ADSORPTION STUDY OF Cr(VI) and Pb(II) FROM AQUEOUS SOLUTION USING ANIMAL CHARCOAL DERIVED FROM COW BONE

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AUGUST, 2011

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AUGUST, 2011

DECLARATION

I declare that the work in the thesis entitled Adsorption Study of Cr(VI) and Pb(II) from Aqueous Solution using Animal Charcoal derived from Cow Bone was performed by me in the Department of Chemistry under the supervision of PROF. V. O. Ajibola and PROF. C. E. Gimba.

The information derived from the literature have been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any university.

Olaniyi, Ibrahim		
Name	Signature	Date

CERTIFICATION

This thesis entitled ‘’ ADSORPTION STUDY OF Cr(VI) and Pb(II) FROM AQUEOUS SOLUTION USING ANIMAL CHARCOAL DERIVED FROM COW BONE ‘’ by Olaniyi, Ibrahim meets the regulations governing the award of the degree of Master of Science of Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literary presentation.

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ABSTRACT

Cow bones (femur and humerus) obtained from Zango abattoir village, Zaria, Nigeria were washed, rinsed with de-ionized water and sundried for a week. The cow bones were further dried in the oven at 105^0C for 72 hours, after which the bones were crushed and calcined in a muffle furnace (model GLM-3+PD/ IND) at 500^0C for 30 minutes. The carbonized bone samples were sieved into particle size 355µm using an Endecott's sieve. Adsorption experiments were carried out at two different temperatures (30^0C and 40^0C), five different timings viz: 5, 10, 20, 40 and 60 minutes, and five different initial metal ion concentrations viz: 10ppm, 20ppm, 30ppm, 40ppm and 50ppm of lead and chromium ions were prepared from the standard stock of each metal ion solutions respectively. The adsorbent (cow bone charcoal) was used to investigate the adsorption of lead and chromium from aqueous solution. The effect of contact time, initial concentration, kinetic studies, mechanism of adsorption and adsorption isotherms were studied. The cow bone charcoal exhibited good sorption capacity, and the adsorption data fitted the Langmuir and Freundlich isotherm; and on the basis of the Langmuir constants, the maximum adsorption capacity was observed for lead (6.21) at 40^0C and 60 minutes, while that of chromium (2.49) was observed at 30^0C and 10 minutes. The kinetic study of lead and chromium adsorption on cow bone charcoal was found to follow a pseudo-second order rate equation. This work showed that cow bone charcoal has good potential as an adsorbent in the treatment of lead and chromium contaminated waste water.

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF STUDY

Heavy metal pollution in the aquatic environment is a major health problem. This is because metals are toxic and non-biodegradable (Clement *et al*., 1995). Chromium is carcinogenic and is relatively wide spread in the environment (Fostner and Whittmann, 1979). It is used in industries such as electroplating, fertilizer, tanning and wood preservation, dyeing and photography industries (Martinez *et al*., 2001). Lead is toxic and also used in lead-acid battery, gunpowder, soldering lead applications among others. These metals found their way into the aquatic environment through wastewater discharge (Gupter *et al*., 2003). Because of their non-biodegradability, they tend to accumulate in aquatic organisms; feeding on such aquatic organisms as fish, crabs, or using such contaminated water can lead to metal poisoning in man. Heavy metals pose health hazards, if their concentrations exceed allowable limits. Even when these limits are not exceeded, there is still the potential of a long term poisoning, since they are known to accumulate within biological systems (Quek *et al.*, 1998). The increasing awareness of the environmental consequences arising from heavy metal contamination of the aquatic environment has led to the demand for the treatment of industrial wastewater before discharge into the aquatic environment (Fostner and Whittmann, 1979).

Adsorption process has been an area of extensive research because of the presence and accumulation of toxic carcinogenic effect on living species (Iqbal and Edyvean, 2004). The most common and harmful heavy metals are aluminium, lead, copper, nickel, chromium

and zinc. They are stable elements that cannot be metabolized by the body and get passed up in the food chain to human beings. When waste is disposed into the environment, a further long- term hazard is encountered. There are possibly more problems from these metals, which interfere with normal bodily functions, than have been considered in most medical circles. Reviewing all vitamins and minerals has shown that most substance that is useful can be a toxin or poison, as well. Metals are known primarily and almost exclusively for their potential toxicity in the body, though commercially, they may have great advantages (Mottet, 1987).

A conventional method for removing metals from industrial effluents includes chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion-exchange and carbon adsorption. Most of these methods suffer with high capital and regeneration costs of the materials (Huang and Wu, 1975). Therefore, there is currently a need for new, innovative and cost effective methods for the removal of toxic substances from wastewaters. Bone char as an adsorbent is an effective and versatile means and can be easily adopted in low cost to remove heavy metals from large amount of industrial wastewaters. Recent studies have shown that heavy metals can be removed using plant materials such as palm pressed fibers and coconut husk (Tan *et al*., 1993), water fern: *Azolla filiculoidis* (Zhao and Duncan, 1997), peat moss (Gosset *et al*., 2002), lignocellulosic substrate extracted from wheat bran (Dupont *et al*., 2003), *Rhizopus nigricans* (Bai and Abraham, 2001), cork and yohimbe bark wastes (Villaescusa *et al*.,2000), and leaves of indigenous biomaterials, *Tridax procumbens* (Freeland *et al*., 1974). Apart from the plant based materials, chemical modification of various adsorbents, phenol formaldehyde cationic matrices (Singanan *et al*., 2006), polyethylonamide modified

wood (Swamiappan and Krishnamoorthy, 1984), sulphur containing modified silica gels (Freeland *et al*., 1974) and commercial activated charcoals are also employed (Verwilghen *et al*., 2004).

1.2 BONE CHARCOAL

Bone charcoal also known as bone black, ivory black, animal charcoal, or a braiser, is a granular material produced by charring animal bones. The bones are heated to high temperatures in the range of 400^0C to 500^oC in an oxygen depleted atmosphere to control the quality of the product as related to its adsorption capacity for applications such as defluoridation of water and removal of heavy metals from aqueous solutions (Pattanayak *et al*., 2000). Bone charcoal consists mainly 90% of calcium phosphate and 10% of carbon. Structurally, calcium phosphate in bone charcoal is in the hydroxyapatite form (Pattanayak *et al*., 2000). Chen *et al*., in 2006 reported the use of bone charcoal to adsorb radio isotopes of antimony and europium ions from wastes and suggested that chemisorption was the main operating mechanism for $^{152}EU^{3+}$ removal from the aqueous solution with a high degree of irreversible fixation on bone charcoal. They claimed that sorption is due to cation exchange of metal ions onto hydroxyapatite. It has been demonstrated that calcium phosphate acts not only as adsorption centres but also enables ion –exchange process. Bone charcoal has lower surface area than activated carbons, but presents high adsorptive capacities for copper, zinc, cadmium (Choy and McKay, 2005).

1.2.1 Bone Charcoal (Granular) Possible Designations

a) Chemical Name : Tricalcium phosphate

b) Chemical Formula: C = (~12%) (Ca_3 (PO_4)$_2$ = (~ 88%)

c) $[Ca_{10}(PO_4)_6(OH)_2]$

1.2.2 Typical Applications of Bone Charcoal

I. Filtration Media: Bone char is used to remove fluoride from water and to filter aquarium water.

II. It is used in the sugar refining industry for decolorizing (Yacoubou and Jean, 2007) (a process patented by Louis Constant in 1812) (Thorpe and Thomas, 1912).This is a concern for vegans and vegetarians, since about a quarter of the sugar in the United States is processed using bone char as a filter (about half of all sugar from sugar cane is processed with bone char, the rest with activated carbon). As bone char does not get into the sugar, sugar processed this way is considered Parve/Kosher.

III. It is used to remove crude oil in the production of petroleum jelly.

IV. Bone char is also used as black pigment. It is sometimes used for artistic painting because it is the deepest available black, though charcoal black is often satisfactory and is often used.

1.3 ADSORPTION

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process (Oremusova, 2007).

Adsorption is operative in most natural, physical, biological and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification (Kopecky *et al*., 1996). Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus, it is energetically favourable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorptions. Some examples of adsorbents commonly used in adsorption experiments are charcoal, silica gel (SiO_2), alumina (Al_2O_3), zeolites, and molecular sieves (Oural, 2003).

1.3.1 Types of Adsorption

Physisorption (physical adsorption): is a type of adsorption in which the adsorbate adheres to the surface only through van der Waals (Weak intermolecular) interactions, which are also responsible for the non-ideal behaviour of real gases. It is characterized by low heats of adsorption of the order of 5 to 10 kCal per mol of the gas. The process of adsorption is similar to the condensation of gas on liquid (Oural, 2003). This suggests that the forces, by which the adsorbed gas molecules are held to the surface of the solid, are similar to the forces of cohesion of molecules in the liquid state. A rise in temperature will increase the kinetic energies of molecules and the molecules will leave the surface, thus lowering the extent of adsorption. Another characteristic of physical adsorption is that the adsorption equilibrium is reversible and is established rapidly. Physical adsorption is

generally observed in the adsorption of various gases on charcoal and is independent of the chemical nature of the substance being adsorbed.

Chemisorption: Here a molecule adheres to a surface through the formation of a chemical bond, as opposed to the van der Waals forces which caused physisorption. Chemisorption is thus highly selective since only certain types of molecules will be adsorbed by a particular solid. This depends on the chemical properties of gas and the adsorbent. Chemisorption is accompanied by much higher heat changes from 10kCal to 100kCal per mole. These heat changes are of the same order as those involved in chemical reactions. Unlike physical adsorption, chemical adsorption is not reversible. Hydrogen is strongly adsorbed by the metals nickel, iron and platinum (Norskov, 1990). In many cases, it has been observed that adsorption is neither physical nor chemical but a combination of the two. Some systems show physical adsorption at low temperature but as the temperature is raised; physical adsorption changes into chemical adsorption (Ruthven, 1984).

1.3.2 Adsorption Isotherms

A plot obtained between the amount of substance adsorbed per unit mass of the adsorbent and the equilibrium (in case of a gas) or concentration (in case of solution) at constant temperature is known as the adsorption isotherm (Sharma and Sharma, 1977).

1.3.3 Langmuir Adsorption Isotherm

In 1916, Irving Langmuir published an isotherm for gases adsorbed on solids, which retained his name. It is an empirical isotherm derived from a proposed kinetic mechanism. It is based on four hypotheses, viz:

1) The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
2) Adsorbed molecules do not interact.
3) All adsorption occurs through the same mechanism
4) At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other already adsorbed molecules of adsorbate, only on the free surface of the adsorbent.

The Langmuir sorption isotherm (Langmuir, 1916) has been successfully applied to many pollutants sorption processes and has been the most widely used sorption isotherm for the sorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that sorption takes place at specific homogenous sites within the sorbent. It is then assumed that once a metal ion occupies a site, no further sorption can take place at that site. The rate of sorption to the surface should be proportional to a driving force which times an area. The driving is the concentration in the solution and the area is the amount of bare surface. If the fraction of covered surface is ø, the rate per unit of surface is:

$$r_a = K_a C (1-ø) \quad \ldots (1.1)$$

The desorption from the surface is proportional to the amount of surface covered:

$$r_d = K_d ø \quad \ldots (1.2)$$

Where K_a and K_d are rate coefficients, r_a is sorption rate, r_d is desorption rate, C is concentration in the solution and ø is fraction of the surface covered.

At equilibrium, the two rates are equal, and:

$$ø = K_a C_e / K_d + K_a C_e \quad \ldots (1.3)$$

Since q_e is proportional to ø

$$ø = Q_e / Q_m \quad \ldots (1.4)$$

The saturated monolayer sorption capacity, q_m can be obtained when ø approaches 1, then $q_e = q_m$

The saturated monolayer isotherm can be represented as:

$$Q_e = Q_m K_a C_e / 1 + K_a C_e \quad \ldots (1.5)$$

The above equation can be rearranged to the following linear form:

$$C_e / Q_e = 1/ K_a Q_m + C_e \, 1 / Q_m \quad \ldots (1.6)$$

Where

C_e = the equilibrium concentration of metal ion (mg/l)

Q_e = amount of metal ion sorbed at equilibrium (mg/g)

Q_m is the maximum adsorption capacity, while K_a is a coefficient related to the affinity between the adsorbent and metal ions and also related to the energy of adsorption. By plotting C_e / Q_e against C_e , Q_m, and K_a can be evaluated from the slope $(1 / Q_m)$ and an intercept of $(1/ K_a Q_m)$.

1.3.4 Freundlich Isotherm

In 1906, Freundlich studied the sorption of a material onto animal charcoal (Freundlich, 1906). He found that if the concentration of solute in the solution at equilibrium, C_e was raised to the power 1/ n , the amount of solute sorbed being Q_e , then

$C_e^{1/n} / Q_e$ was a constant at a given temperature. This fairly satisfactory empirical isotherm can be used for non-ideal sorption and is expressed by the following equation:

$$Q_e = K_f C_e^{1/n} \quad \ldots (1.7)$$

Where

C_e = the equilibrium concentration of metal ion (mg/l)

Q_e = amount of metal ion sorbed at equilibrium (mg/g)

K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively.

The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\text{Log } Q_e = \log K_f + 1/n \log C_e \quad \ldots (1.8)$$

By plotting log Q_e against log C_e, K_f and n can be evaluated from the slope and intercept respectively.

The effect of isotherm shape can be used to predict whether a sorption system is ‘ favourable ‘ or ‘unfavourable ‘ both in fixed- bed systems (Weber and Chakravorti, 1974) as well as in batch processes (Poots *et al*., 1978). According to Hall *et al*., (1966), the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R, which is defined by the following relationship:

$$K_R = 1/ 1 + K_a C_o \quad \ldots (1.9)$$

Where K_R is a dimensionless separation factor, C_o is initial concentration (mg/l) and K_a is Langmuir constant (l/mg). The parameter K_R indicates the shape of the isotherm accordingly.

Table 1.1: Showing K_R values for different isotherm shapes

Values of K_R	**Type of isotherm**
$K_R > 1$	Unfavourable
$K_R = 1$	Linear
$0 < K_R < 1$	Favourable
$K_R = 0$	Irreversible

The plateau on each isotherm corresponds to monolayer coverage of the surface by the metal ions and this value is the ultimate sorptive capacity at high concentrations and can be used to estimate the specific surface area (A). If the area (**σ)** occupied by an adsorbed molecule on the surface is known, the specific surface area (A) in square meters per gram (m^2/g) is given by:

$$A = q_m N_0 \boldsymbol{\sigma} \times 10^{-20} \quad \ldots (1.10)$$

Where N_o is Avogadro's number and **σ** is given in square angstroms.

1.3.5 Factors Affecting Adsorption

The amount adsorbed per gram of solid depends on:

i. The specific area of the solid

ii. The equilibrium solute concentration in the solution

iii. The temperature and

iv. The nature of the molecules involved

1.3.6 Applications of Adsorption

Adsorption finds extensive applications both in the laboratory and in the industry. Some of the important applications are:

i. Adsorption of gases on solids is employed for creating a high vacuum between the walls of Dewar containers designed for storing liquid air or liquid hydrogen. This is achieved by placing activated charcoal between the walls which has already been exhausted to the maximum extent using a vacuum pump. The activated charcoal will adsorb any gas which may appear due to glass imperfection or diffusion through the glass.

ii. Adsorption of gases on solids is also utilized in gas masks which contain an adsorbent or a series of adsorbents. These adsorbents purify the air for breathing by adsorbing all the poisonous gases from the atmosphere. In the same manner, suitable adsorbents can also be employed in the industry for recovering the solvent vapours from air or particular solvents from the mixture of other gases.

iii. Charcoal finds an extensive application in the sugar industry. It is used as a decolouriser for the purification of sugar liquors. It can also be used for removing colouring matter from various other types of solutions.

iv. Adsorption is employed for the recovery and concentrations of vitamins and other biological substances.

v. Adsorption finds extensive applications in chromatography which is based on selective adsorption of a number of constituents present together in a solution or gas.

vi. Adsorption also plays an important role in catalysis. (Sharma and Sharma, 1977).

1.4 JUSTIFICATION

i. In recent years, there has been a considerable interest in the increasing contamination of water bodies by heavy metal ions via industrial activities with resultant effects on man and the environment (Okuo and Ozioko, 2001). For humans, poisoning by most of these metals causes severe dysfunction of the kidney, reproductive system, liver, brain and central nervous system (Manahan, 1994).

ii. Unarguably, this has posed a serious challenge to the Nigerian Government due to the indiscriminate discharge of waste waters containing heavy metal ions by small and medium scale industries.

iii. These industries lack the financial muscle to engage the use of conventional methods of treatments such as ion-exchange resins, precipitation, chemical coagulation, sedimentation and conventional biological treatment (activated sludge) (Vogel, 1989; Herbig, 1966) which are quite effective but unattainable for small and medium scale industries because of the prohibitive cost (Huang and Wu, 1975).

iv. Hence, it is expedient to device or seek alternative methods of removing heavy metal ions from wastewaters by using readily available cheap raw

material like cow bone charcoal via the process of adsorption (Wilson *et al*., 2006).

1.5 AIM

i. To investigate the readily available cheap raw materials like cow bone (which ordinarily contribute to environmental pollution in some areas), in the management of heavy metal poisoning.

ii. To examine the ability of cow bone charcoal as an adsorbent in the adsorption of metal ions from aqueous solution and therefore evaluate its potential in wastewater treatment systems.

1.6 OBJECTIVES

i. To determine the concentration of the selected metal ions before and after adsorption.

ii. To determine the amount of metal ions adsorbed per gram of the charcoal.

iii. To evaluate the sorption characteristics of the adsorbent with respect to Pb^{2+}, and Cr (VI).

iv. To analyze the data obtained from the adsorption experiment via Langmuir and Freundlich isotherms.

v. To evaluate the effect of particle sizes, different contact times and temperatures for each metal ionic strength.

CHAPTER TWO

LITERATURE REVIEW

2.1 POLLUTION

With the ever accelerating use of heavy metals by hospitals, universities, research laboratories, nuclear weapons, and others coupled with the ‘’Atom for peace programme’’ , there is an equally increasing problem of preventing the heavy metal wastes from polluting public air and water supplies. The most toxic metals are nickel, chromium and cadmium. The method is based upon the principle of removing heavy metals with activated charcoal. Activated charcoal is usually good agent for removing heavy metals of colour, tastes and odours from air and water for prevention of environmental pollution (Manzoor, 1995).

Generally, two types of pollution caused by heavy metals are :

i. Metallic air pollutants
ii. Metallic water pollutants

2.1.1 Metallic Air Pollutants

Majority of metallic compounds when present in air exist in a particulate form. To remain airborne, the particle must be very small (generally <10μm) and efficient collection is essential prior to analysis (Ilyin and Travnikov, 2005).

Variety of metallic air pollutants emitted to the atmosphere by industrial process, to affect materials, plants or animals seriously are given in Table 2.1. Metallic air pollution can be protected by activated charcoal particularly using it during chemical wars of radiation, in shape of masks.

Table 2.1: Sources, Annual Emissions and Health Effects of Metallic Air Pollutants (WHO, 2002)

Substance	Sources	Emissions (Tonnes/Years)	Health Effects
Lead	Auto exhaust, industry solid waste disposal, coal combustion, paint	208250	Brain damage, behavioral disorders, convulsions, death.
Vanadium	Coal and petroleum combustion industry	18440	Inhibits formation of phospholipids&S-containing amino acids.
Manganese	Industry,coalcombustion	1623	Fever, pneumonia
Nickel	Coal combustion, industry	6625	Dermatitis, dizziness, headaches, nausea, & carcinogenesis.also $[Ni(CO)_4]$
Cadmium	Industry	1962	Gastrointestinal disorder, respiratory tract disturbances, carcinogenic mutagenic
Mercury	Coal combustion, commercial industry	777	Tremor, skin eruption, hallucinations
Beryllium	Coal combustion, industry	156	Lungs damage, enlargement of lymph glands, emaciation

2.1.2 Metallic Water Pollutants

The disposal without attendant pollution of industrial wastewater containing heavy metals is becoming a matter of increasing concern, because many heavy metals form stable complexes with biomolecules and their presence in even small amounts can be detrimental to plants and animals (WHO, 2002).

Ingestion of polluted waters could cause physiological damage. The extent of this damage would depend upon several factors including:

1) Quantity
2) Concentration
3) Site of desorption
4) Physical half life
5) Biological half life
6) Type of metal radiation and
7) Energy of metal radiation

A suggestion has been proposed for the treatment of wastewater containing heavy metals by using the cheaper activated charcoal as an ion-exchange medium because water pollution falls into eight general categories viz:

1) Sewage
2) Infectious agents
3) Plant materials
4) Organic chemical exotics
5) Mineral chemical substances

6) Sediments

7) Radioactive materials

8) Heat

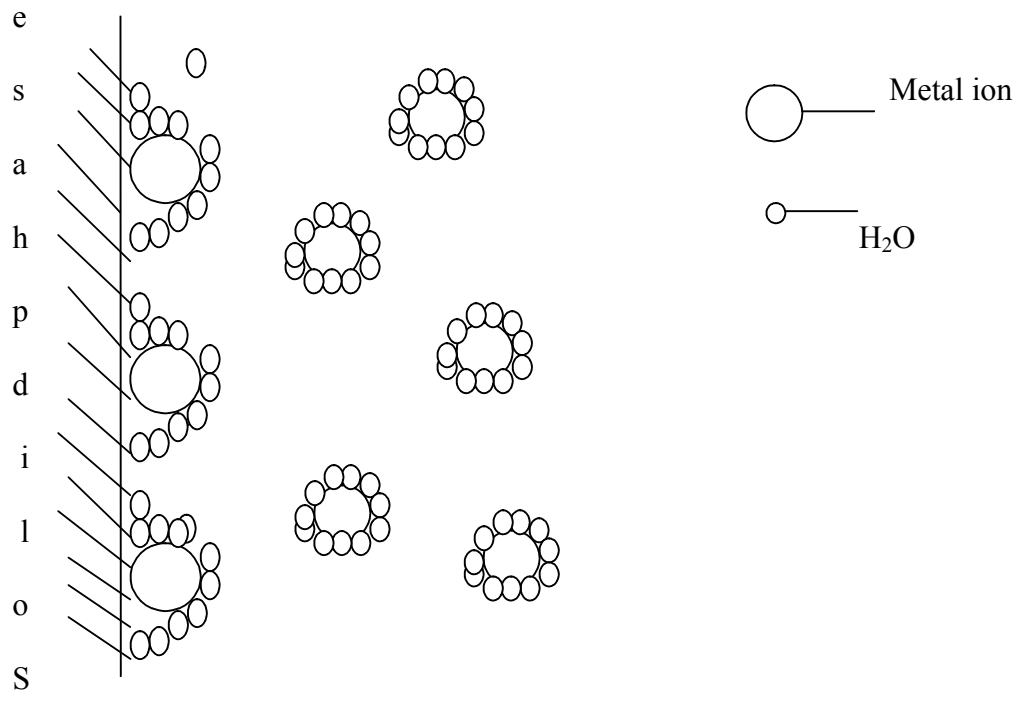


Figure 2.1: Physical picture of the dissolvation of metal ions on adsorption.

(Freeland, 1974)

Table 2.2: Toxic Metals in Natural Waters and Wastewater (EC, 2001)

Elements	Sources	Effects
Cadmium	Industrial discharge, mining, waste metal plating, water pipe	Replaces Zinc bio-chemically, causes high blood pressure, kidney damage, distinction of testicular tissue and red blood cells, toxicity to aquatic biodata.
Chromium	Metal plating, cooling tower water, additive (chromate) normally found as Cr (VI) in polluted water.	Essential trace metallic elements; possibly carcinogenic as Cr (VI)
Copper	Metal plating, industrial and domestic waste, mining, mineral leaching	Essential trace metal ,not very toxic to plants and algae at moderate levels.
Lead	Industry, mining, plumbing, coal, gasoline	Toxic (anaemia, kidney disease, nervous disorder) wild life destroyed.
Manganese	Mining industrial waste, acid mine drainage, microbial action on manganese minerals at low PE	Relatively non-toxic to animals, toxic to plants at high levels, stains materials (bath-clothing).
Mercury	Industrial waste, mining, pesticides, coal	Highly toxic.
Zinc	Industrial waste, metal plating, plumbing	Essential in many metallo-enzymes, toxic to plants at higher levels.
Nickel	Coal combustion industries	Dermatitis, dizziness, headaches, nausea, & carcinogenesis

2.2 ENVIRONMENTAL POLLUTION AND IMPACTS OF EXPOSURE

Heavy metals are metallic elements that are present in both natural and contaminated environments. In natural environments, they occur at low concentrations. However at high concentrations as is the case in contaminated environments, they result in public health impacts. The elements that are of concern include lead, mercury, cadmium, arsenic, chromium, zinc, nickel and copper. Heavy metals may be released into the environment from metal smelting and refining industries, scrap metal, plastic and rubber industries, various consumer products and from burning of waste containing these elements. On release to the air, the elements travel for large distances and are deposited onto the soil, vegetation and water depending on their density. Once deposited, these metals are not degraded and persist in the environment for many years poisoning humans through inhalation, ingestion and skin absorption. Acute exposure leads to nausea, Anorexia, vomiting, gastrointestinal abnormalities and dermatitis (UNEP, 2001).

Table 2.3: Shows the sources, risk levels and health effects from exposure to these Heavy Metals (UNEP, 2001).

Heavy Metal	Sources of Environmental exposure	Minimum Risk level	Chronic exposure toxicity effects
Lead	Industrial, vehicular emissions, paints and burning of plastics, papers, etc.	Blood lead levels Below 10 µg/dl of blood*	Impairment of neurological development, suppression of the hematological system and kidney failure.
Mercury	Electronics, plastic waste, pesticides, pharmaceutical and dental waste	Below 10 µg/dl of blood* Oral exposure of 4mg/kg/day**	Gastro-intestinal disorders, respiratory tract irritation, renal failure and neuro toxicity.
Cadmium	Electronics, plastics, batteries and contaminated water	Below 1 µg/dl of blood*	Irritation of the lungs and gastrointestinal tract, kidney damage, abnormalities of the skeletal system and cancer of the lungs and prostate.

µg/dl*: micrograms per deciliter of blood / Mg/kg**: milligrams per kilogram

On the other hand, persistent organic pollutants are long-lasting non-biodegradable organic compounds that accumulate in the food chain, especially fish and livestock, and pose serious health risks to humans. They dissolve poorly in water and are readily stored in fatty tissues hence may be passed to infants through breast milk. These chemicals include: aldrin, dieldrin, and dichlorodiphenyltrichloroethane (DDT), endrin, heptachlor, toxaphene, chlordane, hexachlorobenzene, mirex, Pesticides and polychlorinated biphenyls (PCBs) all of which are to be phased out and/or eliminated under the international environmental agreements (UNEP, 2001).

2.3 REMOVAL OF HEAVY METALS IN EFFLUENT BY ADSORPTION AND COAGULATION

Due to growing rigorous environmental regulations, limit for heavy metal in drinking water and wastewater becomes more and more strict. The method of ion exchange has been comprehensively employed to remove heavy metals in water bodies currently (Dorfner, 1972; Pajunen, 1987), but the cost is high. There are some reports on the removal of heavy metals in effluent by complexation of the dry biomass (Schiewer and Volesky, 1997; Fourest and Volesky, 1996). Unfortunately, these methods are difficult to use on a large scale. Previous research has reported the methods of biosorption or chemical modified solid surface (Veglio *et al.,* 2000); it takes some time for the adsorption of heavy metals in water bodies, especially, at parts per million (ppm) level.

At present, some coagulants have been used to remove the heavy metals in drinking water and effluent. As the flocs formed by the hydrolysis of aluminum salts and ferric salts have no affinity to heavy metals, the research of special coagulants become a hot focus. Many investigators have developed some composite coagulants, but up to now, only

limited results were obtained (Fourest and Volesky, 1996). Water resources available have decreased quickly, people irrigate with sewage in many regions. Heavy metals in water bodies will accumulate in crops and enter into the food chain ultimately. This influence is not observed in a short term, but it may result in irretrievable loss ten or more years later. The occurrence of the same illness in some regions has a close connection with water pollution. Moreover, it will take several decades for the remediation water bodies and soil polluted by heavy metals. During past decades, a newly environmental protection field is the restoration of water bodies and soil pollution.

In the present study, a kind of particles (10~100 nm) were formed in the course of hydrolysis of tetraethoxysilane, and then it was modified by (3-mercaptopropyl) trimethoxysilane (APS). The large specific surface area of these particles provides myriad active points of –SH for the adsorption of heavy metal, it was first used for the treatment of effluent contaminated by Pb and Cr (Cabatingan and Agapay, 2001).

2.4 CARBONIZATION

Carbonization is the formation of chars from source material which may be material of animal vegetable or mineral origin. Carbonization is generally accomplished by heating the source material usually in the absence of air to a temperature sufficiently high to dry and volatilized the substance in the carbon (Hasler, 1974).Temperature below 600^0C are preferable to produce chars suitable for activation (Cheremisinoff and Ellerbush, 1978), but it was reported that some of animal bone for the purification of brown sugar were done at 700^0C (Albert, 1978). The importance of carbonization is to dry and volatilize some undesirable substance in the carbonaceous samples, as well as to produce fine and closed pores filled with high molecular weight hydrocarbon and tarry materials.

2.5 RESEARCH REVIEWS

Adsorption processes are widely used to remove pollutants from wastewaters. Recently, concern has increased about the long-term toxic effects of water containing these dissolved pollutants. According to Lee *et al*., (1999) the disposal of coloured wastes such as dyes and pigments into receiving waters damages the environment as they are toxic to aquatic life. They also pose a problem because of their carcinogenicity and toxicity (Papic *et al*., 2000) and colour is also an aesthetic problem. Industrialization and urbanization has also added a significant amount of heavy metals being deposited into natural aquatic and terrestrial ecosystems Sanyahumbi *et al*., (1998) stressed that for humans, poisoning by most of these metals causes severe dysfunction of the kidney, reproductive system, liver, brain and central nervous system. Therefore, the need to monitor, control and cleanup heavy metal pollution is becoming more important..

A wide range of carbons exist for possible use as adsorbents. A large number of activated carbons have been prepared from different raw materials, as coconut shells, rice husks, nut shells (Pollard *et al*., 1992), peat moss (Nawar and Doma, 1989) ; peat (Poots *et al*.,1976). Each has its own applications and limitations.

Worral *et al*., (1996) found that soil organic matter controlled the adsorption of isoproturon when organic carbon contents exceeded 2.7%, where as, the clay-size separate became more important in isoproturon adsorption at lower organic carbon contents. Pesticide sorption onto pure clay minerals has been studied extensively (e.g., Bailey and White, 1964; Mcnamara and Toth, 1970; Laird *et al*., 1992; Worrall *et al*., 1996; Celis *et al*., 1997; Moreau-Kervevan and Mouvet, 1998). The adsorption behaviour of natural dirty clay mixtures in soils, however differs from that of pure clays (Christensen *et al*., 1989;

Cox *et al*., 1995) due to complexation with, e.g., Iron oxides, hydroxides, and soil organic substances.

There are a number of published observations that show the utility of using pecan shells as activated carbons for the removal of metal ions and organic compounds (Toles *et al*., 1998, 1999; John *et al*., 1998, 1999; Wartelle and Marshall, 2001; Dastgheib and Rocksraw, 2002a, b). These studies utilized activated carbons that were produced by acid, steam or carbon dioxide activation. These studies showed that acid activation of pecan shells resulted in higher metal ion adsorption than activation by carbon dioxide or steam. This was particularly true when all three activation methods were compared in one publication (Johns *et al*., 1999). The investigations noted above generally observed metal ion binding only in the presence of a single metal ion, usually Copper ion (Cu^{2+}). However, Dastgheib and Rockstraw (2002b) observed metal ion binding to pecan shell carbon in the presence of binary mixtures of various metals. Very little published literature report the competitive binding of a single metal ion in a mixture of metal ions in the presence of by product based activated carbons, although this would be important to ascertain because metal ions do not usually exist in isolation in contaminated waters or wastewaters.

Various processes including chemical precipitation and reverse osmosis, have been developed for removing heavy metal such as cadmium from wastewater (Gaballah and Kibertus, 1998). However, when applied to non-point sources of cadmium contamination such as stormwater runoff, these processes can be expensive to implement. Consequently, interest is growing in the use of sorbents made from low- cost renewable materials, such as solid wood waste or bark. Several natural adsorbents, including algal biomass (Matheickal *et al*., 1999; Yang and Volesky, 1999; Figuiera *et al*., 2000; Romero-Gouzalez *et al*., 2001; davis *et al*;2003), peatmoss (crist *et al*., 1996, 1999), bark (Randall *et al*., 1974; Seki *et al*;

1997; Gaballah and Kibertus, 1998; Al-Asheh *et al*., 2000), and sugar beet pulp (Reddad *et al*., 2002), have been investigated for their ability to sequester Cd from water. Adsorption of Cd from aqueous solutions can take place via two mechanisms, ion exchange and complexation. In the ion-exchange mechanism, Cd binds to anionic sites by displacing protons from acidic groups or existing alkali or alkali earth metals (e.g., Sodium (Na) or Calcium (Ca) from anionic sites at high pH (Crist *et al*., 1996, 1999; Romero-Gonzalez *et al*., 2001).

Gaballah and Kibertus, (1998) suggested that uptake of Copper (Cu) by wood takes place by several mechanisms : reaction between Cu^{2+} species and surface carbonyl groups (RCOOH); hydrogen bonding of hydrated Cu $(H_2O)_6^{2+}$ ions with cellulose; and formation of complexes with surface hydroxyl groups of lignin.

Recently, Min *et al*., (2004) reported on the use of juniper fiber for removing cadmium from aqueous solution. The juniper fiber consisted of a mixture of wood and bark. They observed that base treatment of the juniper fiber increased cadmium adsorption capacity and that adsorption of cadmium was greater for bark compared to wood. However, there was no explanation as to why bark performed better than wood. These researchers focused on improving the sorption capacity by base hydrolysis of surface carboxylate functional groups (RCOOR`).

Research on textile effluent decolourization in recent years has been focused on reactive dyes. Reactive dyes are mainly azo compounds with different reactive groups such as vinyl sulfone, chlorotriazine and also a metal nucleus. They are used to dye both cotton fabric (Cooper, 1992; Philips, 1996) and silk. These dyes impart excellent wash and light fastness properties but have a low fixation level due to hydrolysis. Hence, they are lost to the effluent and alkaline dye bath, accounting for 0.6-0.8g dye/ dm^3 (Gahr *et al*., 1994;

Steenken-Richter and Kermer, 1992). As a result, the management of the spent reactive dye baths has become a challenging and pressing problem.(Robinson *et al*., 2001).

Conventional wastewater treatment plants have low removal efficiency for reactive and other anion soluble dyes due to their stability towards light, wash; heat and oxidizing agents. The operational cost of these physico-chemical treatment processes is also very high. Dye wastewaters are also less treatable through biological aerobic processes. Although biodegradation is a potential possibility of removal of soluble dyes, the reactive dyes are an exception (Waters, 1995). The search for an alternative cost effective adsorbent has been focused on a range of natural raw materials such as sawdust, agricultural waste residues like corn cob, barley husk and wheat straw (Nigam *et al*., 2002), Linseed cake (Liversidge *et al*., 1997) eucalyptus bark (Morais *et al*., 1999), the giant duckweed, Spirodela polyrrza (Waranusantigul *et al*., 2003) just to mention a few. These have been studied for the adsorption of basic and reactive dyes. Biosorption, which involves the use of biological material- like or nonviable, can be used to concentrate and recover or eliminate the pollutants from aqueous solutions. Various workers have investigated the biosorption of various organic pollutants and colour from wastewaters (Tsezos and Bell, 1989; Fu and Viraragbavan, 2001).

Theodore and Reynolds, (1987) defined hazardous wastes as those that may have adverse effects on human and animal health or on the environment when not properly controlled. Wastes generally may exist as solids, liquids, sludge, powders and slurries. About 90% of these wastes exist in liquid or semi-liquid states. Freedman and Bowen (1989) have variously tabulated concentrations of toxic elements in the environment. Copper, being both essential and toxic to human health, can be removed from the environment mostly by chemical treatment and adsorption. Adsorption of heavy metal ions

from aqeous medium has been an area of active research in the recent times. Okeimen and Onyenkpa (1989) used melon (*Citrullus vulgaris*) seed husks for the sorption of Cd^{2+} , Pb^{2+} , Ni^{2+} and Cu^{2+} ions from aqueous solutions. Okeimen and Okundaye (1989) repeated the same feat with thiolated maize (*Zea mays*) cob powder for the removal of Co^{2+} and Cu^{2+} ions from aqueous solution. McPherson and Rowley (1990) reported the effectiveness of old rubber tyre for the removal of Hg^{2+} and Cd^{2+} ions from aqueous solution. Okeimen *et al*., (1991) reported the efficiency of groundnut (*Arachis hypogeal*) husks, modified with EDTA for the sorption of Cd (II) and Pb (II) ions from aqueous medium. Ashiegbu (1995), used thiolated beans (*Vigina unquiculata*) seed husks for the sorption of As (III) and Cr (III) ions from aqueous solution. Okuo and Ozioko (2001) also used chemically treated periwinkle shell for the sorption of Pb (II) and Hg (II) ions. The works of these authors suggest the possibility of developing good adsorbents from agricultural and marine wastes.

Metals like, cadmium, chromium and copper are toxic and may be found in both surface and underground water. The main source of the contamination is either industrial wastes or phosphorus fertilizers. One of the toxic effects of these metals is the accumulation in the physiological system causing osseous and also producing similar symptoms to osteoporoses. Salami and Adekola (2002), studying the adsorption of cadmium by goethite in aqueous solution observed that the adsorption of cadmium with smallest particle size of 0.9nm gave the highest adsorption capacity. A recent research by Gimba *et al*., (2002) on cyanide binding in micro columns with activated carbon matrix from groundnut and coconut shells observed that activated carbon from groundnut shells gave better adsorption than those from coconut shell.

Cellulose is the most abundant naturally occurring bio-polymer. It is made of glucose units, linked by β-1, 4-glycosidic bonds. Adsorptive properties of cellulose, especially with regard to reactive dyes have been well known since long and these have been extensively exploited in the textile industry. Affinity of cellulose towards metals and minerals have also been observed and exploited though to a much lesser extent.

A wide variety of natural products comprising mostly cellulosic matrix, were tried by different workers for the removal of various heavy metals from aqueous and non aqueous solution. These included pine bark (Al-Asheh *et al*., 2000), peanut shell (Wilson *et al*., 2006), sawdust (Argun *et al*., 2007; Sciban *et al*., 2007), cotton (Ozsoy and Kumbur, 2006). Shea butter seed husk (Eromosele and Abarc, 1998). Sunflower stalk (Sun and Shi, 1998). CACM2, an adsorbent extracted from a cactus (Carrillo-Morales *et al*., 2001). Low cost cellulosic materials such as bamboo pulp and sawdust dyed with monochlorotriazine type reactive dyes have been found to remove Cu^{2+}, Pb^{2+}, Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, and Ni^{2+} from their aqueous solutions (Shukla and Sakhardande, 1991).

Recently, an extensive review has been carried out on the possible exploitation of the wood industry by products such as barks, sawdust in the field of heavy metal removal from contaminated effluents. Different sawdust species such as red fir, mango, lime, pine, cedar, teak, barks of pine , oak and spruce have been examined with regards to their adsorption of different heavy metals, namely, Cd, Cr, Cu, Hg, Ni, Pb, and Zn. Functionality of cellulose by impregnating with inorganic substances has been reviewed by Kurokawa and Hanaya (1995).

Elements in every group of the periodic table have been found to be stimulatory to animals. Most metals in the fourth period are carcinogenic. It can be assumed that the carcinogenicity is related to the electronic structure of transition and inner transitional

metals (Luckey and Venugopal, 1977). Since copper is an essential metal in a number of enzymes for all forms of life, problems arise when it is deficient or in excess. Excess copper accumulates in the liver and the most toxic form of copper is thought to be Cu^{+}. Its toxicity is highly pH dependent and it has been reported to be more toxic to fish at lower pH values (Sharma *et al*., 1992). In some respect the intake of essential elements is more critical than for toxic elements. However, epidemiological evidence, such as a high incidence of cancer among coppersmiths, suggests a primary carcinogenic role for copper (Luckey and Venugopal, 1977). The co -carcinogenic character of copper is accepted. A higher incidence of stomach cancer in humans has been found in regions where the Zn: Cu ratio in the soil exceeded certain limits (Luckey and Venugopal, 1977). Lead is a typical toxic heavy metal with cumulative and nondegradative characteristics. Lead is fairly widespread in our consumer society and probably is the most serious toxic metal. Evidence of harmful effects in adults is rarely seen at blood where lead levels are below 80 mg per 100 ml. Human exposure to lead occurs through air, water and food. The passage of lead into and between these media involves many complex environmental pathways. There is a long history of human exposure to abnormally elevated levels of lead in food and drink, due to practices such as cooking in lead-lined or lead glazed pots and the supply of water through lead pipes (Manahan, 1991).

The removal of metal ions from effluents is of importance to many countries of the world both environmentally and for water re-use. The application of low-cost sorbents including carbonaceous materials, agricultural products and waste by-products has been investigated (Nguyen and Do, 2001). In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat (Ho and McKay, 2000), wood (Poots *et al*., 1978), pine bark (Al-Asheh and Duvnjak, 1997), banana pith (Low *et*

al., 1995), rice bran, soybean and cottonseed hulls (Marshall and Johns, 1996), peanut shells (Wafwoyo *et al*., 1999), hazelnut shell (Cimino *et al*., 2000), rice husk (Mishra *et al*.,1997), sawdust (Yu *et al*., 2001), wool (Balkose and Baltacioglu, 1992), orange peel and compost (Azab and Peterson, 1989) and leaves (Zaggout, 2001). Most of these works have shown that natural products can be good sorbents for heavy metals. Indeed, it could be argued that many of these natural sorbents remove metals more by ion exchange than by adsorption. Nevertheless, many previous workers tend to base their analyses on sorption theories. These include: the acidic properties of carboxylic and phenolic functional groups present in humic substances (Bloom and McBride, 1979) (Boyd *et al*., 1981). Some ion exchange reactions, e.g. proton release when metal cations bind to peat (Bloom and McBride, 1979).

CHAPTER THREE

MATERIALS AND METHODS

3.1 CHEMICALS AND REAGENTS

The metal ion solutions**:** Pb^{2+} and Cr (VI) ions were prepared from analar grade (BDH) Pb $(NO_3)_2$ and $K_2Cr_2O_7$ respectively. De-ionised water was used for the preparation of all solutions and adsorption experiments.

3.2 SAMPLE COLLECTION AND PREPARATION

The cow bones (Femur and Humerus) were collected from Zango abattoir village, Zaria, Nigeria. The bones were thoroughly washed to rid them of adhering dirts, rinsed thoroughly with de-ionized water and sun-dried for a week. Afterwards, the bones were taken to the laboratory and further oven-dried for 72 hours at 105^0C (Masri and Friedman, 1974). The dried cow bones were broken into smaller pieces, ground into powder using mortar and pestle and sieved into particle size of 355µm using an Endecott's sieve.

3.3 PRELIMINARY WORK

The physical characteristics carried out on the raw adsorbent were**:** Bulk density, carbonization, moisture content, dry matter, total Ash content, total surface area, volatile content, fixed carbon and pH.

3.3.1 Carbonization

Carbonization of the sized cow bone (Femur and Humerus) powder was carried out at 500^0C for 30 minutes in a muffle furnace (Model GLM-3+PD/IND) manufactured by carbolite, Bramford, Sheffield, England (Gimba *et al*., 2001). 6g each of the raw cow bone powder were measured in batches into 5 large nickel crucibles and calcined at 500^0C in an enclosed environment for a resident time of 30 minutes; this task was repeated until all sample were calcined. Carbonized products from the raw bone sample were aerated and pooled together in a plastic container.

3.3.2 Bulk Density

The bulk density of the adsorbent (cow bone powder) was carried out in the laboratory; the method described in European standards, CEN/ TS, (2005) was employed.

Procedure

This was done by measuring the volume of water displaced when a known weight of the raw sample was dropped into a graduated measuring cylinder.

Calculation

Bulk Density (BD) = M_a/ V_a x 1000kg/l

Where

M_a = weight of sample

V_a = volume of water displaced

3.3.3 Moisture and Dry Matter Content Determination

2g of the raw cow bone (sorbent) sample was weighed out in a preweighed petridish. The sample was placed in the thermostatic oven for 1 hour at a temperature of 105^0C. After which the sample was cooled in a dessicator. The oven dried sample was reweighed and the moisture content was determined (ASTM, 1994).

Calculation:

Moisture content (%) = $W_0 - W_1 / W_0$ x 100%

W_0 = Initial weight of dry sorbent

W_1 = New weight of sorbent after drying

Dry matter (%) = Oven dry weight (g) / Initial sample weight (g) x 100%

3.3.4 Ash Content Determination

Ash content determination was determined using the method employed by Dara (1991) and Aloko and Adebayo (2007). 2g of the sorbent was placed in a preweighed porcelain crucible and transferred into a preheated muffle furnace at a temperature of 500^0C for 2 hours, subsequently; the crucible and its content were cooled in a dessicator. The crucible and its content were reweighed and the new weight was noted. The percentage ash content was calculated with the formula below:

Calculation:

A_c (%) = W_a / W_0 x 100%

W_a = weight of ash after cooling

W_0 = original weight of dry sorbent

3.3.5 Volatile Content Determination

2g of the sample was heated to about 300^0C for 10 minutes in a partially closed porcelain crucible placed in a muffle furnace. The crucible and its content were retrieved and cooled in a dessicator. The difference in weight was recorded and the volatile content determined thus.

Calculation

V_c (%) = [$W_0 – W_a$ / W_0] x 100%

Where

V_c = volatile component in percentage

W_0 = the original weight of dry sorbent

W_a = the weight of matter after cooling

3.3.6 Fixed Carbon Determination

The fixed carbon content was determined using the formula:

F_c (%) = $100 – V_c – A_c - M_c$

Where

V_c = volatile content

A_c = ash content

M_c = moisture content

3.3.7 pH Determination

The pH of the raw sample was determined by dispersing 1.0g sample in 100ml of distilled water and stirred for 1 hour. pH of the supernatant solution was obtained with an electronic pH meter; samples were run in duplicates.

3.4 PREPARATION OF STANDARD SOLUTIONS

De-ionized water obtained from the Chemistry Department of Ahmadu Bello University, Zaria was used in the preparation of all solutions. Stock solutions of the following metal ions were prepared as described below: 1000ppm of Pb^{2+} was prepared by dissolving 1.5985g of lead nitrate, Pb $(NO_3)_2$ in de-ionized water and the volume was made to the mark in a 1000cm^3 volumetric flask using de-ionized water.

1000ppm of Cr (VI) ion was prepared by dissolving 2.8289g of potassium dichromate, ($K_2Cr_2O_7$) in de-ionized water and the volume was made to the mark in a 1000cm^3 volumetric flask using de-ionized water.

3.5 PREPARATION OF METAL ION SOLUTIONS

Metal ion (Pb^{2+} and Cr (VI) ions) solution of varying concentrations 10ppm, 20ppm, 30ppm, 40ppm and 50ppm were prepared using a serial dilution from the standard stock of each metal ion.

3.6 ADSORPTION EXPERIMENTS

The experiment was carried out in a batch mode for the measurement of adsorption capabilities. 1.00g of the adsorbent (bone charcoal) was placed into each of five dry 100ml conical flasks. Different initial metal ion concentrations of 10, 20, 30, 40, and 50mg/l of lead and chromium ions measured from the standard stock of each metal ion were added to each conical flask and made up to the 100ml mark with de-ionized water. The conical flasks were tightly stoppered, then shaken periodically at room temperature on an end-over-end shaker for one hour; after which the reaction mixture was allowed to equilibrate at different contact time of 5, 10, 20, 40 and 60 minutes in a thermostatic water bath maintained at two different temperatures say 30^0C and 40^0C.

At the end of each contact time, the mixture in each conical flask was filtered through Whatman (No 1) filter paper into 120ml plastic bottles. The residual (equilibrium) concentrations of lead and chromium ions in the filtrate were determined by Atomic Absorption Spectrophotometer (AAS). Differences between the initial and final (residual) concentrations were recorded as the amount of each lead and chromium ions removed from solution. In order to obtain the sorption characteristics of the adsorbent with respect to lead and chromium, the Langmuir and Freundlich expressions were used in analyzing the data obtained from the adsorption experiments (Kopecky *et al*., 1996).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 PRELIMINARY INVESTIGATION

Table 4.1 Shows the physicochemical characteristics of cow bone charcoal (femur and humerus).

Table 4.1: Physical characterization of cow bone charcoal (femur & humerus)

Solubility	Insoluble in cold & hot water
Bulk density	1.05g/l
Moisture content	3%
Ash content	66%
Volatile content	22%
Fixed carbon	9%
pH of adsorbent(raw sample)	7.32
pH of carbonized sample	7.55
Percentage dry matter	97%
Colour	Black
Odour	odourless
Appearance	Powdered solid

On investigation, it was observed that the cow bone charcoal had a high bulk density of 1.05g/cm^3 which is an indication of good filterability. That is, it would be able to filter more liquid volume before available cake space is filled. The 66% ash content value obtained for the cow bone charcoal is an affirmation that the cow bone charcoal is rich in inorganic constituents. The 22% low volatile content of the cow bone charcoal showed that this biological material is stable for adsorption experiment.

4.2 ADSORPTION ISOTHERM AND EFFECT OF INITIAL CONCENTRATION

The results obtained on the adsorption of Pb^{2+} and Cr (VI) ions with different particle sizes and at different temperatures, initial concentrations and times were analysed by using the models given by Langmuir and Freundlich which correspond to homogenous and heterogeneous adsorbent surfaces, respectively. The effect of initial concentration was also considered to observe the trend of adsorption. The Langmuir isotherm model assumes uniform energies of adsorption on to the surface and no migration of adsorbate in the plane of the surface (Chang and Frances, 1995).

Table 4.2: Adsorption constants for Langmuir and Freundlich isotherms at particle size 355µm, 30^{o}C and 5min.

	Langmuir constants			Freundlich constants		
Metal ion	Q_M (mg/g)	K_a	R^2	K_F(mg/g)	n	R^2
Pb^{2+}	0.31	0.06	0.984	0.03	0.78	poor
Cr (VI)	0.53	0.11	0.583	$1.72x10^{-3}$	0.28	0.844

A linearised plot of Langmuir and Freundlich isotherm and effect of concentration for Pb^{2+} and Cr (VI) at particle size of 355µm, 30^{0}C and 5 minutes are shown in Fig. 4.1-4.5.

Where Q_M = maximum adsorption capacity

K_a = affinity between the adsorbent and the metal ions

R^2 = rank correlation coefficient

n = adsorption intensity

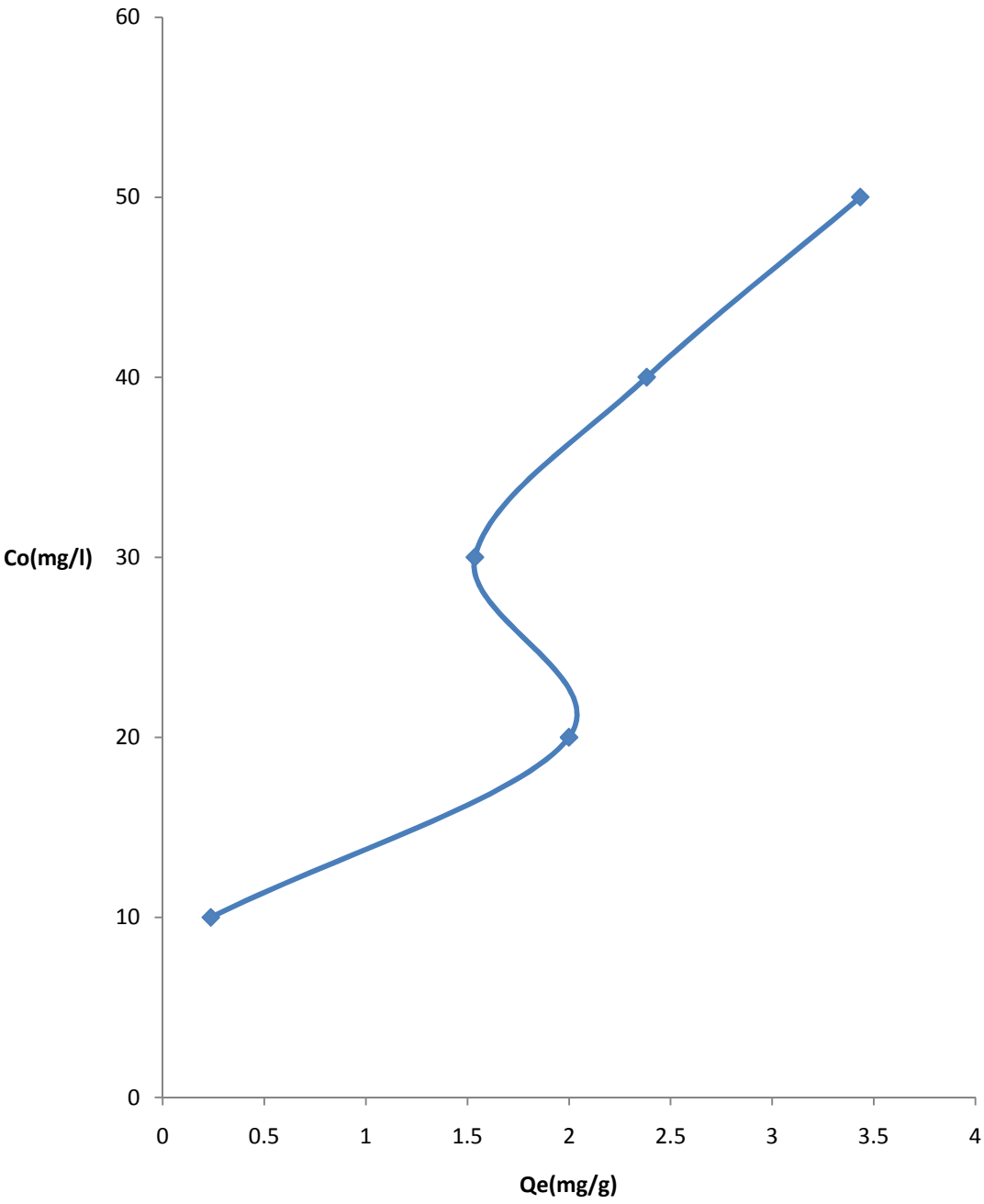


Fig.4.1. Effect of concentration on the adsorption of Pb^{2+} at 355µm, 30°C and 5min

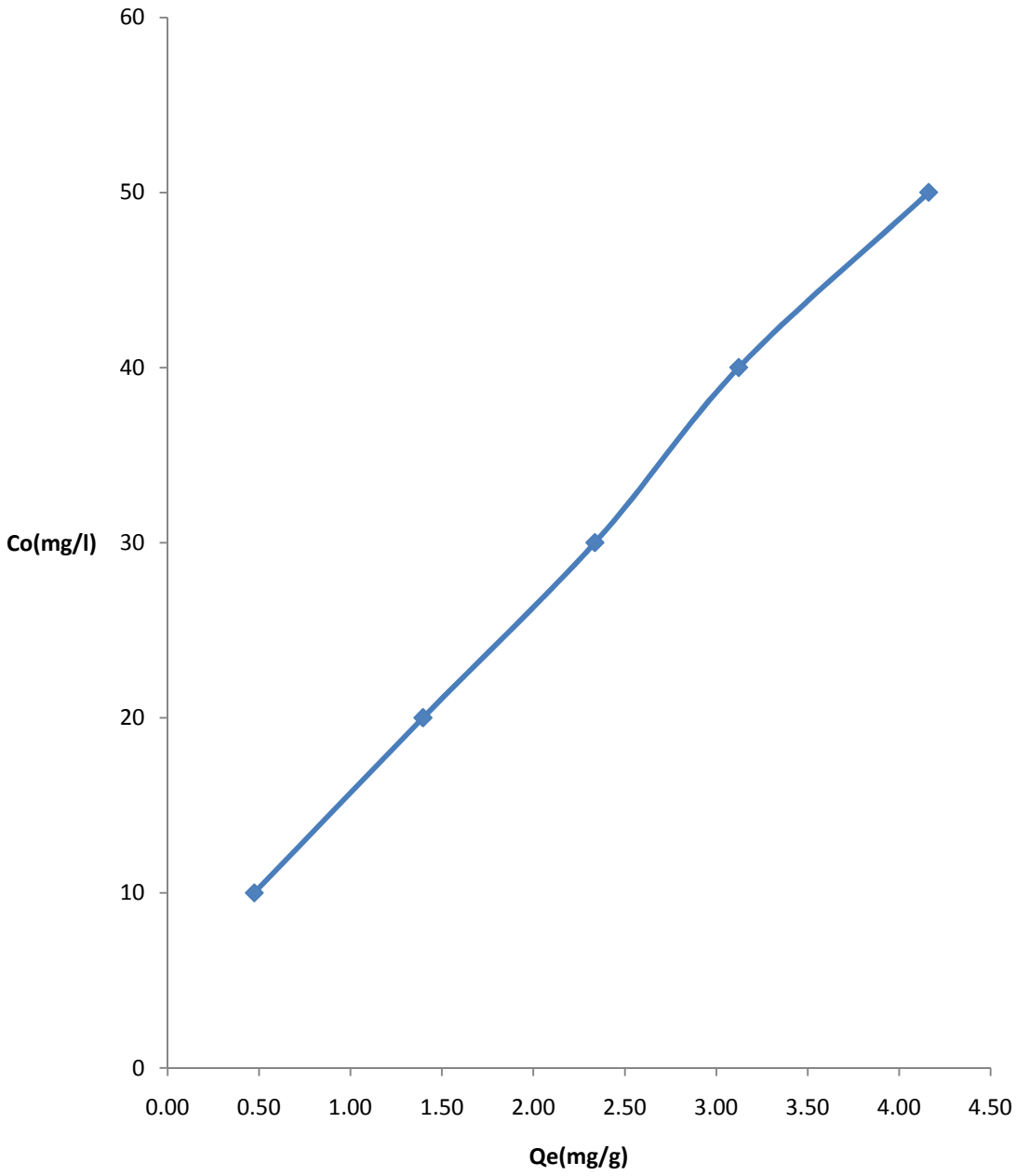


Fig.4.2.Effect of concentration on the adsorption of Cr (VI) at 355µm, 30^{o}C and 5min

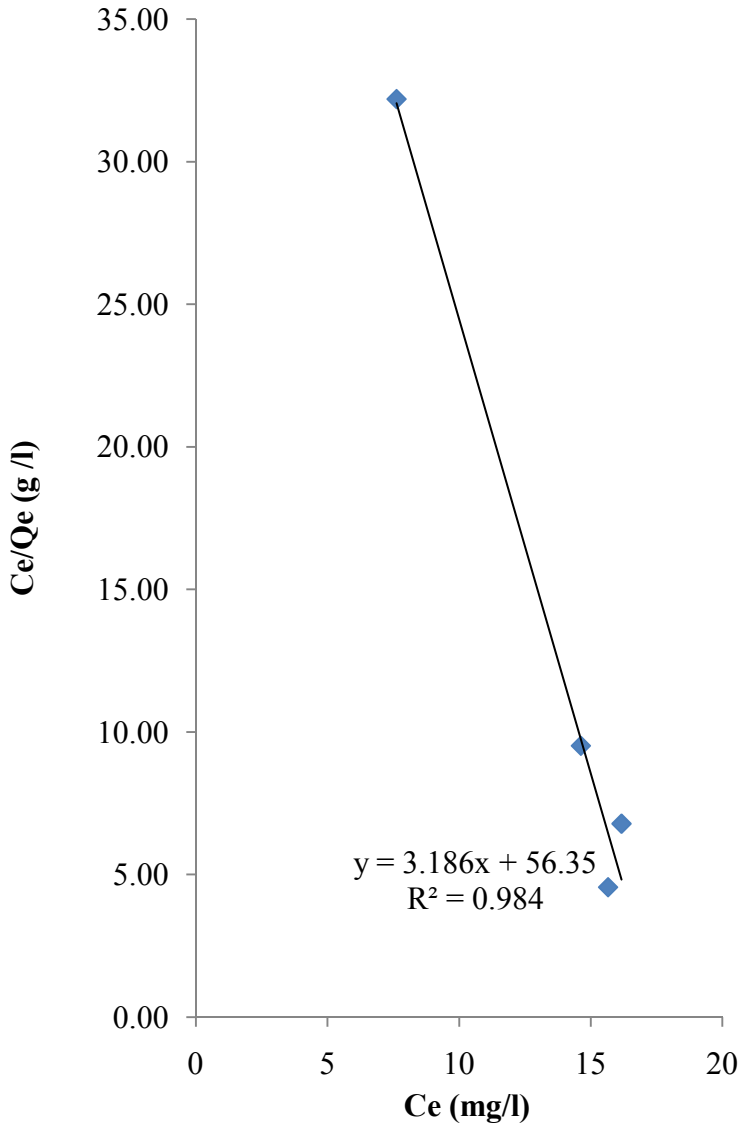


Fig. 4.3.Langmuir isotherm for the adsorption of Pb^{2+}at particle size 355µm,30^0C and5 min

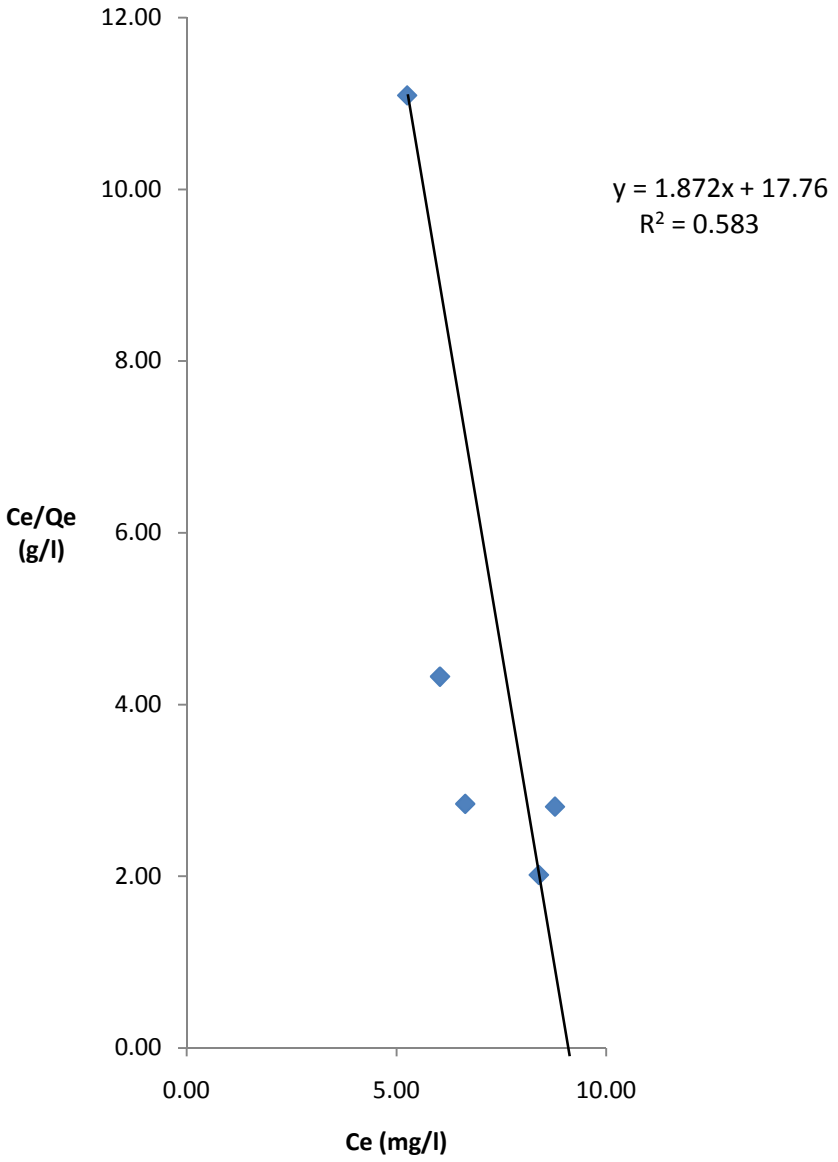


Fig.4.4. Langmuir isotherm for the adsorption of Cr (VI) at particle size 355µm,30^{o}C and 5min

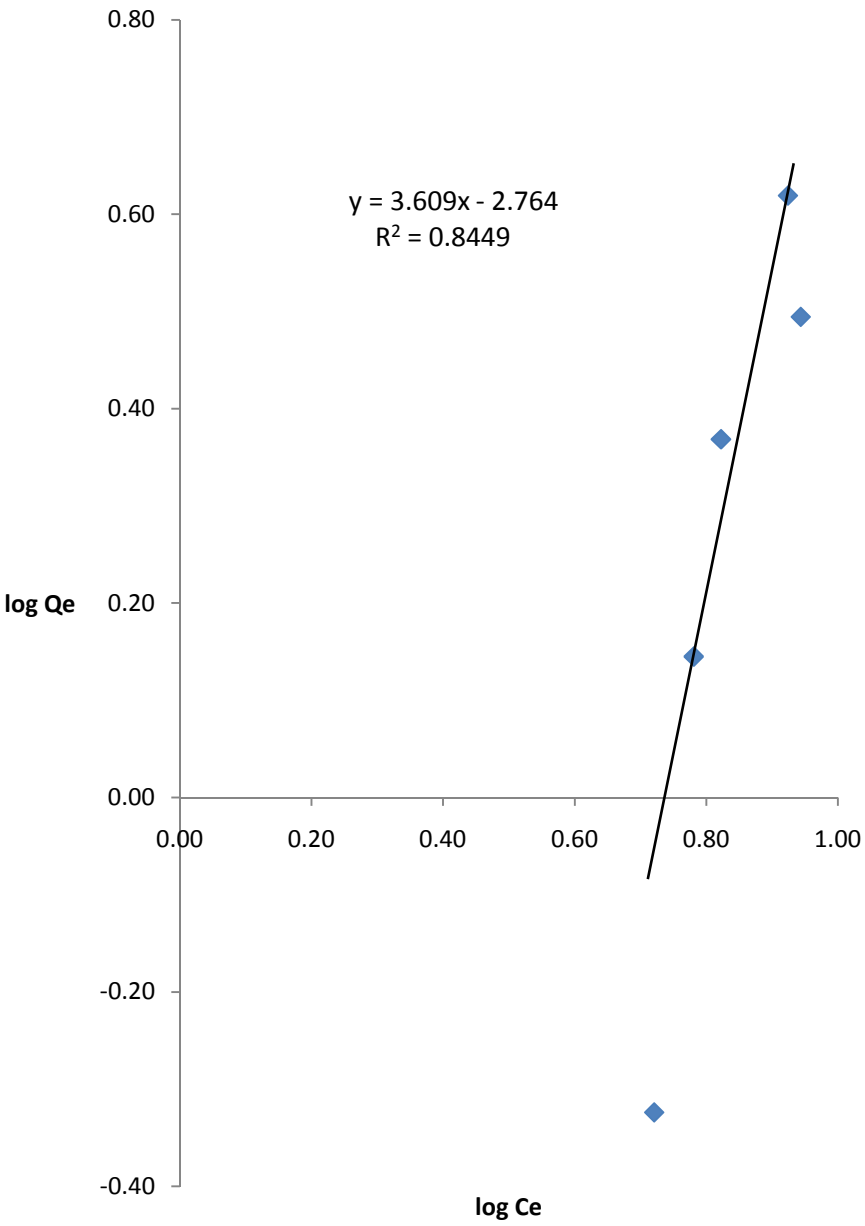


Fig.4.5. Freundlich isotherm for the adsorption of Cr (VI) at particle size 355µm, 30^{o}Cand 5min

Fig.4.1-4.2 shows the effect of initial metal ion concentrations on the adsorption of lead and chromium with 355µm, 30^0C and 5 minutes. It can be observed that at 10mg/l for lead, adsorption increases steadily until there was a decrease at 30mg/l due to saturation of the binding sites. Afterwards, the amount of lead adsorbed became constant. In the case of chromium, as the initial metal ion concentration rises, adsorption increases, while the binding sites were not saturated. Fig.4.3-4.5 showed the linearity of the adsorption process with the Langmuir and Freundlich models. From Table 4.2, it was observed that the binding sites of chromium exceeded that of lead. However, the linear regression coefficient for lead R^2 value exceeded that of chromium with both models. Therefore, lead assumed homogenous adsorption with the Langmuir model at the specified parameters (30^0C and 5 minutes).

Table 4.3: Adsorption constants for Langmuir and Freundlich isotherms at particle size 355µm, 30^{o}C and 10min

	Langmuir constants			Freundlich constants		
Metal ion	Q_M (mg/g)	K_a	R^2	K_F(mg/g)	n	R^2
Pb^{2+}	1.42	0.02	0.876	$1.70x10^{-2}$	0.67	0.937
Cr (VI)	2.49	1.24	0.554	$2.60x10^{-2}$	0.45	0.910

A linearised plot of Langmuir and Freundlich isotherm and the effect of concentration for Pb^{2+} and Cr (VI) at particle size of 355 µm, 30^{o}C and 10min are shown in Fig. 4.6-4.10.

Q_M = maximum adsorption capacity

K_a = affinity between the adsorbent and the metal ions

R^2 = rank correlation coefficient

n = adsorption intensity

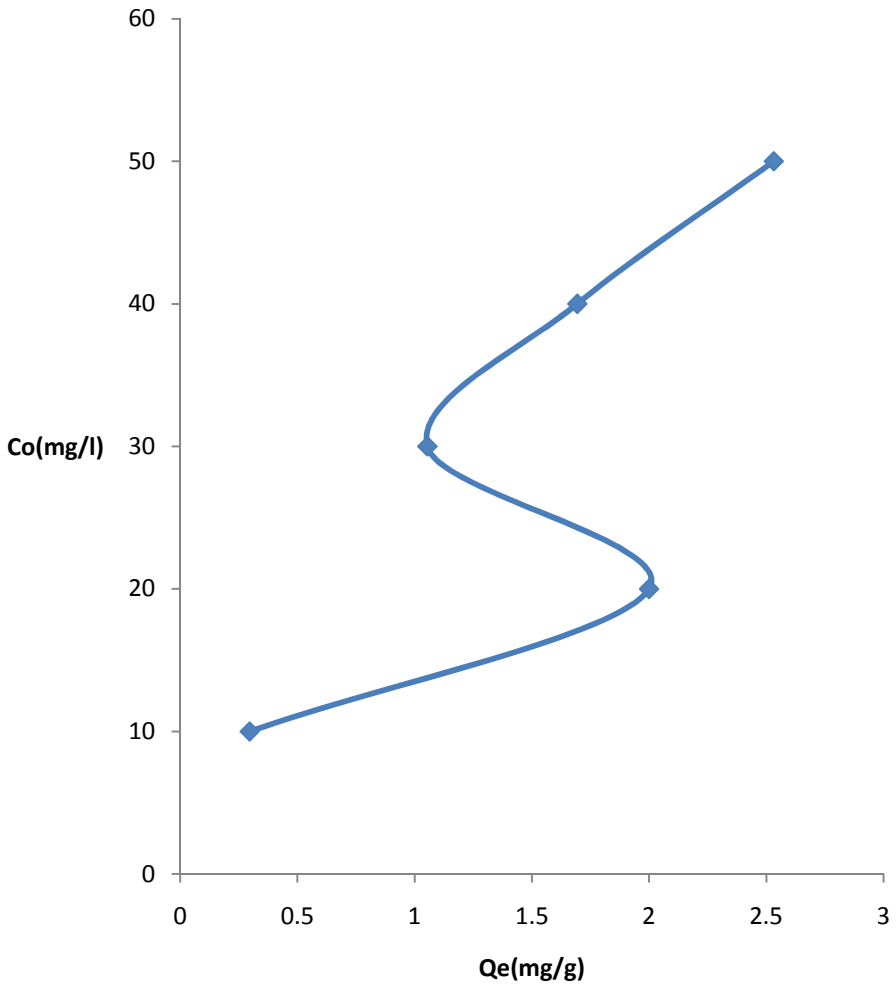


Fig.4.6. Effect of concentration on the adsorption of Pb^{2+} at 355µm, 30^{o}C and 10min

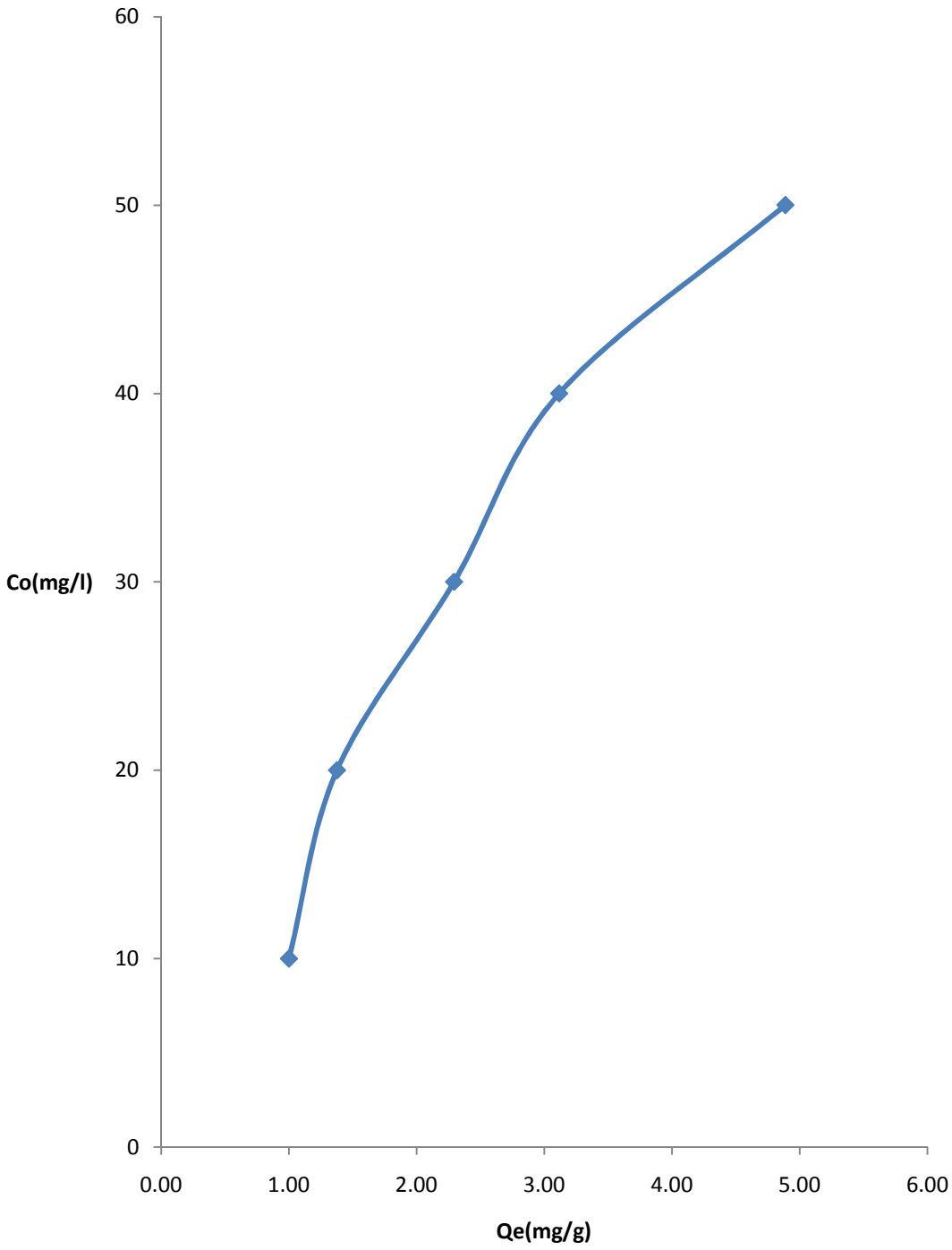


Fig.4.7.Effect of concentration on the adsorption of Cr (VI) at 355µm, 30^{o}C and 10min

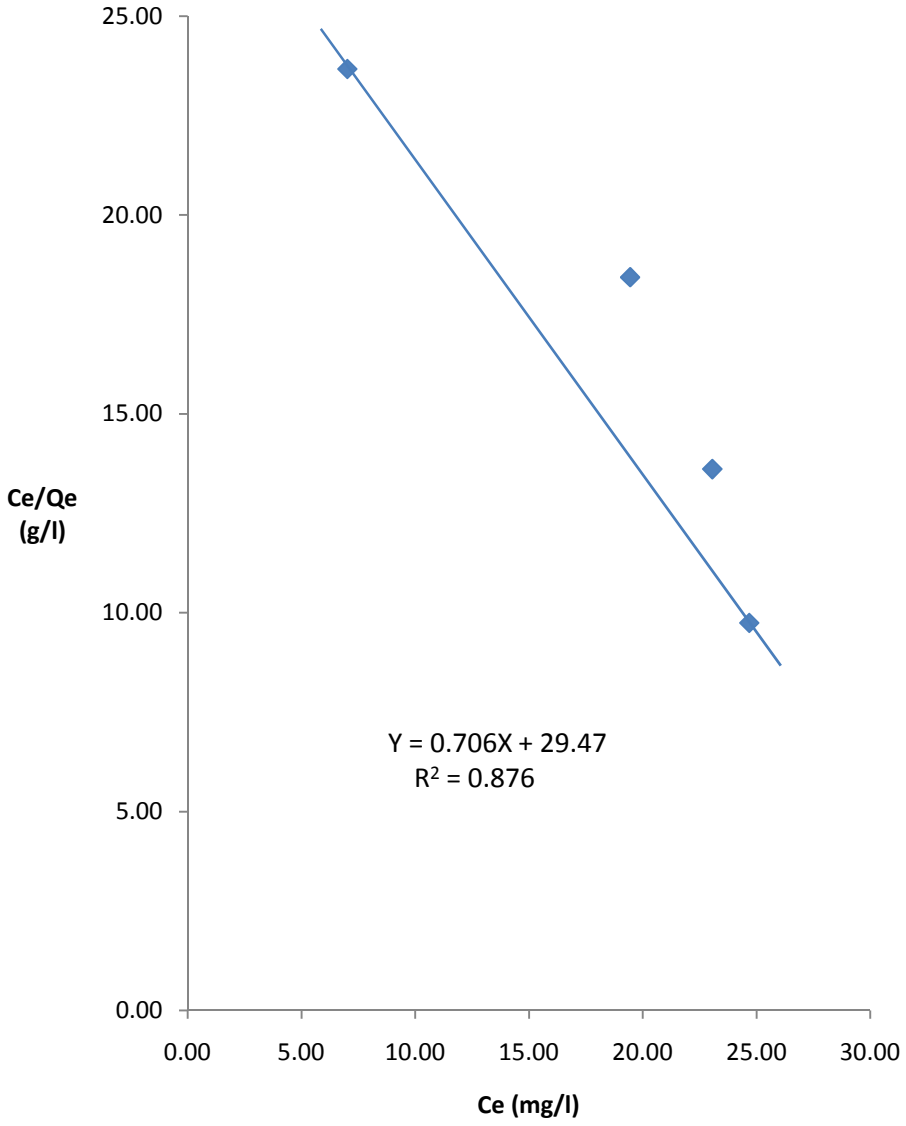


Fig.4.8. Langmuir isotherm for the adsorption of Pb^{2+}at particle size355µm,30^{o}C and 10min

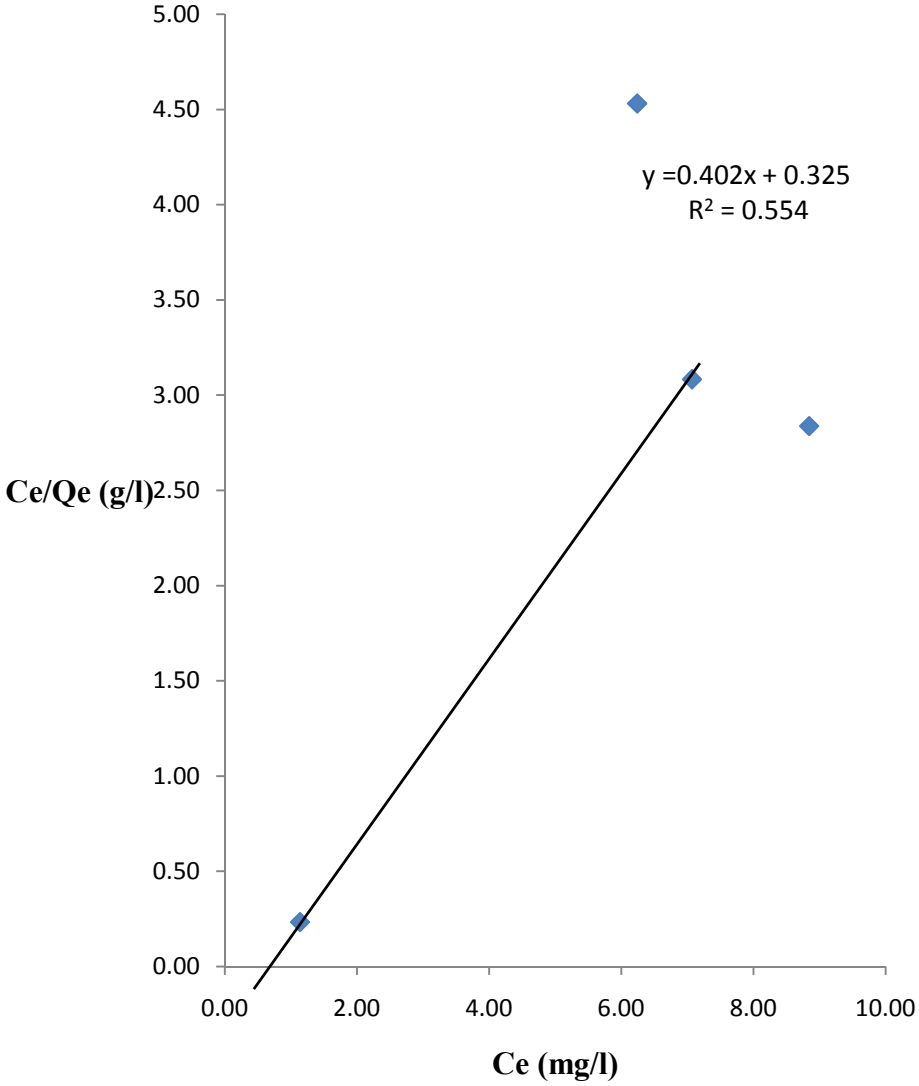


Fig.4.9 Langmuir isotherm for the adsorption of Cr (VI) at particle size 355µm, 30^{o}C and 10min.

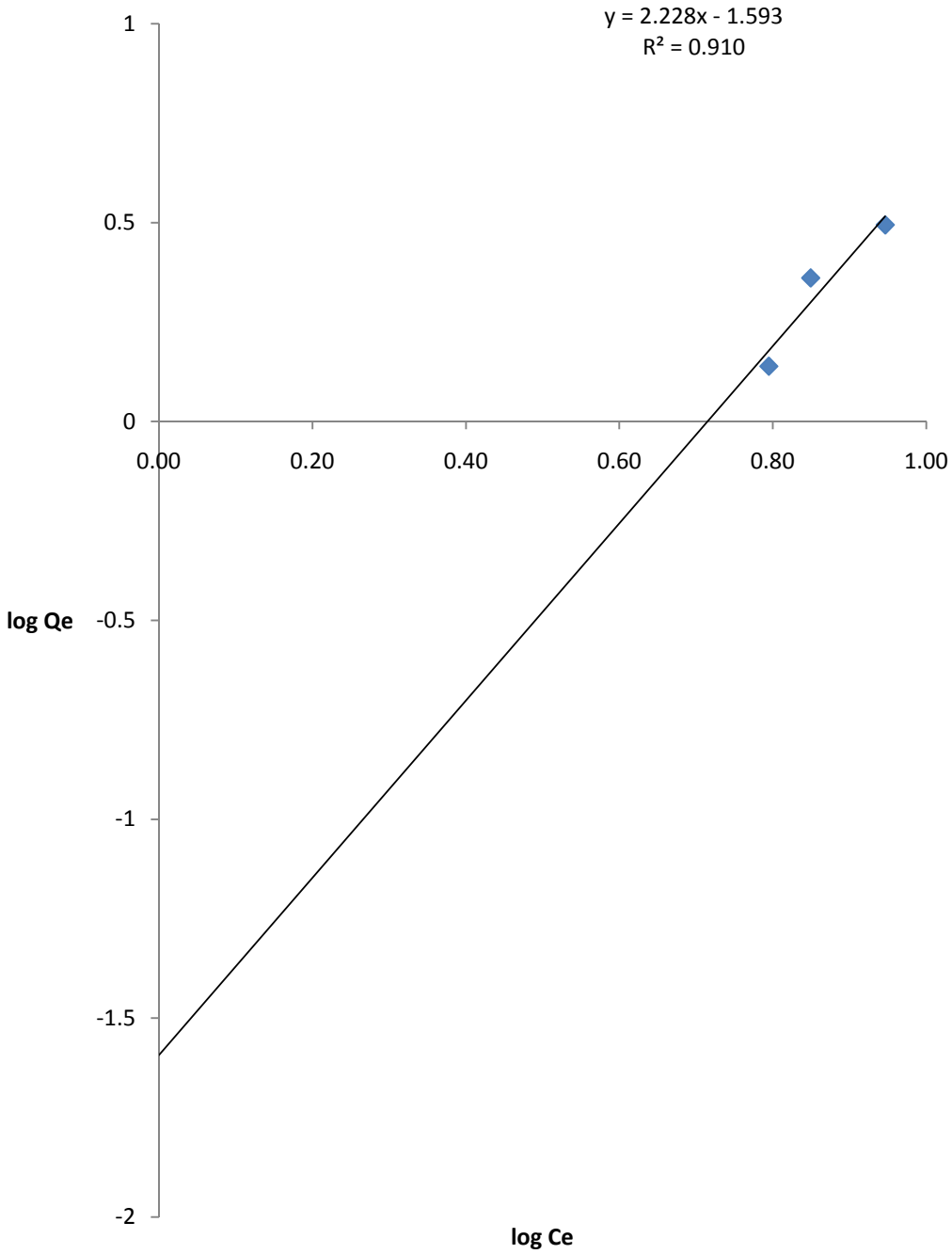


Fig.4.10. Freundlich isotherm for the adsorption of Cr (VI) at particle size 355µm, 30^{o}C and 10min.

Fig.4.6-4.7 shows that the effect of initial concentration on the amount of lead adsorbed at 10 minutes has similar trend with that of 5 minutes. While that of chromium maintained a steady rise at 10 minutes with no saturation. Fig. 4.8-4.10 shows the linearised form of the adsorption process with Langmuir and Freundlich model. From the Langmuir constants, the linear regression coefficient of lead and chromium indicates good linearity with the Freundlich model; but that of lead indicates better, with higher adsorption intensity. Therefore, the adsorption of lead fitted well with the Freundlich model.

Table 4.4: Adsorption constants for Langmuir and Freundlich isotherms at particle size 355µm, 30°C and 20min.

	Langmuir constants			Freundlich constants		
Metal ion	Q_M (mg/g)	K_a	R^2	K_F(mg/g)	n	R^2
Pb^{2+}	-	-	-	$5.3x10^{-4}$	0.39	0.611
Cr (VI)	-	-	-	2.28	3.08	0.502

A linearised plot of Langmuir, Freundlich isotherm and effect of concentration for Pb^{2+} and Cr (VI) at particle size 355µm, 30°C and 20min are shown in Fig.4.11- 4.14.

Where

Q_M = maximum adsorption capacity

K_a = affinity between the adsorbent and the metal ions

R^2 = rank correlation coefficient

n = adsorption intensity

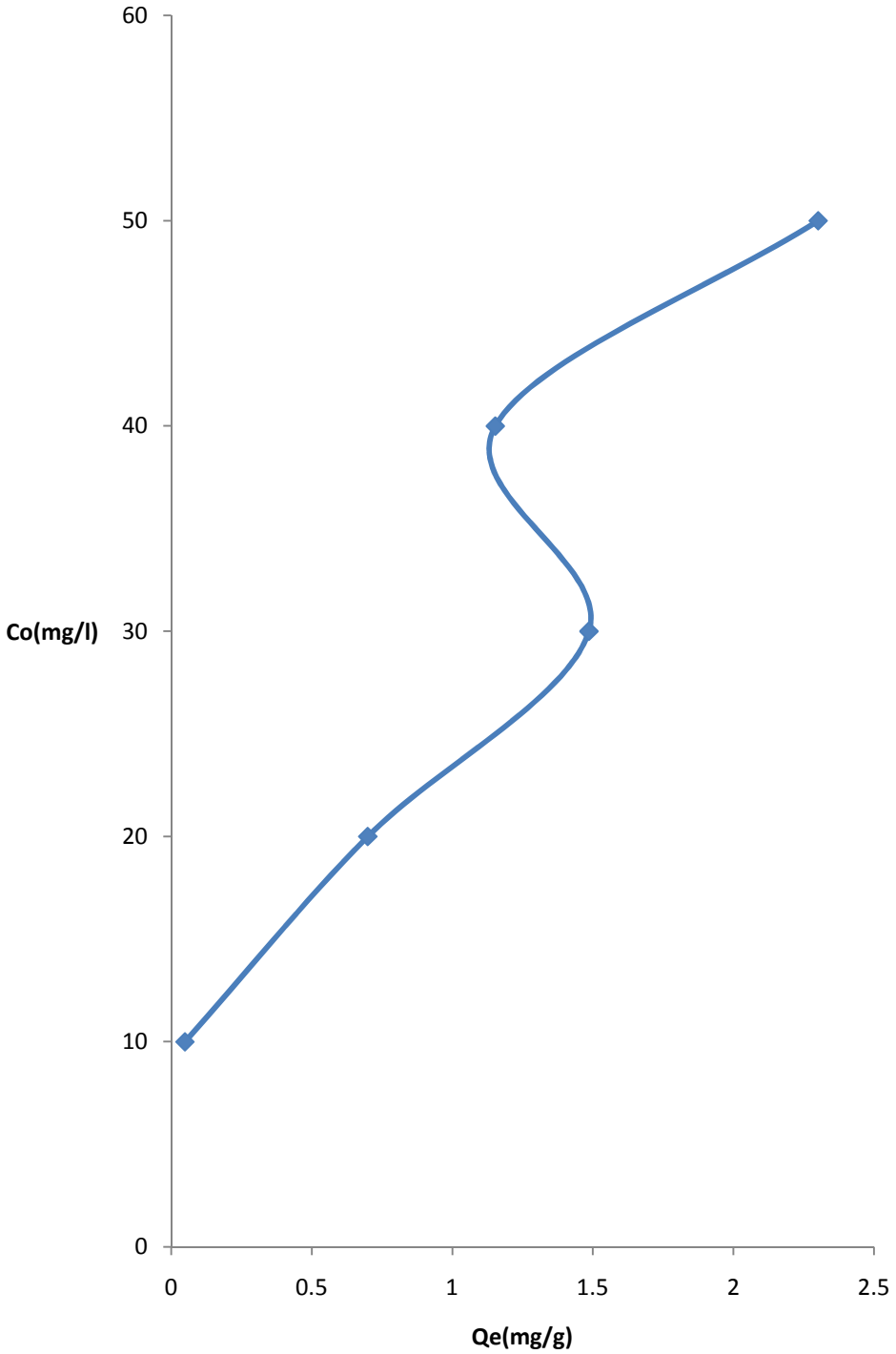


Fig.4.11.Effect of concentration on the adsorption of Pb^{2+} at 355µm, 30^{o}C and 20min

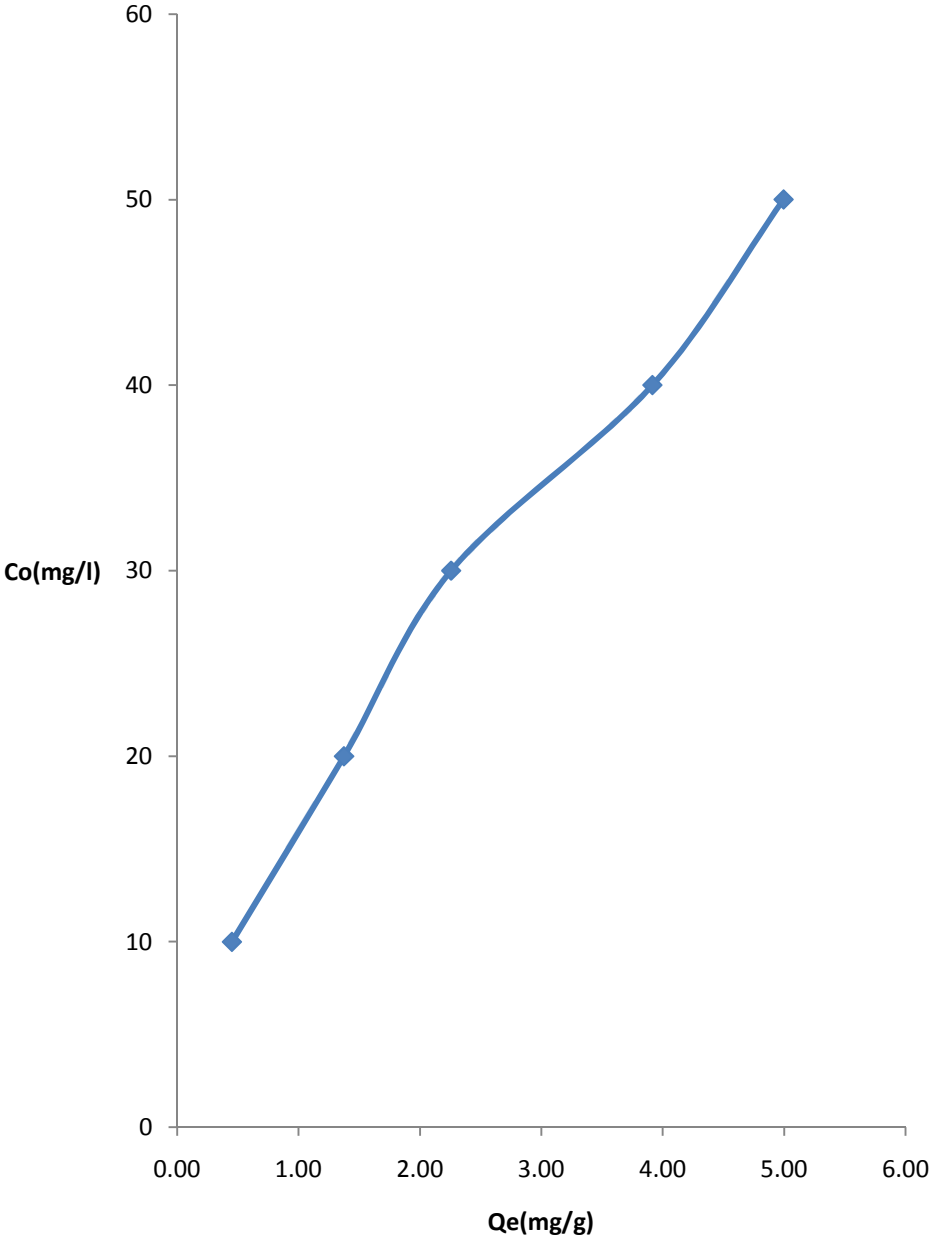


Fig.4.12.Effect of concentration on the adsorption of Cr (VI) at 355µm, 30^{o}C and 20min

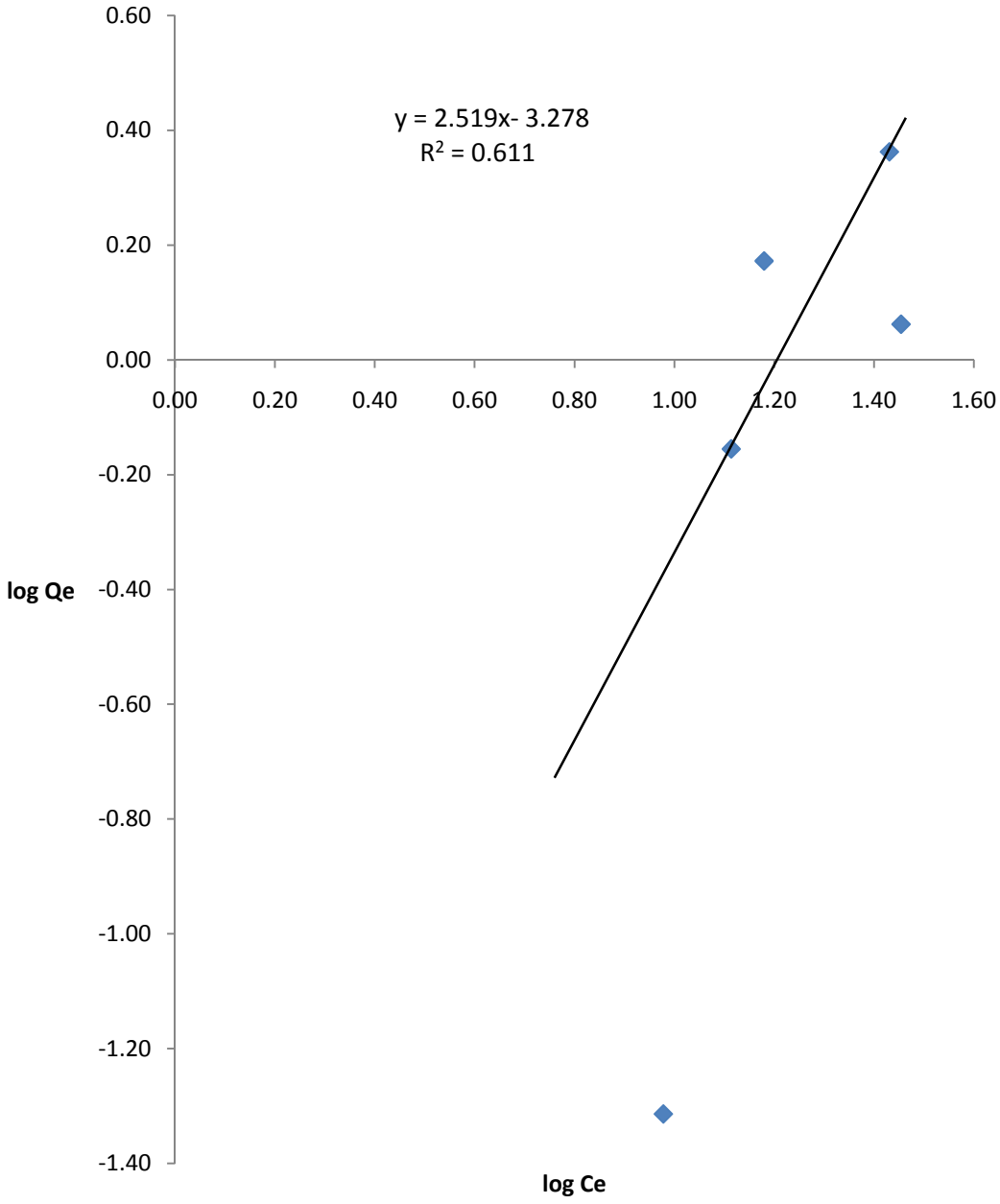


Fig.4.13. Freundlich isotherm for the adsorption of Pb^{2+} at particle size 355µm, 30^{o}C and 20min.

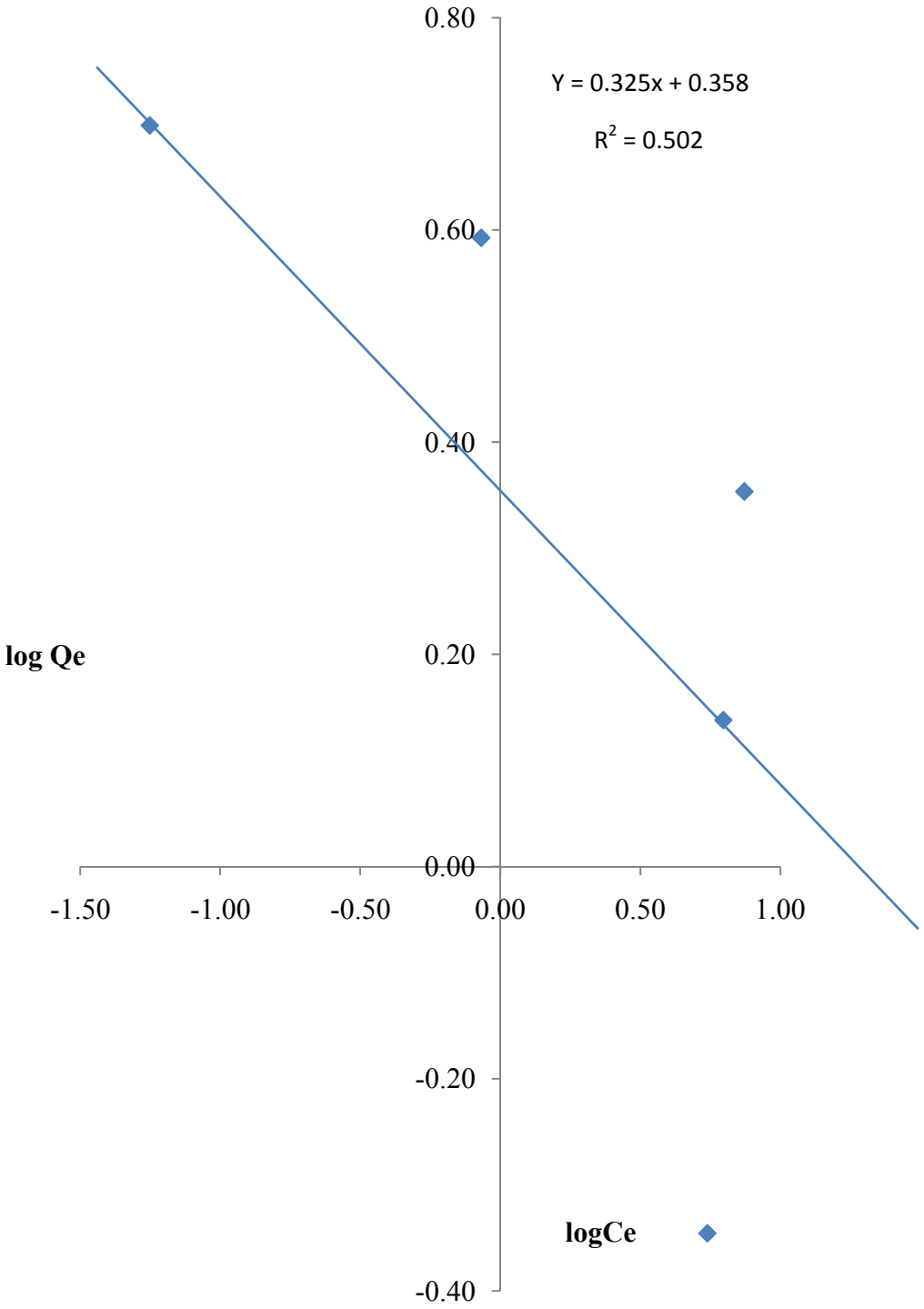


Fig.4.14. Freundlich isotherm for the adsorption of Cr (VI) at particle size 355µm, 30^{o}C and 20min

Fig.4.11-4.14 shows that the effect of initial concentration on the amount of lead adsorbed at 20 minutes rose steadily without saturation from 10mg/l to 40mg/l from which saturation took effect. Afterwards, concentration became steady. While in the case of chromium, adsorption increases with the amount adsorbed. Table 4.4 indicates that the linear regression coefficient for lead with the Freundlich model was fairly higher than that of chromium. Therefore, the Freundlich model indicates better linearity for the adsorption of lead in heterogeneous condition.

Table 4.5: Adsorption constants for Langmuir and Freundlich isotherms at particle size 355µm, 30^{o}C and 40min.

	Langmuir constants			Freundlich constants		
Metal ion	Q_M (mg/g)	K_a	R^2	K_F(mg/g)	n	R^2
Pb^{2+}	-	-	poor	-	-	poor
Cr (VI)	0.88	0.08	0.634	$7.7x10^{-3}$	0.37	0.925

A linearised plot of Langmuir, Freundlich isotherm and effect of concentration for Pb^{2+} and Cr (VI) at particle size 355µm, 30^{o}C and 40min are shown in Fig.4.15- 4.17.

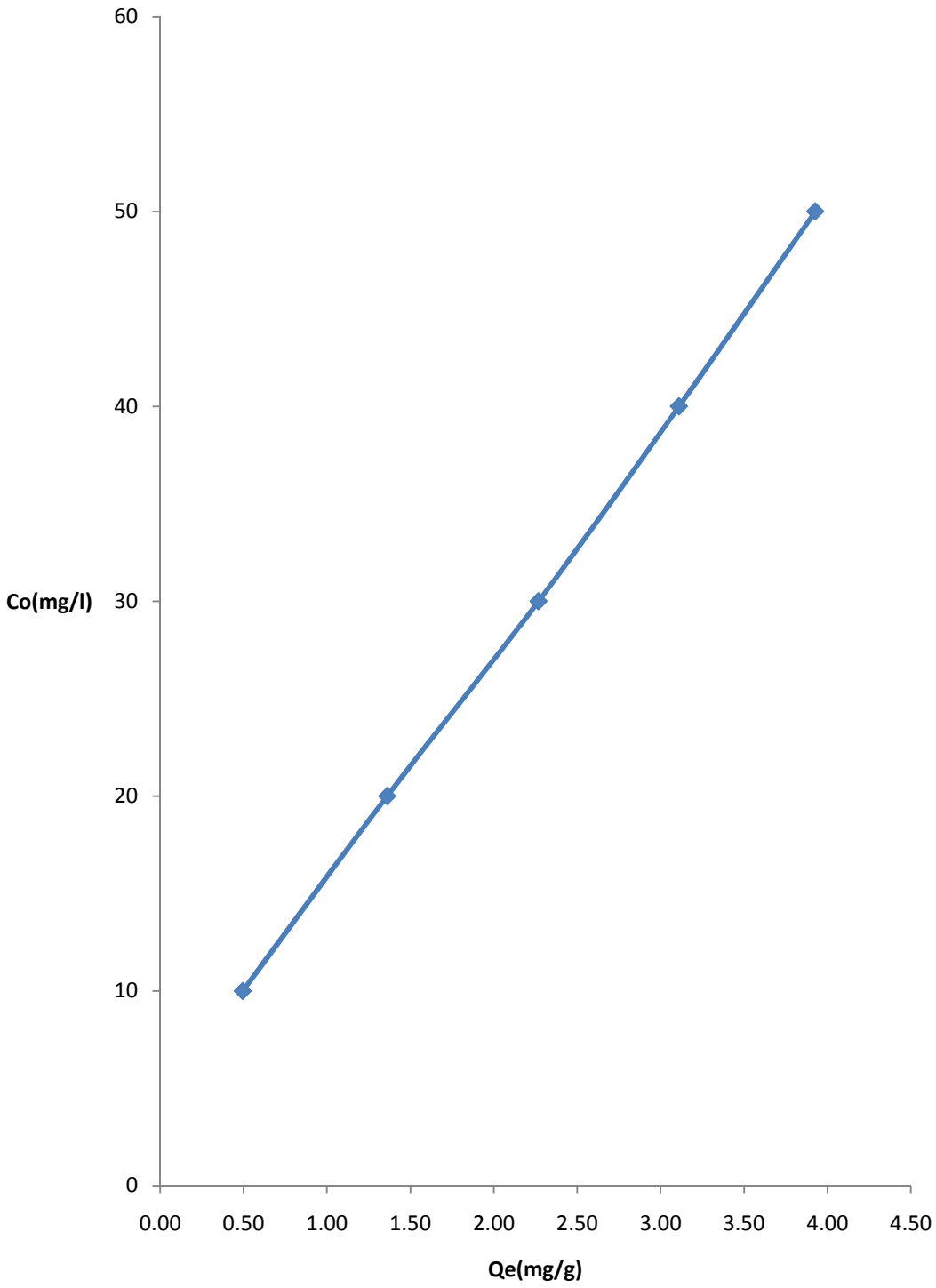


Fig.4.15. Effect of concentration on the adsorption of Cr (VI) at 355µm, 30^{o}C and 40min

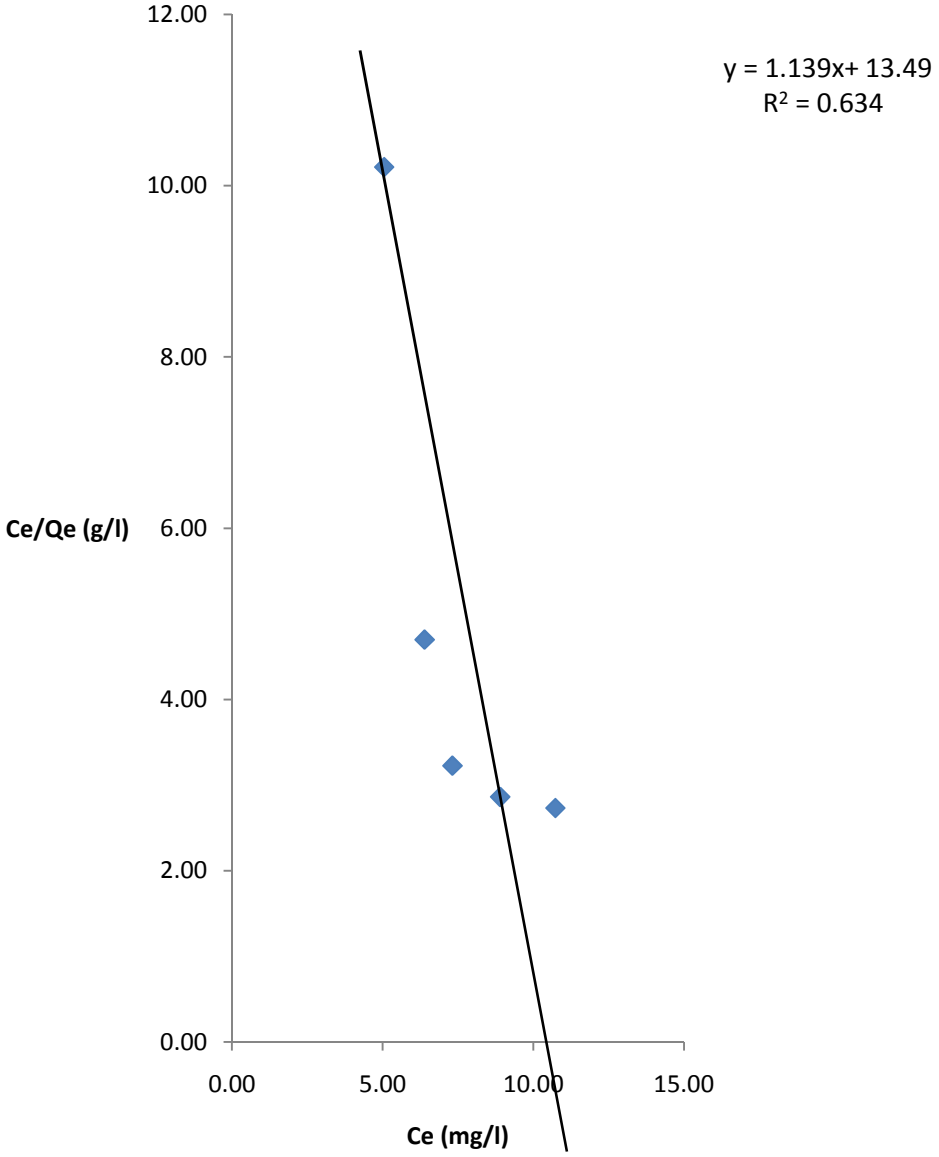


Fig.4.16. Langmuir isotherm for the adsorption of Cr (VI) at particle size 355µm,30^{0}C and 40 min.

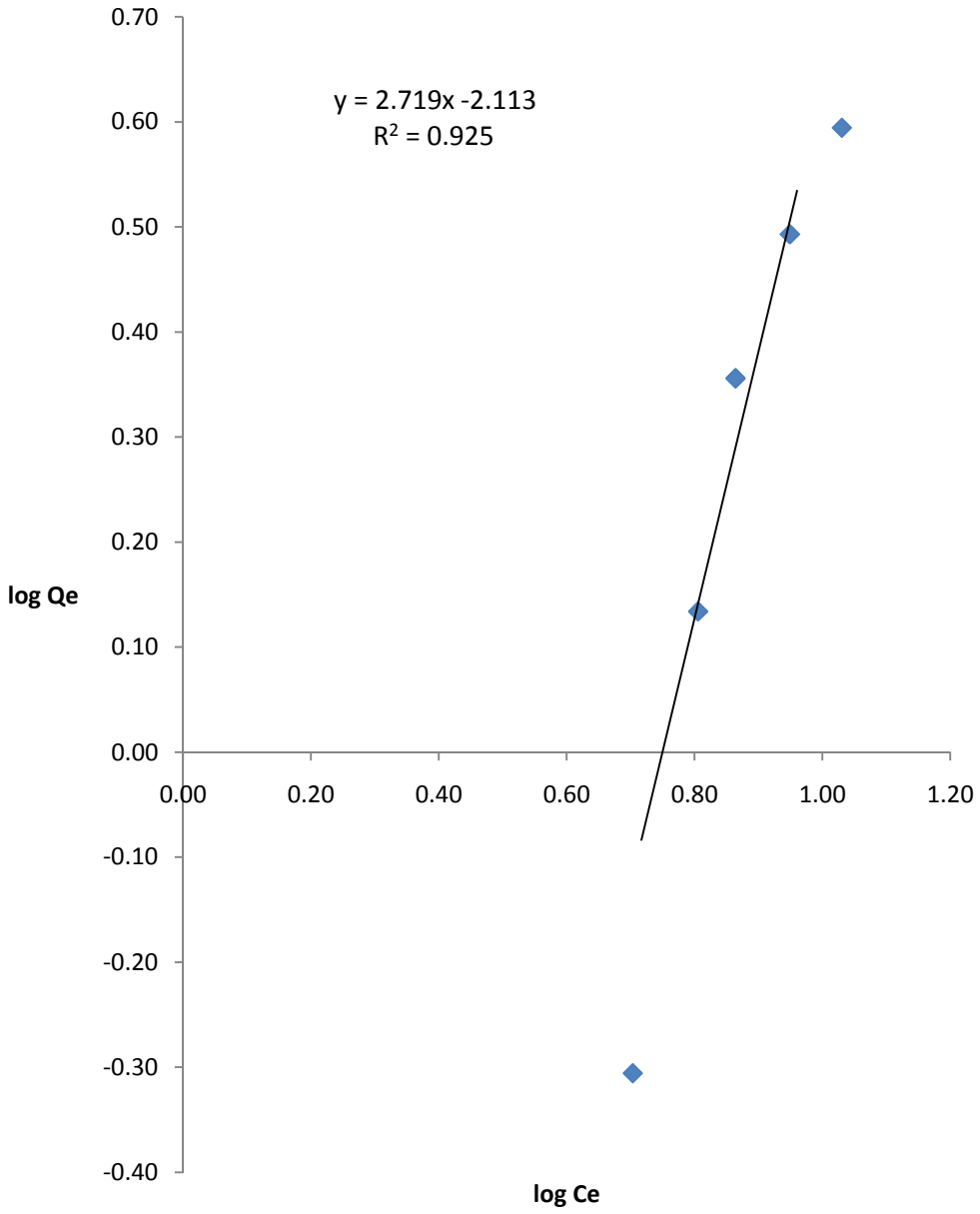


Fig.4.17. Freundlich isotherm for the adsorption of Cr (VI) at particle size 355µm, 30^{o}C and 40min

Fig.4.15. shows that increasing concentrations of chromium at 40 minutes resulted in increased adsorption on to cow bone charcoal. The adsorption of lead was very poor under similar condition. The Langmuir and Freundlich adsorption model in Fig.4.16 and 4.17 above, showed the linearity of the adsorption process. The Freundlich model predicted good adsorption of chromium with a high linear regression coefficient R^2. Therefore, the adsorption of chromium is heterogeneous at 40 minutes, 30^0C and 355 μm particle size.

Table 4.6: Adsorption constants for Langmuir and Freundlich isotherms at particle size 355µm, 30°C and 60min.

	Langmuir constants			Freundlich constants		
Metal ion	Q_M (mg/g)	K_a	R^2	K_F(mg/g)	n	R^2
Pb^{2+}	3.59	0.04	0.965	-	-	poor
Cr (VI)	0.23	0.11	0.623	$1.12x10^{-5}$	0.17	0.841

A linearised plot of Langmuir, Freundlich isotherm and effect of concentration for Pb^{2+} and Cr (VI) at particle size 355µm, 30°C and 60min are shown in Fig.4.18 – 4.22.

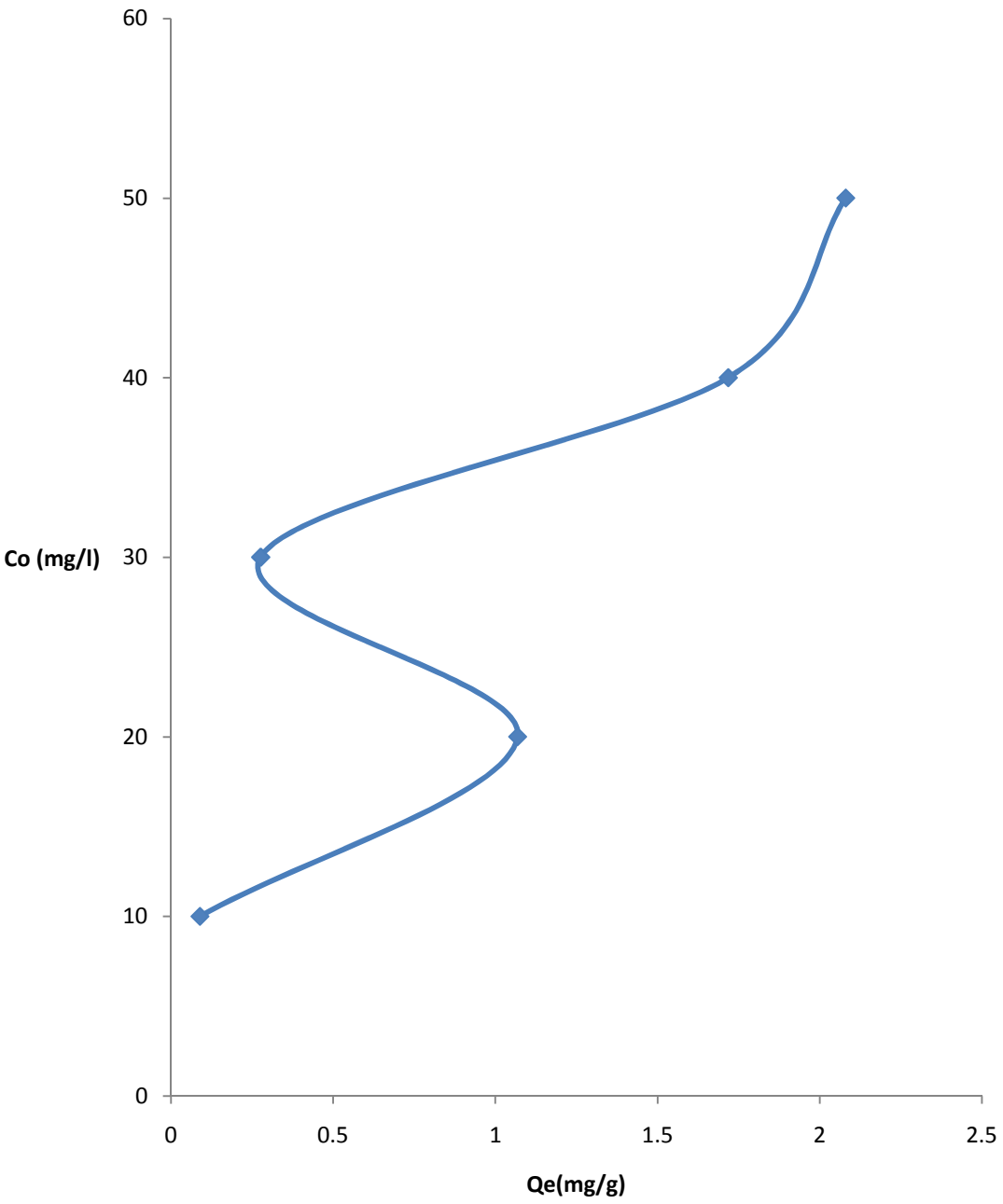


Fig.4.18. Effect of concentration on the adsorption of Pb^{2+} at 355µm, 30°C and 60min

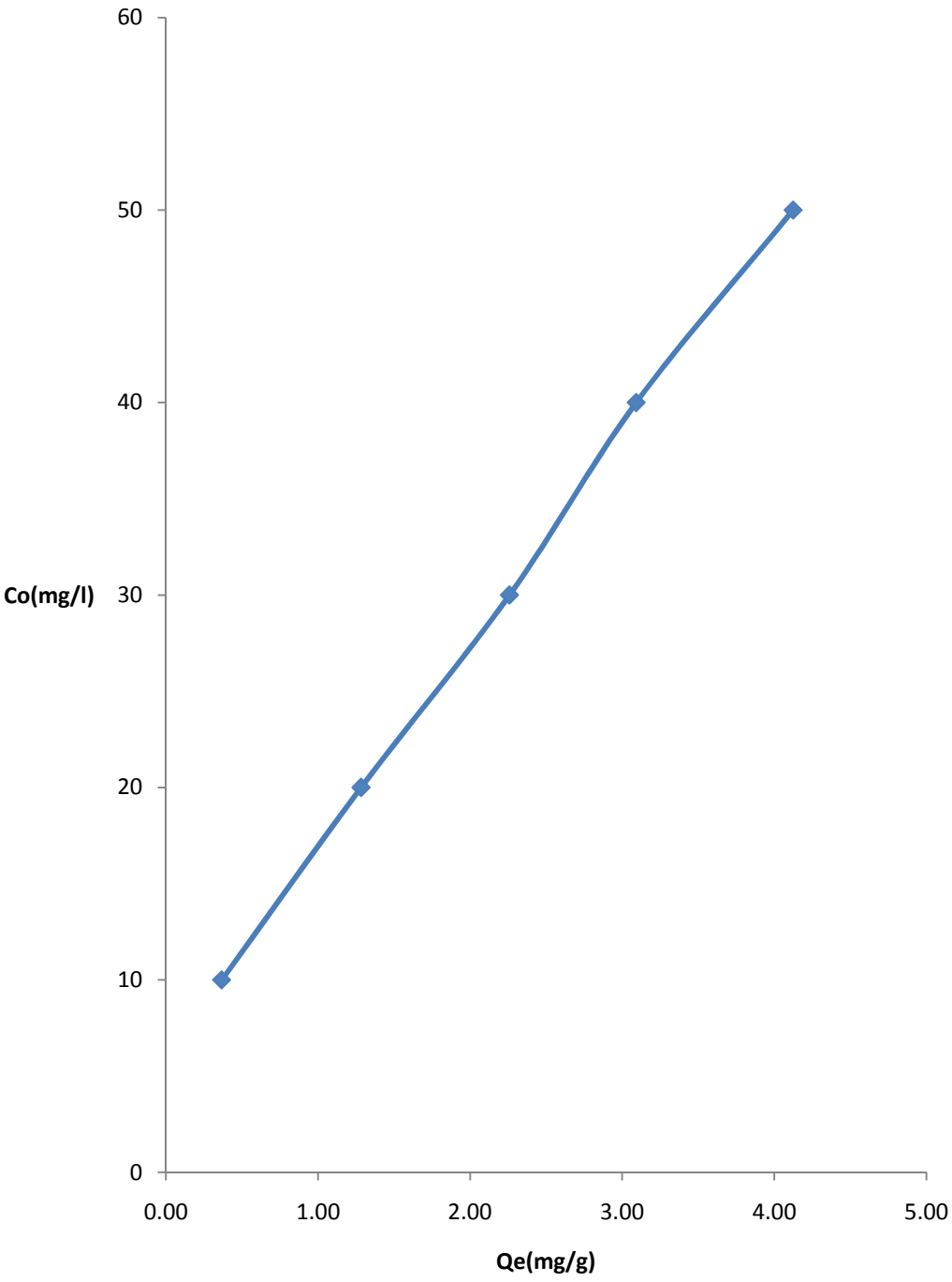


Fig.4.19. Effect of concentration on the adsorption of Cr (VI) at 355µm, 30^{o}C and 60min

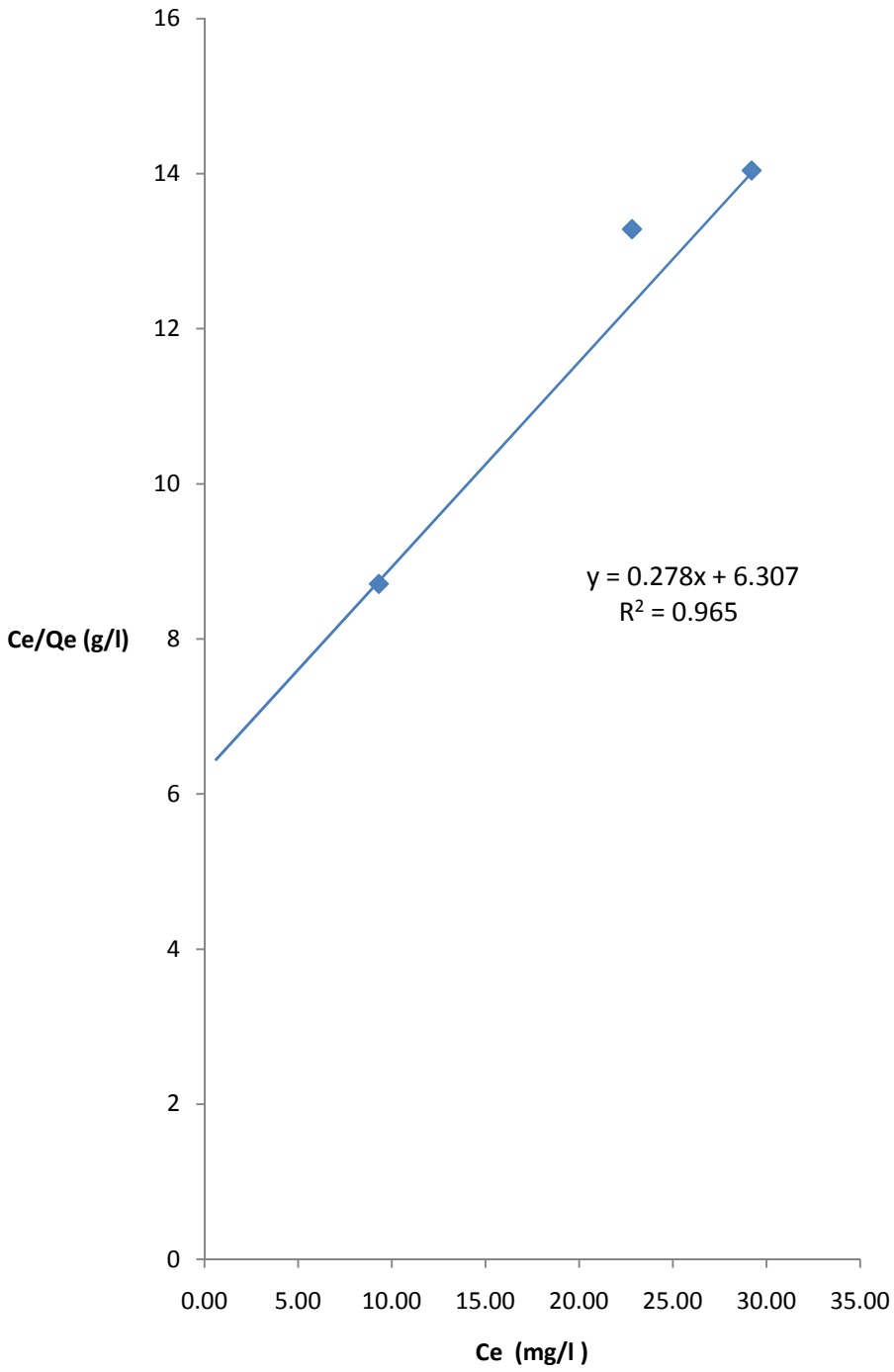


Fig.4.20 .Langmuir isotherm for the adsorption of lead at particle size 355µm, 30^{o}C and 60min.

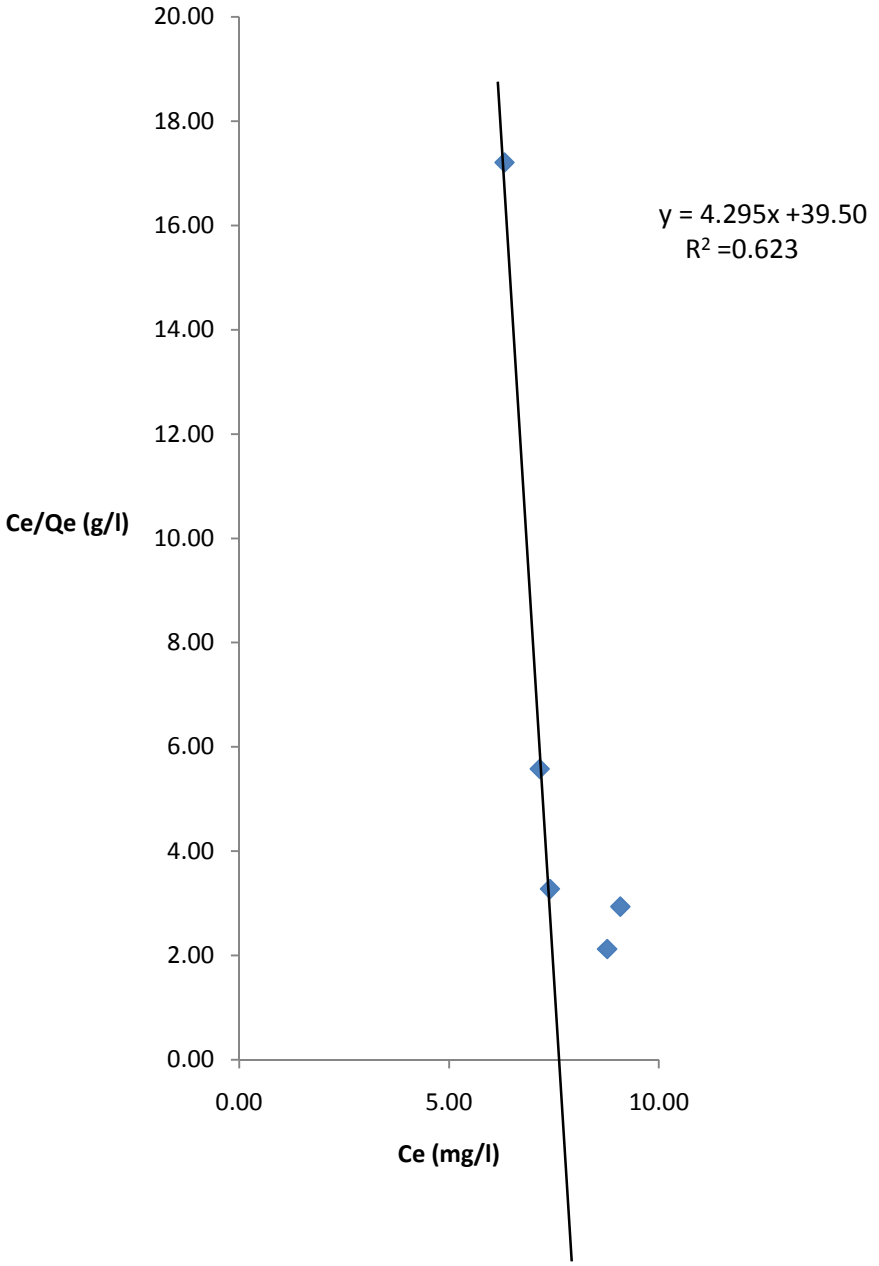


Fig.4.21.Langmuir isotherm for the adsorption of Cr (VI) at particle size 355µm,30^{o} C and 60min.

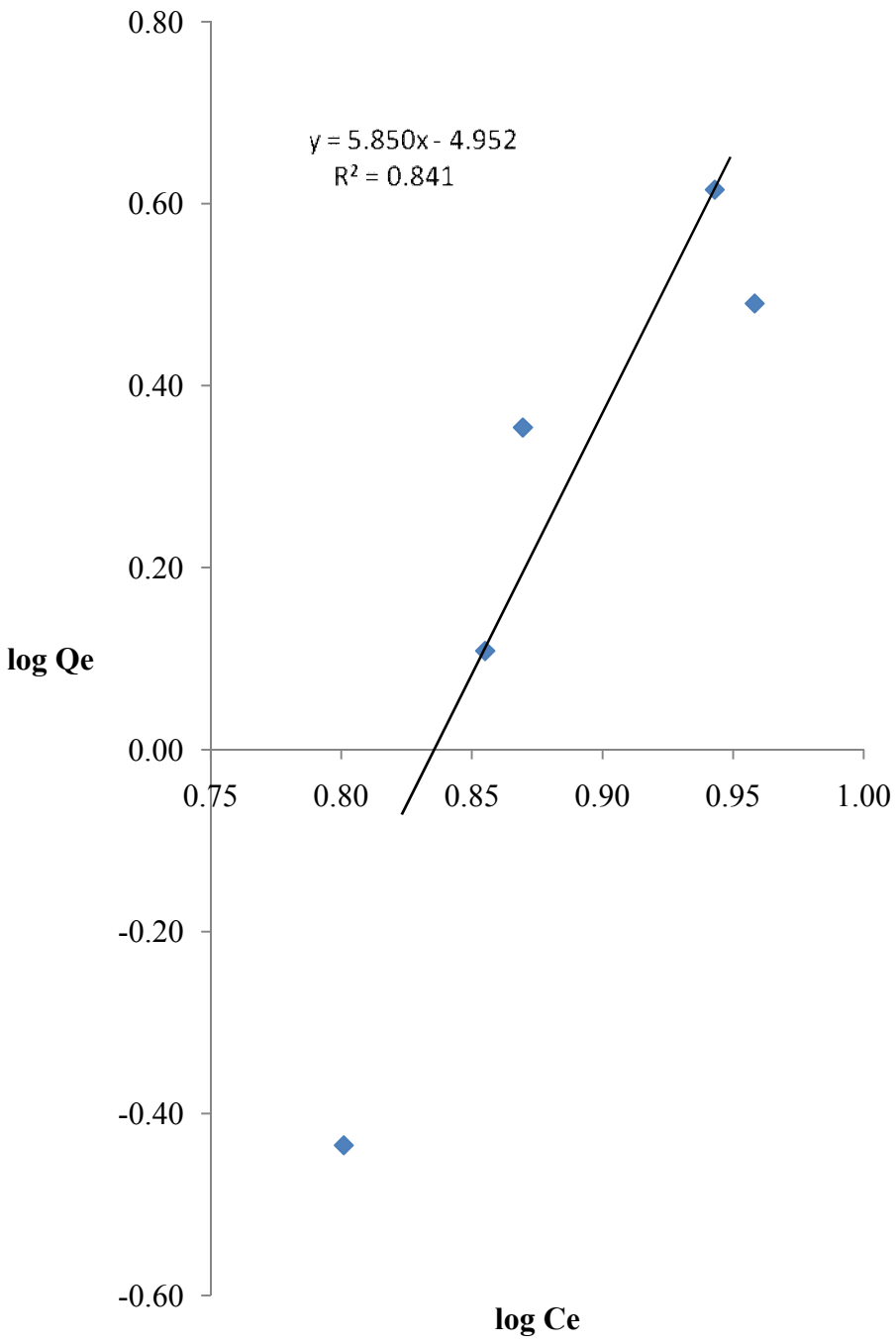


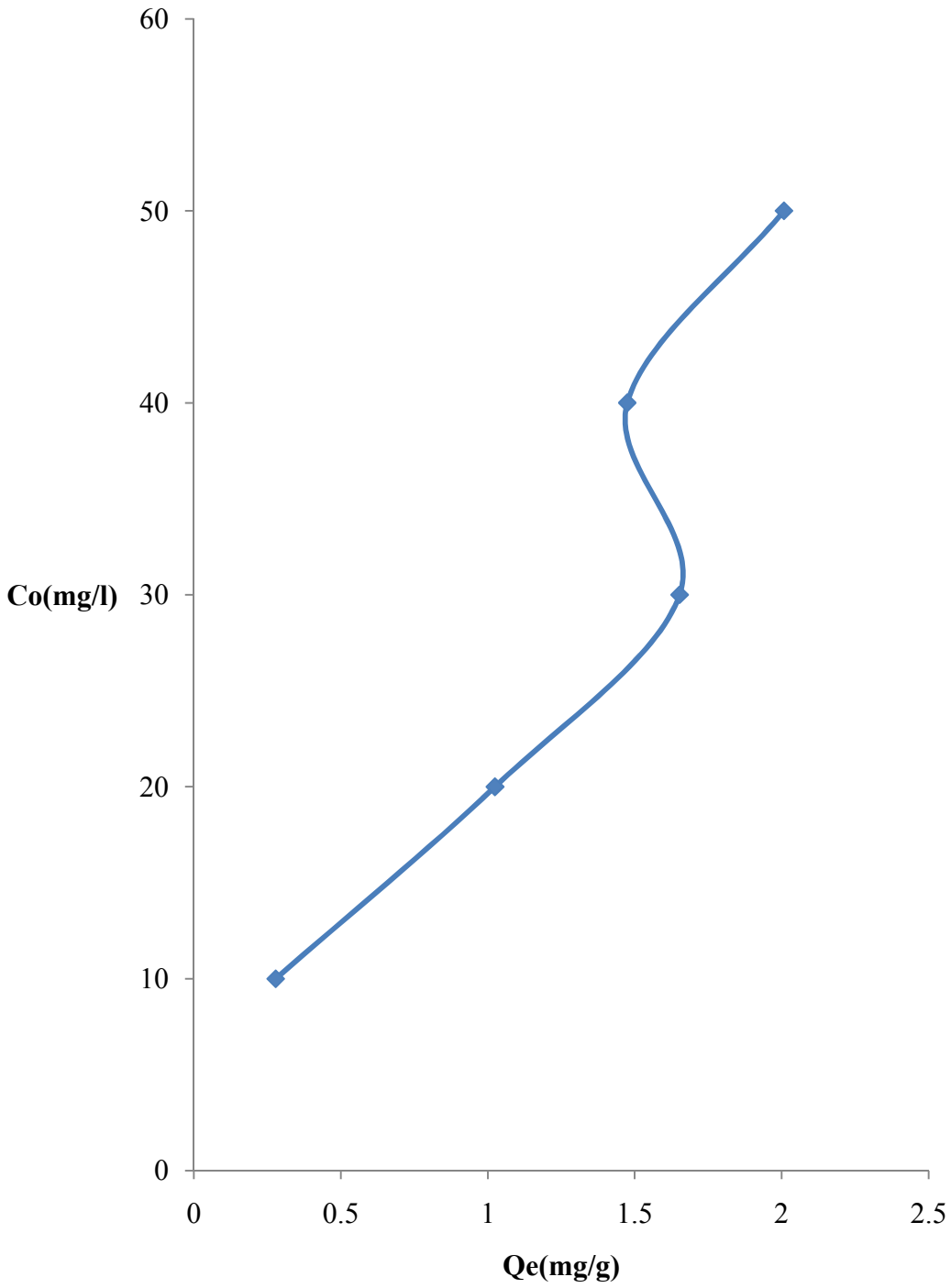
Fig.4.22. Freundlich isotherm for the adsorption of Cr (VI) at particle size 355µm, 30^{o}C and 60min.

Fig.4.18-4.19 shows that the effect of concentration on the amount of lead and chromium increases as the amount adsorbed increases. In Table 4.6 above, showing the Langmuir and Freundlich constants, it can be observed that lead has a higher adsorption capacity (Q_m: 3.59) compared to chromium. The Freundlich model did not show a good fit for the adsorption of lead, but it was very good for the adsorption of chromium with R^2 value of 0.841. However, the linear regression value obtained for lead (R^2 = 0.965) showed better linearity with the Langmuir model. With this value, the adsorption of lead fitted well with the Langmuir model under homogenous condition.

Table 4.7: Adsorption constants for Langmuir and Freundlich isotherms at particle size 355µm, 40^{o}C and different timings (05-60min).

	Langmuir constants				Freundlich constants		
Metal ion	T(min)	Q_M (mg/g)	K_a	R^2	K_F(mg/g)	n	R^2
Pb^{2+}	5	2.56	0.08	0.763	0.06	0.95	0.656
	10	0.69	0.03	0.971	$3.7x10^{-3}$	0.54	0.999
	20	0.49	0.04	0.692	$4.8x10^{-6}$	0.22	0.601
	40	0.84	0.05	0.836	$2.43x10^{-7}$	0.17	0.812
	60	6.21	0.03	0.944	0.01	0.55	0.689
Cr (VI)	5	1.05	0.09	0.470	$1.80x10^{-2}$	0.39	0.759
	10	0.50	0.11	0.667	$1.30x10^{-3}$	0.27	0.890
	20	0.45	0.12	0.645	$8.50x10^{-4}$	0.24	0.883
	40	poor	poor	poor	0.04	0.44	0.716
	60	poor	poor	poor	$7.30x10^{-2}$	0.59	0.541

A linearised plot of Langmuir, Freundlich isotherm and effect of concentration for Pb^{2+} and Cr (VI) at particle size 355µm, 40^{o}C and different timings are shown in the Figures 4.23-4.27.



Fg.4.23.Effect of concentration on the adsorption of Pb^{2+}at 355µm, 40^0C and 5min

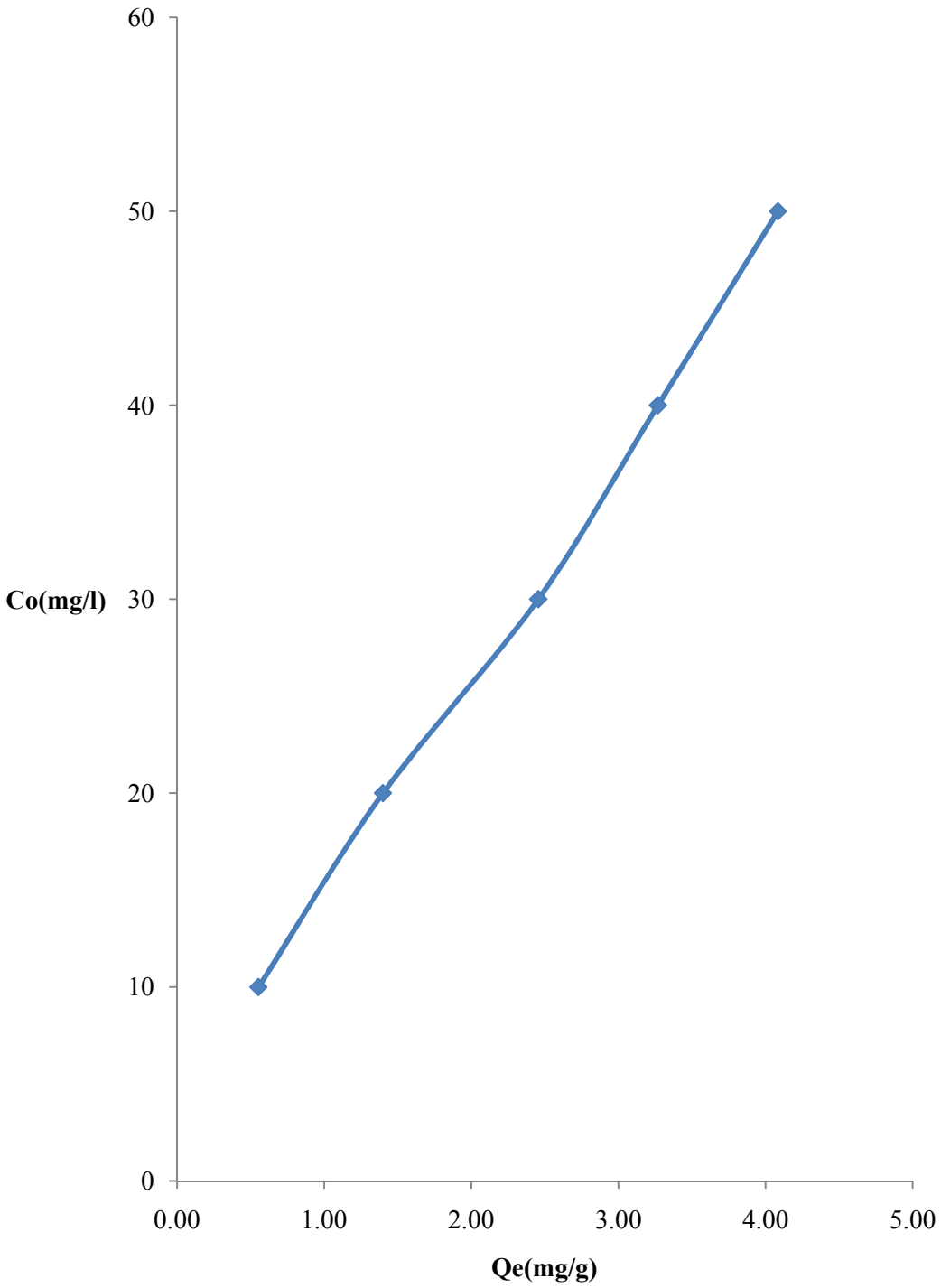


Fig.4.24. Effect of concentration on the adsorption of Cr (VI) at 355µm, 40^0C and 5min

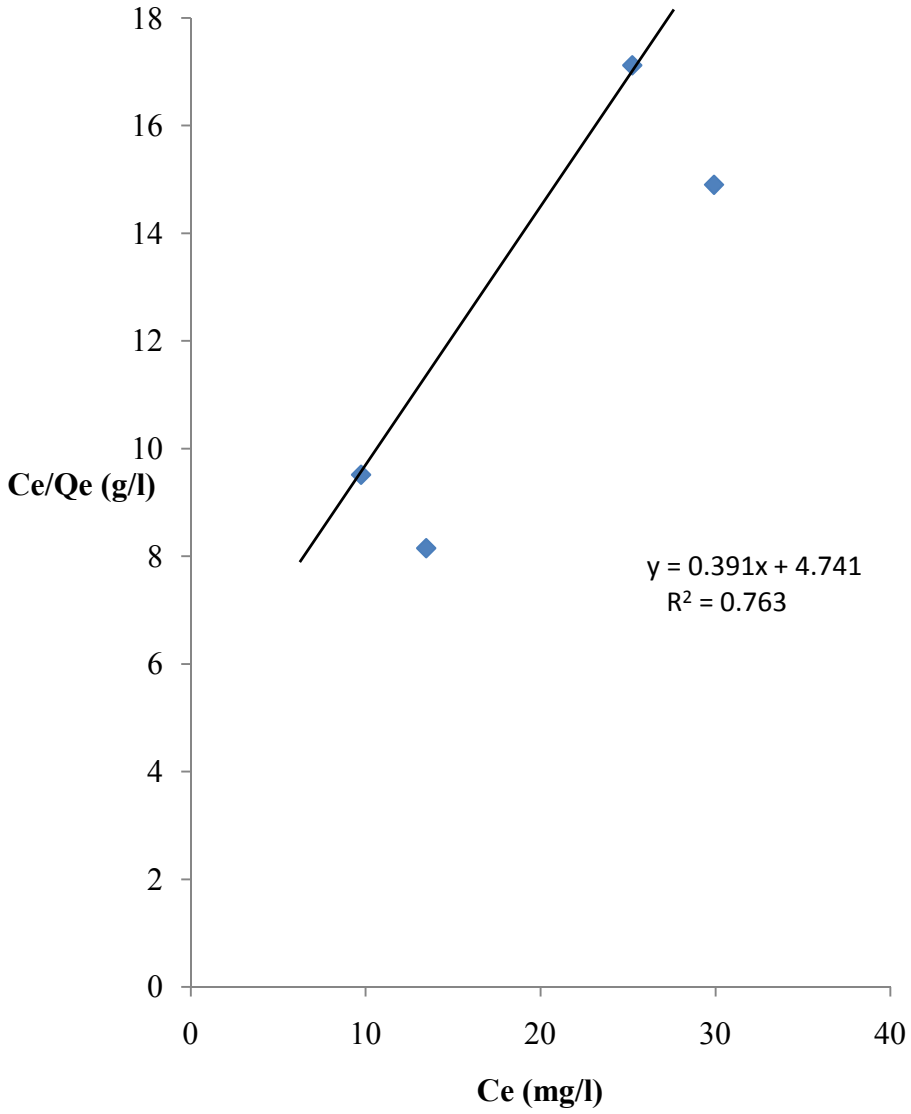


Fig.4.25. Langmuir isotherm for the adsorption of Pb^{2+} at particle size 355µm, 40^{o}C and 5min

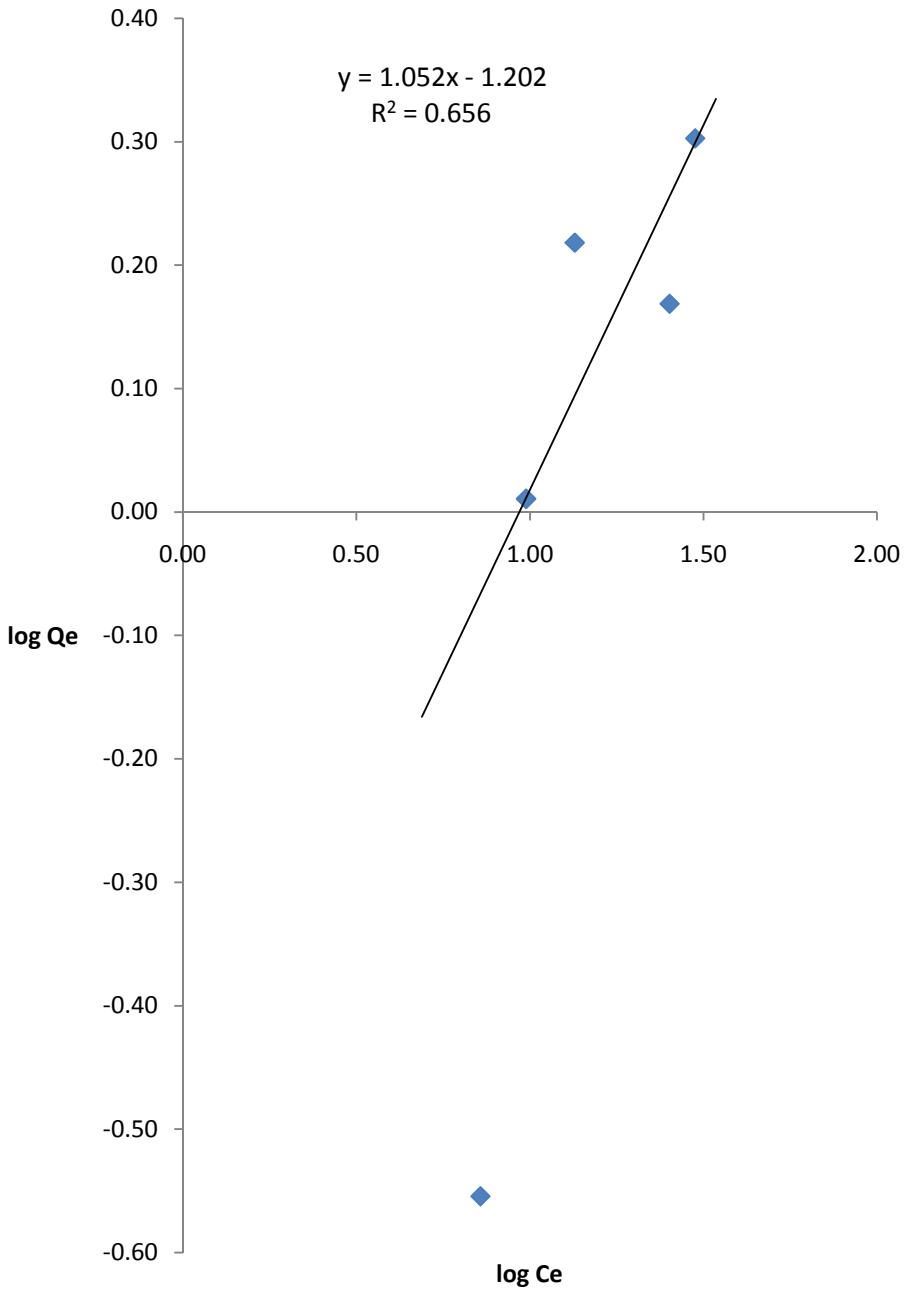


Fig.4.26. Freundlich isotherm for the adsorption of Pb^{2+}at particle size 355µm, 40^{o}C and 5min

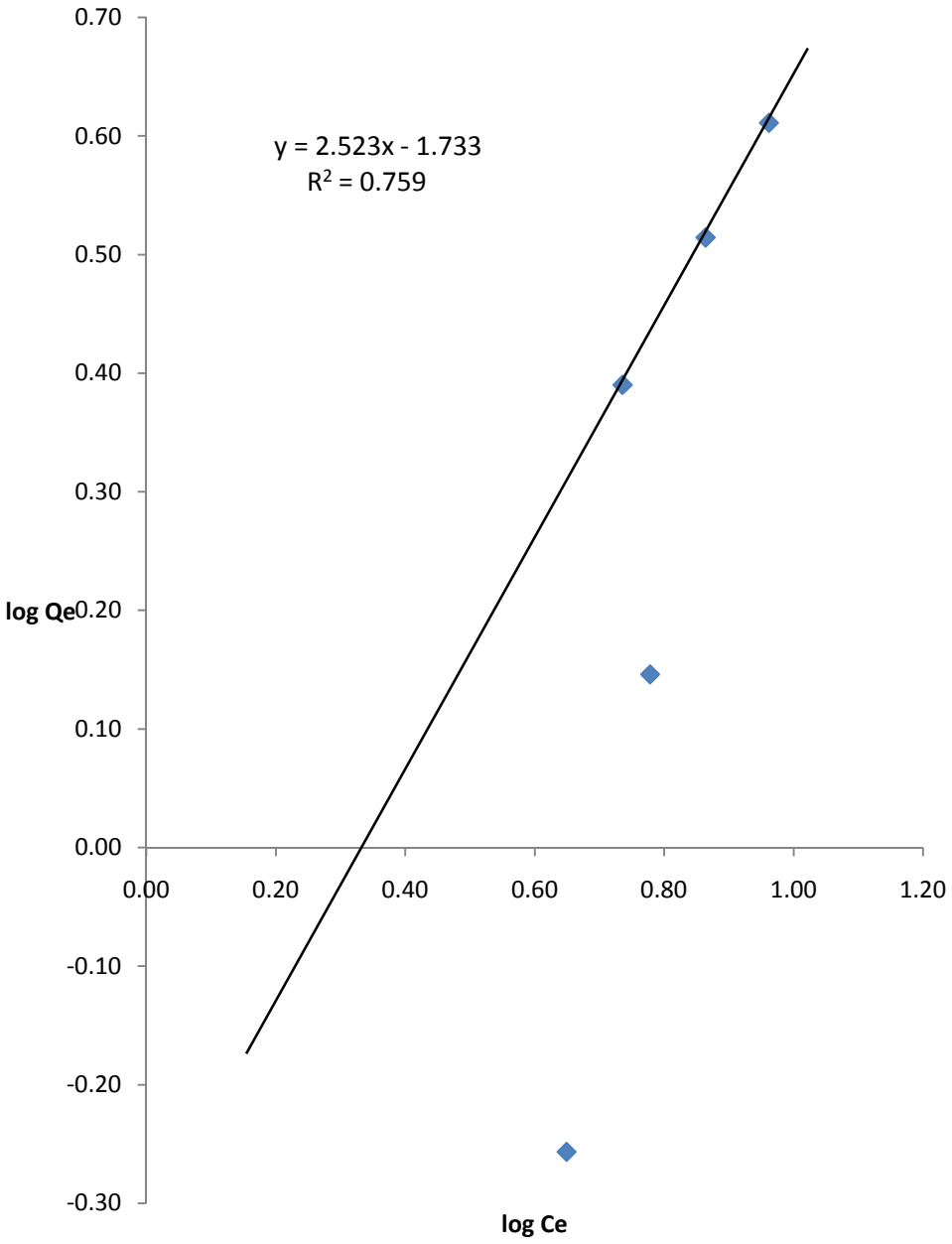


Fig.4.27 .Freundlich isotherm for the adsorption of Cr (VI) at particle size 355µm, 40^{o}C and 5min.

Table 4.7 shows the Langmuir and Freundlich constants for the adsorption of Pb^{2+} and Cr (VI) on cow bone charcoal at particle size 355µm, 40^{o}C and at different timings. Fig.4.23 and Fig.4.24 shows the isotherm plot for the effect of initial concentration on the amount of Pb^{2+} and Cr (VI) adsorbed from aqueous solution on to cow bone charcoal. As shown in these two Figures 4.23 and 4.24, as the initial concentration increases, there was a corresponding increase in the amount adsorbed. Slight saturation was noticed at 40mg/l of lead removal; afterwards, the adsorption progressed further. While in Fig.4.24, as the concentration increases, the amount of Cr (VI) adsorbed from solution also increases with absolute linearity.

Fig.4.25-4.27 shows the Langmuir and Freundlich isotherm plot for Pb^{2+} and Cr (VI). As observed from these Figures, Pb^{2+} has a higher maximum theoretical adsorption capacity of 2.56 than Cr (VI) at 5 minutes of agitation and at 40^{o}C. The adsorption intensity of Pb^{2+} exceeded that of Cr (VI) by greater amount. The correlation coefficient R^2 obtained from the Langmuir plot for Pb^{2+} at 5 minutes is higher compared to Cr (VI), Freundlich model inclusive. Therefore, at 5 minutes, the adsorption of Pb^{2+} is monolayer (homogenous).

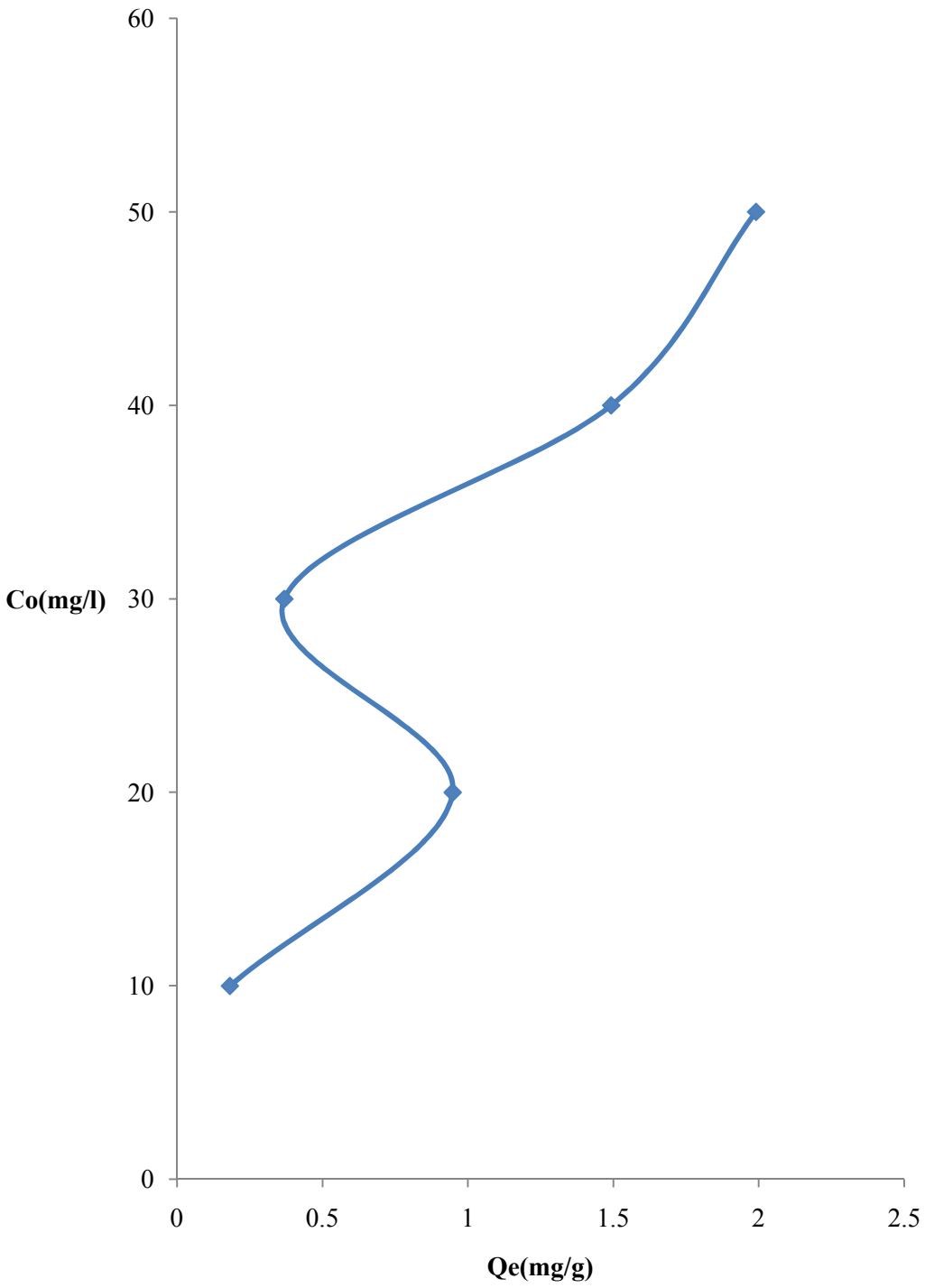


Fig.4.28.Effect of concentration on the adsorption of Pb^{2+} at 355µm, 40^0C and 10min

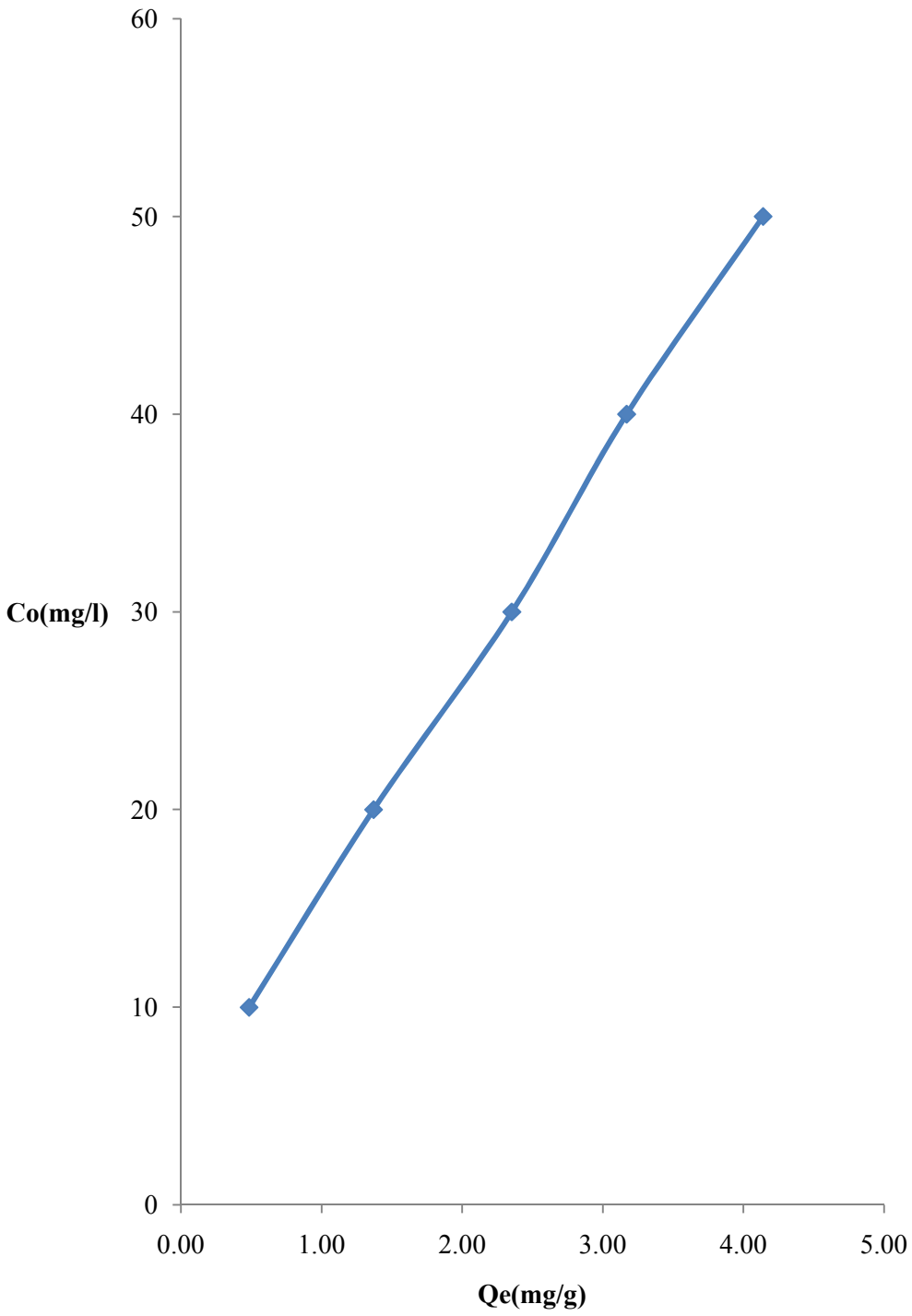


Fig.4.29. Effect of concentration on the adsorption of Cr (VI) at 355µm, 40^0C and 10min

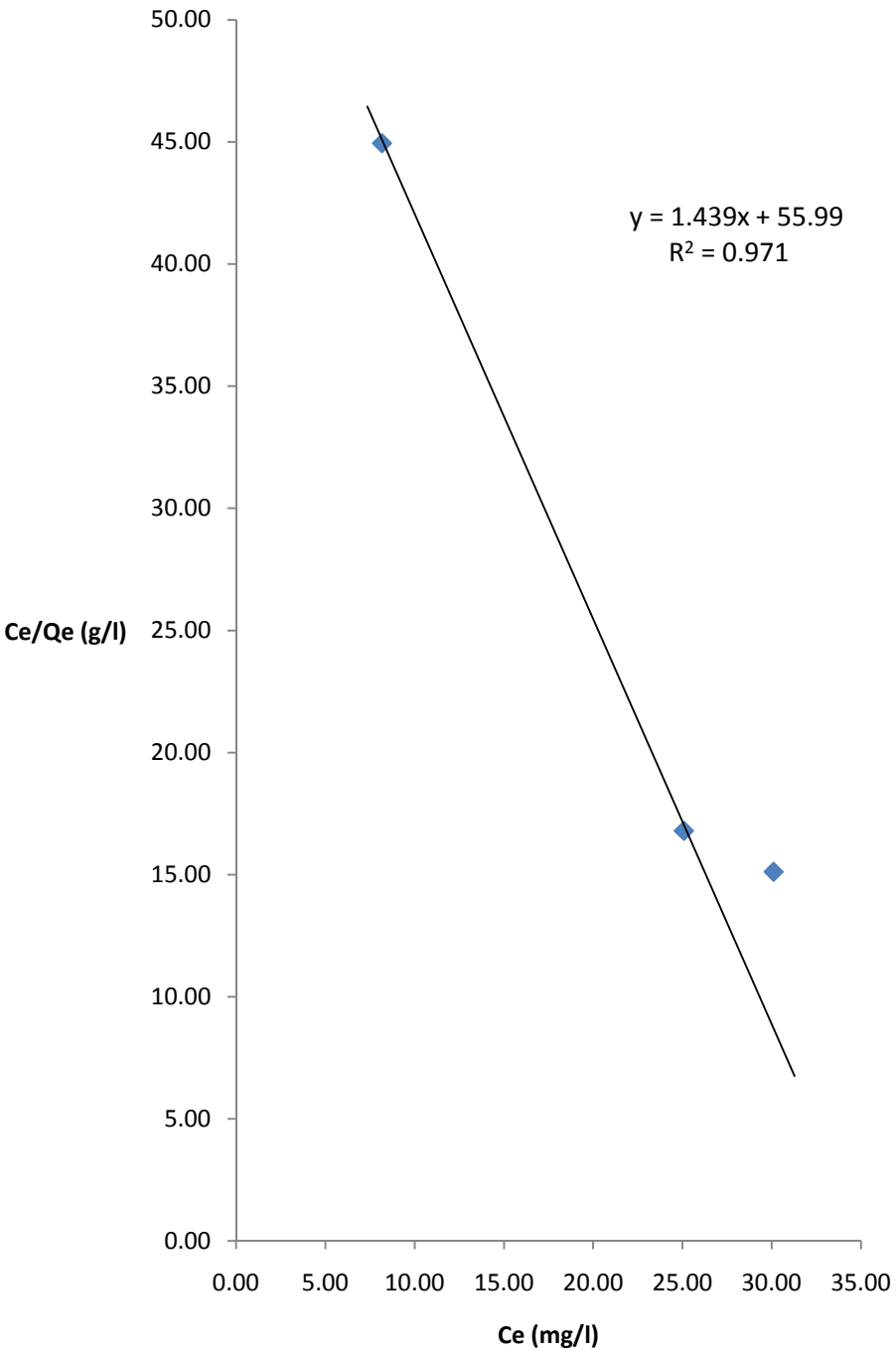


Fig.4.30.Langmuir isotherm for the adsorption of Pb^{2+} at particle size 355µm, 40^{o}C and 10min.

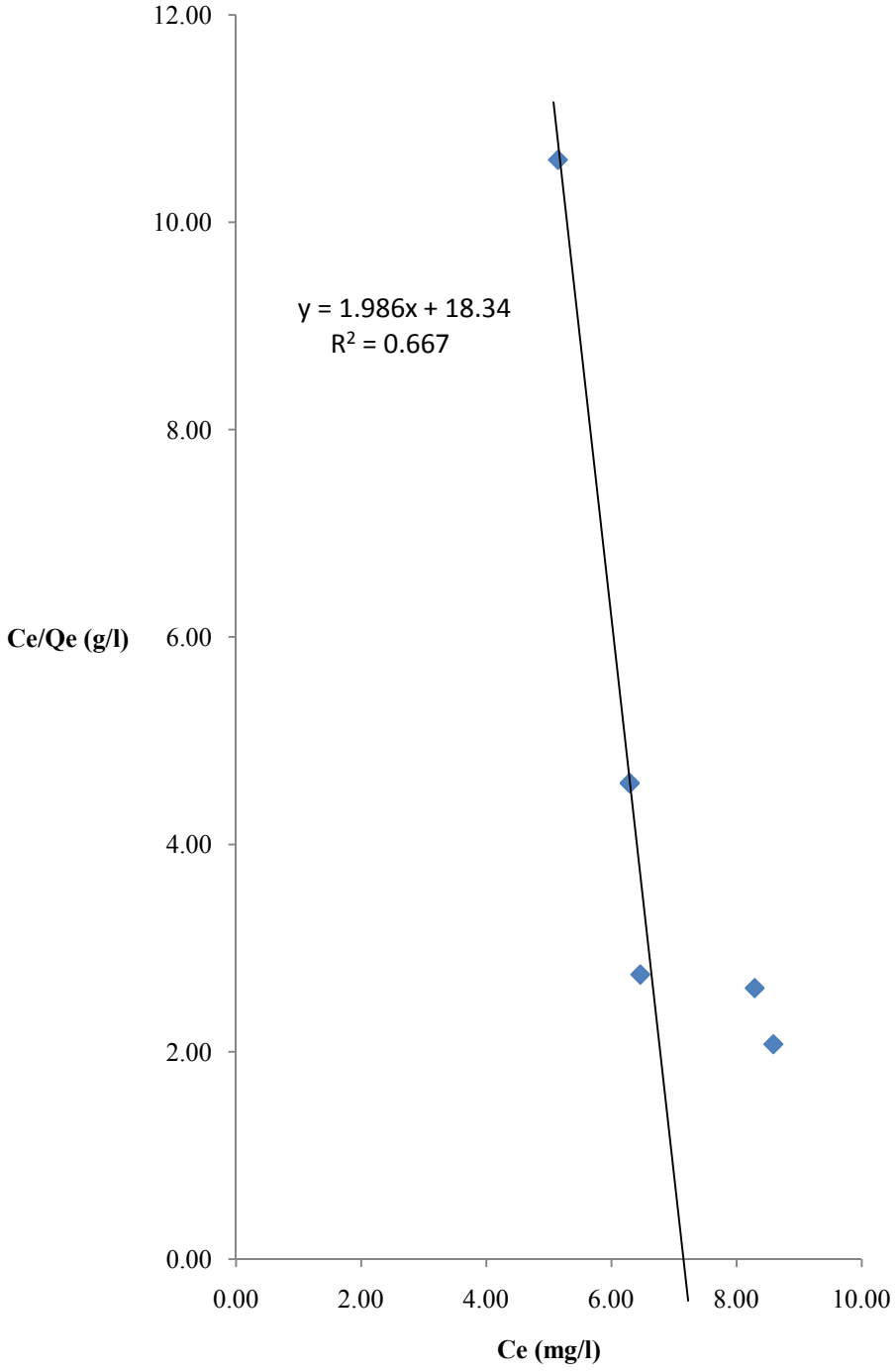


Fig.4.31 .Langmuir isotherm for the adsorption of Cr (VI) at particle size 355µm,40^{o}C and 10min

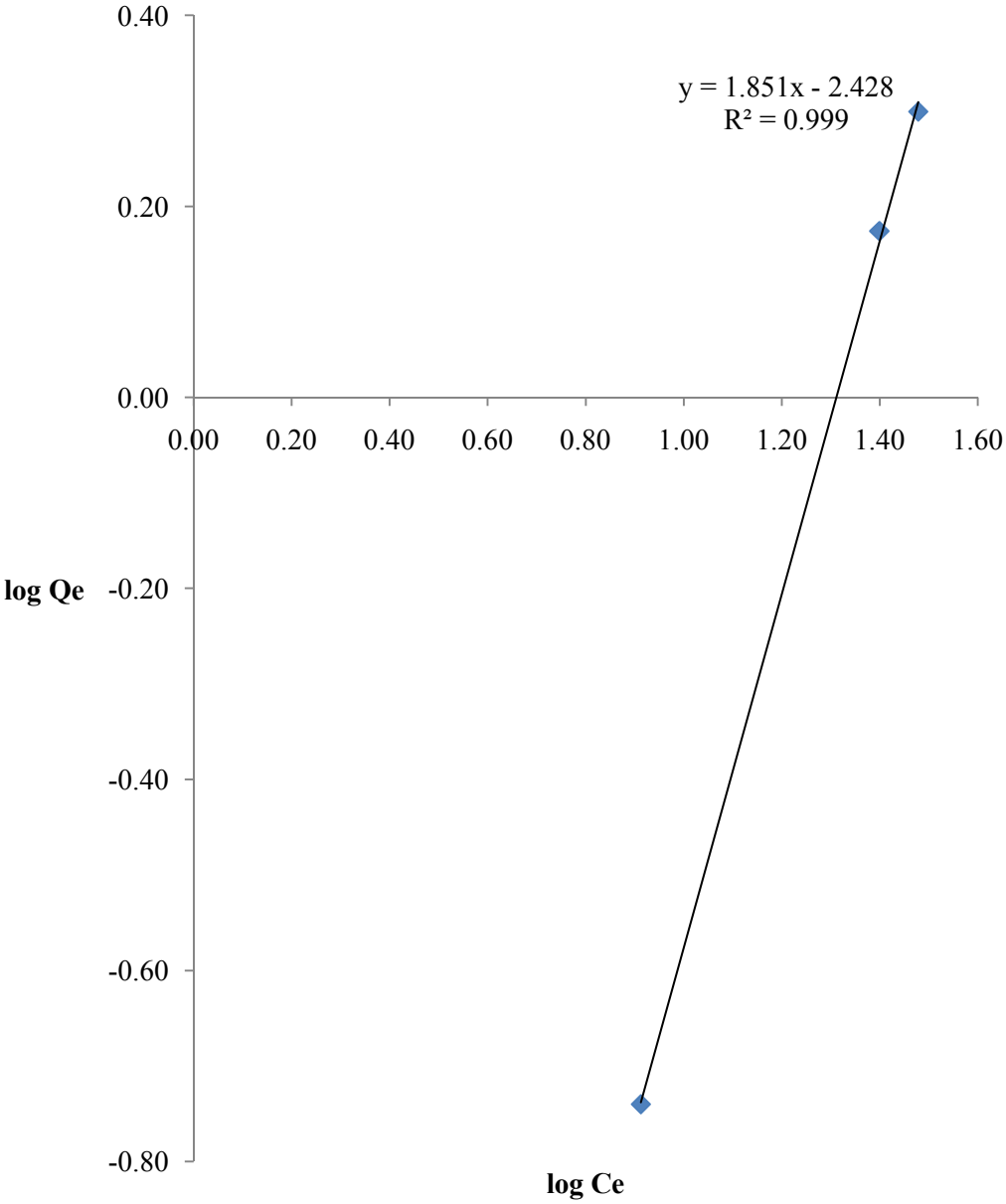


Fig.4.32.Freundlich isotherm for the adsorption of Pb^{2+} at particle size 355µm, 40^{o}C and 10min

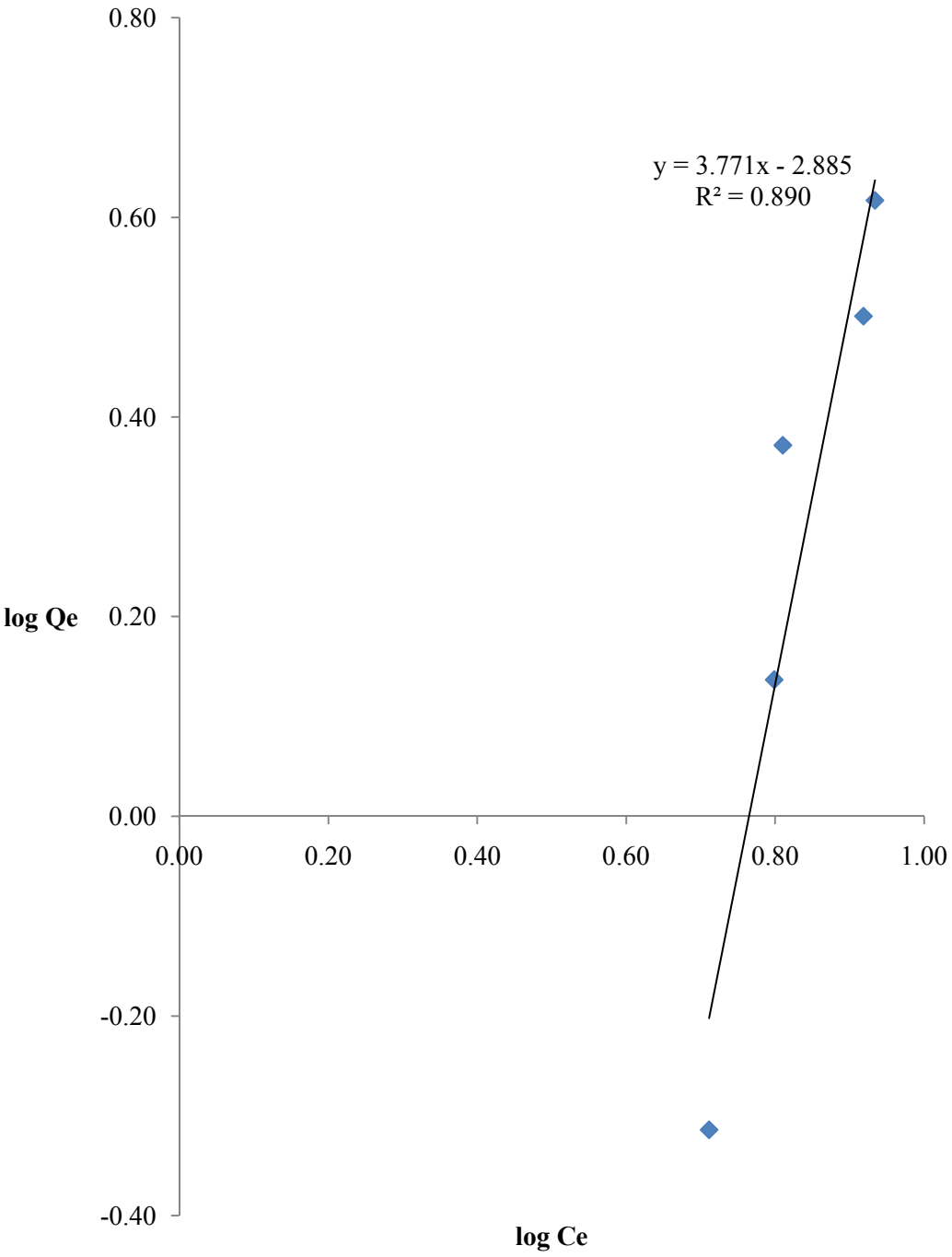


Fig.4.33. Freundlich isotherm for the adsorption of Cr (VI) at particle size355µm,40^{o}C and10min.

Figure 4.28 and 4.29 shows the effect of concentration on the amount of Pb^{2+} and Cr (VI) adsorbed from aqueous solution on to cow bone charcoal. The two figures showed that as the concentration increases, the amount adsorbed increases as well in both cases. However, there was saturation at 30mg/l Pb^{2+} removal; probably the binding sites were saturated at that point. Figure 4.30-4.33 shows the Langmuir and Freundlich isotherm plot for Pb^{2+} and Cr (VI) at 10 minutes and 40^0C . As shown in the figures, both models fitted the adsorption of both metal ions from aqueous solutions with a good correlation coefficient R^2 value. Also, from the constants, the affinity between Cr (VI) and cow bone charcoal that is K_a value was greater than that of Pb^{2+}. The adsorption of Pb^{2+} was more intense; however, the R^2 value of Pb^{2+} with the Freundlich model was greater at 10 minutes. Therefore, the adsorption of Pb^{2+} is heterogeneous.

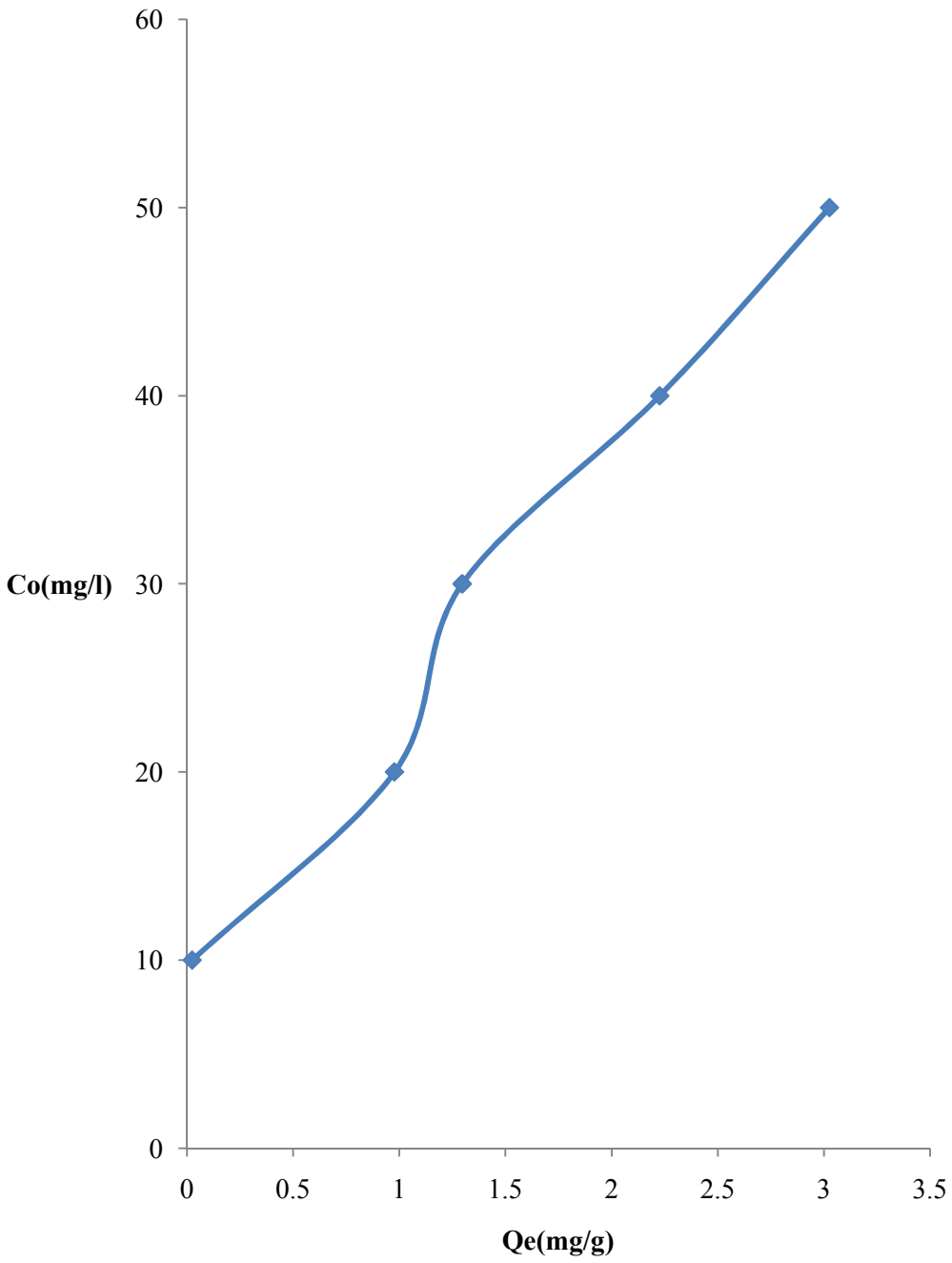


Fig.4.34. Effect of concentration on the adsorption of Pb^{2+} at 355µm, 40^0C and 20min

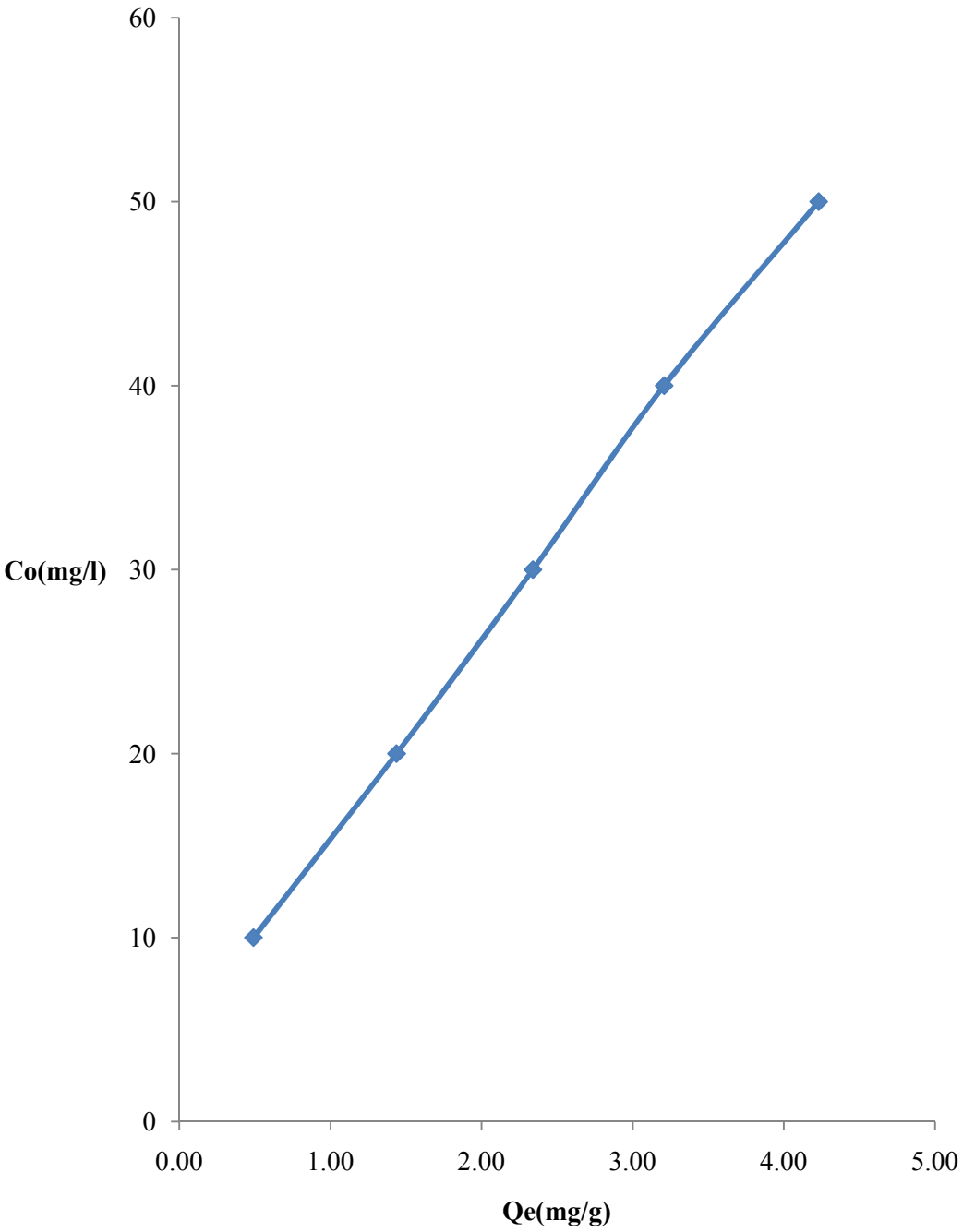


Fig.4.35. Effect of concentration on the adsorption of Cr (VI) at 355µm, 40^0C and 20min

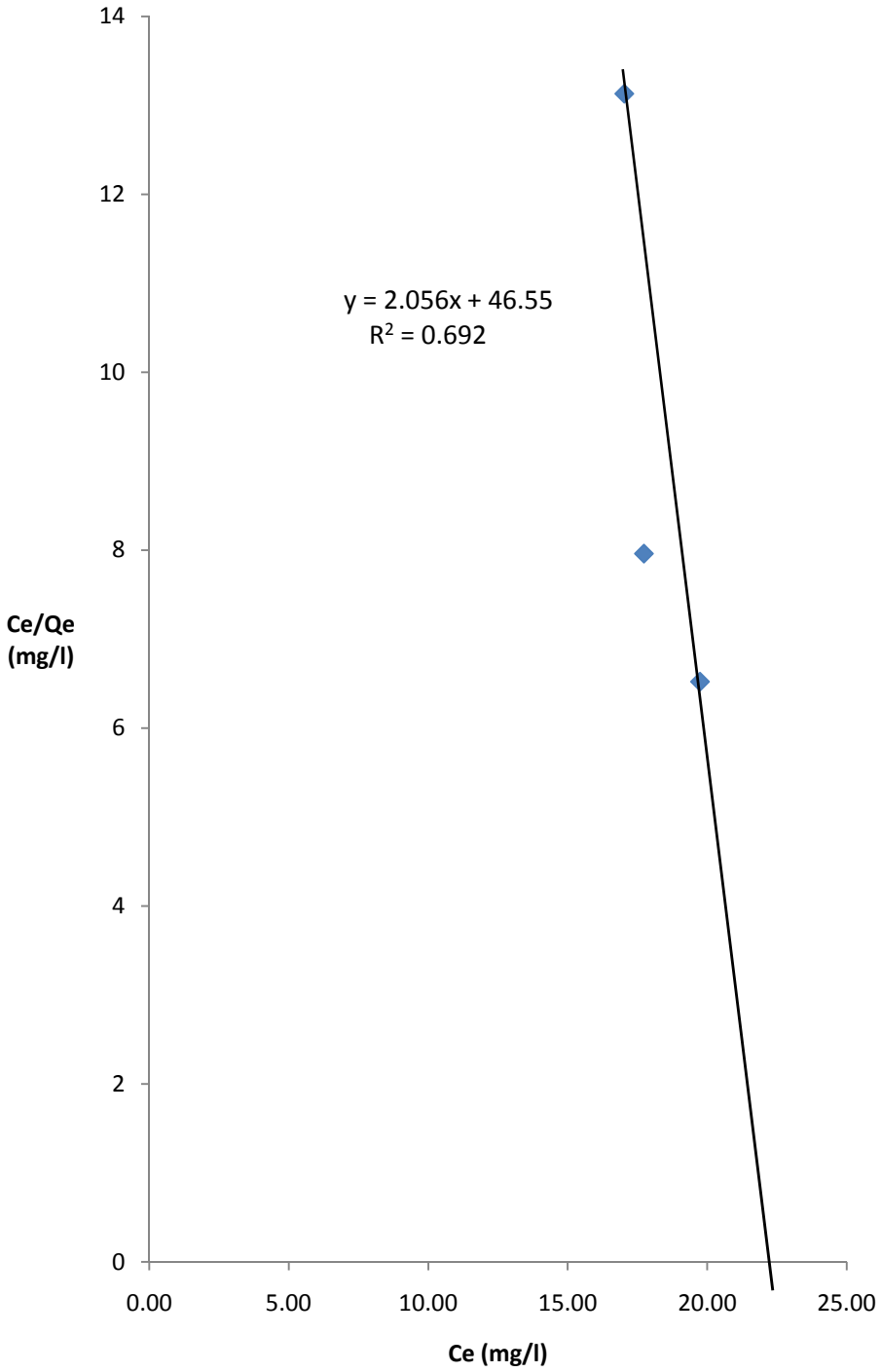


Fig.4.36. Langmuir isotherm for the adsorption of Pb^{2+} at particle size 355µm, 40^{o}C and 20min

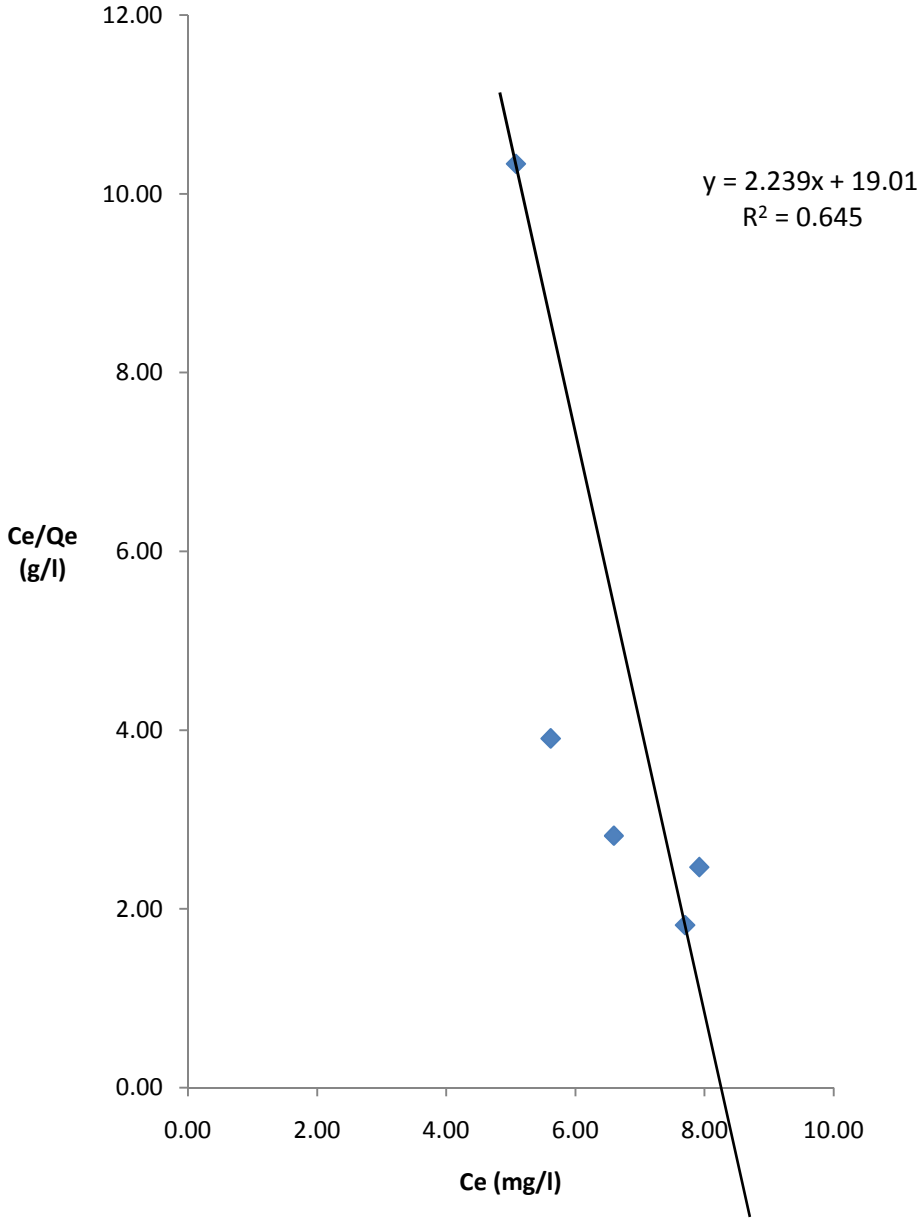


Fig.4.37.Langmuir isotherm for the adsorption of Cr (VI) at particle size 355µm,40^{o} C and 20min

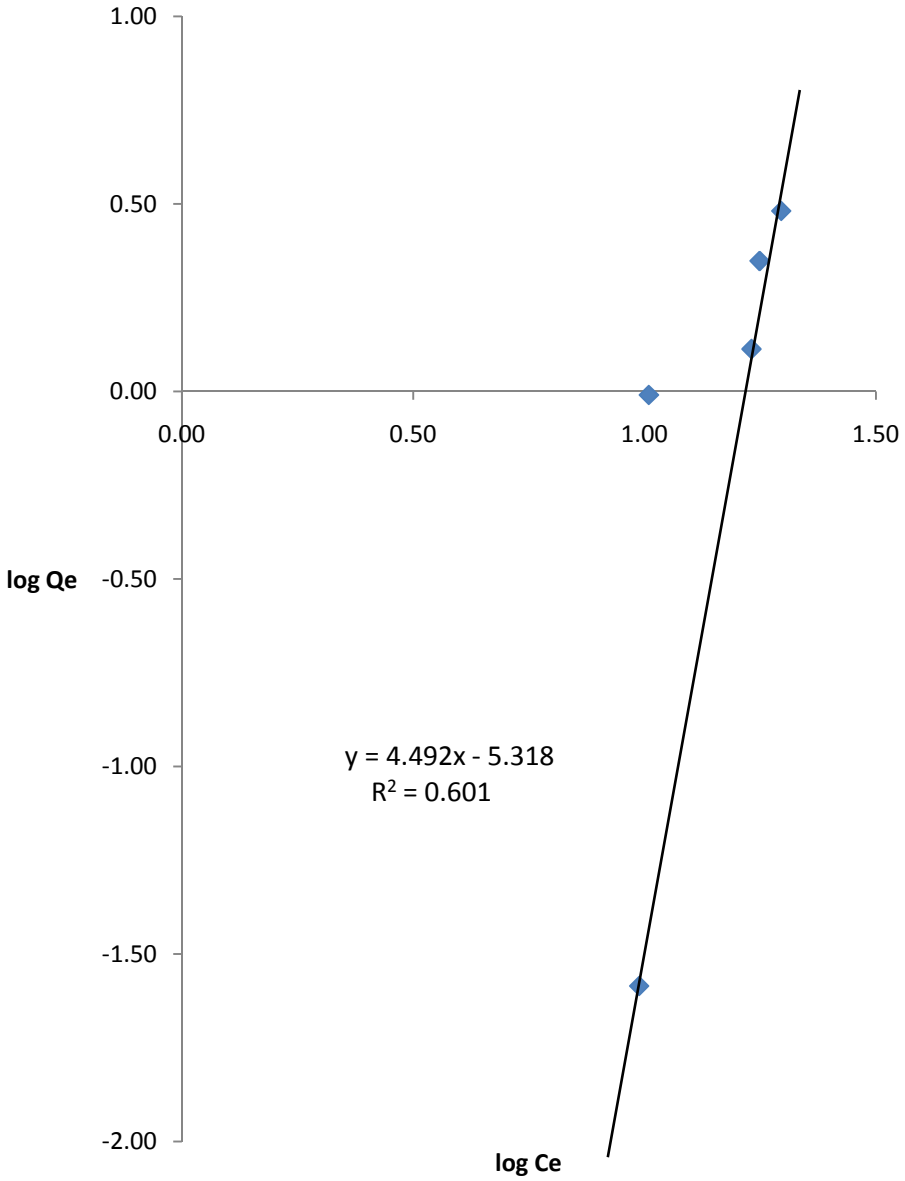


Fig.4.38.Freundlich isotherm for the adsorption of Pb^{2+} at particle size 355µm, 40^{o}C and 20min

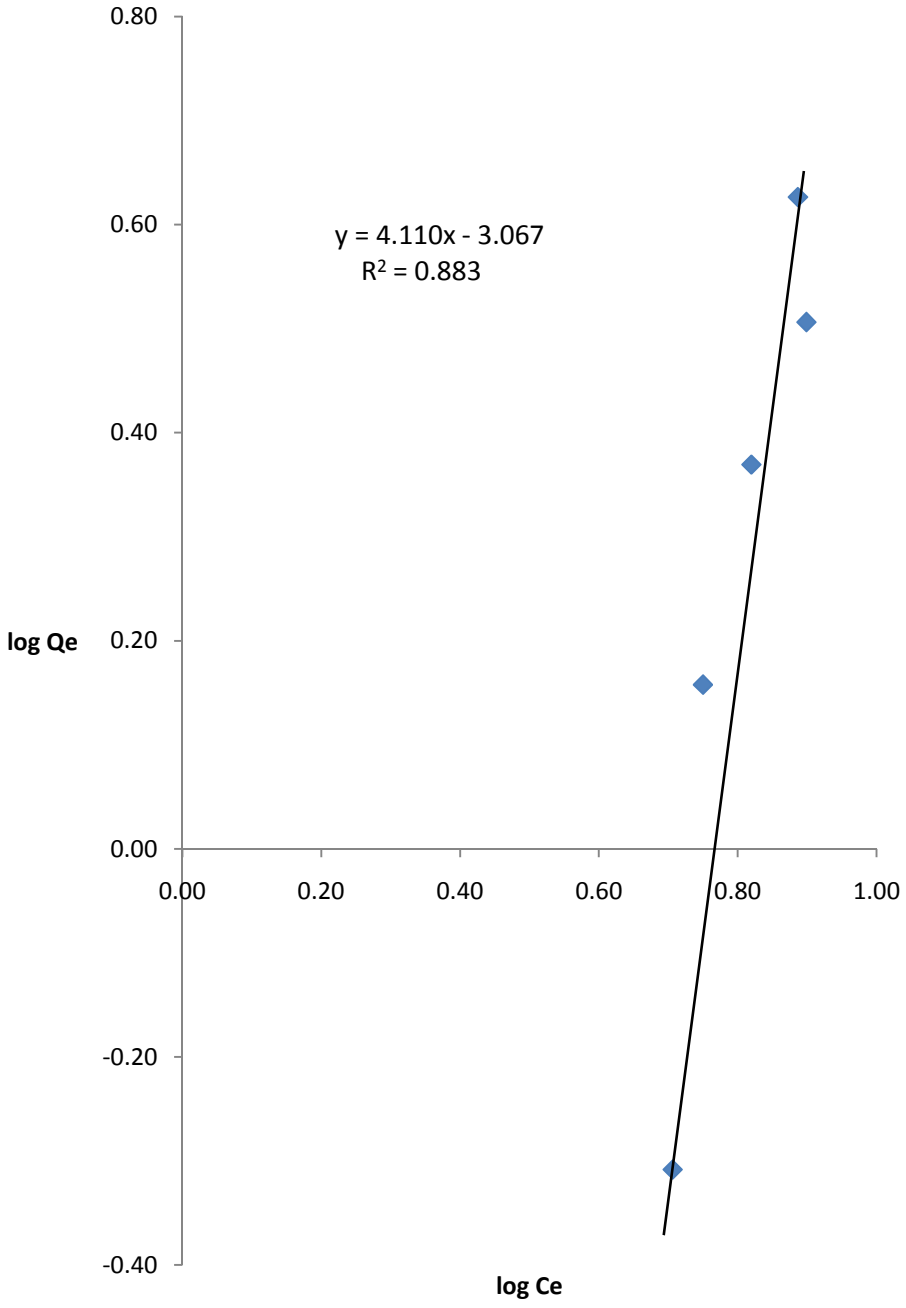


Fig.4.39. Freundlich isotherm for the adsorption of Cr (VI) at particle size 355µm, 40^{o}C and 20min

Figure 4.34 and 4.35 shows the effect of concentration on the adsorption of Pb^{2+} and Cr(VI) at 20 minutes and 40^0C . Both figures showed absolute linearity in their adsorption pattern. As their concentration increases, the amount adsorbed increases in accordance. Figure 4.36 to 4.39 shows the Langmuir and Freundlich isotherm plot for Pb^{2+} and Cr(VI) at 20 minutes and 40^0C. On observation, models showed good prediction for the adsorption of Pb^{2+} and Cr(VI) on to cow bone charcoal. The adsorption intensities for both metal ions were weak, that is less than one; likewise the maximum / theoretical adsorption capacity. The Freundlich model showed better prediction for Cr(VI) with a correlation coefficient value of (R^2= 0.883). Based on this result, the adsorption of Cr(VI) at 20 minutes and 40^0C is heterogeneous.

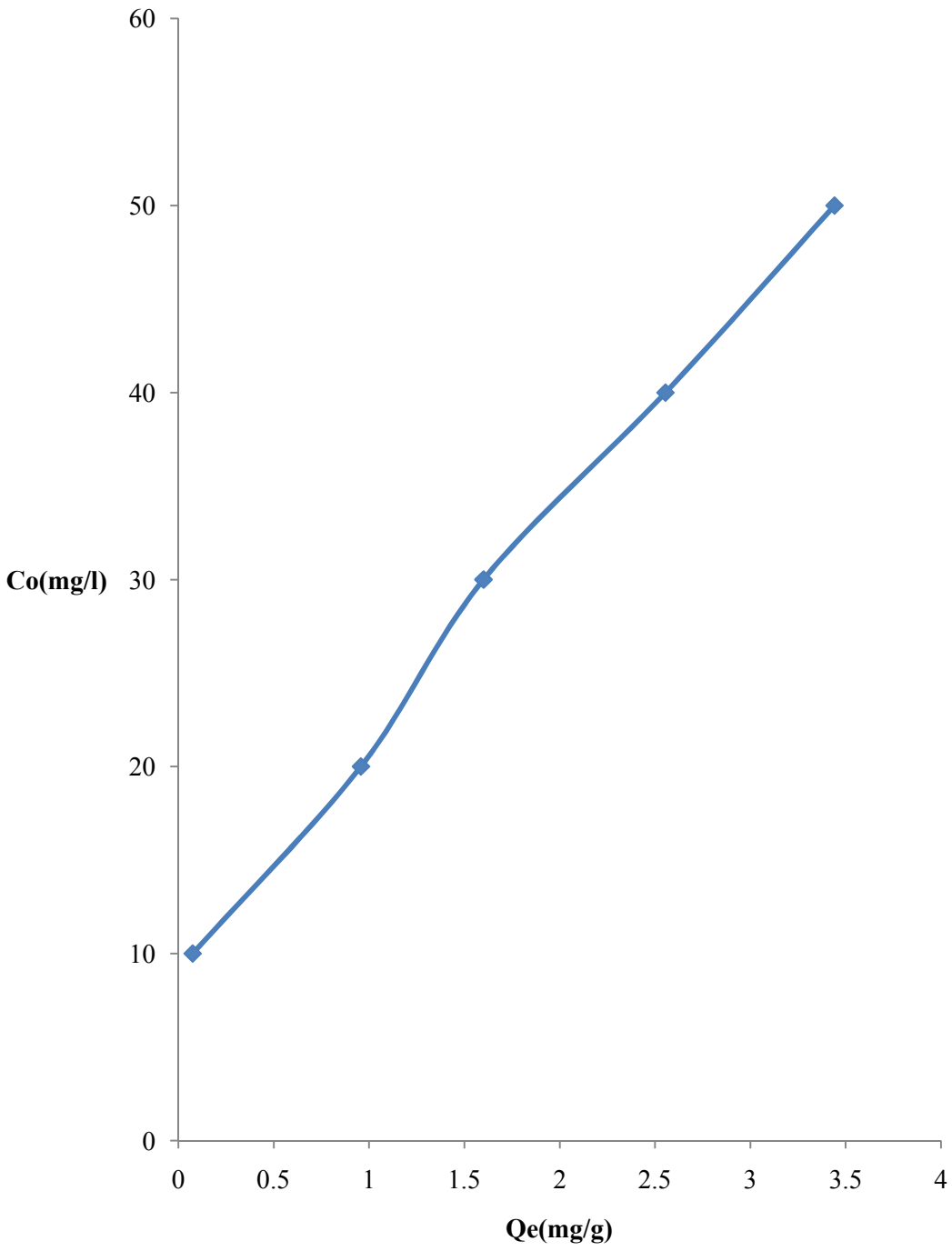


Fig.4.40.Effect of concentration on the adsorption of Pb^{2+} at 355µm,40^0C and 40min

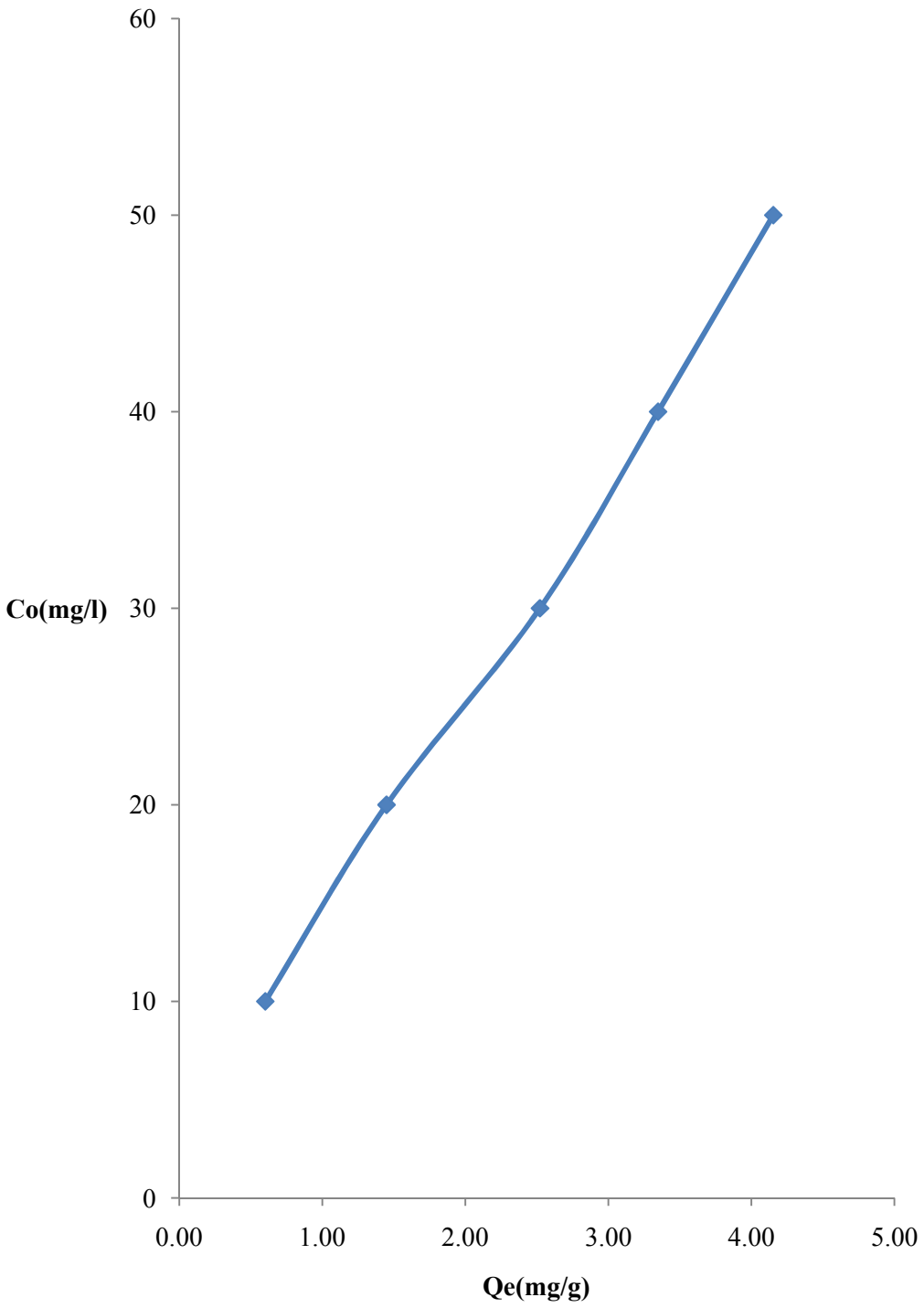


Fig.4.41. Effect of concentration on the adsorption of Cr (VI) at 355µm, 40^0C and 40min

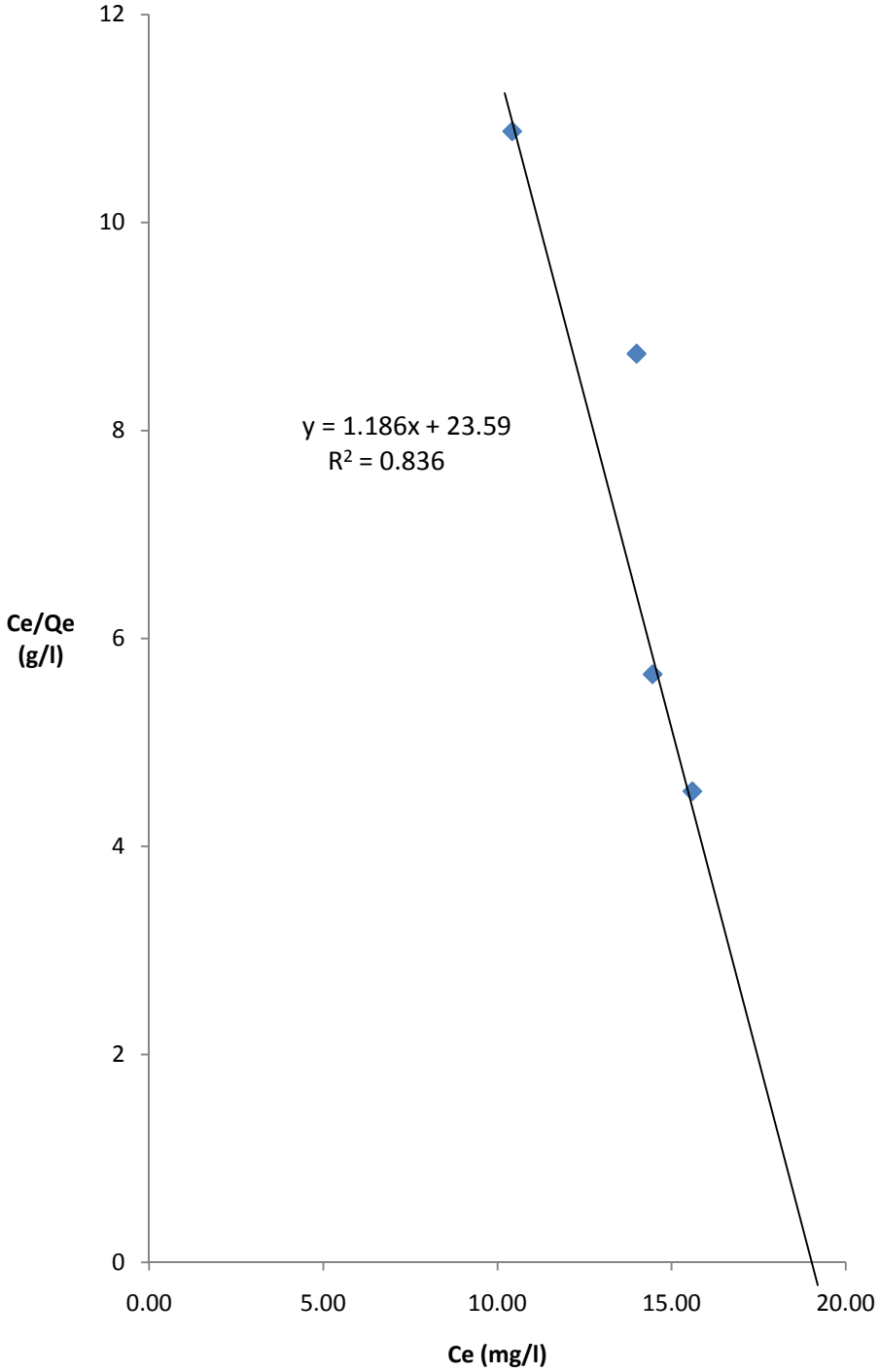


Fig.4.42.Langmuir isotherm for the adsorption of Pb^{2+} at particle size 355µm, 40^{o}C and 40min

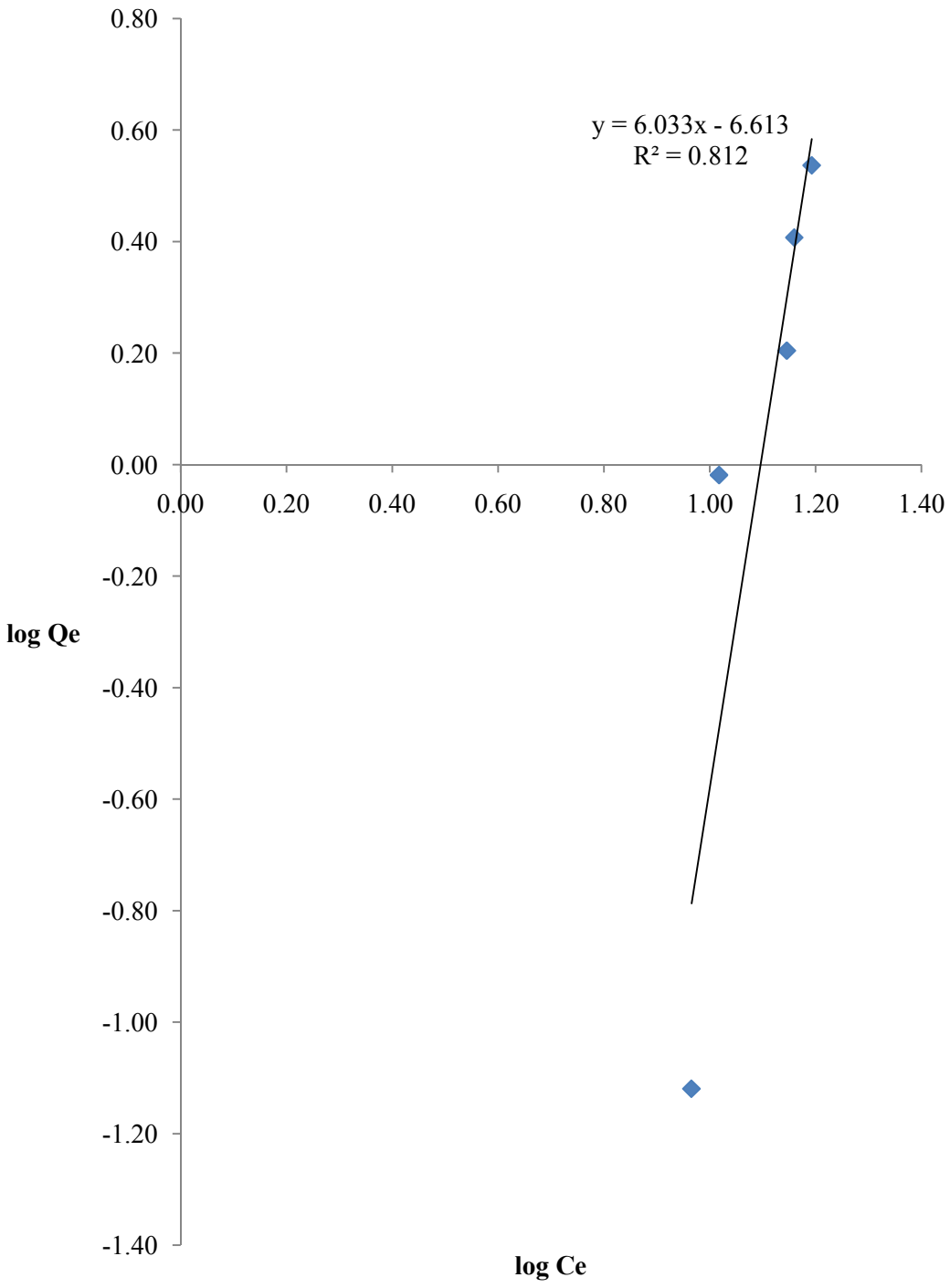


Fig.4.43. Freundlich isotherm for the adsorption of Pb^{2+} at particle size 355µm, 40^{o}C and 40min.

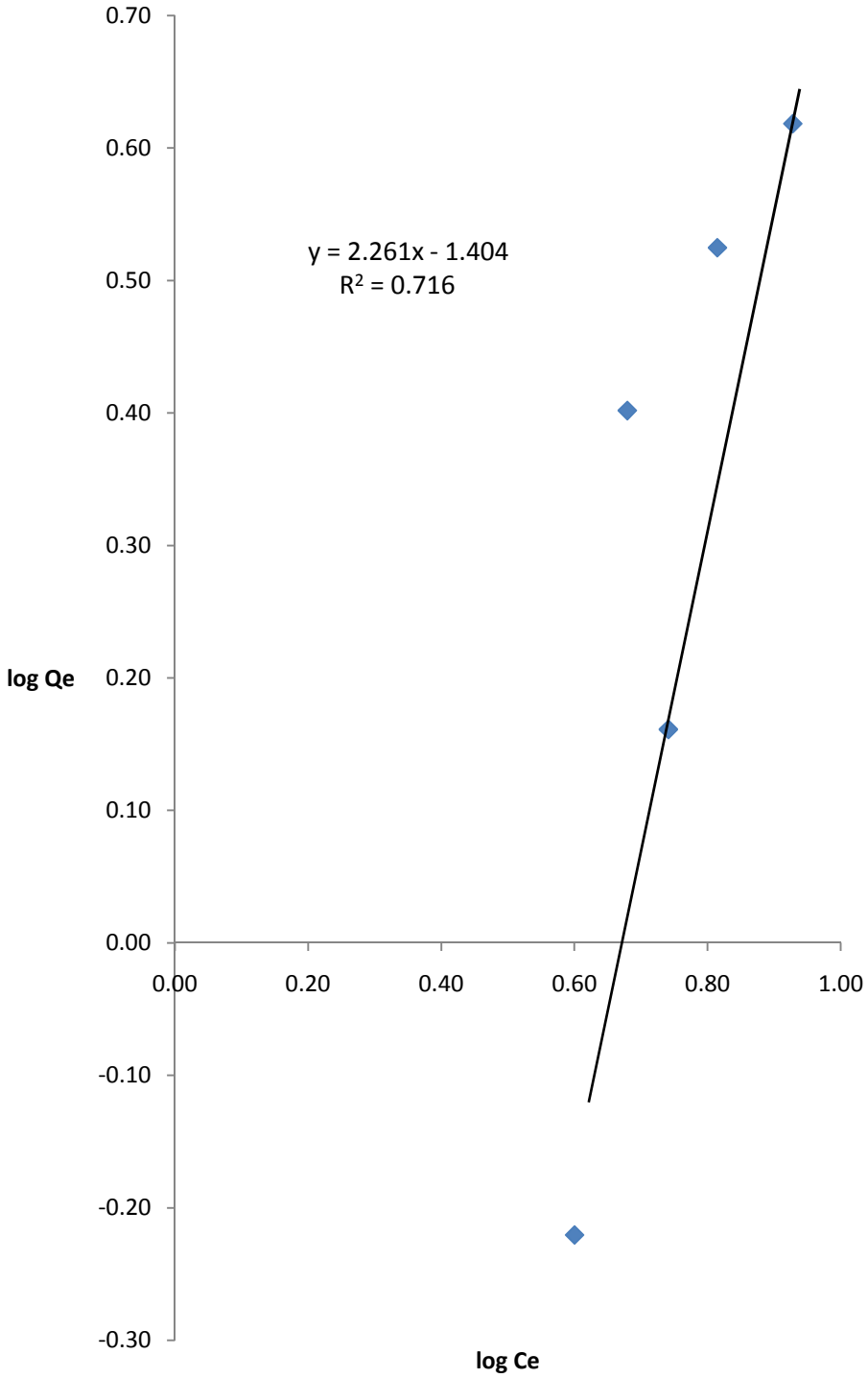


Fig.4.44.Freundlich isotherm for the adsorption of Cr (VI) at particle size 355µm, 40^{o}C and 40min

Figure 4.40 and 4.41 shows the effect of concentration on the adsorption of Pb^{2+} and Cr (VI) on to cow bone charcoal at 40 minutes and 40^0C. The isotherm shape indicates good linearity for the adsorption process. In both cases, the amount adsorbed is a function of concentration; that is, as the initial concentration increases, the amount adsorbed rises as well. Figure 4.42 to 4.44 shows the Langmuir and Freundlich isotherm plot for the adsorption of Pb^{2+} and Cr (VI). From the figures, Pb^{2+} has a good maximum/ theoretical adsorption capacity compared to Cr (VI), whose value was poor; also, adsorption intensities (n) of both metal ions were weak that is less than one. However, the Langmuir and Freundlich isotherm for lead indicates good prediction; while the Langmuir plot for Cr (VI) at 40 minutes did not show a good fit. On the other hand, the Freundlich plot for Cr (VI) indicates good prediction.

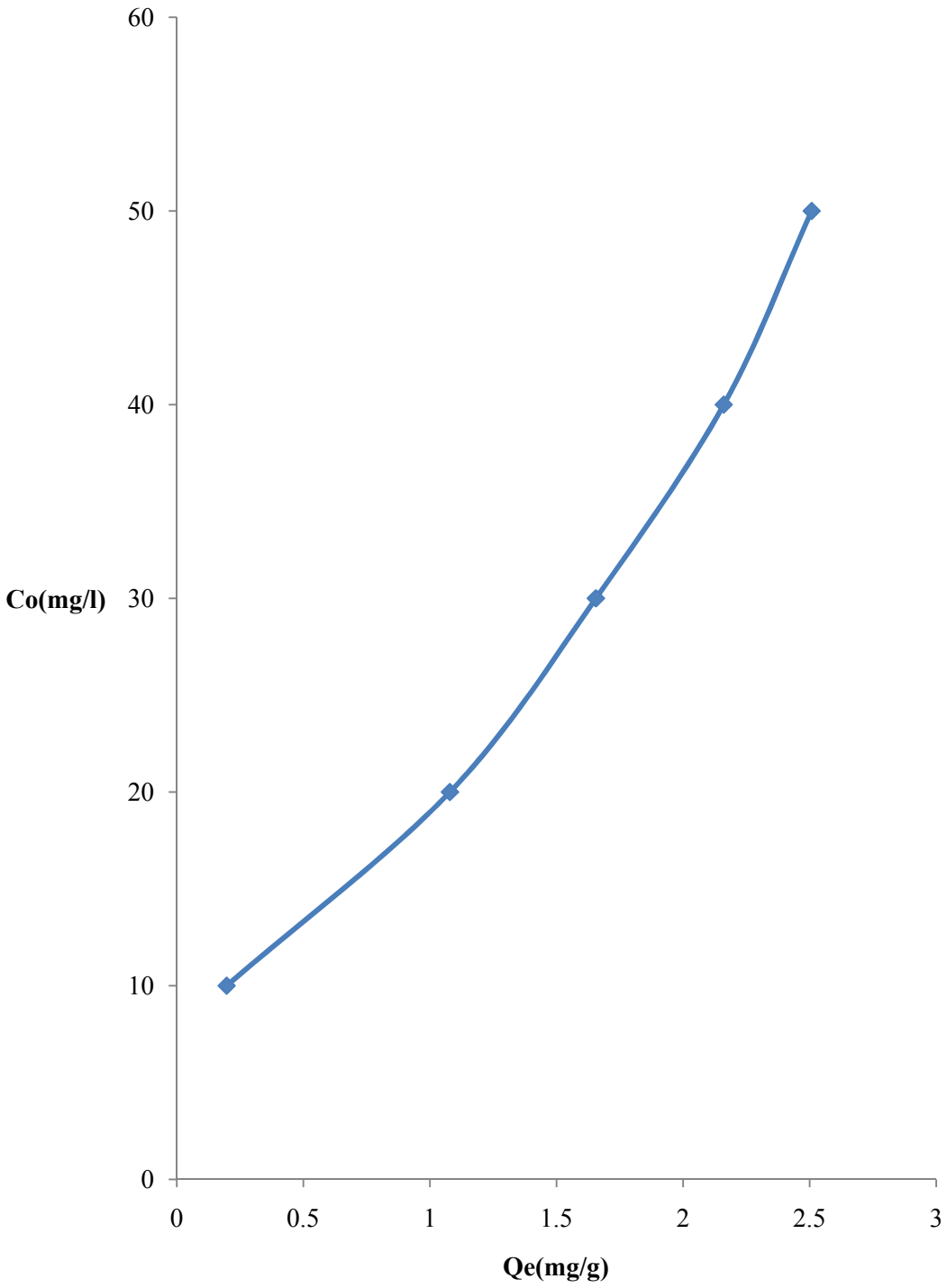


Fig.4.45. Effect of concentration on the adsorption of Pb^{2+} at 355µm, 40^0C and 60min

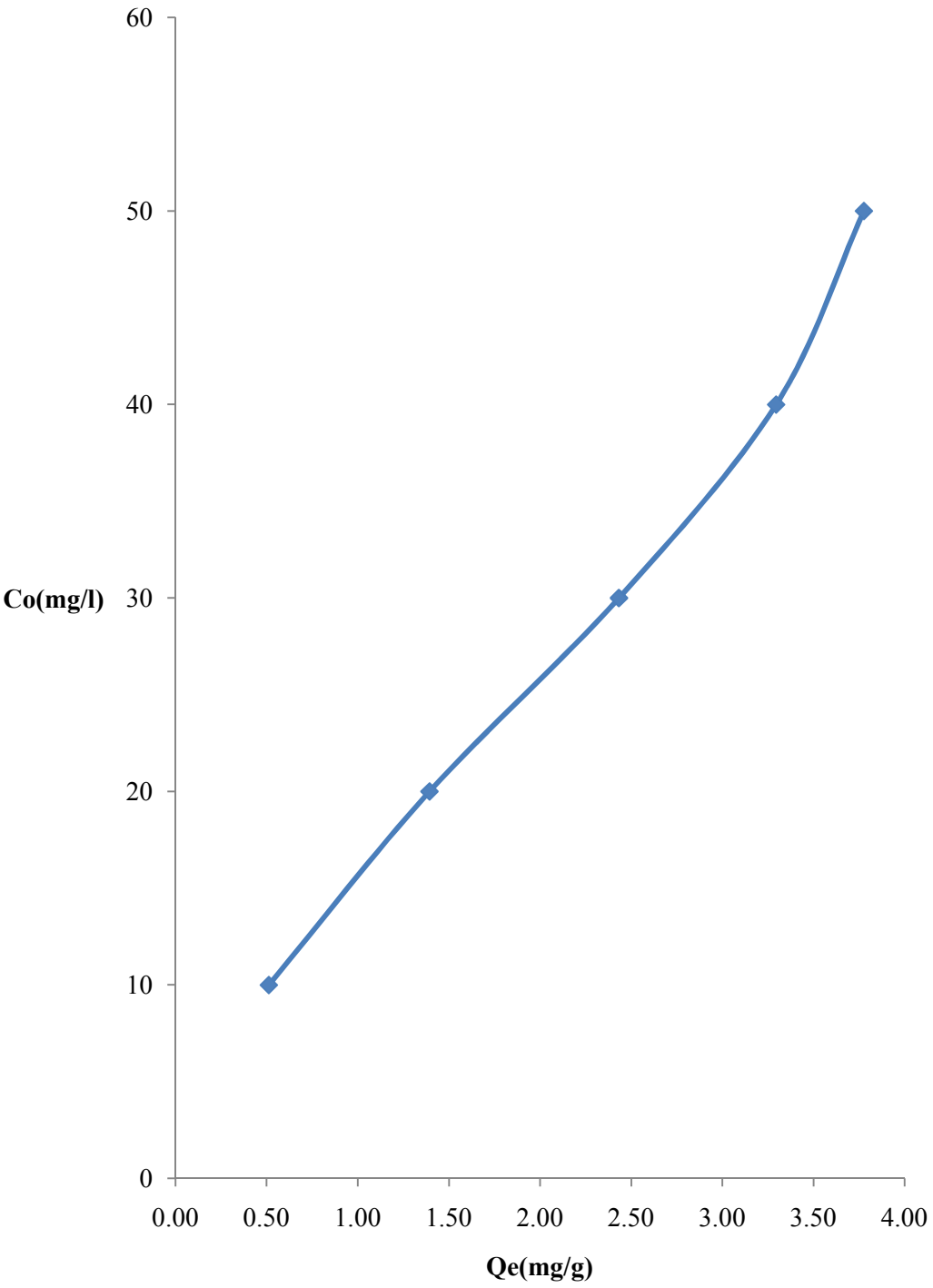


Fig.4.46. Effect of concentration on the adsorption of Cr (VI) at 355µm, 40^0C and 60min

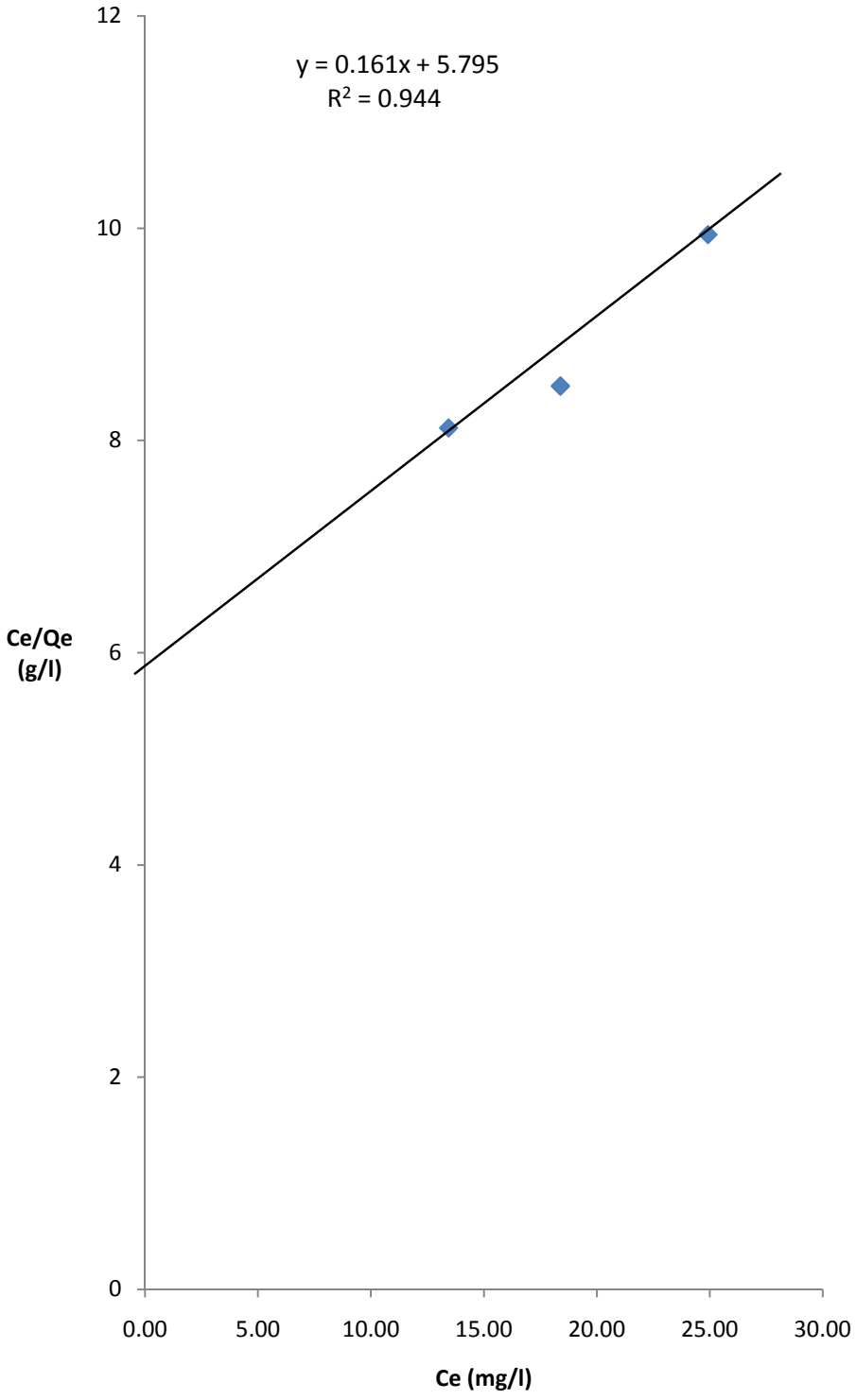


Fig.4.47. Langmuir isotherm for the adsorption of Pb^{2+} at particle size 355µm, 40^{o}C and 60min.

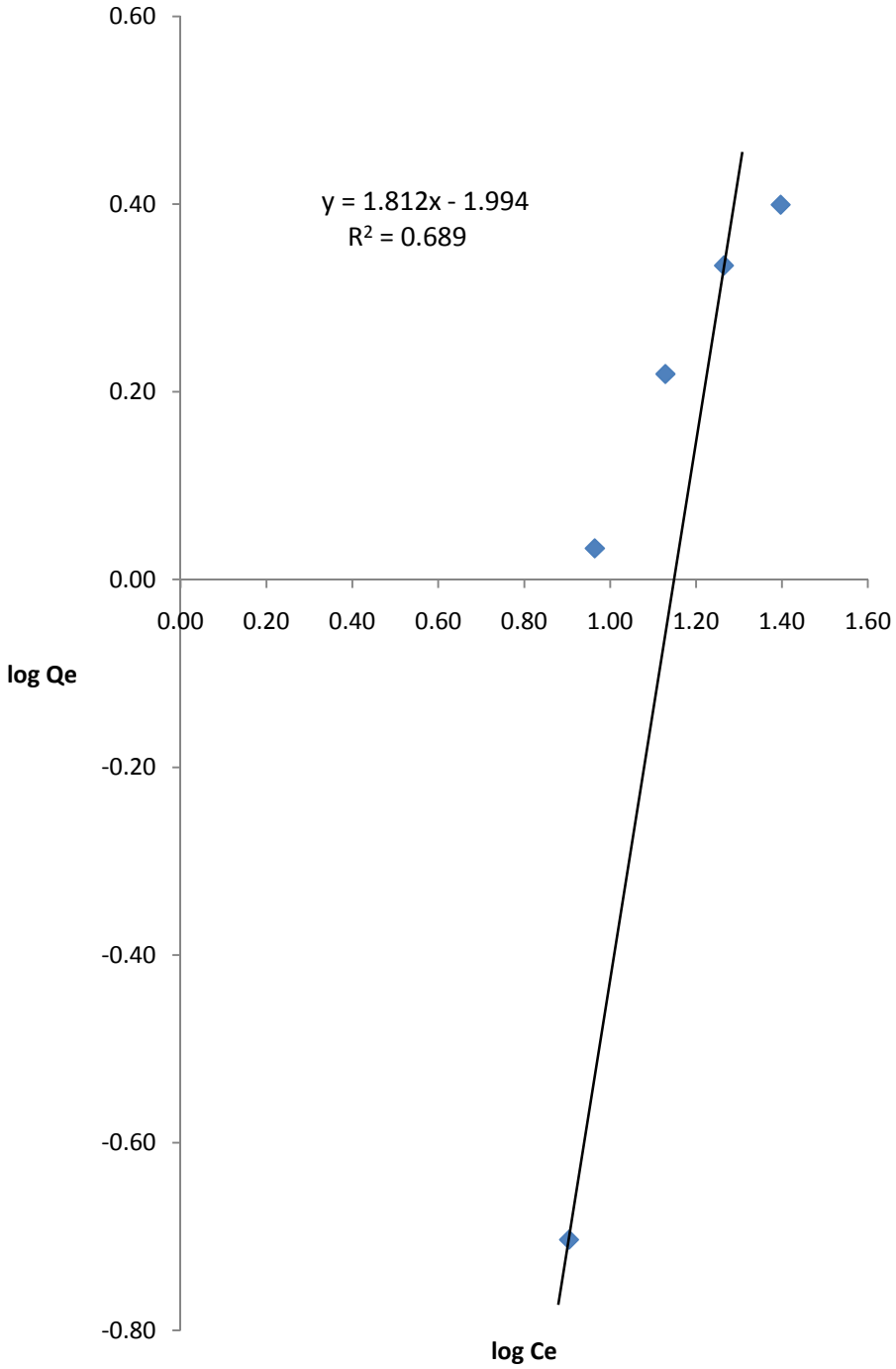


Fig.4.48. Freundlich isotherm for the adsorption of Pb^{2+} at particle size 355µm, 40^{o}C and 60min.

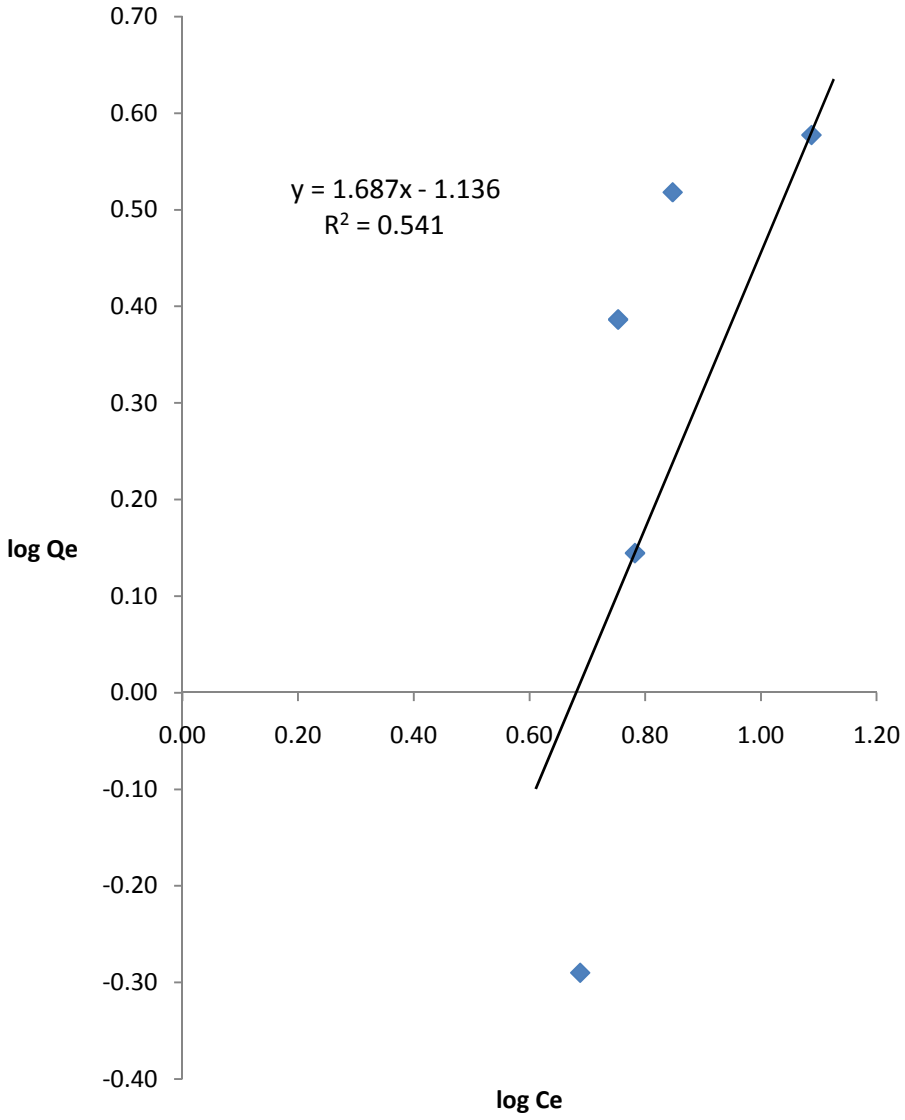


Fig.4.49. Freundlich isotherm for the adsorption of Cr (VI) at particle size 355µm,40^{o}C and 60min

Figure 4.45 and 4.46 above shows the effect of concentration on the adsorption of Pb^{2+} and Cr (VI) on cow bone charcoal at 60 minutes and 40^0C . The two figures showed that as concentration increases, the amount adsorbed also increases. The linearity of these isotherms were represented with Langmuir and Freundlich isotherm in Fig.4.47-4.49.

In Table 4.7, at 60 minutes and 40^0C, Pb^{2+} assumed higher maximum/theoretical adsorption capacity with a value of (6.21mg/g); while that of Cr (VI) was poor. Similarly, the correlation coefficient ($R^2 = 0.944$) for Pb^{2+} shows that Pb^{2+} has a better prediction with Langmuir model, under homogenous condition; while the Langmuir plot for Cr (VI) was not encouraging.

4.3 EFFECT OF CONTACT TIME

Fig.4.50. below shows contact time effect on the cow bone charcoal removal of 30mg/l Pb^{2+} at 30^0C and particle size 355μm. There was a slight increase in the removal of 30mg/l of Pb^{2+} with cow bone charcoal after which there was a decrease at 10 minutes, until it reaches a maximum after 20 minutes of agitation. Afterwards, no further increase was observed. This trend could be due to the saturation of the binding sites on the surface of the adsorbent (cow bone charcoal). In Figure 4.51, the removal of 30mg/l Cr (VI) decline uniformly down the trend as the time increases up to 20 minutes; at this time, the amount adsorbed became constant. Therefore, the affinity for the adsorbate is in the order of Pb^{2+} < Cr (VI).

Fig.4.52. shows contact time effect on the cow bone charcoal removal of 30mg/l Pb^{2+} at 40^0C. There was a sharp decrease after 5 minutes of agitation. The decrease was pronounced at 10 minutes, after which there was a sharp increase at 20 minutes. From 40

minutes of agitation to 60 minutes, the rate of adsorption was constant. While in Figure 4.53, 30mg/l removal of Cr (VI) under similar condition indicates that the amount adsorbed decreased between 10 and 20 minutes, after which there was a sharp increase at 40 minutes of contact time, until it reaches a maximum peak where the amount adsorbed began to regress at 60 minutes. Consequently, the order of affinity for the adsorbate is Cr (VI) < Pb^{2+}. .

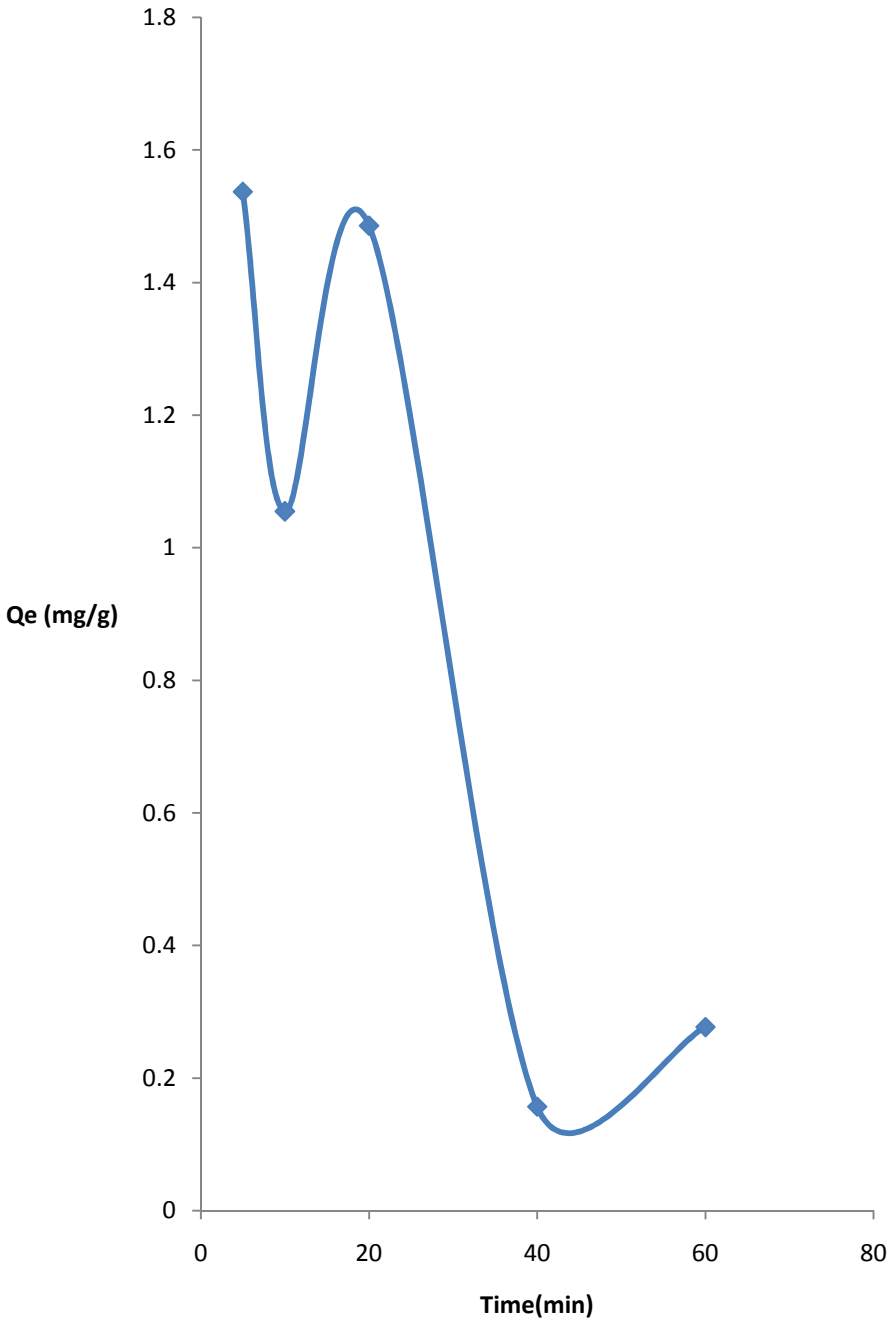


Fig.4.50. Effect of contact time on adsorption at 355µm and 30°C

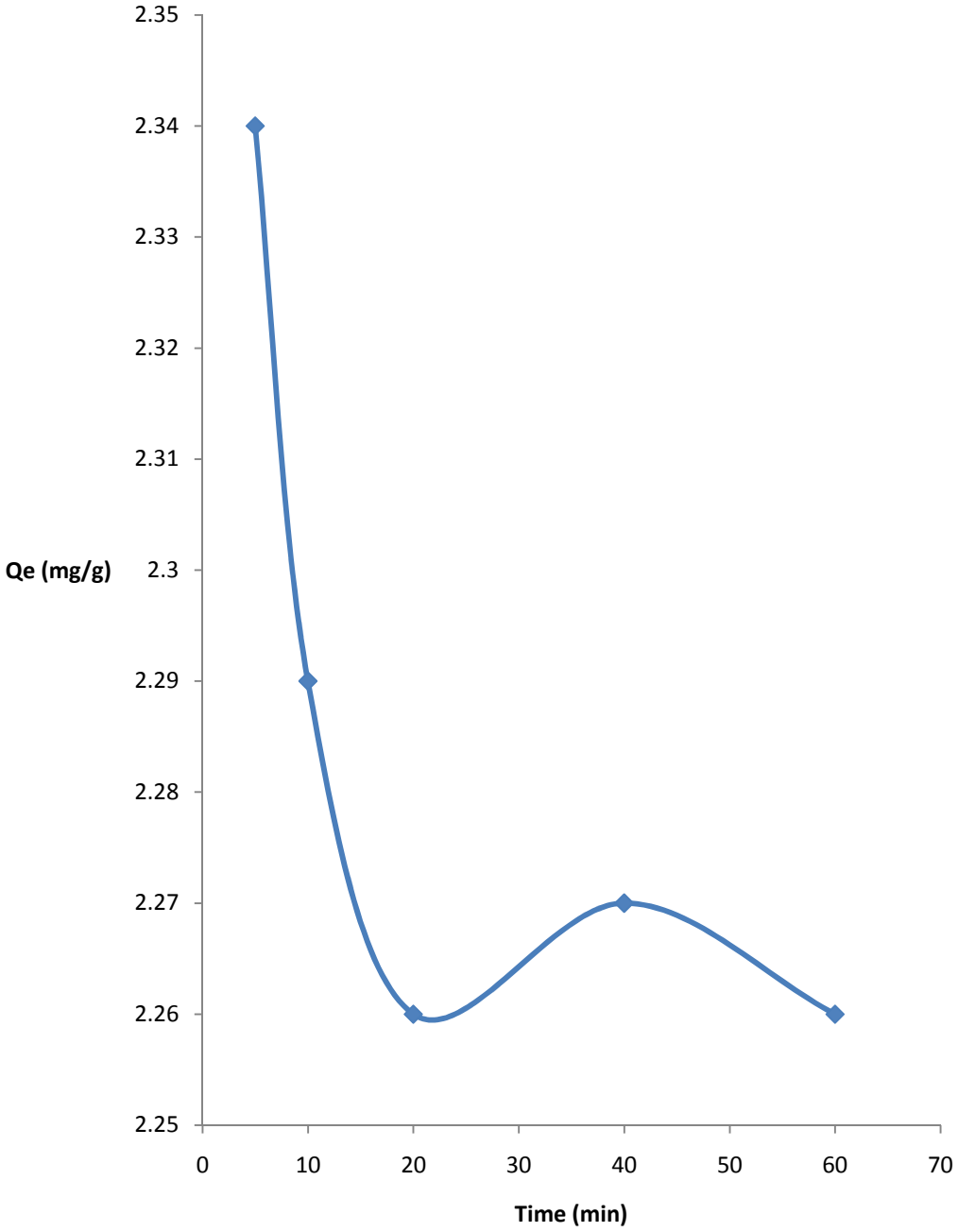


Fig.4.51. Effect of contact time on adsorption at 355µm and 30°C

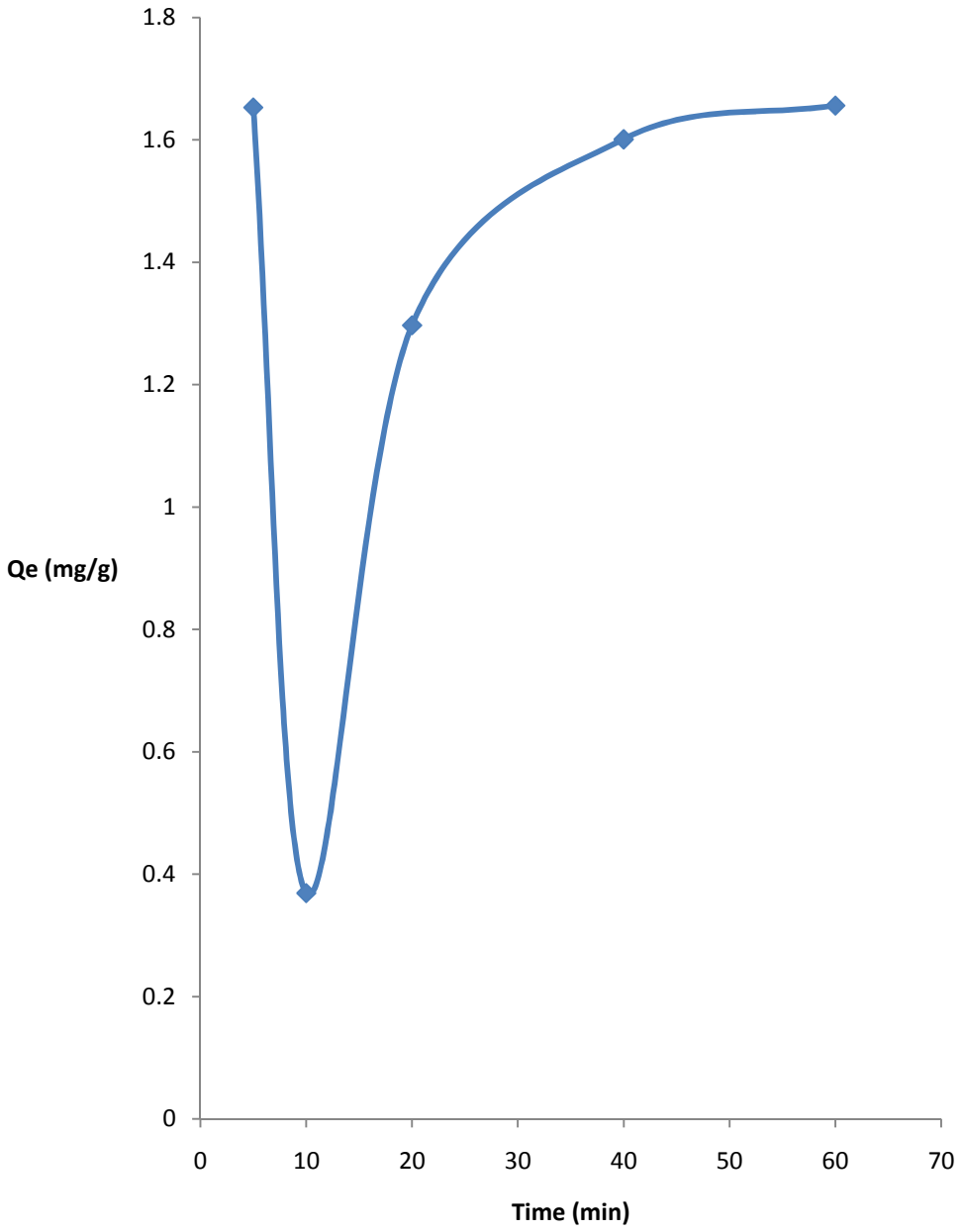


Fig.4.52. Effect of contact time on adsorption, at 355µm and 40^{o}C

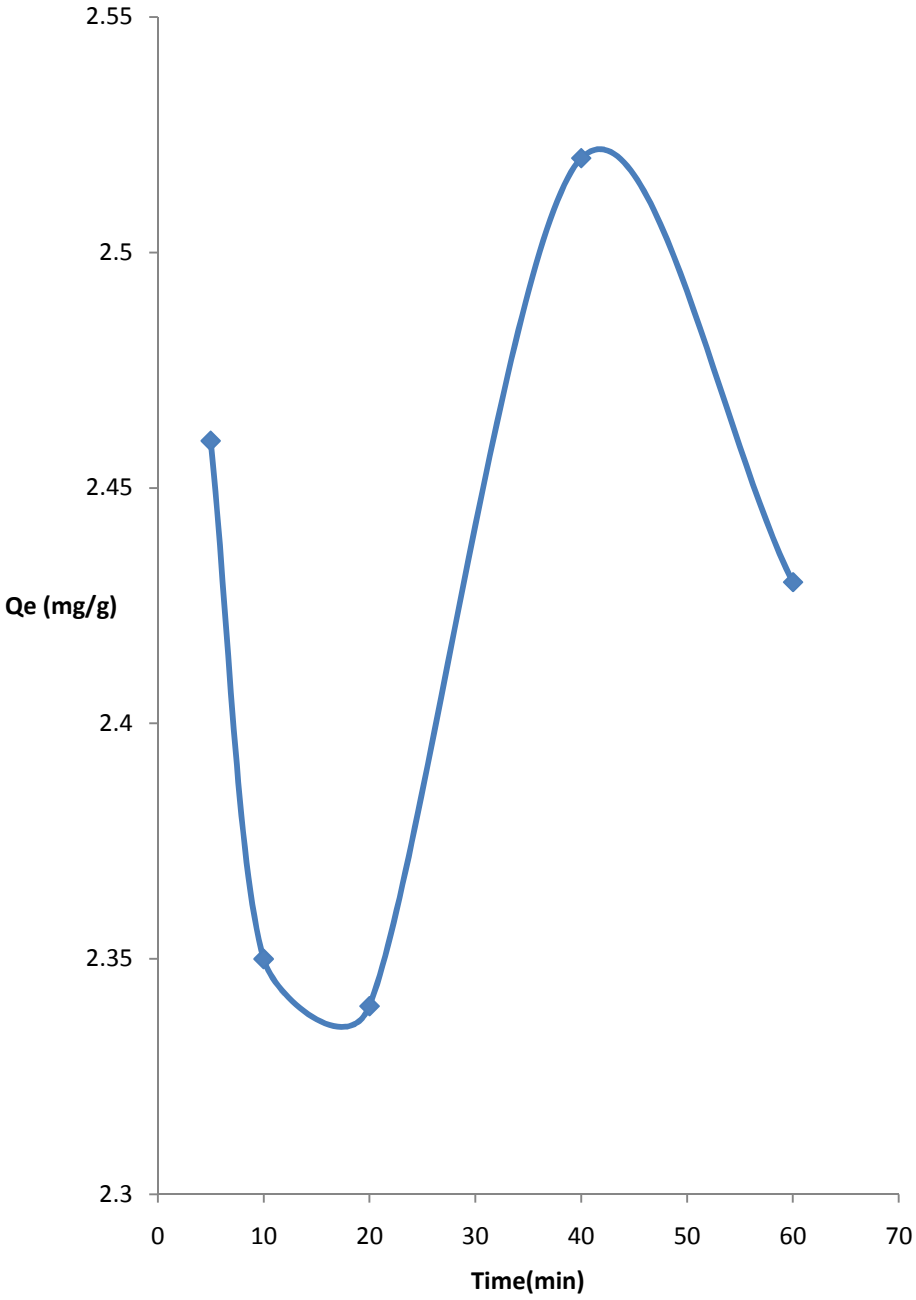


Fig.4.53. Effect of contact time on adsorption, at 355µm and 40°C

4.4 ADSORPTION KINETICS

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Pb^{2+} and Cr (VI) adsorption at three different initial concentrations on cow bone charcoal were analyzed using pseudo-first order and pseudo second order kinetic models. The first order was used to check the adsorption data of Pb^{2+} and Cr (VI) on cow bone charcoal, but the correlation coefficient was not high. However, pseudo second order kinetic model (Ho and McKay, 2000) was successfully applied with high correlation coefficient for explaining kinetic data of an adsorption processes (Ho, 2003). The adsorption of Pb^{2+} and Cr (VI) on cow bone charcoal could be pseudo second order process rather than first order.

The Ho-second order rate equation can be written as

$$dq_t / d_t = K_2 (q_e - q_t)^2 \quad \ldots 4.1$$

Where K_2 is the second order rate constant of adsorption (g/mg/min), q_e is the amount of adsorbate at equilibrium (mg/g) and q_t is the amount of adsorbate on the surface of the adsorbent at any time t (mg/g).

Integrating equation (4.1) above, for the boundary condition t = 0 to t = t and $q_t = 0$ to $q_t = q_t$ gives

$$1 / (q_e - q_t) = 1 / q_e + kt \quad \ldots 4.2$$

Equation (4.2) above, can be rearranged to obtain:

$$t / q_t = 1 / kq_e^2 + 1 / q_e t \quad \ldots 4.3$$

This is the linearised form of Ho-second order model. If the initial sorption rate is

$h_o = kq_e^2$, Eq. (4.3) can be written as :

$$1 / q_t = 1 / h_o + 1/ q_e t \qquad \ldots 4.4$$

Where h_o is the initial adsorption rate; the plot of t / q_t against t in Eq. (4.3) should give a linear relationship from which the constants q_e and h_o can be determined.

Table.4.8. Pseudo second order rate equation constants at different initial concentrations for Pb^{2+} and Cr(VI) adsorption on cow bone charcoal.

Metal ion	Co (mg/l)	q_e (mg/g)	K_2 (g/mg/min)	h_o (mg/g/min)	R^2
Pb^{2+}	10	0.102	39.968	0.399	0.651
	20	1.832	0.016	0.054	0.638
	30	0.205	0.744	0.031	0.788
Cr (VI)	10	0.376	0.889	0.125	0.972
	20	1.280	0.808	1.324	0.998
	30	2.257	3.272	16.677	0.999

Where Co = initial concentration of metal ions

q_e = amount of adsorbate at equilibrium

K_2 = second order rate constant of adsorption

h_o = initial adsorption rate

R^2 = rank correlation coefficient

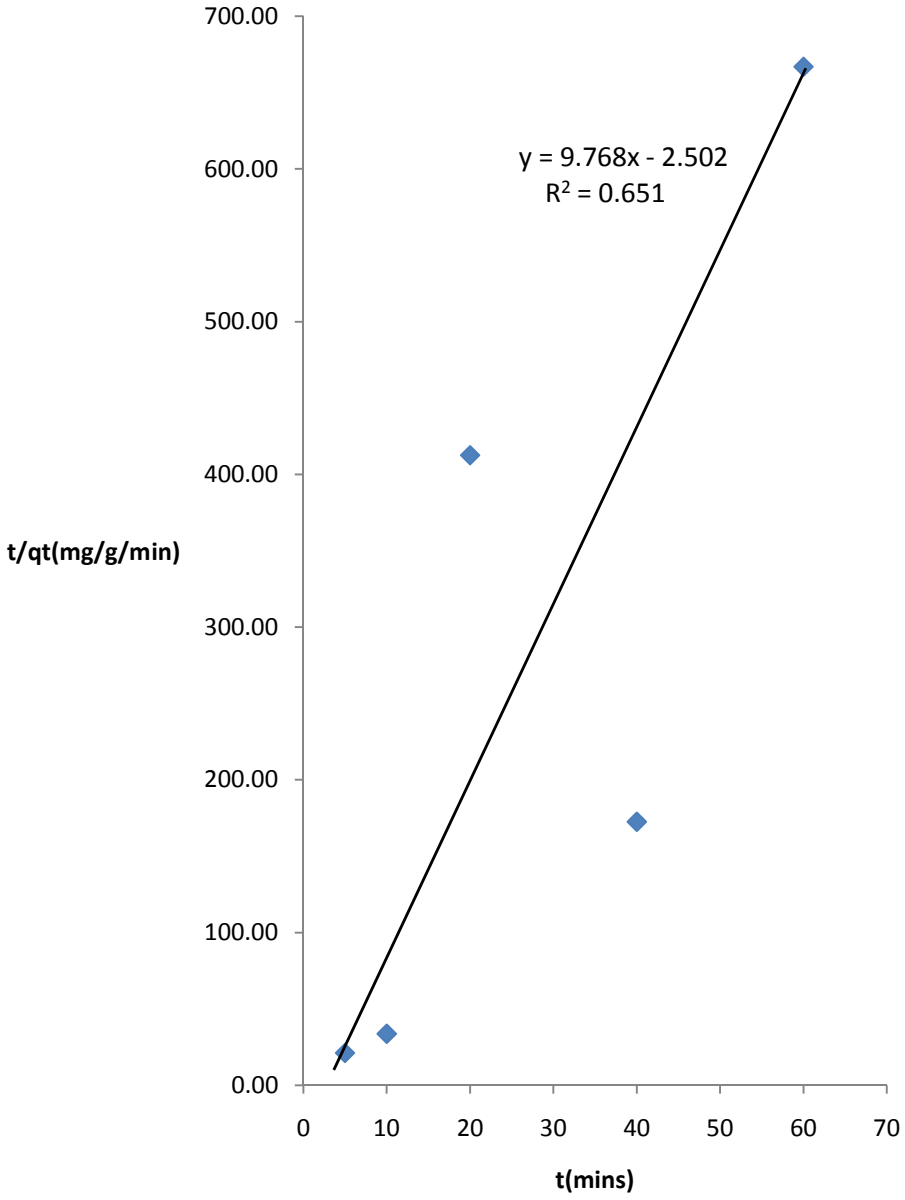


Fig.4.54. Pseudo-second order plot for Pb^{2+} on Cow bone charcoal at 10mg/l

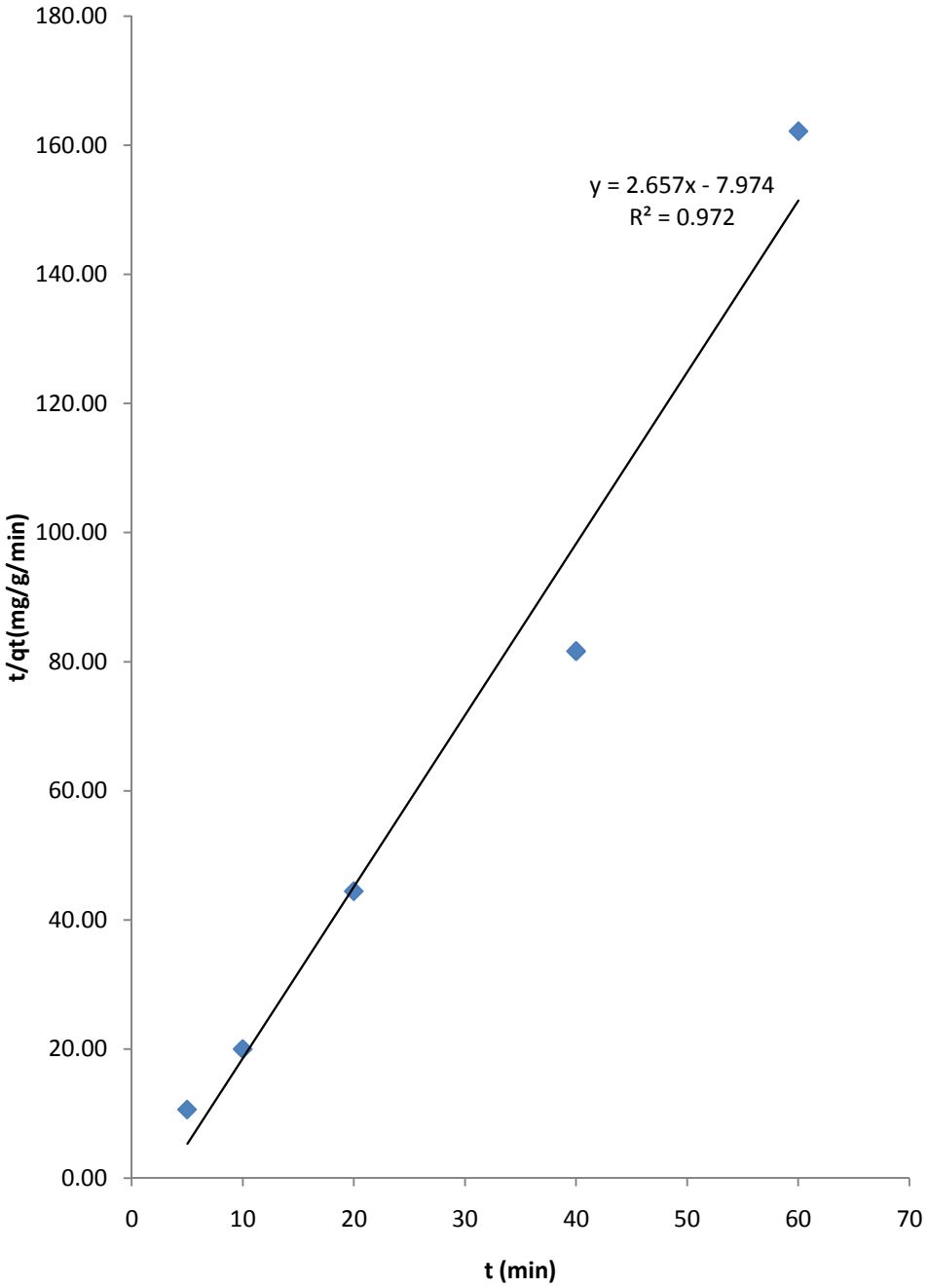


Fig.4.55. Pseudo-second order plot for Cr (VI) on Cow bone charcoal at 10mg/l

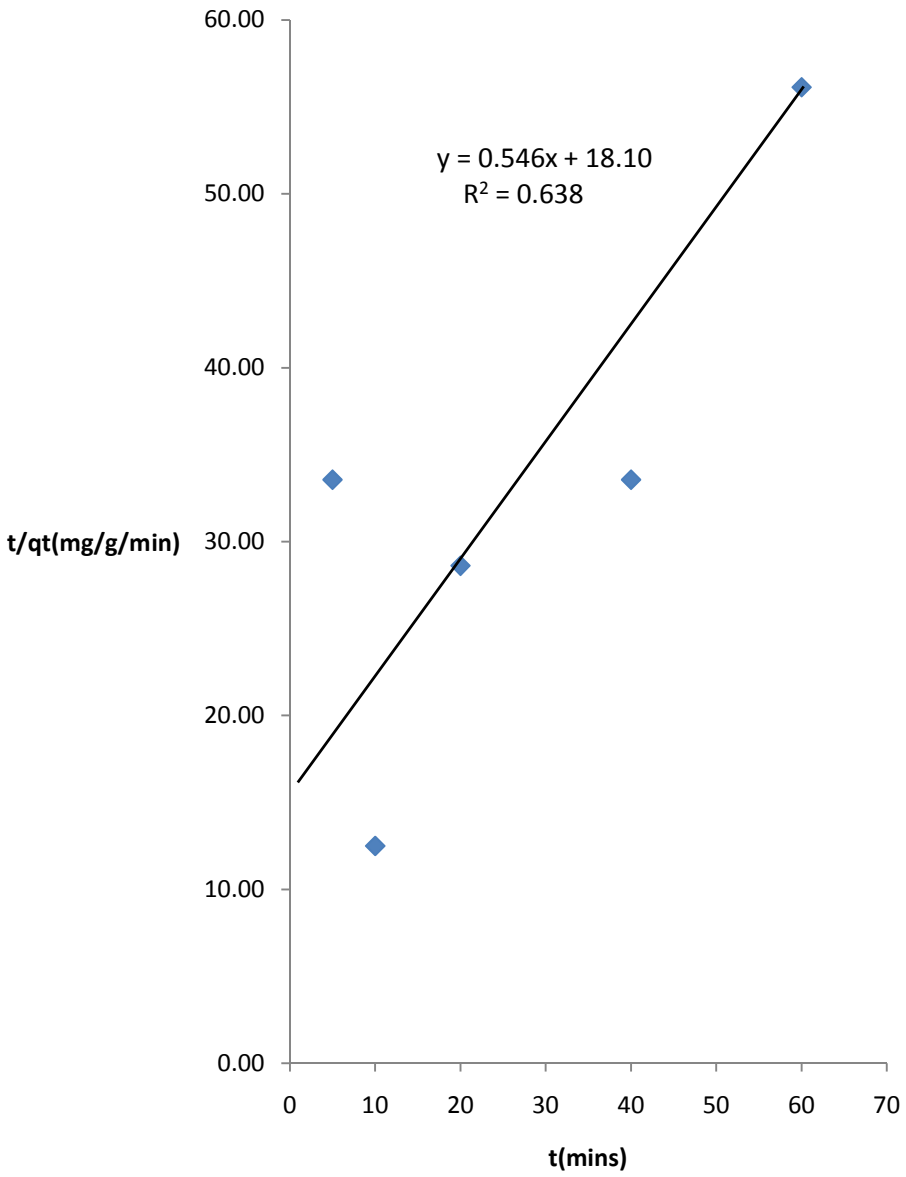


Fig.4.56.Pseudo-second order plot for Pb^{2+} on Cow bone charcoal at 20mg/l

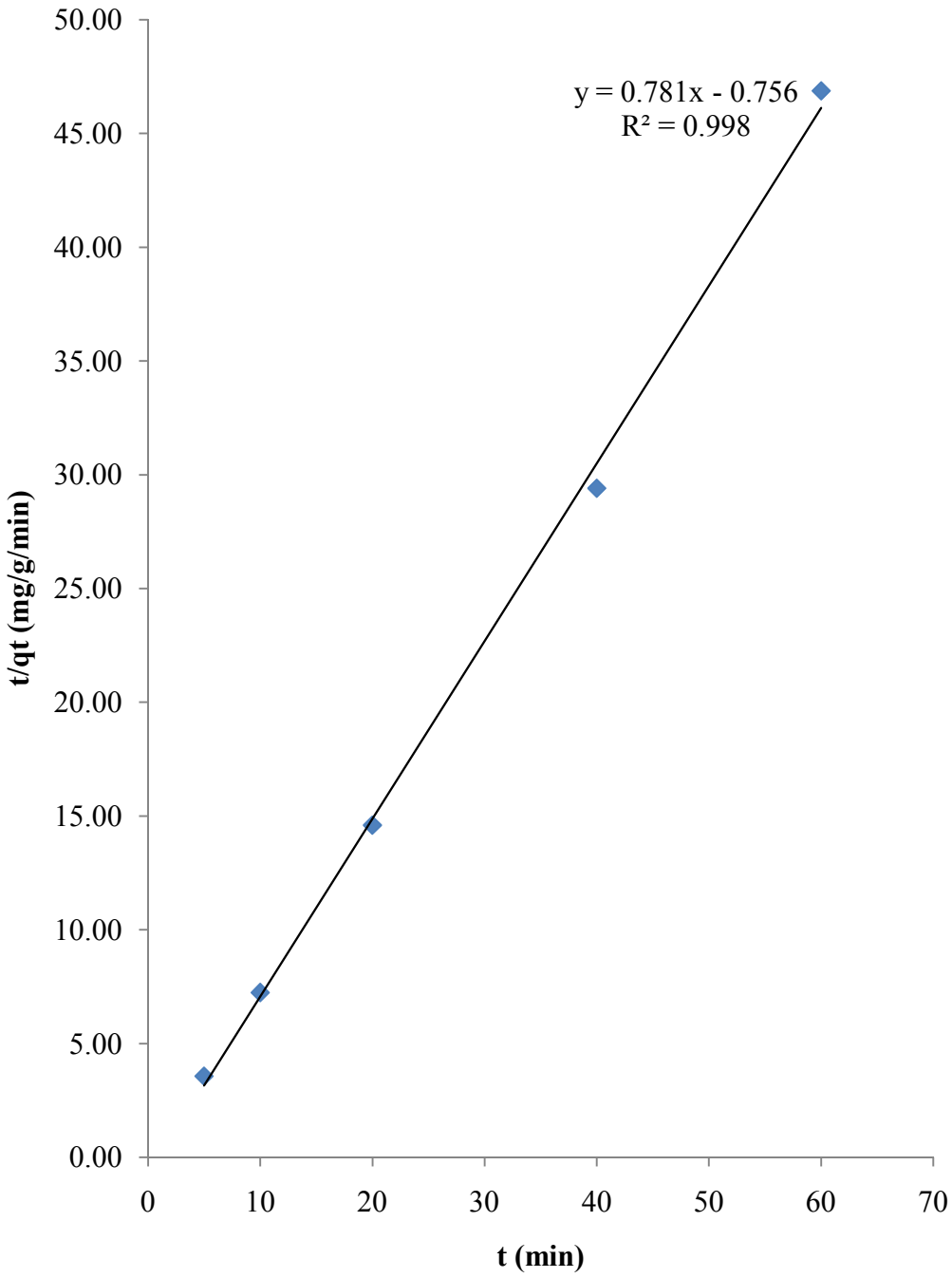


Fig.4.57. Pseudo-second order plot for Cr(VI) on Cow bone charcoal at 20mg/l

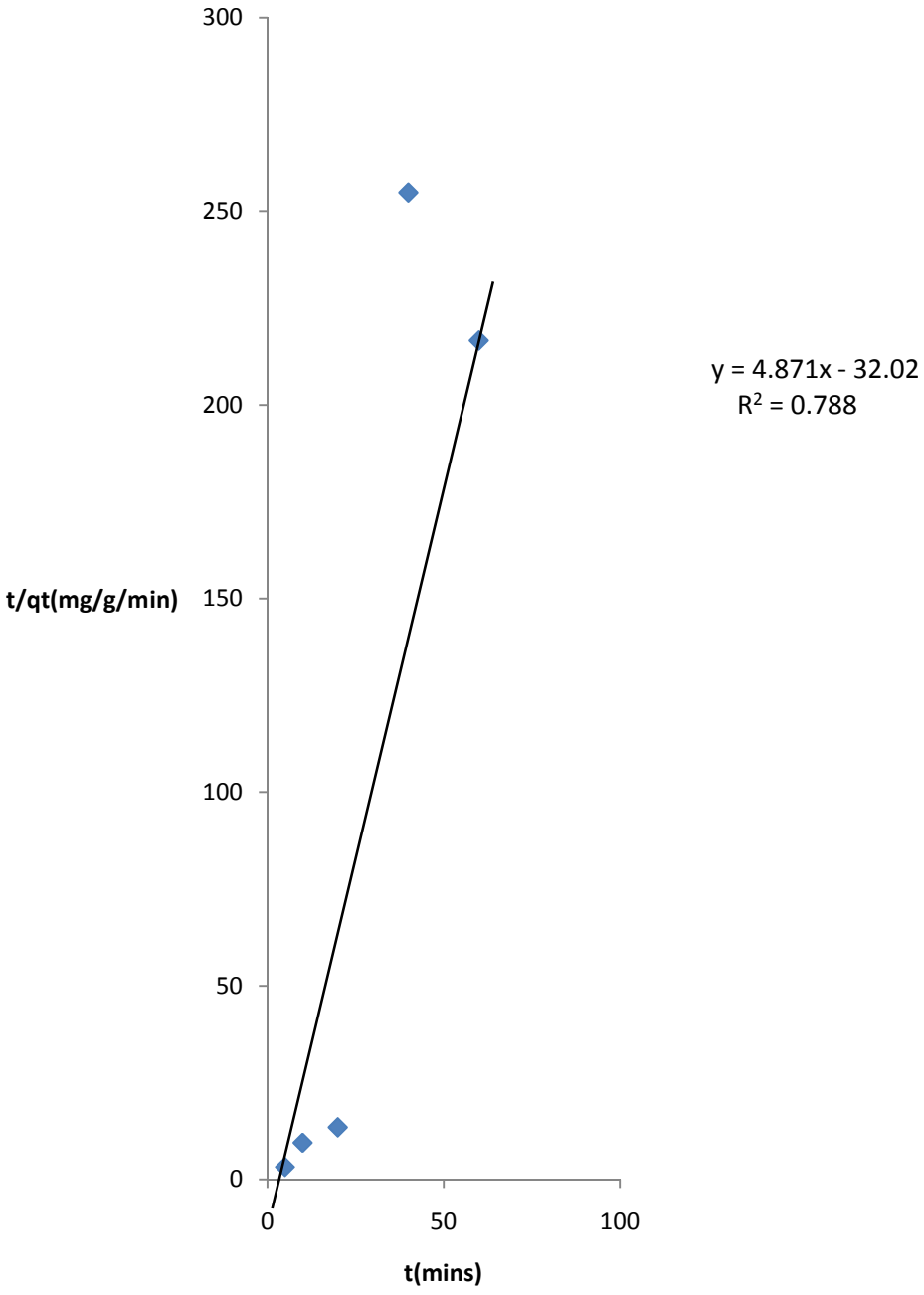


Fig.4.58. Pseudo-second order plot for Pb^{2+} on Cow bone charcoal at 30mg/l

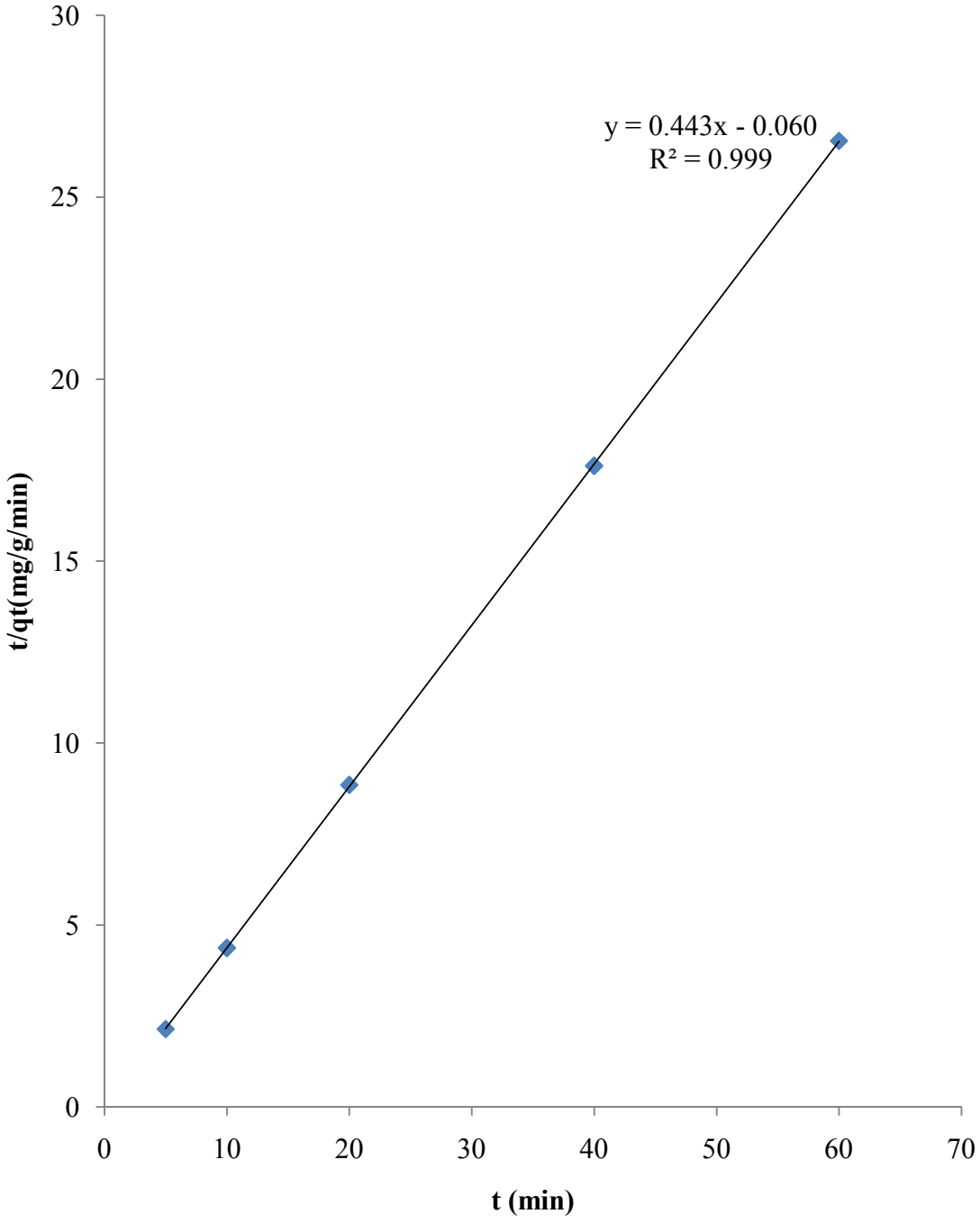


Fig.4.59. Pseudo-second order plot for Cr(VI) on Cow bone charcoal at 30mg/l

Figure 4.54 to 4.59 showed the excellent linearity for three different concentrations of Pb^{2+} and Cr (VI). The calculated values of K_2 and h_0 from pseudo –second order rate equation are shown in Table 4.8.

The data showed good compliance with the pseudo – second order equation. The regression coefficients for the linear plots were better placed. The value of the initial adsorption rates, h_0 was determined by using the values of the intercept of the linear plot in Figure 4.54 to 4.59. In the case of Pb^{2+}, the initial adsorption rate (h_0) decreased with increase in the initial concentration. While h_0 varied from 0.399mg/g/min to 0.031 mg/g/min, the Co varied from 10mg/l to 30mg/l for Pb^{2+}. However, the value of the rate constant (K_2) decreased from 39.968g/mg/min to 0.744g/mg/min with slight fluctuation as the initial concentration increased from 10mg/l to 30mg/l, showing the process to be highly concentration dependent, which was consistent with studies reported (Ho *et al*., 2001).

In the case of Cr (VI), the initial adsorption rate (h_0) increased with an increase in the initial concentration; the h_0 varied from 0.125mg/g/min to 16.677mg/g/min, while the Co varied from 10mg/l to 30mg/l. This could be attributed to the increase in the driving force for mass transfer, allowing more Cr (VI) ion to reach the surface of the adsorbents in a shorter period of time. However, the values of the rate constants (K_2) increased from 0.889g/mg/min to 3.272g/mg/min for an increase of initial Cr (VI) concentration from 10mg/l to 30mg/l. From these parameters, it was found that equilibrium adsorption capacity q_e was also dependent on initial concentration for Pb^{2+} and Cr (VI) . In Table 4.8, it was also observed that Cr (VI) has the highest correlation coefficient R^2 value of 0.999 which

indicates chemisorption type of adsorption while the lowest was observed for Pb^{2+} (R^2= 0.638) which indicates physisorption.

4.5 MECHANISM OF ADSORPTION

Although cow bone charcoal displays relative low surface area ($283m^2/g$). Cow bone charcoal analysis indicates that it consists of calcium phosphate as a major component. It has been demonstrated that calcium phosphate acts not only as adsorption centers but also enables ion- exchange process (Findon *et al*., 1993).

$$\equiv PO^- + H^+ \longrightarrow \equiv POH$$

$$\equiv CaOH_2^+ \longrightarrow \equiv CaOH + H^+$$

In the presence of Pb^{2+}, the following reactions may occur:

$$\equiv POH + M^{2+} \longrightarrow \equiv POM^+ + H^+$$

$$\equiv PO^- + M^{2+} \longrightarrow \equiv POM^+$$

$$\equiv CaOH + M^{2+} \longrightarrow \equiv CaOM^+ + H^+$$

Where M is the metal ion

CHAPTER FIVE

5.1 CONCLUSION

The preliminary studies on bone charcoal obtained from the (femur and humerus) of cow showed the mineral enrichment and effectiveness of this biological material in the removal of lead and chromium from aqueous solutions. Excellent linearity based on the effect of concentration on the amount adsorbed was evidently pronounced at temperature of 40^0C. The kinetics of lead and chromium adsorption on the cow bone charcoal was found to follow a pseudo-second order rate equation. Similarly, the regression analysis of the equilibrium data fitted the Langmuir and Freundlich adsorption isotherms. However, it was observed that the Langmuir isotherm plot for chromium was poor at (30^0C and 20 minutes), (40^0C and 40 minutes) and (40^0C and 60 minutes); while the Langmuir and Freundlich isotherms plot for lead were poor at (30^0C and 20 minutes) and (30^0C and 40 minutes) respectively. The highest maximum adsorption capacity (Q_m) was observed for lead at 40^0C and 60 minutes; while that of chromium was observed at 30^0C and 10 minutes. As the temperature increases, the amount adsorbed increases as well, which indicates endothermic adsorption. The adsorbent, cow bone charcoal is cheap and readily available, therefore it will be useful in the treatment of lead and chromium contaminated wastewater before discharge into the aquatic environment.

5.2 RECOMMENDATION

Cow bone charcoal can be evaluated as an alternative adsorbent to treat waste water containing lead and chromium. It can be applied in developing countries due to low cost and availability of cow bones.

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APPENDICES

i). Adsorption of Cr(VI) ion on cow bone charcoal at particle size 355µm,30^{o}C and 5min.

I.conc. (mg/l)	F. conc.(Ce) (mg/l)	A. ads.(Qe) (mg/g)	% Adsorbed	Ce/Qe	Log Ce	Log Qe
10	5.26	0.47	47.41	11.09	0.72	-0.32
20	6.04	1.40	69.81	4.33	0.78	0.14
30	6.64	2.34	77.86	2.84	0.82	0.37
40	8.78	3.12	78.06	2.81	0.94	0.49
50	8.39	4.16	83.21	2.02	0.92	0.62

ii).Adsorption of Cr(VI) ion on cow bone charcoal at particle size 355µm, 30^{o}C and 10min.

I. conc. (mg/l)	F. conc.(Ce) (mg/l)	A. ads.(Qe) (mg/g)	% Adsorbed	Ce/Qe	Log Ce	Log Qe
10	5.00	0.50	50.03	9.99	0.70	-0.30
20	6.24	1.38	68.82	4.53	0.79	0.14
30	7.07	2.29	76.44	3.08	0.85	0.36
40	8.84	3.12	77.90	2.84	0.95	0.49
50	1.14	4.89	97.72	0.23	0.06	0.69

iii). Adsorption of Cr(VI) ion on cow bone charcoal at particle size 355µm, 30^{o}C and 20min.

I. conc. (mg/l)	**F. conc.(Ce) mg/l**	**A. ads.(Qe) mg/g**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	5.49	0.45	45.13	12.16	0.74	-0.35
20	6.26	1.37	68.72	4.55	0.80	0.14
30	7.43	2.26	75.23	3.29	0.87	0.35
40	0.85	3.91	97.87	0.22	-0.07	0.59
50	0.06	4.99	99.89	0.01	-1.25	0.70

iv). Adsorption of Cr(VI) ion on cow bone charcoal at particle size 355µm,30^{o}C and 40min.

I. conc. (mg/l)	**F. conc.(Ce) (mg/l)**	**A.ads.(Qe) (mg/g)**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	5.05	0.49	49.47	10.21	0.70	-0.31
20	6.39	1.36	68.04	4.70	0.81	0.13
30	7.32	2.27	75.61	3.23	0.86	0.36
40	8.90	3.11	77.76	2.86	0.95	0.49
50	10.73	3.93	78.54	2.73	1.03	0.59

v). Adsorption of Cr(VI) ion on cow bone charcoal (femur and humerus) at particle size 355µm, 30^{o}C and 60min.

I. conc. (mg/l)	**F.conc.(Ce) (mg/l)**	**A. ads.(Qe) (mg/g)**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	6.32	0.37	36.76	17.20	0.80	-0.43
20	7.16	1.28	64.19	5.58	0.86	0.11
30	7.41	2.26	75.32	3.28	0.87	0.35
40	9.08	3.09	77.29	2.94	0.96	0.49
50	8.77	4.12	82.46	2.13	0.94	0.62

vi). Adsorption of Cr(VI) ion on cow bone charcoal at particle size 355µm,40^{o}C and 5min.

I.conc. (mg/l)	**F. conc.(Ce) (mg/l)**	**A. ads.(Qe) (mg/g)**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	4.46	0.55	55.39	8.05	0.65	-0.26
20	6.00	1.40	69.98	4.29	0.78	0.15
30	5.44	2.46	81.85	2.22	0.74	0.39
40	7.31	3.27	81.72	2.24	0.86	0.51
50	9.16	4.08	81.68	2.24	0.96	0.61

vii). Adsorption of Cr(VI) ion on cow bone charcoal at particle size 355µm, 40^{o}C and 10min.

I. conc. (mg/l)	**F.conc.(Ce) (mg/l)**	**A.ads.(Qe) (mg/g)**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	5.15	0.49	48.54	10.60	0.71	-0.31
20	6.29	1.37	68.54	4.59	0.80	0.14
30	6.46	2.35	78.46	2.75	0.81	0.37
40	8.29	3.17	79.27	2.62	0.92	0.50
50	8.59	4.14	82.82	2.07	0.93	0.62

viii). Adsorption of Cr(VI) ion on cow bone charcoal at particle size 355µm, 40^{o}C and 20min.

I. conc. (mg/l)	**F.conc.(Ce) (mg/l)**	**A. ads.(Qe) (mg/g)**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	5.08	0.49	49.18	10.33	0.71	-0.31
20	5.62	1.44	71.91	3.91	0.75	0.16
30	6.60	2.34	78.01	2.82	0.82	0.37
40	7.92	3.21	80.20	2.47	0.90	0.51
50	7.70	4.23	84.60	1.82	0.89	0.63

ix). Adsorption of Cr(VI) ion on cow bone charcoal at particle size 355µm, 40^{o}C and 40min.

I. conc. (mg/l)	F. conc.(Ce) (mg/l)	A.ads.(Qe) (mg/g)	% Adsorbed	Ce/Qe	Log Ce	Log Qe
10	3.98	0.60	60.18	6.62	0.60	-0.22
20	5.51	1.45	72.46	3.80	0.74	0.16
30	4.78	2.52	84.07	1.89	0.68	0.40
40	6.53	3.35	83.69	1.95	0.81	0.52
50	8.47	4.15	83.06	2.04	0.93	0.62

x). Adsorption of Cr(VI) ion on cow bone charcoal at particle size 355µm,40^{o}C and 60min.

I. conc. (mg/l)	F. conc.(Ce) (mg/l)	A. ads.(Qe) (mg/g)	% Adsorbed	Ce/Qe	Log Ce	Log Qe
10	4.87	0.51	51.27	9.50	0.69	-0.29
20	6.06	1.39	69.71	4.35	0.78	0.14
30	5.67	2.43	81.12	2.33	0.75	0.39
40	7.04	3.30	82.41	2.13	0.85	0.52
50	12.22	3.78	75.55	3.24	1.09	0.58

xi). Adsorption of Pb^{2+} ion on cow bone charcoal at particle size 355µm, 30^{o}C and 5min.

I. conc. (mg/l)	**F.conc.(Ce) (mg/l)**	**A. ads.(Qe) (mg/g)**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	7.63	0.237	23.70	32.19	0.88	-0.63
20	18.51	0.149	7.45	124.23	1.27	-0.83
30	14.63	1.537	51.23	9.52	1.17	0.19
40	16.17	2.383	59.58	6.79	1.21	0.38
50	15.66	3.434	68.68	4.56	1.19	0.54

xii). Adsorption of Pb^{2+} ion on cow bone charcoal at particle size 355µm, 30^{o}C and 10min.

I.conc. (mg/l)	**F. conc.(Ce) (mg/l)**	**A. ads.(Qe) (mg/g)**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	7.03	0.297	29.70	23.67	0.85	-0.53
20	12.00	0.8	40.00	15.00	1.08	-0.10
30	19.45	1.055	35.17	18.44	1.29	0.02
40	23.06	1.694	42.35	13.61	1.36	0.23
50	24.68	2.532	50.64	9.75	1.39	0.40

xiii). Adsorption of Pb^{2+} ion on cow bone charcoal at particle size 355µm,30^{o}C and 20min.

I. conc. (mg/l)	**F. conc.(Ce) (mg/l)**	**A. ads.(Qe) (mg/g)**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	9.515	0.0485	4.85	196.19	0.98	-1.31
20	13.01	0.699	34.95	18.61	1.11	-0.16
30	15.14	1.486	49.53	10.19	1.18	0.17
40	28.47	1.153	28.83	24.69	1.45	0.06
50	26.98	2.302	46.04	11.72	1.43	0.36

xiv). Adsorption of Pb^{2+} ion on cow bone charcoal at particle size 355µm,30^{o}C and 40min.

I. conc. (mg/l)	**F.conc.(Ce) (mg/l)**	**A. ads.(Qe) (mg/g)**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	7.68	0.232	23.20	33.10	0.89	-0.63
20	8.08	1.192	59.60	6.78	0.91	0.08
30	28.43	0.157	5.23	181.08	1.45	-0.80
40	22.90	1.71	42.75	13.39	1.36	0.23
50	24.04	2.596	51.92	9.26	1.38	0.41

xv). Adsorption of Pb^{2+} ion on cow bone charcoal at particle size 355µm,30^{o}C and 60min.

I.conc. (mg/l)	**F. conc.(Ce) (mg/l)**	**A. ads.(Qe) (mg/g)**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	9.10	0.09	9.00	101.11	0.96	-1.05
20	9.31	1.069	53.45	8.71	0.97	0.03
30	27.23	0.277	9.23	98.30	1.44	-0.56
40	22.82	1.718	42.95	13.28	1.36	0.24
50	29.20	2.08	41.60	14.04	1.47	0.32

xvi). Adsorption of Pb^{2+} ion on cow bone charcoal at particle size 355µm,40^{o}C and 5min.

I.conc. (mg/l)	**F.conc.(Ce) (mg/l)**	**A. ads.(Qe) (mg/g)**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	7.21	0.279	27.90	25.84	0.86	-0.55
20	9.75	1.025	51.25	9.51	0.99	0.01
30	13.47	1.653	55.10	8.15	1.13	0.22
40	25.25	1.475	36.88	17.12	1.40	0.17
50	29.92	2.008	40.16	14.90	1.48	0.30

xvii). Adsorption of Pb^{2+} ion on cow bone charcoal at particle size 355µm,40^{o}C and 10min.

I. conc. (mg/l)	**F. conc.(Ce) (mg/l)**	**A. ads.(Qe) (mg/g)**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	8.18	0.182	18.20	44.95	0.91	-0.74
20	10.52	0.948	47.40	11.10	1.02	-0.02
30	26.31	0.369	12.30	71.30	1.42	-0.43
40	25.07	1.493	37.33	16.79	1.40	0.17
50	30.09	1.991	39.82	15.11	1.48	0.30

xviii). Adsorption of Pb^{2+} ion on cow bone charcoal at particle size 355µm,40^{o}C and 20min.

I. conc. (mg/l)	**F. conc.(Ce) (mg/l)**	**A. ads.(Qe) (mg/g)**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	9.74	0.026	2.60	374.62	0.99	-1.59
20	10.22	0.978	48.90	10.45	1.01	-0.01
30	17.03	1.297	43.23	13.13	1.23	0.11
40	17.73	2.227	55.68	7.96	1.25	0.35
50	19.74	3.026	60.52	6.52	1.30	0.48

xix). Adsorption of Pb^{2+} ion on cow bone charcoal at particle size 355µm, 40^{o}C and 40min.

I. conc. (mg/l)	**F. conc.(Ce) (mg/l)**	**A. ads.(Qe) (mg/g)**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	9.24	0.076	7.60	121.58	0.97	-1.12
20	10.42	0.958	47.90	10.88	1.02	-0.02
30	13.99	1.601	53.37	8.74	1.15	0.20
40	14.45	2.555	63.88	5.66	1.16	0.41
50	15.59	3.441	68.82	4.53	1.19	0.54

xx). Adsorption of Pb^{2+} ion on cow bone charcoal at particle size 355µm,40^{o}C and 60min.

I. conc. (mg/l)	**F. conc.(Ce) (mg/l)**	**A. ads.(Qe) (mg/g)**	**% Adsorbed**	**Ce/Qe**	**Log Ce**	**Log Qe**
10	8.02	0.198	19.80	40.51	0.90	-0.70
20	9.21	1.0795	53.98	8.53	0.96	0.03
30	13.44	1.656	55.20	8.12	1.13	0.22
40	18.39	2.161	54.03	8.51	1.26	0.33
50	24.92	2.508	50.16	9.94	1.40	0.40