ADSORPTION OF LEAD (II) FROM AQUEOUS SOLUTION USING MIZORAM WOOD CHARCOAL: KINETICS AND ISOTHERMS STUDIES

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Declaration of the Candidate

I, Aawaj Kuloong Rai, hereby declare that the subject matter of this dissertation entitled **"Adsorption of Lead (II) from aqueous solution using Mizoram Wood charcoal: Kinetics and Isotherms studies."** is a record of work done by me, that the contents of this dissertation did not form basis of the award of any previous degree to me or to the best of my knowledge to anybody else, and that the dissertation had not been submitted by me for any research degree in any other University/Institute.

This is being submitted to Mizoram University for the award of the degree of Master of Philosophy in Biotechnology.

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CERTIFICATE

This is to certify that the dissertation entitled **"Adsorption of Lead (II) from aqueous solution using Mizoram Wood charcoal: Kinetics and Isotherms studies**." to Mizoram University for the award of the degree of Master of Philosophy Biotechnology by **Aawaj Kuloong Rai** Registration No. ***MZU/M.Phil./448 of 03/05/2018,*** Research scholar in the Department of Biotechnology, is a record of original research work, based on the results of the experiments and investigations carried out independently by her during the period from 2017-2019 of study, under my guidance and supervision and has not been previously submitted for the award of any degree in any Indian or foreign University.

It is further certified that the scholar fulfils all the requirements as laid down by the University for the purpose of submission of M.Phil. Dissertation.

Place:

Date:

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Dated:

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Abbreviations

HM – Heavy Metal

HMs – Heavy Metals

WHO – World Health Organization

ATSDR – Agency for Toxic Substance and Disease Registry

USEPA – United States Environmental protection agency

EU – European Union Standards

BIS – Bureau of Indian Standard

EU European Union Standards

ISI – Indian Standard Institution

EPA – Environmental Protection Agency

pH – Power of H^+ ions or negative logarithm of activity of H+ ions

AAS – Atomic Adsorption Spectroscopy/Spectrophotometer

FTIR – Fourier-Transform Infrared Spectroscopy

μS – micro siemens

IQ – Intelligent Quotient

(=O) – oxo

(−SH) – thio

(PO_4^{-3}) – phosphate

CNS – Central Nervous System

PNS – Peripheral Nervous System

KXRF – K X-ray fluorescence

ppm – parts per million

hr – hour

min – minute

EPS – exopolysaccharide

rpm – revolutions per minute

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charcoal in different studied different setup of the experiments; **(a)** Effect of pH on the adsorption of fixed amount of Pb (II) ions with fixed amount of adsorbent (0.1 g), **(b)** Effect of Pb (II) ions concentration on adsorption process with fixed amount adsorbent at pH=6, **(c)** Effect of adsorbent dose on the fixed concentration of Pb ions at pH=6 and **(d)** Effect of time on the fixed concentration of Pb ions (10 ppm) with fixed amount of adsorbent at pH=6 at constant temperature 29 °C respectively.

1. Introduction

Heavy metals (HMs) are those elements which have a density higher than that of water and they show toxicity even at very low concentrations. Heavy metal comprises elements which are metals as well as metalloids (Hutton & Symon, 1986; Battarbee *et al.*, 1988; Nriagu & Pacyna, 1988; Nriagu, 1988; Hawkes, 1997). Some examples of heavy metals are arsenic, lead, mercury, cadmium, chromium, thallium, copper, zinc, iron, cobalt, etc. Heavy metals are found naturally in the earth's crust and some of the heavy metals such as zinc, iron, selenium, cobalt, copper, etc. are important to us in trace amount for the normal maintenance of our metabolism. Nevertheless, the higher concentration of heavy metal may be toxic as well. Therefore, different health concerned associations and governing bodies such as World Health Organization (WHO), Agency for Toxic Substance and Disease Registry (ATSDR), United States Environmental protection agency (USEPA), Indian Standard Institution (ISI), etc. have set a limiting concentration of these metals in various cases, such as drinking water.

HMs are the pollutants of the natural water reservoirs because they are not easily degraded biologically. They are persistent and toxic to aquatic as well as terrestrial life forms. The accumulation of HMs in the environment, especially in the water bodies is mainly due to outnumbered pollutants from various industries. They are not only responsible for the pollution of water bodies, but other parts of the environment like soil, air and biosphere as well. They are toxic and potent carcinogen which can cause disorders in the nervous system even at trace amounts (Lalhruaitluanga *et al.*, 2010). Therefore, proper disposal methods of waste products and pollutants should be used before discharging into the environment. One of the important reasons for the pollution caused by heavy metals in the environment is the discharge of wastes from industries which contains heavy metals and it causes serious health problems (Gupta & Ali, 2013). Figure 1 illustrates the schematic representation of bioaccumulation of heavy metal in the food chain by the discharge of toxic heavy metals from the industrial waste into the water. Some of the common sources of heavy metal pollution include, extractive metallurgy processes, electroplating, refining, automobile, battery manufacturing, steel industries, tannery, paint manufacturing, electronic industries (Williams *et al.*, 1998), atomic plants, photography, aerospace (Gupta & Ali, 2013), manufacturing of explosives., glass industries (Lalhruaitluanga *et al.*, 2010), etc. The constituents of these pollutions are mainly arsenic (As), nickel (Ni), zinc (Zn), cadmium (Cd), and lead (Pb) and so on. These heavy metals when accumulated in a high concentration are toxic and may seriously damage the natural aqueous environment when discharged into the water bodies.

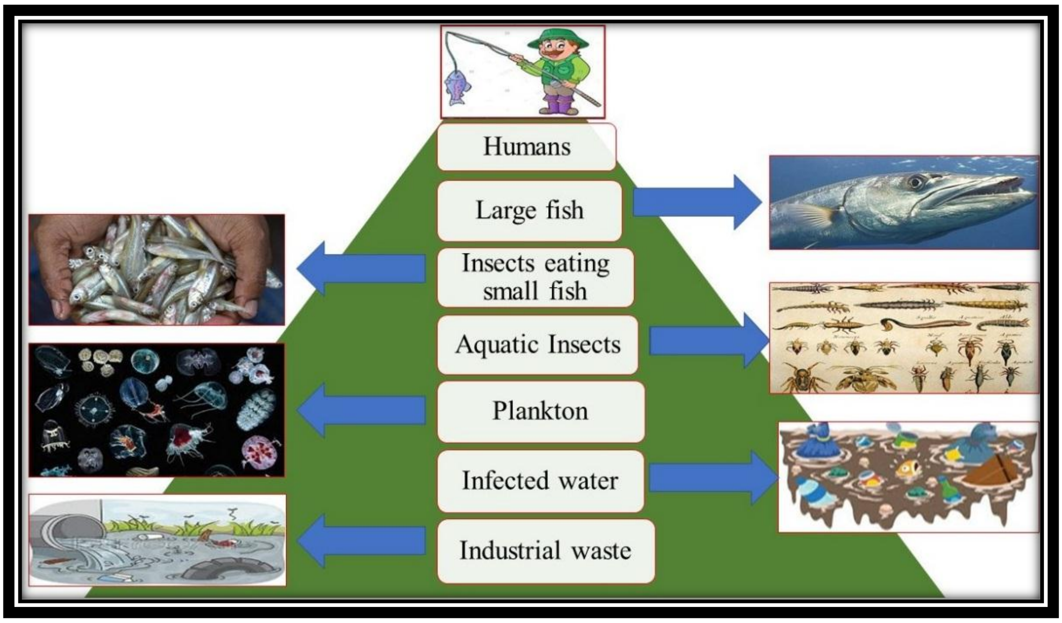

Figure 1. Schematic representation of bioaccumulation of heavy metals from industrial waste.

Different pollutants have been classified mainly into three broad groups, they are; inorganic, organic and biological particles (Gupta and Ali, 2013; Adhoum *et al.*, 2004; Hunsom *et al.*, 2005) Among these three different types of pollutants, the heavy metals come under the inorganic pollutants and unlike the organic pollutants, the heavy metals cannot be degraded easily through natural processes into non- toxic end products (Gupta *et al*., 2001). The level of HMs and their uptake in the various sources like soil, municipality sewage waste, sludge, river, groundwater, leachate, etc. have already been reported (Apak, Hizal, & Ustaer, 1999; Gundersen & Steinnes, 2003; Christensen & Christensen, 2000; Das & Jana, 2006). Due to this fact, they can be easily captivated on to seafood, vegetables and consumption of such contaminated foods by humans can lead the accumulation of heavy metals in the human body, which is referred as 'Bioaccumulation' (Azimi *et al.*, 2016).

Lead (Pb) metal are considered to be most studied heavy metal in toxicology area as compared to other metals (Jalali *et al.*, 2002). In fact, Pb is found to accumulate in the various tissues and organs of the body such as the blood, brain, bones, kidneys, muscles, kidneys, etc. and once they exceed a certain level, are capable of causing serious health problems (Lalhruaitluanga *et al.*, 2010; Lo *et al*., 1999). Pb has a less advantageous role in human health compared to other trace elements like zinc, copper, iron, etc. It shows a neurotoxic behavior in humans which leads to various neurological disorders. The main effect of the lead poison is on the developing children whose nervous system development is hampered which in turn leads to the long-term damage and disorder in their body. Lead poisoning also causes degeneration of mental and intellectual abilities of the children. Generally, Pb poisoning is prominent in children when it accumulates in the body and exceeds the limit above 50 μgL^{-1} in the blood stream. It has been found that the relation between the intelligent quotient (IQ) and Pb level in the blood is inversely proportional to each other. Pb acts as an enzyme inhibitor and Pb (II) ions react with the enzyme's active sites, specially, the functional groups such as oxo (=O), thio (–SH), phosphate (PO_4^{-3}). It also affects the permeability of the cell membrane of various organs. (Morosanu *et al.*, 2017)

Even in developing countries like China, lead poisoning has been a serious health issue, particularly, in case of youngsters and measures of combating this problem has become a challenge and drawn attention to the researchers (Hou *et al.*, 2013). About 70 million people of the whole population is found to be affected by heavy metal poisoning in Bangladesh, West Bengal and other parts of east India (Deliyanni *et al.,* 2015; Peleka & Matis, 2011) and further, lead poisoning may lead to abortions and miscarriage in pregnant woman (Youssef *et al*., 2014).

The provisional guideline value for Pb in drinking water according to World Health Organization (2017) was 0.01 ppm (parts per million), USEPA as 0.015 ppm and EU as 0.01 ppm (Bhattacharjee *et al.*, 2003; Balaria & Schiewer, 2008). According to the reports of Agency for Toxic Substance and Disease Registry (ATSDR), Pb has been listed as the second most hazardous materials which is responsible to pollute the environment (Chatterjee *et al.,* 2016). The lead (Pb) concentration limit for industrial discharged wastewater is found to be 1 ppm (Wang *et al.*, 2017). Environmental Protection Agency (EPA) has set a limit of Pb in the wastewater as 0.05 ppm whereas the Bureau of Indian Standard (BIS) has set its limit as 0.1 ppm.

Membrane filtration, ion-exchange, adsorption, chemical precipitation, nanotechnology treatments, electrochemical and advanced oxidation processes are some of the widely used techniques in the treatment of water contaminated with heavy metals. Although, each of these methods has their own advantages as well as disadvantages. So, there has always been a demand for a cost-effective, feasible, time-saving and safer method for the removal of these different heavy metals.

Among different methods, adsorption method is most effective, especially when activated charcoal is used as an adsorbent due to its high efficiency in capturing the heavy metals (Azimi *et al.*, 2016). Charcoals are found to purify both air as well as water impurities (Mor *et al.*, 2007; Sarin and Pant, 2006). Way back to 3000 years ago, the Egyptians used charcoal for the absorption of gases in the stomach by taking charcoal orally. Whereas Phoenicians have used charcoal with a similar perception for other application such as purification of water. Even though they were not aware of the actual mechanism of action of charcoal in the adsorption of impurities in gas as well as in water. They were using it on the basis of mere observation and evidence of treatments being successful by using charcoal (Russo *et al.*, 2017). Three main requirements for a good adsorbent must be in abundant quantities, easily renewable and cost-effective (Demirbas, 2008).

Mechanism of biosorption is a physicochemical process which involves the removal of various pollutants, such as heavy metals from solution by biological materials (Sahmoune, 2018). The mechanism of binding of heavy metals onto the adsorbent surface is a complicated process. The process of adsorption is basically divided into two broad groups, physical adsorption or physisorption and chemical adsorption or chemisorption. Physisorption is stabilized by van der Waal's interaction whereas complexation, chelation and ion exchange interaction take place in case of chemisorption. Physisorption is a reversible process whereas chemisorption is irreversible. External factors such as pH, temperature, pressure, etc. effects physisorption more than chemisorption. The metal binding of heavy metal onto the adsorbent surface depends on the monolayer sorption in case of chemisorption in contrast to physisorption (Khosa & Ullah, 2018).

Quite a lot of hard work has been done in order to generate biosorbents that can remove heavy metals and organic dies from water. Biosorbents like charcoal are very important because they have various functional groups in their structure which can be helpful for the removal of heavy metals. But they also possess some drawbacks as well. They have less stability and mechanical resistance which makes them practically unacceptable on the industrial basis. In a commercial basis, they face problems with regard to regeneration and they are degraded continuously. The reuse of biosorbents has also been a matter of challenge for various workers in the treatment of wastewater specifically in case of sewage treatment where new and fresh biomass of adsorbent has to be supplied continuously. Taking all the advantages as well as the disadvantages into consideration much emphasis has been put on to accept the challenge of understanding the mechanism of adsorption of heavy metals onto the adsorbents in recent years (Khosa & Ullah, 2018).

*Scope of the work***:**

Wood is one the most abundant and economically important timber product in the state of Mizoram, India. Wood charcoal is mainly used for household purposes and produced by thermal decomposition of wood at a temperature of 600 – 800°C under reduced oxygen supply inside the charcoal kiln. Adsorption phenomena usually depend on many parameters such as adsorbent dose, temperature, pH, metal concentration, time. High surface area with pore size greater than 2 nm can facilitate more adsorption by maintaining the adsorption-desorption equilibrium. Besides this, a large number of functional groups over the surface of adsorbent is another factor to enhanced the adsorption quality of the adsorbent material.

In order to understand the adsorption capability of the charcoal, Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models are the three mostly used isotherm models. Surface phenomena play significant role to adsorb the metal ions over the active center site (functional groups/pores) of the adsorbent (Desta *et al*., 2013). In the present work the adsorption experiments were conducted in batch mode. There are generally two modes of adsorption process, one is the batch mode and the other one is the continuous mode of adsorption experiments. The batch mode is suitable for low scale whereas the continuous mode is for larger scale such as industrial scale. The main motivation behind this present study is to investigate the locally produced wood charcoal as an effective alternative adsorbent concerned with health and to solve the environmental problem so that it would be more valuable for the community. Therefore, the present study was performed to evaluate wood charcoal as an adsorbent for the removal of Pb metal ions from the aqueous solution. Although activated carbon is a preferred adsorbent, widespread use is restricted by its high cost of production (Pan *et al.*, 2009).

Charcoal has been used from ancient time to remove impurities from water. In this study the adsorption process is carried out using locally available wood charcoal (mixture of Nahor (*Mesua ferrea*), Walnut (*Juglans regia*) and Katus (*Castanopsis hystrix*) found in Mizoram. In Mizoram wood being the most important, readily available and regularly used timber, has a lot of important uses in day to day life. From these woods, charcoal is made by local people for their household activities and some are made for commercial purposes as well. Adsorption phenomena usually depends on many parameters such as adsorbent dose, temperature, pH, metal concentration, time. The main motivation behind this present study is to investigate the locally manufactured wood charcoal as an effective alternative adsorbent concerned with health and to solve the environmental problem, so that it would be more valuable for the community. Many studies have been done to investigate the efficiency of adsorbent and subsequently finding cheap and better substitutes for the adsorbent. Herein, the efficiency of raw charcoal was analyzed for the removable of HM from the aqueous solution. The present study focuses only on the raw charcoal (mixture of Nahor (*Mesua ferrea*), Walnut (*Juglans regia*) and Katus (*Castanopsis hystrix,*) to remove toxic heavy metal as Pb ions from the aqueous solution. Therefore, by knowing the novelty of the charcoal materials and its characteristic feature, Mizoram Wood charcoal are expected to be a potent adsorbent for the removal of lead (Pb) from aqueous solution.

1.1.The objectives of the present work are as follows:

- To evaluate wood charcoal as an adsorbent for the removal of Pb ions from aqueous solution by systematic evaluation of the parameters involved such as pH, adsorbent dose, heavy metal concentration and time.
- For further study; Freundlich and Langmuir adsorption isotherms shall be studied and pseudo-first-order, pseudo-second-order, models shall be checked

for the isotherm and kinetics of adsorption to understand the mode of adsorption and rate of adsorption during the experiment using raw charcoal (mixture of Nahor (*Mesua ferrea*), Walnut (*Juglans regia*) and Katus (*Castanopsis hystrix*) as an adsorbent. Besides that, standard change in Gibb's free energy of adsorption at constant temperature shall be checked.

2. Review of literature

Water is the important component that help living organisms to sustain life on earth. There are various sources of water such as lake, pond, river, sea, ground water, etc. To have a clean source of water has become a matter of utmost importance throughout the world. But due to the growing global population, the number of industries in the world is increasing day by day. The water from those industries have many pollutants which are not treated properly while discharging into the environment or they have less effective treatment plans for these waste waters. Thus, to get surplus and clean water, one of the methods is water harvesting which is not that feasible and effective in all parts of the world. The other one is the treatment of the waste water which is more practically applicable at different places. So now a days more emphasis is given on the treatment of waste waters (Pathan & Bose, 2018; Azimi *et al.*, 2016; Chong *et al.*, 2010)**.**

Heavy metals are those elements which have density higher than that of water and they show toxicity even at very low concentrations. In contrast to the name given to them as heavy metals, their toxicity has very less to do with their density rather than their chemical property. (Duruibe *et al.*, 20070). Heavy metals are a special group of pollutants which are bio refractory, toxic (El-Maaty *et al.*, 2014) to different living organisms as they have property of bio accumulation. (Jobby *et al.*, 2018). They are found in the purification system of waters in the waste water treatment plants as they are capable of showing dreaded effects in health, environment and other living organisms (Altun & Kar, 2016). Heavy metals are liberated into the atmosphere from broad range of anthropogenic and natural sources with the magnitude of pollution caused by anthropogenic sources being greater by one or to folds compared to natural sources. (Nriagu, 1988; Liu et al., 2012).

When HMs are consumed by a body above the recommended level, it becomes lethal to the body which is known to be the biotoxic effect of that HM. Each HM has their own specific toxicity and symptoms of it. But in a general sense, there are some common symptoms which are associated with HM poisoning. They are diarrhea, vomiting, nausea, paralysis, problems related to stomach i.e. gastrointestinal diseases, red- rusted stool color, depression, pneumonia, tremor, etc. The toxicity may be of various degree and of different types. In terms of degree, it may be chronic, subchronic and acute. Whereas, in terms of types, it may be neurotoxic, mutagenic, teratogenic or carcinogenic, depending upon the type and form of HM (Duruibe *et al.*, 2007).

Heavy metals have been found to affect various biospheres either it is land, air or water (Jobby *et al.*, 2018). Due to its profound effect in these areas, much concern has been made in their removal (Erdem *et al.*, 2013; Abou *et al.*, 2014). Primarily when these pollutants are liberated in the environment from various anthropogenic sources, they get incorporated and starts to accumulate in the food-chain pyramid at different levels (mentioned in Figure 1). It causes serious health problems in living organisms, with humans being the most affected one at the top of the pyramid as it collects the metal ions in concentrated form (Deliyanni *et al.*, 2015).

Lead is one of the ubiquitous heavy metal found in nature.it can be harmful if the concentration exceeds the normal level (Gupta *et al.*, 2001; Dursun & Pala, 2007). Among the other heavy metals, lead has found to occur more often in waste water

(Morosanu *et al.*, 2017). Lead is a kind of heavy metal which is not that essential but is toxic even at very low concentrations and has a profound effect in human health as it enters into the food chain by various biogeochemical cycles. The biogeochemical cycle of Lead is found to be affected by humans to great extent. It is found in most of the environmental pollutants. (Komárek *et al.*, 2008; Momčilović, *et al.*, 2011). According to studies of Liu *et al*. (2011), the calculated excess ratios of lead isotopes showed that lead poisoning was found to be maximum from Russia and Europe (Liu *et al.*, 2012).

Lead in its inorganic form is absorbed in the body usually through inhalation or by uptake of food and water containing higher levels of HM concentration (Duruibe *et al.*, 2007). Pb being a teratogenic toxin, causes abnormalities in the developmental process of the body which is prevalent highest in case of children. Other adverse effect of lead poisoning are the inhibition of the process of hemoglobin synthesis, kidney and liver problem, cardiovascular diseases, problems of the joints in the body, problems related to reproductive system, psychosis, etc. It mainly affects the nervous system of the body by targeting the two most important components of nervous system, the Central Nervous System or CNS and other one being the Peripheral Nervous System or PNS (Duruibe *et al.*, 2007).

Pb has been found to exist in two forms, organic and inorganic. The organic form is found to be mostly associated with the central nervous system related diseases whereas the inorganic form of Pb is found to be related to the gastrointestinal problems, peripheral nervous system problems and also the central nervous system problems (Lenntech, 2004). The grey matter development in the brain which is responsible for the storage of memory and also determines the intelligence quotient in an individual is hampered by Pb poisoning.

Lead is found to affect the central nervous system, gastrointestinal system and organs such as liver, kidney, etc. It is associated with many diseases either directly or indirectly. Lead poisoning may be associated with diseases such as nephritic syndrome, encephalopathy, anemia, hepatitis, etc. (Momčilović *et al.*, 2011). Lead shows toxicity against multiple organs which may lead to various diseases. In case of albino rat’s recent studies showed that Pb shows toxicity in the testicles (Offor *et al.*, 2017). As lead is a multi-organ toxicant, toxicity of lead can be measured by testing the level of lead in the blood and also in the bones by using instruments like K x ray fluorescence (KXRF). Lead poisoning can be prevented by removing the possible sources of lead (Shukla *et al.*, 2018).

The enamel paints are found to contain lead at concentrations above 1,40,000 ppm (Shukla *et al.*, 2018). Human activities such as the use of gasoline containing lead, combustion of coal, use of fertilizers containing lead, incineration of wastes containing lead, use of batteries, various industrial activities such as extraction of metals, etc. has been the culprit for lead poisoning. It has been found that the primary recipient of lead in the environment from various sources is the atmosphere and the contamination is one to two times greater in terms of anthropogenic sources compared to the natural sources of lead poisoning. The atmospheric contamination of lead is assumed to be started nearly 5000 years ago from south- west Asia when there was no efficient technologies and methods to extract metals (Komárek *et al.*, 2008). Drainage from acid mines, burning of fossil fuel, sulfide ore smelting are the sources which leads to pollution of water bodies like lakes, rivers, streams, ponds, etc.

The provisional guideline value for lead in drinking water according to World Health Organization (2017) was 0.01mg L^{-1}. Lead is one of the most poisonous, heavy metal in our environment, the reports of Agency for Toxic Substance and Disease Registry (ATSDR), listed lead as the second most hazardous materials, polluting our environment. (Chatterjee *et al.*, 2016). According to USEPA, the permissible limit of lead in drinking water is 0.015 mg L^{-1} (Momčilović, *et al.*, 2011) and according to National Agency for Food and Drugs Administration and Control (NAFDAC) (Duruibe *et al.*, 2007). The permissible limit of lead in drinking water according to Indian Standard Institution is 0.05 mg L^{-1} and for water on land is 0.1 mg L^{-1} ((I.S.I. Specification IA: 2490, 1982; I.S.I. Specification IS 10500, 1991).

Recently, water purification has been carried out with several attempts to remove the contamination of heavy metals at a cost effective, eco-friendly way, avoiding the use of harmful chemicals (Pathan and Bose, 2018). Figure 2 illustrate the diagrammatic representation of different processes involved in the removal of heavy metals. Tracing of lead pollution has been done efficiently by the analysis of lead isotopes and their ratios. It has been found to be an important tool the analysis of lead in pollutants (Komárek *et al.*, 2008; Liu *et al.*, 2012). Zinc and Calcium deficiency may increase the adsorption of Pb in the human body (Duruibe *et al.*, 2007).

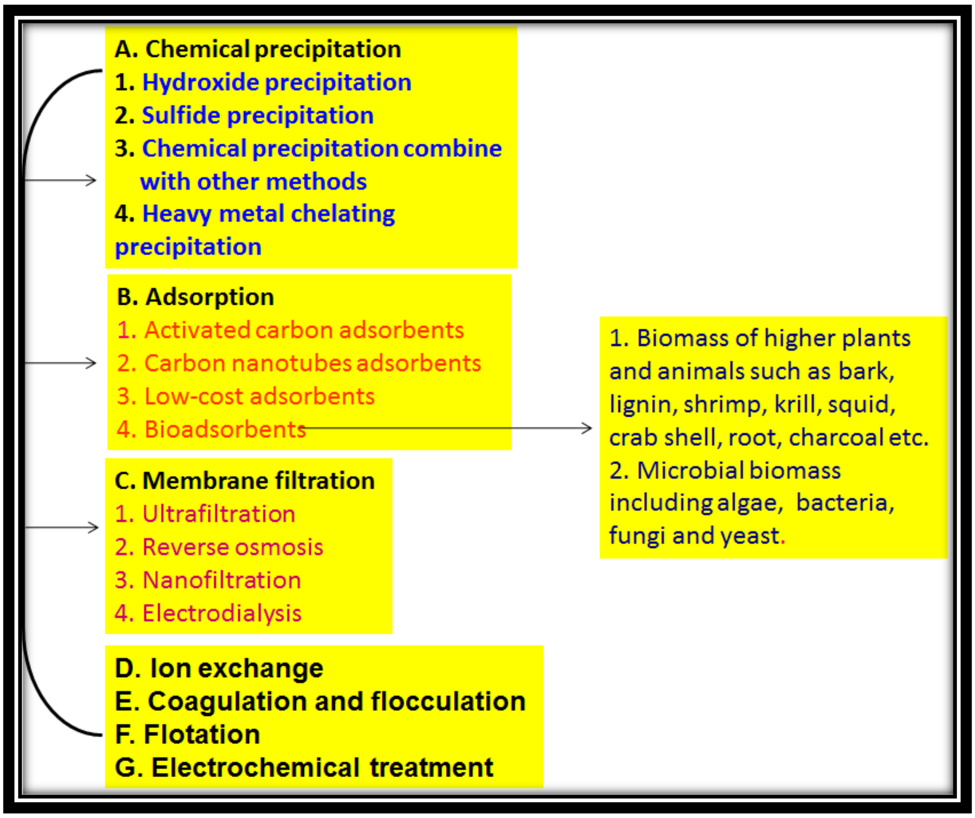

Figure 2. Diagrammatic representation of different processes involved in the removal of heavy metals.

Between the different methods used in the treatment of heavy metal pollution, the adsorption method is found to be most effective and as an adsorbent, activated carbon has been used widely due to its high efficiency in capturing the heavy metals (Chand *et al.*, 1994). Even though the heavy metals such as lead, chromium, cadmium, nickel, etc. are found naturally in the earth's crust, their trace amounts are enough to be toxic to human beings (Karnib *et al.*, 2014). Li *et. al.*, 2008 have found that the separation of Pb (II) have higher competence strength as compared to other toxic metal ions e.g. Cu (II) and Cr (III) from the water solution using peanut husk adsorbent. Their finding data using batch method at different pH and initial concentration (metal ions) revealed that adsorption was low or weak at acidic solution while adsorption is fitted with Freundlich isotherm and Langmuir. The adsorption order using peanut husk adsorbent is found to be as Pb (II)> Cu (II)> Cr (III). Organic pollutants such as metal containing dyes from industrial layouts, phenolic wastes from wastewaters, and heavy metal containing wastes from various sources are found to be removed more efficiently by the biosorption process. Mostly agricultural derivatives and plant based biosorbents has been used by many workers in their research. The use of these materials as biosorbent has many advantages over other adsorbents. It is due to the reason that they are easily available, cost effective, less pollutive, they need not be maintained in an aseptic condition, by the process of desorption separation or recovery of metal ions from the adsorbent, due to which adsorbent can be recycled and reused, formation of biological as well as chemical sludge is lowered cleaning of which itself is a tedious job (Aksu, 2005).

Various biological materials such as *Melocanna baccifera* Roxburgh (bamboo) charcoal (Lalhruaitluanga *et al*., 2010), bromelain immobilized on activated charcoal (Chatterjee *et al*., 2016), activated carbon made from date pits (Abdulkarim *et al*., 2003), activated charcoal prepared from tamarind wood (Acharya *et al*., 2009), activated carbon prepared using cow bone (Cechinel *et al*., 2013), charcoal prepared from fish bone (Wang *et al*., 2017), activated carbon made from biomass of plant *Euphorbia rigida* (Gercel *et al.*, 2007), activated charcoal made from lignocellulosic materials (Largitte *et al*., 2015), activated carbon derived from Eichhornia, an aquatic weed (Shekinah *et al*., 2002; Wakil *et al*., 2014), activated charcoal prepared from rice husk (Youssef *et al*., 2014), activated carbon prepared from pine cone (Momcilovic *et al*., 2011), rapeseed biomass (Morosanu *et al*., 2017), biomass of *Sargassum filipendul* (Verma *et al*., 2016.) etc. have been used for the adsorption of Pb. Debajit Kalita and

S.R Joshi have reported the metallophilic bacteria, *Pseudomonas* sp. W6 isolated from hot water spring of North-East India is capable of bioremediating Pb (II) by producing exopolysaccharide (EPS). This EPS produced by this species made it capable of binding with lead with high affinity (Kalita and Joshi, 2017)

Williams *et al.,* in their study, "Comparison Between biosorbents for the removal of metal ions from aqueous solutions", have compared the bio- absorptive property of the waste from sea weed which was dealginated with alginate fibre and linseed fibre waste (Williams *et al.,* 1998). They have observed the adsorptive property of these adsorbents for the removal of heavy metals such as copper, cadmium and nickel separately and also in the mixed solution. They have found that the alginate fibre were most successful in removing the heavy metals and cadmium being the utmost efficiently removed metal amongst others. Additionally, studies revealed that after the biosorbent reaches their maximum absorptive capacity, their absorption becomes selective. In this study, copper was found to be preferred metal rather than cadmium and nickel ions (Williams *et al.*, 1998). Vikrant Sarin and K.K Pant have used activated charcoal rise husk, eucalyptus bark (EB) in their study "Removal of chromium from industrial waste by using eucalyptus bark" for the removal of chromium (Sarin and Pant, 2006). They found that the maximum removal efficiency of cadmium was seen in case of eucalyptus bark (EB) with the removal percentage being 87.4%. Figure 3, depict schematic representation of the uses of phytotechnology in environment and human welfare.

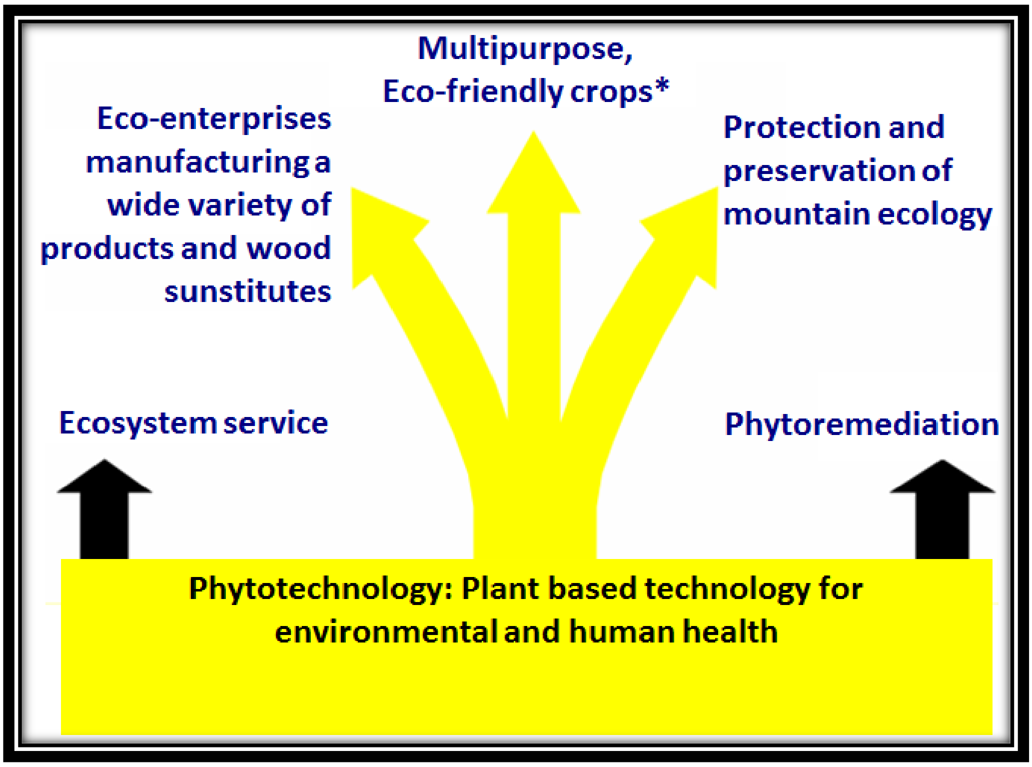

Figure 3. Schematic representation of the uses of phytotechnology in environment and human welfare.

3. Material and Method

3.1. Chemical used:

The Pb (II) stock solution was made from lead nitrate; $Pb(NO_3)_2$, analytical grade) supplied from Merck, India, Ltd., The pH of the solution was adjusted using 0.1 N $NaOH$ and 0.1 N H_2SO_4 solutions. All the solutions were prepared using double distilled water having specific conductance 1–2 μS cm^{-1} at room temperature.

3.2. Methods:

3.2.1. Production of wood charcoal (adsorbent)

Wood charcoal was produced by thermal decomposition inside the charcoal kiln. The oxygen supply inside the charcoal kiln was minimal and maintained to prevent burning to ash and the woods are supplied in 2 to 3 feet depends on the kiln size which can accommodated. Therefore, under the control of oxygen supply, charring of the wood occurs. The charring period take place 2 to 4 hr. These low-cost charcoals are available in the market and mainly used for domestic purposes by the local people. Charcoal was milled with a blender and sieved to particles of 100 mesh screen.

3.2.2. Preparation of lead nitrate (adsorbate)

Stock solution of Pb (1000 mg L^{-1} or 1 ppm) was prepared by weighing 1.5985 g of lead nitrate, $Pb(NO_3)_2$ per liter water in volumetric flask. Initial solutions with different concentrations of Pb (II) were prepared by proper dilution from stock solution. Standard solution of Pb (II) was used for calibration in atomic absorption spectrophotometer.

3.2.3. Batch mode adsorption experiments

The adsorption of Pb (II) ions onto charcoal was investigated in batch mode adsorption process. All batch experiments were carried out in 250 mL conical flasks containing 100 mL of metal solution.

In batch culture experiments, the various factors like effect of pH, metal concentration, time and adsorbent dose were carried out for the study of adsorption of the heavy metal by wood charcoal.

The percentage of adsorption (Ad %), quality of Pb adsorbed at t time (q_t) and equilibrium (q_e) on charcoal can be calculated using the following equations:

$$Ad\% = \frac{(c_0 - c_e)}{c_0} \times 100 \quad (1)$$

$$q_t = \frac{(c_0 - c_t)}{m} \times 100 \quad (2)$$

$$q_e = \frac{(c_0 - c_e)}{m} \times 100 \quad (3)$$

$Ad\%$ is the percentage of Pb adsorption, q_t (mg g^{-1}) are Pb adsorbed on charcoal at time *t*; c_0 (mg L^{-1}) is initial Pb concentration, q_e (mg g^{-1}) are the Pb adsorbed on charcoal at equilibrium, c_e (mg L^{-1}) are equilibrium Pb concentration, c_t (mg/L) are Pb concentration at time *t* and *m* (g) is the mass of adsorbent dose (Liu *et al.*, 2012).

3.2.4. Effect of pH

The effect of pH on the sorption capacity of wood charcoal for Pb (II) ions removal was evaluated within the range of 2.0–7.0 pH (with an interval of 1 pH). The pH of each metal ions solution was adjusted to the required pH value by using 0.1 N

H_2SO_4 or 0.1 N $NaOH$. Then 0.1 g of dried adsorbent was added into the metal ions solution. The reaction mixture was shaken for 6 hr at 150 rpm in a shaking incubator (Model: NBS Bench top refrigerated incubator, INOVA 42 New Brunswick) at temperature 29 ^{o}C to attain adsorption equilibrium. The uncertainty in the measurement of temperature was ± 0.2 ^{o}C. Solution pH was measured by a digital pH meter (Eutech, Model No. pH 510).

3.2.5. Effect of Adsorbent dose

The effect of adsorbent dose was evaluated in the range of 0.1–0.5 g for the removal of Pb (II) having concentration of 10 ppm. The reaction mixture was shaken for 6 h at 150 rpm and 29 ± 0.2 ^{o}C. A high precision electronic balance was used for weighing the adsorbent (Kerro, Model No. BL2203K).

3.2.6. Effect of contact time

The rate of adsorption was evaluated from 15–360 min and 0.1 g of dried adsorbent was added into the metal ions solution. The reaction mixture was shaken for desired time period at 150 rpm, 29 ± 0.2 ^{o}C.

3.2.7. Effect of initial metal ions concentration

The effect of initial metal ions concentration of Pb (II) was evaluated from 10 to 30 mg L^{-1} with fixed adsorbent (0.1 g). Likely, the reaction mixture was shaken for 6 hr at 150 rpm, 29 ± 0.2 ^{o}C.

3.2.8. Detection of various concentration of Pb (II) ions

At the end of all the batch mode experiments, the solutions were separated from the adsorbent by centrifuging (Model: Refrigerated Centrifuge 5810R, 5810R Eppendrof) at 10,000 rpm for 8 min. The concentrations of Pb in the solutions were analyzed using flame atomic adsorption spectrophotometer (AAS) (Model: Shimadzu 7000). The wavelength (λ_{max}) of 193.7 nm was used for the analysis of the Pb (II) solution. The instrument was calibrated with a standard solution within a linear range and a correlation coefficient (R^2) of 0.995 to 1.0 was obtained. In order to reproduce the results, the experiments were conducted in triplicate and the average values were used for the data analysis.

3.2.9. Functional group analysis

FTIR (Fourier Transform Infra-Red) spectroscopy technique was carried out using Shimadzu model- IRAAffinity-1S, 00703 to analyze the nature of adsorbent in absence/presence of Pb (II). FTIR were run within the range of 400- 4000 cm^{-1} in order to know the functional groups and internal binding that are responsible for the attachment of the heavy metal (Pb) on to the surface of the adsorbent.

3.2.10. Isotherm studies

Adsorption on solid surfaces is one of the most powerful techniques for reducing pollutants in industrial and natural systems (Azizian & Bashiri, 2009). According to the Langmuir isotherm adsorption equation, the monolayer approach defined the adsorption as the adhesion or bonding of adsorbates like liquids, fluids or gases on the surface of solid or liquid as an adsorbent by forming the thin film or layer over it. The process can be either chemical or it can be physical. The chemical bonding was found to be stronger than the physical bond and the chemical bound could be in single or multiple layers. The separation of adsorbate from the adsorbent can be done by the process of desorption. There are several factors influencing the adsorption process out of which, the temperature is the most influential factor. The study is usually carried out at a constant temperature using different models of adsorption called adsorption isotherms. There are various adsorption isotherms out of which the most frequently used are Langmuir adsorption isotherm (Langmuir, 1916), which is used to study the monolayer adsorption. Another is Freundlich adsorption isotherm, which is usually applied to study monolayer as well as multilayer adsorption. Similarly, there are other isotherm as well such as Dubinin-Radushkevich isotherm model (Dubinin, & Radushkevich, 1947) which can be used in the study.

According to Irving Langmuir, the process of adsorption takes place in monolayer and it takes place on a homogenous surface. The adsorption of adsorbate takes only at restricted sites of the adsorbent surface and at the time of saturation, all the localized sites are occupied by the adsorbate. Since the process is of a monolayer type, only one atom or molecule of the adsorbate can attach on to a particular adsorbent site. No interaction takes place between the adjacent atoms or ions of the adsorbate because the surface on which they are attached is homogenous in terms of energy (Czepirski, *et al.*,2000)

The distribution of the adsorbate molecules between the liquid phase and the solid phase and the uptake capacity of Pb (II) onto the adsorbent was studied based on the Freundlich isotherm (Freundlich, 1907), using the equation 4.

$$log(q_e) = \log K_f + \left(\frac{1}{n}\right) log C_e \qquad (4)$$

Pb (II) uptake capacity by the adsorbent was also studied by Langmuir isotherm (Langmuir, 1916) using equation (5).

$$\frac{C_e}{q_e} = \left(\frac{1}{q_{max} \quad b}\right) + \frac{C_e}{q_{max}} \qquad (5)$$

where b is the parameter corresponding to adsorption energy and its unit is mg^{-1}. q_{max} (mg of solute g^{-1} of adsorbent) is the maximum adsorption capacity at complete coverage of monolayer.

3.2.11. Kinetics studies

Pseudo-first-order kinetics:

To explain the kinetics of adsorption and to investigate the mechanism of biosorption, pseudo-first-order Lagergren model (Lagergren, 1898) can be applying for solid or liquid systems for adsorption process which is given by equation 6.

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

Applying log both side;

$$log(q_e - q_t) = logq_e - {k_1t}/{2.303} \qquad (6)$$

where q_e (mg g^{-1}) is amount of Pb adsorbed on charcoal at equilibrium, q_t (mg g^{-1}) is amount of Pb adsorbed on charcoal at time t and k_1 (min^{-1}) is the rate constant for the biosorption. The assumption of pseudo-1st-order model is based on the rate which is directly proportional to the number of unoccupied sites.

Pseudo-second-order kinetics:

Similarly, Pseudo-second-order kinetics or Ho and Mac Kay's pseudo-2nd-order kinetics model (Ho and McKay, 1999) can be used to study the nature of adsorption and this model assumed that the rate of adsorption is proportional to the number of squared unoccupied sites. This can be study by using following equation 7.

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \qquad (7)$$

where k_2 is the rate constant for the pseudo-second-order adsorption kinetics and other terms are mentioned in previous equation 6.

4. Results and discussions

4.1. Effect of pH

The pH is one of the important factors that affects the adsorption of heavy metal ions over the surface of adsorbent (Huang *et al.*, 1990; Matheickal *et al.*, 1999). In present work, the effect of pH on the adsorption of Pb (II) onto the wood charcoal are observed at 2 to 7 pH (with an interval of 1) containing of 10 ppm as the initial metal ions concentration and 0.1 g as the adsorbent dose keeping constant temperature as 29 °C. The solutions of 10 ppm are studied at all pH range and the adsorption was clearly observed except at pH 7. It is worthwhile to mentioned that the solutions were clear up to pH 6 and precipitation of Pb (II) ions begins from pH 7. This is due to the precipitation of lead hydroxide at pH 7 and similar results have been reported by several researcher on the precipitation of Pb (II) solution at pH 7 and at higher pH range (Lalhruaitluanga *et al*.,2010). Thus, the effect of pH on the adsorption was not carried out above this pH. Initially, optimization on the pH studies have been carried out and Figure 4 (a) show that the maximum adsorption of Pb ions is observed at pH 6. Therefore, rest of the experiments are carried out to investigate the effect of various factors by choosing pH at 6 (Erdem *et al.*, 2013).

At lower pH, Pb ions are believed to have a competition with the presence of hydrogen ions (H^+) and as a result, the electrostatic interaction of repulsion between the positive Pb (II) ions and adsorbed H^+ ions which further lower the attachment or the adsorption of Pb (II) ions on to the charcoal (adsorbent) surface (Comte *et. al.*, 2008). To support the obtained result extracted from the Figure 4 (a), furthermore, pH_{PZC} calculation have been carried out. The pH_{PZC} value of adsorbent (0.1 g charcoal) has been determined from the plot of change in pH of metal ions solution (10 ppm) taken after 6 hr of incubation at 29 °C versus its initial pH value. Figure 4 (b) shows that the pH_{PZC} value of studied adsorbent is found to be at pH 2. The pH also determines the charge of the active site of the adsorbent due to which protonation as well as deprotonation occurred at the surface of the adsorbent. Thus, pH determines the interaction of the adsorbent with the adsorbate. The pH_{PZC} value is a pH at which the surface charge of the adsorbent is zero and which is determined from pH value at which the change in pH is minimum as shown in Figure 4 (b). This means that the overall surface charge of the adsorbent at this point is neutral. From the idea of pH_{PZC}, the mechanism of the ionization process of the functional groups present on the adsorbent surface and their interaction with the adsorbates can be assumed. It has been found that at pH value greater than the pH_{PZC}, the surface of the adsorbent is negatively charged so this may lead to the adsorption of cationic adsorbate or cationic pollutants more efficiently whereas at pH value lower than the pH_{PZC}, the surface of the adsorbent is positively charged and therefore, this may lead to the adsorption of anionic adsorbates (Fiol and Villaescusa, 2009). The surface of the charcoal below the pH_{PZC} value will be more positively charged and do not allow the Pb ions to attach onto them. This way the maximum adsorption is seen at the higher pH values specially at pH above the pH_{PZC} value where the charcoal surface possesses more negative charges and favor the binding of the positive Pb ions.

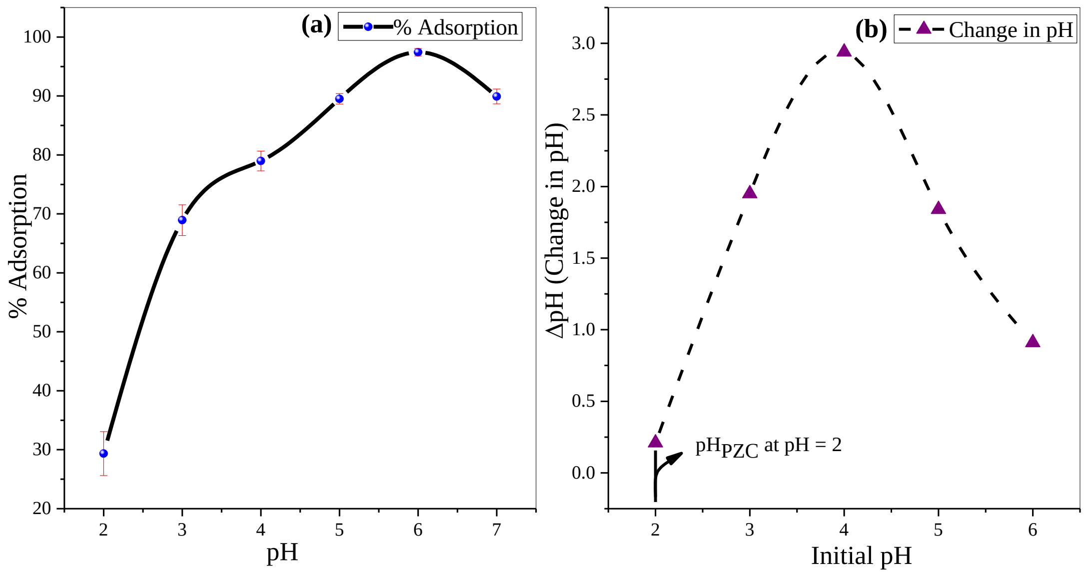

Figure 4. **(a)** Effect of pH on the adsorption percentage of Pb (II) ions and **(b)** determination of pH_{PZC} from the plot of change in pH against initial pH.

4.2. Effect of adsorbent dose

Adsorbent dose is one of the factors taken in the study of adsorption and removal of heavy metals. The effect of adsorbent dose (i.e. charcoal) also plays an important role in the adsorption of Pb from the aqueous solution. The present study shows that different doses of adsorbent ranging from 0.1–0.5 g/100 mL has played a vital role in the adsorption. The adsorption of Pb ions solution (10 ppm) are conducted at constant pH 6 and the temperature (29 °C). The results showed that as the concentration of the adsorbent increases, the percentage of adsorption also increases which can be seen in the Figure 5. This may be due to the fact that as the concentration of adsorbent increases, there will be more surface area for the heavy metals for their adsorption. The maximum adsorption has been observed with adsorbent dose of 0.5 g and its corresponding adsorption percentage is found to be 99.56% which is noted to be highest among all studied doses of adsorbent.

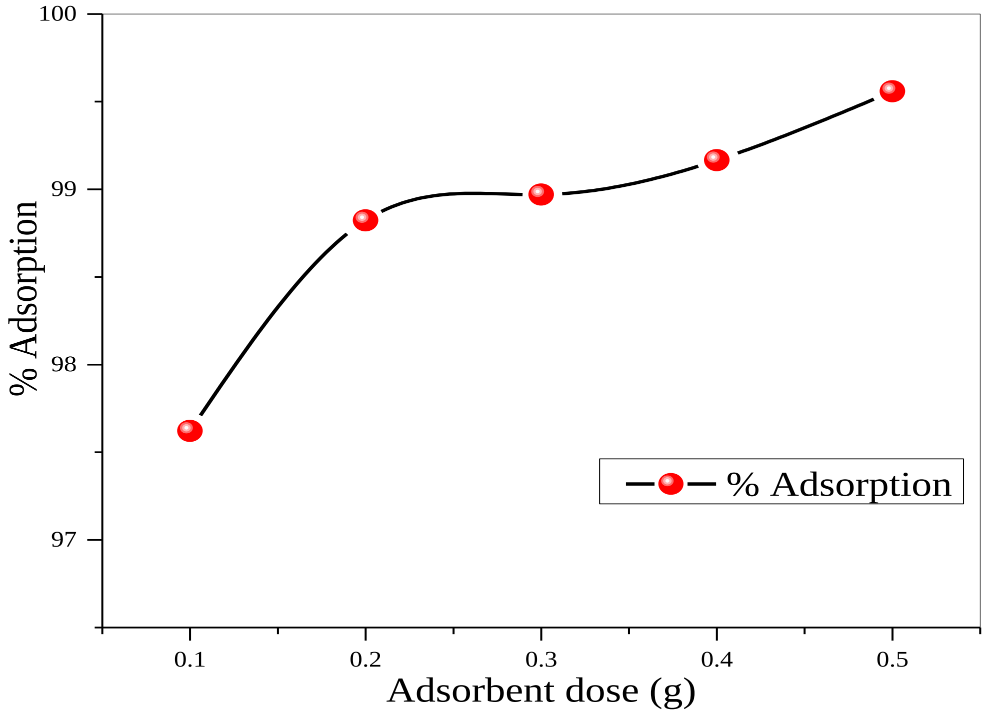

Figure 5. Effect of adsorbent dose on the percentage of adsorption of Pb (II) ions at constant pH and metal ions concentration.

The sharp increase in the adsorption is clearly noted from the optimized 0.1 g of adsorbent dose to 0.2 g of adsorbent dose. However, such sharp increase in adsorption of Pb ions has not been seen from 0.2 g of adsorbent dose but thereafter, gradual increase in adsorption take place with less increments of adsorption up to 0.5 g of adsorbent dose.

4.3. Effect of initial metal concentration

The effect of initial metal ions concentration is also an important factor in case of adsorption studies. In this section, the study has been carried out with different initial metal ions concentration ranging from 10–30 mg/L (i.e. 10 to 30 ppm) in presence of fixed adsorbent dose (0.1 g) at a particular pH 6, temperature, 29 °C and the contact time as 6hr. The results from the present study showed that the increase in concentration of Pb ions has opposite effect on the percentage of adsorption i.e., with the increase in the concentration of Pb ions there is decrease in the percentage of adsorption. The obtained result is illustrated in Figure 6. Such observation is due to the presence of fixed surface area of adsorbent for studied concentrations of Pb ions. The available surface area decreases with increase in concentration of Pb ions and therefore, the remaining surplus metal ions do not have sufficient surface area for the adsorption. Due to this fact, there are more Pb ions in the solution and the percentage of adsorption decreases as the concentration of Pb ions increases. This can also be explained by the fact that the experiment followed through Langmuir mode of adsorption which may responsible to mask the surface charge of adsorbent due to the formation of multilayers onto the surface of the adsorbent. Therefore, the adsorption of metal ions begins to decline slowly from 20 ppm to 25 ppm and it almost remain constant up to 30 ppm metal ions concentration.

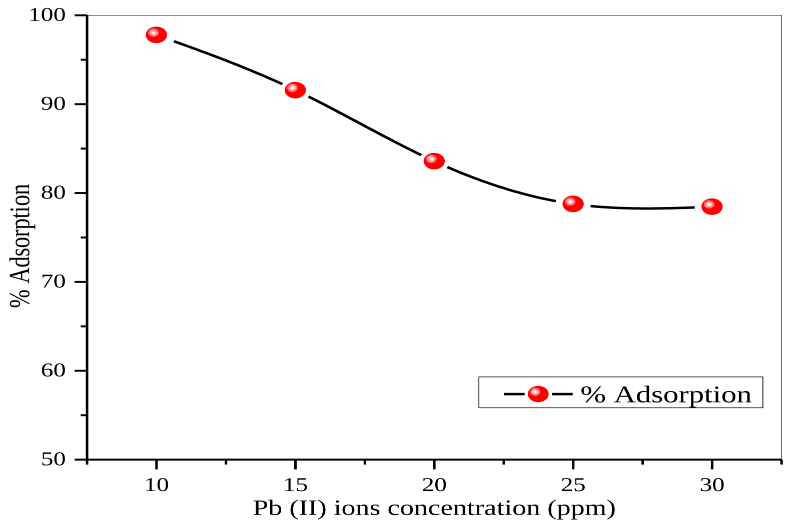

Figure 6. Effect of Pb (II) ions concentration on the percentage of adsorption in a fixed adsorbent dose at constant pH.

4.4. Effect of Time of Contact

Time factor or time of contact is the primary element in the adsorption process to make the efficient adsorbent in industrial application. Effect of time of contact has been performed within the time period ranging from 15–360 min taking 10 ppm of Pb ions concentration at fixed pH 6 and temperature as 29 °C throughout the process. The experimental results showed that as the contact time increases, the percentage of adsorption increases but after certain intermediate range of time period, the percentage of adsorption becomes almost constant which is shown in the Figure 7. Initially, the adsorption of metal ions is abruptly enhanced from 15 min to 60 min of contact time. Thereafter, increase in the percentage of adsorption become slow and remain almost steady reaching maximum adsorption percentage (98.14 %) at the interval of 240 min. However, adsorption percentage appeared to be very slightly decreased after 240 min and it attained 97.16 % with maximum time of contact (360 min). Such observation lead to the conclusion that as the time of contact increases, adsorption of Pb ions facilitated initially till the equilibrium is attained. As the time of contact passes, available surface area gets condense due to the surface occupied by the Pb ions and further adsorption allow to attain the equilibrium between the adsorbed ions and non-adsorbed ions on the surface of adsorbent. Therefore, by passes of time after reaching an equilibrium, adsorption and desorption take place together.

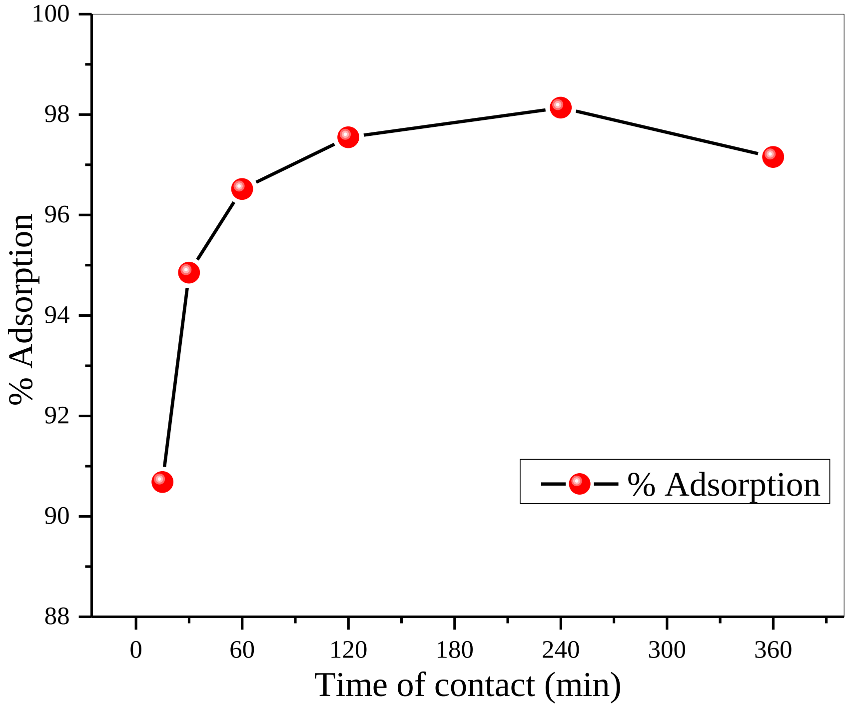

Figure 7. Effect of time of contact on the percentage of adsorption of Pb (II) ions.

4.5. Analysis of FTIR results

Flourier transfer infrared spectroscopy (FTIR) techniques is considered as a powerful technique to analyze various organic or inorganic functional group of the materials. This technique has been used to know the representative functional groups present on the surface of charcoal responsible for the Pb (II) ions attachment or binding. In order to get the information about the stretching and bending vibrations shown by the functional groups, the adsorption spectra for the adsorbent were run between the 40–4000 cm^{-1} range. Figure 8 show FTIR spectra of solid adsorbent for (a) raw charcoal, (b) charcoal loaded with 20 ppm Pb (II) solution and (c) charcoal loaded with 30 ppm Pb (II) solution. Figure 8 contain two sets of spectra; (I) showing spectrum of ‘b’ shifted by 20 scale units and spectrum ‘c’ is shifted by 40 scale units along the y axis (% transmittance) whereas spectra (II) showing a comparative representation of spectra without shifting in scale along y axis. From the Figure 8 (II), it is clearly observed that after treatment of raw charcoal with different concentration of Pb (II) solution, there are change in the % transmittance of raw charcoal. Thus, these results revealed the interaction of the present functional groups over the surface of raw charcoal with Pb (II) ions.

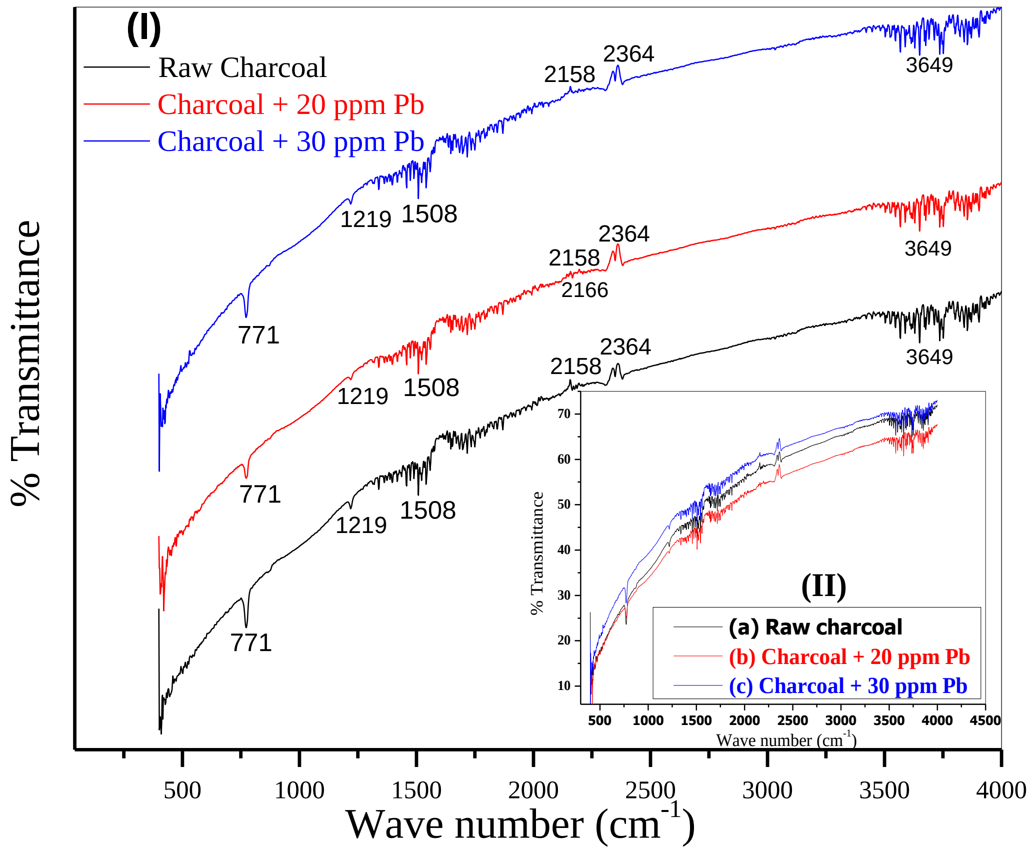

Figure 8. (I) FTIR spectra of **(a)** raw charcoal, **(b)** raw charcoal loaded with 20 ppm Pb (II) ions solution and **(c)** raw charcoal loaded with 30 ppm Pb (II) solution where spectrum (b) and (c) are shifted by 20 and 40 scale units along y axis respectively; **8 (II)** comparative illustration of spectra without shifting in scale along y axis.

A significant peak is observed at a position of 771 cm^{-1} in all spectra (a), (b) and (c) which could be attributed to the C–H stretching vibration. The relative intensity of the peak at 771 cm^{-1} is noted to be slightly more in spectra (a) as compared to (b) and (c). However, this functional group corresponding at 771 cm^{-1} generally is not considered for the specific vibration due to the complex interaction occurring below the 1000 cm^{-1} region as it falls under 'fingerprint zone' (Yazic et al., 2008). Similarly, a peak at 1219 cm^{-1} can be attributed to C–N stretching, C–H bending, C–O stretching vibrations which is found to decrease relatively in (b) and (c) as compared to (a). The peak at a position of 2158 cm^{-1} corresponds to RN–C group, is found to be decreased in case of (b) and (c) when compared to (a), but in case of (b) the peak is shifted to a position 2166 cm^{-1}. The peak at 2364 cm^{-1} position which is associated with phosphene group (P-H sharp), is found to increase in case of (b) and (c) as compared to (a). This may be due to the fact that the corresponding functional groups may help in the binding of Pb ions on to the surface of the adsorbent. The significant peak at position 3649 cm^{-1} to 3584 cm^{-1} broad band (Lalhruaitluanga *et al.*, 2010) and peak at 1508 cm^{-1} corresponded to –OH stretching vibration and N≡O group on the surface of the adsorbent respectively. The band from 2175–2140 cm^{-1} represented S−C≡N stretching whereas 1550–500 cm^{-1} corresponded N≡O stretching. Figure 9 show a schematic representation of charcoal surface with some functional groups and its porosity.

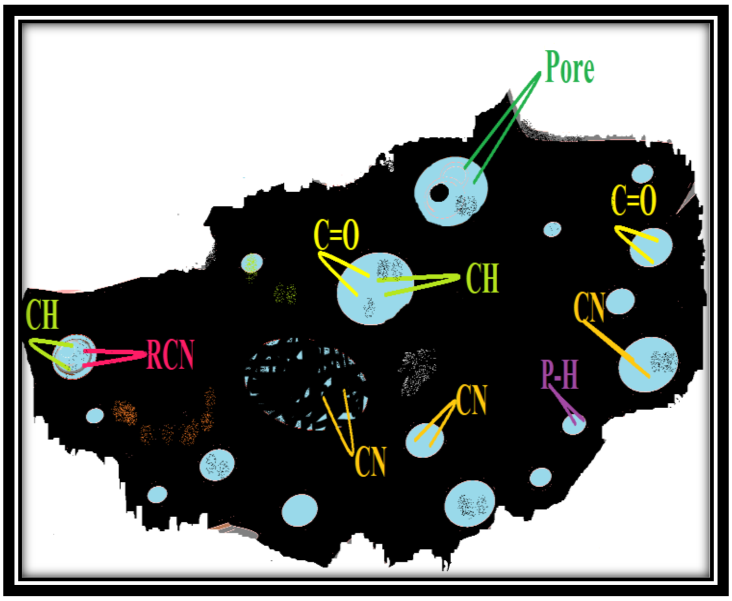

Figure 9. Schematic representation of charcoal surface with some porosity and functional groups.

4.6. Isotherm studies

4.6.1. Langmuir isotherm adsorption:

Adsorption isotherm is a curve which can provide a relationship between the amount adsorbed by the adsorbent and the concentration or amount of adsorbate at fixed temperature. Isotherm studies were carried out using two empirical models such as Langmuir and Freundlich isotherm (next subsection 4.6.2) for the analysis of the data obtained at equilibrium with varying initial concentration of Pb (II) ions. This study has been done by taking Pb (II) solution between 10–30 ppm (with an interval of 5 ppm) in presence of fixed amount of adsorbent dose (0.1 g) at pH 6 and constant temperature of 29 °C. Firstly, Langmuir isotherm adsorption studies were attempt to understand the nature of adsorption of metal ions onto the surface of the raw charcoal. According to Langmuir adsorption isotherm, the surface of the adsorbent has a limited number of identical sites possessing similar energy which allow the equal affinity for adsorbate molecules over the surface of adsorbent to form a monolayer at equilibrium without any interaction among the adsorbate ions or molecules at the vicinity of the adsorbent's surface (Foo & Hameed, 2010). The Langmuir isotherm can be calculated using equation 5 (already discussed in early section 3.2.10) as:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_{max}\ b}\right) + \frac{C_e}{q_{max}} \tag{5}$$

where C_e (mg L^{-1}) is the concentration of Pb (II) solution at equilibrium; q_e is the amount of Pb (II) ions adsorbed per gram of charcoal at equilibrium and q_{max} (mg of solute g^{-1} of adsorbent) is the maximum adsorption capacity at complete coverage of monolayer.

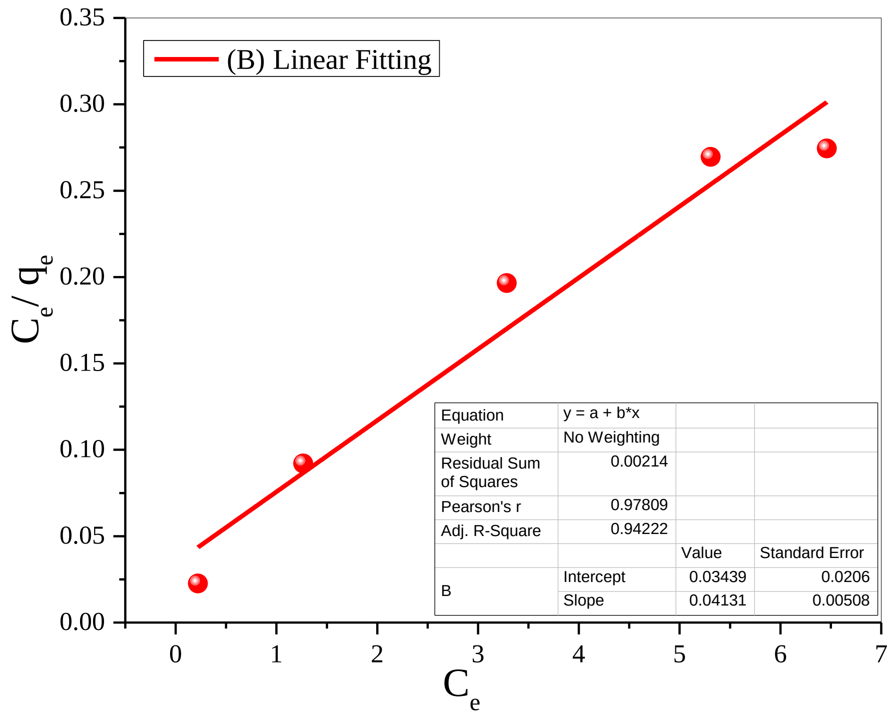

Figure 10. Plot of $\left(\frac{C_e}{q_e}\right)$ versus C_e to evaluate the slope (q_{max}) and the value of b.

The value of q_{max} and b can be calculated from the slope and intercept respectively by plotting $\left(\frac{C_e}{q_e}\right)$ against C_e. The linear fitting made a satisfactory straight line with correlation coefficient (R^2) value of 0.9422. The calculated value for the slope $\left(\frac{1}{q_{max}}\right)$ is 0.04131 and intercept $\left(\frac{1}{q_{max}\ \ b}\right)$ is 0.03439 respectively. The obtained data from Langmuir adsorption isotherm about the q_{max} and b value are mention in the Table 1 along with data of Freundlich adsorption isotherm. The obtained experimental data for the adsorption of Pb (II) ions at its maximum concentration (30 ppm) while treated with 0.1 g of charcoal was 23.539 ppm whereas its corresponding calculated value applying Langmuir isotherm adsorption is found to be 24.21 ppm which is nicely satisfy the result.

Table 1. The parameters related to Langmuir and Freundlich isotherms for the adsorption of Pb (II) ions onto the charcoal (0.1 g) adsorbent.

Heavy Metal	**Langmuir Isotherm**			**Freundlich Isotherm**			
(Pb)	R^2	q_{max}	b	R^2	K_f	$1/n$ (*)	n
	0.942	24.21	1.184	0.941	13.539	0.23985	4.169
Experimental q_e value	23.539						

*$0 < n < 1$.

4.6.2. Freundlich isotherm adsorption:

Freundlich model is based on the adsorption over the heterogeneous surface of adsorbent at low concentration and considered to be interact adsorbed molecules among themselves (Gautam *et al.*, 2014). It is stated that the energy of adsorption which reduced exponentially when there is decreased in the number of adsorbent's active site. Freundlich isotherm can be study using equation 4 (already discussed in early section 3.2.10).

$$log(q_e) = \log K_f + \left(\frac{1}{n}\right) log C_e \tag{4}$$

All the term used in the above equation 4 are mention as;

K_f = capacity of adsorption,

n = intensity of adsorption ($0 < n < 1$),

C_e = Concentration of Pb (II) ions at equilibrium,

q_e = amount of Pb (II) ions adsorbed per gram of charcoal at equilibrium.

The terms K_f and n are constants in the equation 4, whereas it has great significant in Freundlich isotherm adsorption which provides an information about the capacity of adsorption (K_f) and intensity of adsorption (n) whose values lie between 0 to 1. The plot $log(q_e)$ versus $\log(C_e)$ is drawn and made linear fitting with correlation coefficient (R^2) value as 0.941. The n value and K_f from the slope and intercept using equation 4. Data extracted from the Figure 11 and calculated parameters (Table 1) indicated that the value of n i.e., n = 4.169 lies outside the required range i.e., $0 < n < 1$ which suggests the mode of adsorption does not follow Freundlich isotherm adsorption.

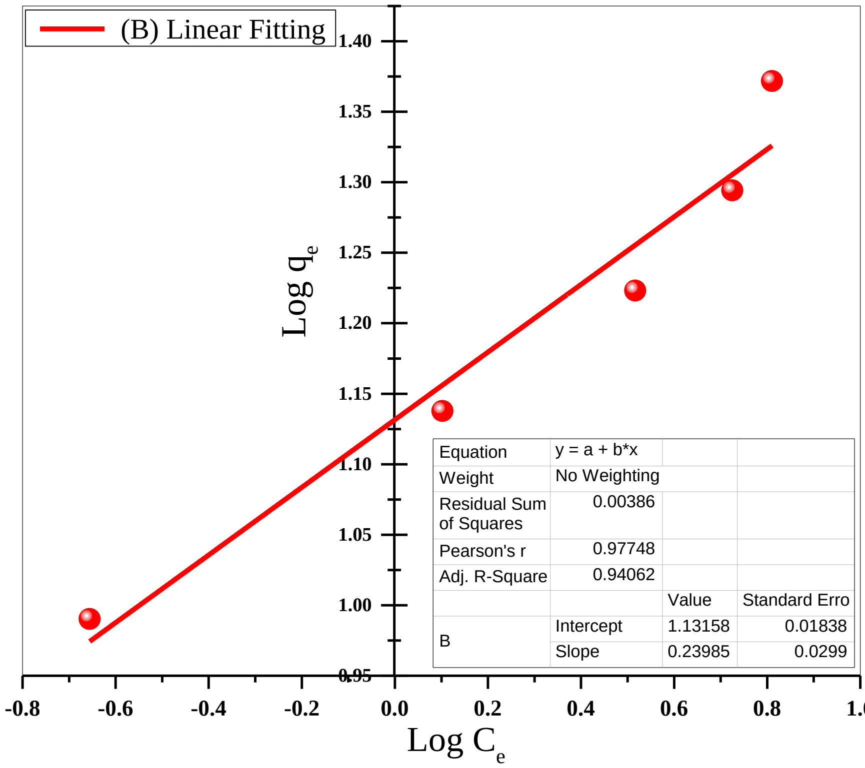

Figure 11. Plot of $log(q_e)$ versus $\log(C_e)$ to evaluate the slope (n) and the K_f.

The overall both type of isotherm studies conclude that the adsorption of Pb (II) ions onto the studied charcoal follow better in Langmuir isotherm adsorption due to energetically favorable process than Freundlich isotherm adsorption.

4.6.3. Separation Factor (R_L): R_L is another parameter which is a dimensional quantity concern with the adsorption process known as separation factor or an equilibrium parameter. Further, it is useful parameter to check the validity or feasibility of Langmuir isotherm adsorption. It can be calculated from the equilibrium parameter (b) i.e., Langmuir isotherm constant and initial concentration of the Pb (II) ions (C_i mg L^{-1}). Separation factor can be evaluate using following equation 8 as;

$$R_L = \frac{1}{1 + bC_i} \tag{8}$$

The separation factor indicated that Langmuir isotherm adsorption is favorable when the R_L value lies between 0 to 1. Figure 12 relates the R_L values with the initial metal ion concentrations. The maximum R_L value at the concentration of Pb (II) ions with 10 ppm indicates close to unity which is considered to be most favorable condition for the adsorption of metal ions. Figure 12 shows increase in the initial concentration of the metal ions with decreased in R_L values which falls within the favorable range. Therefore, it can be concluded that the mode of adsorption is favorable even at higher concentration of metal ions.

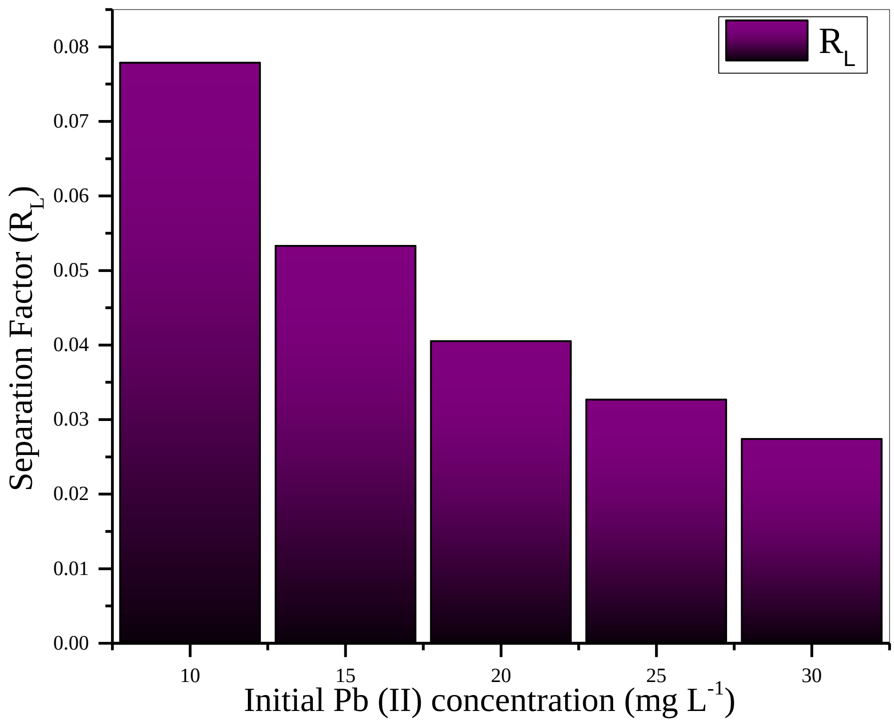

Figure 12. Plot between the calculated separation factor and initial concentration of Pb (II) ions.

4.7. Kinetics

The kinetics of metal ions adsorption onto the given fixed amount of adsorbent deals with respect to time which takes place at constant metal ions concentration and temperature. It is usually explained the potential to trapped the adsorbate into the surface pores of the adsorbent (Saha & Grappe, 2016). Two models can be applied to study the mechanism of adsorption kinetics such as pseudo-first-order and pseudo-second-order kinetics.

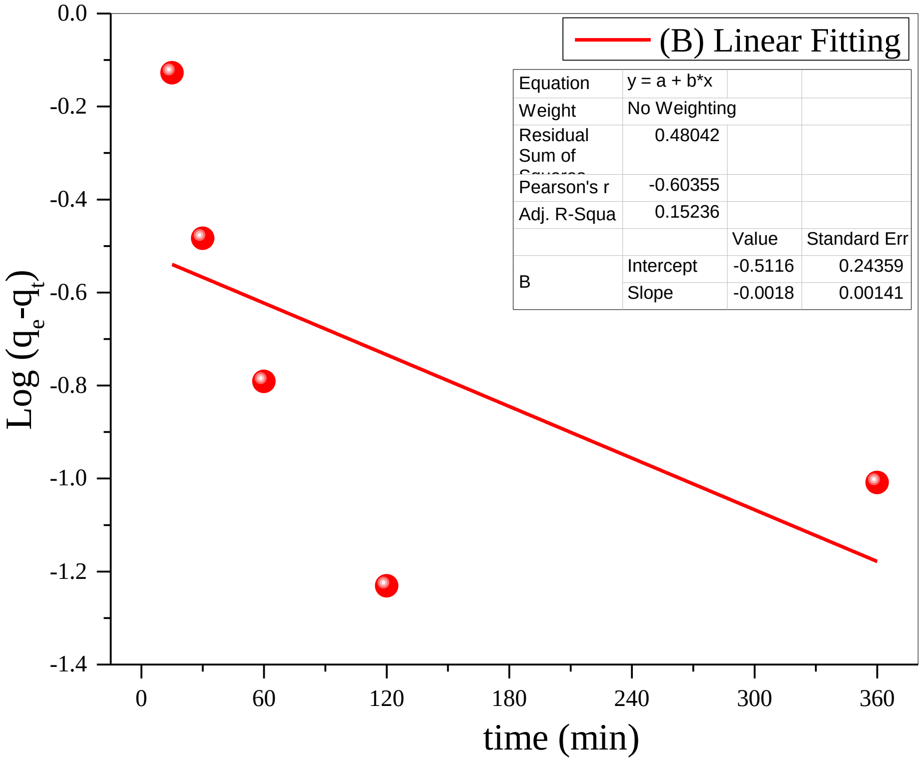

Figure 13. Plot of $log(q_e - q_t)$ versus time (t) to representation the biosorption kinetics of Pb (II) ions onto the wood charcoal using pseudo-first-order kinetic model.

To investigate the adsorption kinetics in solid-liquid system, pseudo-first-order can study using equation (6);

$$log(q_e - q_t) = logq_e - {k_1 t}/{2.303} \quad (6)$$

where q_e (mg g^{-1}) is amount of Pb adsorbed on charcoal at equilibrium, q_t (mg g^{-1}) is amount of Pb adsorbed on charcoal at time t and k_1 (min^{-1}) is the rate constant for the biosorption. The assumption of pseudo- first-order model is based on the rate which is directly proportional to the number of unoccupied sites.

Figure 13 represents the pseudo-first-order kinetics of biosorption of Pb (II) ions onto the wood charcoal where $log(q_e - q_t)$ versus time (t) were plotted and obtained straight line is insignificant with respect to correlation coefficient (R^2 =0.15) value with poor linear fitting. The rate constant (k_1) and adsorption capacity of adsorbent (q_e) at equilibrium are evaluated from the slope and intercept and their values are reflected in Table 2.

Table 2. The parameters related to pseudo-first/second-order kinetics for the adsorption of Pb (II) ions onto the charcoal (0.1 g) adsorbent.

Kinetics	**Pseudo-first-order**			**Pseudo-second-order**			
Parameters	R^2	k_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	q_e (mg g^{-1}) (Experimental)
Value	0.15	0.004	0.308	0.99	0.172	9.766	9.716

Likewise, pseudo-second-order kinetics for adsorption of Pb (II) ions onto the wood charcoal can be calculated using equation 7;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

where k_2 is the rate constant for the pseudo-second-order adsorption kinetics and other terms are mentioned in previously equation 6.

Figure 14 represents the plot of $\left(\frac{t}{q_t}\right)$ versus t where the intercept and slope have been used for the calculation of q_e value and the rate constant (k_2) and their corresponding values are mentioned in Table 2. The linear fitting is found to be good with respect to correlation coefficient (R^2) value. Results indicates the correlation coefficient in case of pseudo-second-order kinetics with $R^2 = 0.99$ value is more significant as compared to the pseudo-first-order kinetic ($R^2 = 0.15$). Furthermore, on comparing the q_e value for both the kinetics models, the experimental q_e value at a maximum time (360 min) of interval is 9.716 mg g^{-1} which is close to the value of 9.766 mg g^{-1} obtained from the studies of second order kinetics. Similarly, result obtained from the pseudo-first-order kinetics (q_e=0.308 mg g^{-1}) could not match with the experimental result (q_e=9.716 mg g^{-1}). Therefore, studies of kinetics results concluded that the rate of adsorption followed pseudo-second-order kinetics for the adsorption of Pb (II) ions onto the wood charcoal.

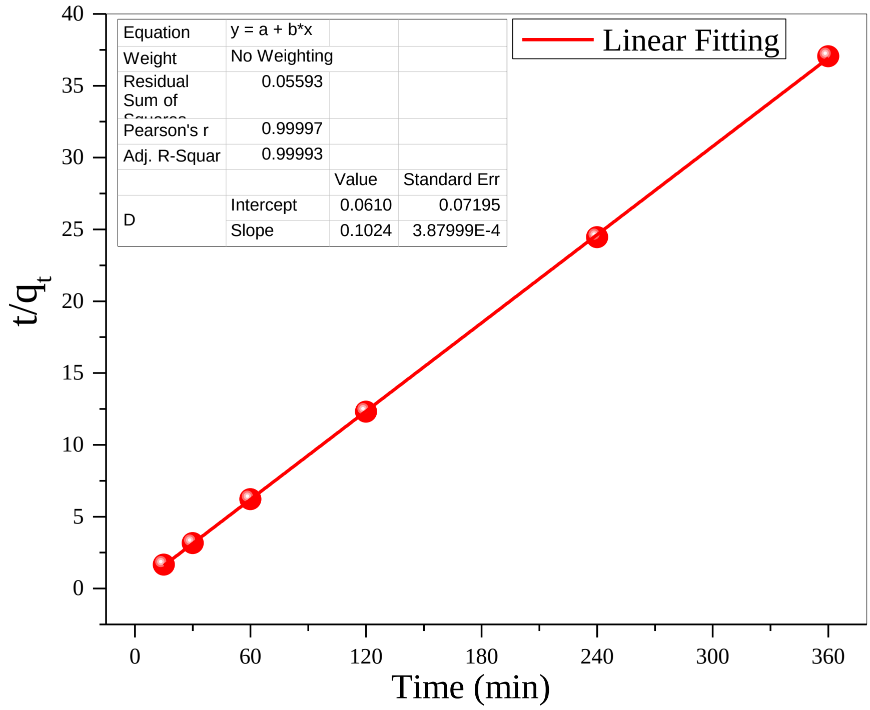

Figure 14. Plot of $\left(\frac{t}{q_t}\right)$ versus t to representation the biosorption kinetics of Pb (II) ions onto the wood charcoal using pseudo-second-order kinetic model.

4.8. Studies of thermodynamic parameter (standard change in Gibb's free energy)

The standard change in Gibb's free energy (ΔG^0_{ad}) is an important thermodynamic parameter to depict the spontaneity and the feasibility of the adsorption process. As all the experiments were performed without varying the temperature or at constant temperature, thus, only standard change in Gibb's free energy for the adsorption of Pb (II) ions by wood charcoal are evaluated and other thermodynamic parameter such as standard change in enthalpy and entropy was beyond the scope of our study (due to fixed temperature of the experiments).The biosorption of Pb (II) ions can be considered as reversible process and represents by a heterogenous equilibrium.

$$Pb^{2+} + \text{biosorbent} \leftrightarrow (\text{Pb} - \text{biosorbent})$$

The standard change in Gibb's free energy (ΔG^0) can be evaluated using equation 9 as follows;

$$\Delta G^0_{ad} = -RT ln K_e \quad (9)$$

K_e represents the equilibrium constant at constant temperature which is calculated by the ratio of adsorbed metal concentration (q_e) on the surface of charcoal (biosorbent) to the non-adsorbed metal concentration (C_e) in the solution at equilibrium (Vikrant Sarin and K.K Pant, 2006). Whereas R is the universal gas constant and T the temperature at Kelvin scale. Figure 15 represent the ΔG^0_{ad} with respect to the different setup of the experiments [(a), (b), (c) and (d)] in order to analyze the feasibility of the adsorption process and all their corresponding data are mentioned in Table 3 [(a), (b), (c) and (d)] The negative value of ΔG^0_{ad} indicates the feasibility as well as spontaneous nature of biosorption (Apiratikul and Pavasant, 2008; Bhatt *et al.*, 2013).

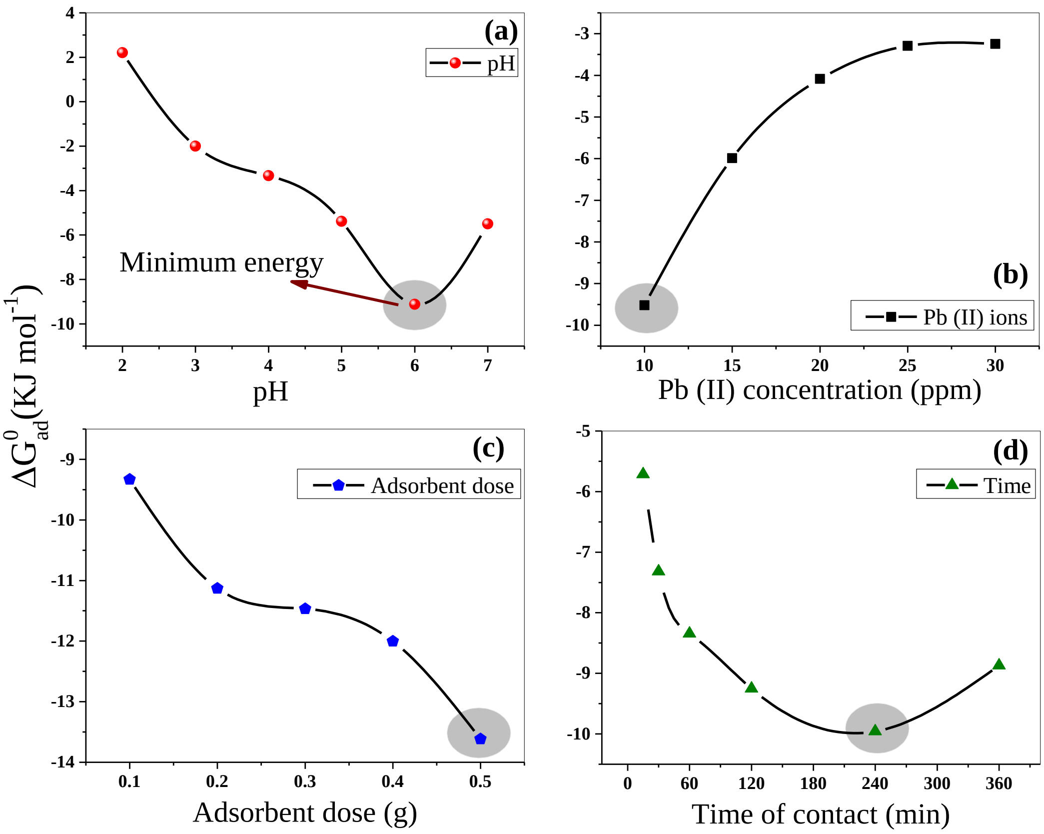

Figure 15. Plots of ΔG_{ad}^{0} versus **(a)** change in pH; **(b)** Pb (II) ions concentration; **(c)** adsorbent dose and **(d)** time of contact during adsorption.

All ΔG_{ad}^{0} values are found to be negative in magnitude except in Table 3 (a) at pH 6 which suggest that the adsorption of metal ions onto the studied adsorbent are feasible and spontaneous in nature. The exceptional case at pH 2 is observed due to the pH_{PZC} value which is noted at pH 2 (discussed in section 4.1) at which the surface charge of the adsorbent is neutral. Therefore, above this pH_{PZC} value, adsorption of positive Pb (II) ions are feasible to adsorbed onto the negative surface charge of adsorbent which is supported by the obtained ΔG_{ad}^{0} values. Figure 15 (a) shows that the increase in pH of the fixed concentration of Pb (II) ions (10 ppm) with fixed amount of adsorbent (0.1 g) decreases with ΔG_{ad}^{0} values and attained a minimum value of

–9.123 kJ mol^{-1} at pH 6 which indicates that the process of adsorption is maximum at pH 6. Similarly, early discussed finding (section 4.1, 4.2, 4.3 and 4.4) on different setup of experiments are well supported with calculated ΔG_{ad}^{0} values and most feasible condition are mentioned and highlighted in Table 3 [(a), (b), (c) and (d)] and Figure 15 [(a), (b), (c) and (d)] respectively.

Table. 3. Evaluation of thermodynamic parameter i.e., standard change in Gibb's free energy for the adsorption of Pb (II) ions on to the wood charcoal in different studied different setup of the experiments; **(a)** Effect of pH on the adsorption of fixed amount of Pb (II) ions with fixed amount of adsorbent (0.1 g), **(b)** Effect of Pb (II) ions concentration on adsorption process with fixed amount adsorbent at pH=6, **(c)** Effect of adsorbent dose on the fixed concentration of Pb ions at pH=6 and **(d)** Effect of time on the fixed concentration of Pb ions (10 ppm) with fixed amount of adsorbent at pH=6 at constant temperature 29 °C respectively.

(a) Effect of pH on the adsorption of fixed amount of Pb (II) ions with fixed amount of adsorbent (0.1 g).[*]					
pH	Initial [Pb^{2+}] (ppm)	C_e (mg L^{-1})	q_e (mg g^{-1})	$\left(\frac{q_e}{C_e}\right)$	ΔG_{ad}^{0} (kJ mol^{-1})
2	10	7.065	2.935	0.416	2.206
3	10	3.106	6.894	2.219	-2.003
4	10	2.102	7.898	3.758	-3.326
5	10	1.048	8.952	8.540	-5.388
6	10	0.258	9.742	37.782	**-9.123**
7	10	1.008	8.992	8.920	-5.497
(b) Effect of Pb (II) ions concentration on adsorption process with fixed amount adsorbent at pH=6.[*]					

Initial $[Pb^{2+}]$ (ppm)	Amount of adsorbent (g)	C_e (mg L^{-1})	q_e (mg g^{-1})	$\left(\frac{q_e}{C_e}\right)$	ΔG^0_{ad} (kJ mol^{-1})
10	0.1	0.221	9.779	44.249	**-9.520**
15	0.1	1.265	13.735	10.856	-5.991
20	0.1	3.284	16.716	5.089	-4.088
25	0.1	5.309	19.691	3.709	-3.293
30	0.1	6.461	23.539	3.643	-3.248

(c) Effect of adsorbent dose on the fixed concentration of Pb ions at pH=6.[*]

Adsorbent dose (gm)	Initial $[Pb^{2+}]$ (ppm)	C_e (mg L^{-1})	q_e (mg g^{-1})	$\left(\frac{q_e}{C_e}\right)$	ΔG^0_{ad} (kJ mol^{-1})
0.1	10	0.238	9.762	41.043	-9.331
0.2	10	0.118	9.882	83.962	-11.129
0.3	10	0.103	9.897	96.087	-11.468
0.4	10	0.083	9.917	118.904	-12.003
0.5	10	0.044	9.956	225.757	**-13.614**

(d) Effect of time on the fixed concentration of Pb ions (10 ppm) with fixed amount of adsorbent at pH=6.[*]

Time (min)	Initial $[Pb^{2+}]$; ppm	C_e (mg L^{-1})	q_e (mg g^{-1})	$\left(\frac{q_e}{C_e}\right)$	ΔG^0_{ad} (kJ mol^{-1})
15	10	0.932	9.068	9.732	-5.716
30	10	0.515	9.485	18.421	-7.319
60	10	0.348	9.652	27.719	-8.345
120	10	0.245	9.755	39.783	-9.253
240	10	0.186	9.814	52.648	**-9.957**
360	10	0.284	9.716	34.162	-8.870

[*] Temperature is 29 ±0.2 °C.

5. Conclusion

Wood charcoal (powder) was found to be more potent to remove Pb (II) ions due to different functional group and additional pore present over the surface of the wood charcoal powder as an adsorbent. Therefore, it enhanced the absorptivity of Pb (II) ions from the aqueous solution which will be an ecofriendly approach. Such important research finding may provide the value for the local community.

From the present work we came to a conclusion that the process of adsorption followed Langmuir adsorption isotherm and the rate of adsorption followed by pseudo second-order kinetics. Batch culture experiments at constant temperature 29 °C revealed that the parameters as limiting factor or variables such as pH, metal ions concentration, time, and adsorbent dose has as significant effect on the mode of adsorption. In fact, effect of pH on the process of adsorption was found to be sensitive and important parameter. This result suggests that change in pH changes the adsorption of Pb (II) ions onto the studied adsorbent which is achieved maximum at pH 6. This can also be supported by the results obtained from the pH_{PZC}value. The pH_{PZC} value was found to be at pH 2 which suggests that the pH above 2 was favorable for the adsorption of positive Pb (II) ions onto the negative surface of charcoal. In case of the effect of adsorbent dose, it was found that as the percentage of adsorption increased, the process of adsorption also increased. This can be interpreted by taking into the view that the surface area of the adsorbent dose increased which resulted in the increase in the percentage of adsorption. The effect of metal ion concentration on adsorption showed that as the concentration of metal ion increased, there was a significant decrease in the percentage of adsorption. This may be due to the fact that as the surface area might have decreased as the metal ion concentration increased. In this case, a fixed (i.e. 0.1 gm) amount of adsorbent for the adsorption of Pb (II) ions suggest that there might be a mono layer formation taking place on the surface of charcoal surface which is also found in the Langmuir adsorption isotherm. The effect of time studies showed that as the time increased, the percentage of adsorption also increased till the equilibrium was attained and thereafter the nature of adsorption showed almost constant due to the adsorption-desorption equilibrium. The maximum adsorption was achieved at a time interval of 4 hr (240 mins). However, with further progression of experiment, it was observed that the percentage of adsorption was being decreased after 6hr. which may be due to the reason that the process of desorption may be taking place on the surface of adsorbent.

In order to study the mode of adsorption, isotherm studies were conducted. Comparing both the Langmuir and Freundlich adsorption isotherms, it was found that the mode of adsorption favored more towards Langmuir adsorption isotherm. Further Kinetics study was also done in order to know the rate of adsorption. From the kinetic studies, it was found that the adsorption process followed pseudo-second-order kinetics. The ΔG_{ad}^{0} was calculated for different factors affecting the process of adsorption i.e. pH, concentration of Pb ions, adsorbent dose as well as for contact time. The evaluated thermodynamic parameter i.e., change in standard Gibbs free energy (ΔG_{ad}^{0}) values are found to be negative in magnitude expect at pH 2 which indicated that the process of adsorption is feasible and spontaneous in nature. FTIR analysis revealed the presence of various functional groups such C–N, C–O, N≡O, C–H, RN–C, P-H, etc. which is consider to be involved in the attachment of Pb (II) ions onto the surface of the adsorbent. Moreover, limited literatures are available with raw wood charcoal with better adsorption percentage. Herein, our studies showed that the Mizoram wood charcoal (mixture of Nahor (*Mesua ferrea*), Walnut (*Juglans regia*) and Katus (*Castanopsis hystrix*) can be used to remove Pb (II) ions from the aqueous solution which can be used in advanced techniques to purify drinking water and this will increase the value for the local community.

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ABSTRACT

ADSORPTION OF LEAD (II) FROM AQUEOUS SOLUTION USING MIZORAM WOOD CHARCOAL: KINETICS AND ISOTHERMS STUDIES

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Adsorption of Lead (II) from aqueous solution using Mizoram Wood charcoal: Kinetics and Isotherms studies

Abstract

Several types of heavy metals have been a subject of major concern for the environment. Heavy metals such as lead, arsenic, copper, cadmium, chromium, nickel, zinc, mercury, etc. are toxic to biological system if exceed the permissible limit in the body. These pollutants are harmful and toxic which are non- biodegradable and causes of various diseases. Heavy metals are actually found in nature and some of them like zinc, iron, molybdenum, etc. are required in trace amounts in the body for normal metabolism. Their toxicity lies in the fact that when they exceed a particular concentration, they become toxic for the living system. This may also be due to the fact that they have the property of accumulating in different organs of the body and the process is called bioaccumulation. There are various natural as well as anthropogenic sources through which these heavy metals get inside the body. The common portal of entry being food and drinking water. Several water purifying systems and methods have been devised in past many years. But each one of them has its own pros and cons. The effort to minimize the cons has become a prime motive of recent researches. Even though newer methods have also come to be known these days. Out of many processes, adsorption has been extensively used in the past many years and charcoal being a good adsorbent which has been used from ancient time to remove impurities from water. In the present study, removal of heavy metal as lead (Pb) has been chosen to remove from aqueous solution

using biosorbent as wood charcoal. Such problem has been attempted by the adsorption technique using locally available wood charcoal found in Mizoram, India. These low-cost charcoals are available in the market and mainly used for domestic purposes by the local people. This available wood charcoal was used as an adsorbent for the removable of Pb (II) ions for the study. Adsorbent was used after milled, blended and sieved to particles of 100 mesh screen. The present study is focused more on the use of a cheap and easy method in order to remove a potent neurotoxic heavy metal Pb. Batch culture experiments at constant temperature 29 °C were done by systematic evaluation of the parameters as limiting factor or variables such as pH, metal ions concentration, time, and adsorbent dose. Results showed that the maximum adsorption of Pb (II) was observed at pH 6 with maximum percentage of adsorption is found to be 97.5%. Also, the study on the time of contact revealed that the most suitable time period for maximum adsorption was attained at 240 min (4hr). Furthermore, pH_{PZC} value is evaluated through traditional approach i.e., pH measurement and it is found to be at lower pH range i.e., at pH 2, which suggest that the adsorption of positive Pb (II) ions is possible only above the value of pH 2. However, adsorption studies of Pb (II) ions is difficult after pH 6 due to the precipitation of Pb (II) ions. Varying of adsorbent dose from 0.1 g to 0.5 g on fixed Pb (II) concentration (10 ppm) has a great impact on adsorption which increase with increase in the adsorbent dose. Likewise, effect of Pb (II) concentration ranging from 10–30 ppm (with an interval of 5 ppm) on the fixed amount of adsorbent (0.1 g) found to be decrease with increase in the concentration due to the more coverage of surface area of studied adsorbent. Time of contact of fixed Pb (II) concentration (10 ppm) with fixed amount of adsorbent (0.1 g) were studied up to 360 min and this result show that the amount of adsorption is more at initial stage which is lower or become almost constant at the end of the studied time range due to attainment of adsorption-desorption equilibrium with adsorbed metal on the adsorbent surface ions and non-adsorbed metal ions in the solution. Adsorption isotherm studies were carried out by applying two mostly used models, Langmuir and Freundlich adsorption isotherm to understand the mode of adsorption. The result shows that the mode of adsorption is followed by Langmuir adsorption isotherm with experimental Pb (II) adsorption value of 23.539 ppm at its maximum concentration (30 ppm) when treated with 0.1 g of charcoal which satisfy the corresponding calculated value applying Langmuir isotherm adsorption (24.21 ppm). The pseudo–first-order and second-order kinetics were also studied to know the type of kinetics. Evaluation of the kinetic data showed the best correlation coefficient value in case of pseudo-second-order kinetics. The FTIR results also showed that various functional such as CN, RCN, NO, etc. are present on the surface of the charcoal which are responsible for the attachment of the Pb (II) ions. Furthermore, to analyze the feasibility of the adsorption process, thermodynamic parameter i.e., change in standard Gibbs free energy (ΔG_{ad}^{0}) for the adsorption have been calculated at constant temperature. Evaluation of ΔG_{ad}^{0} parameter suggest that all the adsorption studies at different setup to calculate the effect of limiting parameter are all negative in magnitude except at pH 2 which indicate that the process of adsorption of Pb (II) ions onto the biosorbent is feasible and spontaneous in nature (except at pH 2). It can be concluded that the studied wood charcoal as a biosorbent has great a potential to efficiently remove

Pb (II) ions from the aqueous solution which can be applied in the purification of Pb contaminated drinking water with further advanced research. The nobility of this work lies on the fact that most of the process for heavy metal removal is cost generating and complex.