

# **INVESTIGATION ON THE ADSORPTION BEHAVIOUR OF LEAD (II) ONTO RICE HUSK POWDER**

**A Dissertation**

**Submitted to Central Department of Chemistry in the Partial Fulfillment  
of the requirements for the Master's Degree in Chemistry**

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Nepal  
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## FOREWORD

The dissertation work entitled "*Investigation on the Adsorption Behaviour of Lead (II) onto Rice Husk Powder*", submitted by *Vijay Das* for the M.Sc. Degree in Chemistry of Tribhuvan University is carried out under my supervision. During the research period, he had worked sincerely and satisfactorily. No part of this thesis has been submitted for any other degree.

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## ACKNOWLEDGEMENT

It is a matter of immense pleasure that I got an opportunity to do this dissertation work under the supervision of Mr. Khagendra Prasad Bohara, Lecturer of Central Department of Chemistry, Tribhuvan University. I would like to express my sincere gratitude to him for his constant support, guidance, inspiration, dedication, care and valuable suggestions.

I would like to express my sincere gratitude to Dr. Kedar Nath Ghimire, Head of the Department, Central Department of Chemistry for providing me the opportunity for this dissertation work.

I am also grateful to Prof. Jaya Krishna Shrestha, Dr. Megh Raj Pokhrel, Dr. Paras Nath Yadav and all the teachers of Central Department of Chemistry for their kind suggestions and inspiration during the research period. I would also like to thank Central Department of Chemistry and my friends for their kind co-operation during my dissertation work.

Similarly I am grateful to Dr. Sita Ram Joshi and Mr. Shailesh Kumar Jha, Nepal Bureau of Standards and Metrology, for providing necessary laboratory facility to conduct the dissertation work in Chemical Lab of NBSM.

At last but not the least, I would like to remember Lekhnath Kandel, and Deepak Gaywali, for their help during the research work.

**Vijay Das**

**2012**

## ABBREVIATIONS

$1/n$  = Adsorption intensity

$A^0$  = Angstrom

AAS = Atomic Absorption Spectrophotometer

$C_e$  = Equilibrium concentration

$C_i$  = Initial concentration of lead (II) in mg/l

CMRH = Chemically Modified Rice Husk

EPA = Environmental Protection Agency

g/l = Gram per Litre

ICP = Inductive Coupled Plasma

$K_1$  = Pseudo-first order rate constant in  $\text{min}^{-1}$

$K_2$  = Pseudo-second order rate constant in  $\text{g mg}^{-1} \text{min}^{-1}$

$K_2'$  = Second order rate constant in  $\text{g mg}^{-1} \text{min}^{-1}$

$K_L$  = Langmuir equilibrium parameter

m mol/g = Millimole per Gram

mg/l = Milligram per Litre

ml = Milliliter

MPL = Maximum Permissible Limit

$q_e$  = Amount adsorbed at equilibrium in  $\text{mg g}^{-1}$

$q_m$  = Maximum adsorption capacity in  $\text{mg g}^{-1}$

$q_t$  = Amount adsorbed at time 't' in  $\text{mg g}^{-1}$

$R^2$  = Correlation coefficient

RRH = Raw Rice Husk

W = Weight of adsorbent in gram

WHO = World Health Organization

$o$  = Initial adsorption rate in  $\text{mg g}^{-1} \text{min}^{-1}$

## ABSTRACT

The application of low-cost adsorbents obtained from agricultural wastes as an alternate to the conventional methods of removing heavy metal ions from waste water has been investigated. Present study deals with the adsorption of lead (II) from aqueous solution on rice husk and its chemically modified form. Rice Husk is a by-product generally obtained from rice mill. The Chemically Modified Rice Husk (CMRH) is obtained by treating raw rice husk with 4M sulfuric acid. Batch studies were performed at an initial concentration of 25 mg/L to evaluate the influence of various parameters like pH, equilibrium time, amount of adsorbent and concentration of adsorbate. Studies showed that pH of aqueous solution affected lead (II) adsorption as a result the removal efficiency increased with increasing pH of the solution. The maximum efficiency was achieved at pH 5. Kinetics and isotherm modeling studies demonstrated that the experimental data best fit a pseudo-second order and Langmuir isotherm model, respectively. The maximum Langmuir adsorption capacity was found to be 143.25 mg/g & 133.81 for CMRH and RRH, respectively. Furthermore, the studies showed CMRH was more favorable than RRH for the adsorption of lead (II) from aqueous solution. In summary, biosorption onto rice husk is a low cost, effective and simple process for treating Pb (II) loaded waste water.

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# **1 Introduction**

## **1.1 General Introduction**

Water is an essential substance to sustain life and is of primary concern to consumers. Human being obtain water from three major sources i.e. rain water, surface water (reservoirs, rivers, streams, ponds and lakes) and ground water (shallow wells, deep tube wells, springs). In our country, ground water is the major sources of water for consumption because of insufficient and unreliable municipal water supply system. A demand of ground water is increasing day by day. Ground water and drinking water should be free from toxic heavy metal. However, water sources are contaminated with numerous heavy metals, such as Antimony (Sb), Chromium (Cr), Copper (Cu), Lead (Pb), Manganese (Mn), Mercury (Hg), Cadmium (Cd), etc, which are significantly toxic to human beings and ecological environments [1]. Heavy metals are elements having atomic weight between 63.5 and 200.6 and specific gravity greater than 5. Heavy metals are not biodegradable and tend to accumulate in living organisms thereby causing diseases and disorders [2].

Among the toxic heavy metals Mercury (Hg), Cadmium (Cd) and Lead (Pb) are called big three heavy metal and are in the limelight due to their major impact on environment. Cd and Pb are potent neurotoxic metals. Lead (II) is heavy metal poison which forms complexes with oxo-groups in enzymes to affect virtually all steps in the process of hemoglobin synthesis and porphyrin metabolism [3]. Lead (II) poisoning in human causes severe damage to kidney, nervous system, reproductive system, liver and brain. Severe exposure to lead has been associated with sterility, abortion, still births and neo-natal deaths [4]. Process industries, such as battery manufacturing, printing and pigment, metal plating and finishing, ammunition, soldering material, ceramic and glass industries, iron and steel manufacturing units generate large quantities of waste water contaminated with lead (II) [4]. In drinking water lead (II) contamination

occurs due to the corrosion and leaching of lead pipes and Pb/Sn solder joints associated with copper service lines used in household plumbing [4].

Lead is soft, bluish-white, silvery, grey metal. It is the element of Group IV A, Period VI of the periodic table of the elements. The chemical symbol is Pb having Atomic number 82 and Atomic weight 207. It has 4 naturally occurring isotopes 208, 206, 207 and 204 in order of abundance. In its natural state, it contains 82 electrons and 82 protons. Its electronic configuration is  $[^{131}\text{Xe}_{54}] 4f^{14}5d^{10}6s^26p^2$  in ground state. In aquatic system Pb usually loses two of the 6p electrons giving it a net charge of +2. The remaining 6s, 2 electrons are the outer shell electrons that exist as a lone pair of electron. This lone pair has significant influence on the reactivity and co-ordination of  $\text{Pb}^{+2}$  ions. Lead can also lose both 6s electrons under severe oxidizing conditions giving it a net positive charge of +4. Lead (IV) is not very stable in this environment. Thus the divalent form Pb (II) controls the fate of lead in aqueous geochemical conditions [5]. Since lead is strongly sorbed, its solubility is low at ambient pH, most natural waters have low concentration of aqueous Pb. In fact, a significant amount of Pb in water, may exist in an undissolved state, and is being transported as colloidal particles [5]. The concentration of Pb in natural waters with pH nears 7 is normally less than 10 ppb [5]. The common species of aqueous lead in acid are  $\text{Pb}^{2+}$  e.g. organic-Pb,  $\text{PbSO}_4$  and  $\text{PbHCO}_3^+$ , and for alkaline solution  $\text{PbHCO}_3^+$ , organic-Pb,  $\text{Pb}(\text{CO}_3)_2^{2-}$  and  $\text{PbOH}^+$ . The behaviors of Pb in solution is largely governed by the size (ionic radius=1.4 Å<sup>0</sup>), valence and electronegativity of the ion. These characteristics contribute to the strength and number of water molecules surrounding the Pb atom. The hydration number for Pb is between 5 to 8 [5].

According to WHO, the maximum permissible limit (MPL) for lead in drinking water is 0.01 mg/l [6]. The permissible level/ limit of lead in waste water as set by EPA are 0.05 mg/l [7]. According to Nepal Standards, the

maximum level of lead in drinking water is 0.01 mg/l [8]. But the maximum permissible limits (MPL) of lead in waste water/ industrial effluent is 0.1 mg/l in Nepal [9]. Because of its toxicity, proper treatment of industrial waste water which release high level of lead into the aquatic and land ecosystem is essential.

There are several methods for removal of heavy metal ions from aqueous solution such as precipitation, ion exchange, reverse osmosis, coagulation, electrolysis, solvent extraction, evaporation and adsorption [10]. However, most of the methods are costly and not economically feasible and also not eco-friendly due to the disposal of residual metal sludge and inefficiency in avoiding secondary pollution. The adsorption technique is the most versatile and effective method for the removal of heavy metal. Adsorption has advantages over the other methods because it is simple in design and requires low operational cost [11].

Activated carbon has been the most widely used adsorbents for removal of heavy metals from the concentrated and dilute effluents. Activated carbon with their large surface area, micro porous character and chemical nature of their surface area have made them potential adsorbent for the removal of heavy metal from industrial effluents. But this technique has not been used by small and medium scale industries because of its high operational cost. For this reason, the researchers are more interested to search for low cost and locally available materials as adsorbent for metal ion removal from the waste water. However efforts have been contributed to develop new adsorbent and improve the existing adsorbent to have an alternative to activated carbon. These materials obtained from industrial waste products such as rubber, agriculture wastes products and by-products [12]. Bio-wastes as adsorbents have gained importance because of their comparable efficiency, easy availability and low cost. The removal of lead (II) has been studied using moss peat [13], Activated carbon from fluted pumpkin seed shell (*Telfairia occidentalis*) [14], Chicken feathers [15], egg shells [16],

Silica ceramics [17], *Tridax procumbens* (Asteraceae) [18] etc. Their sorption capacities are smaller than that of activated carbon. Therefore there is a need for the development of low cost, highly efficient and easily available materials and also need to improve the existing adsorbents by chemical modification. Bio-sorption of heavy metal occurs as a result of physiochemical interactions, mainly ion exchange or surface complex formation between metal ions and the acidic functional groups present on the surface of adsorbent [19].

The wastes and by-products can be modified by various methods like chemical activation, thermal activation, steam activation, etc. The effective surface area of carbon enhances and the surface area of the adsorbent gets modified due to change in functional group of the raw material by the chemical modification process. Due to this, the adsorption capacity of adsorbent increases and the carbon prepared from wastes becomes an excellent adsorbent for the treatment of heavy metals present in the industrial effluents.

Rice husks are an agricultural waste produced as a by-product of the rice-milling industry, generated more than 100 million tons per year in developing country. Rice husk is mostly used as feed for the domestic animals and as fuel in the furnaces of various industries to generate heat.

## **1.2 Adsorption Study**

The phenomenon of accumulation of any substance on the surface of solid or liquid phase as compared to that present in the bulk of the material is called adsorption. The substance adsorbed on the surface is called adsorbate, while the surface to which it gets attached is called adsorbent. Adsorption is a surface phenomenon and at a given temperature and pressure depends on the surface area of the adsorbent [20]. The adsorption of lead (II) ion on raw rice husks and chemically modified rice husks can be studied as batch adsorption method.

In column adsorption method, a column of adsorbent of particular length and internal diameter is made and filled with fixed weight of adsorbent and effluent is allowed to percolate through the column at constant flow rate using flow controller. Effluent samples are collected at each interval of time and examined for residual metal concentration to evaluate the efficiency of the column. The metal concentration before and after adsorption are measured.

In batch study, the sample is pipette out in the Erlenmeyer flask and a definite amount of adsorbent is added to the sample. The pH of sample solution is adjusted by suitable acid (0.1 M, 1 M HNO<sub>3</sub>) solution and base (0.1 M, 1 M NaOH) solution by hit and trial method. The Erlenmeyer flask is shaken vigorously in mechanical shaker at room temperature for prescribed length of time in a shaker at a definite speed. The metal concentration is determined by some appropriate technique. The adsorption of heavy metal {lead (II)} onto the different adsorbents is affected by various parameters such as contact time (min), pH, initial concentration {lead (II) mg/l} and amount of adsorbent used. In order to understand the mechanism and effectiveness of adsorption one of the above parameter is changed by keeping other constant.

From the metal concentration determined before and after adsorption ( $C_i$  and  $C_f$ ) respectively and dry weight of adsorbent ( $w$ ), the volume of sample ( $v$ ), the amount of adsorbate {lead (II)} adsorbed in mg/g at equilibrium is computed by the following formula.

$$q = \frac{(C_i - C_e) v}{w} \text{ mg/g} \dots\dots\dots (i)$$

Where  $C_i$  and  $C_e$  are the initial and equilibrium or final concentrations of the adsorbate {lead (II)} in mg/l respectively,  $v$  is volume of adsorbate solution taken in litre and  $w$  is weight of adsorbent in gram.

The metal removal percentage is defined as the ratio of decrease in metal ion concentration before and after adsorption to the initial concentration of metal in aqueous solution. Percentage removal or removal efficiency is given by

$$\text{Removal \%} = \frac{C_i - C_e}{C_i} \times 100 \% \dots\dots\dots(\text{ii})$$

The distribution ratio for the adsorption process at equilibrium is determined by following equation.

$$D = \frac{q}{C_e} \dots\dots\dots(\text{iii})$$

Where, D is the distribution factor for the adsorption in (l/g).

### 1.3 Chemical Modification of Adsorbent

Conventional treatment technologies for the removal of toxic heavy metals are not economic and further generate huge quantity of toxic chemical sludge. Bio-sorption is an emerging potential alternative to the existing conventional technology for the removal and recovery of metal ions from aqueous solutions. The major advantage of bio-sorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical or biological sludge, regeneration of bio-sorbents and possibility of metal recovery. Agricultural waste materials such as rice husk are abundant sources for significant metal bio-sorption, contain cellulose [21].

Rice husk is an agricultural waste material, outer covering of paddy, *Oryza sativa* and is develop as natural sheaths on rice grains during their growth. It is recovered during refining of rice in mill. It is used mainly as fuels for generating heat in home and industries and also as feed for domestic animals in

our country. The rice husk contains 22 % lignin, 38% cellulose, 20% ash and remaining 20% silica and other organic materials such as pentose sugar [22].

By chemical modification the surface of the adsorbent gets functionalized due to the formation of different functional groups and active sites on the surface of adsorbent. The most common chemicals that can be used for the treatment of adsorbent are acids, bases, oxidants. Chemically modified adsorbent vary greatly in its adsorption characteristics, which in general improves the adsorption capacity probably due to the presence of higher no of active binding sites after modification, better ion exchange properties and generation of new functionality that favours metal uptake. Metal ions are removed by chemically modified adsorbent due to surface complex formation and exchange between metal ions and acidic functional group [19]. A low cost modification considers the cost of chemicals employed and method of modification.

Rice husk is insoluble in water, has good chemical stability, has high mechanical strength making it a good adsorbent and can be used for the treatment of heavy metals in its raw or modified forms using different modification methods [22]. When it is washed, dried, grinded form it is generally called raw rice husk powder [RRH]. The raw rice husk powder which is subjected to some suitable chemical(s) is termed as chemically modified rice husk powder [CMRH].

#### **1.4 Adsorption Isotherms**

Adsorption isotherm is a graphical representation of the amount of adsorbate adsorbed per unit mass of the adsorbent as a function of the amount of the adsorbate left in bulk solution at equilibrium (equilibrium concentration), at constant temperature [23]. The experimental adsorption isotherms have wide applicability for describing adsorption capacity to monitor the feasibility of these processes for a given condition and application of adsorbent. The adsorption



data obtained from the sorption behavior of adsorbate {lead (II) by RRH and CMRH} can be analyzed with the help of well-known isotherm models given by Langmuir and Freundlich.

In 1916, Langmuir established the first quantitative model of adsorption. This model has been successfully applied for the adsorption of solute from a liquid solution, which involves active adsorbent sites, homogenous surface for adsorption with the formation of monolayer coverage and adsorption is independent of the occupation of neighboring sites [20, 24]. The Langmuir adsorption isotherm is given by the following equation.

$$\frac{C}{X} = \frac{a}{1+bC} \dots\dots\dots (iv)$$

Where, C is the concentration of adsorbate, X is the amount of adsorbate adsorbed per gram of adsorbent, 'a' and 'b' are Langmuir constants. In order to establish the maximum adsorption capacity, the linear form of Langmuir adsorption isotherm is provided by the following equation.

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \dots\dots\dots (v)$$

On simplification, equation (v) gives the following equation.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \dots\dots\dots (vi)$$

Where,  $q_e$  is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in (mg/g),  $C_e$  is the equilibrium concentration of the adsorbate in mg/l,  $q_m$  is the maximum adsorption capacity (mg/g) and 'b' is the Langmuir adsorption equilibrium constant 1/mg.

A plot of  $C_e/q_e$  against  $C_e$  gives a straight line with slope  $1/q_m$  and an intercept  $1/q_m b$  from which ' $q_m$ ' and ' $b$ ' can be determined.

According to the 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 ( $K_L$ ), which is given by the relationship.

$$K_L = \frac{1}{1 + bC_i} \text{.....(vii)}$$

Where,  $C_i$  is the initial concentration of the adsorbate (mg/l) and  $K_L$  indicates the shape of isotherm and nature of the adsorption process, [ $K_L > 1$ , unfavorable,  $K_L = 1$ , linear,  $0 < K_L < 1$  favourable,  $K_L = 0$ , irreversible]. The value of  $K_L$  between 0 and 1 indicates thjat adsorption is favorable.

The adsorption data obtained can also be analyzed with Freundlich adsorption model. In 1906, Freundlich established relationship that describes the adsorption phenomenon. The linear form of Freundlich isotherm is given by the equation.

$$q_e = KC_e^{1/n} \text{.....(viii)}$$

Where,  $q_e$  is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g),  $C_e$  is the equilibrium concentration of the adsorbate (mg/l); ' $K$ ' and ' $n$ ' are Freundlich equilibrium coefficient, which are considered to be the relative indicators of adsorption capacity and adsorption intensity.

The logarithmic form of the Freundlich equation is given by

$$\log q_e = \log K + \frac{1}{n} \log C_e \dots\dots\dots (IX)$$

When  $\log q_e$  is plotted against  $\log C_e$ , a straight line is obtained with slope  $1/n$  and intercept  $\log K$ . From this plot, the value of  $1/n$  and  $K$  can be determined. The value of  $1/n$  between 0.1 and 1.0 indicates the favourable adsorption of adsorbate; heavy metal ions.

## 1.5 Adsorption Kinetics

The study of adsorption kinetics describes the solute uptake rate and mechanism of the adsorption phenomenon and evidently this rate controls the residence time of adsorbate uptake at the solid- solution interface. Various sorption kinetic models are in practice to describe the uptake of metals by different adsorbents. The first order kinetic model is used for the reversible reaction with an equilibrium established between liquid and solid phase. The pseudo first order rate equation (Lagergren, 1898), the pseudo second order rate equation (Ho and McKay, 1999) and second order rate equation (Ho et al, 1996) has been used extensively for the description of adsorption kinetics.

This relationship between experimental data and the model predicted value is expressed by correlation coefficient. This helps in determining which reaction model better describes the adsorption of heavy metals onto the adsorbent. A relatively high value of correlation coefficient ( $R^2 \sim 1$ ) indicates that the models successfully describes the kinetics of lead (II) adsorption [25].

### 1.5.1 Pseudo-First Order Kinetic Model

The pseudo first order kinetic model is employed for the reversible reaction with an equilibrium established between liquid and solid phase. The pseudo first order rate equation (Lagergren, 1898) is generally expressed as

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \dots\dots\dots(x)$$

where,  $q_e$  and  $q_t$  are the amount of lead (II) adsorbed per gram at equilibrium and at time 't' in mg/g.  $K_1$  is the rate constant of pseudo-first order adsorption ( $\text{min}^{-1}$ ).

After integration and applying boundary conditions, the linear form of the equation (x), When  $t=0$  to  $t=t$  and  $q_t=0$  and  $q_t=q_t$

$$\text{Log } (q_e - q_t) - \text{log } q_e - \frac{K_1}{2.303} t \dots\dots\dots(x_i)$$

The plot of  $\text{log } (q_e - q_t)$  versus 't' should give a linear relationship, from which  $k_1$  and  $q_e$  can be determined from the slope and intercept of the plot respectively.

### 1.5.2 Pseudo- Second Order Kinetic Model

The pseudo-second order kinetic rate equation (Ho and McKay, 1999) is used to study the kinetics of adsorption of heavy metal which is generally expressed as,

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \dots\dots\dots(x_{ii})$$

Where,  $K_2$  is the rate constant for pseudo-second order adsorption in ( $\text{g mg}^{-1} \text{min}^{-1}$ ),  $q_e$  and  $q_t$  are the amount of metals adsorbed (mg/g) at any time 't' and at equilibrium time(e) respectively.

Integration of equation (xii) and applying boundary condition,  $q_t=0$  at  $t=0$ ,  $q_t=q_t$  at  $t=t$ , gives following rearranged linear form as,

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

If the initial adsorption rate is  $V_0$  (mg/g min),

$$\text{Then } V_0 = K_2 q_e^2$$

The equation (xiii) can be written as

$$\frac{t}{q_t} = \frac{1}{V_0} + \frac{1}{q_e} t \dots\dots\dots (xiv)$$

Experimentally, the value of  $q_e$  and  $K_2$  can be determined from the linear plot of  $t/q_t$  versus 't' with the help of slope and intercept of the plot respectively.

### 1.5.3 Second Order Kinetic Model

The second order adsorption, kinetic rate equation (Lagergren, 1898) is generally expressed as

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} - K_2' t \dots\dots\dots (xv)$$

where,  $q_e$  is the amount of metal ions adsorbed at equilibrium (mg/g),  $q_t$  is the amount of metal ions adsorbed at 't' (mg/g), t is contact time (min) and  $K_2'$  is second order rate constant ( $\text{g mg}^{-1} \text{ min}^{-1}$ ). The plot of  $1/(q_e - q_t)$  versus 't' gives a linear plot, from which  $K_2'$  and  $q_e$  can be determined from the slope and intercept respectively [26].

## 1.6 Methods for the Determination of Metals

Heavy metals are determined by various methods such as gravimetric method, titrimetric methods, anodic stripping voltammetry and instrumental methods. The gravimetric and titrimetric methods are appropriate for the

determination of high concentration of metal. For determination of metal at low concentration, instrumental method is suitable. The instrumental method includes spectrophotometric method, AAS method and ICP method. The lead can be determined by instrumental method i.e. spectrophotometric method, AAS method and ICP method. The spectrophotometric method for lead determination is called Dithiozone Method. The flame AAS method has sensitivity more than that of spectrophotometric method and less than ICP emission spectroscopy. For the ICP instrument high cost required. Many laboratories are exercising in graphite furnace AAS for determination of lead metal.

The concentration of lead can be determined by flame technique of Atomic absorption Spectrophotometer which is operated by Air/Acetylene gas flow under secondary pressure 11.5-14.5 psi. Before the determination of unknown sample solution, the instrument is to be calibrated each and every time to obtain the calibration curve, 'absorbance versus concentration'. With the help of this calibration curve and absorbance, the concentration of unknown solution can be determined. The  $\lambda_{\text{max}}$  for lead metal is 217 nm at slit width 1 nm. For the determination of lead, the calibration curve is obtained by using the lead (II) solutions of concentrations 1, 5, 10 and 15 mg/l. The sensitivity of AAS can be checked by 5 mg/l of lead solution that gives the absorbance 0.2 at  $\lambda_{\text{max}}=217$  nm and slit width is 1 nm. The instrumental detection limits for the determination of lead by flame and graphite tube atomizer are 0.01 mg/l and 0.06  $\mu\text{g/l}$  respectively [27].

## **1.7 Literature Survey**

Removal of heavy metal ions from the aqueous solution by agricultural waste materials is an innovating and promising technology [23]. The efficiency of the waste material derived adsorbents depends upon the capacity, affinity and specificity including its physio-chemical nature. The adsorbents are taken either

in the natural form or modified by some chemical(s) and thermal treatment for increasing their sorption capabilities.

Faroukhsamani et al., [28] studied the bacteria *Chryseomonas luteola* MGI-48 for adsorption and recovery of heavy metal from waste water. The sorption capacity of microorganism was determined for living and dead cells. The maximum capacity for living and dead cells was about 2.08 and 4.20 meq/g (dry cell weight) respectively. The sorption capacity of lead by biomass is depended on lead ion concentration. The best condition for sorption of Pb is pH 7 with 30 minutes contact time. Previous NaOH treatment of biomass also increased its sorption capacity. 0.1 M HCl and EDTA could recover more than 70 % lead adsorbed on cell. Cells were cultured at 30°C in glucose mineral salts at pH 7. The biomass suspended in aqueous heavy metals solution to give a cell density of 0.02 mg/l dry weight biomass (1 dead dry cell=40 g wet cell). The suspension was shaken at 125 rpm for 1 hrs.

Sharain-liew et al., [29] studied cattails (*Typha angustifolia*) leaves as adsorbent for biosorption of Pb (II) from waste water. Batch adsorption studies with dry leaves were conducted and they were able to adsorb Pb(II) from 100 ml of 25 mg/l Pb(II) solution with the optimized dosage of 0.6 g. Adsorption equilibrium was achieved within 8 hrs with an effectively removal of 86.04 %. The sorption kinetic data fitted best to the pseudo-second order model with  $R^2$  of 0.9979. Experimental adsorption capacity at equilibrium was found to be 3.620 mg/g.

Buasri et al., [30] studied natural zeolite clinoptilolite to remove lead from aqueous solution in batch adsorption experiments. Adsorption tests of Pb (II) were carried out using a solid to liquid ratio of 20 g/l and agitation speed of 700 rpm. The effects of particles size of the minerals (75-250  $\mu$ m), solution concentration (100-1200 ppm), initial pH (2-7), contact time (30-180 min) and

temperature (30-75 °C) were examined. The experimental data was analyzed by Langmuir and Freundlich isotherm models. In adsorption studies, residual heavy metal ion concentration reached equilibrium in short duration of 30 min for initial Pb (II) concentration of 100 and 300 ppm. The maximum adsorption capacity is 58.73 mg Pb (II) / g of zeolite at 75 °C, showed that this adsorbent was suitable for lead removal from aqueous media.

Asrari et al., [31] studied the removal of Pb (II) and Zn (II) ions using rice husk in food industrial waste water. The parameters influencing the sorption of Pb and Zn were contact time (5-70 minutes), pH (2-9), adsorbent amount (0.5-3 gm). The percentage removal of  $Zn^{2+}$  and  $Pb^{2+}$  ions increased with an increase in contact time and dosage of rice husk. The binding process was strongly affected by pH and the optimum pH for  $Zn^{2+}$  and  $Pb^{2+}$  ions were 7 and 9 respectively. The maximum adsorption capacity of adsorbent for  $Zn^{2+}$  and  $Pb^{2+}$  ions was calculated from the Langmuir isotherm and found to be 19.617 and 0.6216 mg/g respectively.

Badmus et al., [32] studied the batch removal of heavy metals (Pb, Zn and Cu) from industrial waste water under different experimental conditions using hydrogen peroxide. Experimental results indicate that at pH 6.5, pretreatment analysis gave the following value of Pb 57.63 mg/l; Zn 18.9 mg/l and Cu 13.9 mg/l. Removal of heavy metals was optimum at pH 7.6, at temperature 30°C, 1.5 %  $H_2O_2$  concentration and 60 min holding time, reducing the amount of Pb, Zn and Cu by 83.5, 85.5 and 82.23 % respectively.

Acharya et al., [33] studied the adsorption of lead (II) on activated carbon prepared from Tamarind Wood by Zinc chloride activation. Adsorption studies were conducted in the range of 10-50 mg/l initial lead (II) concentration and a temperature in the range of 10-50°C. The experimental data were analyzed by Freundlich and Langmuir isotherm. Equilibrium data fit well with the Langmuir model and Freundlich model with maximum adsorption capacity of 43.85 mg/g.



The rates of adsorption were found to confirm to pseudo-second order kinetics with good correlation coefficient and the overall rate of lead (II) uptake was found to be controlled by pore diffusion, film diffusion throughout the entire adsorption process.

Wahi et al., [34] prepared activated carbon from palm oil empty fruit bunches (EFB) to remove Hg (II), Pb (II) and Cu (II) from aqueous solutions. The adsorption capacity was determined as a function of adsorbate initial concentration and adsorbent dosage. Adsorption isotherm of metals on adsorbent were determined and compared with Langmuir and Freundlich isotherm models. The maximum adsorption capacities were 52.67, 48.96 and 0.84 mg/g for Hg (II), Pb (II) and Cu (II) respectively as calculated from Langmuir adsorption isotherm equation. The adsorption of Hg (II), Pb (II) and Cu (II) by EFB activated carbon is dependent on the dosage of adsorbent and the initial metal concentration.

Pawebang et al., [35] compare the efficiency of lead removal by egg shell and fish scale at various condition such as pH values, initial concentration and 2.5 g of adsorbent (particle size 40-60 mesh) doses, the results showed that optimum pH values was 4.5 and optimum contact time was 80 min. Egg shell (2.5 g) could adsorb lead 11.25 mg/g, fish scale (2.5 g) could adsorb lead 13 mg/g. So that the fish scale had more potential for lead adsorption than the egg shell.

Liao et al., [36] used carbonate hydroxyapatite (CHAP) synthesized from eggshell waste for removing lead (II) ion from aqueous solution. The effects of pH (2-9), contact time (5-180 minutes), initial concentration (10-500 mg/l) were studied in batch experiments. The maximum uptake of lead ion was obtained at pH 6. Adsorption equilibrium was established in 60 minutes. The adsorption of lead ion by CHAP increased as the initial concentration of lead ion increased in

the medium. The maximum lead ion adsorbed was found to be 101 mg/g. The adsorption of Pb (II) ion on CHAP was correlated well ( $R^2=0.9995$ ) with Langmuir equation as compared to Freundlich isotherm equation under the concentration range studied.

Senthil Kumar et al., [37] used bael tree leaf powder as an adsorbent for removal of  $Pb^{2+}$  ions from aqueous solution through batch technique. The influence of pH, equilibrium contact time, temperature, adsorbent dosage and initial metal concentration were investigated. The experimental isotherm data were analyzed using the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich equations. The highest removal rate was 84.93 % at solution pH 5, contact time 60 min and initial concentration 50 mg/l. The monolayer adsorption capacity is 4.065 mg/g with the correlation coefficient of 0.993. The adsorption of  $Pb^{2+}$  ions followed the pseudo-second order equation, suggesting that adsorption process is presumably chemisorption.

Han et al., [38] studied lead removal by cereal chaff. Variables of the system include biosorption time, chaff dose, and solution temperature. The experimental results were fitted to Langmuir model. According to the elution using the Langmuir equation, the maximum biosorption capacities of lead ion onto chaff was 12.5 mg/g at 293 K.

Martines et al., [39] studied the sorption of lead and cadmium by grape stalk waste (by product from wine production). The effects of contact time, pH, ionic medium, and initial concentration and other metal ion present and ligands were studied in batch experiments at 20°C. Maximum sorption for both metals was found 5.5. The equilibrium process was described well by Langmuir model, with maximum grape stalk sorption capacities of 0.241 and 0.248 mmol/g for Pb and Cd respectively.

After such an extensive literature survey, it was noticed that a little research was done on lead (II) removal by RRH and CMRH. Since thousands of tons of rice husk was produced per year in developing country like Nepal as agricultural waste which is abundantly available, low-cost and has no important use except as fuel in the boiler furnaces to produce heat energy and feeds for domestic animals. So it seems that it is interesting to investigate the efficiency of raw rice husk and chemically modified rice husk for removal of lead (II) from aqueous solution. Therefore, an effort has been made through this dissertation work to study the adsorption capacity of RRH and CMRH as adsorbent for removal of lead (II) from aqueous solution at laboratory condition.

### **1.8 Objectives of the Present Study**

Various conventional methods are available for the removal of heavy metals with a series of limitations. At low concentration, adsorption is the most promising and effective technique and the use of activated carbon are still very popular for waste water treatment but also expensive. In recent year several Studies have been reported for the biosorption of lead using waste materials as low cost adsorbents such as crab shell, fish scale, egg shell, grape stalk, cockle shell and saw dust etc [35, 36, and 39]. Their adsorption capacities, however, are smaller than activated carbon. To explore the efficiency and simplicity of adsorption for water and waste water treatment, further research on low cost adsorbent is necessary to identify widely available and effective agricultural wastes for the adsorption of toxic metals. An agricultural waste which is widely accessible in Nepal is *Oryza sativa* husk. Therefore, an attempt has been made through this dissertation work to explore the use of a low cost, efficient and easily available adsorbent for the adsorption of lead (II) from aqueous solution.

### **1.8.1 General Objective**

The general objective of the present research work is to prepare low- cost biosorbent from rice husk and to investigate its adsorption capacity for the sorption of lead (II) from aqueous solution.

### **1.8.2 Specific Objectives**

The specific objectives of the present research work are as follows:

- I. To prepare, modify and to check efficiency of the adsorbent for the adsorption of lead (II) from aqueous solution.
- II. To investigate the effect of contact time, pH, initial concentration of adsorbate and adsorbent dose for the removal of lead (II) from aqueous solution.
- III. To study the nature of adsorption isotherm for the removal of lead (II) from aqueous solution.
- IV. To study the kinetics of the adsorption process.
- V. To compare the adsorption capacity of acid modified rice husk with raw rice husk as an adsorbent.

## **2 Experimental**

This dissertation work was conducted as batch experiment design in duplicate using raw rice husk and chemically modified rice husk as adsorbent for the removal of lead (II) from aqueous solution.

### **2.1 Apparatus**

- Weighing balance, METTLER AE163, Switzerland
- Hot air oven, Memmert, Germany
- Thomas, Wiley laboratory mill (Grinder), England, UK
- pH meter, Merohm 692, Denmark
- Sieve no 150 mesh, India
- Atomic Absorption Spectrophotometer, Varian Australia, AA240 FS
- Orbital Shaker, Stuart SSL 1, England, UK

### **2.2 Chemical Reagents**

- Sulphuric Acid,
- Sodium bicarbonate,
- Sodium hydroxide,
- Nitric Acid,
- Lead nitrate.

All the chemical reagents used for this dissertation work were of analytical grade, Excelsior, Qualigens fine chemicals, Glaxo Indian Limited, Bombay.

### **2.3 Preparation of Reagents**

#### **2.3.1 Preparation of 1000 mg/l Stock Lead (II) Solution**

The stock lead (II) solution was prepared from lead nitrate, Qualigens, Mumbai, India. It was dried in oven at 105°C for half an hour. The exact 0.8073 g of lead nitrate;  $\text{Pb}(\text{NO}_3)_2$  (purity = 99 % and M. W. = 331.20) was weighed

and transferred into 500 ml of volumetric flask, dissolved completely in distilled water, then 5 ml of concentrated  $\text{HNO}_3$  was added and finally diluted with distilled water up to the mark to get 1000 mg/l solution of lead (II).

### **2.3.2 Working Lead (II) Solution**

From the stock solution of lead (II), working solutions of lower concentration were prepared by diluting with distilled water. First 250 mg/l of lead (II) solution was prepared from 1000 mg/l stock solution. From 250 mg/l of lead solution further required lower concentrations 10, 20, 25, 30, 40, 50, 100, 150, 200 mg/l. were prepared by appropriate dilutions.

### **2.3.3 Preparation of 4 M Sulphuric Acid (Approx)**

4 M  $\text{H}_2\text{SO}_4$  solution was prepared by diluting 55 ml ( $= 4 \times 250 / 18.38$ ) of concentrated  $\text{H}_2\text{SO}_4$  (sp. gravity = 1.84, purity = 98 %, M.W. = 98.08) in 250 ml volumetric flask with distilled water.

### **2.3.4 Preparation of 1 % Sodium Bicarbonate Solution (Approx)**

1 % sodium bicarbonate solution was prepared by dissolving 2.5 g of  $\text{NaHCO}_3$  (purity = 99-101 %, M.W. = 84.01) in 250 ml volumetric flask.

### **2.3.5 Preparation of 1 M Nitric Acid Solution**

1 M nitric acid solution was prepared by diluting 16 ml ( $= 1 \times 250 / 15.78$ ) of concentrated  $\text{HNO}_3$  (sp. gravity = 1.42, purity = 69-71 %, M.W. = 63.01) in 250 ml volumetric flask in distilled water and 0.1 M  $\text{HNO}_3$  was prepared by diluting 10 ml of 1 M  $\text{HNO}_3$  in 100 ml volumetric flask.

### **2.3.6 Preparation of 1 M Sodium Hydroxide Solution (Approx)**

1 M sodium hydroxide solution was prepared by dissolving 10 gm of NaOH pellets (purity = 96 % and M.W. = 40) in 250 ml volumetric flask. Further 0.1 M NaOH solution was prepared by diluting 10 ml of 1 M NaOH in 100 ml volumetric flask.

### **2.3.7 Buffer Solution**

Buffer solution of pH 4.01, 7 and 9, employed for calibration of pH meter is technical buffer pH 4.01 and 7 of trace model: TPL4 are manufactured in WTW GmbH & Co. KG. D82362 Weilheim and that of pH 9 which contains KCl,  $\text{HBO}_3$  and NaOH is from MercSpecialities Private Ltd, Shiv Sagar Estate A, Worli, Mumbai.

## **2.4 Preparation of Adsorbent from Rice Husk**

### **2.4.1 Preparation of Adsorbent from Raw Rice Husk**

Raw Rice husk was collected from local rice mill Balaju, Kathmandu. It was washed thoroughly first with tap water, then with distilled water 3 times to remove dust unwanted particles. It was left at room temperature for 1 day to ooze out excess water. Then it was placed in air dry oven at  $105^{\circ}\text{C}$  to dry for 24 hours. The dried rice husk was grinded in Thomas Wiley laboratory mill to make small particle size, and was sieved by 150 micron mesh to obtain definite particle size. It was stored in clean and dry polyethylene bottle. This raw rice husk powder is considered as potential adsorbent to remove Pb (II) from aqueous solution [RRH]. Its efficiency for lead (II) uptake was further enhanced by chemical modification.

### **2.4.2 Preparation of Chemically Modified Rice Husk Adsorbent**

Raw Rice Husk [RRH] was subjected to chemical modification using 4 M  $\text{H}_2\text{SO}_4$  at laboratory temperature, produce high surface area and high degree of microporosity. The RRH was treated with 4 M  $\text{H}_2\text{SO}_4$  in the ratio of 1:2 (Rice husk powder: 4 M  $\text{H}_2\text{SO}_4$ , w/v) and allowed to soak for 24 hours at room temperature to ensure complete reaction. It was washed with distilled water six times to remove acid residue and was allowed to soak in 1% sodium bicarbonate solution for 24 hours to neutralize the residual acid. Finally, it was again washed with distilled water and was placed in the oven at  $105^{\circ}\text{C}$  for 24 hours. It was termed as chemically modified rice husk powder [CMRH].

By chemical modification the surface of the adsorbent gets functionalized due to the formation of different functional groups and active sites on the surface of the adsorbent.

## **2.5 Adsorption Study**

### **2.5.1 Batch Adsorption Studies**

Batch adsorption experiments were carried out with synthetic working solution of lead (II) of predetermined concentration and adsorbent rice husk, in its raw form as well as in modified form. Most of the chemicals used in this study were analytical grade. The working solutions of various required concentration were prepared by diluting 250 mg/l of lead (II) solution.

In 100 ml Erlenmeyer flask, 25 ml of working solution is pipette out. pH of the solution was adjusted by using 0.1 M, 1 M  $\text{HNO}_3$  and 0.1 M, 1 M NaOH solutions and 25 mg of raw rice husk or chemically modified rice husk was added. The Erlenmeyer flask was shaken for 60 min in mechanical shaker at speed of 200 rpm to attain equilibrium. The equilibrated solution was filtered using Whatman No. 40 filter paper and the filtrate was analyzed for the remaining concentration of lead (II) ions. The metal concentration before and after adsorption were determined by using an Atomic Absorption Spectrophotometer, Varian, Australia, AA 240 FS. All experiments were performed in duplicate and average values were reported.

### **2.5.2 Batch Equilibrium Contact Time Studies**

25 ml of 25 mg/l concentration of lead (II) solution was pipette out in 100 ml Erlenmeyer flask and 25 mg of adsorbents were added to it. It was shaken at shaker speed of 200 rpm for 5, 10, 15, 20, 30, 60, 120 and 180 minutes. Then the sample solution was filtered through Whatman No. 40 filter paper. The metal concentration before and after adsorption were determined by AAS.



### **2.5.3 Batch pH Studies**

Batch pH studies were performed by shaking 25 ml of 25 mg/l of lead (II) solution with 25 mg of adsorbent for 60 min to attain equilibrium over a wide range of initial pH values 1, 2, 3, 4, 5, 6 and 7 by using 0.1 M, 1 M HNO<sub>3</sub> and as well as concentrated HNO<sub>3</sub> and 0.1 M, 1 M NaOH solutions. The samples were shaken in 100 ml Erlenmeyer flask at speed of 200 rpm. The solution was filtered through Whatman No. 40 filter paper. The filtrate was used for determining final concentration by AAS.

### **2.5.4 Effect of Initial Concentration of Lead (II)**

Adsorption isotherm studies were conducted by using initial concentration of lead (II) 10, 20, 25, 30, 40, 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mg/l. 25 ml of different concentration of lead (II) solution were used and were shaken at shaker speed of 200 rpm for 60 min with 25 mg of adsorbent dose for both RRH and CMRH at optimum pH of 5. The remaining lead (II) concentration was determined by AAS. The experimental data were employed to determine maximum adsorption capacity.

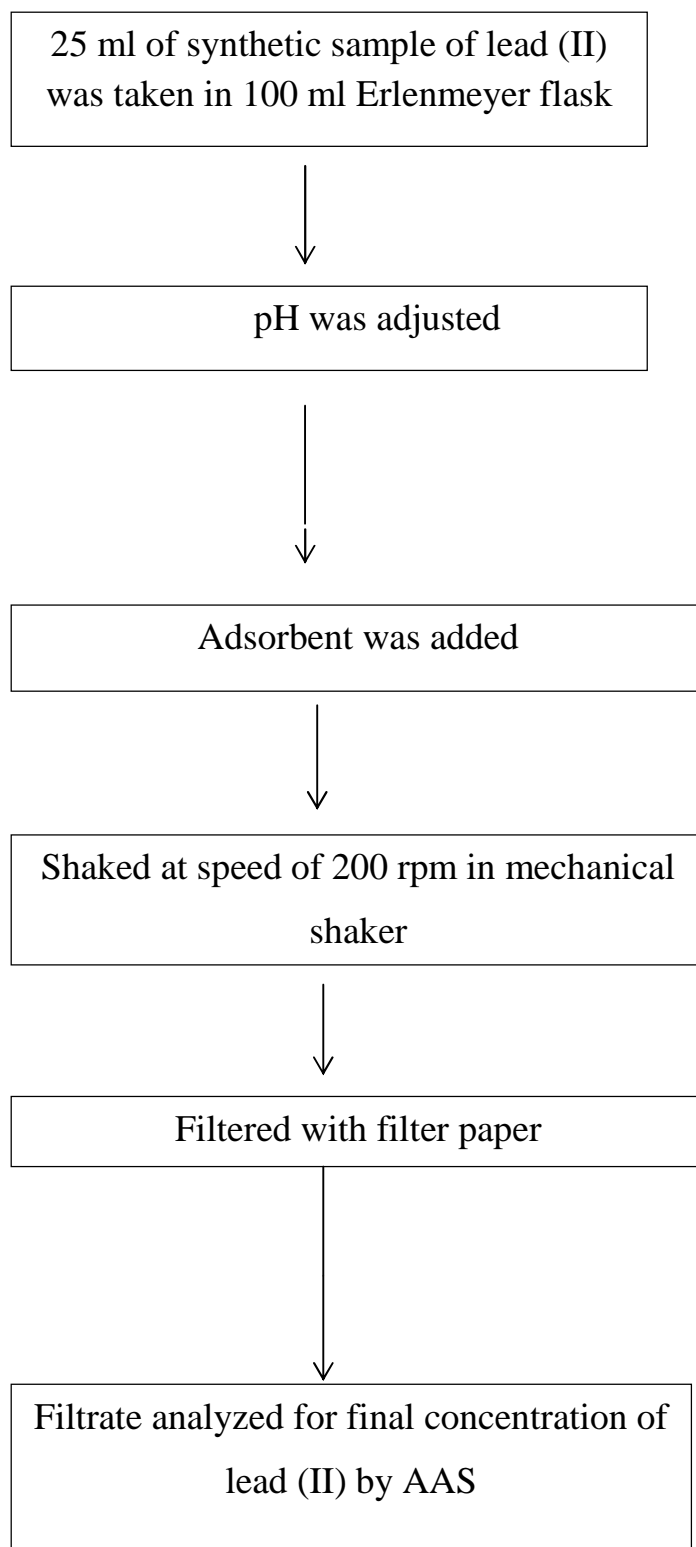
### **2.5.5 Effect of Adsorbent Dose**

The effect of adsorbent dose was performed by taking 25 ml of 25 mg/l initial concentration of lead (II) with pipette in 100 ml Erlenmeyer flask and then the initial pH of each sample was adjusted to 5 using 1 M NaOH and 1 M HNO<sub>3</sub>. The amount of adsorbent (RRH & CMRH) was varied as 5, 10, 20, 25, 40, 50, 60, 80, 100 and 140 mg (was added to different sample). The shaker speed was adjusted to 200 rpm for 60 min and the sample mixture was filtered through Whatman No. 40 filter paper. The lead concentration in filtrate was determined by AAS

### **2.5.6 Batch Kinetic Studies**

The adsorption kinetic experiments were performed at optimum pH 5 for lead (II) adsorption by equilibrating 25 ml of 25 mg/l in 100 ml Erlenmeyer flask with 25 mg of adsorbent. The flask was shaken at shaker speed of 200 rpm. The kinetics was investigated by drawing samples after desired period of contact time and filter through Whatman No. 40 filter paper and concentration before and after adsorption was determined by AAS. The data obtained was tested with pseudo-first order (Lagergren, 1898), pseudo-second order (Ho, 1999 and Ho & McKay, 2000) and second order kinetic models (Ho et al, 1996).

### Flow Chart for Adsorption of Lead (II) on to CMRH and RRH



### 3 Results and Discussion

The adsorption of lead (II) in aqueous solution on RRH and CMRH were examined by optimizing various physiochemical parameters such as contact time, initial pH, initial adsorbate concentration and adsorbent dose.

#### 3.1 Effect of Contact Time

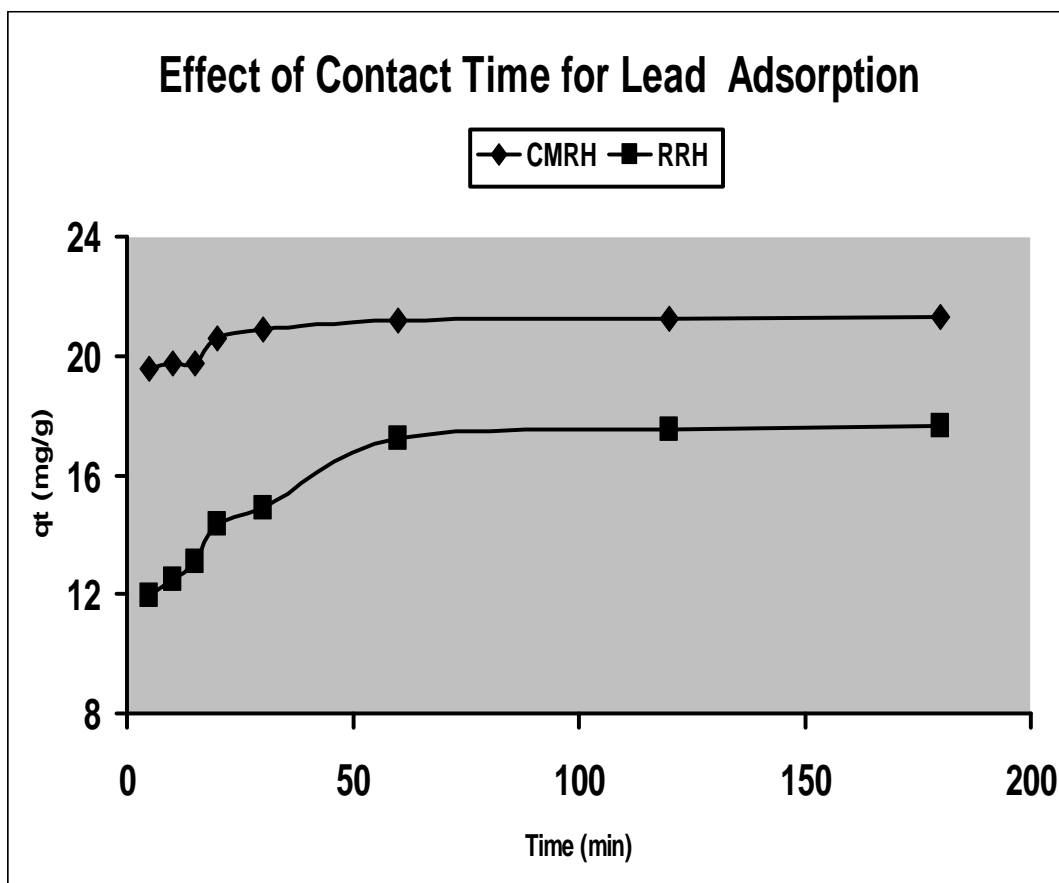
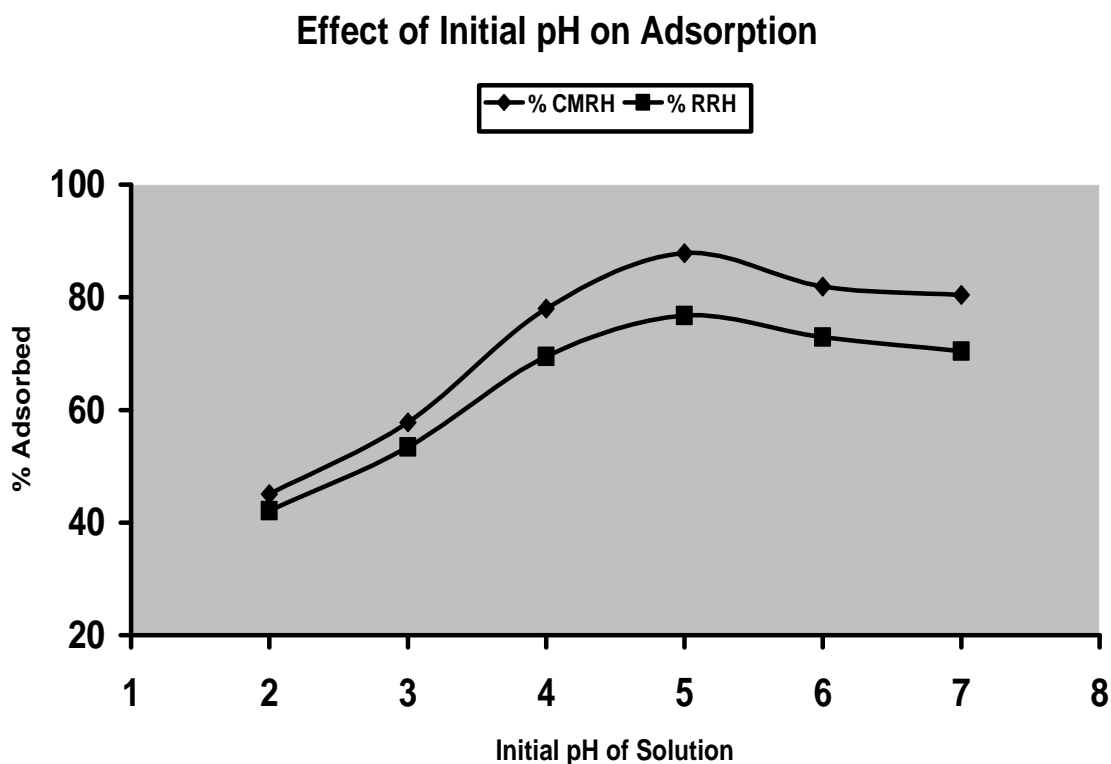


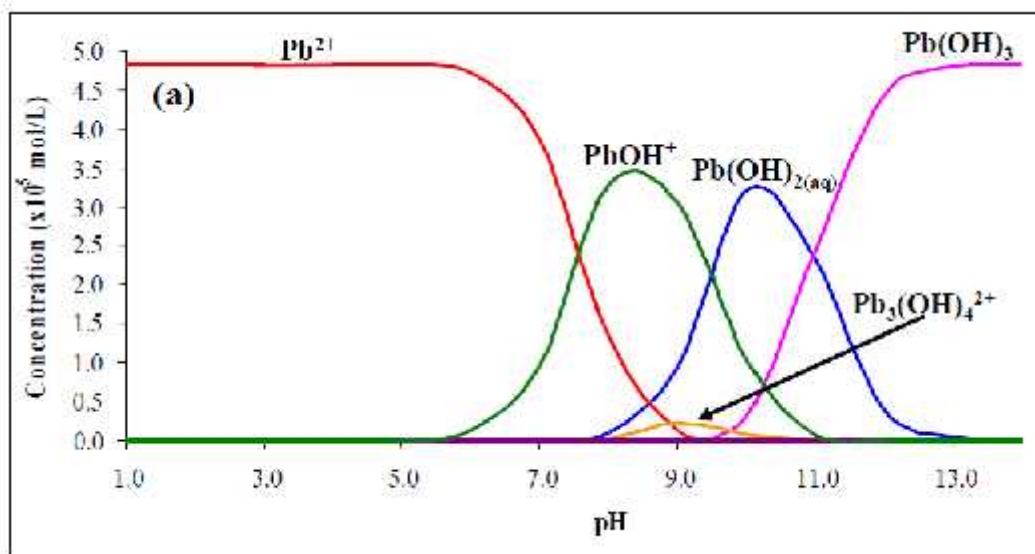
Figure 1:- Effect of Contact Time for CMRH and RRH

The rate of adsorption is the most important for performing the batch adsorption experiment. The experimental study measuring the effect of contact time on the batch adsorption of 25 mg/l lead (II) with 25 mg of adsorbent RRH and CMRH is shown in figure:-1 and table:-1A & 1B which shows the equilibrium contact time for adsorption of lead (II) on to CMRH and RRH reached within the first 60 minutes and beyond this saturation level reached.

From the data, it was found that the adsorption rate was rapid at first because of the presence of large number of adsorption sites or complexation sites so that large amount of lead (II) ion attached selectively to the adsorbent sites within the first 30 min. The rate slowed down gradually till it attained equilibrium at 60 min for both RRH and CMRH beyond which there was no significant increase in adsorption rate due to decrease in active sorption sites in the adsorbent and after reaching the saturation point adsorption becomes constant. Higher adsorption efficiency of CMRH could be attributed to the higher availability of different surface functional groups obtained by chemical modification. Bansode, et al. reported a 24 hours equilibrium time for adsorption of Pb (II), Cu (II) and Zn (II). Similar trend was reported by Ayyappan et al. for the adsorption of Pb (II) by pith carbon, sawdust carbon and bagasse carbon [40].

### 3.2 Effect of pH





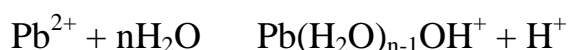
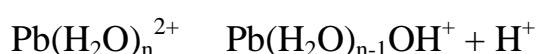
**Figure 2:- Effect of pH for CMRH and RRH and Speciation Diagram of Lead (II) in Aqueous Solution**

The pH of solution is the most important variable governing metal adsorption process because  $H^+$  ions themselves are strong competing ions and partly pH influences the chemical speciation of functional groups available on the adsorbent surface.

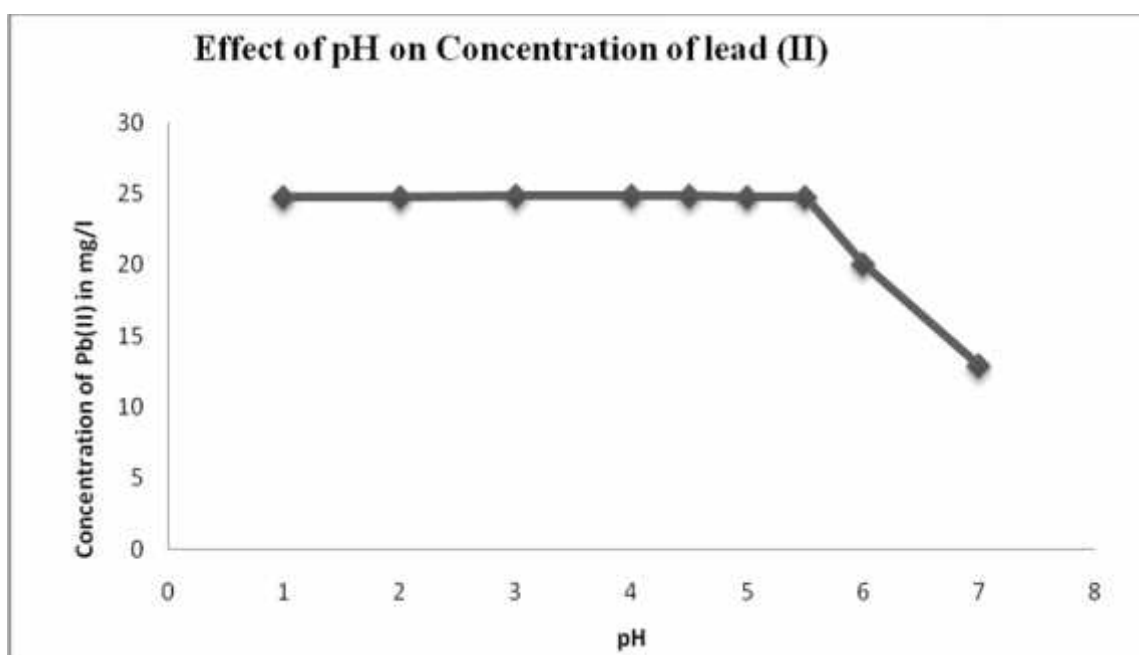
To evaluate the influence of pH on the adsorption, experiments were carried out at initial pH 1 to 7 to avoid metal hydroxide precipitation which occurs at  $pH > 6.5$  for  $Pb(OH)_2$ . The effect of pH on the adsorption efficiencies are shown in figure:-2 and table:-2A & 2B which shows removal of lead (II) increases with increasing in pH and maximum removal value was reached at pH 5 for both RRH and CMRH and on increasing pH above 5.5 precipitation occurred. The low degree of adsorption at low pH can be explained by the fact that at low pH,  $H^+$  ions concentration is high and therefore protons ( $H^+$  ions) can compete with Pb (II) in forming a bond with the surface active sites. These bonded active sites become saturated with  $H^+$  and was inaccessible to Pb (II) ions. In addition when pH increases, there is decrease in positive surface charge because the deprotonation of the adsorbent functional groups occur which results in lower electrostatics repulsion between the positively charged metal ions and

the surface of CMRH and RRH favoring adsorption i.e. with increase in pH of the solution, charges on the surface of RRH and CMRH becomes negative. Thereby leading to an attraction forces between Pb (II) and RRH or CMRH, enhancing adsorption. Hence an increase in adsorption of Pb (II) from solution. Similar results were reported by Yu et al. [41] and Ayyapan et al. for adsorption of Pb (II) by saw dust and carbon derived from saw dust bagasse and pith [40].

The process involved for lead (II) adsorption is given below.

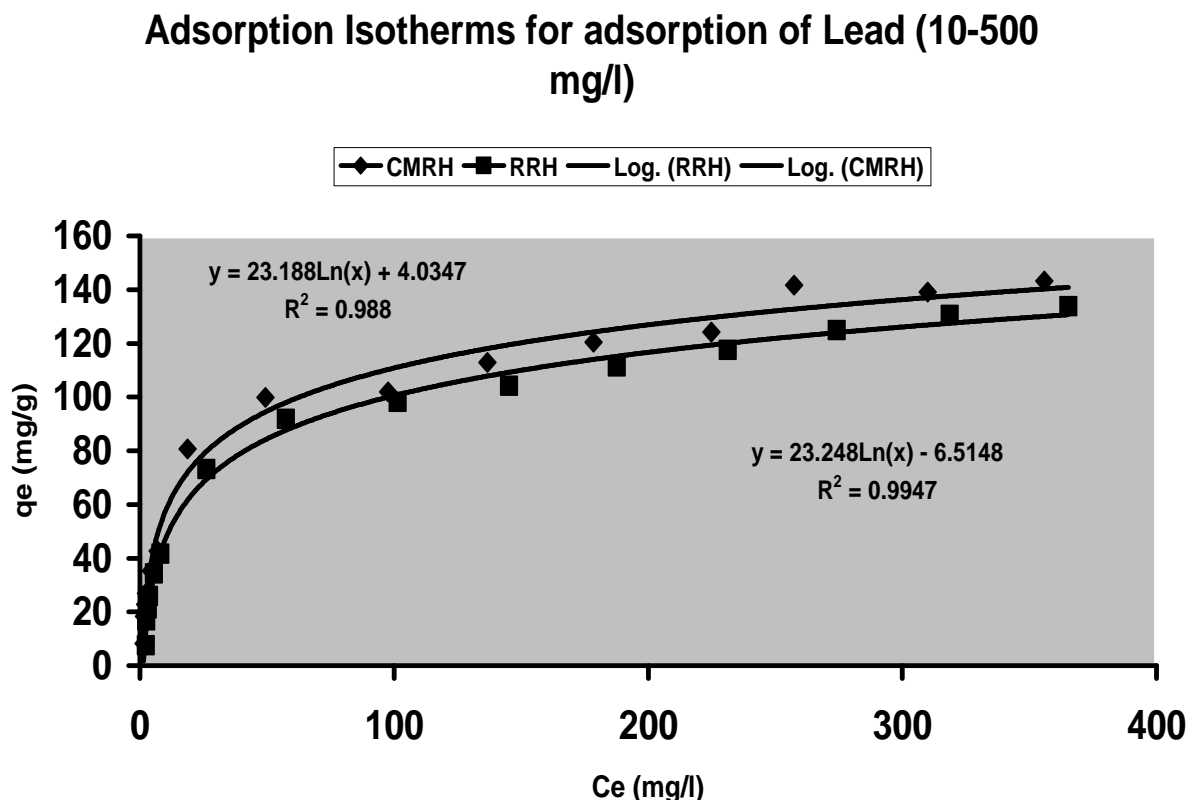


The lead (II) speciation diagram given in figure 2 shows that dominant species is  $\text{Pb}(\text{OH})_2$  at  $\text{pH} > 6$   $\text{Pb}^{2+}$  and  $\text{Pb}(\text{OH})^+$  at  $\text{pH} < 6$  [42]. The maximum removal of lead (II) was occurred around at pH 5 for RRH and CMRH. This is also clear from figure: 3 and table: 3 which shows there is decrease in actual concentration of lead (II) at  $\text{pH} > 5.5$  due to precipitation of lead (II) as hydroxide form.



**Figure 3:-Effect of pH on Lead (II) Concentration (solubility)**

### 3.3 Effect of Initial Concentration



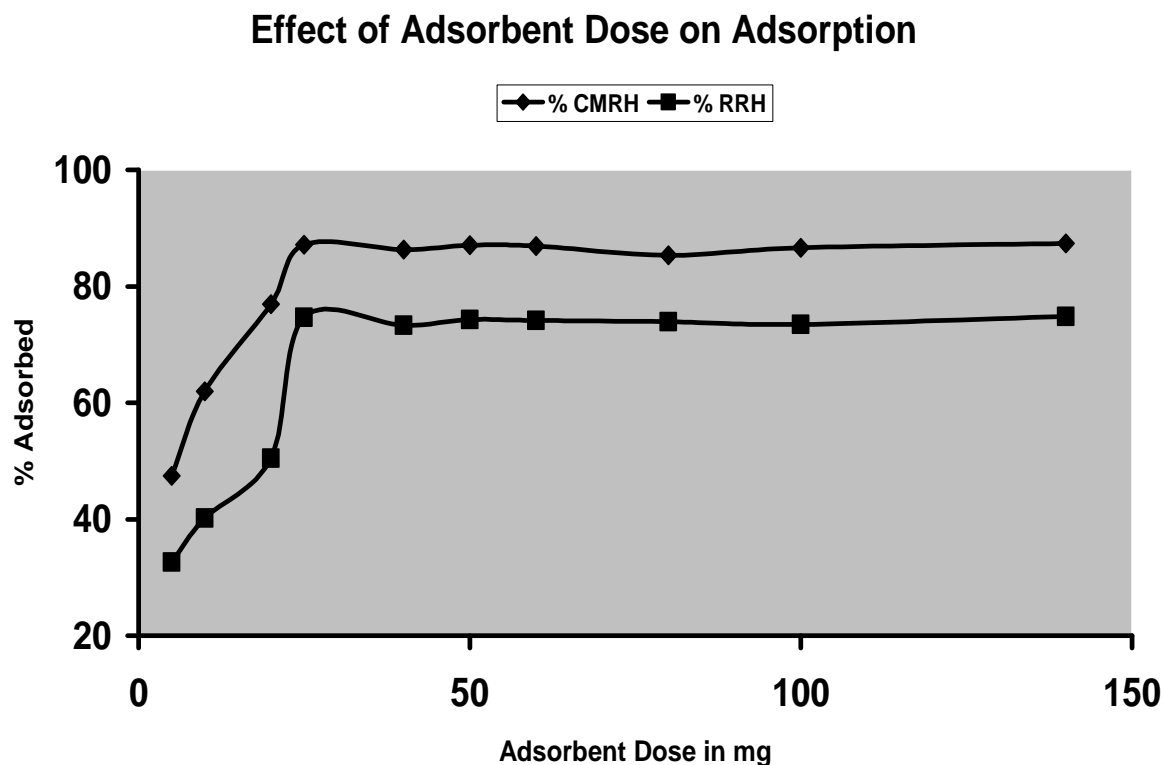
**Figure 4:-Effect of Initial Concentration for CMRH and RRH**

The effect of lead (II) concentration is shown in figure 4 which shows that adsorption of lead (II) on both adsorbents increases with increase in initial concentration of lead (II) solution and attains equilibrium which is attributed to the availability of limited adsorption sites. The increase in concentration of lead (II) increases the mass transfer driving force and therefore increases the rate at which lead (II) ions pass from the bulk solution to the particle surface that would results in higher adsorption [4].

From the result, it was found that on changing the initial concentration of lead (II) from 10 to 500 mg/l the amount adsorbed increased from 8.25 mg/g to 143.25 mg/g at optimum pH 5 for CMRH whereas for RRH, it was increased from 7.56 mg/g to 133.81 mg/g.



### 3.4 Effect of Adsorbent Dose

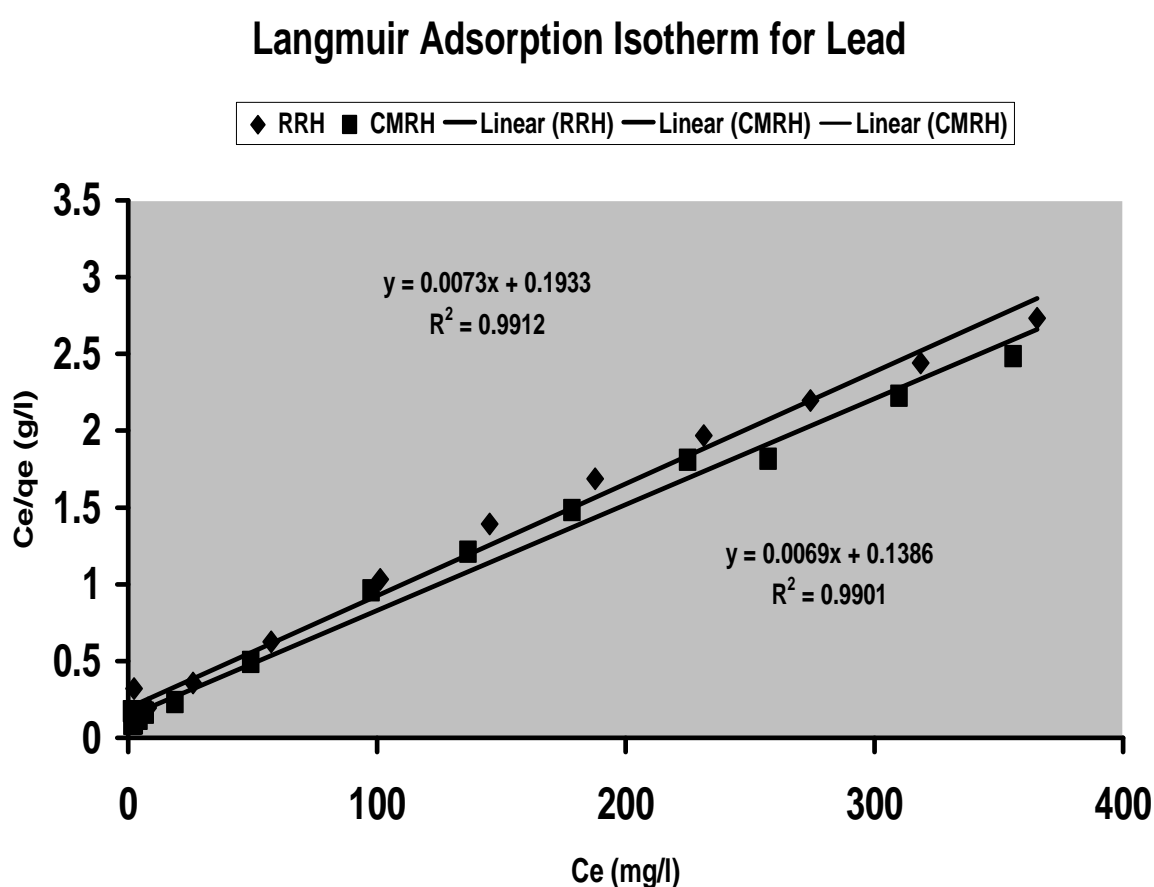


**Figure 5:-Effect of Adsorbent Dose for CMRH and RRH**

The effect of variation of adsorbent amount on the adsorption efficiency of lead (II) ion by RRH and CMRH is shown in figure 5 and table 4A & 4B. The amount of adsorbent was varied from 5 mg to 140 mg and equilibrated for 60 min at pH 5 and at initial lead (II) ion concentration 25 mg/l. The removal of lead (II) ion was found to increase with an increase in adsorbent doses. The removal remains almost unchanged after adsorbent dose of 25 mg for both RRH and CMRH. Increase in adsorption with increase in adsorbent doses attributed to the availability of large surface area and more adsorption sites. At low adsorbent dose, the adsorbent surface becomes saturated with lead (II) ion and the residual lead (II) ion concentration in the solution is large.

### 3.5 Batch Isotherm Studies

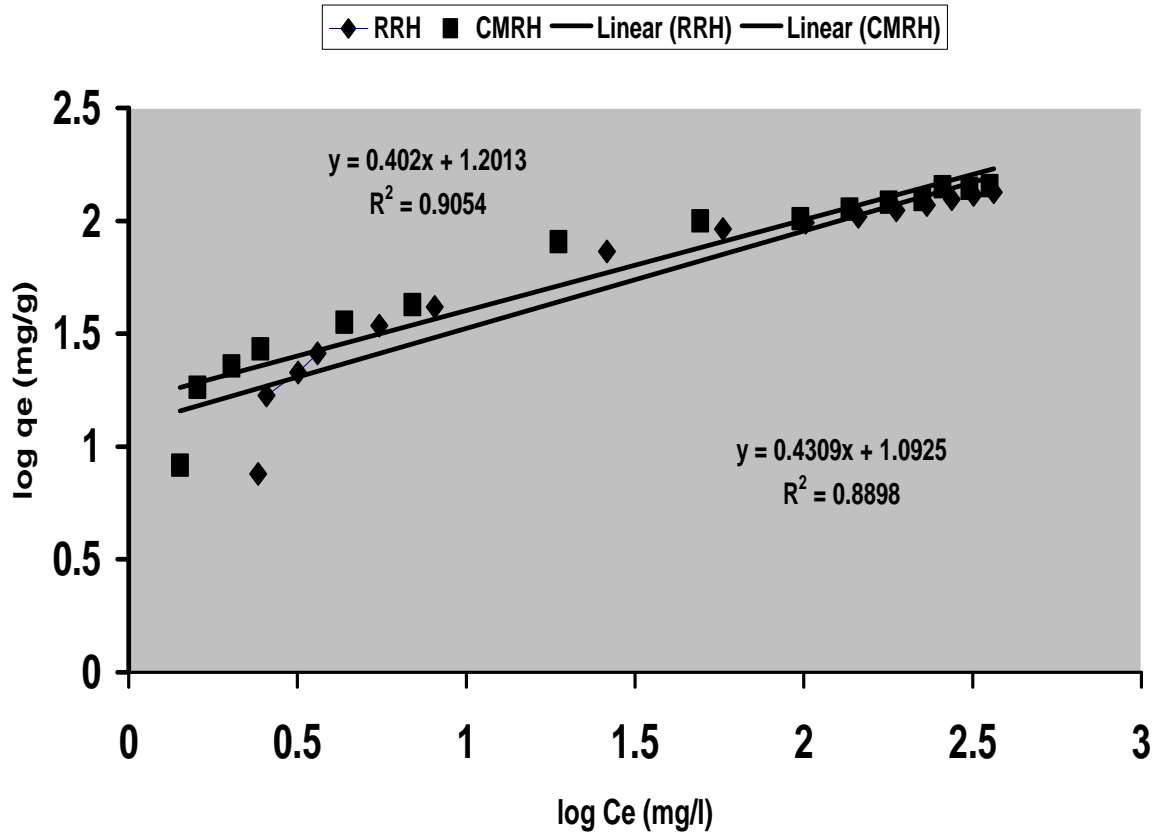
Adsorption of lead (II) onto CMRH and RRH gives the linear relationship with Langmuir and Freundlich isotherm which are shown in figure 6 & 7 and table 5A & 5B. Langmuir and Freundlich parameters shown in table 7 are determined from the slope and intercept of their respective plots. The values of Langmuir equilibrium parameters which are shown in table 8 lies between 0 and 1 indicating that equilibrium data fits well with Langmuir adsorption isotherm.



**Figure 6:-Langmuir Adsorption Isotherm for CMRH and RRH**

The plot for Freundlich adsorption isotherm of RRH and CMRH shows that equilibrium data fits well with Freundlich adsorption isotherm as well. The value  $1/n$  lies between 0 and 1 indicating that adsorption process is favourable.

### Freundlich Adsorption Isotherm for Lead



**Figure 7: Freundlich Adsorption Isotherm for CMRH and RRH**

However, the correlation coefficient value for Langmuir isotherm is found to be greater than that of Freundlich isotherm indicating that the adsorption process is better defined by the Langmuir adsorption isotherm model than by the Freundlich, which indicated the surface homogeneity of the adsorbents. The monolayer adsorption capacities of CMRH & RRH were found to be 143.25 mg/g & 133.81 mg/g respectively for Pb (II).

### 3.6 Batch Kinetic Studies

#### Pseudo second Order Kinetic Model for Adsorption of Lead

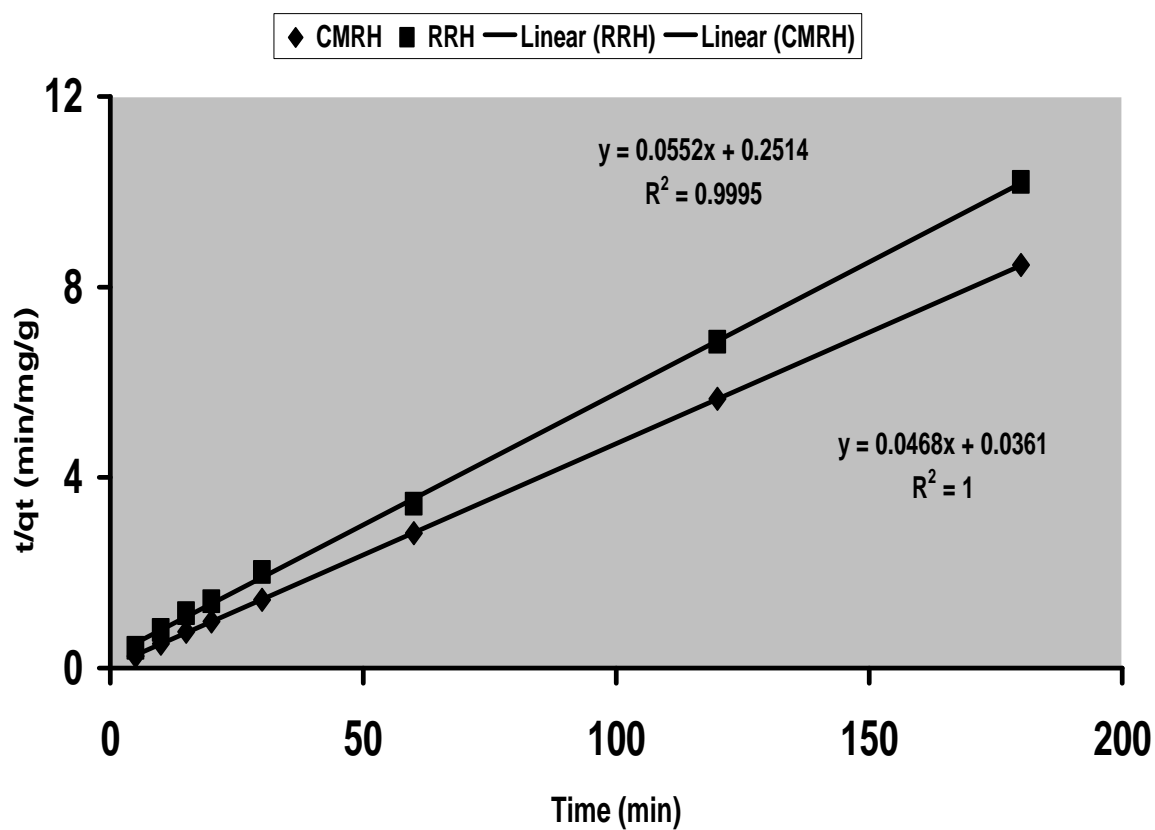
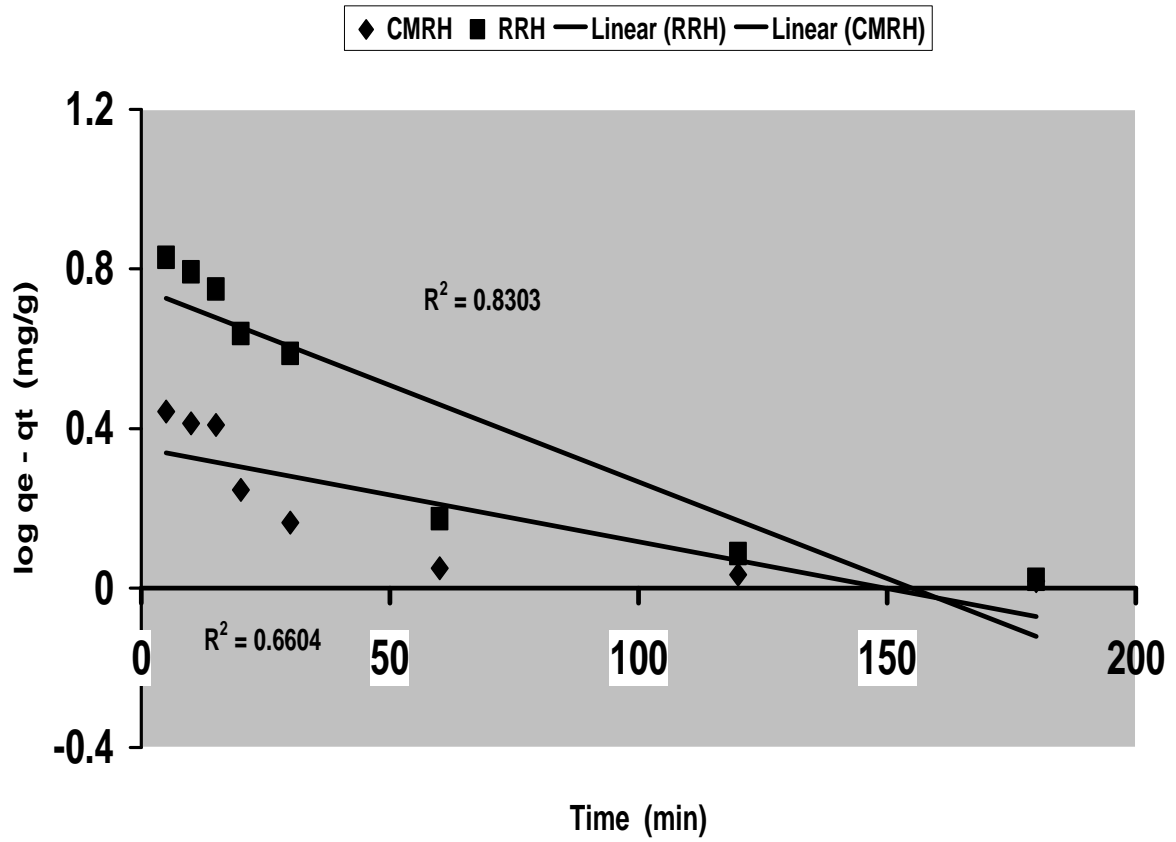


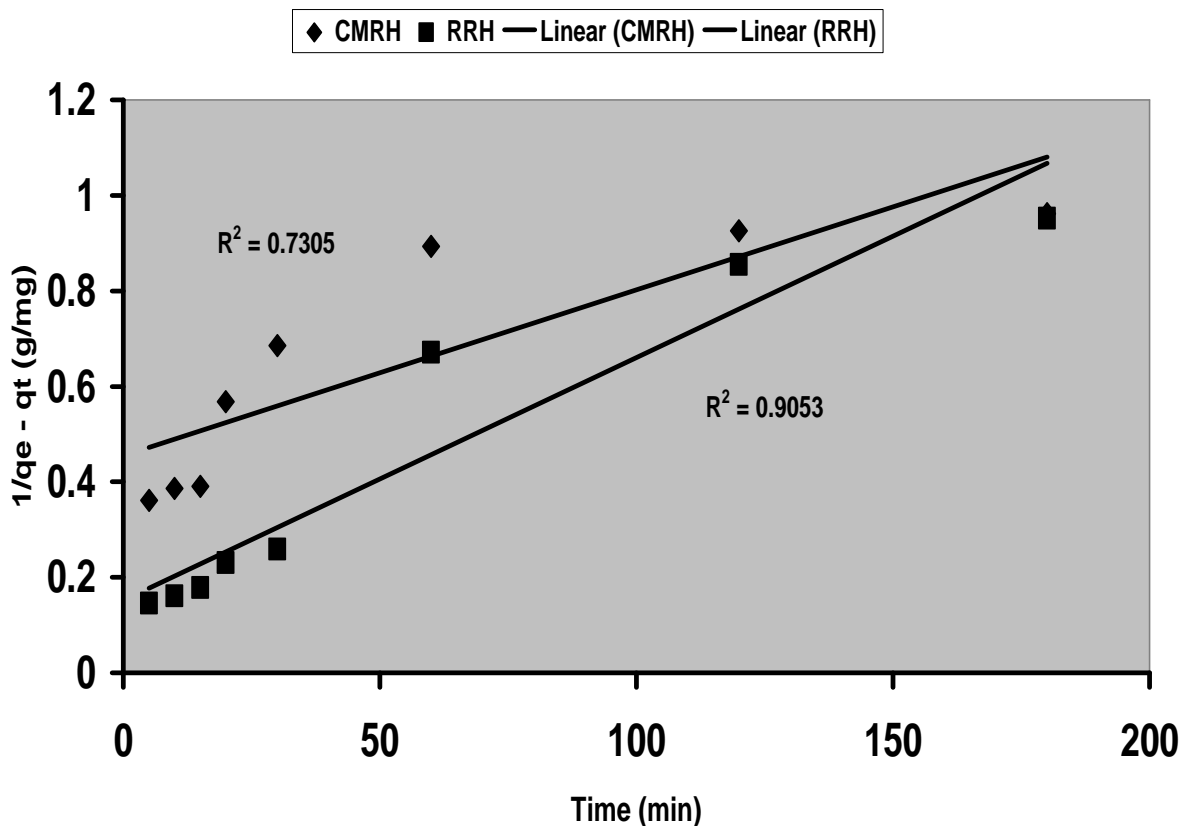
Figure 8:-Pseudo Second Order Kinetic Model for Adsorption of Lead (II) On CMRH and RRH

## Pseudo First Order Kinetic Model for Adsorption of Lead



**Figure 9:-Pseudo First Order Kinetic Model for Adsorption of Lead  
(II) On CMRH and RRH**

## Second Order Kinetic Model for Adsorption of Lead



**Figure 10:-Second Order Kinetic Model for Adsorption of Lead (II) On CMRH and RRH**

Kinetic studies for the adsorption of lead (II) onto RRH and CMRH were studied using pseudo-first order (Langergren, 1898), Pseudo-second order (Ho, et al.1995 and Ho and Mckay, et al. 2000) and second order (Langergren, 1898) models. The kinetic study of lead adsorption by RRH and CMRH is shown in figure 8, 9 & 10 and table 6A & 6B. From the plot and table 9, it can be observed that the correlation coefficient for pseudo second order was found to be close to 1, i.e, 0.9995 for RRH and 1 for CMRH. On other hand, the correlation coefficient ( $R^2$ ) for the pseudo-first order and second order kinetics were lower than that of pseudo-second order for both adsorbents CMRH and RRH.

According to pseudo second order model, the plot of  $t/q_t$  versus ' $t$ ' gives a straight line with positive slope value. Therefore, the adsorption of lead (II) onto

RRH and CMRH follows the pseudo-second order kinetic model. This suggests that rate – limiting step of this sorption process may be chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate [36].

### 3.7 Comparison of the maximum adsorption capacity ( $q_{\max}$ )

Comparison of the maximum adsorption capacity ( $q_{\max}$ ) of the RRH and CMRH with earlier investigated adsorbents are tabulated below. The results reveal that rice husk possesses higher potentiality towards the adsorptive removal of lead (II) from aqueous solution.

S.N.	Adsorbent	$q_{\max}$ (mg/g)	Source
1	Moss peat	117.58	[13]
2	Activated carbon from fluted pumpkin seed shell ( <i>Telfairia occidentalis</i> )	14.286	[14]
3	Chicken feathers	8.3	[15]
4	<i>Tridax procumbens</i> (Asteraceae)	2.90	[18]
5	Egg shell	29.878	[43]
6	Silica ceramics	2.7098	[17]
7	Carbonate hydroxyapatite extracted from eggshell waste	101.00	[36]
8	Raw rice husk (RRH)	131.81	[This work]
9	Chemically modified rice husk (CMRH)	143.25	[This work]

### **3.8 Treatment of the spiked ground water samples**

The suitability of the adsorbent for the adsorptive removal of lead (II) from aqueous solution was tested with the spiked ground water samples. The results are shown in table 10A and 10B. The % adsorption of lead (II) for CMRH was found to be about 95% with the effective dose of 25 mg of adsorbent showing that the adsorption is significantly good demonstrating that the selected bioadsorbent can be successfully used for the removal of lead (II) from water. However, the % adsorption of lead (II) varies with reference to the characteristics of ground water, especially the concentration of other competitive ions in aqueous system such as  $\text{Cd}^{2+}$ .



## 4 Conclusions

In the present work, the removal of lead (II) from abundantly available, low cost adsorbent, rice husk and its chemically modified form was investigated and their efficiency was compared. Basic adsorption experiments indicated that the adsorption of Pb (II) by CMRH and RRH was an adsorbate, adsorbent dependent process and the optimum adsorption capacity for both the CMRH and RRH was achieved at pH 5, contact time of 60 min, initial concentration of 25 mg/l and adsorption dose of 25 mg. The maximum adsorption capacity was found to be 143.25 mg/g & 133.81 mg/g for CMRH & RRH respectively and results revealed that Langmuir adsorption isotherm model was found to be more applicable than Freundlich adsorption isotherm model for the better description of the adsorption behavior of lead (II) ion onto rice husk, indicating surface homogeneity. The kinetic data was analyzed by pseudo-first order, pseudo-second order and second order kinetic models and it was found that the obtained data were best fitted by the pseudo-second order kinetic model, which indicated that chemisorption was the rate – limiting step in the sorption process.

Comparisons of the maximum adsorption capacity of the RRH and CMRH with earlier investigated adsorbents have shown that rice husk possesses higher potentiality towards the adsorptive removal of lead (II) from aqueous solution.

Furthermore, treatment of the spiked ground water samples showed that the adsorption is significantly good demonstrating that the selected bioadsorbent can be successfully used for the removal of lead (II) from aqueous solution.

The effluent water from industries such as paint manufacture industries have high content of lead(II) and it is necessary for such industry to reduce lead (II) to the acceptable level. The use of RRH and CMRH for removal of lead (II) not only solves the problem of sludge disposal but also becomes fruitful for such

industries. Hence it can be concluded that rice husk can be used as an efficient and economical material for the adsorptive removal of lead (II) from waste water. Moreover, its efficiency can be enhanced by chemical modification with sulphuric acid.

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## Annex

**Table 1A:- Effect of Contact Time for CMRH**

Initial lead concentration taken =25 mg/l

Total volume of sample =25 ml

Amount of adsorbents =25 mg

Shaker speed = 200 rpm

S.N.	Time in minutes	Actual initial concentration (C <sub>i</sub> )	Equilibrium concentration of lead (C <sub>e</sub> )	Amount of lead (II) adsorbed, q <sub>t</sub> (mg/g)
1	5	24.86	5.31	19.55
2	10	24.91	5.18	19.73
3	15	24.86	5.1	19.76
4	20	24.76	4.2	20.56
5	30	24.92	4.06	20.86
6	60	24.5	3.3	21.2
7	120	24.8	3.56	21.24
8	180	24.9	3.62	21.28
9	24 hours	24.88	2.56	22.32

**Table 1B:- Effect of Contact Time for RRH**

Initial lead concentration taken =25 mg/l

Total volume of sample =25 ml

Amount of adsorbents =25 mg

Shaker speed = 200 rpm

S.N.	Time in minutes	Actual initial concentration (C <sub>i</sub> )	Equilibrium concentration of lead (C <sub>e</sub> )	Amount of lead (II) adsorbed, q <sub>t</sub> (mg/g)
1	5	24.86	12.9	11.96
2	10	24.91	12.41	12.5
3	15	24.86	11.78	13.08
4	20	24.76	10.41	14.35
5	30	24.92	10.05	14.87
6	60	24.5	7.3	17.2
7	120	24.8	7.28	17.52
8	180	24.9	7.26	17.64
9	24 hours	24.88	6.19	18.69

**Table 2A:-Effect of pH for Adsorption of Lead (II) on to CMRH**

Initial lead concentration =24.38 mg/l

Total volume of sample =25 ml

Amount of adsorbent =25 mg

Shaker speed = 200 rpm

contact time=60 minutes

S.N.	pH	Equilibrium concentration of lead (C <sub>e</sub> )	% removal for CMRH
1	1	24.89	
2	2	14.12	42.08
3	3	10.54	56.79
4	4	5.37	77.97
5	5	2.97	87.82
6	6	4.42	81.87
7	7	4.77	80.43

**Table 2B:- Effect of pH for Adsorption of Lead (II) on to RRH**

Initial lead concentration =24.38 mg/l

Total volume of sample =25 ml

Amount of adsorbent =25 mg

Shaker speed = 200 rpm

Contact time=60 minutes

S.N.	pH	Equilibrium concentration of lead (C <sub>e</sub> )	% removal for RRH
1	1	24.05	
2	2	13.92	42.9
3	3	11.37	53.37
4	4	7.43	69.52
5	5	6.15	74.77
6	6	6.35	73.95
7	7	7.22	70.39

**Table 3:- Effect of pH on Concentration of Lead (II)**

Initial lead concentration =25 mg/l

Total volume of sample =25 ml

Shaker speed = 200 rpm

Shaking time =60 min

S.N.	pH	Actual concentration, mg/l
1	1	24.68
2	2	24.71
3	3	24.78
4	4	24.78
5	4.5	24.81
6	5	24.69
7	5.5	24.75
8	6	20.02
9	7	12.89



**Table 4A:- Effect of Adsorbent Dose for CMRH**

Initial lead concentration =24.38 mg/l

Total volume of sample =25 ml

Shaker speed = 200 rpm

pH 5

Contact time =60 minutes

S.N.	Amount of adsorbent in mg	Equilibrium concentration of lead (II) in mg/l, $C_e$	% removal for CMRH
1	5	12.81	47.47
2	10	9.28	61.94
3	20	5.62	76.95
4	25	3.38	86.14
5	40	3.33	86.34
6	50	3.4	86.05
7	60	3.19	86.91
8	80	3.58	85.32
9	100	4.23	82.65
10	140	4.55	81.34

**Table 4B:-Effect of Adsorbent Dose for RRH**

Initial lead concentration =24.38 mg/l

Total volume of sample =25 ml

Shaker speed = 200 rpm

pH 5

Contact time =60 minutes

S.N.	Amount of adsorbent in mg	Equilibrium concentration of lead (II) in mg/l, $C_e$	% removal for RRH
1	5	13.99	42.62
2	10	14.58	40.2
3	20	12.08	50.45
4	25	6.17	74.69
5	40	6.5	73.33
6	50	6.26	74.32
7	60	6.3	74.16
8	80	6.36	73.91
9	100	6.72	72.44
10	140	7.36	69.81

**Table 5A:- Adsorption Isotherm for Adsorption of Lead (II) on to  
CMRH**

Volume of sample = 25 ml

Amount of adsorbent =25 mg

Shaker speed =200 rpm

pH 5

Contact time = 60 minutes

S.N.	Concentration lead (II) taken in mg/l	Actual concentration $C_i$ (mg/l)	Equilibrium concentration, $C_e$ (mg/l)	Amount of lead (II) adsorbed , $q_e$ (mg/g)	$C_e/q_e$ in g/l	$\log C_e$	$\log q_e$
1	10	9.67	1.42	8.25	0.172	0.152	0.916
2	20	19.86	1.6	18.26	0.088	0.204	1.262
3	25	24.75	2.02	22.73	0.089	0.305	1.357
4	30	29.44	2.46	26.98	0.091	0.391	1.431
5	40	39.72	4.36	35.36	0.123	0.639	1.549
6	50	49.54	6.94	42.6	0.163	0.841	1.629
7	100	99.48	18.8	80.68	0.233	1.274	1.907
8	150	149.32	49.38	99.94	0.494	1.694	1.999
9	200	199.64	97.7	101.94	0.958	1.99	2.008
10	250	249.56	136.74	112.82	1.212	2.136	2.052
11	300	298.86	178.48	120.38	1.483	2.252	2.081
12	350	349.19	224.93	124.26	1.81	2.352	2.094
13	400	399.08	257.38	141.7	1.816	2.411	2.151
14	450	449.04	309.9	139.14	2.227	2.491	2.144
15	500	499.16	355.92	143.24	2.485	2.551	2.156

**Table 5B:- Adsorption Isotherm for Adsorption of Lead (II) on to RRH**

Volume of sample = 25 ml

Amount of adsorbent =25 mg

Shaker speed =200 rpm

pH =5

Contact time = 60 minutes

S.N.	Concentration lead (II) taken in mg/l	Actual concentration $C_i$ (mg/l)	Equilibrium concentration, $C_e$ (mg/l)	Amount of lead (II) adsorbed , $q_e$ (mg/g)	$C_e/q_e$ in g/l	$\log C_e$	$\log q_e$
1	10	9.98	2.42	7.56	0.32	0.384	0.879
2	20	19.38	2.56	16.82	0.152	0.408	1.226
3	25	24.44	3.18	21.26	0.15	0.502	1.328
4	30	29.56	3.62	25.94	0.14	0.559	1.414
5	40	39.84	5.52	34.32	0.161	0.742	1.536
6	50	49.64	8.08	41.56	0.194	0.907	1.619
7	100	99.25	26.15	73.1	0.358	1.417	1.864
8	150	149.3	57.48	91.82	0.626	1.76	1.963
9	200	199.54	101.4	98.14	1.033	2.006	1.992
10	250	249.47	145.26	104.21	1.394	2.162	2.018
11	300	299.11	187.74	111.37	1.686	2.274	2.047
12	350	348.96	231.38	117.58	1.968	2.364	2.07
13	400	399.18	274.26	124.92	2.196	2.438	2.097
14	450	449.21	318.68	130.53	2.441	2.503	2.116
15	500	499.23	365.42	133.81	2.731	2.563	2.126

**Table 6A:- Kinetic Data for Adsorption of Lead (II) on CMRH**

Volume of sample =25 ml

Amount of adsorbent=25 mg

Initial concentration taken =25 mg/l

pH =5

Shaker speed =200 rpm

S.N.	Time in minutes	Actual initial concentration, $C_i$ (mg/l)	Equilibrium concentration, $C_e$ (mg/l)	Amount of lead (II) adsorbed, $q_t$ (mg/g)	$t/q_t$ (min/mg/g)	$q_e - q_t$ (mg/g)	$1/q_e - q_t$ (g/mg)	$\log q_e - q_t$ (mg/g)
1	5	24.86	5.31	19.55	0.2557	2.77	0.361	0.443
2	10	24.91	5.18	19.73	0.5068	2.59	0.3861	0.413
3	15	24.86	5.1	19.76	0.7591	2.56	0.3906	0.408
4	20	24.76	4.2	20.56	0.9727	1.76	0.5681	0.246
5	30	24.92	4.06	20.86	1.4381	1.46	0.6849	0.164
6	60	24.5	3.3	21.2	2.83	1.12	0.8928	0.049
7	120	24.8	3.56	21.24	5.6497	1.08	0.9259	0.033
8	180	24.9	3.62	21.28	8.4586	1.04	0.9615	0.017
9	24 hrs	24.88	2.56	22.32	64.516			

**Table 6B:- Kinetic Data for Adsorption of Lead (II) on RRH**

Volume of sample =25 ml

Amount of adsorbent=25 mg

Initial concentration taken =25 mg/l

pH= 5

Shaker speed =200 rpm

S.N.	Time in minutes	Actual initial concentration, $C_i$ (mg/l)	Equilibrium concentration, $C_e$ (mg/l)	Amount of lead (II) adsorbed, $q_t$ (mg/g)	$t/q_t$ (min/mg/g)	$q_e - q_t$ (mg/g)	$1/q_e - q_t$ (g/mg)	$\log q_e - q_t$ (mg/g)
1	5	24.86	12.9	11.96	0.418	6.73	0.1459	0.828
2	10	24.91	12.41	12.5	0.8	6.19	0.1615	0.7916
3	15	24.86	11.78	13.08	1.147	5.61	0.1782	0.749
4	20	24.76	10.41	14.35	1.394	4.34	0.2304	0.6375
5	30	24.92	10.05	14.87	2.017	3.87	0.2584	0.5877
6	60	24.5	7.3	17.2	3.448	1.49	0.6711	0.1731
7	120	24.8	7.28	17.52	6.849	1.17	0.8547	0.0862
8	180	24.9	7.26	17.64	10.204	1.05	0.9523	0.0212
9	24 hrs	24.88	6.19	18.69	77.047			

**Table 7: Langmuir and Freundlich Parameters for the Adsorption of Lead (II) on to CMRH and RRH**

S.N.	Adsorbents	$q_m$ exp(mg/g)	Langmuir isotherm			Freundlich isotherm		
			$q_m$ (mg/g)	$b$ (L/mg)	$R^2$	$K$ (mg/g)	$1/n$	$R^2$
1	RRH	133.81	136.9863	0.0378	0.9912	15.8964	0.402	0.9054
2	CMRH	143.25	144.9275	0.0498	0.9901	12.3737	0.4309	0.8898

**Table 8: Value for Langmuir Parameters at Different Concentration of Lead (II)for CMRH and RRH**

S.N.	For CMRH			For RRH		
	Concentration of lead taken, mg/l	Actual concentration of lead, mg/l	$K_L$ values	Concentration of lead taken, mg/l	Actual concentration of lead, mg/l	$K_L$ values
1	10	9.67	0.6749	10	9.88	0.7280
2	20	19.86	0.5027	20	19.38	0.5772
3	25	24.75	0.4479	25	24.44	0.5198
4	30	29.44	0.4055	30	29.56	0.4723
5	40	39.72	0.3392	40	39.84	0.3990
6	50	49.54	0.2884	50	49.64	0.3476
7	100	99.48	0.1679	100	99.25	0.2104
8	150	149.32	0.1185	150	149.3	0.1505
9	200	199.64	0.09139	200	199.54	0.1170
10	250	249.56	0.07447	250	249.47	0.09587
11	300	298.86	0.06296	300	299.11	0.08126
12	350	349.19	0.05438	350	348.96	0.07047
13	400	399.08	0.04790	400	399.18	0.06215
14	450	449.04	0.04280	450	449.21	0.05561
15	500	499.16	0.03867	500	499.23	0.05032

**Table 9: Pseudo Second Order Reaction Rate Constant and Correlation Coefficient for the Adsorption of Lead (II) on CMRH and RRH**

S.N.	Adsorbent	Pseudo Second Order		
		$K_2$ g/mg min	$q_o$ mg/g min	$R^2$
1	RRH	0.0121	3.9777	0.9995
2	CMRH	0.0606	27.7008	1

**Table 10: - Lead Adsorption from Spiked Ground Water Samples**

**Table 10A: - Characteristics of Water**

S.N.	Sample	Initial pH	Value of cadmium in ppb	Value of lead in ppb	Total hardness in ppm	Drop in pH
1	Ground water- Balaju,	8.67	0.027	0.858	333.66	7.72
2	Ground (well) water- Pulchowk	8.46	0.064	1.54	421.74	7.65

**Table 10 B: - % Removal of Lead (II) in Spiked Ground Water Samples**

Volume of sample taken =25 ml

pH = 5

Amount of adsorbent =25 mg

Contact time =60 minutes

Shaking speed=200 rpm

S.N.	Type of sample	Type of adsorbent	Actual concentration in mg/l	Equilibrium concentration in mg/l	% of lead adsorbed
1	Ground water- Balaju	RRH	10.6269	1.3783	87.03
		CMRH	10.3872	0.4714	95.46
2	Ground (well) water- Pulchowk	RRH	9.5295	1.5423	83.81
		CMRH	9.8648	0.5264	94.66