ADSORPTION OF LEAD (II) IONS FROM INDUSTRIAL EFFLUENT BY USE OF EGGSHELL

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BSC.

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DECLARATION

Declaration by the Candidate

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DEDICATION

I dedicate this thesis to my parents Major RTD & Mrs. Alexander C. Sirma and my husband Disan C. Lagat who they believed in me while undertaking my studies. Their encouragement and moral support gave me determination to work hard. Thank you so much.

ABSTRACT

Heavy metals are major toxicants found in industrial effluent and have been known to contaminate the water resources. They include metals such as lead, cadmium, arsenic and chromium which pose a significant threat to the environment and public health because of their toxicity, accumulation along the food chain and their recalcitrance in nature. The aim of the study was to investigate the removal of lead (II) ions from raw industrial effluent using low cost sorbent; eggshell. Industrial effluent samples were collected through purposive sampling at the point of discharge before treatment, from the Associated Battery Manufacturing Company in Nairobi. The lead concentration in the effluent samples collected was analyzed by use of the Atomic Absorption Spectrophotometer (AAS) (Spectra AA50). Crushed eggshell of different particle size were added to the sample stirred using magnetic stirrer for 30 minutes to attain equilibrium. After contact time, equilibrium uptake of lead (II) ions by the eggshell was achieved. Filter paper grade 54 was used to filter the eggshell so as to obtain the filtrate. The exact concentration of the filtrate was then determined using the AAS. The experimental research design used was the Randomized block design. This entailed the varying of process parameters like effects of pH, sorbent size, sorbent amount, and contact time in the sampled effluent. Results obtained were analyzed to compare the lead (II) ions removal efficiency between raw and boiled eggshells. All the data represents the mean of three independent experiments. Data analysis was performed using statistical function of the Microsoft excel 2007. Maximum adsorption of Pb^{2+} on eggshell was observed at pH = 5. Adsorption equilibrium was established in about 120 minutes and the mass of eggshell used was 10 g/L of particle size using sieve No. 355µm. The data generated were fitted on three adsorption models, Langmuir, Freundlich and Temkin models to determine the best fit model. Langmuir model was the best fitted model on the raw eggshell with a correlation coefficient $R^2 = 0.994$ and adsorption capacity of 11.63 mg/g, this was followed by Freundlich $R^2 =0.926$ and then the Temkin Isotherm $R^2 = 0.875$. The results showed that the egg shell removed the lead (II) ions from the industrial effluent from 19.2 mg/L to 0.2023 mg/L which is below the recommended water quality standards for effluent discharge to public sewers within optimum conditions.

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ACRONYMS

AC	Activated Carbon
AAS	Atomic Absorption Spectrophotometer
ABM	Associated Battery Manufacturers
$CaCl_2$	Calcium Chloride
$CaCO_3$	Calcium Carbonate
$Ca(OH)_2$	Calcium Hydroxide
$(CaPO_3)$	Calcium Phosphate
EMCA	Environmental Management and Coordination Act
$(FeCl_3)$	Ferric Chloride
$(FeSO_4)$	Ferrous Sulfate
g/L	Grams per liter
HCl	Hydrochloric Acid
HNO_3	Nitric Acid
$KAL\ (SO_4)_2 \,.\, 12H_2O$	Alum
KEBS	Kenya Bureau of Standards
$MgCO_3$	Magnesium Carbonate
mg/L	Milligrams per liter
mL	Milliliter
NEMA	National Environmental Management Authority

Pb $(NO_3)_2$	Lead (II) nitrate
PPM	Parts Per Million
RPM	Revolution per minute
TDS	Total Dissolved Solids
µm	Micrometer
WHO	World Health Organization

DEFINITION OF TERMS

Adsorption: mass transfer process by which a substance is transferred from liquid phase to surface of solid phase and become bound by physical and chemical interaction.

Adsorbent: material used in the adsorption process to remove the heavy metal from industrial effluent.

Atomic Absorption Spectrometer: Analytical equipment used to measure quantities of chemical elements in environmental samples by measuring adsorbed radiations of chemical element of interest

Adsorption Isotherm: defined by graphical representation showing the relationship of the amount of the heavy metal adsorbed by unit weight of the adsorbent**.**

Bisorption: Selective sequestering of metal soluble species that result in the immobilization of metal by microbial cells. The process is metabolically passive and does not require energy.

Conventional methods: Traditional methods used in the treatment of industrial waste water effluent such as chemical precipitation, reverse osmosis, coagulation and flocculation.

Heavy metals: Metallic chemical element that has relatively high density, specific gravity greater than 5.0 g/cm^3 and its toxic to human beings.

Low cost Adsorbent: these are materials that are locally and easily available which require little processing, are abundant in nature and considered as a byproduct or waste from an industry and may be used in the adsorption of heavy metals.

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CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Fast population growth, rapid rate of urbanization, waste generation from domestic and industrial sources have rendered many water sources unwholesome, hazardous to man and the environment in many countries including Kenya. The water resources requirement is continuously increasing in the world while on the other hand water is becoming unfit due to rapid rate of pollution through indiscriminate disposal of solid and liquid waste. This therefore necessitates the treatment of industrial waste waters in order to allow industrial effluent to be disposed off without bringing about any associated dangers to the human health and the natural environment (Nordberg *et al.***,** 1979).

Metals enter the ecosystem primarily through indiscreet disposal of chemical and metal wastes from industrial, domestic and agricultural activities. Heavy metals include elements such as lead, cadmium, mercury, chromium and arsenic that are highly toxic when adsorbed into the body (Nordberg *et al.***,** 1979). Being non-biodegradable, these metals accumulate in the tissues and organs of living organisms thereby affecting the normal body process. They are toxic and carcinogenic substances with no essential function to the human body but only detrimental effects (Parmar and Thakur, 2013).

Lead is one of the heavy metals that occur naturally in the environment. It is among the earliest metals recognized (Garty, 2001) and has been used since 5000 BC for application in metal products, cables, building materials, storage batteries, electrodes in the process of electrolysis, ammunitions and pipelines. It is also used in the glass of computer and television screens where it shields the viewer from radiation.

Lead (II) ions are hazardous in the environment since they bind strongly to particles such as soil sediments and sewage sludge and hence its removal from the environment is of great concern. It can enter the human body through uptake of water (20%), food (65%), and air (15%) and has the most damaging effect on human health (Nurchi and Villaescusa, 2008). It can cause damage to central nervous system, kidney, liver, reproductive system and basic cellular processes. Toxic symptoms associated with lead (II) ions include; anaemia, insomnia, rise in blood pressure, headache, dizziness, irritability, weakness of muscles, hallucination, disruption of biosynthesis of haemoglobin and renal damages (Naseem and Tahir, 2001). Studies have shown that lead affects even unborn children it enters the foetus through the mother’s placenta leading to serious damage to the nervous and brains of the unborn children (Babel and Kurniawan, 2003).

Most of the lead concentrations found in the environment are due to increased anthropogenic activities such as industrial processes, fuel and solid waste combustion. There are several industries responsible for the release of waste water containing lead (II) ions to the environment include; painting, coating, refineries, photographic materials, explosives, automotive, steel and storage battery industry (Garvrilescu, 2004).

Conventional methods used in the treatment of industrial waste water containing heavy metals include; solvent extraction, chemical precipitation (Wang *et al.,* 2004), ion exchange and electrochemical treatment (Kurniawan *et al.,* 2006). These technologies have advantages as well as limitations which include incomplete metal removal, high capital costs, high reagent and energy requirements, and generation of toxic sludge or other waste products that require disposal (Cho and Kim, 2003; Göksungur *et al.*, 2005). These challenges have facilitated the search for new technologies that can reduce the heavy metal concentrations to environmentally acceptable levels especially with the increasingly strict discharge limits.

Adsorption of heavy metals is a current technology employed in removal of the toxic metals from industrial waste streams. Several studies have been able to prove the effectiveness of sorption for the heavy metal removal (Arunlertaree *et al.*, 2007; Tolga *et al.*, 2003; Rashed, 2003). It is preferred due to low operating cost and possibility of metal recovery, minimization of chemical toxic sludge, being cost effective for treatment of large volumes of waste water containing low pollutant concentration and offers high efficiency in detoxifying effluents. Agricultural materials (banana peel, cassava waste, rice husks) are treated as waste products and may have great potential as inexpensive heavy metal sorbents (Abia *et al.*, 2003; Nurchi and Villaescusa, 2008).

In this study, the sorbent material studied is the eggshell. Normally, most of the eggshell is disposed of into the environment and contributes to air pollution due to decomposition (Tsai *et al.*, 2008). Eggshell is a ceramic material arranged in 3 layer structure and has well developed intrinsic pore structure and pure calcium carbonate as an important constituent (Stadelman, 2000). It is abundant in generation and composed of calcium carbonate which is calcite and known to adsorb metals. The eggshell is thus proposed to be used as an alternative to the chemical calcium carbonate used in chemical precipitation method in the treatment of industrial effluent.

1.2 Problem statement

Currently industrial liquid and solid waste management has become one of the most challenging tasks to manage because tonnes of industrial pollutants are being disposed of without sufficient treatment as prescribed by the National Environmental Management Authority (NEMA). Lead metal pollution is a major and serious problem to the environment because of its toxicity and associated negative effects on human health.

Standards have been set about water quality by Kenya Bureau of Standards (KEBS) and World Health Organization (WHO) to reduce health hazards. According to Environmental Management and Coordination Act (Water Quality Regulations, 2006), guideline values for discharge of lead into public sewers are at a concentration of 1 mg/L, into public water is 0.01mg/L and for drinking and bottled water also has a set standard of 0.05 mg/L of lead concentration. Government agencies concerned have the authority to monitor the industrial waste water disposal to safeguard the water bodies against pollution.

Despite set standards and the current technologies employed in the treatment of industrial effluent, water pollution from lead (II) ions contamination is still present. This has attracted a lot of attention to scientists to carry out studies to help in study of environmental pollution from heavy metal bearing effluents (de Carvalho *et al.*, 2003).

The current technologies employed in the removal of toxic industrial lead metal ions normally produce waste water containing concentrations beyond the regulated standards resulting in environmental degradation. The chemical precipitation method by use of lime; for example generates abundant amount of lead contaminated gypsum sludge which is toxic and its disposal is cumbersome even though the method is cost effective. On the other hand, ion exchange process is considered expensive, due to the cost of the synthetic ion exchange resins, which are non-biodegradable and not selective enough to allow an efficient recovery of heavy metals present in waste water. As for the solvent extraction method is limited to streams containing more than 1 g/L of the targeted heavy metal (Valdman and Leitel, 2000) while the use of the activated carbon adsorbent is limited due to the depleted source of commercial coal and increase in their prices with increase in the quality of coal (Babel and Kurniawan, 2003). In order to curtail the risk of pollution problem from the effluent, it is necessary to accurately treat the waste water before discharging to the environment.

Based on the problems discussed above, this study provided an alternative method of lead removal in industrial effluents using locally available material. In this study, the industry of interest is a battery manufacturing industry. It uses lead metal as one of the major raw materials, because of its conductivity, resistance to corrosion, and the reversible reaction between lead oxide and sulphuric acid that makes them rechargeable. Battery industry waste water effluent contains lead (II) ions that contribute to water contamination (Altas *et al*., 2005). The study entailed the removal of lead (II) ions from raw industrial effluent from Associated Battery Manufacturing Company in Nairobi, by use of waste eggshell. In this scenario, the principle of re-use in waste management was also applied.

1.3 Objectives of the Study

1.3.1 General Objective

The general objective of the study was to investigate the removal of lead (II) ions from raw battery industrial effluent by use of eggshell powder in order to prevent pollution of environment.

1.3.2 Specific Objectives

The research study was guided by the following specific objectives:

i. To determine the levels of lead (II) ions, total dissolve solids (TDS), pH level in raw industrial effluent obtained from associated battery manufacturing company in Kenya;

ii. To determine the optimal pH, sorbent size, sorbent dose and contact time for effective in the removal of Pb (II) ions using raw and boiled eggshells from the raw battery industrial effluent;

iii. To compare the experimental equilibrium data for both raw and boiled eggshell using the adsorption equilibrium models.

1.4 Research Hypothesis

1.4.1 General hypothesis

The bisorption technique of industrial waste water treatment by use of waste eggshell in a battery manufacturing company can aid in the removal of lead and prevent pollution of water bodies from heavy metals.

1.4.2 Statistical hypothesis

H_0: Waste eggshell is not effective in the removal of lead (II) ions from the raw industrial waste water effluent.

H_0: There is no significant difference in the removal of lead (II) ions by use of either boiled or raw eggshells from the raw industrial effluent.

1.5 Justification of the Study

The water contamination by heavy metals through discharge of industrial waste water is a an environmental problem. Unlike other pollutants that are susceptible to biological degradation, heavy metals are dangerous environmental pollutants due to their toxicity and strong tendency to concentrate in the environment and along the food chain. Lead metal and its compounds are toxic to human if its concentration in drinking water is above the recommended levels. The human body cannot process or eliminate the lead metal thus leading to bioaccumulation in fatty tissues and internal organs such as the brain, heart, kidney, liver, pancreas, and nervous system. This leads to neurotoxicity, hypertension, reduced intelligence, and hyperactivity syndrome (Naseem and Tahir, 2001). Therefore, the removal and recovery of lead is important for environmental and health protection.

Lead is a constituent of effluent in battery manufacturing industries. Most of the industries use the conventional means of treatment of the industrial effluent which generally involve chemical precipitation. The techniques are challenging in terms of disposal of the toxic sludge produced, inadequate lead removal and are very expensive especially in a developing country like Kenya. Therefore, this study sought to address these problems by investigating the use of eggshell as a low cost sorbent and assess the extent the eggshells can remove lead from industrial waste water effluent. On the other hand eggshell constitutes significant waste disposal problems for the food industry and investigation into re-use of the waste product is of great importance.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This chapter highlights conventional methods used in the treatment of the industrial waste water effluent, sorbent materials studied in the removal of heavy metals, instrumentation of the atomic absorption spectrometer, equilibrium adsorption isotherm models and similar studies recorded in literature.

2.2 Methods used in the treatment of industrial lead effluent

There are many methods used in removal of heavy metal ions such as chemical precipitation, ion exchange, and chemical oxidation. There are other advanced purification of different physiochemical methods such as active carbon adsorption, membrane filtration, electrochemical treatment technologies and reversed osmosis. These treatments of industrial effluent have their challenges and economic importance.

2.2.1 Chemical precipitation

Chemical precipitation is the commonly used technology used in treatment of industrial effluent. Metal hydroxides such as sodium hydroxides and calcium hydroxides are used. It involves the conversion of heavy metal ions into insoluble metal hydroxides, which precipitate from aqueous solutions. Equation 2.1 shows the reaction equation: (Wang *et al.*, 2004).

$$\mathbf{M^{2+}_{(aq)} + 2\,(OH)^{-} \longrightarrow M(OH)_{2(s)}}\text{.................}\textbf{Equation 2.1}$$

Where: M^{2+} represents the heavy metal ion

$M\,(OH)_2$ represents the insoluble hydroxide which is basic.

This method is most widely used because of its simplicity, low capital investment especially when waste water contains high concentration of heavy metals and safe operation. It has some limitation in that, when the concentration of heavy metals is low it is uneconomical (Wang *et al.*, 2004). Heavy metals are not recovered in this method, large quantities of chemical precipitants are required and there are large volumes of toxic sludge produced and sediments which requires further treatment. In addition, the generated toxic sludge requires license for disposal. The precipitation method also has slow metal precipitation as well as poor settling hence requires improved system design for the waste water treatment (Aziz *et al.*, 2008).

2.2.2 Ion exchange

Ion-exchange method is used in removal of heavy metals from industrial waste water. A solid insoluble resin containing ions of similar charge to the heavy metal ions is placed in the waste water solution. The resin has special ability to exchange its cations with the metals in waste water (Kurniawan *et al*., 2006). The removal of heavy metal ions by ion-exchange resins is affected by certain variables such as pH, contact time, temperature, and the initial metal concentration (Gode and Pehlivan, 2006). Ionic charge also plays an important role in ion-exchange process. Iron exchange method is attractive due to high treatment capacity, no sludge disposal problems, high removal efficiency, and fast kinetics. Despite the advantages, the method is expensive, non selective, non-biodegradable, and uneconomical for effluents with low metal ion concentration. It also cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the waste water (Kurniawan *et al*., 2006).

2.2.3 Coagulation and flocculation

Coagulation process destabilizes colloidal particles and then flocculation of the unstable particles into bulky floccules (El Samrani *et al.,* 2008). Colloidal particles are usually less than 1 µm in size and have poor settling characteristics and contribute to the colour and turbidity of water. Waste water is adjusted to basic pH and coagulating chemicals are added to overcome the electrostatic repulsion of suspended colloidal particles. Coagulants that are used include the alum (KAL $(SO_4)_{2.}$ 12 H_2O), ferrous sulfate ($FeSO_{4)}$ and ferric chloride ($FeCl_3$), resulting in the effective removal of waste water particulates and impurities by charge neutralization of particles (El Samrani *et al.,* 2008*)*. The main advantage of this method is that it takes a shorter time to settle out and has improved sludge settling. Its limitation is in the sludge production, expensive chemical additives and extra operational cost for sludge disposal and treatment.

2.2.4 Electrochemical methods

Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state. It is known for its good reduction yields and less toxic sludge production. The technology involves relatively large capital investment, expensive electricity supply and corrosion of the electrodes. (Kurniawan *et al.*, 2006).

2.2.5 Flotation

The method has been used for a long period due to low holding times and inexpensive operation. Air is passed through waste water and as the air rises, it separates solids and other liquids from solution. Waste water containing higher metal concentration is then removed from the overall solution. Flotation has several advantages, high metal selectivity, removal efficiency, low operating cost, and production of more concentrated sludge (Rubio *et al*., 2007). Its limitation is that it is only used in waste water containing less than 150 mg/L of heavy metal, high initial capital cost and maintenance operation.

2.2.6 Reverse Osmosis

Reverse osmosis is a membrane separation technique that makes use of osmotic pressure and very small membrane pores. Pressure greater than osmotic pressure of water is applied, that forcefully forces the waste water to permeate through the membrane. The process is a highly effective means of water purification but very expensive due to high pressure required for separation (Kurniawan *et al.,* 2006).

2.2.7 Adsorption

Adsorption is one of the most important procedures for removal of heavy metals from the environment. It involves the introduction of solid adsorbent into the waste water and heavy metals bound to it. The main properties for heavy metal removal are strong affinity and high loading capacity (Sari *et al.,* 2007). It requires a simple design and operation and produces treated effluent of high quality. In some cases the sorbent used can be regenerated by suitable desorption process.

2.2.7.1 Activated Carbon Adsorbents

Activated carbon (AC) adsorbents are majorly used in the removal of heavy metal contaminants from the industrial effluents. Any carbon material can be used to make activated carbon; however, commercial activated carbon is manufactured from some carbon sources such as wood, shells, peat, coal and oil products (Babel and Kurniawan, 2003). It is a well known adsorbent due to its large micropore, mesopore volumes, high adsorption capacity and large surface area. The major drawbacks are the poor economic feasibility, limited applicability and effectiveness, and the short lifetime often due to low and expensive regeneration capacities. Activated carbon also requires complexing agents to improve removal performance for inorganic matter not attractive to small-scale industry (Bailey *et al.,* 1999)

2.2.7.2 Low-Cost Adsorbents

A low-cost adsorbent is defined as one which requires little processing, abundant in nature, or is a by-product or waste material from another industry (Bailey *et al.,* 1999). This may include agricultural wastes, industrial by-products and wastes and natural substances. There are several studies carried out in the use of these low cost adsorbents for the treatment of heavy metals wastewater. Bhattacharyya and Gupta, (2008) reviewed the adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite. Babel and Kurniawan, (2003) reviewed the use of low-cost adsorbents for heavy metals uptake from contaminated water. Researchers have investigated use of industrial by-products such as lignin from pulp and paper industry which is a byproduct of cellulose production (Betancur *et al.,* 2009) to treat waste water.

2.2.7.3 Eggshells as low cost adsorbent

Eggs are widely used in bakeries, food restaurants, hotels and some food manufacturers and the eggshell is always considered as waste. The eggshell generation is high in Kenya and its disposal is cumbersome. According to Stadelman (2000), eggshell accounts for about 9-12 % of its total weight depending on egg size. Chemical composition of the egg shell comprises calcium carbonate ($CaCO_3$) (94%), magnesium carbonate ($MgCO_3$) (1%), calcium phosphate ($CaPO_3$) (1%) and organic matter (4%). Porous structure of the eggshell is about (7,000-17,000 pores) (William and Owen, 1995) which makes it attractive to be used as an adsorbent. Eggshells also have whipping, gelling and emulsification properties in addition to their high quality protein (Butcher and Miles, 1996).

The eggshell may be used as a low-cost adsorbent for removal of ionic metals from the aqueous solution due to the calcium carbonate ($CaCO_3$) content (Kuh and Kim, 2000; Tsai *et al.*, 2006). Eggshell is known to have good adsorptive properties mainly attributed to the intrinsic pore structure, calcium carbonate and protein acid mucopolysaccharide that can be developed to a good adsorbent. Protein acid mucopolysaccharide has several important functional groups such as carboxyl, amine and sulfate that can bind heavy metals ion to form ionic bond (Surasen, 2002). Eggshell has the capacity to act as a neutralizing agent, hence any aqueous solution equilibrated with the eggshell becomes more basic and heavy metals can precipitate and deposit on egg shell particles (Brown and Lemay, 1985).

2.2.8 Biosorbents in treatment of industrial effluent

Biosorbents are biological materials used in heavy metal removal. According to Scott (1992) bisorption has gained important credibility due to efficiency in heavy metal removal and low cost of the biosorbents. The major advantages is high effectiveness in reduction of metal ions, cheap biosorbents, binding process is rapid, reversible and requires minimal energy for activation. Typical biosorbents can be derived from three sources as follows: non-living biomass such as bark, lignin, shrimp, krill, squid, crab shell; algal biomass; microbial biomass, such as; bacteria, fungi and yeast (Apiratikul and Pavasant, 2008b).

2.3 Principle of Atomic Absorption Spectrophotometer

Atomic Absorption Spectrophotometer (AAS) is an analytical technique for measuring quantities of chemical elements present in environmental samples through measuring absorbed radiation by chemical element of interest. The method is based on the absorption of ultraviolet or visible light by gaseous atoms. AAS is the most sensitive technique used to analyze metal impurities. A monochromator is used to select the specific wavelength of light absorbed by the sample and to exclude other wavelength. Specific wavelength of light allows for determination of specific element of interest when in the presence of other elements. A detector measures the wavelength of light transmitted by the sample and compares them to the wavelength which originally passed through the sample. Signal processor integrates the changes in wavelength absorbed which appear in the read outs as peaks of energy absorption at discrete wavelength (García and Báez, 2012). A block diagram of atomic absorption spectrometer is shown in Figure 2.1.

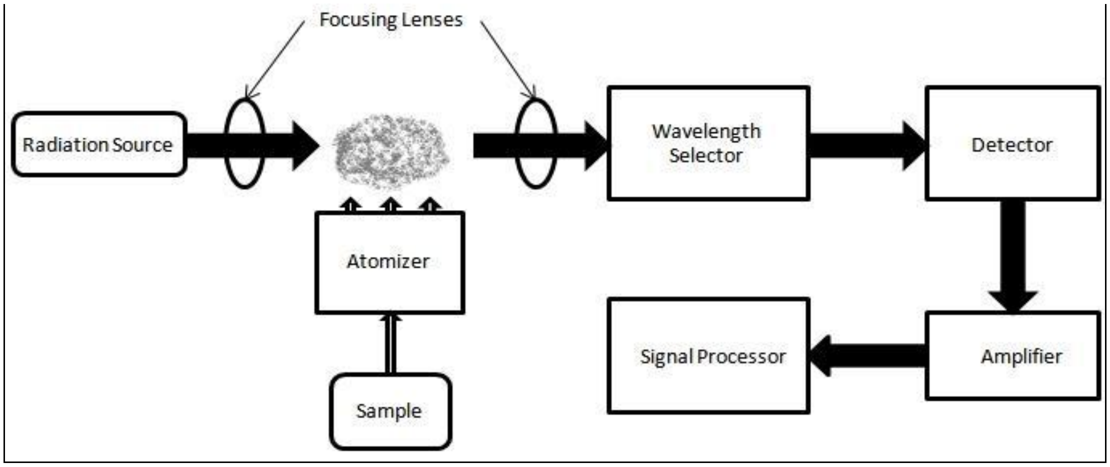

Figure 2. 1: Schematic diagram of Atomic Absorption Spectometer (García and Báez, 2012).

The sample is converted into atomic vapours by spraying the solution into the flame. A hollow cathode lamp containing the element to be determined is used as the light source. The wavelength spread is extremely narrow; both for the emission line of the light source and the absorption line of the same element in the flame. For this reason there is no interference from spectral line of other elements (García and Báez, 2012). As the hollow cathode light is directed at sample solution sprayed, some of the light is absorbed by atomized sample component and the rest passes through. The selected spectral line is isolated from the emerging beam by a monochromator and the ratio of its intensity (I) to that of the source (I_0) is measured by a photocell or multiplier. The amount of light absorbed depends on the number of atoms in the light path provided the flame is hot enough to convert a chemical species to free atoms. When the rate of aspiration and the flame conditions are kept constant, the absorbance (log I_0 / I) will be directly proportional to the concentration of the given metal sample, as governed by Beer Lambert's law (A= έbC); where A is the absorbance, C is the concentration of the sample; b is the path length of the radiation and έ is the absorption coefficient. There are several types of interference that might occur with the use of the AAS as described below:

2.3.1 Chemical Interference

Chemical interference is caused by the inability of the flame to atomize the desired compound in the sample. It is observed when the flame temperatures are not sufficient to dissociate the desired compound from its chemical bonds. It is mainly associated with alkaline earth salt such as Barium (Ba), Beryllium (Be) and Calcium(Ca) **(**García and Báez, 2012).

2.3.2 Ionization Interference

Ionization interference occurs when the flame is too hot making large proportions of atoms in the sample to ionize hence, causing them to absorb at different radiation line. Introduction of excess of the other metal ions in the flame which are more easily ionizable than the metal of interest helps to eliminate this. The use of cooler air hydrogen flame solves the problem (García and Báez, 2012).

2.3.3 Matrix or bulk interference

Matrix or bulk interference is caused by either change in viscosity of solution or large excess of extraneous ions. A sample that is more viscous than the standard provided it can result in difference in sample uptake due to changes in nebulization efficiency. This is corrected by matching closely the matrix composition and standard.

2.3.4 Spectral Interference

Spectral interference occurs due to direct overlapping lines from the primary radiation source and absorption line of another element in the atom cell. It is caused by a large number of species present in the flame that are capable of broadband absorption radiation. It is very rare; however, it occurs when the lines are within the band pass of the monochromator overlap with each other's spectral profile (within 0.01 nm). Example are the non-specific absorption at 217.0 nm which affects lead (NaCl gives a strong molecular absorption of this wavelength) and the $Ca(OH)_2$ absorption band on barium is at 553.55

nm. This interference is usually eliminated by use of background correction, which includes:

i. Preparing a blank solution with its matrix similar to that of the analyte so that the absorption of the blank is a measure of the background.

ii. Measuring the absorbance at wavelength close to the resonance line used in determination, the measured absorbance is used to correct the absorbance signal at the resonance line.

iii. Use of a broadband continuous source or radiation in conjunction with the hollow-cathode line source, both free analyte atoms and molecular species in the flame cathode line of the hollow cathode. The continuous radiation from the continuous source is absorbed over a bandwidth of wavelength passed by the monochromator (usually 0.1-0.2 nm), while the free analyte atom absorbs in a narrow range (0.005-0.001 nm) from the continuous source is due almost entirely to the components of the background (García and Báez, 2012).

2.4 Removal Efficiency

The heavy metal amount adsorbed per unit sorbent is calculated using equation 2.2 (de carvalho *et al.,* 2003)

$$\mathbf{Q = (C_0 - C_f) \times (V/M) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ Equation 2.2}}$$

Where: Q is the specific metal adsorbed,

V Volume of effluent solution,

C_0 Initial concentration of metal in solution,

C_f Final concentration of metal in solution,

M Mass of sorbent.

The percentage of heavy metal adsorbed is computed as shown in equation 2.3:

% lead removed = (C_0 – C_f / C_0) x 100……………..Equation 2.3

Where:

C_0 Initial concentration of metal in solution

C_f Final concentration of metal in solution

2.5 Adsorption Isotherms

2.5.1 Equilibrium of sorption

The analysis of the adsorption process requires equilibrium, where the metal ions are partitioned between the adsorbent and the liquid phase as a function of the metal concentration. The adsorption process provides ultimate data used in the applicability of the particular sorption process using a specific adsorbent and is described by fitting the experimental points in model (Park *et al.,* 2007). There are several equilibrium adsorption models used in the assessment of the sorption performance such as Langmuir, Freundlich and Temkin models among others.

The adsorption isotherm generated represents the relationship between the amount adsorbed per unit weight of solid sorbent and the amount of solute (heavy metal) remaining in the solution at equilibrium. Adsorption isotherm equations are used to study the nature of adsorption with the basic purpose of optimization of design of adsorption units for removal of pollutants from waste waters. The information obtained from the data is important in comparing different adsorption media used (Eskandarpour *et al.,* 2008).

2.5.1.1 Langmuir Model Equation

Langmuir is commonly used for isotherm modeling derived from simple mass kinetics and gives information on monolayer adsorption. It represents the equilibrium distribution of metal ions between solid and liquid phases (Langmuir, 1918). It produced a good agreement with wide variety of experimental data. It is mainly based on four assumptions (Subramanyam and Das, 2009):

- All adsorption occurs through the same mechanism,
- The surface of the adsorbent is uniform, that is all the adsorption sites are equal,
- Adsorbed molecules do not interact, once the adsorbed molecule occupies a site, no further adsorption takes place,
- At the maximum adsorption, only a monolayer is formed on the outer surface of the adsorbent and after that no further adsorption takes place,

Langmuir is linearized to four different types where type 1 is the most commonly used linear expression to study the relationship between concentration of solute in liquid phase and solid phase at equilibrium conditions as shown in equation 2.4 (Subramanyam and Das, 2009),

$$\frac{1}{qe} = \frac{1}{Qmax} + \frac{1}{bQCe}$$ .... **Equation 2.4**

Where: $\mathbf{q_e}$ Amount of solute adsorbed per unit weight at equilibrium,

$\mathbf{Q_{max}}$ Indicates the maximum monolayer sorption capacity of sorbent (mg/g),

Q Sorption capacity

b Langmuir constant related to the energy of sorption(l/mg),

$\mathbf{C_e}$ Equilibrium concentration of the metal ion or solute.

Separation Factor ($\mathbf{R_L}$)

The behaviour of the Langmuir isotherm in relation to the adsorption process is determined by use of the dimensionless constant separation factor. The factor is able to tell whether the shape of the isotherm is favourable. The factor is given by equation 2.5. (Subramanyam and Das, 2009),

$\mathbf{R_L=1/ (1+bCo)}$ **……………………………………Equation 2.5**

C_0 = Initial concentration of heavy metal

b = Langmuir constant related to the energy of adsorption L/mg

R_L = shape of the isotherm ($0 < R_L < 1$) indicates favourable adsorption

2.5.1.2 Freundlich Model Equation

This model is more widely used but provides no information on the monolayer adsorption capacity in contrast to Langmuir model. It is based on heterogeneous surfaces (Freundlich, 1906). The model is capable to describe the adsorption of organic and inorganic compounds on a wide variety of adsorbents including biosorbents. The model is represented by equation 2.6;

$$\text{Log Qe} = \text{Log Kf} + 1/\text{n Log Ce}$$ ……………………… **Equation 2.6**

Where:

C_e Equilibrium concentration of the metal ion in bulk concentration (mg/L),

K_f Freundlich constant related to sorption capacity of adsorbent mg/g). The K value represents the steepness of the isotherm the higher the K value the greater the adsorption intensity,

Q_e Amount of solute adsorbed per unit weight,

n is the Freundlich exponent related to adsorption intensity (g/L) (when the n value is between 1 and 10, it represents effective adsorption condition),

1/n is the adsorption intensity or heterogeneity factor the Freundlich exponent related to the curvature of the isotherm, ($1/n < 1$ indicates normal adsorption, $1/n > 1$ is cooperative adsorption, 1/n = 1 isotherm adsorption is linear and occurs at very low solute concentration with low loading of the adsorbent (Site, 2001).

A plot of Log q_e versus Log C_e gives the Freundlich isotherm constants K_f and n values which are determined from the intercept and slope, respectively.

2.5.1.3 Temkin Model Equation

The isotherm contains a factor that explicitly takes into account the adsorbent –adsorbate interactions, by ignoring the extremely low and large values of concentrations. The model also assumes effect of some direct interactions such as adsorbate particles and suggests decrease in adsorption heat of all molecules in the layer is due to interactions. Temkin model assumes that the fall of heat of adsorption is linear rather that logarithmic (Ho *et al.*, 2002).

Equation 2.7 shows the equation of the Temkin model;

$$qe = BInAT + BInCe$$ ………………………. **Equation 2.7**

C_e - Concentration of adsorbate in solution at equilibrium (mg/L),

A_T - Temkin isotherm equilibrium binding constant (L/g)

q_e - Amount of metal adsorbed per unit weight of adsorbent (mg/g)

B - Constants related to heat of sorption J/mol, A graphical plot of the Temkin isotherm is X against $InC_{e.}$ A straight line graph is obtained whose slope is given by **A** the y intercept **B** constant.

2.6 Related studies

Katarzyna (2005), did a study on the sorption of chromium (III) ions (Cr $(NO_3)_3$. $9H_2O$ from POCh Gliwise S. A., Poland aqueous solutions by use of eggshell as a low cost sorbent. The concentration of chromium (III) ions was analyzed by Inductive Coupled Plasma spectrometry ICP – AES plasma spectrometer. Mathematical models describing kinetics and equilibrium sorption was used in the experiment. The effects of process parameters such as pH, temperature, sorbent and initial concentration of chromium (III) ions was performed on process kinetics, temperature and pH on process equilibrium. According to the experiment crushed eggshells exhibited relatively high sorption capacity compared to other sorbent and was evaluated as 21-160 mg/g. The study further recommends research to be carried out to verify whether the sorbent could be used in removal of other heavy metals apart from chromium.

Tolga *et al.*, (2007) investigated on the removal of lead by bisorption applied to storage battery industry waste water. The bisorption performance was carried out by use of micro-organisms *Rhizopus arrhizus* to remove the lead (II) ions. The average lead (II) ions concentration in storage battery wastewater was 3.0 mg/L and it reduced to value below 0.5 mg/L. Effects of media condition such as pH, temperature, bisorption of lead ions to *Rhizopus arrhizus* was investigated on batch reactor. Optimum bisorption condition was found to be initial pH 4.5, temperature 30^0C, biomass 1.0g/L. The discharge limit of the battery waste water was 2 mg/L as per the national environmental regulation in Turkey but after the bisorption process the lead concentration was 0.157 mg/L which is far below the maximum discharge limit. The maximum bisorption capacity was obtained at 2.643 mg Pb (II)/g of micro-organism. This study recommended new studies to be done for further metal exclusion from the industrial waste water.

Arunlertaree et *al*., (2007) investigated on the use of the hen and duck egg shell to remove lead from battery organization in Bangkok. The characteristic and chemical composition of eggshell was investigated and analyzed by AAS. The data was statistically processed using least significance difference of 95% confidence level. The experiment was done under unadjusted pH of 1.35 – 1.45. Equilibrium model was used to determine the adsorption isotherm and Freundlich model was the best. The limitation of this study was use of real waste water for unadjusted final pH for several batch studies.

Kalyani *et al*., (2010) assessed the use of hen eggshell for its ability to remove lead from aqueous solution in batch bisorption system. The study was done by collecting eggshells from Andhra University college of Engineering hostel and kitchen waste. The lead (II) ions were prepared by dissolving its corresponding nitrate salt in distilled water. The bisorption capacity onto eggshell was evaluated by use of Langmuir, Freundlich, Redlich – Peterson and Temkin bisorption models to describe the isotherm constants. The experimental data was correlated with the kinetic model. The maximum bisorption capacity was 29.87 mg/g. The study did not apply the eggshell bisorption process on real industrial waste water but obtained the lead (II) ions concentration by analytical preparation.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction

This chapter summarizes the procedures, equipment and materials that were used while carrying out the analysis. Adsorption experiments were conducted to investigate the effects of pH, amount of the eggshell, size of the powdered eggshell and the contact time on the adsorption of the eggshell. All the experiments were performed in triplicate at room temperature.

3.2 Chemical reagents

The reagents that were used during the experiment include; sodium hydroxide, hydrochloric acid and nitric acid of analytical grade.

3.3 Equipment and glassware

Several types of glassware was used during the experiment such as; beakers, desiccators, volumetric flasks 250 mL, round bottomed flasks 250 mL, polyethylene bottles and measuring cylinders.

The equipment and materials used include: oven, filter funnels, incubator, Whatman filter papers grade 54, mesh sieves of different sizes, spatulas, pH meter (Model No. 86505), adhesive stickers, rotary shaker, grinder, analytical balance (RADWAG AS220.R2), thermometer and atomic absorption spectrophotometer (AAS) (Varian Spectra AA50).

3.4 Sampling and Preparation

3.4.1 Effluent

Purposive sampling was employed to obtain the raw samples at the effluent discharge point before the pre-treatment process from Associated Battery Company as shown in figure 3.1. The samples were filtered into polyethylene containers and covered with polyethylene lid which had been previously washed in 20 percent dilute nitric acid and rinsed in distilled water to avoid contamination.

For the determination of lead in the effluent, 50 mL of the sample was transferred into a 250 mL conical flask and digested using 3:1 v/v of concentrated HCl and HNO_3 (concentrated aqua ragia) then placed in fume cupboard to break all the matrices of lead compounds into lead (II) ions during analysis. The sample was then covered using aluminum foil to prevent spillage and then placed on a hot plate at temperatures between (80-140) ºC until about 10 mL of the solution remained. The solution was then allowed to cool, filtered into a 50 mL volumetric flask and filled to the mark with deionized water. This was then followed by analysis of initial concentration of lead by use of the atomic absorption spectrophotometer (Spectra AA50).

Figure 3.1 shows the waste water flow diagram with indication of the sampling point.

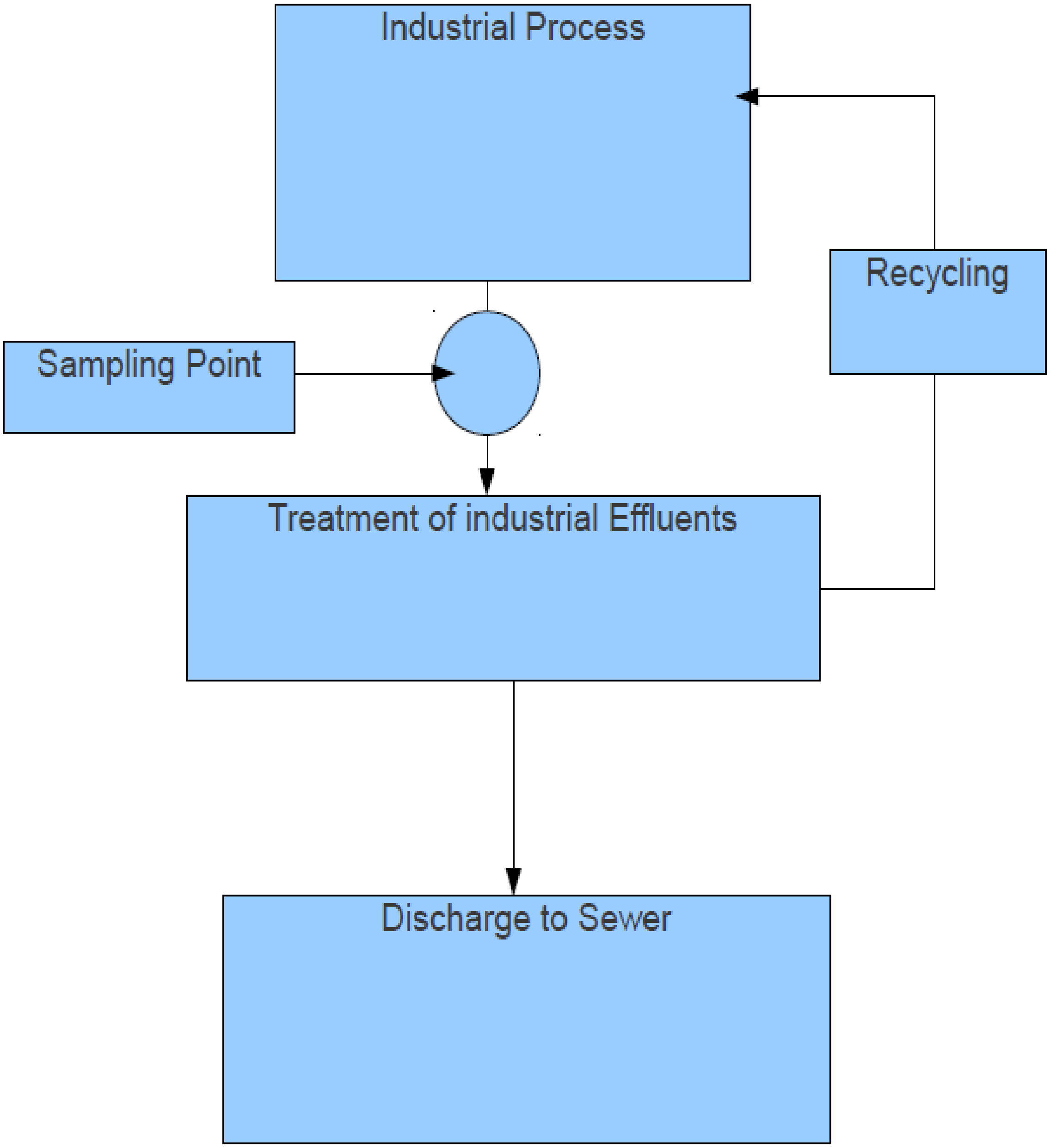

Figure 3.1: Schematic waste water flow diagram with indication of sampling point

(Source: Associated Battery Manufacturers, 2013)

3.4.2 Eggshell

The waste eggshell samples were collected from the Tusky's bakery shops in Eldoret town. The samples were then washed with tap water several times to remove any traces of particles that may interfere with the procedure. Waste eggshell were then rinsed with distilled water followed by air-drying. Samples were then placed in the incubator at 40 ^{0}C for 30 minutes to reduce the chances of decomposition and then cooled to room temperature. The dried eggshells were then crushed using pestle and mortar to obtain fine powder. The powdered samples were screened through a set of sieves to get geometrical size of sieve No. (355, 425, 500, 600, 710) µm packed in stopped containers and stored in desiccators depending on size for use during the experiment (Figure 3.2).

As for the boiled eggshells they were exposed to high temperatures of (above 100 ^{0}C) for 45 minutes to break down the chemical composition, air dried, placed in the oven for 2 hours at 100 ^{0}C to dry, cooled to room temperature. The boiled eggshell were then ground and screened through a set of sieves to get a geometrical size of different sieve sizes similar to the raw eggshell. The ground boiled eggshell were then packed in stopped airtight containers and stored in desiccators for use during the experiment.

Washing of the eggshells

Air dying and placing in the incubator to remove moisture content

Figure 3.2 : Preparation of Adsorbent : Eggshell
(Source: Author, 2013)

3.5 Preparation of Standards for Instrument Calibration

The stock solution was prepared by weighing 0.1607g of 99.5% purity of Pb $(NO_3)_2$ and transferred into 100 mL volumetric flask and diluted to the mark with 10% v/v of dilute nitric acid and deionised water. Working standards of (0, 2.5, 5.0 and 10) ppm were prepared from the stock by serial dilution with deionised water. A standard calibration curve was obtained using a series of varying concentrations of the standards for lead metal. The calibration curve obtained for the lead metal was linear with correlation co-efficient of approximately 1(0.999) (see appendix A1).

3.6 Experimental design

The randomized block design was used in this experiment, the principle of randomization and replication was considered. The samples were divided into 4 homogenous groups called blocks where they had similar concentrations and amount of the industrial effluent. Several treatments were assigned to the experimental units. The independent variables evaluated included; pH, sorbent size, sorbent amount, and the contact time. These treatments were analyzed for both raw and boiled eggshells in triplicate. The layout in figures 3.3, 3.4, 3.5 and 3.6 indicated the randomized block design layout used in the data analysis.

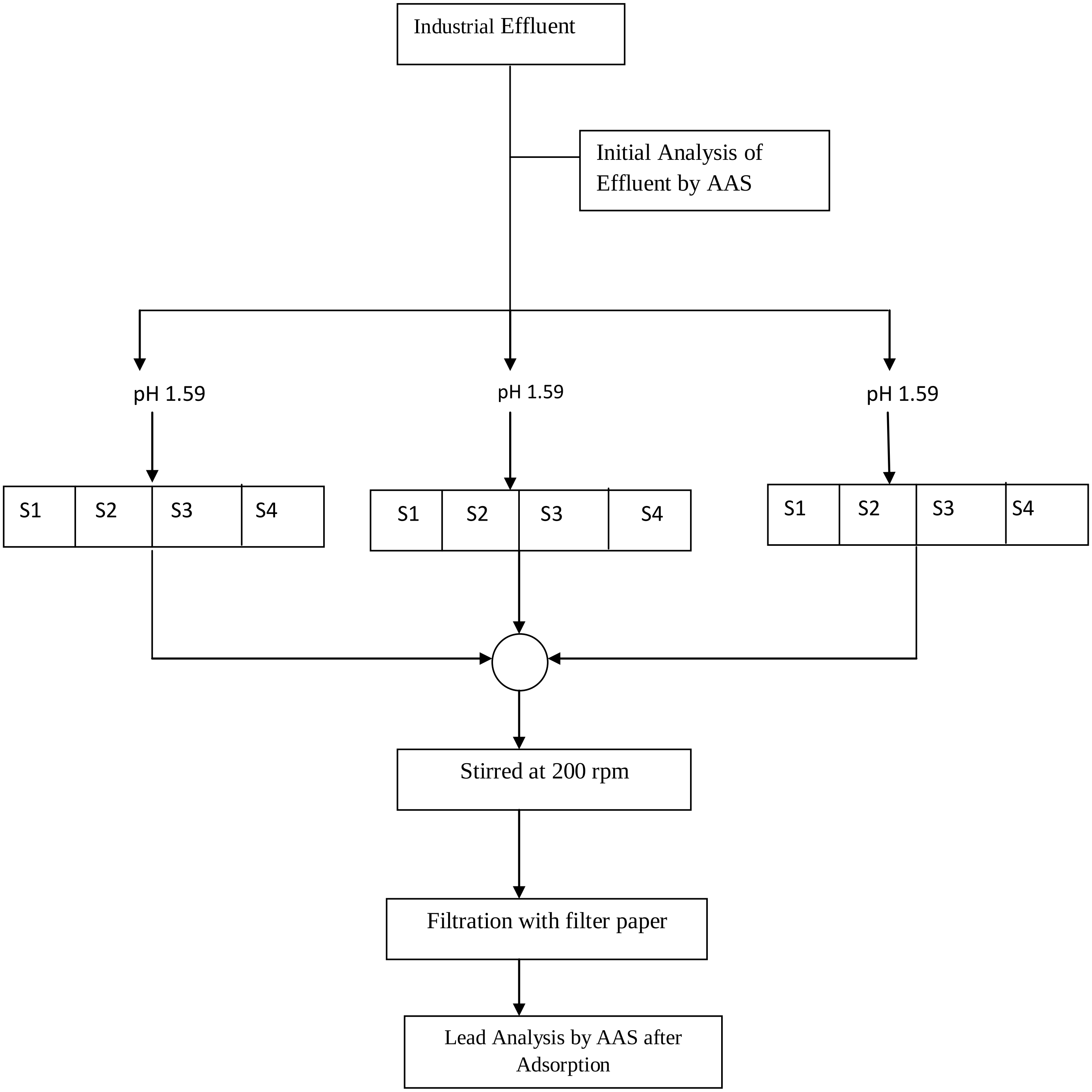

Figure 3.3: Batch Experiment layout for testing effect of eggshell particle size (S1…S4) on removal of lead (II) ions in 100 mL effluent

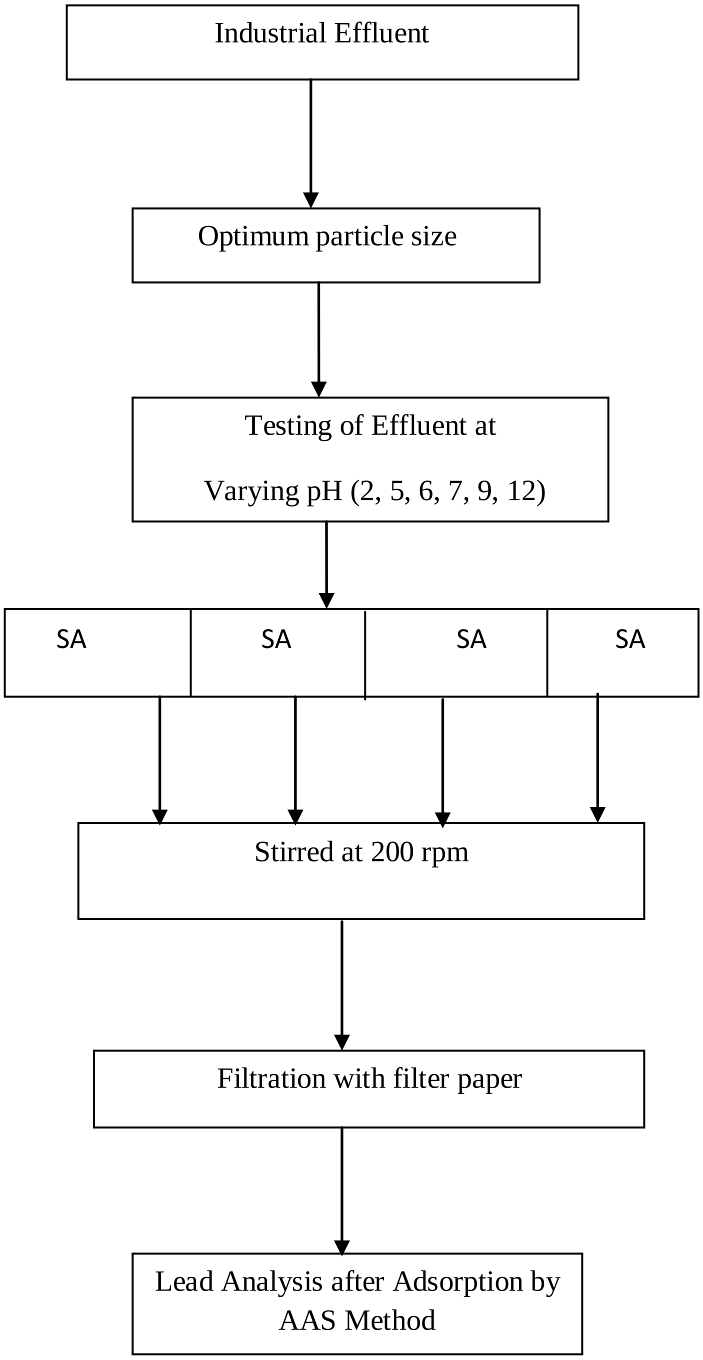

Figure 3.4: Batch experiment layout for testing the effect of pH on removal of lead (II) ions in 100 mL effluent by use of eggshell sorbent at optimum particle size

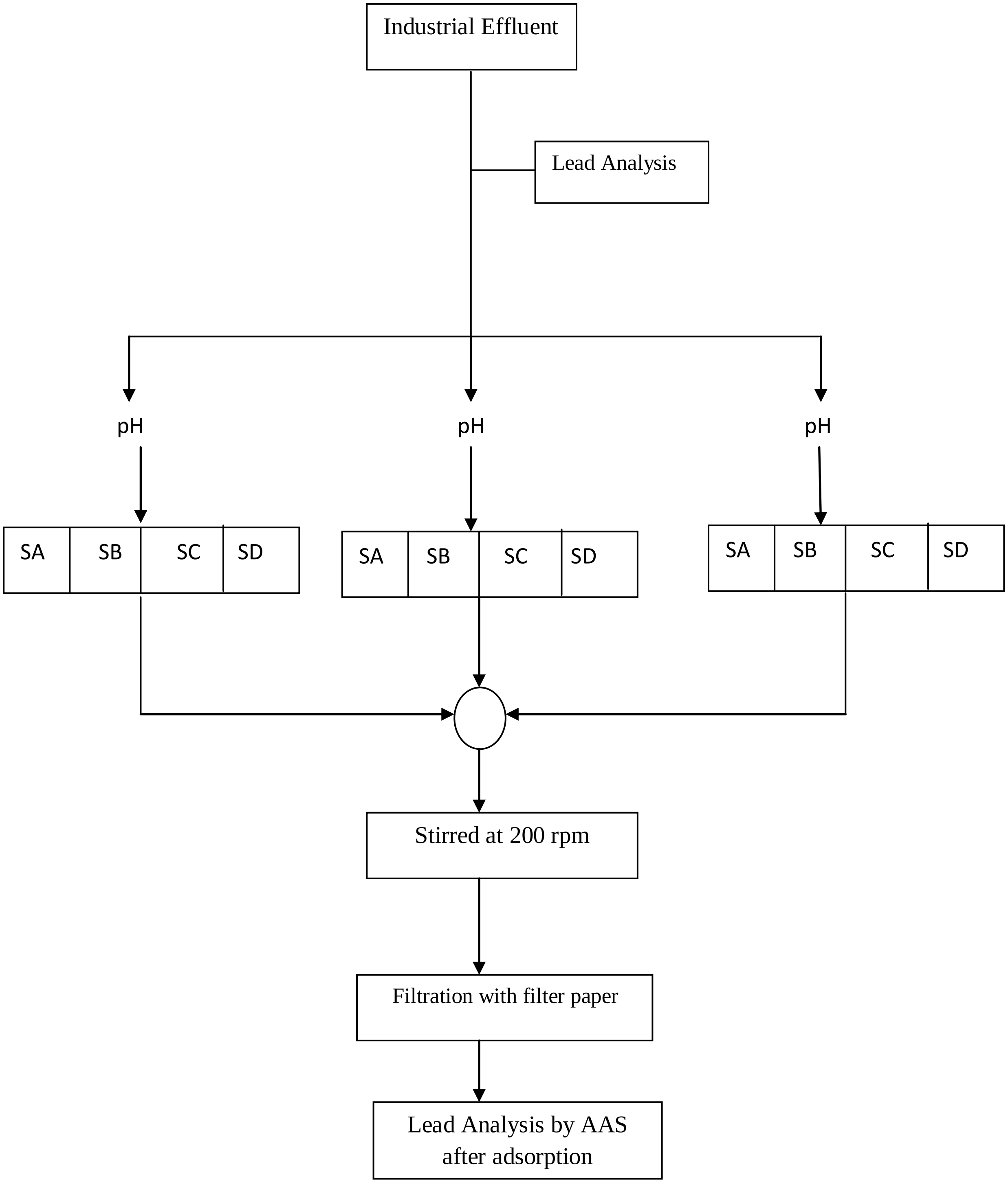

Figure 3.5: Experiment layout for testing the effect of the different masses (SA to SD) of eggshell using optimum particle size and pH on removal of lead (II) ions in 100 mL effluent

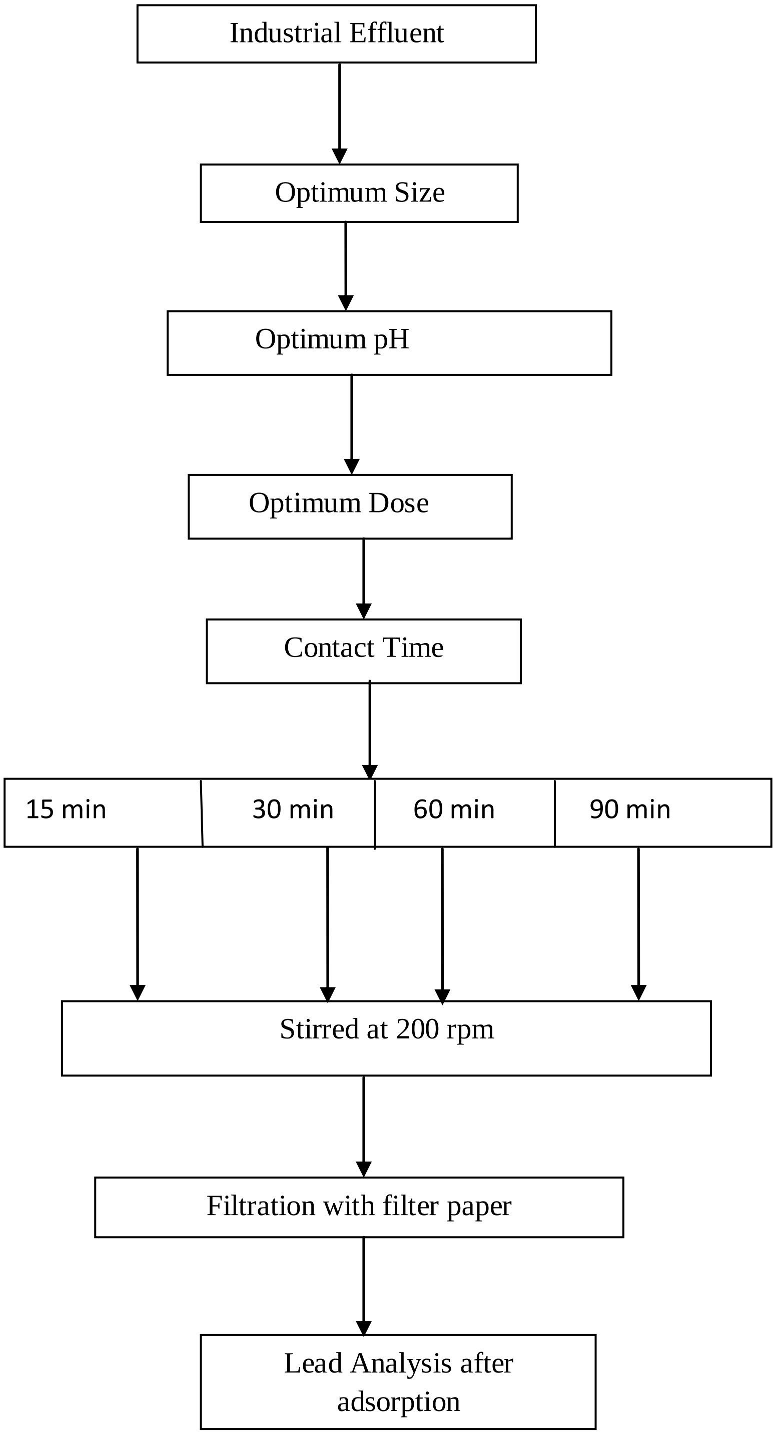

Figure 3.6: Experiment layout for testing the effect of contact time on removal of lead (II) ions by use of eggshell at optimum (particle size, pH, sorbent dose)

3.7 Adsorption experiment

The initial lead concentration of the effluent was analyzed by using AAS Spectre AA50. Pre-determined test was carried out to determine the optimum pH for the experiment. In order to adjust the pH small amounts of 1M sodium hydroxide were added to achieve the desired pH. Magnetic stirrer helped in agitation to obtain a homogenous solution. The samples acidity or alkalinity was determined by use of pH meter. To achieve data precision the experiment was analyzed in triplicate. An effluent sample of 100 mL was transferred to a conical flask. The crushed eggshell added to the samples, and then stirred with a magnetic stirrer for 30 minutes to attain equilibrium. After the contact time, the equilibrium uptake of lead (II) ions by the eggshell was achieved. Whatman filter paper of grade 54 was used for filtering the eggshell to obtain the filtrate. The exact concentration of the lead (II) ions in the filtrate was then analyzed using the atomic absorption spectrometer.

3.7.1 Effect of Particle size

Sieve analysis was performed using a stack of sieves where each lower sieve had a smaller aperture size than the sieve above it. Sieving was performed by hand until the powder passes through the sieve. Sieve sizes Nos. (355, 425, 500, 600, 710) µm were used to achieve different particle sizes of eggshell. Eggshell was placed in 250 mL conical flasks that had been previously filled with 100 mL effluent sample. Using a magnetic stirrer the mixture was stirred at 200 rpm for 30 minutes and filtered. Lead (II) ions concentration in the filtrate was determined using atomic absorption spectrometer (Spectra-AA50).

3.7.2 Effect of pH

Batch sorption experiments were carried out at the different pH (2, 5, 6, 7, 9 and 12) each for a 100 mL industrial effluent sample 1 g of eggshell was added of particle size sieve No. 355µm. Using a magnetic stirrer the mixture was then stirred for 30 minutes at 200 rpm and the solution filtered. The final concentration of Pb^{2+} (lead (II) ions) in the filtrate was analyzed using the Spectra-AA50 to determine the optimal pH of adsorption.

3.7.3 Effect of mass of eggshell

Batch sorption experiments were performed by placing different masses (0.1 g, 0.5 g, 1 g, 1.5 g, 2 g, 4 g, 6 g, 8 g,) of particle size of sieve No.355µm of eggshell in 250 ml conical flask and introducing 100 ml of effluent sample at a pH of 5. Using a magnetic stirrer the mixture was then stirred for 30 minutes at 200 rpm and the solution filtered using filter No. 54. The final concentration of Pb^{2+} in the filtrate was determined using Atomic Absorption Spectrometer (Spectra-AA50) and used to find the optimal dose of powdered eggshell for adsorption.

3.7.4 Effect of contact time

Batch sorption experiments were performed by adding 1 g eggshell of particle size of sieve No. 355µm in a 250 mL conical flask and introducing 100 mL of effluent sample at a pH 5. Using a magnetic stirrer the mixture was then stirred at 200 rpm for different time intervals of (15, 30, 60, 90, 120, 150 and 180) minutes. The solution was filtered after each interval with filter No. 54. Lead (II) ions concentration in the filtrates was analyzed using atomic absorption spectrometer (Spectra- AA50) and the results used to establish the optimal contact time to be used in the experiment. The results from these experiments are presented and discussed in the next chapter.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Characteristics of Industrial Effluent

Industrial effluent sample was obtained from the Associated Battery Manufacturing Company in Nairobi Kenya. The industry uses lead antimony alloy as its main raw material for added strength and improved electrical properties; this therefore allows presence of other metals although their quantities are negligible. Most of the raw materials used within the company have range of quantities of heavy metals depending on the packaging as shown in Appendix A2.

The effluent sample collected before the pretreatment process was characterized and results presented Table 4.1. From the assessment of the effluent, the sample indicated it was strongly acidic (pH 1.59 +/- 0.1), black greyish in colour. Initial lead concentration (19.2 mg/L), pH (1.59) and total dissolved solids (2454 mg/L) was found to be higher than what required in the Environmental Management and Cordination Act (Water Quality Regulations) 2006. The analysis of the values of total dissolved solids (TDS), pH and the general nature of the waste water was essential to characterize the industrial effluent.

The quantities of other heavy metals such as Arsenic (As), Copper (Cu), Cadmium (Cd), Zinc (Zn) and Nickel (Ni) in the sampled effluent were below the set government values on environmental regulations. The negligible quantities of these other elements from the battery industrial effluent confirmed that lead (Pb) is the main heavy metal present with a concentration of 19.2+/- 0.005 mg/L of the sampled effluent hence chosen for adsorption using the eggshell.

These results are consistent with those reported in other studies, according to Sumeth and Ura (2012), their survey of three batteries manufacturing industries showed the levels of pH ranging from 1.6 to 2.9 while the Pb (II) ions concentration ranged from 5 to 15 mg/l.

This implies the level of pollutants in the lead acid battery waste water varies depending on the raw materials and methods adopted in battery making. The appropriate treatment method to be used depends on the effluent characteristics such as; pH, lead metal concentration, and total dissolved solids (TDS).

Table 4.1: Levels of Pb, TDS and pH of Industrial Effluent before Pre-treatment process and compared with NEMA Water Quality Standards

EFFLUENT ANALYSIS			
Parameter	**Mean Value of each parameter analyzed in the effluent**	**NEMA Water Quality Standards for Effluent Discharge to Public sewers (EMCA,2006)**	**NEMA Water Quality Standards for Effluent Discharge to Environment (EMCA,2006)**
Lead (mg/L)	19.20	1.0	0.01
TDS (mg/L)	2454	2000	1200
pH	1.59	6-9	6.5-8.5

4.2 Effects of various parameters on the removal of Pb^{2+} ions by use of boiled and raw egg shells

4.2.1 Effect of particle size

The initial Pb^{2+} concentration of solution was fixed at 19.2 mg/L, unadjusted pH and the fixed volume of 100 mL of the lead effluent, the particle size of the eggshell ranged from sieve size No. (355 to 710) µm. The results (Fig. 4.1) of the variation of percentage removal of efficiency against particle size shows, with increased particle size the adsorption decreases.

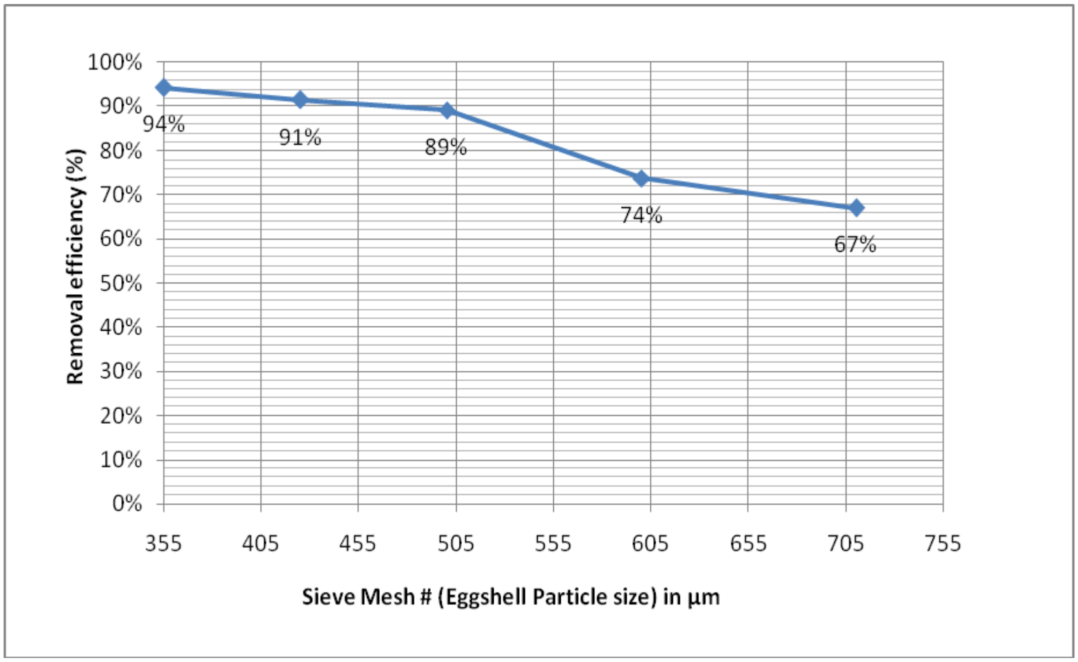

Figure 4.1: The effect of particle size on removal efficiency (Dosage of eggshell: 10 g/ L; shaking speed: 200 rpm and temperature: 293 K)

The adsorption of lead (II) ions basically depends on the surface area and particle size of the adsorbent. Sieve No. 355 µm had the highest removal efficiency of 94% (Appendix A3), from the study the smaller the particle size, the more lead (II) ions were adsorbed due to increased surface area available. This implies that adsorption is surface phenomenon and the rate of adsorption increased with decrease in particle size in agreement with other studies (Kalyani *et al.*, 2010; Badmus *et al.*, 2007).

4.2.2 Effect of pH

The results of the effects of pH on removal efficiency are shown on the graph on Figure 4.2 and appendix A4; where adsorption of lead (II) ions was studied at room temperature by varying pH of metal solution from pH 2 to pH 12.

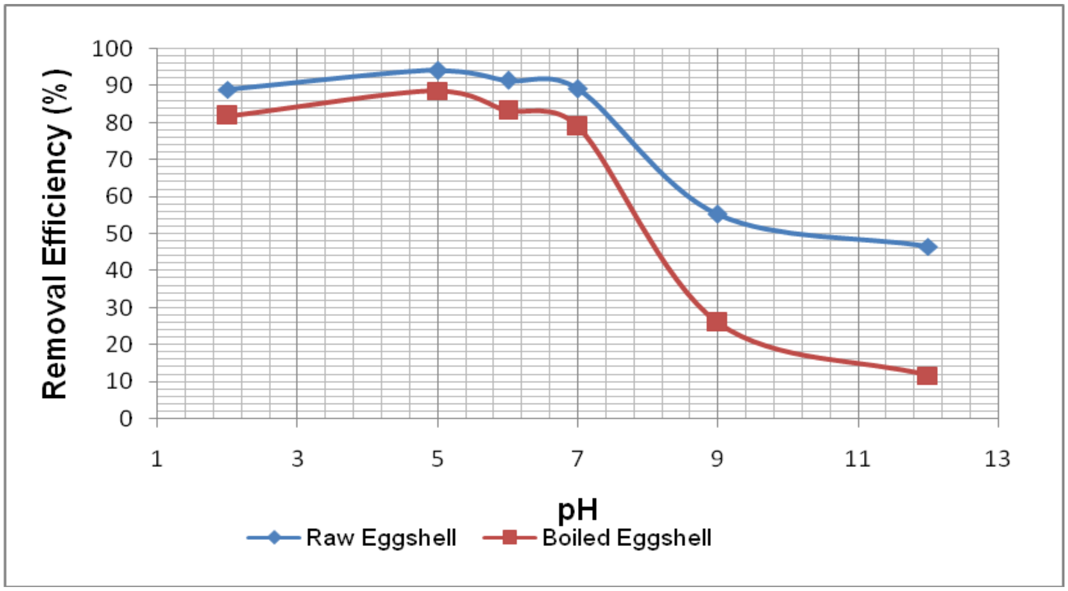

Figure 4.2: The effect of pH on removal efficiency (Dosage of eggshell: 10 g/ L; shaking speed: 200 rpm and temperature: 293K)

From the experimental results, the percentage metal removal efficiency increased gradually with increased pH of solution range from pH 2 to pH 5. The optimum pH observed was 5 with a percentage removal efficiency of 94.2% for raw eggshell and 88.6% for boiled eggshell (appendix A4). At pH 5 the competition of the hydrogen ions was minimized and the formation of the metal ions precipitate was avoided thus enhanced metal adsorption. Further increase in pH caused a gradual decrease in adsorption of the lead (II) ions (Figure 4.2). Lead removal recorded minimum values were found to be at pH 12.

From the results, the pH of the industrial effluent is clearly an important parameter that controls the adsorption capacity of lead (II) ions uptake by eggshell, and has a major effect on the protonation and the deprotonating of the active sites. The pH value of a strong solution influences not only the site dissociation of biomass surface but also the solution chemistry of heavy metals (Parmar and Thakur (2013).

According to Katarzyna, (2005) the effect of pH is as a result of ion-exchange mechanism of sorption in which the carbonate group in the eggshell plays a dominant role in the cation – exchange properties. Under low pH, lead removal is inhibited due to the competition of cations between hydrogen and lead (II) ions on the sorption sites. The low pH indicates high protons concentration hence more sorbent groups bind with the protons and less groups are available for the lead (II) ions.

At higher pH values of the effluent exposes the carbonate groups in the eggshell increasing the negative charge density on the sorbent surface. This favours the cationic adsorption and this result in increased Pb (II) ions uptake by the eggshell. Further increase of pH beyond 7, shifts the equilibrium of the reaction to the left. This favour desorption, since there is increased concentration of hydroxyl ions. Similar trends have been reported in literature for the pH dependence on adsorption of Pb (II) ions (Park *et al.*, 2007; Arunlertaree *et al.*, 2007, Badmus *et al.*, 2007).

4.2.3 Effect of adsorbent mass

The effect of the eggshell dose was investigated by varying the amount from (0.1 g, 0.5 g, 1 g, 1.5 g, 2 g, 4 g, 6 g and 8 g). For all the runs initial concentration of Pb (II) ions was fixed at 19.2 mg/L. Figure 4.3 and appendix A5 show the results of the effects of sorbent dose on the sorption of Pb (II) ions. From the Figure showing the effect of eggshell dose as a function of the percentage removal, it was observed that Pb (II) ions percentage removal efficiency increased with increasing dose of the eggshell up to 2 g in 100 mL and then further increase of sorbent dose resulted in minimal removal efficiency.

The increase in percentage removal with increase in adsorbent mass contributed to increased surface area as a result of increased amount of sorbent eggshell with large amount of active exchangeable sites for adsorption as noted by Babel & Kurniawan, (2003) on the low cost sorbent on heavy metal uptake from contaminated water. However, there was no significant increase in percentage removal efficiency with increase in adsorbent dose between 2 g and 8 g. This suggests that after a certain dose of eggshell the maximum adsorption is attained and hence the amount of ions bound to the adsorbent and the amount of free ions remain constant even with further addition of dose of adsorbent.

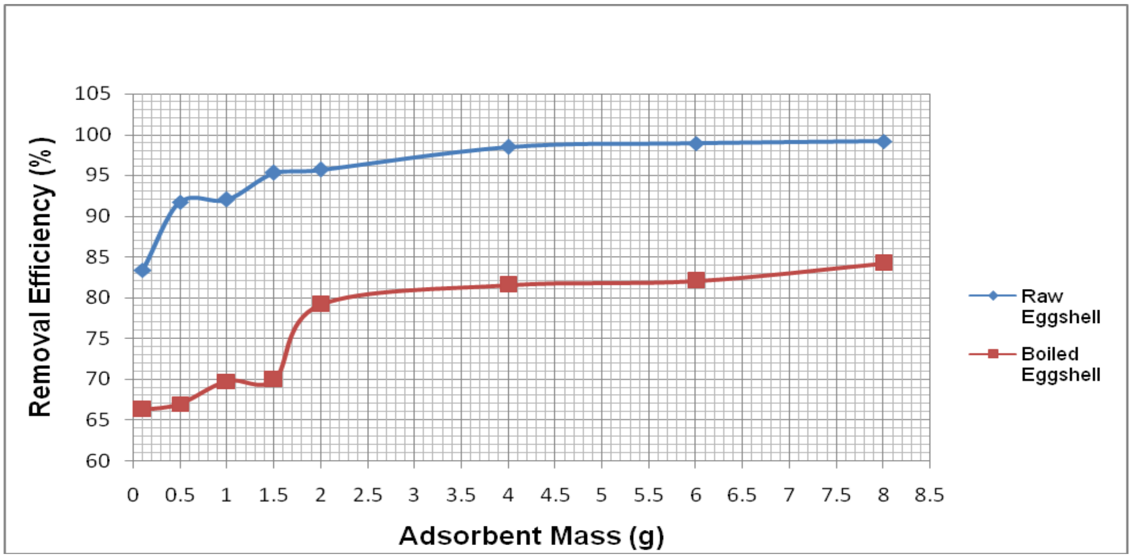

Figure 4.3: The effect of adsorbent mass (g) dosage of eggshell on removal efficiency: 10 g/ L; effluent pH: 5; shaking speed: 200 rpm and temperature: 293 K)

During the experiment a further increment of the adsorbent dosage of eggshell beyond 10 g/L resulted in increased neutralization and consequential overflow of the sampled effluent. Hence 1g of the eggshell was considered optimum for use to increase the accuracy levels of the results since the amount was most stable as compared to the quantities above 1g in 100 mL of effluent.

4.2.4 Effect of contact time

The results are shown in Figure 4.4; a sharp increase in adsorption was noted within the first 60 minutes and then increased slowly reaching maximum adsorption between 90 and 180 minutes; showing the percentage removal efficiency of Pb^{2+} ions using the eggshell increases with increase in contact time.

After 120 minutes, there was no significant increase in uptake capacity with further increase in contact time and this suggests that equilibrium had been attained. Further increase in contact time did not cause improvement in adsorption because of saturation of the active sites. The maximum percentage removal efficiency was 99% for raw eggshell and 89% for the boiled eggshell (appendix A6).

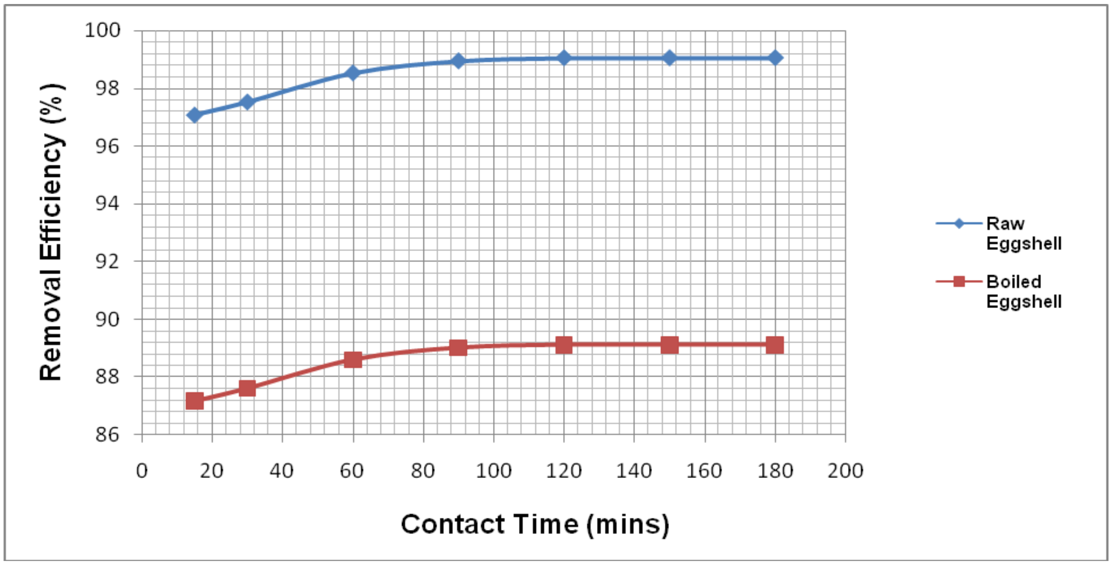

Figure 4.4 : The effect of the contact time on removal efficiency: 10 g L−1; effluent pH: 5; shaking speed: 200 rpm & temperature: 293 K)

Contact time had an effect on the adsorption process and similar trends have been reported in literature; when activated carbon from the periwinkle shell was used on the removal of heavy metal from industrial waste waters (Badmus *et al.*, 2007). He noted that the fast rate of adsorption at the initial stages may be explained by the availability of abundant active sites on the adsorbent surface which gradually got exhausted with increase in contact time.

Das and Mondal (2011) on the other hand highlighted that adsorption process rapidly occurs in the initial stages and is controlled by diffusion process from the bulk to the surface and after some contact time the adsorption controlled process stagnates due to the less available adsorption sites.

4.3 Adsorption Isotherm

Equilibrium data are important in evaluating the adsorption capacity of the adsorbent. The equilibrium models are a useful guide to further experimental work and predict the ability of certain adsorbent to remove a pollutant. The adsorption isotherm offers the best representation of the adsorbate concentration and the quantity of material adsorbed (Subramanyam and Das, 2009). The equilibrium adsorption process in this study was described by fitting the experimental points on equilibrium adsorption models.

In this study the experimental data for removal of lead (II) ions from industrial waste water using eggshell were fitted to the Langmuir, Freundlich and Temkin models to assess the different adsorption isotherms and their ability to correlate the experimental data. These models are frequently used to describe the adsorption process and for that reason they were tested in this work. The experiment entailed the removal of Pb^{2+} ions using raw and boiled eggshells from raw industrial effluent at a constant pH = 5, particle size (sieve No. 355µm), sorbent amount (1g), optimum contact time of 120 minutes, and was conducted at room temperature (293K).

Linear regression technique was used to determine all the isotherm parameters. Correlation coefficient (R^2) was calculated to measure the goodness of fit of the experimental data on the isotherm models using the linear regression. The applicability of the isotherm equation was compared by judging the correlation coefficient.

The calculations used in the graphical representation of the Langmuir, Freundlich and Temkin isotherms for both the raw and the boiled eggshell are represented in appendixes A7 and A8.

4.3.1 Langmuir Adsorption Isotherm

Langmuir isotherm gives information on the monolayer adsorption capacity. Figures 4.5 and 4.6 illustrate the adsorption isotherm data for Pb (II) ions adsorption using the raw and boiled eggshells respectively from raw industrial effluent.

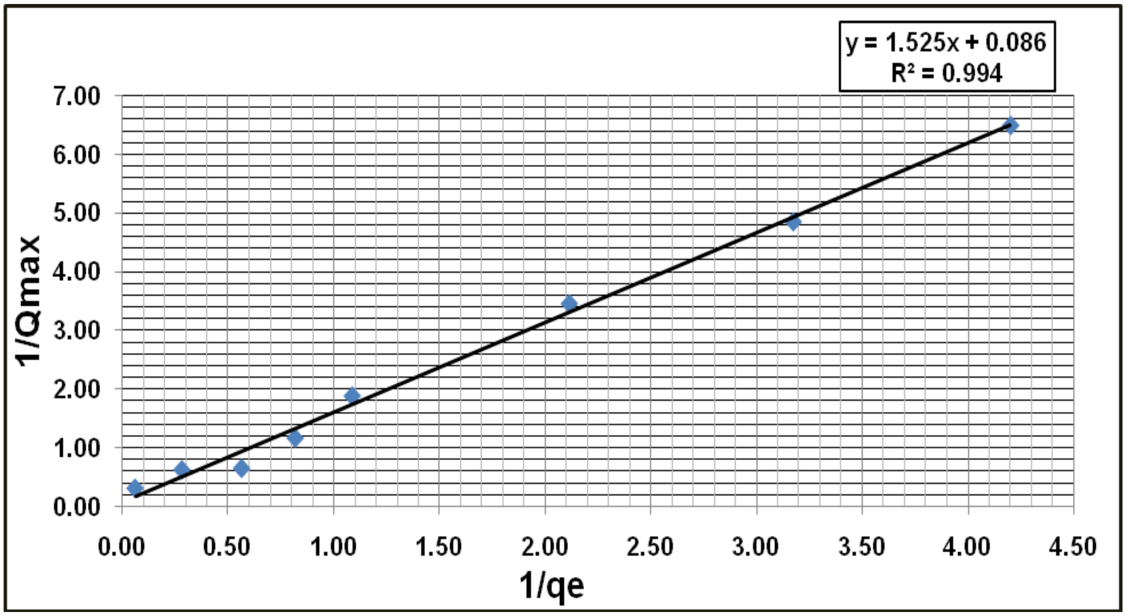

Figure 4. 5: Langmuir Isotherm for the raw eggshell

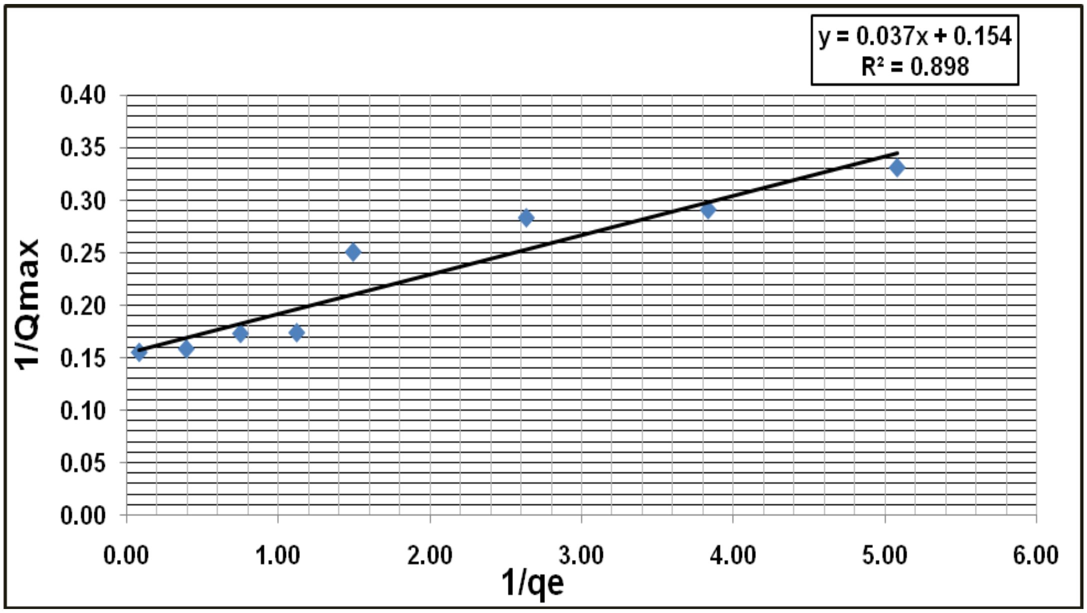

Figure 4.6 : Langmuir Isotherm for the boiled eggshell

Table 4. 2: Langmuir Isotherm Model

	Adsorption Capacity of sorbent Q_{max} (mg/g)	**Langmuir constant related to energy of sorption b (L/mg)**	**Correlation coefficient R^2**	**Error**	**Separation factor (R_L)**
Raw egg shell	11.63	0.0564	0.994	0.045	0.480
Boiled eggshell	6.494	4.162	0.898	0.005	0.013

The raw eggshell had a higher correlation coefficient $R^2 = 0.994$ and maximum monolayer adsorption capacity (Q_{max}) of 11.63 mg/g which is equivalent to 11.63 mg of Pb (II) ions per 1 g of eggshell. Boiled eggshell had correlation coeficient $R^2 = 0.898$ and adsorption capacity (Q_{max}) of 6.494 mg/g equivalent to 6.494 mg of lead (II) ions adsorbed per gram of eggshell under optimum adsorption conditions of the study.

From the values calculated in comparison with other models, it is apparent that Langmuir isotherm is appropriate for adsorption of Pb (II) ions signifying monolayer coverage and homogenous distribution of lead (II) ions onto the sorbent eggshell with no interaction between adsorbed species. The proper fitting of the experimental data to the Langmuir model suggests the adsorption sites having equal activity towards lead (II) ions adsorption from the effluent.

In order to determine whether the Langmuir isotherm was favourable the separation factor (R_L) (equation 2.3) was used. Based on the dimensionless separation factor on Langmuir model for raw eggshell was (0.480) while for boiled eggshell was (0.013). This shows that the shape of the Langmuir isotherm was favourable since the values range between ($0 < R_L < 1$) hence favourable adsorption.

4.3.2 Freundlich Adsorption Isotherm

The freundlich isotherm model is known for giving an empirical relationship and study heterogeneity and surface energy. In this study the adsorption of lead (II) ions to the eggshell surface with the assumption that different sites with different energies are involved.

The figures 4.7 and 4.8 indicates Freundlich adsorption isotherm for the Pb(II) ions removal using raw and boiled eggshell, respectively.

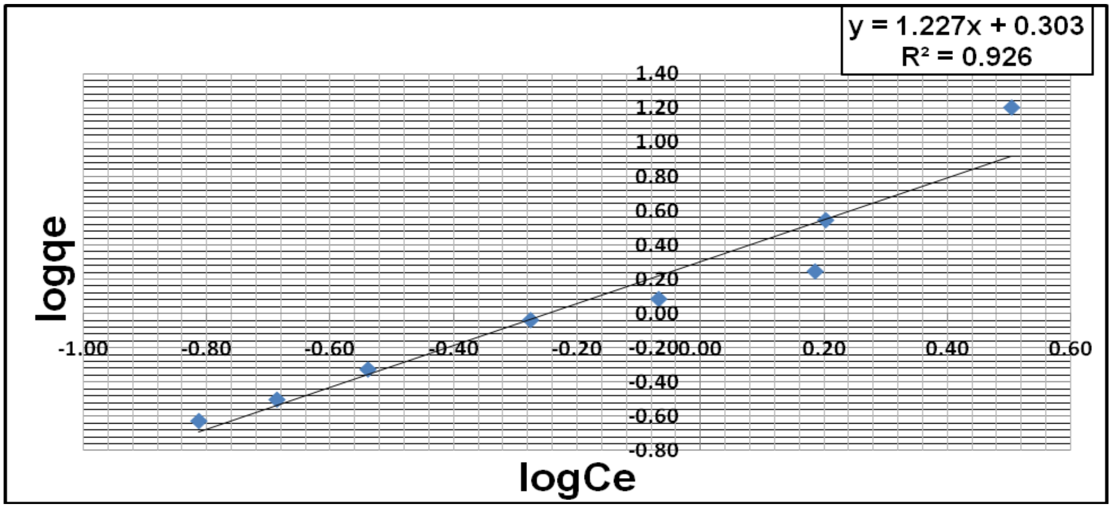

Figure 4. 7: Freundlich Isotherm for the raw eggshell

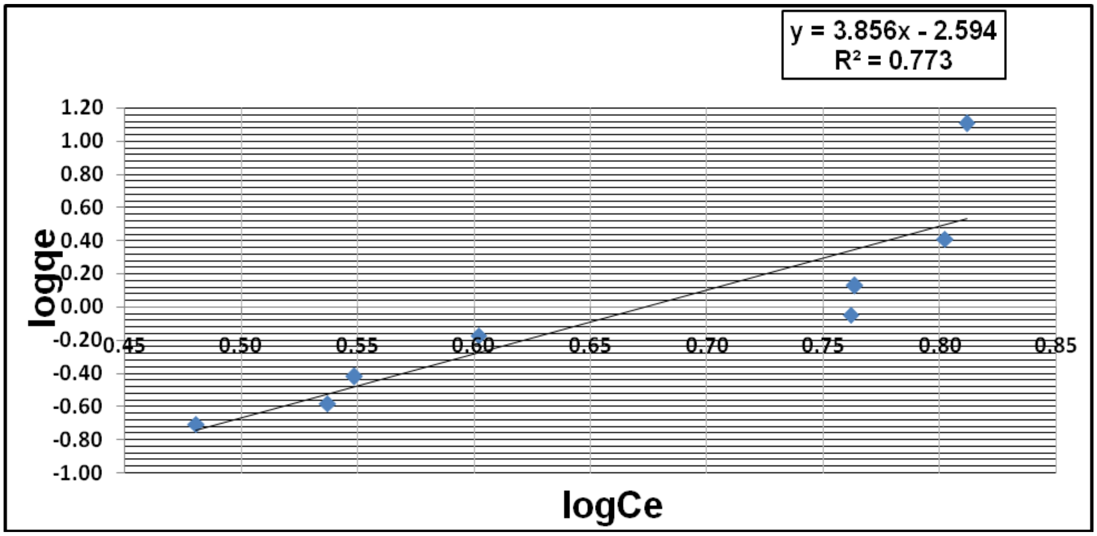

Figure 4.8 : Freundlich Isotherm for the boiled eggshell

The results of the graphical representation are presented in Table 4.3

Table 4. 3: Freundlich Isotherm Model

	Freundlich constant related to sorption capacity K (mg/g)	**Heterogeneous Factor (1/n) g/L**	**Freundlich exponent related to adsorption intensity (n)**	**R^2**	**Error**
Raw egg shell	2.009	1.227	0.815	0.926	0.141
Boiled Eggshell	$2.55 *10^{-3}$	3.856	0.259	0.773	0.852

According to Site (2001) favourable adsorption tends to occur when the n value is between 1 and 10. The larger the value of n the smaller the 1/n value implying stronger interaction between the adsorbent and adsorbate,1/n above 1 indicates cooperative adsorption while when n value equal to 1 indicates linear adsorption leading to identical adsorption energies for all the sites. In addition when 1/n is below 1 it indicates normal adsorption. In this study the raw eggshell had a higher K value (2.009 mg/g) than for the boiled eggshell ($2.55 *10^{-3}$ mg/g), indicating the raw eggshell has more adsorption capacity.

Therefore according to the experimental results the raw eggshell had a higher correlation coefficient (R^2) =0.926 compared to the boiled eggshell with R^2 = 0.773 as well as a higher adsorption capacity of 2.009 mg/g.

4.3.3 Temkin Adsorption Isotherm

The Temkin model takes into account the interaction between the eggshell and the lead (II) ions to be adsorbed and is based on the assumption that the free energy of sorption is a function of surface coverage. Adsorption in these case is considered by uniform distribution of binding energies, up to some maximum binding energy. Figures 4.9 and 4.10 show the graphical representation of the Temkin isotherm.

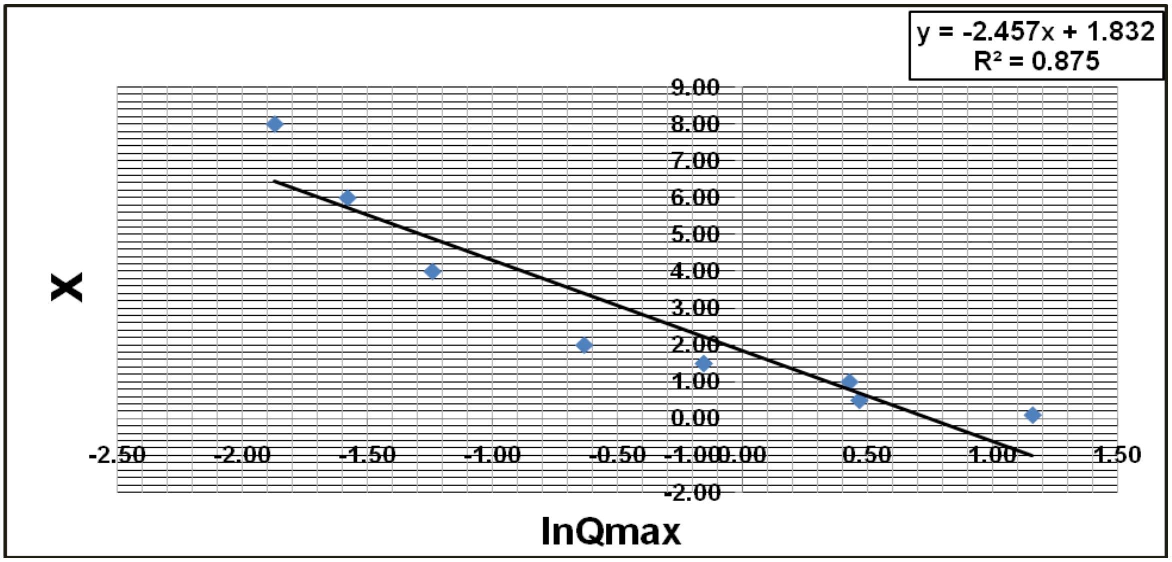

Figure 4.9 : Temkin Isotherm for the raw eggshell

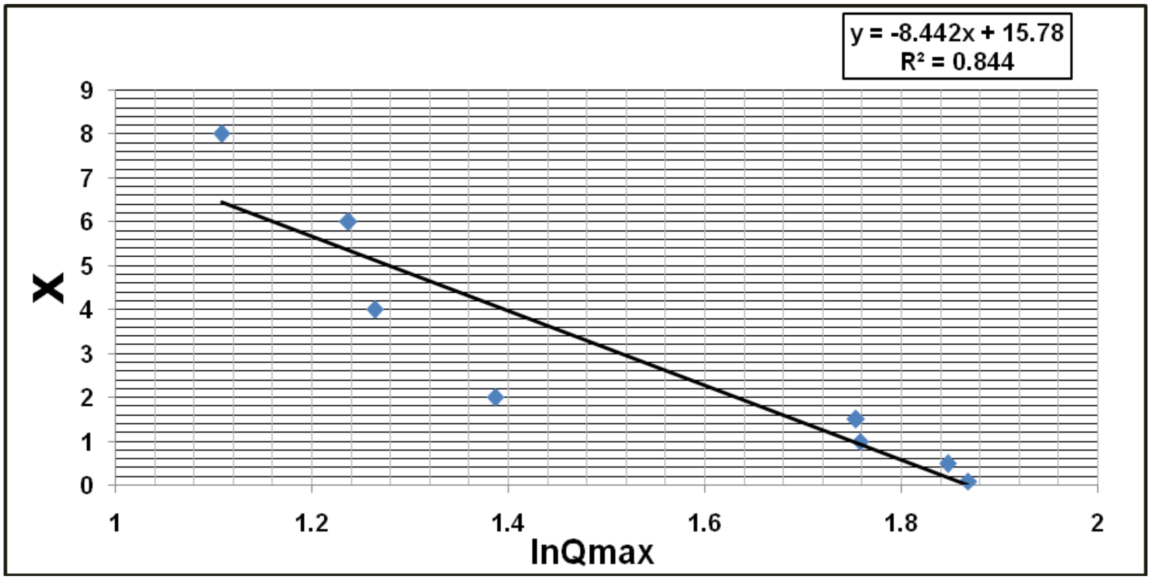

Figure 4.10 : Temkin Isotherm for the boiled eggshell

Table 4. 4: Temkin Isotherm Model

	A_T (L/mg) Constant related to adsorption capacity	**B (J/mol) Intensity of Adsorption**	**Error**	**R^2**
Raw egg shell	0.4744	-2.457	0.379	0.875
Boiled eggshell	0.1542	-8.442	1.479	0.844

Temkin isotherm fitted the experimental data because it takes into account of occupation of more active adsorption sites first although not better than Langmuir and Freundlich isotherms discussed above. The raw eggshell had a higher correlation coefficient $R^2 = 0.875$ with a higher heat of sorption of -2.457 J/mol and boiled eggshell had correlation coeficient $R^2 = 0.844$ and with lower heat of adsorption of -8.442 J/mol.

4.4 Performance of eggshell

According to the study the raw eggshell had better adsorption capacity compared to the boiled eggshell. This is visible from the results obtained in the regression analysis calculated. The adsorption capacity for the raw eggshell was 11.63 mg/g while that for the boiled eggshell was 6.494 mg/g. Thus it is clear that raw eggshell has better functional effects in treatment of industrial effluent containing Pb (II) ions than the boiled eggshell.

From literature eggshell has good adsorption characteristics due to chemical composition. The structure of the eggshell consists of 3 layers; cuticle layer on outer surface, calcareous and inner lamellar layer. Calcareous and lamella layer contain the matrix with protein fibre bonded to calcium carbonate (Stadelman, 2000). The mechanism of sorption of heavy metals by eggshell is through ion exchange to carbonate groups. The eggshell membrane layer has large surface area and constructed of a network of fibrous proteins that comprise of carboxyl and the amine groups which also contribute to adsorption (Tsai *et al.*, 2006). The raw eggshell has higher protein fibre comprising of substituting groups; carboxyl, sulphonic groups and amine groups (Allen and Koumanova, 2005; Polamesanaporn, 2001), than boiled eggshell where the fibrous protein has been denatured limiting efficient adsorption of Pb (II) ions.

The results are consistent with those studied by Park *et al.,* (2007) where efficient removal of Pb was observed with raw eggshell than the calcined eggshell which adsorbed cadmium and chromium. This was attributed to the difference in adsorption preference to the chemical composition of the adsorbent after exposure to different treatments.

Arunlertaree *et al.,* (2007) observed that the natural eggshell for both the hen and duck eggshell had higher adsorption capacity compared to the boiled hen and the duck eggshell. He attributed the performance to the natural eggshell having more protein fibre which comprise of carboxyl and amine groups that promotes adsorption.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The appropriate waste water treatment depends on the effluent characteristics while the sorption capacity depends on the adsorbent being investigated and the nature of the waste water being treated. From this study, eggshell showed promising removal of the lead (II) ions from aqueous solution as low cost sorbent and may be considered as an adsorbent for the lead (II) ions in industrial waste water effluent.

The chemical nature of the eggshell makes the adsorbent an attractive material to be used in the removal of lead (II) ions. Its neutralization capacity gives the eggshell an exceptional performance in the treatment of strongly acidic waste water from battery industrial effluent. The final samples after introduction of eggshell sorbent had pH levels ranging from (6 to 8) +/- 0.1 depending on the sorbent dosage subjected to.

The experiment carried out showed that the adsorption depends on contact time, pH and sorbent dosage. The experimental results showed that the lead (II) ions adsorption is pH dependent and the maximum adsorption of lead occurred at pH = 5 with 94% for raw eggshell and 88% for boiled eggshell, mass of the eggshell used was 1g, optimum particle size was through sieve No. 355µm and equilibrium contact time was 120 minutes. The shaking speed at 200 rpm provided extra energy for formation of new bonds between the Pb (II) ion and the eggshell surface.

Within the finest conditions the adsorption of lead (II) ions using raw eggshell had final concentration in the effluent of 0.2023 mg/L with removal efficiency of 98.9% which is below the EMCA guideline values on water quality (2006) for discharge of lead into public sewers at a concentration of 1 mg/L. The final lead concentration using the boiled eggshell within the optimum conditions was 2.109 mg/L (89%), which is above the guideline values.

The statistical isotherm model equations were satisfactory in predicting adsorption capacity of the eggshell under variable conditions. Equilibrium data for lead (II) ions removal showed the adsorption of lead was represented by the Langmuir, Freundlich and the Temkin isotherms. The experimental data for the adsorption process fitted best in the Langmuir isotherm model with correlation coefficient ($R^2 = 0.994$) followed by Freundlich ($R^2 = 0.926$) and the Temkin ($R^2 = 0.875$) isotherm model for the raw eggshell. The boiled eggshell had lower values of the correlation coefficient since its adsorption capacity was lower. The adsorption capacity using the Langmuir isotherm of the raw eggshell was at 11.63 mg/g while the boiled egg shell was at the 6.494 mg/g confirming the monolayer coverage.

It is clear from the study that the raw eggshell is better adsorbent than the boiled eggshell in the treatment of industrial effluent containing lead (II) ions. This could be attributed to the nature of the chemical composition. From literature the raw eggshell had good adsorptive characteristics due to its composition of polysaccharide fibres and collagen- protein which contains substituting group sites (hydroxyl, amine, sulphonic groups) whose bonding sites were broken when subjected to higher temperatures hence reduced adsorption capacity (Tsai *et al.*, 2006). In conclusion eggshell is abundant in supply and the adsorbent may be used in treatment of industrial waste water containing lead (II) ions due to the level of efficacy as seen in the study.

5.2 Recommendations for further studies

The study shows that metal uptake by the adsorbent eggshell is highly dependent on the active binding sites and the functional groups present on the adsorbent.

The study recommends the following areas for further studies:

- Further research need to be done to enhance the existing adsorption capacity through addition of functional groups on the surface of the adsorbent, in order to meet the EMCA guidelines of discharge to environment of 0.01mg/L. This may be achieved through studies to modify the adsorbent through chemical treatment as long as it is environmentally friendly,

- Proper disposal of used adsorbents; recovery of the heavy metals adsorbed and later recycle them for efficiency purpose which may be easily recovered through the smelter furnace.

- Further studies on the structural behavior in relation to the adsorption properties of the eggshell that may give information for designing batch sorption system and how it can be applied in an industrial set-up. This may include more analysis on the physicochemical nature of the eggshell since it affects rate and capacity of adsorption. This may assist in designing sorption columns (bed/column design) to improve efficiency,

- More research on the treatment of waste water to bring the concentration of toxic heavy metals below recommended release limit in order to conserve the living systems and the environment.
- Further research on durability and regeneration of the adsorbent for recycling and re-use is recommended
- Lastly I recommend the use of the eggshell in the treatment of raw industrial effluent containing Pb (II) ions.

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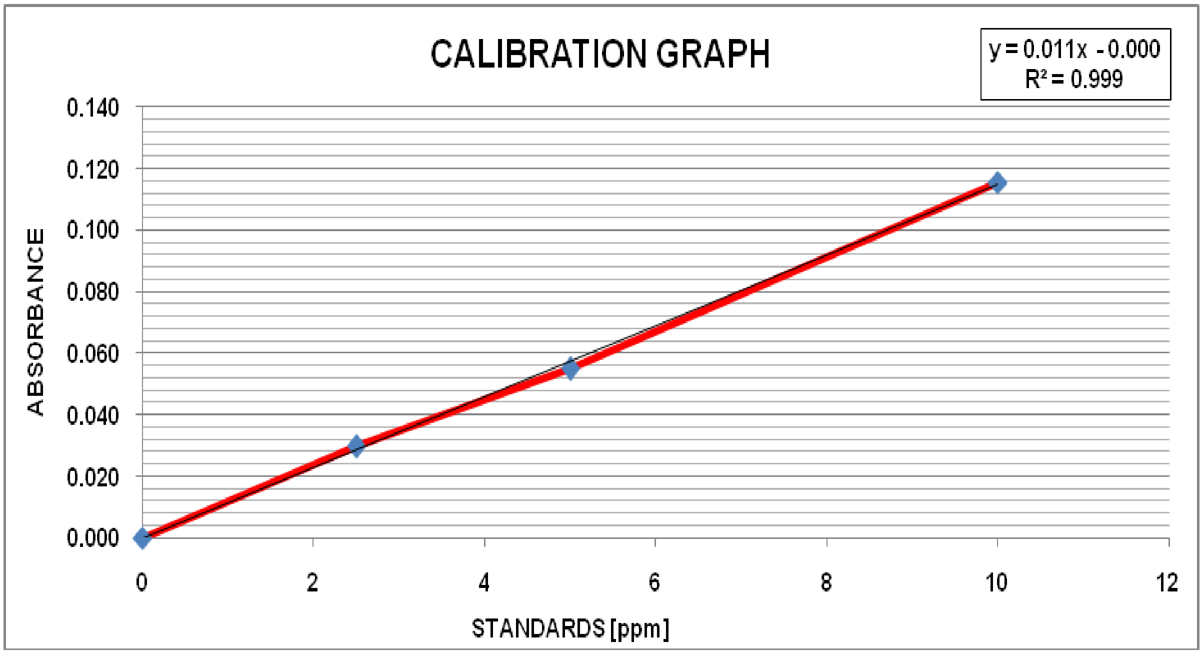
APPENDICES

Appendix AI : Calibration of the Atomic Absorption Spectrophotometer (AAS)

Stds (ppm)	Absorbance	% RSD
0	0.000	0
2.5	0.030	2.7
5	0.055	2.4
10	0.116	2.1



Appendix AII: Potential heavy metals in the industrial effluent and their quantities

Heavy Metal	**Quantities**
Sb (Antimony)	1.8 – 2.0
As (Arsenic)	0.21 - 0.26
Sn (Tin)	0.1 - 0.14
Cu (Copper)	0.02 - 0.05
Fe (Iron)	0.003 max
Ag (Silver)	0.01 max
Zn (Zinc)	0.005 max
Se (Selenium)	0.015 - 0.035
Cd (Cadmium)	0.005 max
Ni (Nickel)	0.01 max

(Source: Associated Battery Manufacturers, 2013)

EXPERIMENTAL DATA ON THE PARAMETERS

Appendix A III: Experimental data on effect of particle size on Lead (II) ions adsorption

		Raw Eggshell	
Sieve No.	**Initial Pb^{2+} conc.(mg/L) (C_o)**	**Final Pb^{2+} Conc. (mg/L) (C_e)**	**Removal Efficiency (%)**
355	19.1076	1.088	94%
425	19.1076	1.629	91%
500	19.1076	2.058	89%
600	19.1076	5.024	74%
710	19.1076	6.305	67%

Appendix A IV: Experimental data on effect of pH

		Raw Eggshell		**Boiled Eggshell**	
pH	**Initial Pb^{2+} Conc.(mg/L) (C_o)**	**Final Pb^{2+} Conc. (mg/L) (C_e)**	**Removal efficiency (%)**	**Final Pb^{2+} Conc (mg/L) (C_e)**	**Removal Efficiency (%)**
2	19.1076	2.0992	89.014	3.4666	81.8573
5	19.1076	1.1157	94.1612	2.1771	88.606
6	19.1076	1.6365	91.4356	3.1934	83.2871
7	19.1076	2.0623	89.207	4.0244	78.9382
9	19.1076	8.5578	55.2125	14.1327	26.0362
12	19.1076	10.2236	46.4944	16.8836	11.639

Appendix A V: Experimental data on effect of adsorbent mass

		Raw Eggshell		**Boiled Eggshell**	
Mass of Eggshell (g)	**Initial Pb Conc. [mg/L]**	**Final Pb^{2+} Conc. [mg/L]**	**Removal Efficiency [%]**	**Final Pb^{2+} Conc. [mg/L]**	**Removal Efficiency [%]**
0.1	19.2012	3.1855	83.4102	6.4773	66.2662
0.5	19.2012	1.5927	91.7052	6.3422	66.9700
1	19.2012	1.53118	92.0261	5.8011	69.7878
1.5	19.2012	0.8949	95.3396	5.7764	69.9167
2	19.2012	0.8301	95.6768	4.0001	79.1673
4	19.2012	0.2891	98.4946	3.5385	81.5715
6	19.2012	0.2059	98.9200	3.4458	82.0545
8	19.2012	0.1539	99.1985	3.0268	84.2373

Appendix A VI: Experimental data on effect of contact time

		Raw Eggshell		Boiled eggshell	
Contact Time (Min)	**Initial Conc. [mg/L]**	**Final Pb^{2+} Conc. [mg/L]**	**Removal Efficiency [%]**	**Final Pb^{2+} Conc. [mg/L]**	**Removal Efficiency [%]**
15	19.2012	0.5586	97.0909	2.4653	87.1609
30	19.2012	0.4730	97.5369	2.3796	87.6069
60	19.2012	0.2817	98.533	2.1884	88.603
90	19.2012	0.2023	98.9464	2.109	89.0164
120	19.2012	0.1822	99.0511	2.0889	89.1211
150	19.2012	0.1818	99.0532	2.0885	89.1232
180	19.2012	0.1818	99.0534	2.0884	89.1234

EQUILIBRIUM MODELLING

Appendix A VII: Adsorption capacity at various equilibrium concentrations for raw eggshell

Mass (g)	qe={[Co-Ce]V/m}	1/qe	Qmax= Qce	1/Qmax	Log qe	Log Ce	In Ce
0.1	16.02	0.0624	3.1854	0.3139	1.2045	0.5032	1.1586
0.5	3.52	0.2839	1.5927	0.6279	0.5467	0.2021	0.4654
1	1.77	0.5659	1.5311	0.6531	0.2472	0.1849	0.4260
1.5	1.22	0.8194	0.8549	1.1697	0.0865	-0.0681	-0.1568
2	0.92	1.0887	0.5301	1.8864	-0.03689	-0.2756	-0.6347
4	0.47	2.1150	0.2891	3.4596	-0.3253	-0.5390	-1.2412
6	0.32	3.1726	0.2059	4.8569	-0.5014	-0.6864	-1.5804
8	0.24	4.2001	0.1539	6.4977	-0.6232	-0.8128	-1.8715

Appendix A VIII: Adsorption capacity at various equilibrium concentrations for boiled eggshell

(g)	qe={[Co-Ce]V/m}	1/qe	Qmax	1/Qmax	lnCe	Log qe	Log Ce
0.1	12.72	0.0786	6.4773	0.1544	1.8683	1.1046	0.8114
0.5	2.57	0.3888	6.3422	0.1577	1.8472	0.4102	0.8022
1	1.34	0.7463	5.8011	0.1724	1.7580	0.1271	0.7635
1.5	0.89	1.1173	5.7764	0.1731	1.7538	-0.0481	0.7617
2	0.67	1.4898	4.0001	0.2499	1.3863	-0.1731	0.6021
4	0.38	2.6314	3.5385	0.2826	1.2637	-0.4202	0.5488
6	0.26	3.8308	3.4458	0.2902	1.2371	-0.5833	0.5373
8	0.20	5.0776	3.0268	0.3304	1.1075	-0.7057	0.4810

Appendix A IX: Laboratory apparatus used during Analysis

WEIGHING SCALE

pH Meter

ATOMIC ABSORPTION
SPECTROMETER, SPECTRA AA50

(Source: Author, 2013)