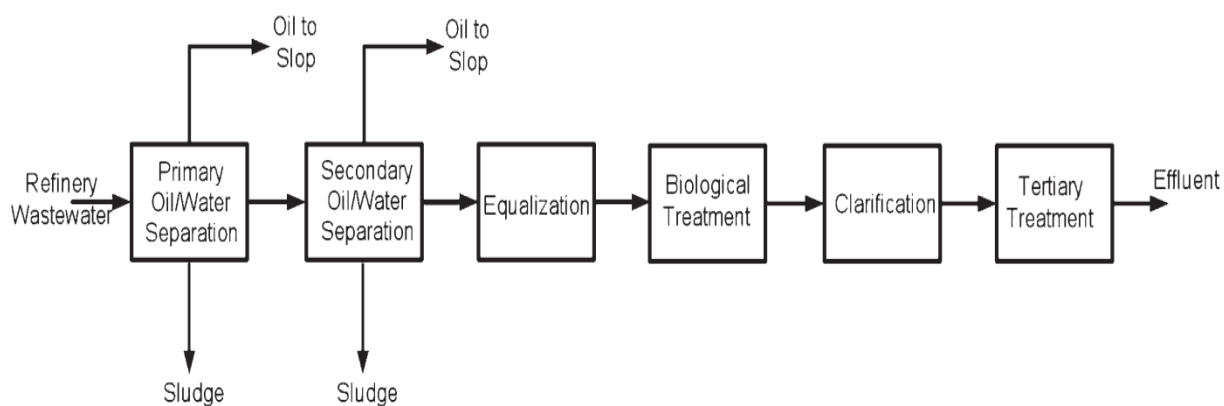


Figure 2.2: Typical Refinery Wastewater Treatment⁽¹⁵⁾.

An oil refinery or petroleum refinery is an industrial process plant where crude oil is processed and refined into more useful petroleum products, such as gasoline, diesel fuel, asphalt base, heating oil, kerosene, and liquefied petroleum gas.

Oil refineries are typically large sprawling industrial complexes with extensive piping running throughout, carrying streams of fluids between large chemical processing units. In many ways, oil refineries use much of the technology of, and can be thought of as types of chemical plants. The crude oil feedstock has typically been processed by an oil production plant. There is usually an oil depot (tank farm) at or near an oil refinery for storage of bulk liquid products⁽¹⁶⁾.

2.5 Major Products:

Petroleum products are usually grouped into three categories: light distillates (LPG, gasoline, naphtha), middle distillates (kerosene, diesel), heavy distillates and residuum (heavy fuel oil, lubricating oils, wax, asphalt). This classification is based on the way crude oil is distilled and separated into fractions (called distillates and residue) as in the above drawing⁽¹⁷⁾.

- Liquefied petroleum gas (LPG)
- Gasoline (also known as petrol)
- Naphtha
- Kerosene and related jet aircraft fuels
- Diesel fuel
- Fuel oils
- Lubricating oils
- Paraffin wax
- Asphalt and tar
- Petroleum coke

Oil refineries also produce various intermediate products such as hydrogen, light hydrocarbons, reformat and pyrolysis gasoline. These are

not usually transported but instead are blended or processed further on-site. Chemical plants are thus often adjacent to oil refineries. For example, light hydrocarbons are steam-cracked in an ethylene plant, and the produced ethylene is polymerized to produce polyethylene⁽¹⁷⁾.

Figure 2.3 is a schematic flow diagram of a typical oil refinery that depicts the various unit processes and the flow of intermediate product streams that occurs between the inlet crude oil feedstock and the final end products.

The diagram depicts only one of the literally hundreds of different oil refinery configurations. The diagram also does not include any of the usual refinery facilities providing utilities such as steam, cooling water, and electric power as well as storage tanks for crude oil feedstock and for intermediate products and end products⁽¹⁸⁾.

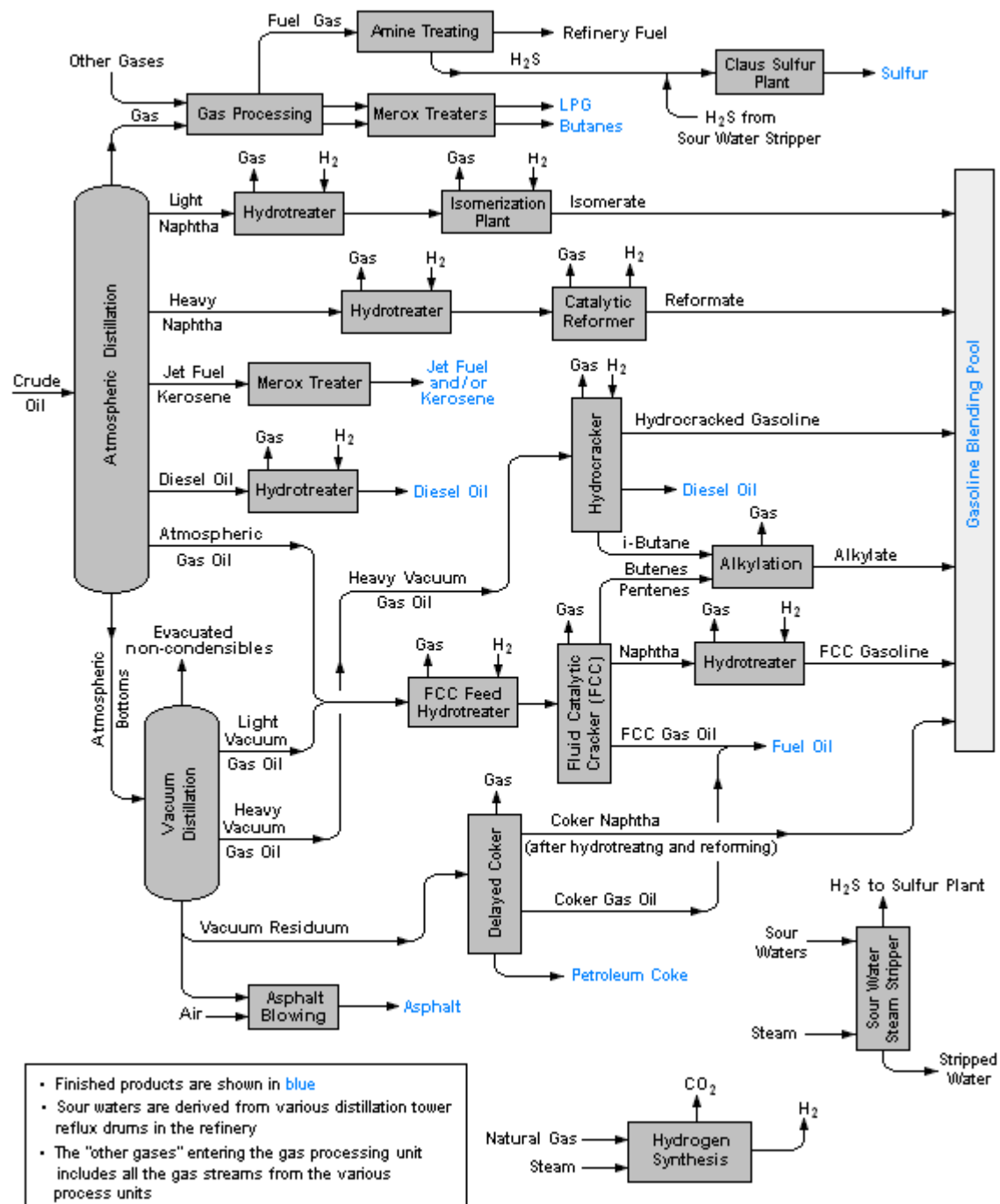


Figure 2.3: Schematic Flow Diagram of a Typical Oil Refinery⁽¹⁸⁾.

Refineries which use a large amount of steam and cooling water need to have an abundant source of water.

Oil refineries therefore are often located nearby navigable rivers or on a sea shore, nearby a port. Such location also gives access to transportation by river or by sea^(18, 19).

2.6 Heavy Metals:

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb)⁽²⁰⁾.

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain⁽²¹⁾.

Heavy metals are dangerous because they tend to bioaccumulation. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted⁽²²⁾.

Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy

metals into streams, lakes, rivers, and groundwater^(23, 24).

The following table shows the regulation limits industrial wastewater contains of heavy metals discharged from petroleum refineries⁽²⁴⁾..

Table 2.2 : The regulation limits of the heavy metals in the industrial wastewater⁽²⁴⁾ ..

| Heavy metals | Maximum limit concentration ppm |
|--------------|---------------------------------|
| Arsenic | 0.5 |
| Lead | 1.0 |
| Mercury | 0.02 |
| Cadmium | 0.5 |
| Chromium | 0.1 |
| Zinc | 0.005 |
| Copper | 3.0 |
| Iron | 1.0 |
| Tin | 2.0 |

Table 2.3 : The Iraq regulation limits of the heavy metals in the industrial wastewater⁽²⁵⁾ ..

| Heavy Metals | Maximum limit concentration in ppm |
|---------------|------------------------------------|
| Lead(Pb) | 0.1 |
| Arsenic(As) | 0.05 |
| Copper(Cu) | 0.2 |
| Nickel(Ni) | 0.2 |
| Selenium(Se) | 0.05 |
| Mercury(Hg) | 0.005 |
| Cadmium(Cd) | 0.01 |
| Zinc(Zn) | 0.2 |
| Chrome(Cr) | 0.1 |
| Aluminum(Al) | 5.0 |
| Barium(Ba) | 4.0 |
| Boron(B) | 1.0 |
| Cobalt(Co) | 0.5 |
| Iron(Fe) | 2.0 |
| Manganese(Mn) | 0.5 |
| Silver(Ag) | 0.05 |

2.7 Effects of Chromium on the Environment:

Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials. Low-level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and damage too circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium⁽²⁶⁾.

2.8 Water Released from Petroleum Refinery:

Wastewaters released by crude oil-processing industries are characterized by the presence of large quantities of crude oil products, polycyclic and aromatic hydrocarbons, phenols, metal derivatives, surface-active substances, sulfides, naphthylenic acids and other chemicals. Due to the ineffectiveness of purification systems, wastewaters may become seriously dangerous, leading to the accumulation of toxic products in the receiving water bodies with potentially serious consequences on the ecosystem⁽²⁷⁾.

In the last few years, the world has moved from treatment into recovery and recycling process for economical reasons and for a sustainable development, and mainly to maintain a safe environment for aquatic life and human health⁽²⁸⁾.

During the year 2011 the feed wastewater to the treatment unit around 850 m³/hr in the Daura refinery.

Almost all petroleum refineries are located on rivers which provide them with process water and serve as a disposal source for their effluents.

The petroleum refining industry is well known as a high consumer of water.

On account of their character and concentration, petroleum refinery wastewater is included among other industrial effluent which is particularly harmful to the receiving water⁽²⁹⁾.

2.9 Treatment Technologies of Heavy Metals Removal:

2.9.1 Coagulation / Flocculation:

Flocculation is the stirring or agitation of chemically-treated water to induce coagulation. The terms coagulation and flocculation are often used interchangeably. More specifically, “coagulation” is the reduction of the net electrical repulsive forces at particle surfaces by addition of coagulating chemicals, whereas “flocculation” is the agglomeration of the destabilized particles by chemical joining and bridging. Flocculation enhances sedimentation or filtration treatment system performance by increasing particle size resulting in increased settling rates and filter capture rates.

In other words, coagulation involves the reduction of surface charges and the formation of complex hydrous oxides. Flocculation involves combining the coagulated particles to form settleable floc. The coagulant (alum, ferric chloride, ferrous sulfate, ferric sulfate, etc.) is mixed rapidly then stirred to encourage formation of floc prior to settling. The coagulant's role here is to destabilize the colloidal suspension by reducing the attractive forces, thereby lowering the energy barrier and enabling particles to aggregate.

A number of coagulation mechanisms including charge neutralization, double layer compression, bridging and sweep, have been postulated dependent on the physical and chemical properties of the solution, pollutant and coagulant⁽³⁰⁾.

Coagulation / Flocculation has been known to be capable of removing heavy metals from aqueous solutions. EPA investigated the use of lime softening and coagulation(using ferric sulfate or alum) for removal of such heavy metals as Pb(II) , Cd(II),Cr(III),Cr(IV),etc⁽³¹⁾.

2.9.2 Activated Carbon Adsorption:

Activated carbon adsorption is a demonstrated wastewater treatment technology that uses activated carbon to remove dissolved organic pollutants from wastewater. The activated carbon is made from many carbonaceous sources including coal, coke, peat, wood, and coconut shells. The carbon source material is “activated” by treating it with an oxidizing gas to form a highly porous structure with a large internal surface area. For very large applications, an on-site regeneration facility is more economical.

Competitive adsorption between compounds has an effect on adsorption. The carbon may preferentially adsorb one compound over another. This competition could result in an adsorbed compound being desorbed from the carbon. This is most pronounced when carbon adsorption is used to treat wastewater with highly variable pollutant character and concentration.

Activated carbon adsorption shows considerable promise for removing the last trace of metal (in the range of 1-2 ppm) following other treatment. However, the suitable type of activated carbon for some heavy metals treatment is unavailable and it is highly cost and has limited efficiency. Molecular structure, solubility, etc., all affect absorbability of activated carbon. Moreover, excess amounts of chemical reagents will be needed

for pH adjustment and regeneration. Additionally there are some weight losses of carbon which result from attrition and carbon oxidation⁽³²⁾.

2.9.3 Ion Exchange:

A common process employed to remove heavy metals from relatively low-concentration waste streams, such as electroplating wastewater, is ion exchange. A key advantage of the ion exchange process is that the metal contaminants can be recovered and reused.

Another advantage is that ion exchange may be designed to remove certain metals only, providing effective removal of these metals from highly contaminated wastewater. A disadvantage is that the resins may be fouled by some organic substances.

Ion exchange is a demineralization process in which the cations and anions in wastewater are selectively exchanged for ions in the insoluble resin material. When the resin capacity is used up, it is regenerated by using high concentrations of the original ion that is exchanged from the resin. The resins of ion exchange consist of an organic or inorganic network structure with attached functional groups.

Ion exchange is suitable for the following⁽³³⁾ .:

- . Removal and recovery of heavy metals from very dilute solutions.
- . Recovering plating solution drag from rinse water
- . Return of the purified water for reuse.
- . Concentrating effluents prior to conventional treatment
- . Removing trace pollutant after a conventional treatment process

The economics of ion exchange are related to the capacity of the resin to exchange ions and to the quantity of regenerate required. The regenerating solution containing the concentrated metal salts requires further treatment prior to its reuse⁽³⁴⁾. Moreover a filtration, carbon absorption step must precede the ion exchange process to prevent resins fouling and pH adjustment is required for final disposal or reuse⁽³⁵⁾.

2.9.4 Cementation:

Cementation is a metal –replacement process in which a solution containing the dissolved metallic ions comes in contact with a more active sacrificial metal such as iron (iron or aluminum scraps) for an oxidation-reduction spontaneous reaction to occur.

The using of metal scraps for heavy metals treatment can lower the chemical costs and simplify the treatment operation by eliminating the need for careful dosage of chemical. It needs at least 4 hours for complete treatment⁽³⁶⁾.

2.9.5 Foam Floatation:

The foam floatation is addition of a surface active agent that has a hydrophobic part (containing the long hydrocarbon chain) of opposite charge to the Inorganic ions to be separated. A finely divided, insoluble compound forms which surface active and may be floated to the surface of the solution and as foam above the solution attached to rising air bubbles. This technique is more appealing in the field of environmental technology for the removal of low concentrations noxious metals which are not effectively removed by chemical precipitation.

This technique is simple, capable of reducing the contaminant concentrations well down the environmental standards and need small space. However, chemical costs are higher than chemical precipitation method and it is require pH adjustments⁽³⁷⁾.

2.9.6 Evaporation / Distillation:

Distillation is the oldest demineralization process. It consists of evaporating a part or all of the water from a saline solution and subsequent condensation of mineral-free vapor. The energy requirements are very high for the system. One modification of the simple distillation process is multiple-effect evaporation, where water is evaporated in different stages at different pressures. Another modification is distillation with vapor compression. This system utilizes the latent heat of the compressed steam to preheat and evaporate the incoming water. Both modifications conserve energy, but the energy requirements are quite large.

Evaporation concentrates the total salts and impurities in the recovered solution however; it has been proved effective for recovering valuable metal salts from electroplating waste solutions without sludge formation. This technique needs relatively high capital costs and evaporating costs. Additionally these systems are complex and their application in wastewater treatment is not feasible⁽³⁸⁾.

2.9.7 Eelectrodialysis:

Electrodialysis is also a demineralization process. In this process, an electrical potential is used to transfer the ion through ion-selective membranes. The energy requirement is directly proportional to the concentration of salts in the water being treated. An electrical voltage is applied in cells.

The separation is accomplished by the selective transport of ions through ion – exchange membranes under the influence of an electrical potential applied across the membrane . The electrodialysis cell is circular with anode and cathode compartments separated by perflurosulfonic acid membranes which are mechanically strong and chemically resistant. Bing a flexible unit operation, electrodialysis can operate in batch or continuous mode.

Electrodialysis has used in heavy metal recovery from plating rinse wastewater. It is suitable for recovery of ionized species from metal finishing wastewater without sludge forming . However, it is not economical for treatment of very dilute solutions or to produce effluent of less than 1 ppm of pollutant level and the membrane may not have a perm-selectivity of unity and therefore allow passage of the co-ions (different ions of the same charge). Additionally the life of membrane is limited and they may be fouling. pH adjustment at low values is also required to prevent the decrease in membrane performance due to scale formation⁽³⁹⁾.

2.9.8 Biological Treatment:

The objective of the activated sludge processes is to remove soluble and insoluble organics from a wastewater stream and to convert this material into a flocculent microbial suspension that is readily settle able and will permit the use of gravitational solids liquid separation techniques.

The activated sludge processes can tolerate up to 10 ppm of heavy metals (copper, nickel, zinc, and hexavalent chrome) either singly or in combination without any adverse effect on aerobic sludge digestion⁽³⁹⁾.

2.9.9 Insoluble Starch Xanthate(ISX):

ISX process has been considered as an effective alternative for heavy metals removal and recovery. ISX is proved by reacting highly cross linked starch with sodium hydroxide and carbon disulfide. Magnesium sulfate is also added to give the product stability and to improve the sludge settling. This process as an ion-exchange material removes the heavy metal ions and replaces them with sodium and magnesium. However, ISX can be added as a slurry or solid form and as a percent to a filter.

Recovery of heavy metals can be achieved by treatment of the starch xanthate with 4N HNO₃ in the form of nitrate and sulfate salts, or by incineration which will produce metal oxides.

It is not economic to use ISX treatment, if the initial metal concentration exceeds 100 ppm. Furthermore, using of HNO₃ in wastewater process is almost undesirable and a huge amount of sludge is

generated by ISX. For those reasons, the using of this process to treatment of wastewater is limited⁽⁴⁰⁾.

2.9.10 Electrochemical Treatment:

Using electricity to treat water was first proposed in UK in 1889. The application of electrolysis in mineral beneficiation was patented by Elmore⁽⁴¹⁾.

Electrocoagulation (EC) with aluminum and iron electrodes was patented in the US in 1909. The electrocoagulation of drinking water was first applied on a large scale in the US in 1946.

Because of the relatively large capital investment and the expensive electricity supply, electrochemical water or wastewater technologies did not find wide application worldwide then. Extensive research, however, in the US and the former USSR during the following half century has accumulated abundant amount of knowledge. With the ever increasing standard of drinking water supply and the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades.

There are companies supplying facilities for metal recoveries, for treating drinking water or process water, treating various wastewaters resulting from tannery, electroplating, dairy, textile⁽⁴¹⁾.

2.10 Selection of Proper Technique:

Technically all previously mentioned technologies are capable of achieving heavy metals removal. But none of these processes can be considered exactly as an ideal method.

The best technology to be utilized is a function of the following:

- . Quality of wastewater to be treated.
- . Initial concentration in wastewater.
- . Compatibility of effluent with regulations.
- . The availability of local skills for design, construction and O&M.
- . The existing of other metals ions or pollutant in wastewater.
- . Economics.
- . The formation of undesirable by product.
- . Complexity of operation and the need for excessive labor or space.
- . Mode of plant operation (batch or continuous).

Among all the previously proposed methods and in accordance with the new modern proposed criteria for the environmental control systems, adsorption technology seems to be the most promising methods for heavy metals removal. In this work, it is expected that the adsorption would be an ideal choice for heavy metals removal for many reasons as it would be stated in chapter three⁽⁴¹⁾.

2.11 Heavy Metals and pH:

As metals enter the treatment process, they are in a stable, dissolved aqueous form and are unable to form solids. The goal of metals treatment by hydroxide precipitation is then to adjust the pH (hydroxide ion concentration) of the water so that the metals will form insoluble

precipitates. Once the metals precipitate and form solids, they can then easily be removed, and the water, now with low metal concentrations, can be discharged. Metal precipitation is primarily dependent upon two factors: the concentration of the metal, and the pH of the water.

Heavy metals are usually present in wastewaters in dilute quantities (1 - 100 mg/L) and at neutral or acidic pH values (<7.0). Both of these factors are disadvantageous with regard to metals removal. However, when one adds caustic to water which contains dissolved metals, the metals react with hydroxide ions to form metal hydroxide solids. Note from Table 1 that high pH corresponds to high hydroxide concentrations. Visual representations of the pH values that promote metal precipitation are displayed in the next seven figures. Each figure represents the solubility of an individual metal at various pH values⁽⁴²⁾.

All of the figures illustrate how the solubility of a particular metal is directly controlled by pH. The y-axis (2.1-2.7) displays the concentration of dissolved metal in the wastewater, in milligrams/liter (mg/lit.). Notice the wide variation in scale. The upper part of the scale shows a dissolved concentration of 100 mg/L. The lowest number on the scale is 0.001 mg/L. These solubility graphs display regions where the metals are soluble or insoluble. The region above the dark lines (the shaded areas) for each metal signifies that the metals should precipitate as metal hydroxides.

This is referred to as the precipitation region. The region below or outside of the dark lines illustrates where the metals are dissolved in solution, no precipitation occurs, and no metal removal takes place⁽⁴²⁾.

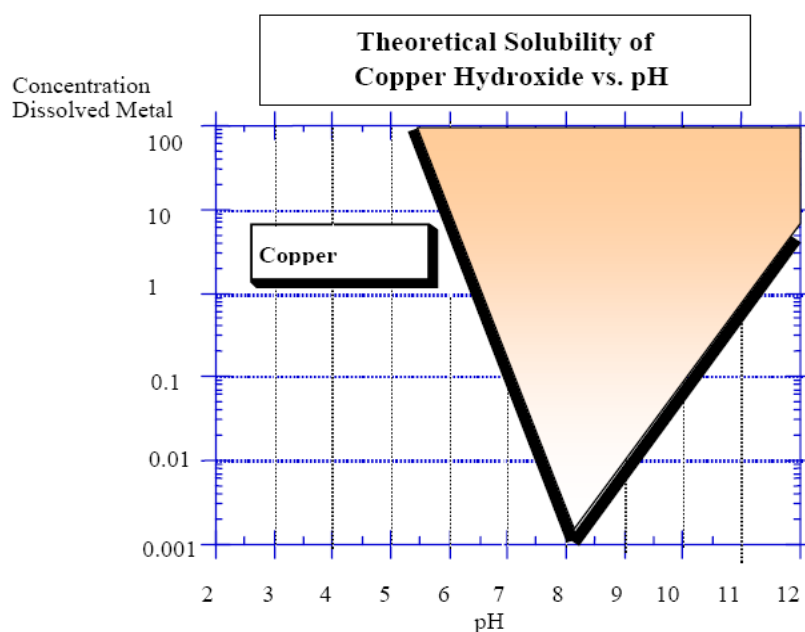
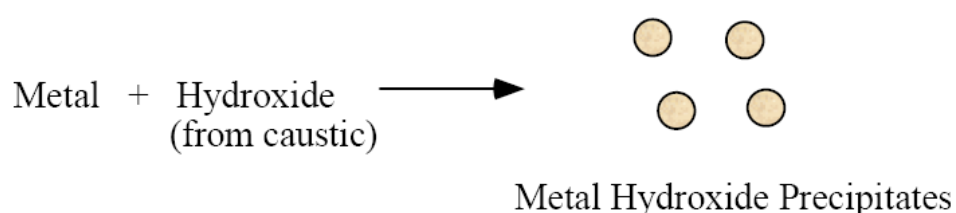


Figure 2.4: Theoretical Solubility of Copper Hydroxide⁽⁴²⁾.

With the exception of silver, notice that all of the metals display a minimum concentration at a particular pH. For example, in Figure 1, the lowest possible dissolved concentration of copper is approximately 0.001 mg/lit., which occurs at a pH value of 8.1.

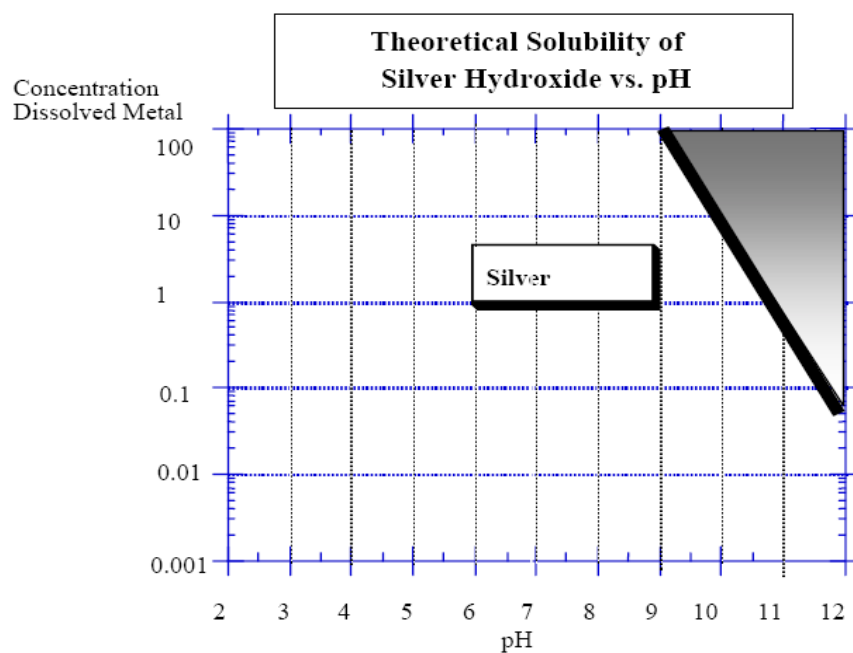


Figure 2.5: Theoretical Solubility of Silver Hydroxide⁽⁴²⁾.

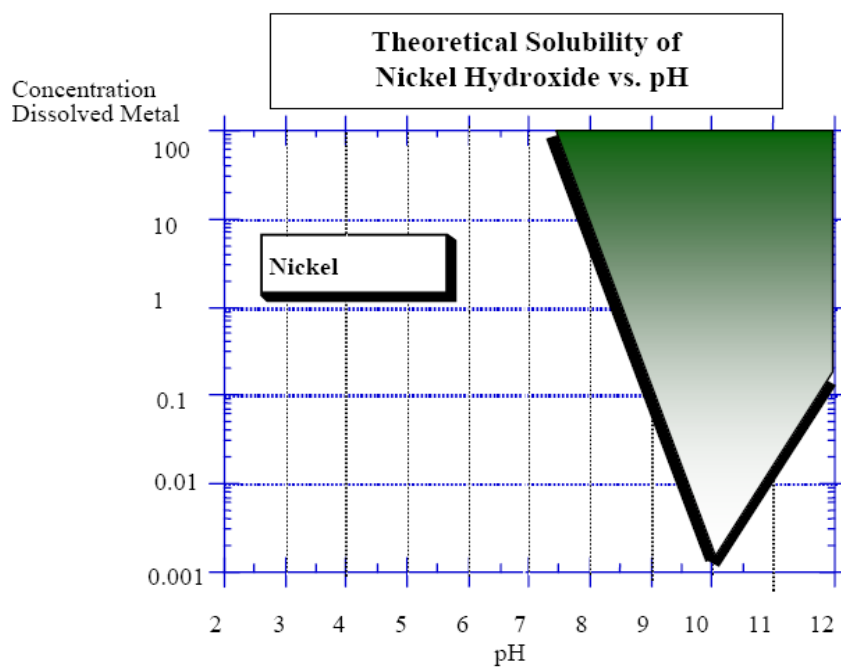


Figure 2.6: Theoretical Solubility of Nickel Hydroxide⁽⁴²⁾.

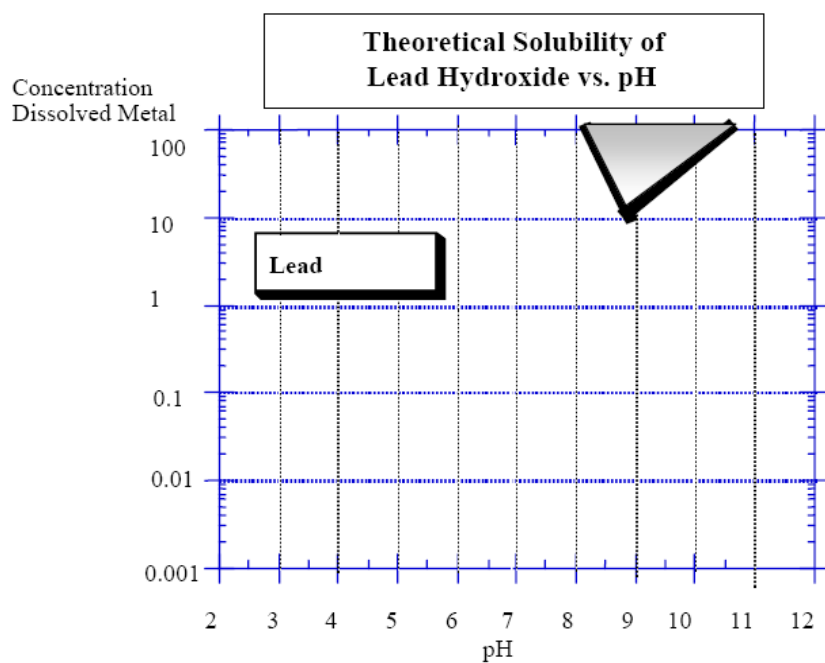


Figure 2.7: Theoretical Solubility of Lead Hydroxide⁽⁴²⁾.

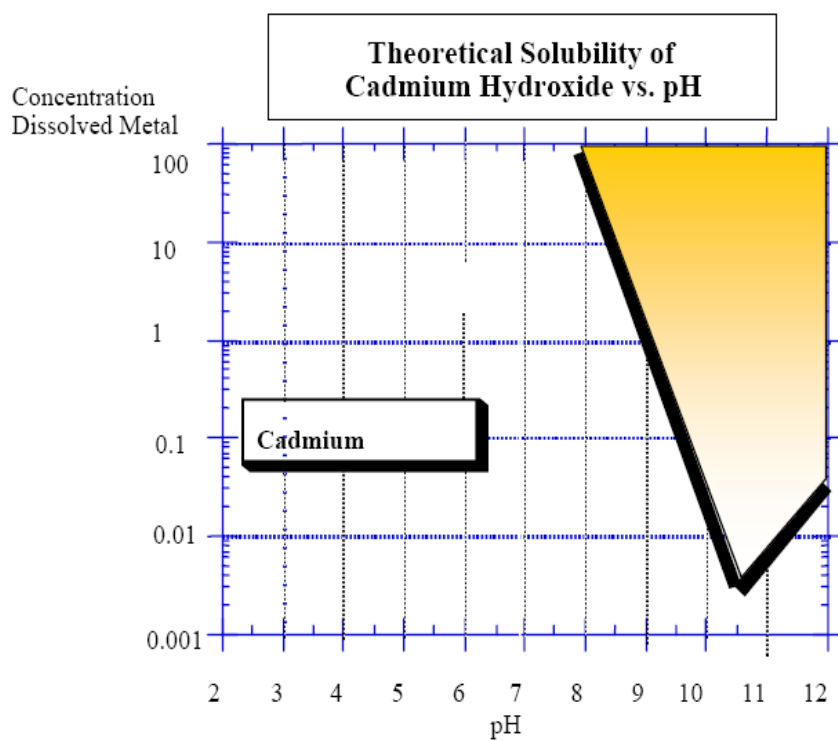


Figure 2.8: Theoretical Solubility of Cadmium Hydroxide⁽⁴²⁾.

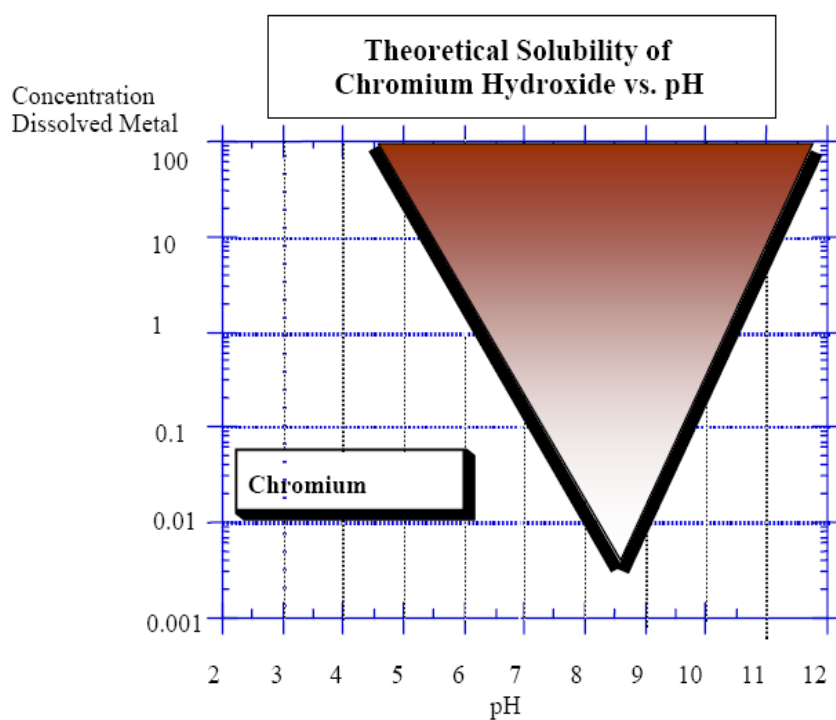


Figure 2.9: Theoretical Solubility of Chromium Hydroxide⁽⁴²⁾.

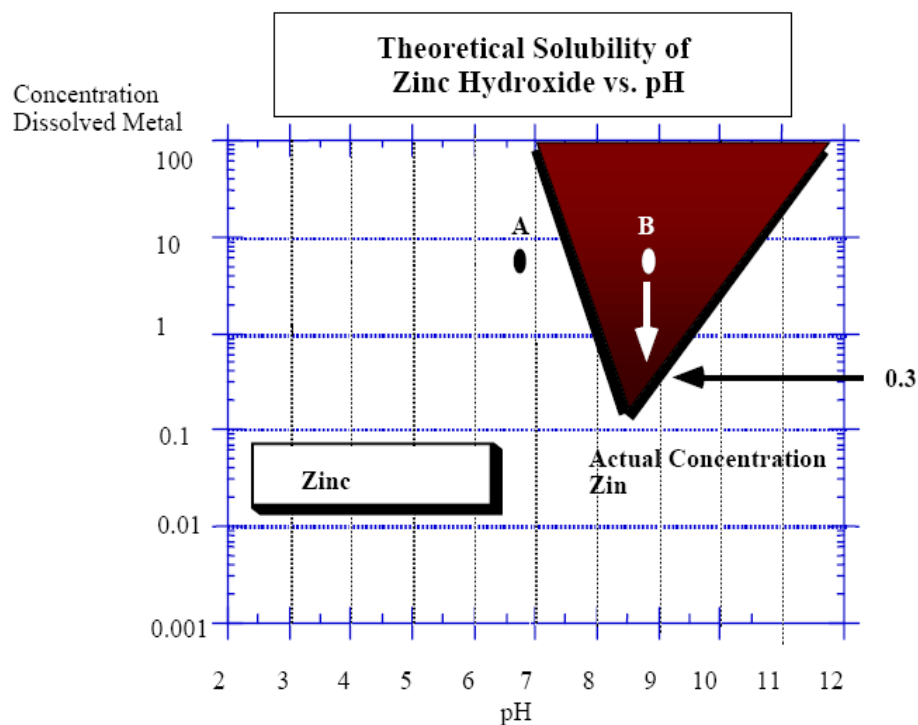


Figure 2.10: Theoretical Solubility of Zink Hydroxide⁽⁴²⁾.

Thus, simply adjusting the pH from 6.8 to 8.6 has effectively precipitated most of the dissolved metal from the water. Since all metals display similar effects, it is clear that the adjustment of pH is critical when the metal is to be removed from the wastewater.

However, the metals now exist in another phase or state (*i.e.*, as small solid particles). Metal removal is not complete until these metal solids are physically removed from the wastewater, typically by subsequent sedimentation and filtration processes⁽⁴²⁾.

2.12 Background Review:

2.12.1 Ion Exchange method:

The use of natural zeolites as an ion exchanger for the removal of heavy metal ions from water and wastewater could be applied by Otilia et al⁽⁴¹⁾. in two main mechanisms, namely batch system and ion exchange columns (as packed bed or fluidized bed)⁽⁴²⁾.

Ion exchange has historically proven Paull et al⁽⁴³⁾, in certain applications, to be an effective method for the metal finishers to minimize waste, ensure effluent compliance, provide water recycle, and even produce a concentrate suitable for recycle back to the process bath. One of the more interesting innovations in ion exchange technology over the past few decades has been the Recoflo short bed ion exchange process. Typical applications using this process involve the recovery of nickel salts from rinse water, the removal of contaminants from chromic acid plating solutions, and the removal of Al from anodizing and etching baths⁽⁴³⁾.

Inan, et al⁽⁴⁴⁾ showed that the removal of zinc ions from aqueous solution using natural Turkish zeolite, clinoptilolite, under different experimental conditions was investigated. Zeolite was used as a low cost adsorbent to remove zinc ions from water changing initial zinc concentration, pH and zeolite particle size. Langmiur and Freundlich isotherm models were tested to describe the adsorption data of Bigadic clinoptilolite about zinc ion uptake capacity. The results showed that the pretreatment with NaCl increased removal efficiency about 50 %. There were no significant effect changing pH's and zeolite particle sizes. According to experimental data the Langmuir isotherm model has been fitted better than Freundlich⁽⁴⁴⁾.

2.12.2 Adsorption method:

The alginate (a natural polymer obtained from marine algae) was tested as adsorbent material to remove bivalent ions (Pb(II); Cd(II)) from synthetic wastewater, due to its good affinity for the bivalent metal ions. The adsorption of the heavy metals was studied as a function of contact time between the alginate and the synthetic . Iulia et al⁽⁴⁴⁾. investigated that the polymeric micro particles with controlled porosity appear to be a suitable alternative to develop a method for heavy metal removal from industrial wastewater⁽⁴⁵⁾.

Waly et al⁽⁴⁶⁾. were studied the adsorption of Cd (II), Al (III), Co (II) and Zn (II), by adsorption technique using Cement Kiln Dust CKD which, is both a waste and a pollutant. The batch experiments showed that the most effective pH range was found to be 5.5 to 8. Time-dependent experiments for the removal efficiency of heavy metals (HM) ions showed that Al (III) required a shortest contact time, for Zn (II) and

Cd (II), binding to the CKD was rapid and occurred within 20 to 40 min and completed for Co (II) within 4 hrs. High sorption capacities were observed for the four HM ions⁽⁴⁶⁾.

The ability of water hyacinth (*Eichhornia crassipes* Mart. Solms.) to absorb and translocate cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), and nickel (Ni) was studied by Shao et al⁽⁴⁷⁾.

Translocation ability was defined as the quantity of Cu, Pb, Cd, Ni, and Zn translocated in the plant's tissues, and was expressed as a root/shoot ratio. The ratio results were in the order of Cu>Pb>Cd>Ni>Zn. Water hyacinth plants had a high bioconcentration of these trace elements when grown in water environments with low concentrations of the five elements. Generally, the concentration of these five elements in the roots was 3 to 15 times higher than those in the shoots. The concentrations in the root tissue were found in the order of Cu>Zn>Ni>Pb>Cd. The absorption capacity for water hyacinth was estimated at 0.24 kg/ha for Cd, 5.42 kg/ha for Pb, 21.62 kg/ha for Cu, 26.17 kg/ha for Zn, and 13.46 kg/ha for Ni. This study shows water hyacinth to be a promising candidate for phytoremediation of wastewater polluted with Cu, Pb, Zn, and Cd⁽⁴⁷⁾.

The ability of light expanded clay aggregate to remove lead and cadmium from paint industry's effluents was studied by Malakootian et al.⁽⁴⁸⁾ at different levels of adsorbent, contact time and pH in April 2008. For this purpose, lead and cadmium removal from paint industry effluents were studied in batch reactors. In this study, different amounts of LECA (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 g/L) were investigated. The amount of adsorbed lead and cadmium exposure to Leca increased from 1.41 to 3

mg/g and 0.22 to 0.75 mg/g, respectively. The maximum removal efficiency for Pb was 93.75 % at pH = 7 and exposure to 10 g/L of LECA, while for cadmium, it was nearly 89.7 % at the same condition. In this study, adsorption process of lead and cadmium was fitted with Freundlich adsorption isotherm (R^2 Pb = 0.97 and R^2 Cd = 0.98). The sufficient contact time was deemed 1-2 h for lead and cadmium. According to the results, LECA is recommended as a low cost and available adsorbent to remove lead and cadmium from industrial wastewater⁽⁴⁸⁾.

The adsorptive removal of Zn(II), Cd(II) and Pb(II) from single and binary metal ion aqueous solution using natural clinoptilolitic zeolite tuff, a regional low-cost naturally available adsorbent, and granulated activated carbon, an adsorbent conventionally applied in wastewater treatment, was studied by Mirjana et al.⁽⁴⁹⁾. The competitive adsorption equilibrium of three binary mixtures (Cd(II)/Zn(II), Zn(II)/Pb(II) and Pb(II)/Cd(II)) with different ratios of initial metal ion concentrations, on both adsorbents, was determined in batch mode at 25°C.

Langmuir and Freundlich isotherms were used to interpret the adsorption data of the investigated systems. The results indicate that the Langmuir isotherm fits the data better in both single and binary component systems. Natural zeolite and granulated activated carbon showed similar adsorption capacity for Pb(II), although granulated activated carbon had higher adsorption capacity for Zn(II) and Cd(II) than natural zeolite. The order of metal ion selectivity on both adsorbents is Pb(II) > Cd(II) > Zn(II).. The binary equilibrium of adsorption showed competitive nature. For all studied metal ions (Zn(II), Cd(II) and Pb(II)) the natural zeolite and granulated activated carbon metal ion adsorption

capacity in the case of binary systems (adsorption) are lower than those obtained for a single metal systems (adsorption), and are significantly influenced by the ratios of initial metal ion concentrations in the binary water solutions⁽⁴⁸⁾.

Chen et al ⁽⁵⁰⁾. investigated the applicability of maghemite Fe_2O_3 nanoparticles for the selective removal of toxic heavy metals from electroplating wastewater. The maghemite nanoparticles of 10 nm were synthesized using a sol–gel method and characterized by X-ray diffraction _XRD_ and transmission electron microscopy TEM. The surface area of the nanoparticles was determined to be 198 m² /g using the Brunauer–Emmett–Teller method. Batch experiments were carried out to determine the adsorption kinetics and mechanisms of Cr_VI_, Cu_II_, and Ni_II_ by maghemite nanoparticles. The adsorption process was found to be highly pH dependent, which made the nanoparticles selectively adsorb these three metals from wastewater. The adsorption of heavy metals reached equilibrium rapidly within 10 min and the adsorption data were well fitted with the Langmuir isotherm. Regeneration studies indicated that the maghemite nanoparticles undergoing successive adsorption–desorption processes retained original metal removal capacity.

Mechanism studies using TEM, XRD, and X-ray photoelectron spectroscopy suggested that the adsorption of Cr_VI_ and Cu_II_ could be due to electrostatic attraction and ion exchange, and the adsorption of Ni_II_ could be as a result of electrostatic attraction only⁽⁵⁰⁾.

Nomanbhay et al ⁽⁵¹⁾. Investigated and focuses on understanding biosorption process and developing a cost effective technology for

treatment of heavy metals-contaminated industrial wastewater. A new composite biosorbent has been prepared by coating chitosan onto acid treated oil palm shell charcoal (AOPSC).

Chitosan loading on the AOPSC support is about 21% by weight. The shape of the adsorbent is nearly spherical with particle diameter ranging 100~150 μm . The adsorption capacity of the composite biosorbent was evaluated by measuring the extent of adsorption of chromium metal ions from water under equilibrium conditions at 25°C. Using Langmuir isotherm model, the equilibrium data yielded the following ultimate capacity values for the coated biosorbent on a per gram basis of chitosan: 154 mg Cr/g. Bioconversion of Cr (VI) to Cr (III) by chitosan was also observed and had been shown previously in other studies using plant tissues and mineral surfaces. After the biosorbent was saturated with the metal ions, the adsorbent was regenerated with 0.1 M sodium hydroxide. Maximum desorption of the metal takes place within 5 bed volumes while complete desorption occurs within 10 bed volumes. Details of preparation of the biosorbent, characterization, and adsorption studies are presented. Dominant sorption mechanisms are ionic interactions and complexation⁽⁵¹⁾.

The study by Amir et al.⁽⁵²⁾, removal of cadmium, lead and nickel from industrial wastewaters has been investigated by using tea waste as a natural adsorbent. The research is a bench scale experimental type and analyses have performed by using different amounts of adsorbent in solutions with 5 different concentrations of each metal and also in a mixed combination. Besides, the effect of various amounts of tea waste used in adsorption efficiency experiments has been investigated. Results indicate that the removal efficiency is highest for lead and is minimum

for cadmium. About 94 and 100% lead removal were achieved by using 0.5 and 1.5g adsorbent for solutions having concentrations of 5 and 10 mg/L Pb. Whereas, 1.5g teawaste can treat nickel solution of 5 mg/L concentration with an efficiency of not more than 85.7%. For cadmium, the efficiency was only 77.2% in the same conditions.

On the other hand, for mixtures of metals and by applying 0.5 g tea waste, they considered a 3.5% decrease in lead removal efficiency and a 13.2% decrease in nickel adsorption for a mixed solution of 5 mg/L⁽⁵²⁾.

The adsorption potential of the kaolinite clay for the removal of lead ions from aqueous solutions was tested by Waid et al⁽⁵³⁾. The measured adsorption isotherms at the different temperatures 298.15 K, 308.15 K and 318.15 K were found to be perfectly fit to the Langmuir isotherm equation. A high adsorption capacity was calculated. An increase in the retention capacity with increasing temperature was measured.

The adsorption process was found to be endothermic with an estimated mean enthalpy change of 135.2 kJ/mol. The measured adsorption kinetic data at different temperatures proved that not only intraparticle diffusion controls the adsorption process but also surface adsorption contributes to the control of rate of adsorption. The influence of pH in the acidic range was investigated. The measured increase in the adsorption rate at higher pH values (4.9) was explained through the influence of H⁺ ions on the complex ion formation⁽⁵³⁾.

Green algae, especially *Cladophora* species, are generally considered as the best bioindicator of aquatic bodies contamination by nutrients as well as by heavy metals. Therefore, the object of this study by Eva

et al.⁽⁵⁴⁾ was to investigate to which extent toxic metals (Ni, V, Cd, Pb, Cr) are present in algal biomass and to establish the bioaccumulation coefficients in correlated algae / water environments in a sewage lagoon, which represents the tertiary stage of a refinery waste water treatment plant (Slovnaft, Bratislava). Due to the orographic depression between the Eastern Alps and Western Carpathians and the characteristic atmospheric circulation with predominance of NW wind direction, the deposition of heavy metal aerosols from closed industrial activities is expected to contribute to bioaccumulation capacities of algae for these elements. The water of the refinery sewage lagoon has been monitored for BOD, COD, petroleum hydrocarbons, pH, BTX, halogenated hydrocarbons, some polyaromates, phosphates, ammonium, sulfates and suspended matter. From the viewpoint of heavy metal contents in agricultural composts, a management scenario for algal biomass reutilization, i.e. recycling nutrients and proteins back into the biosphere, via compost processing, is proposed⁽⁵⁴⁾.

Nasim et al.⁽⁵⁵⁾ showed that The adsorption process is being widely used by various researchers for the removal of heavy metals from waste streams and activated carbon has been frequently used as an adsorbent. Despite its extensive use in the water and wastewater treatment industries, activated carbon remains an expensive material. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon.

Therefore there is an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of heavy metals should be studied in detail. ⁽⁵⁵⁾.

Various adsorbents such as bentonite, activated carbon, conductive electroactive polypyrrole composites were employed by Hossein et al⁽⁵⁶⁾. The conductive polypyrrole composites were prepared using different surfactants such as sodium dodecylbenzenesulfonate, hydroxypropylcellulose, poly(vinyl alcohol) and poly(ethylene glycol) in the presence of FeCl₃ as an oxidant respectively.

The results indicate that the type of three adsorbents and surfactants have a great effect on the removal of arsenic⁽⁵⁶⁾.

Apipreeya et al⁽⁵⁷⁾ showed that Eucalyptus bark could be effectively employed as a raw material for the production of activated carbon. The obtained activated carbon was utilized as adsorbent for treating synthetic wastewater containing Cu(II) and Pb(II). The optimum pH for the adsorption of Cu(II) and Pb(II) was 5. The adsorption reached equilibrium within 45 minutes for the whole range of initial heavy metal concentrations (0.1-10 mM)⁽⁵⁷⁾.

Rais et al⁽⁵⁸⁾ showed that the potential of Pinus roxburghii bark as an adsorbent for the removal of heavy metals such as Cr(VI), Ni(II), Cu(II), Cd(II) and Zn(II) from aqueous solution at ambient temperature was investigated.

Adsorption capacity of the material was found to be 4.15, 3.89, 3.81, 3.53 and 3.01 mg g⁻¹ for Cr(VI), Zn(II), Cu(II), Ni(II) and Cd(II), respectively, at an initial metal ion concentration of 50 mg L⁻¹ at pH 6.5. The effect of concentration, contact time, adsorbent dose, solution pH,

adsorbent particle size, salinity and hardness on the adsorption of Cr(VI) were studied in detail in batch experiments. The equilibrium contact time for Cr(VI) adsorption was found to be 1 h. Adsorption equilibrium data fit well to the Freundlich isotherm in the concentration range studied. The maximum adsorption (96.2%) was recorded at pH 3 for the initial Cr(VI) concentration of 50 mg L⁻¹. The adsorbed metal ions from industrial wastewater were recovered using 0.1 M HCl solution. The column operation was found to be more effective compared to batch process. The percent recovery of Cr(VI) from industrial wastewater by column operation and batch process was found to be 85.8 and 65%, respectively. The results show that *Pinus roxburghii* bark can be used as a cost-effective adsorbent for the removal and recovery of Cr(VI) from wastewater⁽⁵⁸⁾.

The research by Nadeem et al ⁽⁵⁹⁾. reports the adsorption of Cu and Zn ions from aqueous solutions at low concentration range (5-100 mg/L) in batch systems using Rice Husk Ash as an adsorbent, which is abundantly available as agricultural waste. The present study emphasizes on the experimental development of the optimum parameters such as equilibrium time, pH and initial concentration.

Equilibrium data obtained have been fitted to the Langmuir, Freundlich, Tempkin and Dubinin - Radushekevich (DR) adsorption isotherms. Freundlich isotherm best fits the experimental results. Kinetic modeling of first order and pseudo-second order showed that the pseudo-second order equation was the most appropriate for the description of Zn (II) and Cu (II) adsorption by Rice Husk Ash⁽⁵⁹⁾.

Direct and indirect electrochemical oxidation by using boron doped diamond anode (BDD), direct electrochemical oxidation by using ruthenium mixed metal oxide (Ru-MMO) electrode, and electrofenton and electro coagulation by using iron electrode were investigated by Kahraman et al. ⁽⁶⁰⁾ for the treatment of petroleum refinery wastewater (PRW). The results have been given at the best operational conditions which were obtained for each electrochemical method. The results obtained from electrochemical methods were compared to each other ⁽⁶⁰⁾.

The single component adsorption of heavy metal ions named Lead (II), Copper(II), Chromium(III) and Cobalt(II) onto granular activated carbon (GAC) from water aqueous solution has been investigated by Jenan ⁽⁶¹⁾ in batch and fixed bed adsorber. A mathematical model was developed to simulate the experimental data⁽⁶¹⁾.

Heavy metals are strictly regulated and must be treated before being discharged to the environment. A simple and efficient treatment process for removal of heavy metals is essentially necessary. Suad ⁽⁶²⁾ study the performance of continuous flow electro coagulation system, with reactor which consists of a ladder series of twelve electrolytic cells, each cell containing stainless steel cathodes and iron or aluminum anode, has been inspected. The treatment of synthetic solutions containing Zn(II),Cu(II),Ni(II),Cr(II),Cr(III),Cd(II) and Co(II),has been investigated. Several working parameters, such as pH, current density, flow rate and metal ion concentrations were studied in an attempt to achieve a higher removal capacity⁽⁶²⁾.

Kadirvelu et al ⁽⁶³⁾.investigated the adsorption of mercury (II) from aqueous solutions onto an activated carbon under varying conditions of

agitation time, metal ion concentration condition, adsorbent dose and pH to assess the kinetic and equilibrium parameter. Both Freundlich and Langmuir adsorption isotherm models fitted the experimental data well.

Robert et al ⁽⁶⁴⁾ showed that the Aluminum particles are reacted with heavy metal ions in a first acidic aqueous solution to form heavy metallic particles that are suitable for recycling and reuse when recovered from the first aqueous solution. The first residual aqueous solution may also contains ferrous ions obtained by acid redissolving a co-precipitated heavy metal hydroxide and ferrous hydroxide sludge that is produced in the treatment of a dilute chelated heavy metal solution. The first residual aqueous solution with heavy metals substantially removed is recycled and reused as the ferrous reagent for treating said dilute chelated heavy metal bearing solution. The process disclosed herein is useful for treating both dilute and concentrated wastes and wastewaters generated by industries such as metal plating and metal etching and printed circuit board fabrication . Robert ⁽⁶⁴⁾ showed that the Heavy metal ions react with iron particles in acidic aqueous solution to form heavy metallic particles that are suitable for recycling and reuse when recovered from the aqueous solution. Chelating agents that are present are deactivated by bonding to ferrous ions produced from the iron particles. An alkali metal hydroxide is utilized to precipitate remaining heavy metal ions including ferrous and ferric ions which are recycled to the acidic aqueous solution ⁽⁶⁴⁾.

Chegrouche⁽⁶⁵⁾. studies the feasibility of zinc adsorption onto natural bentonite. Equilibrium adsorption isotherm is analyzed to obtain the Langmuir and Freundlich constants. The equilibrium isotherm shows that the data correlate well with Freundlich and Langmuir model and that the adsorption is physical in nature.

Bhattacharyya⁽⁶⁶⁾ used kaolinite, montmorillonite and their poly (oxo zirconium) and tetrabutylammonium derivatives for removing Cd(II) from aqueous solution. Batch experimental studies were carried out under various Cd(II) concentrations, amounts of clay adsorbents, pH, interaction time and temperature. The uptake of the metal was initially very fast but generally slowed down indicating diffusion into interior of the adsorbent particles.

The adsorption process was more akin toward second order reaction mechanism. The suitability of the adsorbent was tested by fitting the adsorption data with Langmuir and Freundlich Isotherm, which gave good fits with both isotherms.

Yavuz et al⁽⁶⁷⁾. studied the adsorption isotherm of copper, nickel, cobalt and manganese from aqueous solution by kaolinite. The sorption of these metals on kaolinite conforms to linear form of Langmuir adsorption equation. Martins⁽¹⁰⁵⁾ et al. applied the Langmuir adsorption model to the adsorption of cadmium and zinc ions onto aquatic moss. The experimental results obtained for each metal fit to Langmuir isotherm model.

Teker et al⁽⁶⁸⁾ investigated the removal of copper(II) and cadmium(II) ions from aqueous solutions, by adsorption on activated carbon. The adsorption data obtained with the adsorbent correlates well with the Freundlich and Langmuir adsorption models. They determined the adsorption isotherm for heavy metal ions from aqueous solutions by activated carbon. These adsorption isotherms were seen to be consistent with Freundlich adsorption isotherm.

Singh⁽⁶⁹⁾ studied the adsorption of cadmium and zinc in single and multi-component system using activated carbon. Adsorption data follow both the Freundlich and Langmuir models.

Tekin et al⁽⁷⁰⁾ determined and correlated the adsorption isotherm of polyvinylimidazole (PVI) onto kaolinite, with common isotherm equations such as Langmuir and Freundlich isotherm models.

2.12.3 Precipitation method:

Chang et al.⁽⁷¹⁾ were studied the Heavy metals precipitation methods and various chromium reduction methods for wastewater samples. Wastewater samples containing chrome was tested with the following methods: (1) sodium metabisulfite, (2) ferrous sulfate, and (3) dimethyl dithio carbonate, ferrous sulfate, and (4) alum. It was found that (a) the first three treatment methods are all effective for chromium reduction or absorption, (b) the fourth method is not as effective for chromium reduction as the other three, (c) the efficiency of heavy metals precipitation process was influenced by the method of chromium reduction used prior to precipitation, and (d) in order to effectively precipitate heavy metals out of wastewater sample, coagulants (or coprecipitants) and polymer must be used. It was also found that by using a proper combination of chromium reduction and precipitation methods, the treated wastewater sample can meet the discharge limits.

A series of experiments was carried out by Muhammad et al.⁽⁷²⁾ to assess the viability of treating refinery wastewater using coarse sand for the removal of heavy metals from the refinery wastewater. The results

showed high removal efficiencies for iron (Fe) (49%), copper (Cu) (53%) and zinc (Zn) (59%) in the coarse sand filled wetlands⁽⁷²⁾.

Vohra et al⁽⁷³⁾ showed that the overall results from several synthetic wastewater matrices that are similar to pretreated petroleum refinery wastewater (PPRWW) using titanium dioxide (TiO₂) mediated PhotoCatalytic Degradation (PCD) process show that under several different environmental conditions, organic pollutant phenol, and inorganic contaminant ammonia can be removed from the concerned wastewaters using the PCD process⁽⁷³⁾.

Hille et al⁽⁷⁴⁾ were described utilizes alkalinity generated by the alga *Spirulina* sp., in a continuous system to precipitate heavy metals. The design of the system separates the algal component from the metal containing stream to overcome metal toxicity. The primary treatment process consistently removed over 99% of the iron (98.9 mg/l) and between 80 and 95% of the zinc (7.16 mg/l) and lead (2.35 mg/l) over a 14-day period. In addition the pH of the raw effluent was increased from 1.8 to over 7 in the post-treatment stream⁽⁷⁴⁾.

Patoczka et al⁽⁷⁵⁾. showed that the ferric salts are capable of removing heavy metals present in soluble, complexed, chelated, colloidal, emulsified and particulate form. This method is particularly applicable for treatment of low-volume industrial streams, where disposal of relatively large quantities of sludge generated, is still an economically competitive solution when compared to other treatment options; in particular hauling for off-site disposal of the whole wastewater stream⁽⁷⁵⁾.

The Results, obtained by Galiulin et al⁽⁷⁶⁾. on the accumulation of heavy metals in plants and the screening of effective metal-accumulating

plants under laboratory and field conditions, have been analyzed and generalized with the intention of assessing the potential of phytoremediation as an emerging technology for the purification of industrial wastewater contaminated by heavy metals⁽⁷⁶⁾.

Amount of a water soluble ethylene dichloride- ammonia polymer having a molecular weight of from about 500 to about 10,000 daltons that contain from about 5 to about 50 mole percent of dithiocarbamate salt groups to react with heavy metals in industrial wastewater system; (d) passing treated industrial wastewater through a submerged membrane, wherein submerged membrane is an ultra filtration mem A method of removing one or more heavy metals from industrial wastewater by use of a membrane separation process is disclosed by Deepak.⁽⁷⁷⁾ Specifically, the following steps are taken to remove heavy metals from industrial wastewater: (a) collecting an industrial wastewater containing heavy metals in a receptacle suitable to hold industrial wastewater; (b) adjusting the pH of system to achieve hydroxide precipitation of heavy metal in industrial wastewater; (c) adding an effective brane or a microfiltration membrane; and (e) optionally back-flushing membrane to remove solids from the membrane surface⁽⁷⁷⁾.

Kenneth⁽⁷⁸⁾ studied An improved method to remove metals, including molybdenum, from industrial wastewater, by chemical precipitation of the metals, followed by settling and dewatering of the precipitate⁽⁷⁸⁾.

Uchiumi ⁽⁷⁹⁾ have designed and synthesized the highly functional chelating agents to collect and recover only hazardous substances(Cu(II), Cd(II), Sb(III), As(III), and Pb(II)) in the waste waters from high technology factories, and evaluated the capabilities of these agents as the

treating stuff for waste water. Design of the members and stereo-chemical configuration of coordination atoms is an important point in the development of the chelating agents having functions adequate to target metal ions. In this work the following chelating agents were synthesized: 2-mercapto-N-2-naphthalenyl acetamide(thionalide) resin of S,O-coordination, S-(Methylphenylthiocarbamoyl) sulfen amide(MPTCS)resin of S,N-Coordination and N-Benzoyl-S-dimethylthiocarbamoyl sulfen amide(BDTCS) resin of S,N-coordination⁽⁷⁹⁾.

Johnny ⁽⁸⁰⁾ showed that a system is provided for removing dissolved metals from industrial wastewater by electro coagulation. The system includes an electro coagulation reactor with a DC power supply having an insulation support enclosure with positive and negative electrode plates disposed thereon⁽⁸⁰⁾.

Overflow from an anaerobic, sulphate reducing, reactor was used Robert ⁽⁸¹⁾ to precipitate copper, iron and zinc from aqueous solutions. Two predictive methods, one generated empirically using data from synthetic solutions and one based on thermodynamic speciation software were evaluated. Both methods could accurately predict zinc precipitation. The inability of the software packages to account for amorphous and colloidal precipitates led to inaccurate models for copper and iron. The empirical models could account for this, but not the presence of organic acids. These factors could be incorporated into future models to enhance their accuracy⁽⁸¹⁾.

2.12.4 Biological method:

The study by Kulbat et al ⁽⁸²⁾ were indicated that the concentrations of seven heavy metals (Zn, Cu, Pb, Cd, Cr, Ni, Ag) in wastewater were rather low. After treatment, the metals concentration met criteria given in the Regulation of the Minister of Environmental Protection of Aug.1, 2002, that was valid at the time of the investigations. Analysis of effectiveness of metals removal during wastewater treatment processes undoubtedly indicates the fundamental role of biological treatment stage in metals removal⁽⁸²⁾.

Chipasa et al. ⁽⁸³⁾ studied the accumulation and removal of heavy metals (Cd, Cu, Pb, Zn) by a biological wastewater treatment system. Heavy metal contents in the influent and effluent wastewater were compared. Also, the heavy metal contents in the sludge before and after anaerobic digestion were compared⁽⁸³⁾.

Biosorption experiments for Chromium (Cr (VI)), Copper (Cu (II)), Cadmium (Cd (II)) and Nickel (Ni (II)) were investigated in study by Korrapati et al ⁽⁸⁴⁾ using nonliving biomass of different *Pseudomonas* species. Maximum Cr (VI) removal reached around 40% and its removal increased with the increase of Cr (VI) influent. Cu (II) removal was at its maximum value in presence of Cr (VI) as a binary metal, which reached 95% of its influent concentration. Concerning to Cd (II) and Ni (II) similar removal ratios were obtained, since it was ranged between 36 to 90% and their maximum removal were obtained in the case of individual Cd (II) and Ni (II)⁽⁸⁴⁾.

Hille et al ⁽⁸⁵⁾. studied the Overflow from an anaerobic, sulphate reducing, reactor was used to precipitate copper, iron and zinc from aqueous solutions. Two predictive methods, one generated empirically using data from synthetic solutions and one based on thermodynamic speciation software were evaluated. Both methods could accurately predict zinc precipitation. The inability of the software packages to account for amorphous and colloidal precipitates led to inaccurate models for copper and iron. The empirical models could account for this, but not the presence of organic acids. These factors could be incorporated into future models to enhance their accuracy⁽⁸⁵⁾.

Vasanthi et al ⁽⁸⁶⁾. studied that the Biosorption technology is used for the removal of heavy metal ions, focusing on Cu(II) and Ni(II) from dilute metal-bearing wastewater streams. Biosorbents tested out so far include leaves (neem, mango, banana, guava, papaya, etc) and citrus peels (lemon, orange and pomelo). Parameters varied include biosorbent dosage, metal ion concentration, reaction time, pH and temperature⁽⁸⁶⁾.

Analyses were carried out using different methods of analyzing and measuring the concentration of heavy metals, mainly to determine the adsorption capacity of different biomass material as well as the active groups involved in biosorption. From the results obtained, the sorption mechanism may be determined, hence enables the design of a sorption column or wastewater treatment beads that may be used to adsorb and later recover metal ions from wastewater⁽⁸⁶⁾.

An increase in population initiating rapid industrialization was by Emmanuel et al ⁽⁸⁷⁾. to consequently increase the effluents and domestic wastewater into the aquatic ecosystem. Heavy metals are major toxicants

found in industrial wastewaters; they may adversely affect the biological treatment of wastewater. Conventional methods for the removal of heavy metals from waste waters are often cost prohibitive hence, there is a need for cheap methods for effluent treatment. The residual metallic ion concentrations were determined using an Atomic Absorption Spectrophotometer (AAS). The results obtained after contacting for 120 minutes showed that Neem leaves achieved the percent removal of 76.8, 67.5, 58.4 and 41.45 for Cu(II), Ni(II), Zn(II) and Pb(II) ions respectively. The percent removal of Ni₂₊ ions was 68.75 with an effective dose of 1.0 g of Neem leaves (bioadsorbent). The ability of Neem leaves to absorb metal ions as shown from the results can be used for the development of an efficient, clean and cheap technology for effluent treatment⁽⁸⁷⁾.

Gardea et al ⁽⁸⁸⁾. showed that the Biosorption is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluents. Microorganisms as well as plant- and animal-derived materials have been used as biosorbents by many researchers. Biomaterial immobilization and chemical modification improves the adsorption capacity and stability of biosorbents⁽⁸⁸⁾.

Biosorption experiments over Cu(II), Cd(II), Pb(II), Cr(III), and Ni(II) demonstrated that biomass Cu(II) adsorption ranged from 8.09 to 45.9 mg g⁻¹, while Cd(II) and Cr(VI) adsorption ranged from 0.4 to 10.8 mg g⁻¹ and from 1.47 to 119 mg g⁻¹, respectively. Mechanisms involved in the biosorption process include chemisorption, complexation, surface and pore adsorption-complexation, ion exchange, microprecipitation, hydroxide condensation onto the biosurface, and surface adsorption.

Chemical modification and spectroscopic studies have shown that cellular components including carboxyl, hydroxyl, sulfate, sulfhydryl, phosphate, amino, amide, imine, and imidazol moieties have metal binding properties and are therefore the functional groups in the biomass. Column studies using support matrices for biomass immobilization such as silica, agar, polyacrilamide, polysulfone, alginates, cellulase, and different cross-linking agents have been performed to improve the biomass adsorption capacity and reusability⁽⁸⁸⁾.

The removal of heavy metals from our environment especially wastewater is now shifting from the use of conventional adsorbents to the use of biosorbents. The presence of heavy metals in the environment is of major concern because of their toxicity, bioaccumulating tendency, and threat to human life and the environment. In recent years, many low cost sorbents such as algae, fungi bacteria and lignocellulosic agricultural by-products have been investigated by Igwe et al ⁽⁸⁹⁾ for their biosorption capacity towards heavy metals. In this comprehensive review, the emphasis is on outlining the occurrences and toxicology of heavy metals and the biosorption capacity of biosorbents compared to conventional adsorbents⁽⁸⁹⁾.

The work by Donghee ⁽⁹⁰⁾ investigate the treatment of tin-plating wastewater containing low concentration of chromium by using biosorption and to understand the principle of removal of heavy metals and to develop the process for removal of heavy metals from wastewater⁽⁸⁸⁾.

Biosorption experiments for Cr(VI), Cu(II), Cd(II) and Ni(II) were investigated by Hany ⁽⁹¹⁾ in this study using nonliving biomass of

different *Pseudomonas* species. The applicability of the Langmuir and Freundlich models for the different biosorbent was tested⁽⁹¹⁾.

Biosorbents and chemically modified biosorbents were prepared and compared by Xie ⁽⁹²⁾ with commercial ion-exchange resins to determine their metal-binding capacity, the range of metals bound, the effects of pH, temperature, contact time, interference by common salts and the effect of multiple cycles of metal binding and elution⁽⁹²⁾.

Biosorbents were prepared from microorganisms isolated from pristine and metal impacted (acid mine drainage) environments and included heterotrophs, methanotrophs, algae, sulfate reducers, and exopolysaccharide-producing cultures. The chemical modifications examined included encapsulation in polysulfone resin, acid, alkali, carbon disulfide, phosphorus oxychloride, anhydrous formamide, sodium thiosulfate, sodium chloroacetic acid, and phenylsulfonate treatments⁽⁹²⁾.

2.12.5 Filtration method:

The complexation- membrane filtration techniques have been shown Barakat et al ⁽⁹³⁾. to be promising alternative techniques for removal of heavy metals from water. This study focused on the use of a clean and novel technology of membrane-based hybrid processes containing multiple polymeric functional groups to remove heavy metals, particularly Cu(II), Ni(II) and Cr(III), from synthetic wastewater. The process has been divided into the following three stages: firstly, heavy metal bonding (adsorption) by a bonding agent, secondly, wastewater

filtration to separate the loaded bonding agent by ultra filtration membrane, and thirdly, bonding agent regeneration. The scientific approach is based on that cationic forms of heavy metals are first complexed by a bonding agent in order to increase their molecular weight with a size larger than the pores of the selected membrane that can be retained. Advantages of that technology over the other conventional technologies are the low energy requirements, feasible and economic, very fast reaction kinetics, and the high selectivity of separation⁽⁹³⁾.

Ortaggi et al⁽⁹⁴⁾ showed that The presence in the environment of large quantities of toxic heavy metals (i.e. cobalt, chromium, lead, cadmium, zinc, etc.), poses serious health risks to individuals, hence the development of novel methods to eliminate toxic contaminants from wastewaters in efficient and economically viable ways is highly desirable. In this work we assayed the ability of a polyamine polymer, polyethylenimine (PEI) and its carboxylated derivative PEI-COOH to complex a selection of twenty two heavy metals and remove them from contaminated water by an ultra-filtration technique⁽⁹⁴⁾. They found that PEI is able to complex efficiently and reduce the concentration of eleven heavy metals (Ag, Al, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn and Zn) to almost a third. In some cases, PEI is very efficient to remove also Cr and Sn to a concentration less than 0.1 ppm. Interestingly, PEI-COOH derivative is able to remove eight heavy metals (Ag, Al, Cd, Co, Cu, Ni, Pb, and Zn) to a concentration less than 0.4 ppm hence increasing the efficiency of polyamine polymers used so far. In conclusion, the use of carboxylated-PEI in conjunction with the ultra filtration technique is a valuable tool that may be used for industrial applications to remove a large number of heavy metals⁽⁹⁴⁾.

Uchiumi et al⁽⁹⁵⁾ had designed and synthesized the highly functional chelating agents to collect and recover only hazardous substances(Cu(II), Cd(II), Sb(III), As(III), and Pb(II)) in the wastewaters from high technology factories, and evaluated the capabilities of these agents as the treating stuff for wastewater. Design of the members and stereo-chemical configuration of coordination atoms is an important point in the development of the chelating agents having functions adequate to target metal ions. In this work the following chelating agents were synthesized: 2-mercapto-N-2-naphthalenyl acetamide(thionalide) resin of S,O-coordination, S-(Methylphenylthiocarbamoyl) sulfen amide(MPTCS)resin of S,N-Coordination and N-Benzoyl-S-dimethylthiocarbamoyl sulfen amide(BDTCS) resin of S,N-coordination.⁽⁹⁵⁾

Mangrove ecosystems are shown by Yim⁽⁹⁶⁾ to be effective in treating different types of wastewater but the ecological functioning of the system might be damaged by the pollutants contained in wastewater .Removal efficiencies of heavy metals from normal strength industrial wastewater were very high in mangrove microcosms planted with *Kandelia candel* (>90%) but the removal efficiencies of heavy metals from strong wastewater (10 times the normal strength) were reduced, except for Cu⁽⁹⁶⁾.

Wastewater containing copper and cadmium can be produced by several industries. The application of both reverse osmosis (RO) and nanofiltration (NF) technologies for the treatment of wastewater containing copper and cadmium ions to reduce fresh water consumption and environmental degradation was investigated by Mirjana et al⁽⁴⁸⁾.

Synthetic wastewater samples containing Cu(II) and Cd(II) ions at various concentrations were prepared and subjected to treatment by RO and NF in the laboratory. The results showed that high removal efficiency of the heavy metals could be achieved by RO process (98% and 99% for copper and cadmium, respectively). NF, however, was capable of removing more than 90% of the copper ions existing in the feed water⁽⁴⁸⁾.

The effectiveness of RO and NF membranes in treating wastewater containing more than one heavy metal was also investigated. The results showed that the RO membrane was capable of treating wastewater with an initial concentration of 500 ppm and reducing the ion concentration to about 3 ppm (99.4% removal), while the average removal efficiency of NF was 97%. The low level of the heavy metals concentration in the permeate implies that water with good quality could be reclaimed for further reuse⁽⁴⁸⁾.

2.13 Theoretical Models of Adsorption:

Most of adsorption theories have been developed for gas-solid system because the gas state is better understood than liquid. Till now the statical theories developed for gas-solid system have been applied to liquid-solid systems with little confidence in designing of the equipment⁽⁹⁷⁾.

Adsorption isotherm equations are used to describe experimental sorption data. The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinity of the sorbent⁽⁹⁸⁾.

2.13.1 Langmuir Isotherm:

One particular mathematical form of an isotherm which is often found to fit experimental data is so called Langmuir isotherm.

The Langmuir model is probably the best known and most widely applied sorption isotherm. It has produced a good agreement with a wide variety of experimental data. The Langmuir isotherm is applied to homogeneous sorption⁽⁹⁸⁾.

Langmuir isotherm was derived in 1916 by Irving Langmuir⁽⁹⁸⁾. The Langmuir isotherm equation is represented as follows:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad \dots 2.1$$

By rearranging equation 2.1 to

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \quad \dots 2.2$$

The values of the Langmuir constants q_m and b can be calculated by least square methods or graphically by plotting C_e/q_e against C_e ⁽⁹⁹⁾.

The Langmuir isotherm is valid for description of single layer adsorption on a surface containing a finite number of binding sites. It is the simplest theoretical model for monolayer adsorption which was developed from either kinetic derivation or thermodynamic derivation⁽¹⁰⁰⁾.

The Langmuir isotherm is developed by assuming:

- Fixed number of accessible sites are available on the adsorbent surface.
- Each site can hold one adsorbate molecules.
- All sites are energetically equivalent.
- There is no interaction between molecules adsorbed on neighboring sites.
- Adsorption is reversible

Yavuz et al⁽¹⁰¹⁾ studied the adsorption isotherm of copper, nickel, cobalt and manganese from aqueous solution by kaolinite. The sorption of these metals on kaolinite conforms to linear form of Langmuir adsorption equation. Martins et al. ⁽¹⁰²⁾ applied the Langmuir adsorption model to the adsorption of cadmium and zinc ions onto aquatic moss. The experimental results obtained for each metal fit to Langmuir isotherm model.

The Langmuir isotherm can be extended for multicomponent system to give the following form ⁽¹⁰³⁾.

$$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}}{1 + \sum_{i=1}^N b_i C_{e,i}} \quad \dots 2.3$$

Where $C_{e,i}$ is the equilibrium concentration of component i in multicomponent system, $q_{e,i}$ is the equilibrium uptake of the component i , and b_i is the single component Langmuir parameter for component i .

2.13.2 BET Isotherm :

Brunauer⁽¹⁰⁴⁾, Emmett and Teller (BET) developed a simple model isotherm for multilayer adsorption. The BET model assumes that a number of layers of adsorbate accumulate at the adsorbent surface and that the Langmuir isotherm model applies to each layer. BET equation is limited by the assumption of uniform energies of adsorption and it may be deduced either from kinetic consideration or the thermodynamics of the adsorption process the BET model is based on a number of rather serious idealization as follows ⁽¹⁰⁰⁾:

- Each molecule in the first adsorbate layer is considered to provide one site for the second and subsequent layers.
- The molecules in the second and subsequent layers which are in contact with other adsorbate rather than with the surface of the adsorbent, are considered to behave as saturated liquid. The BET equilibrium isotherm equation takes the simplified form:

$$q_e = \frac{q_m b C_e}{(C_s - C_e)[1 + (b + 1)^{C_e/C_s}]} \quad \dots 2.4$$

where C_s is the saturation concentration of the adsorbent.

2.13.3 Freundlich Isotherm:

Herbert Max Finley Freundlich⁽¹⁰⁵⁾, a German physical chemist, presented an empirical adsorption isotherm for non-ideal systems in 1906⁽¹⁰⁵⁾. The Freundlich isotherm is the earliest known relationship describing the sorption equation and has widely been used for many years. This fairly satisfactory empirical isotherm can be used for nonideal sorption and involves heterogeneous sorption and is expressed by the following equation⁽¹⁰⁵⁾:

$$q_e = K_f C_e^{1/n} \quad \dots 2.5$$

And the equation may be linearized by taking logarithms as follows:

$$\text{Log}(q_e) = \frac{1}{n} \text{Log}(C_e) + \text{Log}(K_f) \quad \dots 2.6$$

Where K_f and $1/n$ are empirical constants dependent on several environmental factors. The constants in the Freundlich isotherm can be determined by plotting $\text{Log}(q_e)$ vs. $\text{Log}(C_e)$, and the linear line obtained gives a slope which is the value of $1/n$ and y-intercept is $\text{Log}(K_f)$.

The intercept is an indicator of adsorption capacity and the slope is adsorption intensity. A relatively slight slope (and hence a high value of

n) indicates that adsorption is good over the entire range of concentration studied, while a steep slope (and hence small value of n) means that adsorption is at high value concentrations. A greater value of the intercept K_f indicates a higher capacity for adsorption than a smaller value.

2.13.4 Linear Isotherm:

The linear isotherm model describes the accumulation of solutes by adsorbent as directly proportional to the solution concentration ⁽¹⁰⁶⁾as follows:

$$q_e = K_D C_e \quad \text{.....2.7}$$

The constant of proportionality or distribution coefficient K_D is often referred to as partition coefficient. Gharaibeh⁽¹⁰⁶⁾ et al. studied the removal of heavy metals, namely Cr(II), Pb(II), Ni(II), Cd(II) and Zn(II) from aqueous solution. Linear, Langmuir and Freundlich isotherms are used for analysis of experimental data. All three models may give close results at low concentrations but the Freundlich isotherm gives the best fit for the data.

2.13.5 Redlich-Peterson Isotherm:

Jossens⁽¹⁰⁷⁾ et.al modified the three parameter isotherm first proposed by Redlich and Peterson (1959), to incorporate the features of the Langmuir and Freundlich isotherms . It can be described as follows:

$$q_e = \frac{AC_e}{1 + BC_e^{g_R}} \quad \dots 2.8$$

It has three isotherm constants, namely A, B and g_R ($0 < g_R < 1$). These can be evaluated from the linear plot represented by equation 2.13 using a trial and error optimization method:

$$\ln\left(A \frac{C_e}{q_e} - 1\right) = g_R \ln(C_e) + \ln(B) \quad \dots 2.9$$

2.3.6 Combination of Langmuir-Freundlich Model :

The sips model for single component is given by:

$$q_e = \frac{bq_m C_e^{1/n}}{1 + bC_e^{1/n}} \quad \dots 2.10$$

The competitive sips model ⁽¹⁰⁶⁾ related to the individual isotherm parameters is expressed in the following equation:

$$q_{e,i} = \frac{q_{m,i} b_i C_e^{1/n}}{1 + \sum_{i=1}^N b_i C_{e,i}^{1/n_i}} \quad \dots 2.11$$

Where $C_{e,i}$ is the equilibrium concentration of component i in multicomponent system, $q_{e,i}$ is the equilibrium uptake of the component i , and b_i is the single component Langmuir parameter for component i .

Chapter Three

Experimental Work

3.1 Introduction:

Experimental work is conducted to investigate the removal of heavy metals from industrial wastewater from petroleum refinery by adsorption using kaolinite as an adsorbent. The heavy metals used are Zn (II), Cr (III) as nitrate metal ions salt. It was suggested to investigate the state of Zinc(II), Chromium (III) with the addition of Kaolinite and neglect the other heavy metals (Cu(II), Ni(II), Cd(II) and Co(II)) for their low concentration in the wastewater discharged from the Daura Petroleum Refinery.

The experiments runs were carried out by batch experiments with studied multi variable (time of treatment, mass of adsorbent and the metals consternation) effect on removal efficiency. All the experiments were carried out in the Laboratory of Chemical Engineering Department University of Technology and Daura Petroleum Refinery in Baghdad – Iraq also in the Environmental Research center- University of Technology.

3.2 Materials:

| | |
|---|---|
| Product name | Kaolinite, powder |
| Company | Sigma-Aldrich Company (UK) Ltd |
| Composition | $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ |
| Bulk density, Kg/m^3 | 432 |
| BET surface area, m^2/g | 20.3 |
| pH | 4-5 |

3.2.1 Adsorbent:

The adsorbent used was Kaolinite as a powder supplied by Petroleum Research and development center, Baghdad-Iraq. The physical properties listed in Table 3.1 were measured by Thermo Chemistry Laboratory, Environmental Research Center, University of Technology, and also in the Power Laboratory Department, Daura Petroleum Refinery, Baghdad – Iraq, and the shape of internal structure is measured by Light Microscope as shown in Fig. 3.1

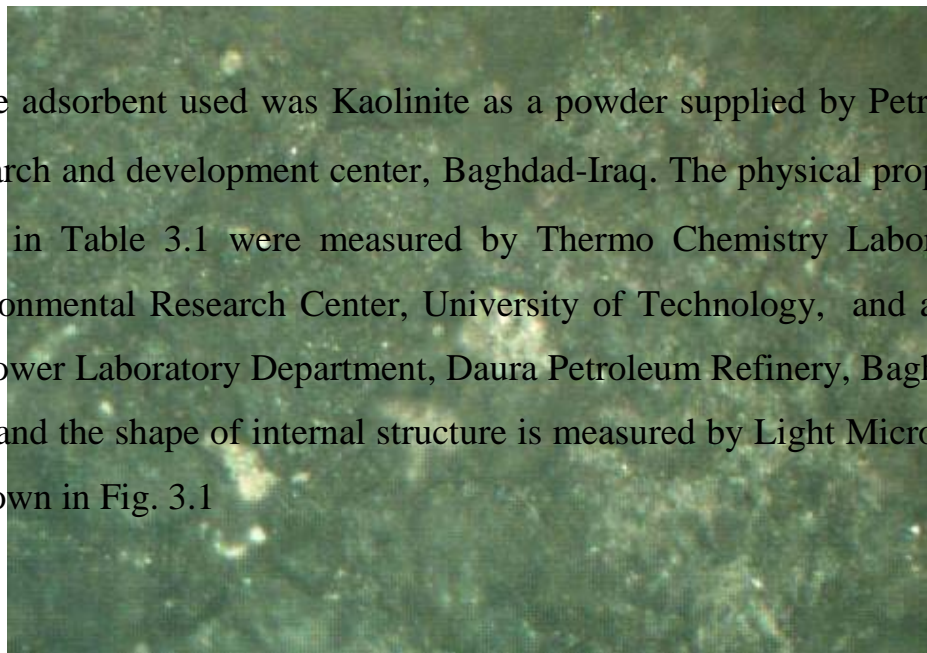


Table 3.1: Physical properties of Kaolinite⁽⁵⁵⁾.

Figure 3.1: kaolinite structure 100X.

3.2.2 Adsorbate:

Metal ions used as nitrate salt are $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The chemicals used are annular grade produced by Fluka and Aldrich-Sigma. All experiments used distilled water.

3.3 Equipments:

- Shaking water bath supplied by Mickle Laboratory Engineering Company Ltd. to agitate the kaolinite / aqueous metal ion mixture
- Pye Unicam pH meter model 292 to measure the pH of the solution
- Millipore membrane filter model Millex , pore size $0.45\mu\text{m}$

- Analytical balance model R300S, Sartorius, Company, to weigh the materials
- Centrifuge model Omnifuge 2.0 RS, Heraeus Sepatech Company
- Perkin Elmer model AAnalyst 400 Atomic absorption spectrometer (AAS) operating with air-acetylene flame: to measure metal ion concentration. The analysis on the AAS for each sample was carried out in triplicate.

3.4 Preparation of Metal Ion Solution:

The third section of the experimental work was prepared different weights of Zinc (II), Chromium (III) as the following: (0.3-1.5)ppm and (0.01-0.07)ppm for solutions of Cr(III) and Zn(II) respectively were prepared. The required amount of metal salt was dissolved into 1liter of distilled water and stir. The masses used are listed in Table 3.2.

Table 3.2, Metal ion salt

| Metal ion | Metal salt | Concentration ppm |
|------------------|---|--------------------------|
| Zn(II) | Zn(NO₃)₂ | 0.0093 |
| Cr(III) | Cr(NO₃)₃.9H₂O | 0.266 |

3.5 Batch Experiments:

Batch experiments were used to obtain the equilibrium isotherm curves and then the equilibrium isotherm data for each metal ion. In batch mode the following experiments were carried out :

- Effect of kaolinite weight on adsorption process.
- Effect of time of treatment on adsorption process.
- Effect of the initial metal ion weight on the adsorption process.

All experiments were carried out at $25^{\circ}\text{C} \pm 1$. The desired pH (6.5) was adjusted using 0.1 M NaOH and 0.1 M HNO_3 .

3.5.1 Effect of kaolinite Weight:

The experiment was used to determine the optimum weight of kaolinite used for removal of metal ions. The experiment was carried out using 5 tubes of 30 ml in volume. A volume of 10 ml portion of the metal ion solution of a concentration (0.0093) ppm Zn (II) and (0.026) ppm Cr (III) were placed in 30 ml tubes containing different amount of kaolinite (0.01-1.0) g. A series of tubes were then shaken at a constant speed of 250 r.p.m in a shaking water bath at temperature $25^{\circ}\text{C} \pm 1$ and agitated continuously for 3 hr. The experiment was adjusted at the pH of the solution which was (6.5) for Zn (II) and Cr (III). After shaking the kaolinite was separated by centrifuge model Omifuge 2.0 RS then by filtration through a membrane filter 0.45 μm . The filtrate was analyzed

for the remaining metal ion concentration by atomic absorption spectrometer (AAS).

The optimum mass of adsorbent was obtained by plotting the mass of adsorbent versus the percentage removal which are given in chapter four.

3.5.2 Effect of the Initial Heavy Metal Weight:

The optimum masses of kaolinite which were 1.5, and 1.0 g and the optimum pH of solutions which was to be fixed at (6.5) was used for Zn(II) and Cr(III) respectively. The experiment was used to obtain the equilibrium isotherm curves for single metal ions by plotting the mass of solute adsorbed per mass of adsorbent, q_e , against the equilibrium concentration of the solution, C_e , and then to obtain the equilibrium isotherm parameters.

A volume of 10 ml of metal ion solution in different initial concentration of (0.01-0.07)ppm Zn(II) and (0.3-1.5)ppm Cr(III) was placed in five tubes containing the fixed mass of kaolinite.

The tubes were then shaken at a constant speed of 250 r.p.m. in a shaking water bath at different temperatures of $25^{\circ}\text{C} \pm 1$ for (3) hrs. The shaker bath consists of temperature controller that controls the temperature for the required value. A temperature indicator provided in the shaker is used to monitor the experimental temperature. After shaking the kaolinite was separated by centrifuge and filtration through a membrane filter $0.45\mu\text{m}$. The filtrate was analyzed for the remaining metal ion concentration by atomic absorption spectrometer AAS.

The uptake of metal ions in single system was calculated by the difference in their initial and final concentration (equilibrium concentration). A mass balance states that the amount of solute (adsorbate) adsorbed onto the solid (adsorbent) must be equal to the amount of solute removed from the solution. In mathematical term as it is given below⁽⁵⁶⁾:

$$q_e = \frac{V}{W} (C_o - C_e) \quad \dots\dots\dots 3.1$$

Where

V = Volume of solution (Liter)

W = Weight of adsorbent in batch experiments (gm)

C_o and C_e = are expressed in mg solute per unit liter of solution and the adsorption graphs are presented on mg/g basis.

The percentage adsorption is calculated as follows:

$$\% \text{ Adsorption} = \frac{(C_o - C_e)}{C_o} * 100 \quad \dots\dots\dots 3.2$$

3.5.3 Effect of Time:

Kinetic experiment is used to obtain the external mass transfer coefficient k_f and the pore diffusion coefficient D_p by using a well stirred batch contactor. The solute concentration is measured with time using atomic absorption spectrometer.

A volume of one liter Pyrex beaker was used and a magnetic mixer. The beaker was filled with 50 ml of metal ion solution of known concentration of 0.0093 Zn(II) and 0.266 ppm Cr(III) and the agitation started before adding the kaolinite. At time zero, the calculated weight of kaolinite was added, and then the samples were taken at every 5-40 min during the experiment.

The weight of kaolinite used to reach an equilibrium concentration is calculated as mentioned in equation 3.1 and by using Langmuir equation.

$$W = \frac{V(C_o - C_e)}{\frac{q_m b C_e}{1 + b C_e}} \dots\dots\dots 3.3$$

Where b is a constant.

The experiments were carried out at constant temperature $25^{\circ}\text{C} \pm 1$ and the pH of solution was adjusted to the required pH by adding of diluted HNO_3 or NaOH (0.1 M).

Chapter Four

Results and Discussion

4-1 Introduction:

In batch experiments, the effect of three variables , namely (mass of adsorbent as Kaolinite, shaking time, and the initial metal ion concentration on the removal of Cr(III) & Zn(II)) from natural wastewater Petroleum Refinery liquor by adsorption onto Kaolinite as an adsorbent was studied.

4-2 Effect of Different Operation Variables on the Removal of Cr(III) and Zn(II):

4.2.1 Effect of Kaolinite Weight:

The effect of mass of Kaolinite on adsorption of metal ions at constant adsorbate concentration was studied for the purpose of determining the optimum adsorbent mass that will bring a best removal.

The results of the dependence of metals ions namely Cr(III) and Zn(II) on the mass of Kaolinite of size 0.6 mm at 25°C are shown in Figs. 4.1 and 4.2. These figures represent the plotting of the percentage removal of metal ions against the mass of the Kaolinite respectively.

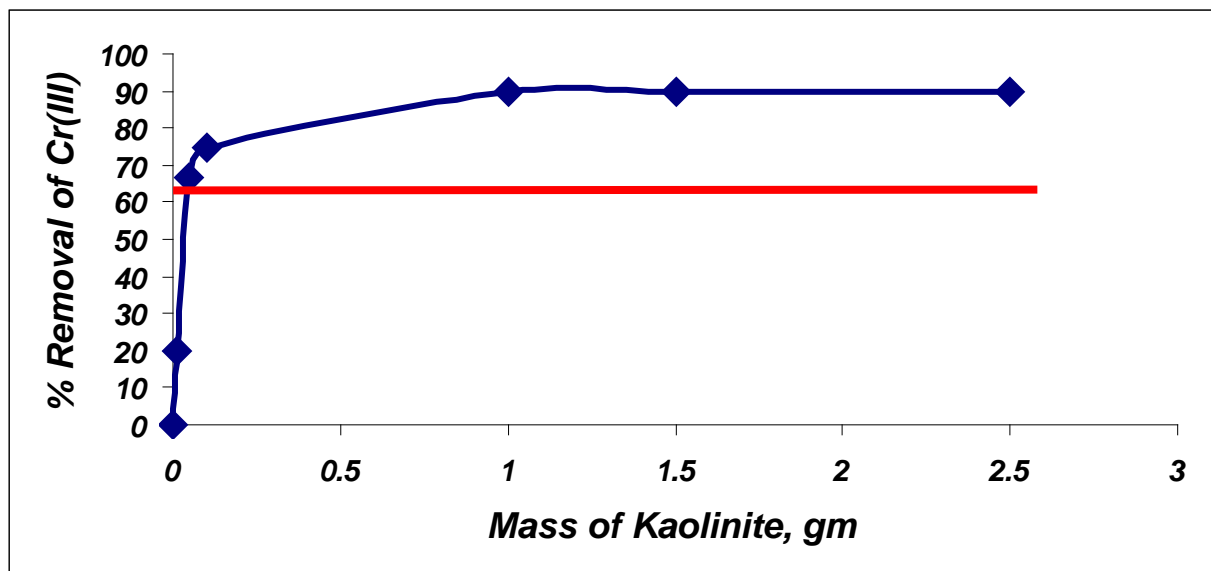


Fig.4.1: The effect of Kaolinite mass on adsorption of Cr(III).

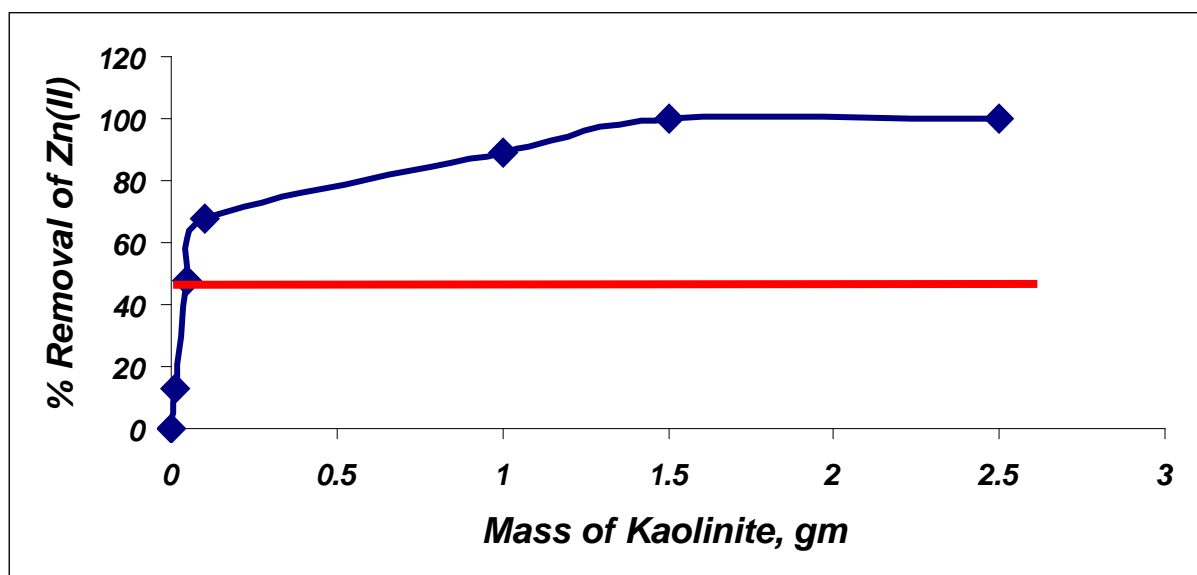


Fig.4.2, The effect of Kaolinite mass on adsorption of Zn(II)

These figures can clearly show that the percent removal of metal ions increases with increasing weight of Kaolinite up to a certain value depending on metal ions and then there is no further increase in

adsorption for metal ions, therefore, the optimum mass of Kaolinite selected were 1.0 and 1.5 g/10ml for Cr(III) and Zn(II) respectively. The increase in the percent removal of metal ions with increase in mass of Kaolinite is due to the greater availability of adsorption sites or surface area of adsorbent. The adsorption of Cr(III) by Kaolinite will increase in adsorption with mass of adsorbent can be contributed to increased surface area and the availability of more binding sites for adsorption.

The red line in these figures represent the regulation limits of Cr(III) and Zn(II) discharged into industrial wastewater from petroleum refineries.

We can see from the previous figures that the removal percent of zinc is higher than that of chrom because the ability of zinc is higher than of chrom. These notes were agreement by the following authors ;

Shekinah et al. (2002), Badmus et al. (2007) reported similar finding for Pb(II) adsorption by activated carbon. Esmaeili et al. (2008) also show the same result for adsorption of Cu(II) by activated carbon prepared from algae graciloria and explained that an increase in adsorbent mass provides great surface area. Mor et al. (2007) studied the adsorption of Cr(III) by activated charcoal and explained that the increase in adsorption with mass of adsorbent can be contributed to increased surface area and the availability of more binding sites for adsorption. Rengaraj and Moon (2002) obtained the same results for adsorption of Co(II) by ion exchange resins.

4.2.2 Effect of Mixing Period:

The mixing period is the average time spent by the liquid in the agitation stage and is thus the time of contact between the wastewater and Kaolinite added. The removal of metal ions Cr(III) and Zn(II) using Kaolinite, as a function of Mixing time is presented in Figs. 4.3 and 4.4.

The mixing time is an important variable which controls the adsorption and plays an important role in the adsorption mechanisms. The experiments were performed by varying mixing time of the samples ranging from 10 to 60 minutes after adding adsorbent. The optimum mass of adsorbents used was obtained from the previous experiments.

The adsorption of these metal ions increases rapidly with increasing mixing time up to a certain value of mixing value depending on the metal ions then the removal reached steady state.

From these figures it can be indicated that the percent removal of metal ions Cr(III) and Zn(II) increase rapidly until it reaches a certain value and then be almost constant so that there is no necessary to increase the mixing period after this point.

Based on the present work the optimum mixing time chosen for Cr(III) and Zn(II) were 40, 30 minutes respectively for adsorption of these metals in single component system.

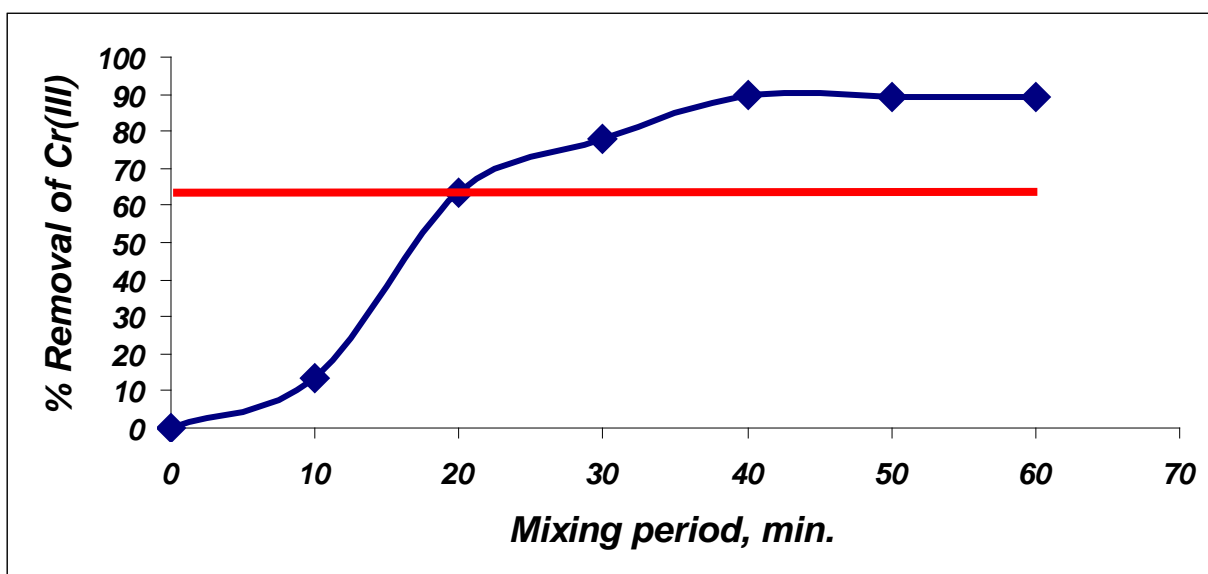


Fig.4.3: The effect of mixing time on adsorption of Cr(III) by Kaolinite

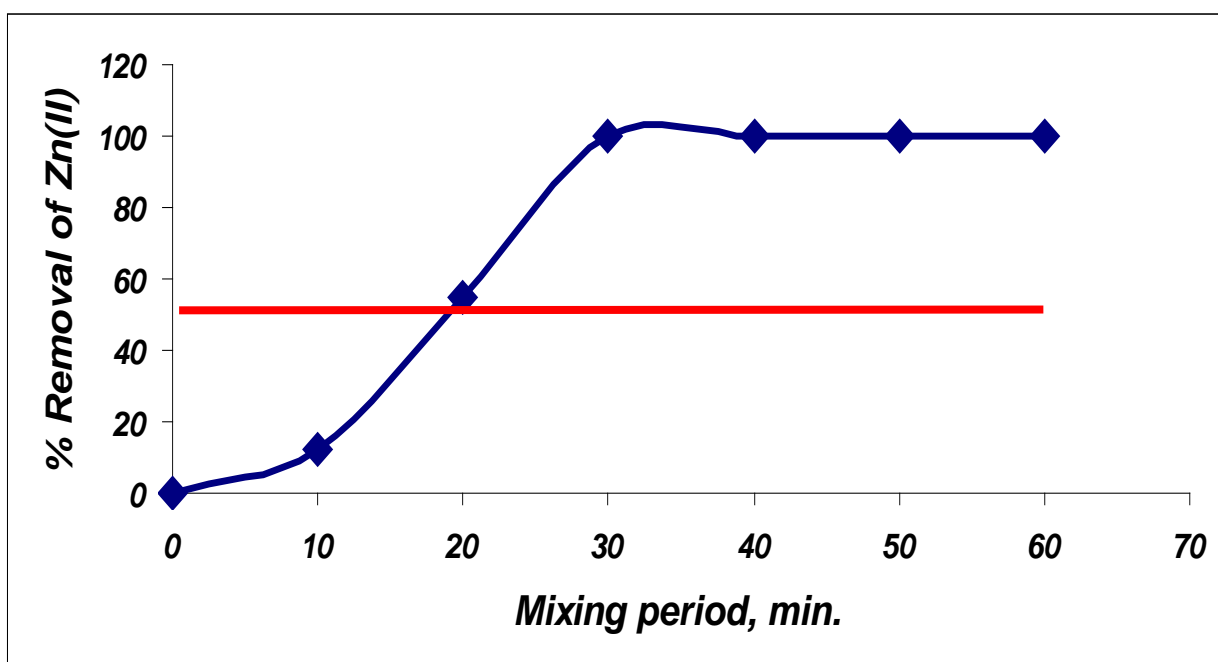


Fig.4.4: The effect of mixing time on adsorption of Zn(II) by Kaolinite.

The red line in these figures represent the regulation limits of Cr(III) and Zn(II) discharged into industrial wastewater from petroleum refineries.

The same behavior has been reported by Mohan and Singh (2002) for adsorption of Cd(II) and Zn(II) using activated carbon, Hashem (2007) for adsorption of Pb(II) using okra waste, Esmaeili et al. (2008) for adsorption of Cu(II) using activated carbon and Teker et al. (1999) for adsorption of Cu(II) and Cd(II) by activated carbon from rice hulls. All those investigators show that the removal of metal ions increased with an increase the mixing time of the solution.

4.2.3 Effect of Initial Concentration:

The effect of initial concentration of Cr(III) and Zn(II) in the feed industrial wastewater on the removal efficiency as shown in figures (4.5) and (4.6) respectively at constant mixing time and weight of adsorbent was obtained from the previous experiments.

these figures shows the influence of initial concentration of the Cr(III) and Zn(II) in the feed industrial wastewater on adsorption at constant mixing periods and using constant Kaolinite addition (optimum value 1.0, 1.5 gm)respectively.

These figures indicates that the percent removal of the metal ions increase with increasing the initial concentration of the Cr(III) and Zn(II) in the feed industrial wastewater until it reaches a certain value.

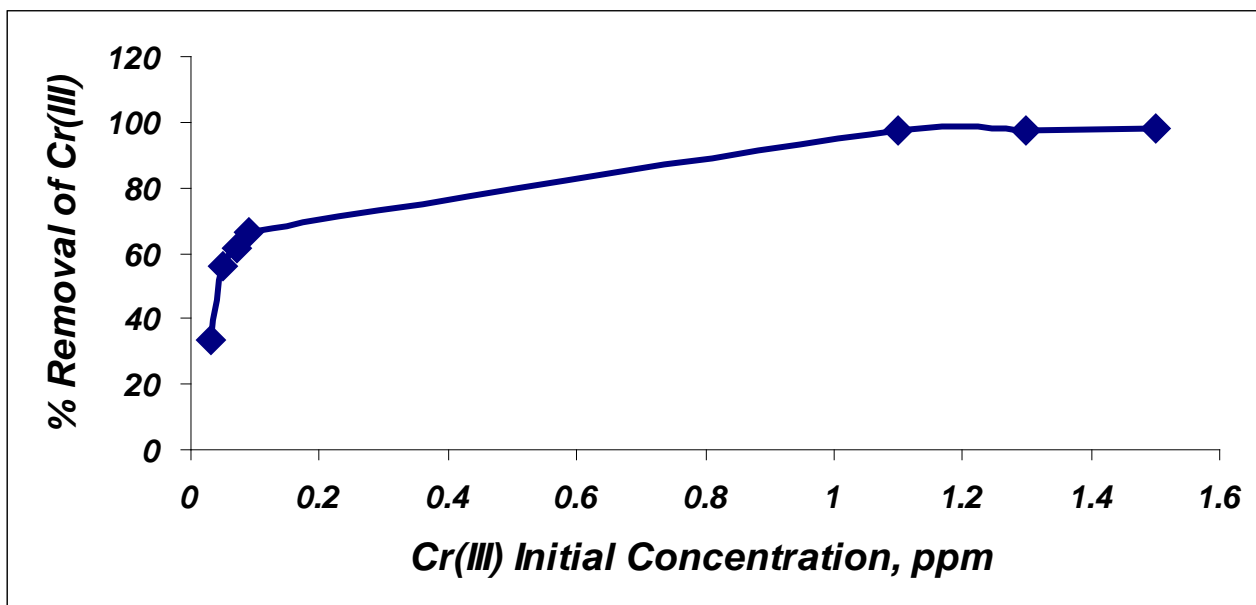


Fig.4.5: The effect of initial concentration of Cr(III) on adsorption by Kaolinite.

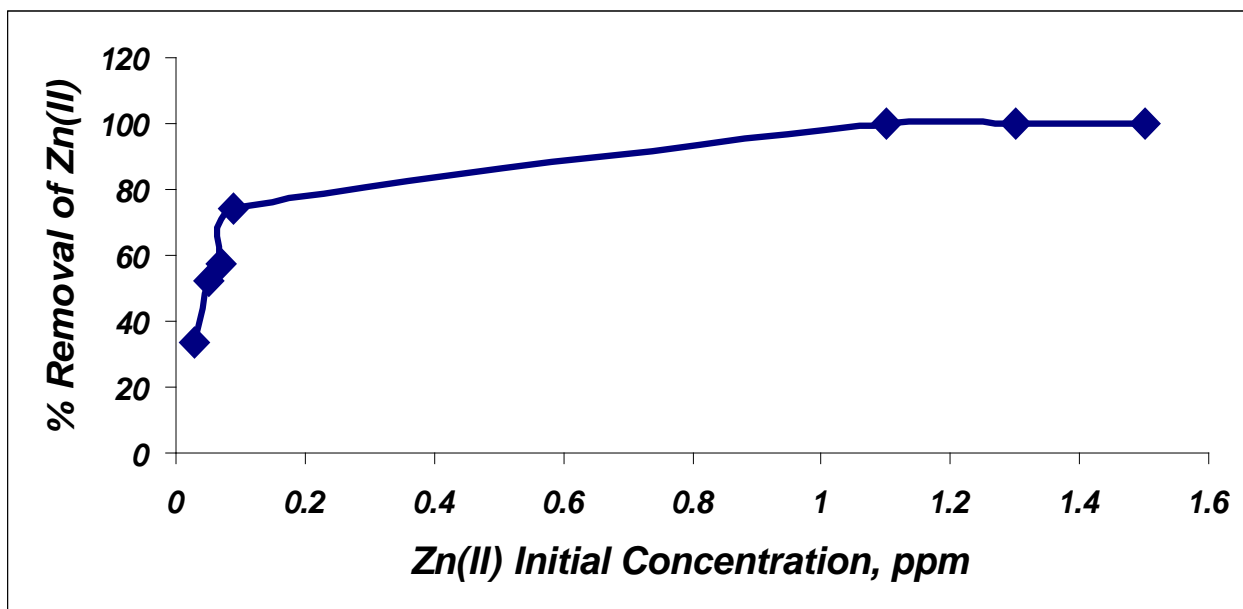


Fig.4.6: The effect of initial concentration of Zn(II) on adsorption by Kaolinite.

4.3 The Best Conditions:

From all of the above figures, the best conditions for the high removal efficiency of Cr(III) and Zn(II) can be obtained as shown below:

Kaolinite weight = 1.0 gm for the Cr(III), 1.5gm for Zn(II) removal.

Mixing period = 40 min. for the Cr(III), 30min. for the Zn(II).

Initial conc. of the Cr(III) and Zn(II)= 1.5 ppm, 1.1 ppm respectively.

The residual Chromium conc. in the effluent = 0.03 ppm

The residual Zinc conc. in the effluent = zero ppm

4.4 Equilibrium Isotherm Experiments:

The adsorption isotherm curves were obtained by plotting the weight of the solute adsorbed per unit weight of the adsorbent (q_e) against the equilibrium concentration of the solute (C_e). The values of q_e for each metal ion were calculated using equation 3.1 in chapter three and listed in Table B-1 and Table B-2 appendix B. Figs. 4.7 and 4.8 show the adsorption isotherm curve for single metal ions Cr(III) and Zn(II) onto Kaolinite at 25°C respectively.

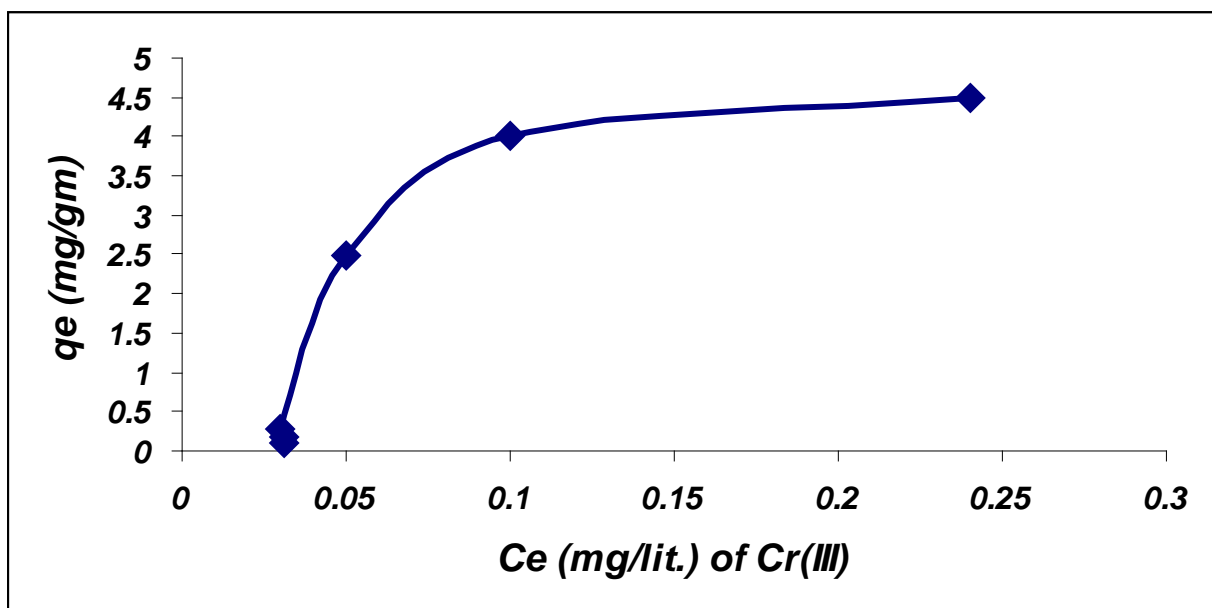


Fig.4.7: Adsorption isotherm for Cr(III) onto Kaolinite.

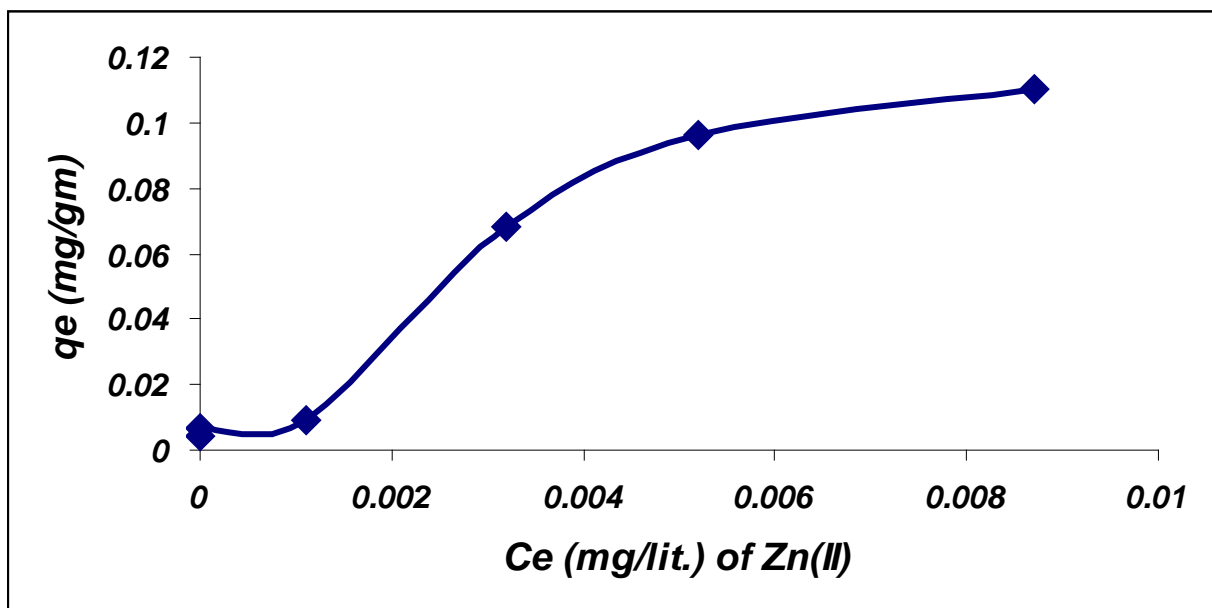


Fig.4.8: Adsorption isotherm for Zn(II) onto Kaolinite.

Chapter Five

Conclusions and Recommendations

5.1 Conclusions:

In the present work the adsorption of metal ions named Zn(II), Cr(III) onto Kaolinite for single component system lead to the following conclusions:

1. From the experimental tests concerned with industrial wastewater discharged from the Daura Petroleum Refinery, it was found that these wastewater were acidic ($\text{pH} = 6.5$) and polluted with chromium and Zinc at relatively concentration of greater than 0.5 mg/lit.
2. In batch adsorbed the pore diffusion model has been successfully applied to the adsorption of metal ions onto Kaolinite in single component system.
3. For adsorption treatment, Kaolinite can be used for this process. The optimum Kaolinite dosage was found by a number of tests to be about 1 gm, and 1.5 gm; this gives an acceptable removal of Chromium and Zinc metal of about (90% and 100%).
4. For the mixing time in the experimental work it was found that mixing process was continued for 40, 35 min. at speed of 250 rpm to achieve the efficient removal of chromium and Zinc metal.
5. The settling time (30-40) min. is to be sufficient to obtain a removal efficiency of about 90% of chromium and Zinc metal further time did not improve the recovery.

6. The optimum conditions for adsorption process wastewater treatment in the case study were:

For the removal of the chromium metal:

| Kaolinite addition | mixing period | Cr initial conc. |
|--------------------|---------------|------------------|
| 1.0 gm | 40 min. | 1.5 mg/lit. |

For the removal of the Zinc metal:

| Kaolinite addition | mixing period | Zn initial conc. |
|--------------------|---------------|------------------|
| 1.5 gm | 30 min. | 1.1 mg/lit. |

7. The efficiency of the addition of the Kaolinite to adsorbed the chromium and the Zinc metals was found to be increasing with the increasing the initial concentrations of the chromium and the zinc in the feed industrial wastewater.
8. The Zinc concentration could be decreased from a value of 1.1 to zero mg/lit. in the effluent from the adsorption process and that for chromium from a value of 1.5 mg/lit. to 0.03mg/lit.

5.2 Recommendations:

1. The experimental tests should be carried out daily on the effluents to ensure and keep uniform specifications that is able to recycle and reuse.
2. This study may be extended by investigate the effluence of Kaolinite on the other heavy metals.
3. For further study the effect of pH can be investigated on the adsorption process.
4. The operators of the plant should be trained on the plant run, knowing how to operate the plant especially the process of Kaolinite adding, and the process of adsorption.
5. For future works it is preferable to study and evaluate the plant efficiency for removing of the pollutant. That is representing an observation about plant operation.
6. The high efficiency of removal the chrome and Zinc metals (90% and 100% respectively) and the level of pH of the effluent, can be lead to reuse the water which out from the treatment unit as a fresh water.
7. This study may be extended by using the low cost material such as clays as an adsorbent for removal of heavy metals. The use of clay mineral as adsorbent is limited by low hydraulic permeability of packed clay. Hence it is recommended to increase the permeability of clay in order to used it as an adsorbent in fixed bed adsorber.
8. This work can be extended to study the multi-component adsorption of three metal ions onto Kaolinite .

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Appendix A

Analytical Technique

Analytical Technique;

Atomic adsorption spectrometer (AAS) was used to measure the metal ion concentration. AAS parameters are:

- Lamp : Hallow cathode lamp
- Fuel : Acetylene
- Oxidant : Air

The procedure for analysis by AAS is:

- Choose the proper hallow cathode lamps.
- Select the proper slit width and adjust the hallow cathode current.
- Light the flame and regular the flow of the fuel and oxidant,
- Prepare of AAS standard solution.
- At the first run the distilled water as blank. The adsorbance should be zero(o ppm, 0 abs.) is a data point for the subsequent calibration curve.
- Run a series of standards of the element under analysis and construct a calibration curve by plotting the concentrations of the standard against the absorbance signal.
- Run the samples and determine the concentration from the calibration curve.
- Read the metal ion concentration value in mg/l from the calibration curve.

Fig. A.1 shows the calibration curve. The analysis on AAS of each samples was carried in triplicate and the mean was computed for each set of values.

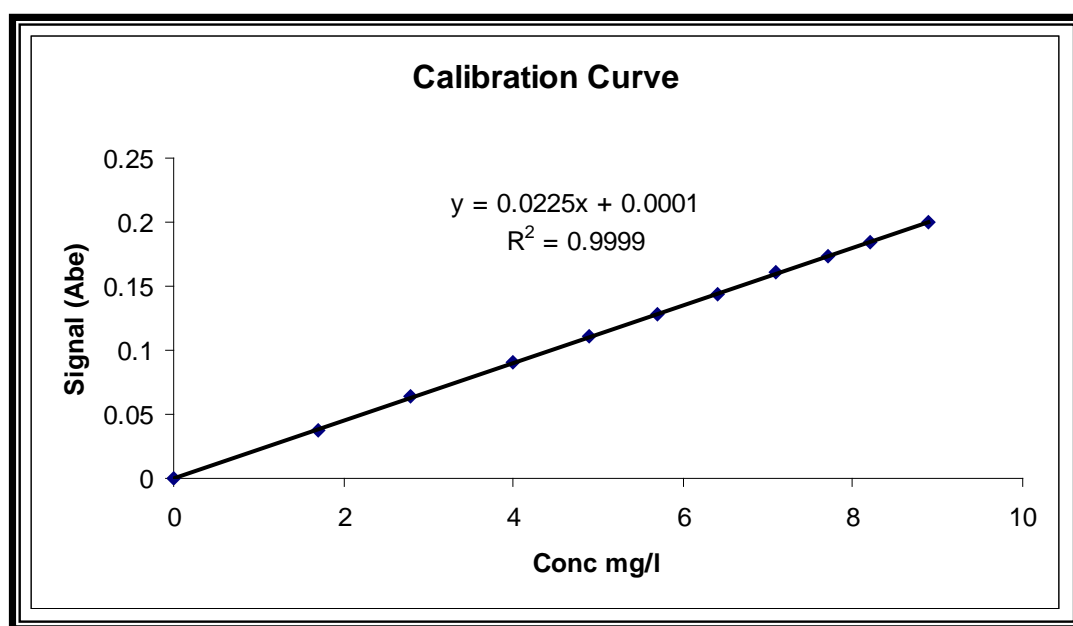


Fig. A.1, Calibration curve in AAS

In the present work the operating conditions for the AAS are shown in the table A.1 below:

Table A.1, Operating conditions for the AAS

| Metal ion | Lamp current | Wavelength | Slit width |
|-----------|--------------|------------|------------|
| Cr(III) | 25 | 357.87 | 2.7/0.8 |
| Zn(II) | 30 | 240.73 | 1.8/1.35 |

Appendix B

Batch Experiments Results

a: Effect of Kaolinite Dose

Table B-1, Effect of Kaolinite Mass on adsorption of Cr(III):

| W (g) | C _e (mg/L) | % Removal | q _e mg/gm |
|----------|--------------------------|--------------|-------------------------|
| 0 | 0.3 | 0 | - |
| 0.01 | 0.24 | 20 | 4.5 |
| 0.05 | 0.1 | 66.66667 | 4 |
| 0.1 | 0.076 | 74.66667 | 2.5 |
| 1 | 0.03 | 90 | 0.27 |
| 1.5 | 0.031 | 89.66667 | 0.179333 |
| 2.5 | 0.031 | 89.66667 | 0.1076 |

Table B-2, Effect of Kaolinite mass on adsorption of Zn(II):

| W (g) | C _e (mg/L) | % Removal | q _e mg/gm |
|----------|--------------------------|--------------|-------------------------|
| 0 | 0.01 | 0 | - |
| 0.01 | 0.0087 | 13 | 0.11 |
| 0.05 | 0.0052 | 48 | 0.096 |
| 0.1 | 0.0032 | 68 | 0.068 |
| 1 | 0.0011 | 89 | 0.0089 |
| 1.5 | 0 | 100 | 0.006667 |
| 2.5 | 0 | 100 | 0.004 |

b: Effect of Mixing Period of Solution:**Table B-3**, Effect of Mixing period on adsorption of Cr(III) :

| Time Min. | C _e (mg/L) | % Removal |
|--------------|--------------------------|--------------|
| 0 | 0.3 | 0 |
| 10 | 0.26 | 13.33333 |
| 20 | 0.11 | 63.33333 |
| 30 | 0.066 | 78 |
| 40 | 0.03 | 90 |
| 50 | 0.032 | 89.33333 |
| 60 | 0.032 | 89.33333 |

Table B-4, Effect of Mixing period on adsorption of Zn(II) :

| Time Min. | C _e (mg/L) | % Removal |
|--------------|--------------------------|--------------|
| 0 | 0.01 | 0 |
| 10 | 0.0088 | 12 |
| 20 | 0.0045 | 55 |
| 30 | 0 | 100 |
| 40 | 0 | 100 |
| 50 | 0 | 100 |
| 60 | 0 | 100 |

c: Effect of Cr(III) initial concentration:**Table B-5**, Effect of Cr(III) Initial Concentration on adsorption of Cr(III)
:

| Cr(III) Initial Conc. ppm | Ce (mg/l) | % Removal |
|--|----------------------|----------------------|
| 0.03 | 0.02 | 33.33333 |
| 0.05 | 0.022 | 56 |
| 0.07 | 0.027 | 61.42857 |
| 0.09 | 0.03 | 66.66667 |
| 1.1 | 0.03 | 97.27273 |
| 1.3 | 0.03 | 97.69231 |
| 1.5 | 0.03 | 98 |

Table B-6, Effect of Zn(II) Initial Concentration on adsorption of Zn(II)
:

| Zn(II) Initial Conc. ppm | Ce (mg/l) | % Removal |
|---|----------------------|----------------------|
| 0.03 | 0.02 | 33.33333 |
| 0.05 | 0.024 | 52 |
| 0.07 | 0.03 | 57.14286 |
| 0.09 | 0.023 | 74.44444 |
| 1.1 | 0 | 100 |
| 1.3 | 0 | 100 |
| 1.5 | 0 | 100 |

معالجة المياه الصناعية الملوثة من المصافي النفطية (إزالة المعادن الثقيلة)

أعداد

علي حاتم احمد

(بكالوريوس في الهندسة الكيماوية – 2004)

بإشراف

أ.د. ثامر جاسم محمد

الخلاصة

يتناول البحث دراسة معالجة المياه الملوثة الصناعية في مصفى الدورة بواسطة عملية الأمتزاز , لإزالة المعادن الثقيلة ايونات الكروم الثلاثية وايونات الزنك. معدل المياه الملوثة المطروحة من مصفى الدورة تقدر بحوالي ($850 \text{ m}^3/\text{hr}$), لذلك فإن لها تأثير كبير على تلوث مياه النهر .

أجريت التجارب بعملية الأمتزاز بالوجبات بواسطة الكاولين بالمواصفات حجم الفراغات ($0.45\mu\text{m}$) كعامل ممتاز . أخذت العينات المعالجة من المياه الملوثة بعد عملية (API separator) وأخضعت لعملية الأمتزاز . ضبطت العينة إلى المستوى المطلوب من تركيز ايونات الكروم وايونات الزنك بواسطة إذابة كميات محددة من أملاح المعادن عند pH ثابت ويساوي (6.5) .

درست تأثير عدة متغيرات عملية مثل وزن المادة المازة (الكأولين) $(0.01 - 2.5) \text{ gm}$,
زمن المزج $(10-60) \text{ min}$, التركيز الابتدائي لايونات الكروم والزنك $(0.03-1.5) \text{ gm}$.
لتحقيق أعلى نسبة إزالة .

أن النتائج التي تم التوصل إليها خلال التجارب المختبرية تظهر أن نسبة إزالة المعادن
الثقيلة لكل من الكروم والزنك تزداد بزيادة وزن المادة المازة (الكأولين) و بزيادة زمن المزج.
حتى تصل إلى 100% وبعد إجراء التجارب تبين أن الظروف المثلى لمعالجة هي
 $(1.0 \text{ and } 1.5) \text{ gm}$, وزمن المزج $(30 \text{ and } 40) \text{ min}$, والتركيز الابتدائي
 $(1.1 \text{ and } 1.5) \text{ mg/lit}$ لكل من الكروم والزنك على التوالي.

أظهرت النتائج المختبرية بأن التركيز المتبقي لكل من الكروم و الزنك بعد معالجة المياه
الملوثة هي $(0.03, 0.0) \text{ ppm}$ على التوالي , وهذه القيم تتوافق مع الحدود المسموح بها
للخصائص القياسية المعتمدة من قبل منظمة الصحة العالمية والمواصفات العراقية .