USE OF MESO AND MICRO POROUS ACTIVATED CARBON PRECURSOR TO DEAD BIOMASSES FOR THE REMOVAL OF HEAVY METAL TOXIC IONS FROM AQUEOUS SOLUTIONS

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in

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By

LALHMUNSIAMA

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DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES
MIZORAM UNIVERSITY,
TANHRIL, AIZAWL- 796004

August, 2013

Mizoram University
Greater Deeds Remain
ESTD MIZORAM UNIVERSITY 2000
(A central University under the Act of Parliament)
Department of Chemistry
School of Physical Sciences

Dr. Diwakar Tiwari
Professor

CERTIFICATE

This is to certify that the thesis entitled *'Use of meso and micro porous activated carbon precursor to dead biomasses for the removal of heavy metal toxic ions from aqueous solutions'* submitted by ***Mr. Lalhmunsiama,*** for the degree of ***Doctor of Philosophy*** in the Mizoram University, Aizawl, Mizoram, embodies the record of original investigations carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the award of the Ph.D degree. This work has not been submitted for any degree in any other university.

Dated: 5 August, 2013

(DIWAKAR TIWARI)
Supervisor

Declaration of the Candidate

I, Lalhmunsiama, a Ph.D scholar in Department of Chemistry, Mizoram University, Aizawl, Mizoram, do hereby solemnly declare that the subject matter of this thesis is the record of the work done by me. I have duly worked on my Ph.D thesis under the supervision of Prof. Diwakar Tiwari, Department of Chemistry, Mizoram University. This is being submitted to the Mizoram University for the degree of Doctor of Philosophy in Chemistry and further, I solemnly declared that I have not submitted this work to any other University or Institute for any other degree.

I also declare that the present investigation relates to bonafide research works done by me and the title of the thesis is **'USE OF MESO AND MICRO POROUS ACTIVATED CARBON PRESURSOR TO DEAD BIOMASSES FOR THE REMOVAL OF HEAVY METAL TOXIC IONS FROM AQUEOUS SOLUTIONS'.**

Dated 5th August, 2013

(LALHMUNSIAMA)
Candidate

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Lalhmunsiama

CONTENTS

1. INTRODUCTION

Water is among the most important basic necessities of human and it is an essential element for life; however lack of potable water is wide-spread in many countries. Therefore, the shortage of fresh/potable water is known to be a major environmental concern around the globe. Although water is abundantly available on earth; according to the survey of World Health Organisation (WHO), 97.5% of water on the earth is having very high salt content and the remaining 2.5% is as fresh water. Moreover, 70% of the fresh water is frozen in the polar icecaps and the remaining 30% is either as soil moisture or in underground aquifers. Less than only 1% of the World's fresh water (or about 0.007% of all water on earth) is readily accessible for direct human consumption (El-Ghonemy, 2012; Shanmugam *et al*., 2004). Therefore, this small proportion of freshwater is under immense stress due to rapid population growth, industrialization, urbanization and unsustainable consumption of water in industry and agriculture. According the United Nations prediction, between two and seven billion people will face water shortages by the year 2050. About 80 countries, comprising 20% of the world populations are suffering from serious water shortage (United Nations, 2006). In developing countries the problem is more aggravated due to the lack of proper management, unavailability of professionals and financial constraint etc. (Azizullah *et al*., 2011). More than 2.2 million people die every year in these countries due to drinking of contaminated water and inadequate sanitation facilities (WHO and UNICEF, 2000). Meanwhile, water resources are coming under intense pressure and several reports indicated that water resources problems are going to be more critical in the future worldwide (Matondo, 2002). The world population is increasing exponentially while the availability of freshwater is declining. Yet even where the supplies are sufficient, they are increasingly at risk because of enhanced water pollution (Azizullah *et al*., 2011).

In general, water pollution is the contamination of water bodies; rivers, lakes, oceans, aquifers and groundwater. The polluted water cause chemical, physical or biological changes in the quality of water and consumption of this may leads to several harmful effects towards the living organisms. There are several classes of water pollutants but mainly caused by human activities. The main chemical pollutants of surface water as well as the ground water were broadly divided into organic pollutants and inorganic pollutants. The organic pollutants are mainly as pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, greases, pharmaceuticals etc. (Ali *et al*., 2012). On the other hand, the inorganic pollutants are usually substances of mineral origin. Metals and salts are among the common inorganic pollutants. Heavy metals are the most important categories of inorganic water pollutants (Hu *et al*., 2010). Due to rapid increase in industrialization and urbanization in recent past caused an enhanced use of several heavy metal toxic ions in various industries such as electroplating, metal processing, textile, battery manufacturing, tanneries, petroleum refining, paint, pesticides, pigment manufacture, printing and photographic industries etc. resulted in excessive release of toxic metals into the environment which ultimately resulted in tremendous load on the environment particularly the aquatic environment. This has caused greatly the deleterious water quality leading to significant environmental imbalances (Khamis *et al*., 2009; Ahmaruzzaman, 2011).

As stated the discharge of untreated or partially treated industrial or urban wastes is posing a severe environmental impact. The remediation of aquatic environment contaminated with heavy metal toxic ions is one of the key issues around the globe because of the acute toxicity showed by these heavy metals towards the aquatic-life, plants and animals including human being. Moreover, the heavy metals poses serious health and environmental problems due to their non-biodegradability, persistency in nature and tendency to accumulate once entered into the biological system (Kumar and

Bandyopadhyay, 2006; Ji *et al*., 2012; Tofighy and Mohammadi, 2011). Although, several heavy metals were essential at trace level however, enhanced uptake caused for several toxic effects and biological disorders. Heavy metals can form compounds within the bio-system which tends to be potentially carcinogenic and mutagenic even at very low levels (Martin, 1985; Madoni *et al*., 1996)

The increasing scarcity of freshwater and its supplies led to the utilization of reclaimed water. The planned potable reuse, a process by which reclaimed water is eventually incorporated into drinking water supplies is one of the sources for diverse water portfolios. The reclaimed water is, however, contained with unregulated contaminants of emerging concerns, which include pharmaceuticals, household chemicals, personal care products, disinfection by-products, insecticides, and suspended endocrine disruptors along with the heavy metals toxic ions (Laws *et al*., 2011; Ternes, 1998; Kolpin *et al*., 2004; Wells *et al*., 2009). Although most of these contaminants are present at very low level, the toxicity and their fate makes a greater concern and shows necessity of its careful treatment (Tiwari *et al*., 2011).

All these factors are indicative of a need to develop or to identify an appropriate technique which is suitable to produce good clean potable drinking water/freshwater to conserve water and energy. The selection of materials with natural abundance having the net charge and porosity makes the material suitable for the cost effective and environment benign treatment technology.

The two dead biomass *viz*., rice husk and areca nut waste were chosen as precursor materials as to obtain the activated carbons. Further, the large surface area of activated carbons were tried to immobilize the iron and manganese oxides onto the pores and surfaces of activated carbons. These materials were then employed in the remediation of the waters contaminated with the Cd(II), Cu(II),Pb(II),As(III) and As(V). Rice husk is one of abundant agricultural by-product; 96% of which is generated in developing countries and the annual world rice production is about 571 million tonnes resulting approximately 140 million tonnes of rice husk were available annually for utilization (Chen *et al*., 2011). Rice husks are usually used as a low-value energy resource, burned in the field, or discarded, which are unfavourable to the atmospheric environment (Guo and Rockstraw, 2007). However, due to its typical composition, rice husk is reported to be a potential inexpensive adsorbents (Mishra *et al*., 2007) and studies also shown that rice husk is suitable for the production of activated carbons in the removal of organic pollutants as well as inorganic pollutants (Zhu *et al*., 2012; Awwad *et al*., 2010). On the other hand *areca* nut which is also known as betel nut is very popular chewing nut in different part of the world. The annual total world production is reported to be 0.64 million tonnes; indeed 51% is produced from India itself (http://www.crnindia.com/commodity/arecanut.html). *Areca* nut waste is regarded as low value biomass and its wide use caused for huge amount of bio-waste introduced into the environment (Sasmal *et al*., 2012). It was reported that this waste could have possible use in the attenuation/removal of cadmium, copper and lead from aqueous solutions (Li *et al*., 2012b, Zheng *et al*., 2008). Therefore, these dead biomasses could be exploited to obtain the micro to meso-porous activated carbons (ACs). These ACs possibly be cost effective and possessed with high specific surface area hence, could show an enhanced applicability in the waste water treatment strategies. Further, the suitability and selectivity of these ACs could be enhanced by selective and suitable modification of ACs. Keeping in view, the iron or manganese oxide small sized particles were immobilized onto the surface and pores of the AC samples and employed in the remediation of heavy metal contaminated aquatic environment. Additionally, such applications of dead biomasses may ultimately alleviate the problems of disposal and management of these waste by-products in general.

1.1. TOXICITY OF HEAVY METALS

'Heavy metals' is a general collective term applying to the group of metals and metalloids with an atomic density greater than 6 g/cm^3 (O'Connell, 2008). Unlike organic pollutants, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various biological disorders (Ngah and Hanafiah, 2008). The metals of major environmental concern are arsenic (arsenic is a metalloid, but is usually classified as a heavy metal), cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel and zinc (Bhattacharyya and Gupta, 2008).

1.1.1. Cadmium

Cadmium is a naturally occurring metal and known as an extremely toxic in any of its chemical forms *viz.*, chloride, sulphate, sulphide, carbonate, oxide, and others (Mahmoud and Haggag, 2011). As compared to other heavy metals, cadmium and its compounds are relatively water soluble therefore mobile in soil and water and tend to bio accumulate (Sud *et al*., 2008). The main pathway through which cadmium enters into environment is via industrial processes such as electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium-nickel batteries, fertilizers, pesticides, mining, pigments and dyes, textile operations and refining (Rao *et al*., 2010). In late 1940's, the effect of cadmium on human became popularized due to the *itai–itai* disease, the most severe form of chronic cadmium (Cd) poisoning caused by prolonged oral Cd ingestion which developed in numerous inhabitants of the Jinzu River basin in Toyama Prefecture (Kasuya, 2000; Inaba, 2005). In addition to direct exposure from air and drinking water, the potential exposure to cadmium is mainly from crops grown in the contaminated water and soil environment, which transports the metal into food chain (Amoyaw *et al*., 2009). Acute exposure to cadmium fumes may cause flu like symptoms including chills, fever, and muscle ache. More severe exposures can cause tracheo-bronchitis, pneumonitis, and pulmonary edema. Symptoms of inflammation may start hours after the exposure and include cough, dryness and irritation of the nose and throat, headache, dizziness, weakness, fever, chills, and chest pain (Jarup, 1998). The accumulated cadmium in human body caused erythrocyte destruction, nausea, salivation, diarrhoea and muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity, hypertension, proteinuria, kidney stone formation and testicular atrophy (Mohan and Singh, 2002; Kula *et al*., 2008). Cadmium is known as carcinogenic to human body and occupational exposure with cadmium is associated with cancers of lung, prostate, pancreas, and kidney. It is classified as a category 1 carcinogen (human carcinogen) by the International Agency for Research on Cancer (IARC) due to its potent characteristics with lung cancer (Waisberg *et al*., 2003). The mechanisms of acute Cd toxicity involve the depletion of glutathione and protein-bound sulfhydryl groups, resulting in enhanced production of reactive oxygen species such as superoxide ion, hydrogen peroxide, and hydroxyl radicals which in turn produces lipid per oxidation, and results in DNA damage (Liu *et al*., 2009). In addition, Cd^{2+}ions may replace Zn^{2+}ions in some enzymes, thereby affecting the enzyme activity in biological systems (Nagarethinam and Gurusamy, 2005) and the binding capability of cadmium to various biological components, such as protein and metallothionein enhances the cadmium toxicity in the human body (Klaassen *et al*., 2009).

1.1.2. Copper

Copper is widely used metal and there are many potential sources of its pollution. The main sources include industries such as plating, mining and smelting, brass manufacture, electroplating, petroleum refining and Cu-based agrochemical industries. Copper is an essential trace ion required at trace level for the human health but potentially toxic at high level intake (Aydin *et al.,* 2008; Demirbas *et al.,* 2009). The human body has natural mechanism to maintain an optimum copper level. Cu functions as a co-factor and requirements for structural and catalytic properties in a variety of important enzymes involved in an array of biological processes as required for growth, development, and maintenance. However, children under one year age have not yet developed this mechanism and are more vulnerable to the toxic effects of copper (Gaetke and Chow, 2003; HDR Engineering Inc**.,** 2001). Excessive intake of copper to human body may lead to severe mucosal irritation, hepatic and renal damage, capillary damage, gastrointestinal irritation and central nervous system irritation (Ngah and Hanafiah, 2008). Kidney, liver and gastrointestinal systems are sensitive targets of oral exposure to copper toxicity (Lei *et al*., 2008). Presence of higher concentrations (>5 mg/l) in the body is showed many health problems such as kidney damage, high fever, haemolysis and vomiting and excess copper in the marine system is showed to damage marine life and damage the gills, liver, kidneys, the nervous system and changing sexual life of fishes (Hossain *et al*., 2012).

1.1.3. Lead

Lead is a heavy metal which has specified characteristics such as resistant to corrosion, conductivity and the special reversible reaction between lead oxide and sulphuric acid (Bahadir *et al*., 2007), therefore it is widely employed in process industries which can be regarded as the anthropogenic sources. The process industries include battery manufacturing, metal plating, industries engaged in lead–acid batteries, paint, oil, metal, phosphate fertilizers, electronic, and wood production. It is also used in storage batteries, insecticides, plastic water pipes, food, beverages, ointments and medicinal concoctions for flavouring and sweetening**.** Other main sources of lead are combustion of fossil fuels and smelting of sulphide ore (Gupta and Rastogi, 2008; Singh *et al*., 2008). The growth of lead-acid battery is increases tremendously with increasing the number of automobile vehicles. The largest consumer of lead is storage battery industry, followed by the petroleum industry in producing gasoline additives (Gurel *et al*., 2005). In spite of its usefulness, lead contamination is become one of the most pervasive/prevalent and elusive threat to the environment and public health (Solener *et al.*, 2008). It is highly toxic to organisms including humans, even at extremely low concentrations (Lalhruaitluanga *et al.*, 2010). Lead as Pb^{2+} ion has a large affinity for the thiol (-SH) and phosphate ion (PO_4^{3-}) containing enzymes, ligands and biomolecules, thereby inhibiting the biosynthesis of haeme units, affecting membrane permeability of kidney, liver and brain cells. These result in either reduced functions or complete breakdown of these organs. Lead forms complexes with oxo-groups in enzymes to affect virtually all steps in the process of haemoglobin synthesis and porphyrin metabolism (Ademoroti, 1996). Hence, lead poisoning in human causes severe damage to the kidney, nervous system, reproductive system, liver and brain which results in sickness or death. Severe exposure is associated with sterility, abortion, stillbirth and neonatal deaths (Sekhar *et al.*, 2004). It is also reported that**,** in children, lead causes a decrease in intelligent quotient (IQ) score, retardation of physical growth, hearing impairment, impaired learning, as well as decreased attention and classroom performance (Okoye *et al.*, 2010). Hence, considering the toxicity and environmental risk, Pb(II) is one of the most important heavy metal for its removal or recovery from the terrestrial environment.

1.1.4. Arsenic

Arsenic is one of the most toxic chemicals in the environment and imposes a great threat to the health of millions of people in many different countries of the World (Li *et al.*, 2012a). Arsenic exists in four different oxidation states, +5(arsenate), +3 (arsenite), 0 (arsenic), and −3 (arsine). The +3 and +5 oxidation states are the major concern in case of environmental exposure. Among these two, As(III) is seemingly more toxic than As(V) (Desesso *et al.*, 1998). The major sources of arsenic include natural weathering reactions, biological activity, geochemical reactions, volcanic emissions and anthropogenic activities.

Mining, combustion of fossil fuels, use of arsenic pesticides, herbicides, crop desiccants, use of arsenic additives to livestock feed and agriculture waste are the main anthropogenic sources (Mohan and Pittman, 2007, Chen *et al.*, 2007b). The acute toxicity in humans includes gastrointestinal discomfort, vomiting, diarrhoea, bloody urine, anuria, shock, convulsions, coma, and death. Moreover, skin lesions, blackfoot disease, peripheral neuropathy, hepatomegaly, heme metabolism problem, bone marrow depression, diabetes, renal disorder are found to be associated with chronic exposure to inorganic arsenic (Micheal and Hughes, 2002). Inorganic arsenic is one of the earliest identified human carcinogens. Evidence for arsenic as a human carcinogen comes from studies of arsenic ore smelters, pesticide workers, and people exposed to arsenic-containing drinking water. Although skin cancers are most frequent, bladder, lung, kidney and liver cancers are also reported to be associated with arsenic (Rosemann, 2003). The cancer risk due to arsenic is mainly attributes to the presence of As(III) as observed from epidemiological studies (Tinwell *et al.*, 1991) anyhow ingested As(V) undergoes reaction in which it is alternately reduced to As(III) (Yokohira, 2010). Due to all these threat to human health, speciation/removal of arsenic from the water bodies is very important to protect the human life.

Table 1: Permissible limits of various toxic heavy metals (WHO, (2004); USEPA, (2012); IS (10500); EU, (1998)).

Metals	Industrial effluent discharge (mg/L)				Permissible limit for potable water (mg/L)			
	Indian Standard			WHO				
	Inland surface	Public sewer	Marine coastal areas	Inland surface water	Indian standard	WHO	USEPA	EU standard
As	0.2	0.2	0.2	-	0.01	0.01	0.01	0.01
Cd	2.0	1.0	2.0	0.1	0.01	0.003	0.005	0.005
Cu	3.0	3.0	3.0	0.05 -1.5	1.5	2.0	1.3	2.0
Pb	0.1	1.0	2.0	0.1	0.05	0.01	0.015	0.01

1.2. HEAVY METALS REMOVAL TECHNIQUES

Heavy metal pollution is one of the most important environmental problems. Natural as well as anthropogenic sources increase to produce and discharge heavy metals into aquatic environment which become a key issue around the globe. Various methods are developed and suggested in the removal of heavy metals from wastewaters and the most widely used methods include chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation, flocculation, flotation and electrochemical treatment (Fu and Wang, 2011; Ornek *et al*., 2007; Wang and Chen, 2009).

Chemical precipitation was traditionally employed to remove heavy metal toxic ions from aqueous solutions. It is relatively simple to operate in which chemical reacts with heavy metals ions to form insoluble precipitates and the treated effluent can be recovered by sedimentation or filtration. In spite of its advantages, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level (Juttner *et al*., 2000) and usually insufficient to meet strict regulatory requirements (Lee and Davis, 2001).

Membrane filtration has received public attention for the wastewater treatment since it is capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis is employed for heavy metal removal from wastewater (Juang and Shiau 2000; Barakat, 2011). However, the studies of risks of using membrane filtration for trace metal analysis elucidate that membrane filtration cannot accurately assess the labile or the dissolved metal fraction from aqueous solutions at least for some selected metal ions (Hedberg *et al.*, 2011).

The other method coagulation-flocculation is employed to treat heavy metals in wastewater in which coagulants such as aluminium sulphate, ferrous sulfate and ferric chloride etc. are used to neutralize particulates and impurities by charge neutralization of particles to form amorphous metal hydroxide precipitates (Pang *et al.*, 2011; El-Samrani *et al.*, 2008). Flotation is a process based on imparting the ionic metal species in waste waters hydrophobic by use of surface active agents and subsequent removal of these hydrophobic species by air bubbling (Polat and Erdogan, 2007). It provides several advantages over the more conventional methods where in the case of high throughput of modern equipment, low sludge generation and the high efficiency of the separation schemes (Rubio *et al.*, 2002). Electrochemical heavy metal wastewater treatment techniques are regarded as rapid and well-controlled that require fewer/no chemicals, provide good reduction yields and produces less sludge, but electrochemical technologies involves high initial capital investment and the expensive electrical supply (Emamjomeh and Shivakumar, 2009; Segundo *et al.*, 2012).

Although all above techniques can be employed for the treatment of heavy metal wastewaters, it is important to mention that the selection of the most suitable treatment techniques depends on the initial metal concentration, the pollutant species in the wastewater, overall treatment cost, operational mode of equipment, plant flexibility, reliability and environmental impact etc. (Kurniawan *et al*., 2006; Eccles, 1995). It is reported that the applications of these traditional treatment techniques need enormous cost and continuous input of chemicals, which become impracticable and unconventional. This may cause an additional environmental damage (Tiwari *et al*., 2007). Therefore, interestingly; the adsorption process may offer to remove even inorganic and organic complex metals that could not be removed by conventional treatment methodologies (Daifullah *et al*., 2003; Mishra and Tiwari, 2002; Volesky, 1994).

1.3. ADSORPTION

Adsorption is a surface phenomenon. It arises due to the residual unbalance forces on the surface of the solids and liquids. As a result of these unbalance forces, the surface of a solid has a tendency to attract and retain the molecules of other species on its surface. As these molecules remain on the surface of the solid, their concentration is higher at the surface than in the bulk of the solid. The phenomenon is called adsorption. The substance, onto which surface the adsorption takes place is called an adsorbent while the molecular species that get adsorbed are called adsorbate. In some cases adsorption and absorption occur together. In such cases, the substances gets uniformly distributed into the bulk of the solid but at the same time, its concentration is higher at the surface than in the bulk, such phenomenon is called “sorption”. Instead of using an adsorption, the term sorption and bio-sorption is used since the adsorption phenomenon is not clear. Bio-sorption can be defined as a non-directed physio-chemical interaction that may occur between metal species and the materials of bio origin.

Adsorption method is versatile and simple to perform for the removal of water pollutants (Daus *et al*., 2004) and it is one of most preferable, effective and economical for its capability to remove even trace amount of metal pollutants from aqueous solutions (Hossain *et al*., 2012; Song *et al*., 2010). Moreover, the adsorption process offers flexibility in design and operation. In many cases it provides high-quality treatment methods for the treatment of different effluents. In addition, adsorption is sometimes reversible and adsorbents can be regenerated by suitable desorption process (Fu and Wang, 2011)

1.3. 1. CLASSIFICATION OF ADSORPTION

Adsorption is generally classified on the basis of the nature of interactions between the atoms, molecules or ions of the adsorbates and the adsorbents.

1.3.1.1. Physisorption

Physisorption is the adsorption which is dominated by physical interaction rather than chemical bonding. The adsorbates are held to the surface of the adsorbent by physical forces such as van der Waal's forces. It is generally resulting with the binding of the adsorbate particles in several consecutive layers which usually favours the lowering of temperature. Physisorption is a spontaneous, rapid and reversible process, which requires small activation energy. Adsorption equilibrium is quickly established and the molecular structure of the solid does not change with physisorption except few molecular solids (Bond 1984; Butt *et al*., 2006).

1.3.1.2. Chemisorption

Chemisorption is based on the chemical forces which arise due to transfer or sharing of electrons between the adsorbate and the adsorbent. The enthalpy of adsorption is much greater as compared to the physisorption. The adsorbates are often bound to the specific binding site, relatively immobile and irreversible. It is usually slower than physisorption and temperature dependent which indicates the presence of activation energy barrier (Butt *et al.,* 2006).

1.3.1. 3. Electrostatic adsorption

This type of adsorption is mainly due to the attractive Coulombic forces operative between electrically charged adsorbent surface and the oppositely charged adsorbate species. This is mostly observed in adsorption from aqueous solutions. It is usually the ionic exchange type; however, ion exchange need not be necessarily an electrostatic process. The exchange adsorption is specific, not always reversible and occurs slowly and the heat of adsorption is usually smaller than that of chemisorption (Helfferich, 1962)

1.3.2. FACTORS AFFECTING ADSORPTION PROCESS

Adsorption at solid – solution interface is influenced by several parameters *viz*., nature of adsorbent, nature of adsorbate, temperature, pH and concentration of the adsorbate and the presence of foreign species.

1.3.2.1. Nature of adsorbent

In general, an increase in surface area of adsorbent enhances the adsorption due to increase in the number of sites available for adsorption (Kurbatov, 1948). Adsorbents with higher surface charge will have a greater tendency to adsorb oppositely charged trace elements while similar charged trace elements (adsorbate) results in lesser uptake by the adsorbent (King *et al*., 1974). The studies of the adsorbents with pores demonstrated the enhance impact of meso-pore volume for the adsorption of the same adsorbates (Hsieh and Teng, 2000)

1.3.2.2. Nature of adsorbate

The adsorption process also depends on the size, shape and chemical nature of the adsorbate. The uptake of the adsorbate depends upon the polarity and the presence of active sites on the adsorbent. Studies on the competitive adsorption of metal ions showed that the properties of the adsorbate play a vital role in the adsorption process (Trivedi *et al*., 2001; Terdkiatburana *et al*., 2008).

1.3.2.3. pH of the solution

The pH is a very important parameter controlling the extent of adsorption of trace elements. The solubility and speciation/state of the adsorbate is strongly depend on the pH of the solution which further greatly affect the adsorption process (Say *et al*., 2001; Bayramoglu *et al*., 2003, Wang, *et al*., 2008). Further, the pH can extensively affect the surface charge of the adsorbent which in turn direct the electrostatic adsorption of ions and colloids. In addition, the acidity and basicity of solution can influence the composition and properties of adsorbent surface and this in turn put forth some effect on adsorption (Gundersen and Steinnes, 2003; Bonten, 2008). The anions or cations of hydroxides used for adjustment of pH compete with trace ions in ion exchange process which is particularly observed in the adsorption of mono–valent or bi–valent ions (Chen and Wang, 2007a).

1.3.2.4. Sorptive concentration

The adsorption at solid–solution interface obviously depends on the bulk sorptive concentrations. Usually, the amount adsorbed increases with increasing the sorptive concentration. The concentration of trace quantity adsorption often conform either Langmuir or Freundlich adsorption isotherms. Several researchers successfully utilized the Langmuir adsorption isotherm for studying the adsorption of metal ions (Sangi *et al*., 2008; Yeddou and Bensmaili, 2007, Hu *et al*., 2010). In addition, Freundlich adsorption isotherm is also found better suitable for the adsorption study of cations and anions on solid surfaces (Chiban *et al*., 2011; Liu *et al*., 2012b). However, in some cases, other isotherms such as Redlich and Peterson Isotherm, Tempkin Isotherm, Sips formulation, etc. are obtained as a better fit to study adsorption at various sorbtive concentrations (Allen *et al*., 2003; Sips, 1948, Foo and Hameed, 2010).

1.3.2.5. Temperature

Temperature is usually considered as an important factor of adsorption at liquid–solid interfaces. The rise in temperature of solution influences the kinetics and thereby promoted the adsorption which is attributed to the acceleration of some steps, originally slow or even due to the change in the adsorption mechanism towards the chemisorption (Li *et al*., 2009; Benes *et al*., 1980). The uptake of the adsorbate normally increases with increase in temperature which could be used in evaluating the activation energies (Al-Degs *et al.,* 2008; Kikuchi *et al*., 1979; Silber *et al*., 2012). On the other hand, it has been observed that the certain adsorption decreases with increase in temperature (Anayurt *et al*., 2009; Rahmani *et al*., 2010); while in some cases, the effect of temperature on trace adsorption is found to be small and nearly constant over a wide range of temperature (Hu *et al*., 2010; Yasemin, 2007).

1.4. ADSORBENTS FOR HEAVY METALS

Various adsorbents are employed for the removal of heavy metals from aqueous solutions. The role of dead biomasses in the removal of heavy metal toxic ions from aqueous waste/effluent waters has received an increase attention during recent past because of its fairly good exchange capacity, large abundance and also cost effectiveness. Numerous researchers investigated heavy metal removal by using dead biomasses such as saw-dust of *Pinussylvestris* (Kaczala *et al*., 2009), microalgae such as *Sargassum sp*. (Padilha *et al*., 2005), leave powder of rubber (*Heveabrasiliensis*) and *Moringa oleifera* (Ngah and Hanafiah, 2008; Reddy *et al*., 2012), *Viscum album* (Erenturk and Malkok, 2007), Peat (Brown *et al*., 2000) etc. Moreover, the attention of many researchers is diverted towards the biomaterials which are by-products or the waste from large scale industry or agriculture waste materials. Agricultural waste materials are considered as economic and environmentally benign due to their unique chemical composition, availability in abundance, renewable, low cost. Therefore, seems an efficient and viable option for heavy metal remediation (Sud *et al*., 2008). Literature studies reveal that agricultural waste materials: rice husk (Ajmal *et al*., 2003), tea waste (Amarasinghe and Williams, 2007), coconut shell (Amuda *et al*., 2007; Song *et al*., 2010), olive cake (Doyurum and Celik, 2006), grape stalk (Villaecesa *et al*., 2005), sugar bagasse (Mohan and Singh, 2002), peanut shell (El-Shafey, 2007), apricot stone (Soleimani and Kaghazchi, 2008), wheat bran (Farajzadeh and Monji, 2004), banana and orange peels (Annadurai *et al*., 2002), modified sugar beet pulp (Reddad *et al*., 2002), sunflower stalk (Hashem *et al*., 2006), corncobs (Vaughan *et al*., 2001), coffee waste (Orhan and Buyukgungor, 1993), apple waste (Maranon and Sastre, 1991), peanut hull (Johnson *et al*., 2002), cotton (Roberts and Rowland, 1973), tamarind seed, coconut shell, almond shell, ground nut shell and walnut shell (Agarwal *et al*., 2006), palm kernel fibre (Ho and Ofomaja, 2005) etc. were successfully applied for the removal of heavy metals from aqueous solutions.

Chitin and chitosan-derivatives are one of the most effective adsorbents due to low cost and high contents of amino and hydroxyl functional groups which show significant adsorption potential for the removal of various aquatic pollutants including heavy metal toxic ions. The high adsorption potential of chitosan for heavy metals is mainly due to high hydrophilicity encountered with large number of hydroxyl groups of glucose units, presence of several functional groups, high chemical reactivity of these groups, and flexible structure of the polymer chain (Bhatnagar and Sillanpaa, 2009). As the chitosan itself can dissolve in acidic medium, the use of cross-linking agent or with some modifying cation process like coating, the dissolution of chitosan can be improved, allowing chitosan composites to work well even in acidic condition. Therefore, chemical modifications that lead to the formation of chitosan derivatives, grafting chitosan and chitosan composites have gained much attention recently (Ngah *et al*., 2011).

Industrial waste materials were also investigated as potential and low cost adsorbents for the removal of the heavy metals from wastewaters. Red mud, a residue from bauxite refining was reported to exhibit an adsorption towards the anionic and cationic metal pollutants (Altundogan *et al*., 2002; Zhu *et al*., 2007b). Fly ash derived from coal combustion was also found to remove the arsenic and other metal cations from aqueous solutions (Balsamo *et al*., 2010; Papandreou *et al*., 2007). Lignin is a natural adsorbent usually obtained from a waste of paper mill. It is an amorphous cross-linked resin that possesses an aromatic three-dimensional polymer structure containing a number of functional groups making it potentially useful as an adsorbent material for removal of heavy metals from water (Guo *et al*., 2008; Wu *et al*., 2008). Other industrial wastes such as furnace slag, fermented slurry, waste from fertilizer industry and leather industry etc. were also employed in the removal of heavy metals from aqueous solutions (Xue, 2009; Namasivayam and Yamuna, 1995; Ahmaruzzaman, 2011)

Sand is one of the natural filter media and widely used as an adsorbent in the waste water treatment plant for the removal of organic pollutants (Bahgat *et al*., 1999; Hamoda *et al*., 2004) as well as inorganic pollutants such as heavy metals (Diels *et al*., 2003; Fonseca *et al*., 2009). Several researchers have developed techniques for coating metal oxides onto the surface of sand to overcome the problem of using metal oxide powders in water treatment. Many reports have shown the importance and suitable application of these surface coatings in controlling metal contamination in aqueous environment (Han *et al*., 2006; Benjamin *et al*., 1996; Tiwari *et al*., 2011). Zeolites, naturally occurring hydrated aluminosilicate minerals is widely utilized in the treatment of wastewaters contaminated with heavy metal toxic ions. It is observed that zeolites possess fairly good removal capacity for the heavy metal ions from aqueous wastes (Erdem *et al*., 2004; Motsi *et al*., 2009). The application of clay and clay minerals is another important materials employed in wastewater treatment. Clay materials received a greater interest in recent past because of their low cost; porosity with variable charge carried by clay materials makes them suitable for the remediation of aquatic wastes contaminated with heavy metal toxic ions. Moreover, natural abundance exaggerates its use in such treatment strategies. Literature survey reveals the applicability of variety of clay and modified clay materials in the removal of organic pollutants as well as inorganic pollutants in the waste water treatment because of their high specific surface area, chemical and mechanical stability, surface functional groups, surface properties, low cost, ion exchange capacities etc. (Lee and Tiwari, 2012, Vieira *et al*., 2010). There are several classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite are assessed as heavy metal adsorbents (Ahmaruzzaman, 2008).

1.5. ACTIVATED CARBON

Activated carbon (AC) is a common term used to describe carbonaceous material with well developed and high internal porosity; hence possesses a large specific surface area. Activated carbon can be produced from a variety of carbonaceous rich materials such as wood (130,000 tonnes/year), coal (100,000 tonnes/year), lignite (50,000 tonnes/year), coconut shell (35,000 tonnes/year), and peat (35,000 tonnes/year) are most commonly used bio materials (Pollard *et al*., 1992). Activated carbon texture includes a wide range of pores that can be classified according to their width in micro-pores (< 2 nm) meso-pores (2 – 50 nm) and the macro-pores (> 50 nm) (Moreno Castilla, 2004). Regarding pore size, most commercially available activated carbons are micro-porous having large specific surface area. These micro-porous activated carbons are excellent adsorbents for small size molecules. On the other hand, meso-porous activated carbons are useful for the adsorption of large size molecules. In order to increase the ability of activated carbon towards the sorption capacity, the pore network should be developed during activated charcoal prepared by applying various physical or chemical treatments (Dias *et al*., 2007). The method for the preparation of activated carbon is broadly divided into two methods: (1) Physical activation and (2) Chemical activation. In physical activation, the raw material with less than 25% moisture, is carbonized first at 400 - 500 ^{o}C to eliminate the bulk of the volatile matter and then the carbon is subjected to oxidizing gases usually carbon dioxide or steam at 800-1000 ^{0}C. Chemical activation involves the incorporation of chemical agents such as zinc chlorides or inorganic acids such as phosphoric acid, nitric acid, sulphuric acid which is mixed with the precursor in proper ratio and carbonized at temperatures up to 800 ^{0}C in the absence of air or in presence of inert gases. Ammonium salts, borates, calcium oxide, ferric and ferrous compounds, manganese dioxide, nickel salts and hydrochloric acid are also used for activation (Mohan and Pittman Jr., 2006; Mohammad-Khah and Ansari, 2009).

The specific surface area of activated carbon varies depending on precursor (Stavropoulos and Zabaniotou, 2009), activation process (Ahmedna *et al*., 2000a), pore size (Karagoz *et al*., 2008) and additives or even chemicals used (Yin *et al*., 2007). By choosing an appropriate activation conditions, activated carbon can possess thespecific surface area as high as up to 2000 m^{2}/g (Mohan and Pittmann Jr., 2006). The functional groups containing oxygen, hydrogen, sulphur and nitrogen are generally present in activated carbon and the main functional groups which, in general, are considered to be responsible for uptake of pollutants include carboxyl, hydroxyl, carbonyl, phenols, lactone and quinone groups. The unique adsorption behaviour of activated carbon can be significantly influenced by these functional groups (Budaeva *et al*., 2010; Matos *et al*., 2011).

Among common adsorbents, activated carbon is undoubtedly the most effective materials for the wastewater treatment due to its large specific surface area, porous structure, high performance and low cost (Haro *et al*., 2012; Dais *et al*., 2007). Several reports showed the successful application of activated carbon in the treatment of aquatic environment contaminated with heavy metal toxic ions (Park and Kim, 2005; Rivera-Utrilla *et al*., 2003; Jusoh *et al*., 2007). The removal of lead, cadmium, zinc, and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot stone were studied and the good removal capacity of activated carbon was observed with very comparable cost (Kazemipour *et al*., 2008). Variety of raw materials were used for the preparation of activated carbon such as waste tire (Betancur *et al*., 2009), bamboo (Lo *et al*., 2009), saw dust (Srinivasakannan *et al*., 2004), sewage slugde (Liu *et al*., 2010a), chicken waste and coal (Cui *et al*., 2007), marine plants (Ncibi *et al*., 2009), pine cone (Momcilovic *et al*., 2011), etc. Agricultural wastes/by products is a rich source for activated carbon production due to their large abundance, low cost, low ash content and reasonable hardness (Ahmedna *et al*., 2000b); therefore, conversion of agricultural wastes into activated carbon is a promising alternative to solve environmental problems and also to reduce the costs of activated carbon preparation. The agriculture waste/by products such as wheat and corn straw (Lanzetta and Di Blasi, 1998), apricot stone (Aygun *et al*., 2003), almond shell (Marcilla *et al*., 2000), rice hulls (Yalcin and Sevinc, 2000), rice straw (Oh and Park, 2002), hazelnut shell (Demirbas, 2009), sugarcane baggase (Ahmedna *et al*., 2000a), grape stalk (Deiana *et al*., 2009), coconut waste (Kadirvelu and Namasivayam, 2003) were among the material employed for the production of activated carbons for the wastewater treatment.

1.5.1. Modification of activated carbon

Various methods are developed to modify the nature and concentration of functional groups in activated carbon. Acid treatment of carbon is generally employed to oxidize the porous carbon surface as it increases the acidic property. This removes the mineral elements and improves the hydrophilic nature of surface. Acidic functional groups (i.e., oxygen functional groups containing proton donors) on carbon surfaces is examined for the removal of heavy metals from water and found to be highly favorable because metal ions have a tendency to form metal complexes with the negatively charged acid groups (Bhatnagar *et al*., 2013). It is reported that surface modification of commercial activated carbon by using citric acid significantly improves copper adsorption capacity. After acid treatment the activated carbon surface becomes more homogeneous (Chen *et al*., 2003). The activated carbon prepared from *Camellia oleifera* shell by water vapor gasification was modified with phosphoric acid resulted in high specific surface area i.e., 1608 m^2/g; showed high sortion capacity for methylene blue (Kang *et al*., 2011). The adsorption of Cr(VI) from aqueous solution by using granular activated carbon (GAC) along with modified granular activated carbon was investigated and the results showed that the activated carbon modified with nitric acid possessed lower specific surface area but an enhanced oxygen functional groups hence, showed higher adsorption capacity for water pollutants comparing to GAC (Huang *et al*., 2009). A commercial activated carbon Chemviron F 400 was oxidized by nitric acid and utilized in the treatment of heavy metal toxic ions. It was reported that a significant changes in physical properties such as surface area decreases and pore size were occurred oxidizing with nitric acid. This enabled the material with substantially high sorption capacity (Vladimir and Malik, 2002). The activated carbon prepared from the apricot stone material by chemical activation with sulphuric was also found to be effective adsorbents for the removal and recovery of Pb(II) from wastewaters (Mouni *et al*., 2011). Tajar *et al*., 2011 reported that the low cost activated carbon was obtained from a nut shell; an agriculture waste by chemical activation with phosphoric acid. The material was further modified by using sulfurizing agent (SO_2) successfully and utilized in the removal of cadmium from aqueous solutions. Tannic acid immobilized activated carbon was synthesized and utilized in the adsorption of heavy metal toxic ions such as Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) studied under the batch experimentation. This immobilization resulted in a reasonable improvement in the removal capacity of activated carbon (Ucer *et al*., 2006). Hydrochloric acid was used for the modification of activated carbon obtained from coconut shell. Further, the AC was employed to remove Cr(VI) from aqueous solutions and it was observed that hydrochloric acid treatment caused to increase the numbers of surface oxygen groups thus, increasing the adsorption active sites and enhanced the removal efficiency of Cr(VI) (Park and Jang, 2002).

Several studies are carried out to determine the effect of basic treatment on activated carbon. Generally, base (alkaline) treatment of AC produces positive surface charge which in turn favors in adsorption of negatively charged species. Therefore, the basic treatment of AC is beneficial in enhancing the adsorption of especially organic species (like phenol) from aqueous solution (Bhatnagar *et al*., 2013). The activated carbon obtained from oil palm empty fruit bunch was modified by using ammonia solution and hence, employed in the adsorption of 2, 4- dichlorophenol. It was observed that the surface modification of the activated carbon by ammonia was shown to increase the adsorption capacity of 2,4-dichlorophenol. This was explained as the basic surface functional groups created by the nitrogen incorporation rendered the activated carbon more basic; and thus found a surface that carries more positive charge (Shaarani and Hameed, 2011). The commercially available CWZ-series activated carbon was treated with gaseous ammonia. The treatment was carried out at elevated temperature ranged from 400 – 800 ^{0}C for 2 hours. The activated carbon treated with ammonia showed an enhance sorption capacity for phenol comparing to untreated materials; however the enhancement was depended to the treatment temperature and porous structure of the studied activated carbon (Przepiorski, 2006). Thermal tailoring of bituminous granular activated carbon (GAC) by ammonia gas at 500 -800^{0}C for 60 minutes showed fourfold improvement in perchlorate adsorption as determined by rapid small scale column tests. The most favorable improvement was occurred for the samples activated at the temperatures between 650 – 700 ^{0}C. The study showed that the modification of activated carbon by using ammonia appeared to be an effective method to enhance the adsorption of perchlorate from aqueous solution (Chen *et al*., 2005a; Chen *et al*., 2005b). The commercial activated carbon were modified by high temperature treatment in the presence of ammonia, nitrogen or hydrogen in the first approach and the second modification was done through carbonization followed by activation of N-enriched polymers and coal tar pitch using CO_2 and steam as activation agents. The adsorption of p-chlorophenol on activated carbon with basic properties was investigated and it was reported that Langmuir monolayer adsorption capacity was related to the porous structure and the amount of basic sites present onto the solid surface (Grabrowska *et al*., 2010). In addition to ammonia treatment, the activated carbon was modified by using basic chemical such as sodium hydroxide (Chiang *et al*., 2002) and urea (Stavropoulos *et al*., 2008) as to increase the surface functional groups.

Carbon materials were treated by ozone; common oxidizers to investigate the mercury attenuation at varying temperature conditions. It is found that ozone treatment dramatically increases the mercury capture capacity of carbon surfaces by factors up to 134, but the activity is easily destroyed by exposure to the atmosphere, to water vapour, or even by mild heating (Manchester *et al*., 2008). Commercial activated carbon (Filtrasorb 400) was treated with different ozone doses in order to study the effect of ozone treatment on their surface properties, and was investigated the behavior of these carbon samples in the adsorption of 1-naphthalenesulphonic, 1,5 naphthalene-disulphonic and 1,3,6-naphthalenetrisulphonic acids. The results indicated that the sorption process was taken place mainly by the π-π dispersion interactions between the aromatic ring electrons of the naphthalene sulphonic acids and the basal plane of the activated carbon. The adsorption capacity of aromatic sulphonic acids was decreased as the pH was increased (Rivera-Utrilla and Sanchez-Polo, 2002).The impact of ozonation on textural and chemical surface characteristics of two granular activated carbons (GAC) namely F400 and AQ40, and their ability to adsorb phenol, *p*-nitrophenol and *p*-chlorophenol from aqueous solutions was studied and reported elsewhere (Alvarez *et al*., 2005). The porous structure of the ozone-treated carbons remained practically unchanged with regard to the virgin GAC. However, an important modification of the chemical surface and hydrophobicity was observed by FTIR spectroscopy. The studies suggested that dispersive interactions between π-electrons of the ring of aromatic carbon and that of the carbon basal planes were thought to be the primary forces responsible for the physical adsorption. Activated carbons were prepared by carbonization at 900 ^{0}C and activated in presence of CO_2 and steam at 850 ^{0}C using cherry stones as precursor material. The obtained products were ozone-treated at room temperature. It was found that the treatment of activated carbon with ozone combined with heat treatment enabled it to control the acidic–basic characters and the strength of carbon surface (Jaramillo *et al*., 2010).

To improve the performance of activated carbon for specific contaminants removal, several researchers conducted various methods to modify the surface characteristics of activated carbon. The granular activated carbon were impregnated with the anionic surfactants sodium dodecyl sulfate, sodium dodecyl benzene sulfonate and dioctylsulfosuccinate sodium. It was observed that the surfactant-impregnated activated carbons could remove an enhanced level of Cd(II) than the bare activated carbon from aqueous solutions (Ahn *et al*., 2009). The bituminous coal based activated carbon was modified by using dicocodimethylammonium chloride, tallowtrimethyl-ammonium chloride, cetyltrimethylammonium chloride and cetylpyridinium chloride surfactants. The cationic surfactant tailored activated carbons was employed effectively in the removal of perchlorate below to its detection levels and this was 30 times higher than the virgin activated carbon

(Parette and Cannon, 2005). It was also reported that the modification was done by using micro wave radiation. The experiment was carried out by using microwave radiation under N_2 atmosphere. A gradual decrease in the surface acidic groups was observed with the modification, while the surface basicity was enhanced to some extent, which gave rise to an increase in the pH_{pzc} value. The micro-pores were then extended into larger pores, resulting in an increase in the pore volume and average pore size. Adsorption studies showed enhanced adsorption of methylene blue by the modified activated carbons (Liu *et al.*, 2010b).

Application of low temperature oxygen plasma was proposed to modify activated carbons (ACs) for enhancing their adsorption toward dibenzothiophene in a model diesel fuel. The results showed that the use of oxygen plasma modification caused to enhance the carbon surface oxygen-containing groups; thus significantly improved their adsorption capacities. Fixed-bed breakthrough experiments showed that the working loading capacity of the modified ACs for dibenzothiophene was increased by 49.1% compared to the original AC (Zhang *et al.*, 2012). The oxygen plasma treatment of activated carbon fibers (ACFs) was carried out to introduce oxygen-containing groups onto carbon surfaces. Experimental results showed that the hydrochloride removal efficiency was increased with the number of plasma treatment times up to around 300%, resulting from newly formed oxygen-containing functional groups (especially phenolic and carboxylic) on carbon surfaces (Park and Kim, 2004). The granular activated carbon was treated with dielectric barrier discharge plasma in an attempt to enhance the sorption capacity of several metal ions. A mechanism of the metal ion adsorption on the activated carbon surface was proposed as ion exchange type occurred between the metal cations from the aqueous solution and hydrogen ions on to the activated carbon surface. The improvement in adsorption was attributed because of the change in surface chemical structure of the activated carbon rather than the modification of the surface physical structure (Lee *et al*., 2005). The modification of activated carbon was also done by using micro-organisms and it was dented as biological modification. The biological modified activated carbon were then utilized in the removal of organic pollutants such as phenol, pesticides etc. (Ha and Vinitnantharat, 2000; van der Hoek *et al*., 1999).

1.6. METAL OXIDES

Recent studies suggested that many nano-sized metal oxides exhibit very favourable sorption to heavy metals in terms of high capacity and selectivity, which would result in better removal of toxic metals ions from aqueous solution. Among the available adsorbents of nano-sized metal oxides, ferric oxide, manganese oxide, aluminium oxide, titanium oxide, magnesium oxide, cerium oxide etc. were classified as the promising adsorbents for heavy metal removal from aqueous solutions (Hua *et al*., 2012). There was an enhanced attention towards the use of nano-sized manganese oxide and iron for cleaner treatment technologies. It was reported that nano-sized manganese dioxide showed significantly higher sorption capacity comparing to its bulk counterpart because of its polymorphic structures and higher specific surface area (Wang *et al*., 2011). The manganese- modified sand was successfully utilized for the removal of Cu(II) and Pb(II) (Tiwari *et al*., 2011) whereas the activated carbon modified with manganese oxide was employed for the treatment of copper and cadmium (Fan and Anderson, 2005). The successful application of either manganese oxide or immobilized nano-sized manganese oxide adsorbents showed promising behaviour in the effective sorption of cationic or anionic pollutants such as arsenic, strontium, cesium, cadmium and zinc from aquatic environment (Trivedi and Axe, 1999; Mishra and Vijaya, 2007; Lenoble *et al*., 2004; Su *et al*., 2010).

The modification of several solids by immobilizing the iron oxide nano-particles was also found to be promising materials for the wastewater treatment. Iron oxides, hydroxides and oxide hydroxides consist of arrays of Fe ions and O^{2-} or OH^- ions. In comparison with minerals existing in soil, iron oxides have relatively high specific surface area and surface charge, and they often regulate free metal concentration in soil through adsorption reactions (Schewertmann and Taylor, 1989)**.** Studies on arsenic removal by iron modified activated carbon shows that preloaded granular activated carbon with iron greatly improved its arsenic adsorption capacity. Moreover, iron preloaded carbon could get over 200 times higher bed volume than virgin carbon (Chen *et al*., 2007b). Reed *et al*., (2000) reported the removal of As(III), As(V), Hg(II) and Pb(II) by Fe-oxide impregnated activated carbon was more effective than its non-impregnated counterpart. The modification of sand surface was done with iron and was then applied in the treatment of Cu(II), Cd(II) and Pb(II) contaminated waters. It was found that the iron oxide nano-particles were immobilized onto the sand surfaces which enabled it efficient and potential materials in the remediation of wastewater contaminated with these heavy metal toxic ions (Lee *et al*., 2012). It was also reported that the municipal sewage sludge was modified with iron oxide and successfully utilized for the removal of Cu(II), Cd(II), Ni(II) and Pb(II) in batch method (Phuengprasop *et al*., 2011). The other materials such as a resin shellac, waste silica, zeolites, methane fermentation sludge, ceramic prepared from mud were reported as modified/impregnated with iron oxide and found suitable for the treatment of wastewaters contaminated with cationic or anionic pollutants under batch methods as well as fixed bed column experiments (Gong *et al*., 2012; Unob *et al*., 2007; Chen *et al*., 2012; Han et al., 2009; Qian *et al*., 2009).

1.6. SCOPE OF THE STUDY

The deleterious quality of the aquatic environment is a global concern. Therefore, the viable and efficient treatments technologies in the remediation of aquatic environment are one of the key issues need to be addressed by the environmental engineers. In a line, the removal/speciation of heavy metal toxic ions from aqueous waste or effluent waters is to be performed prior to its discharge into the water bodies in order to protect the aquatic environment and terrestrial life. In this regard, dead biomasses are one of the possible natural materials available abundantly for the treatment of waste waters. But in order to enhance the sorption capacity of these dead biomasses, micro- to meso-porous activated carbons could be obtained as precursors to these dead biomasses. These activated carbons are supposed to possess significantly large specific surface area, which is available for adsorption of several metallic impurities. It was observed that the seemingly high specific surface area of the activated carbons could be utilized to impregnate the small or nano-sized manganese or iron oxides as to enhance further the removal capacity and suitability of these materials towards several trace metallic impurities particularly the heavy metal toxic ions. The metal oxides of manganese and iron are known to be efficient, effective and suitable materials toward the heavy metal toxic ions including arsenic, cadmium, copper, lead, etc. because of its high specific surface area and acid-base character under varied pH condition. Moreover, these materials showed their limitations in the treatment technologies because of the floc formation and difficulty in settling properties. However, the impregnation of manganese and iron oxides nano-particles onto the solid substrates exaggerates the applicability of these materials. Therefore keeping in view, the present investigation is an attempt to exploit fully the naturally available two dead biomasses *viz*., the rice hulls and *areca* nut wastes to obtain the activated carbons. These, activated carbons could be more viable, eco-friendly and cost effective materials to be employed in such treatment technologies. Further, the ACs samples were utilized a solid substrate materials to immobilize the small sized manganese and iron oxides within the pores and surfaces of ACs samples. These solids were then employed in the treatment of wastewaters contaminated with heavy metal toxic ions under the batch and column reactor operations. The treatment method proposed is an alternative technology to be employed in the remediation of aquatic environment contaminated with several heavy metal toxic ions *viz*., arsenic(III),arsenic(V), cadmium (II), copper (II) and lead(II). These studies provide an initial but important input data for the large scale or pilot plant scale treatment of water bodies contaminated with heavy metal toxic ions.

2. METHODOLOGY

2.1. MATERIALS

2.1.1. Rice hulls and *areca* nut waste

Rice hulls were collected from rice mill at Aizawl, Mizoram, India and the *areca* nut wastes, i.e., the waste produced while the nut is processed for chew, were collected from the local shop of Samtlang, Aizawl, Mizoram, India.

2.1. 2. Chemicals and reagents

The chemicals and reagents used in the experiments were of AR grade and procured from various sources. The de-ionized water was further purified by the Millipore water purification system (Milli-Q^+). The following chemicals are employed in the present investigation.

List of chemicals and reagents

S.No.	Chemical	Source
1	Cadmium(II)sulphate	Kanto Chemical Co. Inc., Japan
2	Copper(II) sulphate	Duksan Pure Chemicals Co. Ltd., Korea
3	Lead nitrate	Junsei Chemical Co. Ltd., Japan
4	Sodium metaarsenite	Wako Pure Chemical Industries Ltd., Japan
5	Disodium hydrogen arsenate heptahydrate	Wako Pure Chemical Industries Ltd., Japan
6	Manganese nitrate hexahydrate	Junsei Chemical Co. Ltd., Japan
7	Iron (III) nitrate enneahydrate	Wako Pure Chemical Industries Ltd., Japan
8	Sulphuric acid	Merck, India
9	Ammonia solution	Merck, India
10	Sodium hydroxide	Duksan Pure Chemicals Co. Ltd., Korea
11	Nitric acid	DuksanPure Chemicals Co. Ltd., Korea

Rice

Rice hulls

***Areca* nut**

***Areca* nut waste**

2.2. METHODS

2.2.1. Preparation of activated carbon (AC)

The raw materials, rice hulls and *areca* nut waste were washed with de-ionized distilled water to remove any adhering impurities. Dried at room temperature and the solid materials were digested in conc. H_2SO_4 and the content was kept at 120 ^{0}C for 2 hours. The carbonized carbon obtained was washed with distilled water till the filtrate solution reached to its pH~4.0. Again dried at 70 ^{0}C and the samples were titrated with small volume of NH_3 solution to neutralize excess acids. The sample was washed with distilled water and completely dried at 70 ^{0}C. The solid sample was cooled at room temperature and grounded to obtain fine powders. Further, this carbonized carbon was activated by using muffle furnace at 800 ^{0}C in N_2 environment for 6 hour and the activated carbon obtained from rice hulls (AC(R)) and areca nut waste (AC(N)) were used for batch experiment as well as for the preparation of manganese coated activated carbons MCAC(R) and MCAC(N) and iron coated activated carbons (ICAC(R) and ICAC(N)).

2.2.2. Preparation of manganese moated activated carbon (MCAC)and iron coated activated carbon (ICAC)

The manganese coated activated carbon (MCAC) was prepared by taking 60 g of AC in a round bottom flask with 100 mL of 0.025M manganese nitrate solution (pH~9). Similarly, the iron coated activated carbon (ICAC) was prepared by taking 60 g of AC in a round bottom flask with 100 mL of 0.025M iron nitrate solution (pH~9). The mixture was kept in a rotary evaporator at 60 ^{0}C at the rotating speed of 30 rpm. Further, almost 90% of the water was removed by applying slowly the vacuum. The slurry was taken out in a beaker and kept in a drying oven at 90 ^{0}C as to dry it completely. Further, the sample was kept for 2 hours at 110 ^{0}C for the stabilization of immobilized manganese-oxide or iron oxide particles. The samples were taken out from the oven and cooled at room temperature and washed with distilled water and dried again at 60 ^{0}C. These samples were then used for further investigations.

2.2.3. Stability of MCAC and ICAC

The manganese or iron particles aggregated onto the surface of activated carbon were assessed for its stability against the pH effect by varying the solution pH from pH 2.0 to 10.0. To this effect, 0.5 g of solid was taken in 100 mL of distilled water at different initial pH values and then kept in an automatic shaker at 25 ^{0}C for 24 hrs. The solutions were then filtered using the 0.45 µm syringe filter. The filtrates were then subjected for its total manganese or iron content using the atomic absorption spectrometer (AAS; Fast Sequential Atomic Absorption Spectrometer Model AA240FS, Varian).

2.2.4. Characterization of the material

Characterization of the solid samples were done by SEM/EDX data in which the surface morphology and composition of these solids AC, MCAC and ICAC were obtained by using SEM (Scanning Electron Microscope) machine (FE-SEM-Model: SU-70, Hitachi, Japan) equipped with energy dispersive X-ray spectroscopy EDX system. XRD data was collected using the X-Ray Diffraction machine i.e., PANalytical, Netherland (vide model- X'Pert PRO MPD). The XRD data was collected with the scan rate of 0.034 of 2θ illumination at an applied voltage of 45 kV with the observed current of 35 mA, using CuK_{α} radiations having the wavelength 1.5418 Å. The functional groups present in these solids were observed by FT-IR analytical methods (Bruker, Tensor 27, USA by KBR disk method). Further, the amount of manganese and iron content in the MCAC and ICAC as well as ACs samples were determined by standard US EPA (United States Environmental Protection Agency) (www.epa.gov/osw/hazard/testmethods/sw846/pdfs/3050b.pdf) method 3050B. The specific surface areas of these samples were obtained by using the Protech Korea BET surface area Analyzer (Model ASAP 2020).

2.2.5. Determination of pH_{pzc} of the solids

The pH_{pzc} (point of zero charge) of these solids was determined using the known method as described earlier (Rivera-Utrilla *et al*., 2001; Khormaei *et al*., 2007). 500 mL of double distilled water was added to an Erlenmeyer flask, capped with cotton and was slowly and continuously heated until boiling for 20 min to expel the dissolved CO_2. The flask was capped immediately to prevent re-absorption of atmospheric CO_2 by water. Then, 50 mL of 0.01M NaCl solution was prepared from CO_2 free water in different flasks and the pH of each solution in each flask was adjusted to pH values of 2.0, 4.0, 6.0, 8.0, 10.0 and 12.0 by adding 0.1M HCl or 0.1M NaOH, solutions. 0.15 g of the solid sample was then added in each flask and the flasks were always capped tightly and agitated for 24 hours at 25^oC. The samples were taken out and immediately check the final solution pH using previously calibrated pH meter (HANNA pH 213, Microprocessor pH meter, USA). The pH_{pzc} was taken as the point at which the curve crossed the line of final pH equals to initial pH.

2.2.6. Speciation studies

The speciation studies was performed for As(III), As(V), Cd(II), Cu(II) and Pb(II) using the $MINEQL^+$ (Version 4.5), a geochemical computer simulation program. The input parameters were taken as initial concentration of Cd(II): 10 mg/L, Cu(II): 10 mg/L and Pb(II): 10 mg/L and As(III) and As(V): 7.5 mg/L at a constant temperature 25^oC. The thermodynamic equilibrium constants used were given in Table 2, 3, 4, 5 and 6. The species distribution of these metal ions as a function of pH is further obtained and presented in figures in results and discussion chapter.

Table 2: Various equilibrium constants used for the speciation of Cd(II) in aqueous solutions at 25 ^{0}C.

Equilibrium	Log K
$Cd^{2+} + 3H_2O \leftrightarrow Cd(OH)_3^- + 3H^+$	-32.505
$Cd^{2+} + 4H_2O \leftrightarrow Cd(OH)_4^{2-} + 4H^+$	-47.288
$Cd^{2+} + H_2O \leftrightarrow Cd(OH)^+ + H^+$	-10.097
$Cd^{2+} + 2H_2O \leftrightarrow Cd(OH)_2\ (aq) + H^+$	-20.294
$2Cd^{2+} + H_2O \leftrightarrow Cd_2(OH)^{3+} + H^+$	-9.397

Table 3: Various equilibrium constants used for the speciation of Cu(II) in aqueous solutions at 25 ^{0}C.

Equilibrium	Log K
$2Cu^{2+} + 2H_2O \leftrightarrow Cu_2(OH)_2^{2+} + 2H^+$	-10.594
$Cu^{2+} + 3H_2O \leftrightarrow Cu(OH)_3^-$	-26.879
$Cu^{2+} + 4H_2O \leftrightarrow Cu(OH)_4^{2-} + 4H^+$	-39.980
$Cu^{2+} + H_2O \leftrightarrow Cu(OH)^+ + H^+$	-7.4970
$Cu^{2+} + 2H_2O \leftrightarrow Cu(OH)_2\ (aq.) + 2H^+$	-16.497

Table 4: Various equilibrium constants used for the speciation of Pb(II) in aqueous solutions at 25 ^{0}C.

Equilibrium	Log K
$Pb^{2+} + 2H_2O \leftrightarrow Pb(OH)_2\ (aq) + 2H^+$	-17.094
$Pb^{2+} + H_2O \leftrightarrow Pb(OH)^+ + H^+$	-7.597
$4Pb^{2+} + 4H_2O \leftrightarrow Pb_4(OH)_4^{4+} + 4H^+$	-19.988
$2Pb^{2+} + H_2O \leftrightarrow Pb_2(OH)_3^+ + H^+$	-6.397
$Pb^{2+} + 3H_2O \leftrightarrow Pb(OH)_3^- + 3H^+$	-28.091
$Pb^{2+} + 4H_2O \leftrightarrow Pb(OH)_4^{2-} + 4H^+$	-39.699
$3Pb^{2+} + 4H_2O \leftrightarrow Pb_3(OH)_4^{2+} + 4H^+$	-23.888

Table 5: Various equilibrium constants used for the speciation of As(III) in aqueous solutions at 25 ^{0}C.

Equilibrium	Log K
$AsO_3^{3-} + H^+ \leftrightarrow HAsO_3^{3-}$	13. 414
$AsO_3^{3-} + 3H^+ \leftrightarrow H_3AsO_3$	34.744
$AsO_3^{3-} + 2H^+ \leftrightarrow H_2AsO_3^-$	25.454
$AsO_3^{3-} + 4H^+ \leftrightarrow H_4AsO_3^+$	34.439

Table 6: Various equilibrium constants used for the speciation of As(V) in aqueous solutions at 25 ^{0}C.

Equilibrium	Log K
$AsO_4^{3-} + H^+ \leftrightarrow HAsO_4^{2-}$	11.500
$AsO_4^{3-} + 2H^+ \leftrightarrow H_2AsO_4^-$	18.460
$AsO_4^{3-} + 3H^+ \leftrightarrow H_3AsO_4$	20.700

2.2.7. Batch reactor studies

Batch experiments were performed to obtain adsorption data with the effect of sorptive pH, initial sorptive concentration, and contact time and background electrolyte concentrations. The stock solutions of 100 mg/L of As(III), As(V), Cd(II), Cu(II) and Pb(II) of 1.0 L of each sorptive were prepared by dissolving the appropriate amounts of their salts in the distilled water and the desired concentration for the batch reactor experiments were obtained by the successive dilution method. The adsorption of As(III), As(V), Cd(II), Cu(II) and Pb(II) was investigated by taking 0.25 g of activated carbon (AC)/or manganese coated activated carbon (MCAC)/or iron coated activated carbon (ICAC) in 0.10 L of sorptive solution. The solution mixture was equilibrated by using automatic shaker (KUKJE, Shaking Incubator, Korea model 36-SIN-125) for 24 hours at 25±1 ^{0}C. The sorptive solution pH was always done, prior to the addition of solids, by addition of drops of

0.1 mol/L HNO_3 or 0.1 mol/L NaOH. The equilibrated solution was then filtered by using 0.45 µm syringe filter and the pH of the solution was again measured and it was reported as the final pH throughout. The bulk metal concentration was measured using Fast Sequential Atomic Absorption Spectrometer (Model AA240FS, Varian). The data was then utilized to calculate the removal percentage of the metal ions. The percentage removal of the target metal ion was calculated using the equation

$$\% \, Removal = \frac{C_0 - C_e}{C_0} \times 100 \qquad \ldots (1)$$

where $C_0$and $C_e$are the initial and final sorptive concentrations, respectively.

2.2.7.1. Effect of pH

pH is an influential parameter in metal uptake from the aqueous solution since it determines the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbents as well the adsorbate in the solution (El-Ashtoukhya *et al*., 2008). Literature studies reveal that, generally, adsorption of metal ions which exists as cations increases with increasing pH up to certain pH value then decreases again with further increase in pH (Kula *et al*., 2008; Reddy *et al*., 2012, Ahmaruzzaman, 2011) or the adsorption continuously increases with increasing pH with maximum percent uptake at alkaline medium (Tajar *et al*., 2009; Lee *et al*., 2012). This may be explicable that the adsorption of cations in strongly acidic medium is very low which is due to a competition occurred between the excess of hydrogen ions and cations or positive metal ions towards the same actives sites of solid surface which suppresses the metal ions adsorption from the solution. Increasing the pH causes for a decrease in H^+ ion concentrations due to successive de-protonation. This results with gradual increase in negative charge density onto the solid surface that enables to favour more adsorption of the cations (Depci *et al*., 2012; Rao *et al*., 2006). On the other hand, the metal with anion species such as chromium, arsenic etc., may exhibit decrease in the percent tadsorption with increasing the solution pH (Gupta and Babu, 2009; Singh *et al*., 2009; Deedar *et al*., 2009). An increase in pH even by a single unit may cause an abrupt change in amount adsorbed (Anayurt *et al*., 2009), but somehow the adsorption which is not much affected by change in pH are also reported (Meena *et al*., 2005). Therefore, there is specific pH range which may favour the uptake of certain metal ions by adsorption processes.

The effect of pH of the sorptive solution was conducted by maintaining the solution pH between pH 2.0 to 10.0 with the metal concentrations of ~10 mg/L. Further, the sorption experiments were conducted as detailed before Section 2.2.7. The results obtained were reported as percentage removal as a function of final pH of the sorptive solution.

2.2.7.2. Effect of sorptive concentration

In the batch reactor operations, the initial concentration of metal ions in the solution plays a key role as to determine the driving force operative to overcome the mass transfer resistance between the aqueous and solid phases (Dang *et al*., 2009). The amount adsorbed by a definite weight of adsorbent increases with an increase in sorptive concentrations. However, the percentage adsorption usually decreases with an increase in sorptive concentrations due to the fact that at low concentrations, relatively larger number of active sites are available onto the solid surface for lesser number of sorbing ions but increasing the sorptive concentration for the same dose of solid relatively lesser number active sites are present which results in less percent removal of the metal ions (Mishra *et al*., 2007). The effect of sorptive concentration was studied by several researchers and further employing the data to various isotherms such as Freunlich, Langmuir, Sips or Tempkin, etc. adsorption isotherm in order to understand the interaction mechanism between the adsorbate species and the adsorbents at the solid-solution interface (Foo and Hameed, 2010).

The effect of initial metal concentration was studied between 1.0 mg/L to 25.0 mg/L for Cd(II), Cu(II) and Pb(II) and As(III) and As(V). The optimum pH was selected based on the speciation of the metals as pH 4.5 for As(III) and As(V), pH 4.0 for Cu(II) and pH 5.0 for Cd(II) and Pb(II).

2.2.7.3. Effect of contact time

The study of sorption kinetics in wastewater treatment is significant as it provides important insights into the reaction pathways and the mechanism of sorption reactions (Wu *et al*., 2001; Zou *et al*., 2006). The removal of heavy metals to reach its apparent equilibrium state is varied from one metal to another and found to be affected by the nature of adsorbent and its available adsorption sites. However, the kinetic characteristic in a sorbent depends not only on the presence of the active metal sites but also depends on the accessibility of the metal site without sterical hindrance (Lasheen *et al*., 2012). Studies on the effect of contact time for the adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) ions by using tannic acid immobilized activated carbon shows that increase in contact time up to 60 minutes significantly enhanced the amount of metal ions adsorbed using a constant dose of adsorbent (Ucer *et al*., 2006). On the other hand, the times needed to reach the equilibrium for the adsorption of Zn(II) varied as 1 hour, 3 hours for clarified sludge and rice husk ash, respectively. Furthermore, 4 hours was needed for the activated alumina and Neem (*Azadirachta*) bark (Bhattacharya *et al*., 2006). All these equilibrium time clearly inferred the sorption kinetic always varies for different adsorbents and adsorbate ions.

The effect of contact time was studied at different interval of time upto 24 hours keeping the initial concentration of the metal ~10 mg/L at the sorptive pH 4.5 for As(III) and As(V), pH 4.0 for Cu(II) and pH 5.0 for Cd(II) and Pb(II).

2.2.7.4. Effect of background electrolyte concentration

The change in background electrolyte concentrations is an important parameter revealing the nature of binding of the sorptive ions onto the solid surface. The background electrolytes dependence data by soil minerals is usually used to distinguish between nonspecific and specific adsorption (Hayes *et al*., 1988). Outer sphere complexes involved only electrostatic or van der Walls interactions and are strongly affected by the ionic background electrolytes in the aqueous phase, whereas inner sphere complexes involved with stronger covalent or ionic bonds were only weakly affected by the background electrolyte concentrations (Spark, 1995). Hence, keeping in view the background electrolyte concentrations was increased from 0.001 mol/Lto 1.0 mol/L $NaNO_3$ in the sorption of As(III) and As(V), Cd(II), Cu(II) and Pb(II) by these solids keeping the initial metal concentration ~10 mg/L and pH ~4.0 as constant. The results were reported as percent removal as a function of the concentration of the background electrolytes.

2.2.8. Adsorption isotherm modelling

A wide variety of equilibrium isotherm models such as Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich-Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherms are formulated based on the different basic assumption. Some of these models have gained more importance than others due to their simplicity and, in some cases, due to their ubiquitous applicability. Accuracy of an isotherm model is generally a function of the number of independent parameters in the model, while its popularity in relation to process application is generally a function of its mathematical simplicity (Malek and Farooq, 1996). Adsorption equilibrium is established when the sorptive solution is in contact with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is apparently in a dynamic balance with the interface concentration. Usually, the mathematical correlation which constitutes an important role towards the modelling analysis, operational design and applicable practice of the adsorption system, is usually depicted by graphically expressing the solid phase against its residual concentration. Its physicochemical parameters together with the underlying thermodynamic assumptions provide information of the adsorption mechanism, surface properties as well as the degree of affinity of the adsorbents (Foo and Hameed, 2010).

The distribution of metals between the liquid and solid phases is generally described by using Langmuir and Freundlich adsorption isotherms. Therefore, among the several adsorption Isotherm models, these two models are the most common models to formulate adsorption equilibrium data.

2.2.8.1. Langmuir adsorption isotherm

Langmuir isotherm model (Langmuir, 1918) assumes monolayer adsorption i.e., the adsorbed layer is in molecular thickness and adsorption can only occur at a fixed number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites. In its derivation, Langmuir isotherm refers to homogeneous adsorption; all sites possess equal affinity for the adsorbate with each molecule possesses constant enthalpies and sorption activation energy (Kundu and Gupta, 2006).

The linearized Langmuir adsorption model (Erdem and Ozverdi, 2005) in its usual form is adopted for the estimation of maximum metal uptake (q_0) at various initial concentrations:

$$\frac{C_e}{q} = \frac{1}{q_o b} + \frac{C_e}{q_o} \qquad ...(2)$$

where q is the amount of solute adsorbed per unit weight of adsorbent (mg/g) at equilibrium; C_e the equilibrium bulk concentration (mg/L); q_o the Langmuir monolayer adsorption capacity, i.e., the amount of solute required to occupy all the available sites in unit mass of solid sample (mg/g) and *'b'* is the Langmuir constant (L/g).

2.2.8.2. Freundlich adsorption isotherm

Freundlich isotherm (Freundlich, 1906) is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. Nowadays, Freundlich isotherm is widely applied in heterogeneous systems especially for organic compounds or highly interactive species on activated carbon and molecular sieves (Foo and Hameed, 2010). The simple form of Freundlich equation (Lim et al., 2008) was taken as equation (3):

$$\log a_e = \frac{1}{n}\log C_e + \log K_f \qquad ...(3)$$

Where a_e and C_e are the amount adsorbed (mg/g) and bulk sorptive concentration (mg/L) at equilibrium, respectively, and K_f and $\frac{1}{n}$ are the Freundlich constants referring to adsorption capacity and adsorption intensity or surface heterogeneity, respectively.

2.2.9. Adsorption kinetic modelling

The kinetic models such as pseudo-first-order model, pseudo-second-order models and Elovich equation are usually employed to describe the reaction order of adsorption system and thereby utilized to obtain the adsorption capacity of the materials employed (Ho, 2006). Moreover, the other models such as intra particle diffusion, first-order reversible reaction model and the Weber and Moris sorption kinetic model are also employed to describe the adsorption kinetics of heavy metal ions (Li *et al*., 2007; Febrianto *et al*., 2009). The pseudo-first-order equation and pseudo-second-order equations are the most widely used kinetic models to explain the adsorption of a solute from the aqueous solution and it is reported that the pseudo-second-order kinetic model is best fitted to the kinetic data collected for dyes and metal ions removal in large quantity comparing to pseudo-first-order kinetic model (Ho and McKay, 1999). The applicability of pseudo-second-order kinetic model to the metal ions describe the chemisorptions as the predominant process involving sharing or exchange of electrons between the adsorbent and the adsorbate as the valency forces and ion exchange (Momcilovic *et al*., 2011; Ho and McKay, 2000).

The data obtained for the effect of contact time were employed for pseudo first-order-rate kinetic and pseudo-second-order-rate kinetic models in order to establish the best fitted observed sorption data for all the studied systems.

2.2.9.1. Pseudo-first order kinetic model

The pseudo-first order kinetic model (Ghaemi *et al*., 2011) was utilized using the following equation (4):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad \ldots(4)$$

Where q_t (mg/g) is the amount of the metal ion adsorbed at time *t*. The value of $k_1$and $q_e$can be obtained from the slope of the plot of log(q_e-q_t) versus *t*.

2.2.9.2. Pseudo-second order kinetic model

The pseudo-second order kinetic equation (Shin *et al*., 2011) is expressed as in equation (5):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \ldots(5)$$

Where q_e^2 is the maximum adsorption capacity (mg/g) and k_2 (g/mg/min) is the adsorption rate constant of pseudo-second order. Linear plot were drawn between the $\frac{t}{q_t}$ against *t* and values of q_e and k_2 can be evaluated by using the slope and intercept, respectively.

2.2.10. Column reactor studies

The column experiments were performed using a glass column (1.0 cm inner diameter) packed with 1.0 g of AC/or MIAC/or ICAC which was kept in the middle of the column; below and above to this, 1g each of bare sand (30-60 BSS in size) was placed and then it was filled with small sized glass beads. The metal solutions (i.e., Cd (II), Cu (II), Pb(II), As(III) and As(V)) with initial concentration of 10.0 mg/L; initial pH=4.0 was pumped upward from the bottom of the column using Acuflow Series II, High-Pressure liquid chromatograph; at a constant flow rate of 1.00 mL/min. Effluent samples were then collected using Spectra/Chrom CF-1 fraction collector. The total bulk sorptive concentration was measured using AAS. The data obtained were further utilized to optimize the removal capacity of these solids under the dynamic conditions using the Thomas equation (Thomas, 1944):

$$\frac{C_e}{C_o} = \frac{1}{1 + e^{(K_T(q_o m - C_o V))/Q}} \qquad ...(6)$$

where C_e is the sorptive concentration in the effluent (mg/L); C_0 is the sorptive concentration in the feed (mg/L); K_T the Thomas rate constant (L/min/mg); q_o is the maximum amount of adsorbates loaded (mg/g) under the specified column conditions; *m* the mass of adsorbent packed in column (g); *V* the throughput volume (L) of sorptive solution; and *Q* the flow rate of pumped sorptive solution (L/min). A non-linear regression was conducted using the column data by the least square fitting for two unknown parameters i.e., K_T and q_o.

3. RESULTS AND DISCUSSION

3.1. Characterization of the activated carbon (AC), manganese coated activated carbon (MCAC) and iron coated activated carbon (ICAC)

3.1.1. SEM-EDX Analysis

3.1.1.1. Surface morphology and elemental composition of activated carbon (AC) samples

The surface morphology and elemental composition of the activated carbon precursor to dead biomasses viz., rice hulls (AC(R)) and areca nut waste (AC(N)) were obtained by SEM-EDX analysis. The SEM images of the activated carbon samples were returned in Figure 1(a) and 1(b), respectively for AC(R) and AC(N). Surface morphology of AC samples showed, very porous surface structure of these solids and the pores are very unevenly distributed on the surface. The pore size varied for these solids; relatively(R) showed slightly bigger pore size comparing to the AC(N) sample. The pores on the AC(N) surface were opened partly, however, mostly distributed evenly on the surface. The energy dispersive X–ray spectro-photometric (EDX) analysis results of AC(R) showed distinct peaks for silicon, carbon, oxygen and sulphur whereas the AC-N showed significant peaks for carbon, oxygen and sulphur only (*cf* Figures 2(a) and 2(b), respectively for AC(R) and AC(N)). Moreover, the elemental composition of the AC(R) and AC(N) were given in the Table 7 and Table 8, respectively included with weight and atomic percentage of elements present in these two solids.

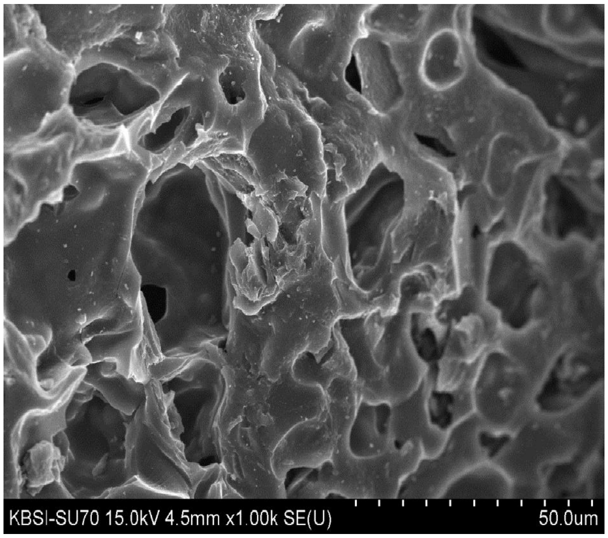

Figure 1(a): SEM image of AC(R)

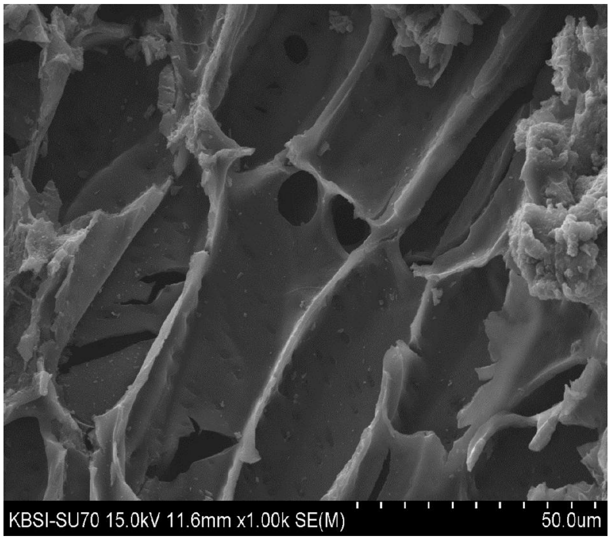

Figure 1(b): SEM image of AC(N)

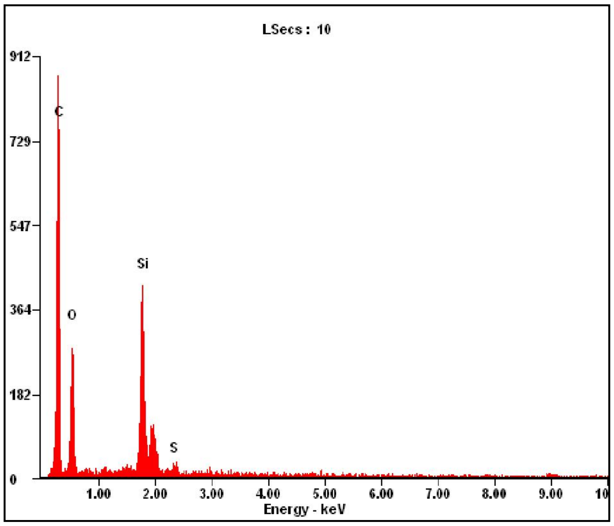

Figure 2(a): EDX graphfor AC(R)

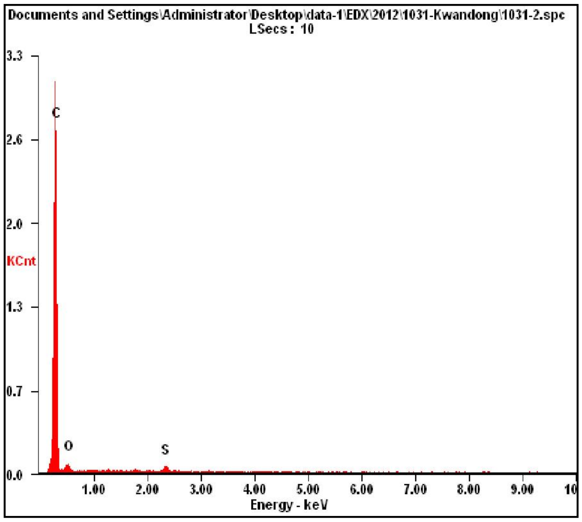

Figure 2(b): EDX graph for AC(N)

Table 7: Weight percentage of the element shown by AC, MCAC and ICAC samples (SEM-EDX analysis)

Materials	*CK*	*OK*	*SiK*	*SK*	*MnK*	*FeK*
AC(R)	69.90	4.02	8.49	0.60	-	-
AC(N)	94.88	21.00	-	1.11	-	-
MCAC(R)	49.00	26.87	7.82	0.61	15.71	-
MCAC(N)	72.86	16.56	-	1.25	9.33	-
ICAC(R)	83.75	10.11	34.94	1.39	-	4.93
ICAC(N)	34.83	34.06	27.31	0.31	-	3.65

Table 8: Atomic percentage of the element shown by AC, MCAC, ICAC samples. (SEM-EDX Analysis)

Materials	*CK*	*OK*	*SiK*	*SK*	*MnK*	*FeK*
AC(R)	78.03	17.28	4.48	0.20	-	-
AC(N)	96.51	3.07	-	0.41	-	-
MCAC(R)	64.33	26.48	4.39	0.30	4.51	-
MCAC(N)	82.99	14.16	-	0.53	2.32	-
ICAC(R)	90.08	8.16	24.21	0.56	-	1.72
ICAC(N)	47.77	35.07	15.92	0.16	-	1.08

3.1.1.2. Surface morphology and elemental composition of manganese coated activated carbon (MCAC)

The SEM images of MCACs solids enable the surface morphology of these solids. It is clearly viewed that the surface structure of ACs was greatly changed with the impregnation of manganese (*cf* Fiugures 3(a) and 3(b), respectively for MCAC(R) and MCAC(N)). It was previously reported that the nano-sized manganese dioxide exhibit an adsorption superior to its bulk counterpart because of its polymorphic structures and higher specific surface area (Wang *et al*., 2011). The SEM images of MCACs in Figure 3(a) and 3(b) showed that manganese dioxide particles were significantly aggregated on the surface as well as pores of the AC. The particles are predominantly small in size and unevenly distributed on the surface of the AC samples. The particles are partly clustered at places onto the surface. Moreover, the EDX data obtained and shown graphically in Figures 4(a) and 4(b), respectively for MCAC(R) and MCAC(N), showed a distinct additional peak of manganese. Similarly, the weight and atomic percentage of the elements present as estimated by the EDX analysis were returned in Tables 7 and 8, respectively for MCAC (R) and MCAC(R) samples. The results clearly demonstrated that a reasonable amount of manganese was impregnated onto the solids of AC (i.e., 15.71 % and 9.33 % in weight and 4.51 % and 2.32 % in atoms for MCAC(R) and MCAC(N), respectively. These results conferred that manganese were successfully immobilized on both activated carbon samples as obtained by the rice hull and areca nut waste.

3.1.1.3. Surface morphology and elemental composition of iron coated activated carbon (ICAC)

Similar to MCAC, the surface morphology of iron impregnated sample was obtained and shown in figures 5(a) and 5(b), respectively for ICAC(R) and ICAC(N) solids. The surface morphology of these two solids were altered significantly in presence of iron as clear from the SEM images of its precursors ACs (vide figures 1(a) and 1(b)). The SEM images of ICAC(R) and ICAC(N) showed that small or even nano-sized iron oxide (possibly -Fe_2O_3 or -FeOOH mineral phases) particles were significantly aggregated clustered onto the surface of AC samples or even within the pores of the ACs. However, at places the particles were clustered within the pores of ACs. The particles were distributed unevenly and predominantly small in size. Further, the SEM-EDX analysis suggested, reasonably significant weight and atomic percentage of iron was occurred indicated again that iron is predominantly immobilized onto the AC surface (*cf* Figures 6(a) and 6(b) as well as Tables 7 and 8, respectively for ICAC(R) and ICAC(N)). These results, therefore, indicated that the iron oxide particles were significantly impregnated on to the surface of AC(R) and AC(N). Previous studies showed that iron was impregnated on granular activated carbon based adsorbents for the removal of arsenic and an iron loading of 7% in weight was observed (Gu *et al.,* 2005). Four iron doped activated carbon was prepared by hydrolysis and it was observed that iron content increases linearly with hydrolysis time. The iron contents was increased from 1.5 -9.4% in weight while increasing the hydrolysis time from 1- 24 hours (Fierro *et al.,* 2009). Iron impregnation was applied to modify the tablet ceramic adsorbents and the iron content after modification was 19.1% (Chen *et al.,* 2012).

3.1.2. Estimation of manganese and iron content in the samples

The amount of manganese or iron content present in the solids i.e., ACs and MCACs and ICACs were obtained by the standard US EPA 3050B method. Results clearly demonstrated that the amount of manganese present in MCAC(R) and MCAC(N) were 1577 mg/kg and 1305 mg/kg, respectively. Whereas, very insignificant amount of manganese was present in the respective ACs samples i.e., 4.5 mg/kg in AC(R) and 5.5mg/kg in AC(N). These results are in conformed to EDX analysis obtained previously. On the other hand the amount of iron impregnated was found to be 2221 mg/kg and 2442 mg/kg, respectively for ICAC(R) and ICAC(N). The corresponding ACs samples were containing the iron 39.75 mg/kg and 107.5 mg/kg, respectively for AC(R) and AC(N) samples.

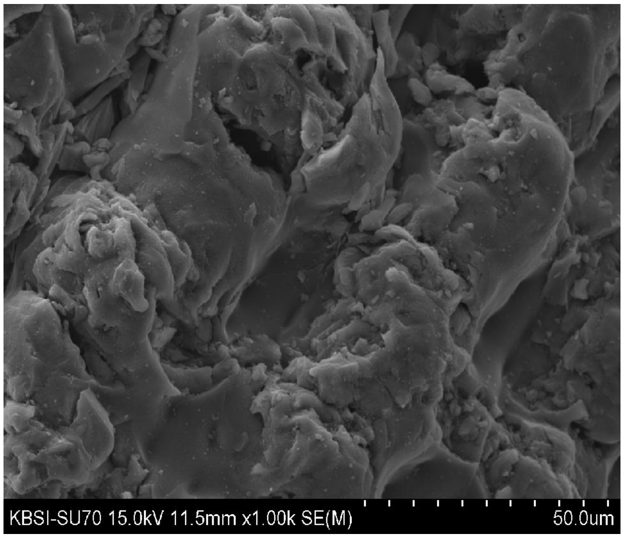

Figure 3(a): SEM image of MCAC(R)

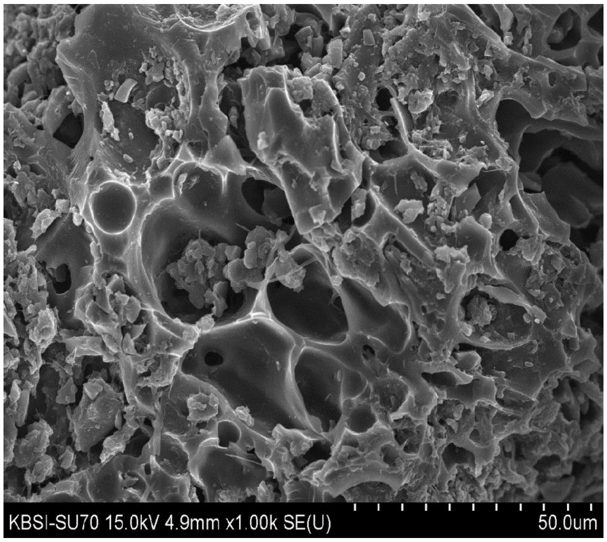

Figure 3(b): SEM image of MCAC(N)

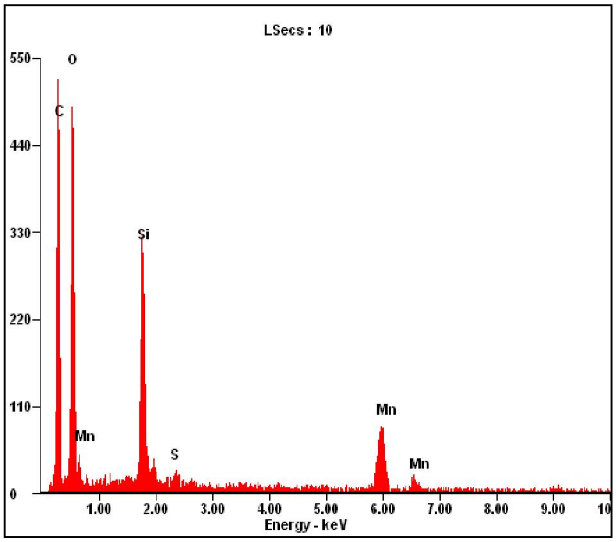

Figure 4(a): EDX graph of MCAC(R)

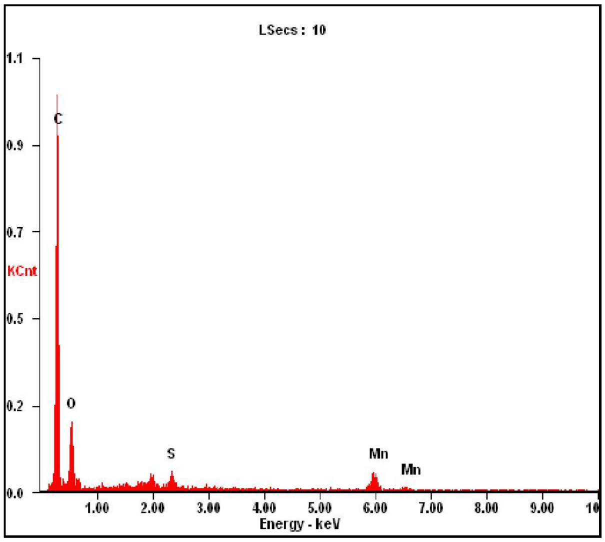

Figure 4(b): EDX graph of MCAC(N)

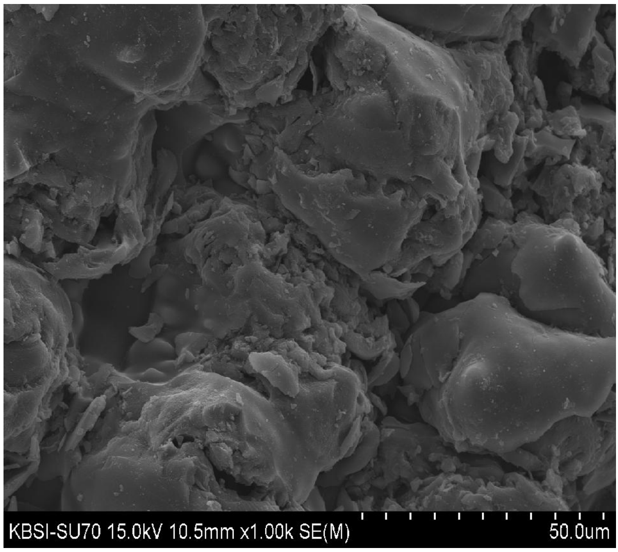

Figure 5(a): SEM image of ICAC(R)

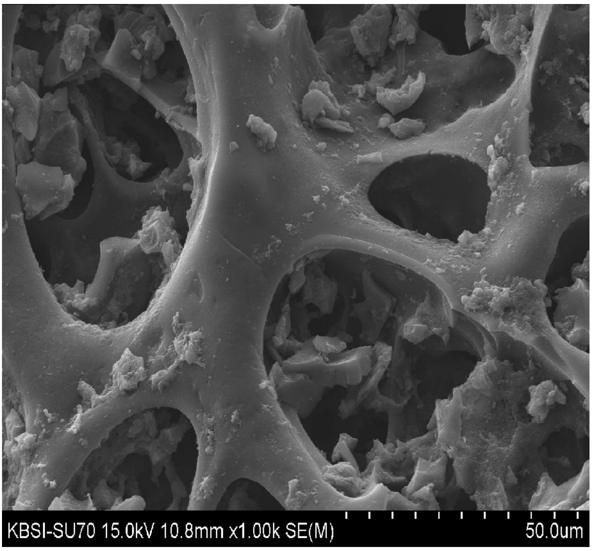

Figure 5(b): SEM image of ICAC(N)

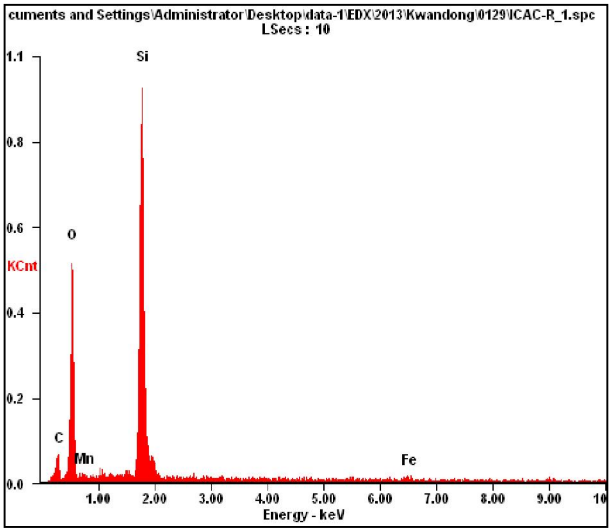

Figure 6(a): EDX graph of ICAC(R)

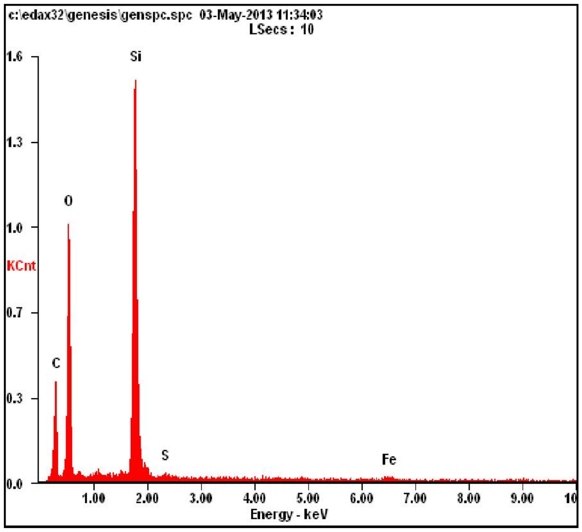

Figure 6(b): EDX graph of ICAC(N)

3.1.3. Stability of manganese and iron coated activated carbon

The stability of the manganese or iron coating is one of important parameter at least against the acid or base attack and such studies enabled the wide applicability of the solids in the waste water treatment. Therefore, keeping in view the stability tests were performed in the wide range of pH i.e., between pH 2.0 to 10.0 for MCAC and ICAC samples. The results obtained were returned in Table 9 and graphically in figures 7(a) and 7(b), respectively for MCACs and ICACs samples.

It was observed that the manganese were strongly impregnated on to the surface as well as pore of the activated carbon within the pH region 4.0 to 10.0 since there was insignificant amount of manganese was leached into the bulk solution. However, some but significant amount of manganese was desorbed from pH~3 and below. Therefore, it may be concluded that the MCAC samples possessed reasonably a good stability within the pH region 3.0 to 10.0. On the other hand, at pH 2.0, a significant amount of iron was desorbed, however, beyond this pH almost a negligible amount iron was leached out into the bulk solution. These results conferred that manganese/or iron occupied the surface of AC firmly and likely to have strong chemical binding with the substrate. Moreover, these results suggest the possibility of employing these materials over the wide pH range in the wastewater treatment.

Table 9: The amount of Manganese and iron leached at various pH

pH	Mn(mg/L)		Fe(mg/L)	
	MCAC(R)	MCAC(N)	ICAC(R)	ICAC(N)
2.0	7.55	5.19	2.57	3.23
3.0	3.65	3.14	0.03	0.03
4.0	1.98	2.40	0	0
5.0	1.33	1.63	0	0
6.0	1.13	1.50	0	0
7.0	0.66	1.05	0	0
8.0	0.64	0.47	0	0
9.0	0.16	0.29	0	0
10.0	0	0	0	0

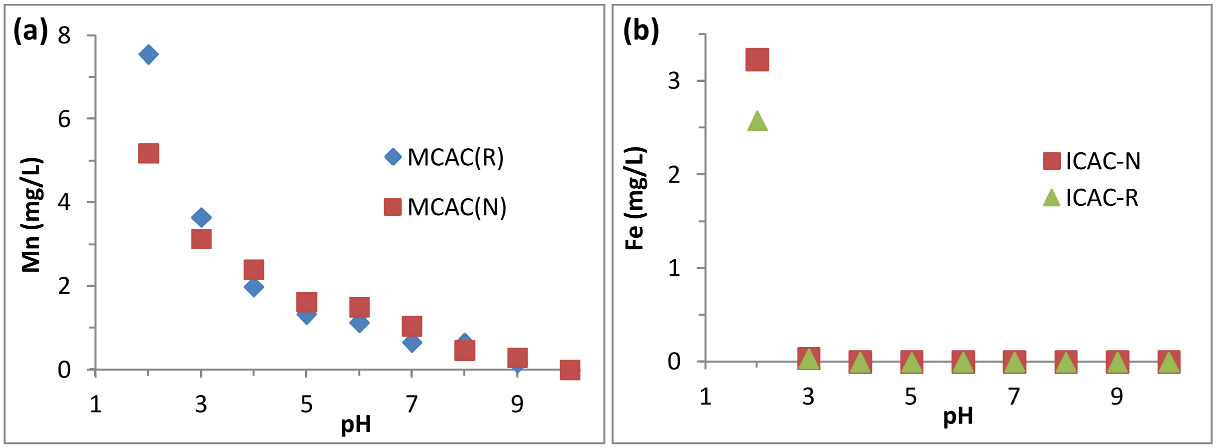

Figure 7: Stability of (a) manganese and (b) iron impregnation on the AC samples as a function of solution pH

3.1.4. Fourier-transform infra-red spectroscopic (FT-IR) analysis

FT-IR data was obtained for the activated carbons precursor to rice hulls and *areca* nut waste along with the manganese and iron oxide immobilized activated carbons. The results were presented graphically in Figure 8(a) and 8(b), respectively for the *areca* nut and rice hulls based samples. Carbon samples could possess various functional groups having different surface structures *viz*., aliphatic, aromatic, cyclic since the IR bands were observed at around 1480 cm^{-1} and regions around 1110 cm^{-1} for both these ACs. Predominant and broad peak appeared at around 3470-3495 cm^{-1} were ascribed to the stretching vibration of –OH groups (carboxyl, alcohol or phenols) etc. or it may be attributed to the absorption of some atmospheric water during FT-IR measurements (Gun'ko *et al.,* 2005; Gupta *et al.,* 2011a). However, it was reported that the IR bands occurred at around 3300 and 3250 cm^{-1} were indicative of the hydroxyl groups, but, usually the band is shifted at around 3500 cm^{-1} in case of non-bonded alcohols, phenols and carboxylic acids (Gomez-Serrano, 1996). Further, peaks in between 2930 and 2910 cm^{-1} was assigned to the C-H stretching and C-H scissoring bands, respectively (Gupta *et al.,* 2011b). Moreover, it was suggested that the peaks at 2800-2900 cm^{-1} was indicated to the existence of aldehyde groups (Gun'ko *et al.,* 2005). The weak peaks occurred at around 1460 cm^{-1} showed the C-H vibration in $–CH_2–$ deformation (Puziy *et al.,* 2002). Moreover, the bands occurred in between 1600 and 1400 cm^{-1} (more predominant in the *areca* nut ACs) could be assigned as C=C vibrations. It was pointed that the peaks in the region 1350 and 900 cm^{-1} was due to the C-O or C=O vibrations (Al Bahri *et al.,* 2012). Similarly, a vibration band occurred around 870 cm^{-1} was obtained because of external bending of –C-H for different substituted benzene ring (Kong *et al.,* 2013). The peak at around 450- 475 cm^{-1} was assigned as the stretching vibrations of Fe-O (Gupta *et al.*, 2011b; Rodulfo-Baechler *et al.*, 2004). This peak was present in both ACs samples as well with less intensity indicating that the bare ACs also included with some iron oxide. This is reaffirmed the digestive analysis data conducted previously. Similarly, peaks at around 840 cm^{-1} inferred to the υ_s vibrations of Si-O-Si or δ-Fe-OH vibrations predominant in the rice hulls activated carbon samples (Li *et al.*, 2010). On the other hand, a Mn-O stretching vibration usually occurred at 940 cm^{-1} (Nakamoto 1997), but none of the samples showed peak in this region could be suggested that the content of manganese was too low hence; the vibration intensity was almost negligible in this region.

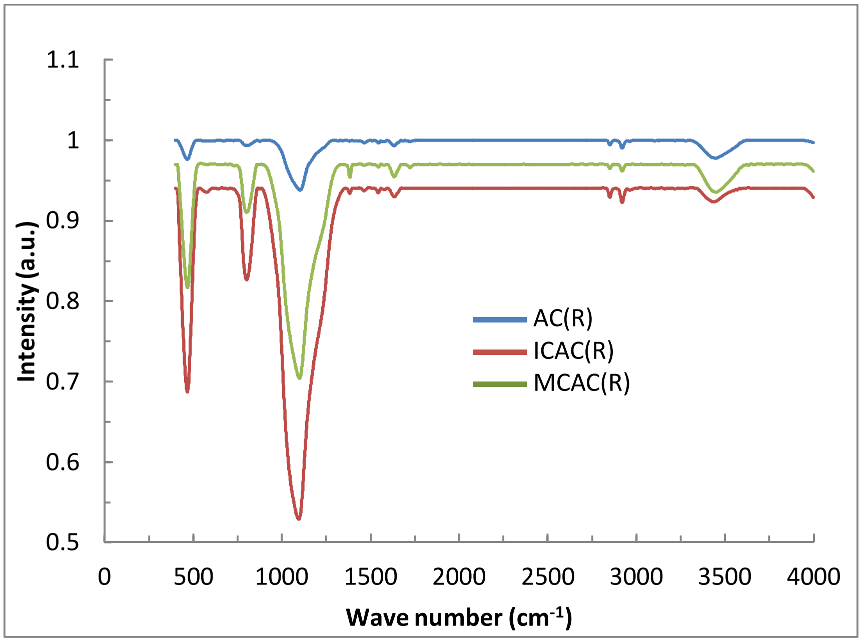

Figure 8(a): FT-IR data for the AC, MCAC and ICAC solids obtained from rice hulls

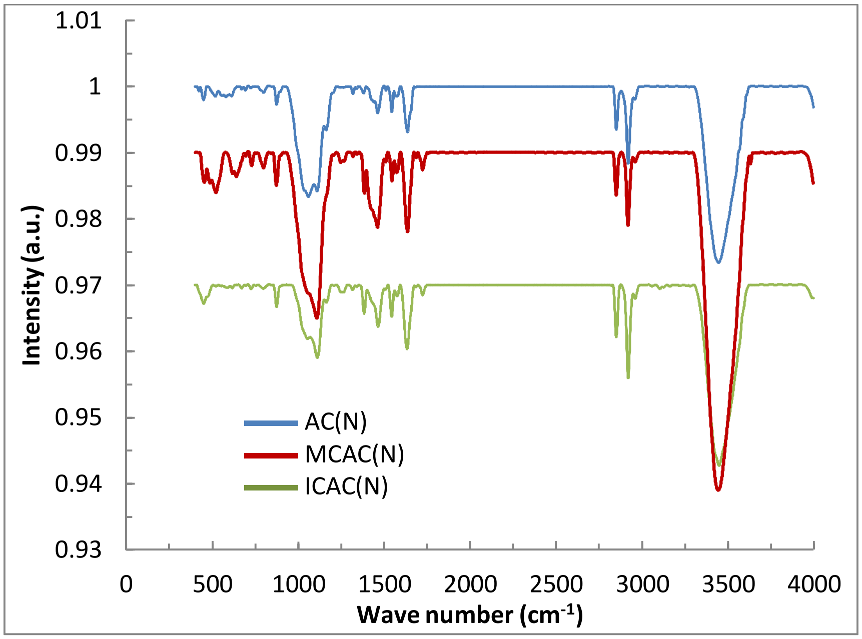

Figure 8(b): FT-IR data for the AC, MCAC and ICAC solids obtained from *areca* nut waste.

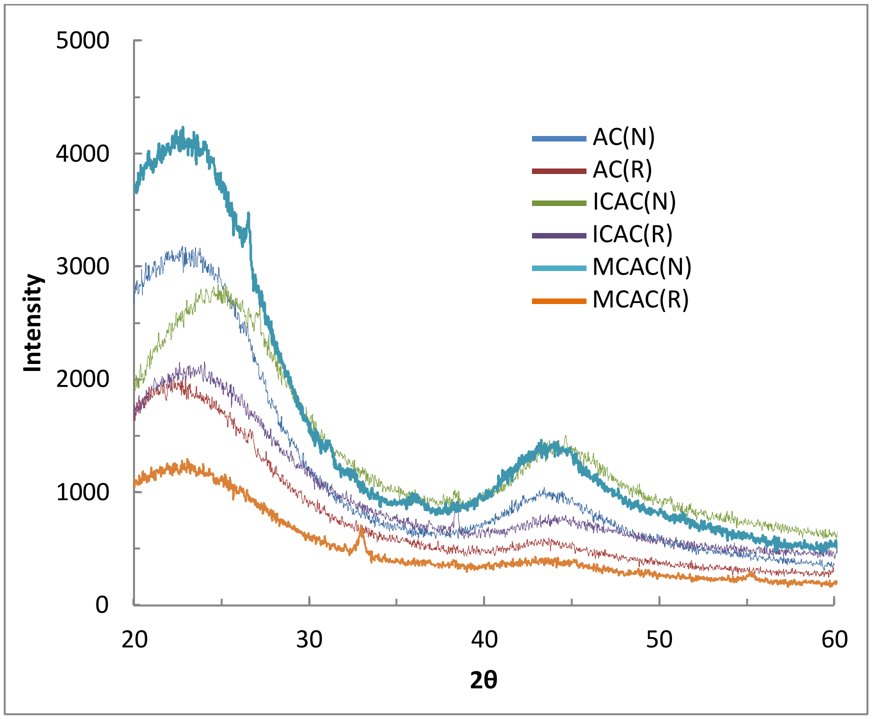

Figure 9: XRD data for various samples of ACs, IIACs and MIACs.

3.1.5. X-ray diffraction (XRD) analysis

Further, these solids were subjected for the X-ray diffraction analysis and the results were presented graphically in Figure 9. It was observed that activated carbon of rice hulls possessed diffraction peak at 2θ value of 22.5 which showed a characteristic peak of amorphous silica (Liu *et al.,* 2012a). Similarly, the AC of *areca* nut showed very broad diffraction peak almost in the same region indicating, perhaps, the amorphous, silica. The XRD data further indicated that ACs have no ordered crystalline structure since no sharp reflections were observed for these samples. A similar XRD pattern was obtained for the ICAC-R or ICAC-N samples except a weak but sharp peak at the 2θ value of 39 which was an indicative of *akaganeite* (β-FeOOH) (Vitela-Rodriguez and Rangel-Mendez 2013). Possibly the other diffraction peaks of the *akaganeite* at 2θ value of 35 was missing because of low content of iron or weak diffraction at this 2θ value (Depci, 2012). On the other hand, the MCACs samples could not show sharp diffraction peaks in the XRD pattern except a weak diffraction peak at the 2θ value of 32.5 (MCAC-R), possibly, due to the presence of Mn_3O_4 mineral phase (Si *et al.* 2009). No other characteristic peaks were observed in the MCACs samples. This was, perhaps, because of the low content of impregnated manganese onto the solid ACs surfaces. Previously, it was reported that no significant X-ray diffraction peak was observed with the manganese or iron impregnated solids using different substrates, because of the amorphous iron or manganese was deposited or the particles were significantly small to diffract or even because of very low content of iron/manganese (Corapcioglu and Huang 1987; Depci 2012; Muniz *et al.,* 2009; Tiwari *et al.,* 2011).

3.1.6. BET specific surface area

The specific surface areas of these solids i.e., ACs, MCACs and ICACs samples were determined by using the BET analyser and results were returned in Table 10. The results show that the activated carbon obtained from rice hulls and areca nut waste contain very high specific surface area. The specific surface area of ACs was slightly decreased in presence of iron or manganese oxides since the iron or manganese oxides, perhaps, occupied the spaces and hence decreased the specific surface area. However, the presence of iron or manganese oxides enabled the solids towards the effective and efficient removal of heavy metal toxic ions from aqueous solution. The similar decrease in specific surface area was reported previously in the case of iron doped activated carbon sample (Fierro, 2009).

Table 10: BET specific surface area obtained for ACs, MCACs and ICACs solids

Solid materials	BET specific surface area (m^2/g)
AC(R)	322.14
MCAC(R)	315.82
ICAC(R)	303.79
AC(N)	379.77
MCAC(N)	371.04
ICAC(N)	370.88

3.1.7. pH_{pzc} (point of zero charge) of the samples used

The pH_{pzc} (point of zero charge) is defined as the pH value at which the net charge of the solid surface is zero i.e., the surface of the material carries neither positive nor negative charges (Khormaei *et al.*, 2007). Point of zero charge determination of these solids is also important in elucidating the adsorption mechanism involved at solid solution interface. At pH lower than PZC, the solid carries a net positive surface charge which results in an electrostatic repulsion with metal cations and causes low sorption. On the other hand, at pH higher than

PZC, the surface carries a net negative charge because of the acidic dissociation of surface functional groups and metal cations may likely to be attracted by the solids. This result in an enhanced uptake of metal cations (Lee *et al.*, 2012; Reddy *et al.*, 2012). The pH_{pzc} obtained for these solid samples were obtained by the simple acid base titrations at constant ionic strength and temperatures. Results obtained are summarized in Table 11.The presence of iron or manganese oxide caused for a slight decrease in pH_{pzc} values of these ACs samples.

Table 11: The pH_{pzc} obtained for ACs, MCACs and ICACs samples

Solid materials	pH_{pzc}
AC(R)	6.6
MCAC(R)	6.5
ICAC(R)	6.1
AC(N)	6.7
MCAC(N)	6.5
ICAC(N)	6.2

3.2. Speciation studies

The speciation studies were conducted by using the MINEQL geochemical computer program (version 4.5) and the equilibrium constants used were given in the previous Chapter and Section 2.2.6. The results obtained with speciation studies could enable to understand the sorption studies or to deduce the mechanism involved at solid/solution interface. Therefore, a complete speciation studies were carried out in a wide range of pH i.e., pH 2.0 to 10.0.

3.2.1. Speciation of Cd(II)

The speciation data obtained by the MINEQL geochemical program for Cd(II) is presented graphically in Figure10(a). The results show that up to pH 8.8 the cadmium exits as Cd^{2+}soluble cationic species. Beyond the pH 9.0 the cadmium turns into insoluble $Cd(OH)_2$

species and above the pH 10.0, the $Cd(OH)_2$ is the only dominant species. In between pH 8.0 to 10.0; maximum of 5.1 % of cadmium exists as $Cd(OH)^+$ species.

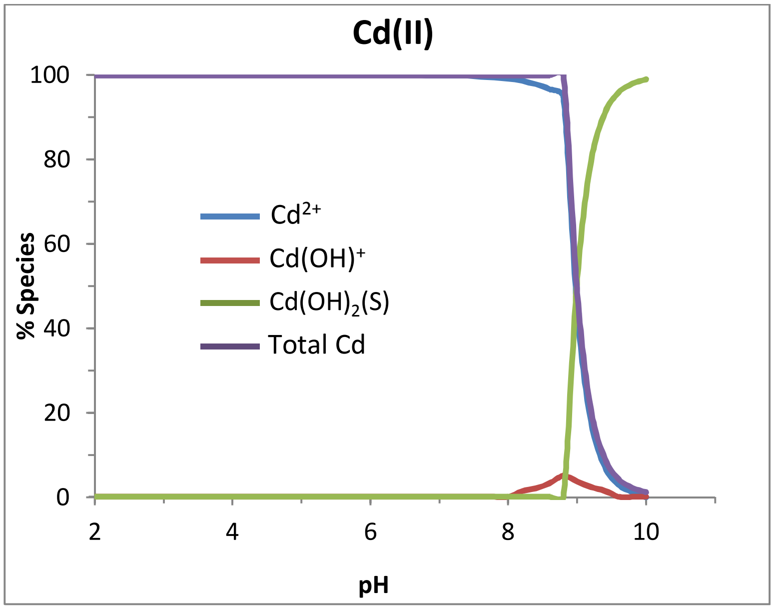

Figure 10(a): Percentage distribution of various species of Cd(II) as a function of pH Cd(II): 10.0 mg/L; Temperature: 25^0C

3.2.2. Speciation of Cu(II)

The speciation results (Figure 10(b)) obtained for Cu((II) show that copper exists as the ionic form of Cu^{2+} up to pH ~5.5, beyond that it starts precipitating as insoluble tenorite species. The insignificant $Cu(OH)^+$ species was formed between pH 5.0-7.0 with a maximum of 1.4 % only. Cu(II) shows formation of insoluble tenorite species at lower pH comparing to other metal ions. Therefore, in order to carry out the adsorption experiments without precipitation for Cu(II), it was suggested to perform the sorption studies at lower pH values i.e., ~pH 4.0.

3.2.3. Speciation of Pb(II)

The percent species of Pb(II) with variation of pH is returned in Figure 10(c). Lead exists as Pb^{2+} up to pH 6.2 and beyond this pH it starts precipitating as $Pb(OH)_2$. $Pb^{2+}$is completely precipitated beyond pH~7.0. It was also observed that insignificant amount of $Pb(OH)^+$ occurs with a maximum of 3.9 % in between pH 5.0-7.0.

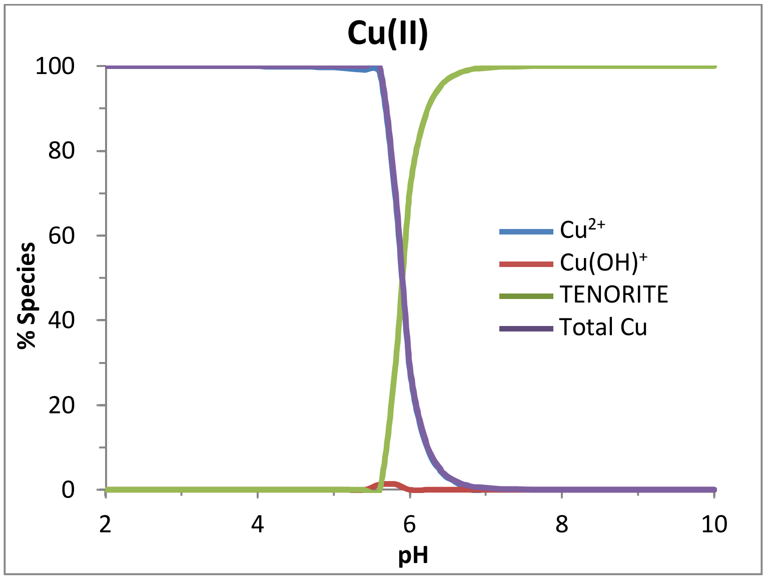

Figure 10(b): Percentage distribution of various species ofCu(II) as a function of pH
Cu(II): 10.0 mg/L; Temperature: 25^0C

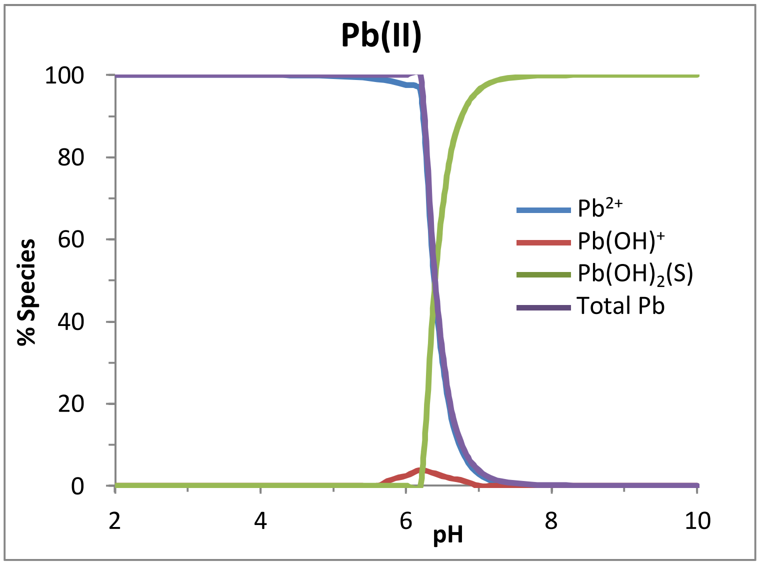

Figure 10(c): Percentage distribution of various species of Pb(II) as a function of pH
Pb(II): 10.0 mg/L; Temperature: 25^oC

3.2.4. Speciation of As(III) and As(V)

The speciation of As(III) and As(V) in aqueous solution at different pH values are studied and results are returned in Figure 10(d) and 10(c), respectively for As(III) and As(V). It is observed that As(III) exists as H_3AsO_3 uncharged species up to pH ~8.0 beyond which it dissociates and the anionic $H_2AsO_3^-$ species are dominant. On the other hand, As(V) exists predominantly as $H_2AsO_4^-$ and H_3AsO_4 species at lower pH i.e., up to pH ~6.8 and above pH 6.8, the anionic species $HAsO_4^{2-}$ species is fully dominant.

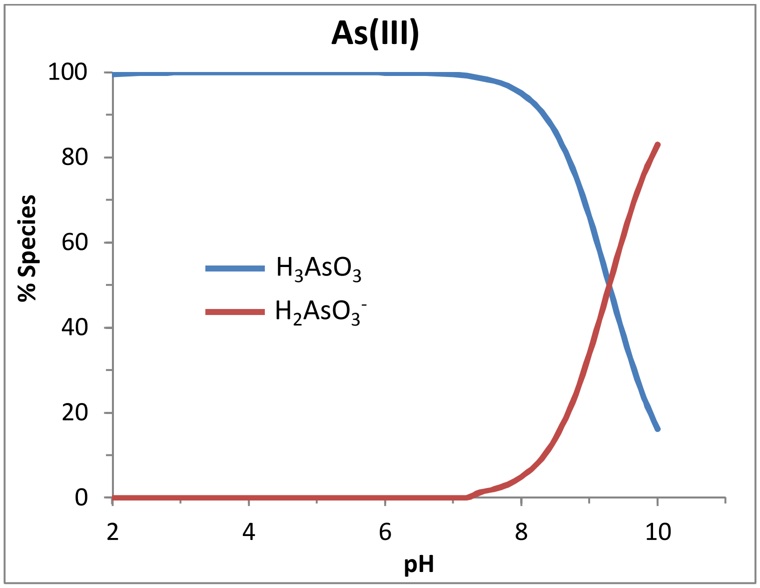

Figure 10(d): Percentage distribution of various species of As(III) as a function of pH. [As(III)]: 7.50 mg/L; Temperature: 25^0C

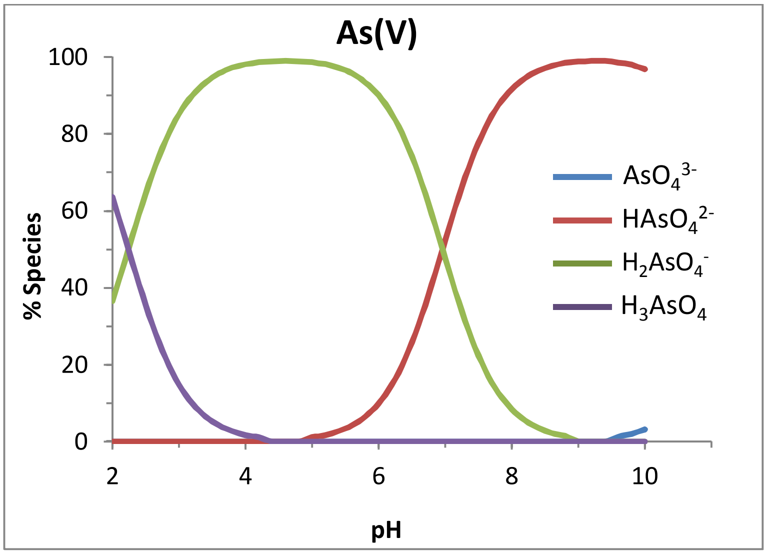

Figure 10(e): Percentage distribution of various species of As(V) as a function of pH. As(V): 7.50 mg/L; Temperature: 25^0C

3.3. BATCH REACTOR STUDIES

3.3.1. Effect of pH

3.3.1.1. Cadmium (II)

The change in solution pH affects greatly the surface charge of the adsorbents as well the speciation of the adsorbate ions. Therefore, the pH dependence sorption studies help in to deduce the mechanism involved at solid/solution interface (Momcilovic *et al.,* 2011; Tiwari *et al.,* 2007). The sorption data was obtained by varying the initial pH 2.0 to 10.0 and at constant initial Cd(II) concentration 10.0 mg/L. The results obtained were presented graphically in Figure 5(a) and 5(b), respectively for AC-N and AC-R based solids. Also presented in the Tables 12(a), 12(b), 12(c), 12(d), 12(e) and 12(f), respectively for the AC(R), MCAC(R), ICAC(R), AC(N), MCAC(N) and ICAC(N). Figures clearly indicated that increasing the pH from 2.0 to 10.0 of the sorptive solution caused for a gradual increase in the adsorption of Cd(II) by these solids. More precisely, it was noted that increasing the pH from 2.39 to 10.11 for AC-N; 2.58 to 10.23 for MCAC-N; 2.00 to 9.69 for ICAC-N caused to increase in Cd(II) uptake respectively, from 8.15 % to 100.0% for AC-N; 13.24% to 100% for MCAC-N and 31.23% to 100 % for ICAC-N. Similarly, increasing the pH from 2.29 to 10.18 for AC-R; 2.57 to 10.38 for MCAC-Rand 205 to 9.30 for ICAC-R caused to increase in the Cd(II) removal, respectively from 10.90% to 100.0%; 15.38% to 100.0% and 36.26 to 100.0%. This could be explicable with the help of the surface properties of solid surface along with the speciation of sorbing species. The speciation of Cd(II) as given in Figure 10(a) indicated that cadmium exists as positively charged Cd^{2+} form low pH to pH 8.8 and beyond that the cadmium converted into $Cd(OH)_2$ (S) species which occurs 100% at pH 9.4. However, in between, cadmium also exists as one of insignificant species $Cd(OH)^+$ maximum of 5.1% at pH 8.8. In other words in wide range of pH cadmium exists in cationic form and carries net positive charge. On the other hand the pH_{pzc} of the adsorbents (Table 11) was found to be6.7, 6.6, 6.5, 6.5, 6.2 and 6.1, respectively for the solids AC-N, AC-R, MCAC-N, MCAC-R, ICAC-N and ICAC-R. This suggested that below this pH the surface of these solids carries a net positive charge and beyond this it contains a net negative charge. Therefore, the lower value of sorption was occurred at lower pH since a strong to moderate electrostatic repulsion takes place between the Cd^{2+} and the positively charged solid surface. Moreover, at high acidic conditions i.e., at very low pH around pH 2.0-3.0, perhaps, a competition could occur between the excess of hydrogen ions and metal ions towards the same sites of solid surface which suppressed further the Cd(II) adsorption. Increasing the pH caused for a decrease in H^+ ion concentrations due to successive de-protonation. This resulted with gradual increase in negative charge density onto the solid surface which enables to favour more adsorption of the metal ions (Zhu *et al.,* 2007a). The observed data was supported the modelling and experimental data obtained to analyse the surface properties of the bio sorbents *viz*., natural bamboo saw dust (Zhao *et al.,* 2012a). Moreover, the results were in a line to previous findings obtained with activated carbon prepared from *Ceiba pentandra* hulls (Rao *et al.,* 2006), Van apple pulp (Depci e*t al.,* 2012)and manganese oxide coated carbon nanotubes (Wang *et al.,* 2007) in the removal of several metal cations. Moreover, at very high pH values i.e., beyond pH 9.0, there could be a mixed effect of adsorption and co-precipitation of Cd(II) on the surface of solids resulted to a complete removal of these ions i.e., about 100% uptake of Cd(II) by these solids (Lee *et al.,* 2010; Lee *et al.,* 2012).

In general the specific surface reactions for metal oxide coated samples may be represented as follows (Pretorious and Peter, 2001; Han *et al*., 2006)

$$\equiv MOH + Cd^{2+} \rightarrow \equiv MO^{-}Cd^{2+} + H^{+} \qquad ...(7)$$

$$\equiv MO^{-} + Cd^{2+} \rightarrow \equiv MO^{-}Cd^{2+} \qquad ...(8)$$

$$2(\equiv MOH) + Cd^{2+} \rightarrow (\equiv MO^{-})_2Cd^{2+} + 2H^{+} \qquad ...(9)$$

$$2(\equiv MO^{-}) + Cd^{2+} \rightarrow (\equiv MO^{-})_2Cd^{2+} \qquad ...(10)$$

Table 12 (a): Effect of pH in the removal of Cd(II) by AC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.29	9.82	8.75	0.43	10.90
3.54	9.82	7.92	0.76	19.35
4.61	9.82	7.34	0.99	25.25
5.27	9.82	7.06	1.10	28.11
6.48	9.82	4.94	1.95	49.69
7.46	9.82	2.52	2.92	74.34
8.37	9.82	1.28	3.42	86.97
9.28	9.82	0.33	3.79	96.64
10.18	9.82	*	3.93	100.00

*Below the detection limit

Table 12(b): Effect of pH in the removal of Cd(II) by MCAC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.57	9.82	8.31	0.60	13.24
3.61	9.82	7.05	1.11	27.70
4.96	9.82	6.36	1.38	31.47
5.72	9.82	5.75	1.63	36.35
6.81	9.82	4.02	2.32	50.81
7.73	9.82	2.54	2.91	69.65
8.89	9.82	1.10	3.49	86.05
9.92	9.82	0.27	3.82	96.84
10.38	9.82	*	3.93	100.00

*Below the detection limit

Table 12(c): Effect of pH in the removal of Cd(II) by ICAC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.05	10.15	6.47	1.47	36.26
3.41	10.15	6.14	1.60	39.51
5.65	10.15	4.67	2.19	53.99
6.10	10.15	3.54	2.64	65.12
6.51	10.15	3.02	2.85	70.25
6.60	10.15	2.62	3.01	74.19
7.00	10.15	1.02	3.65	89.95
8.18	10.15	*	4.06	100.00
9.30	10.15	*	4.06	100.00

*Below the detection limit

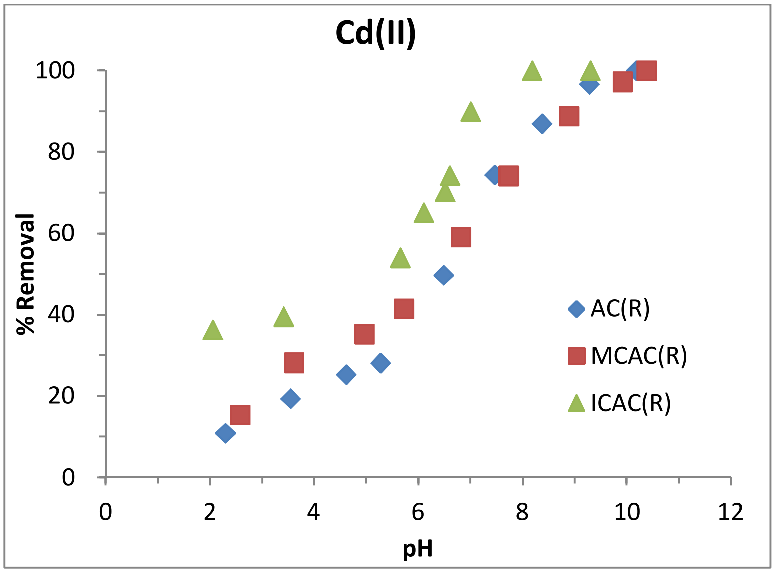

Figure 11(a): Effect of pH in the removal of Cd(II) by using AC(R), MCAC(R) and ICAC(R)

Initial sorptive concentration: ~10 mg/L; Temperature: 25±1 ^{0}C

Table 12(d) : Effect of pH in the removal of Cd(II) by AC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.39	9.82	9.02	0.32	8.15
3.27	9.82	8.34	0.59	15.07
4.51	9.82	7.48	0.93	23.83
5.30	9.82	7.29	1.01	25.76
6.52	9.82	5.26	1.82	46.44
7.27	9.82	2.63	2.87	73.22
8.54	9.82	1.75	3.23	82.18
9.27	9.82	0.42	3.76	95.72
10.11	9.82	*	3.93	100.00

*Below the detection limit

Table 12(e): Effect of pH in the removal of Cd(II) by using MCAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.58	9.82	8.52	0.52	13.24
3.70	9.82	7.10	1.08	27.70
4.82	9.82	6.73	1.24	31.47
5.56	9.82	6.25	1.43	36.35
6.75	9.82	4.83	1.99	50.81
7.89	9.82	2.98	2.74	69.65
8.92	9.82	1.37	3.38	86.05
9.76	9.82	0.31	3.80	96.84
10.23	9.82	*	3.93	100.00

*Below the detection limit

Table 12(f): Effect of pH in the removal of Cd(II) by ICAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.00	10.15	6.98	1.27	31.23
3.64	10.15	6.1	1.62	39.90
5.79	10.15	4.55	2.24	55.17
6.14	10.15	4.45	2.28	56.16
6.46	10.15	4.1	2.42	59.61
6.64	10.15	3.58	2.63	64.73
6.95	10.15	2.43	3.09	76.06
8.12	10.15	*	4.06	100.00
9.69	10.15	*	4.06	100.00

*Below the detection limit

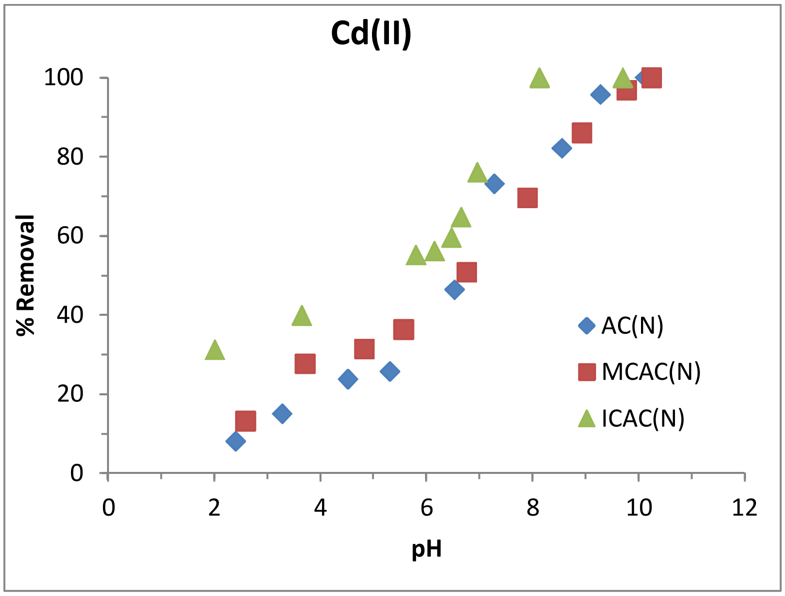

Figure 11(b): Effect of pH in the removal of Cd(II) by AC(N), MCAC(N) and ICAC(N)

Initial sorptive concentration: ~10 mg/L; Temperature: 25±1 ^{0}C

3.3.1.2. Copper (II)

The effect of pH on the adsorption of Cu(II) was evaluated between initial pH 2.0 to 10.0 and the initial concentration of Cu(II) was taken as ~10.0 mg/L. The results obtained were presented in Table 13(a-f) and graphically in Figure 12(a) and 12(b), respectively for rice hulls and *areca* nut waste based solids. These figures clearly indicated that, in general, increasing the initial pH from 2.0 to 10.0 of the sorptive solution significantly caused for an apparent increase in the adsorption of Cu(II). More quantitatively, it was observed that increasing the pH from 2.23 to 10.34 for AC(R), 2.25 to 10.2 AC(N), 2.59 to 10.58 for MCAC(R) and 2.54 to 10.63 for MCAC(N) caused to increase in Cu(II) removal respectively by 15.44 % to 100%, 11.81% to 100%, 29.97% to 100 % and 26.34 to 100%. The low removal of Cu(II) at lower pH is attributed to the competition of Cu(II) ions with H^+ ions as well as the surface charge properties of the adsorbents (Dai *et al*., 2010). The deprotonation reaction of H^+ ions and the complexation reaction of Cu(II) with the surface functional groups could be ascribed as (Benhammou *et al*., 2005):

$$\text{S-OH} + \text{OH}^- \leftrightarrow \text{S-O}^- + \text{H}_2\text{O} \qquad \ldots(11)$$

$$\text{S-O}^- + \text{Cu}^{2+} \leftrightarrow \text{S-O-Cu}^+ \qquad \ldots(12)$$

$$\text{S-O}^- + \text{Cu(OH)}^+ \leftrightarrow \text{S-O-Cu(OH)} \qquad \ldots(13)$$

This resulted with gradual increase in negative charge density onto the solid surface as increasing the pH. Further, this could favour the sorption of metal ions onto solid surfaces (Tajar *et al*., 2009; El-Ashtoukhya *et al*., 2012). The figure further showed that the removal was reached to 100 % at pH 10.0. Moreover, the speciation of Cu(II) showed that the formation of insoluble tenorite appeared from pH 5.2 and existed as the dominant beyond this pH. Hence, the higher uptake of Cu(II) at higher pH is, perhaps, due to the adsorption along with precipitation of the Cu(II) onto the solid surfaces (Chen *et al*., 1996; Tiwari *et al*., 2011).

Table 13(a): Effect of pH in the removal of Cu(II) by AC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.23	9.91	8.38	0.61	15.44
3.41	9.91	7.64	0.91	22.91
4.57	9.91	6.92	1.20	30.17
5.62	9.91	6.07	1.54	38.75
6.18	9.91	4.02	2.36	59.43
7.47	9.91	1.95	3.18	80.32
8.36	9.91	0.67	3.70	93.24
9.22	9.91	0.11	3.92	98.89
10.34	9.91	*	3.96	100.00

*Below the detection limit

Table 13(b): Effect of pH for the removal of Cu(II) by MCAC-R.

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.59	9.91	6.94	1.19	29.97
3.67	9.91	5.72	1.68	42.28
4.89	9.91	4.73	2.07	52.27
5.91	9.91	3.88	2.41	60.85
6.77	9.91	2.71	2.88	72.65
7.93	9.91	1.03	3.55	89.61
8.85	9.91	0.52	3.76	94.75
9.74	9.91	0.07	3.94	99.29
10.58	9.91	*	3.96	100.00

*Below the detection limit

Table 13(c): Effect of pH in the removal of Cu(II) by ICAC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.22	10.24	9.772	0.19	4.57
3.49	10.24	8.045	0.88	21.44
4.28	10.24	6.601	1.46	35.54
5.56	10.24	4.894	2.14	52.21
5.83	10.24	4.046	2.48	60.49
6.95	10.24	0.182	4.02	98.22
7.86	10.24	0.067	4.07	99.35
8.42	10.24	0.016	4.09	99.84
9.16	10.24	*	4.10	100.00

*Below the detection limit

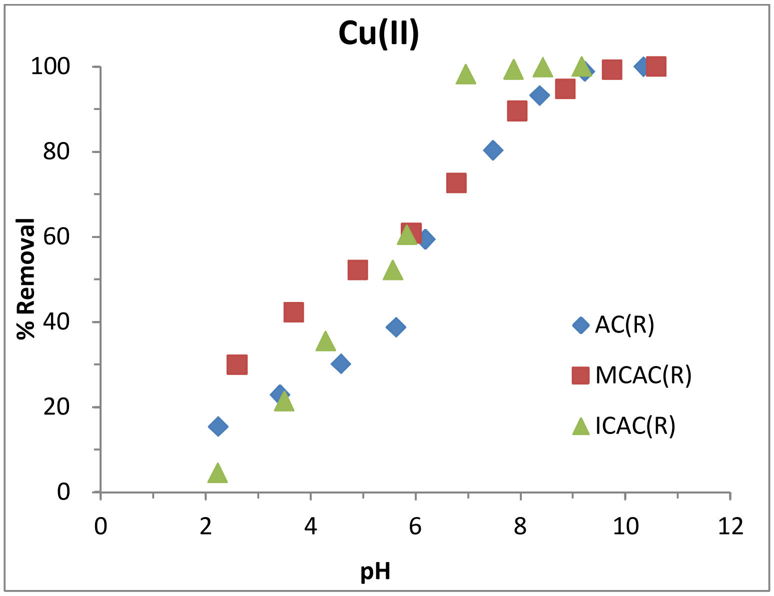

Figure 12(a): Effect of pH in the removal of Cu(II) by AC-R, MCAC-R and ICAC-R

Initial sorptive concentration: ~10 mg/L; Temperature: 25±1 ^{0}C

Table 13(d): Effect of pH in the removal of Cu(II) by AC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.25	9.91	8.74	0.47	11.81
3.21	9.91	7.76	0.86	21.70
4.46	9.91	7.04	1.15	28.96
5.27	9.91	6.21	1.48	37.34
6.38	9.91	4.10	2.32	58.63
7.19	9.91	2.32	3.04	76.59
8.25	9.91	0.71	3.68	92.84
9.36	9.91	0.08	3.93	99.19
10.20	9.91	*	3.96	100.00

*Below the detection limit

Table 13(e): Effect of pH in the removal of Cu(II) by MCAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.54	9.91	7.30	1.04	26.34
3.56	9.91	5.43	1.79	45.21
4.91	9.91	4.91	2.00	50.45
5.96	9.91	3.94	2.39	60.24
6.83	9.91	2.89	2.81	70.84
7.76	9.91	1.22	3.48	87.69
8.92	9.91	0.57	3.74	94.25
9.91	9.91	0.08	3.93	99.19
10.63	9.91	*	3.96	100.00

*Below the detection limit

Table 13(f): Effect of pH in the removal of Cu(II) by ICAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.24	11.36	10.893	0.19	4.11
3.78	11.36	8.247	1.25	27.40
4.23	11.36	7.557	1.52	33.48
5.58	11.36	4.399	2.78	61.28
5.87	11.36	3.865	3.00	65.98
6.85	11.36	0.488	4.35	95.70
7.94	11.36	0.058	4.52	99.49
8.15	11.36	*	4.54	100.00
9.33	11.36	*	4.54	100.00

* Below the detection limit of AAS

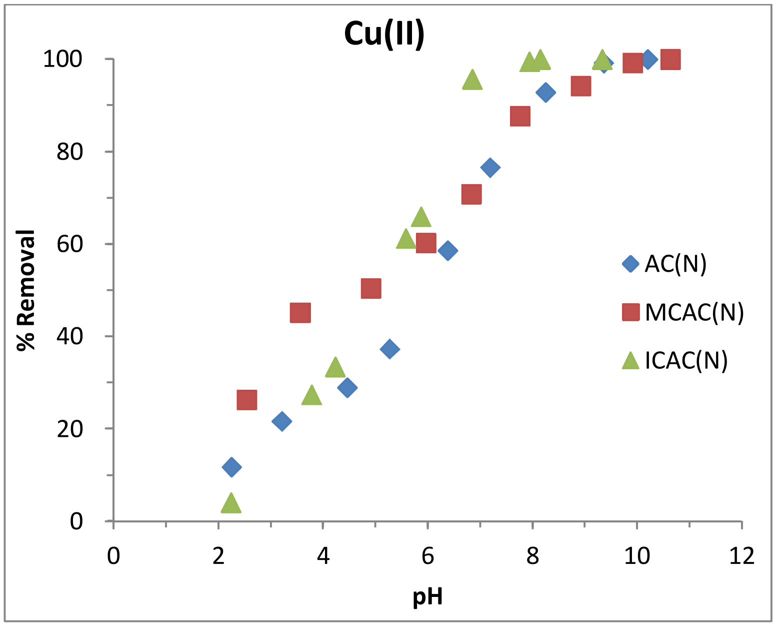

Figure 12(b): Effect of pH in the removal of Cu(II) by AC(N), MCAC(N) and ICAC(N)

Initial sorptive concentration: ~10 mg/L; Temperature: 25±1 ^{0}C

3.3.1.3. Lead (II)

The sorption of Pb(III) by the ACs, MCACs and ICACs solids were obtained and the percent removal of Pb(II) as a function of pH is presented graphically in Figures 13(a) AND 13(b) respectively for the rice hulls and areca nut waste based solids. The pH dependence data is also appended in Table 14(a-f). The results show that increasing the pH from 2.18 to 10.15 for AC-R, 2.24 to 10.21 for AC-N, 2.78 to 10.33 for MCAC-R and 2.88 to 10.43 for MCAC-N caused to increase in the Pb(II) removal respectively from 18.19% to 100 %, 14.47% to 100 %, 31.86 to 100% and 28.14% to 100%. The complete removal at high basic medium might be a mixed effect of adsorption and co-precipitation of the metal ions onto the solid surface (Farley *et al*., 1985; Lee *et al*., 2010). As discuss before, the lower percentage at low pH is explicable with the fact that there is a strong competition occurred between the excess of hydrogen ions and cations or positive metal ions (i.e., Pb^{2+}) towards the surface actives sites of solid. This may cause to suppress the adsorption of $Pb^{2+}$from the solution. However, a gradual increase in pH caused for acidic dissociation of surface functional groups and providing a negatively charged surface. Moreover, there was a significant decrease in H^+ ion concentrations in sorptive solutions as well. This could result in greater electrostatic attraction of metal cations towards the negatively charged surface of the adsorbents; followed by a formation of, perhaps a strong chemical bond onto the solid surfaces which apparently caused to enhance the uptake of Pb(II) by these solids (Depci *et al*., 2012).

Table 14(a): Effect of pH in the removal of Pb(II) by AC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.18	9.95	8.14	0.72	18.19
3.47	9.95	7.56	0.96	24.02
4.62	9.95	6.63	1.33	33.37
5.48	9.95	5.26	1.88	47.14
6.39	9.95	3.40	2.62	65.83
7.21	9.95	1.74	3.28	82.51
8.27	9.95	0.44	3.80	95.58
9.41	9.95	0.05	3.96	99.50
10.15	9.95	*	3.98	100.00

*Below the detection limit

Table 14(b): Effect of pH in the removal of Pb(II) by MCAC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.78	9.95	6.78	1.27	31.86
3.81	9.95	5.21	1.90	47.64
5.14	9.95	4.46	2.20	55.18
5.92	9.95	3.28	2.67	67.04
6.78	9.95	2.24	3.08	77.49
8.05	9.95	0.82	3.65	91.76
9.04	9.95	0.25	3.88	97.49
9.96	9.95	0.04	3.96	99.60
10.33	9.95	*	3.98	100.00

*Below the detection limit

Table 14(c): Effect of pH in the removal of Pb((II) by ICAC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.04	9.86	8.66	0.48	12.17
3.27	9.86	7.62	0.90	22.72
5.32	9.86	1.05	3.52	89.35
6.29	9.86	0.46	3.76	95.33
6.68	9.86	0.89	3.59	90.97
6.95	9.86	0.57	3.72	94.22
7.55	9.86	0.39	3.79	96.04
8.25	9.86	0.36	3.80	96.35
9.9	9.86	0.18	3.87	98.17

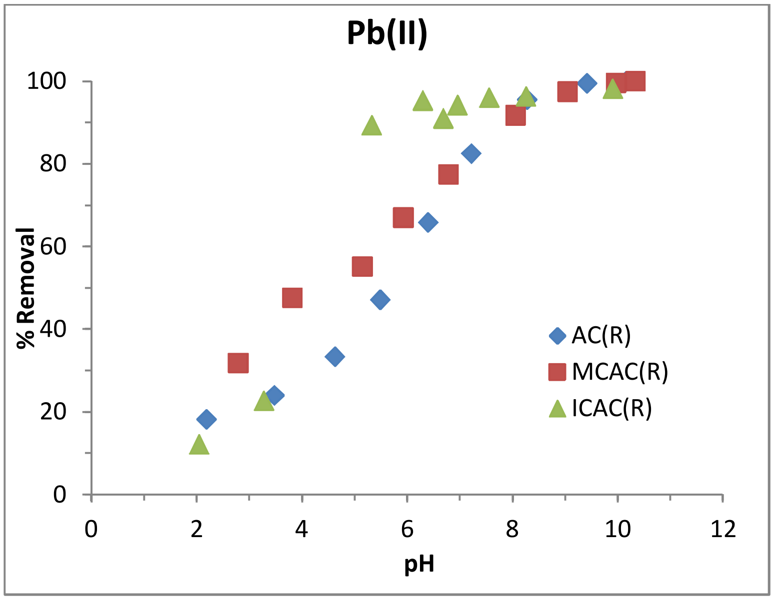

Figure 13(a): Effect of pH in the removal of Pb(II) by AC(R), MCAC(R) and ICAC(R)

Initial sorptive concentration: ~10 mg/L; Temperature: 25±1 ^{0}C

Table 14(d): Effect of pH in the removal of Pb(II) by AC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.24	9.95	8.51	0.58	14.47
3.40	9.95	7.72	0.89	22.41
4.51	9.95	6.73	1.29	32.36
5.63	9.95	5.74	1.68	42.31
6.32	9.95	3.97	2.39	60.10
7.48	9.95	1.89	3.22	81.01
8.17	9.95	0.50	3.78	94.97
9.52	9.95	0.06	3.96	99.40
10.21	9.95	*	3.98	100.00

*Below the detection limit

Table 14(e): Effect of pH in the removal of Pb(II) by MCAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.88	9.95	7.15	1.12	28.14
3.93	9.95	5.67	1.71	43.02
5.06	9.95	4.58	2.15	53.97
5.72	9.95	3.62	2.53	63.62
6.93	9.95	2.73	2.89	72.56
8.15	9.95	0.86	3.64	91.36
8.76	9.95	0.29	3.86	97.09
9.88	9.95	0.04	3.96	99.60
10.42	9.95	*	3.98	100.00

*Below the detection limit

Table 14(f): Effect of pH in the removal of Pb(II) by ICAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.08	9.86	9.29	0.23	5.78
3.49	9.86	8.62	0.50	12.58
5.52	9.86	2.23	3.05	77.38
6.17	9.86	0.54	3.73	94.52
6.62	9.86	0.27	3.84	97.26
6.92	9.86	0.74	3.65	92.49
7.35	9.86	0.59	3.71	94.02
7.89	9.86	0.46	3.76	95.33
9.66	9.86	0.19	3.87	98.07

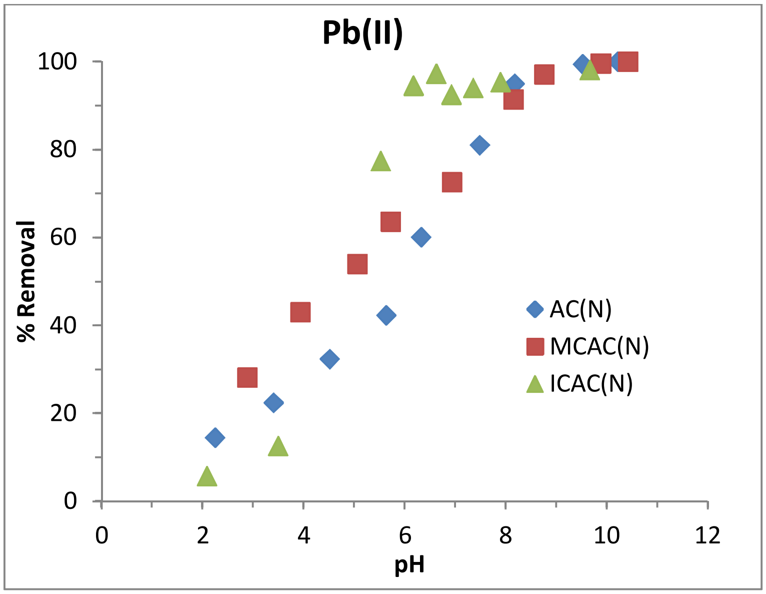

Figure 13(b): Effect of pH in the removal of Pb(II) by AC(N), MCAC(N) and ICAC(N)

Initial sorptive concentration: ~10 mg/L; Temperature: 25±1 ^{0}C

3.3.1.4. Arsenic (III) and Arsenic (V)

The effect of pH was studied with the initial concentration of ~10 mg/L for As(III) and As(V) between the pH range 2.0-10.0. The data obtained for As(III) were given in Table 15(a-d) and graphically in the Figures 14(a) and 14(b), respectively for rice hulls and *areca* nut based solids. Whereas the results for As(V) were returned in Table 16(a-d) and presented graphically in Figures15(a) and 15(b), respectively or rice hulls and *areca* nut based solids. The figures were plotted as the percent removal of the metals as a function of final pH of the sorptive solution. The results clearly conferred that the uptake of these two ions was greatly affected by the change in solution pH. Increasing the solution pH from 2.0 to 10.0 caused a continuous decrease in percent adsorption of As(III) and As(V). This could be explained from the speciation of As(III) and As(V) as discussed earlier, it was mentioned that As(III) existed as H_3AsO_3 species up to pH ~8 and As(V) existed as H_3AsO_4 and $H_2AsO_4^-$ species up to pH ~6.8. Moreover, the surface properties of the solids, i.e., pH_{pzc} also greatly affected the uptakes of As(III) and As(V) onto the surface of these solids. The pH_{pzc} obtained for the six samples were given in Table 11. The surface of AC, MCAC and ICAC was likely to be positively charged at lower pH i.e., below pH_{pzc} as expressed below:

$$\equiv \mathrm{S-OH_2^+} \leftrightarrow \underset{pH_{pzc}}{\equiv \mathrm{S-OH}} \leftrightarrow \equiv \mathrm{S-O^-} \qquad ...(14)$$

This perhaps caused to increase the uptake of these ions at lower pH (Tian *et al*., 2011). The maximum removal was observed at pH ~2.0 with 71.61% for As(III) and 76.21% for As(V). The probable mechanism was proposed as specific arsenic sorption and $\mathrm{OH^-}$ release from the surface (Xu *et al.,* 2002). The ion exchange mechanism could be represented as follows:

$\mathrm{S-(OH)+\ H_2AsO_4^-\ \ \ldots\ldots\ldots\ldots\ldots\ S-(H_2AsO_4)+\ \ OH^-}$ ...(15)

and/or

$\mathrm{S-(OH)+\ HAsO_4^{2-}\ \ \ldots\ldots\ldots\ldots\ldots\ S-(HAsO_4)_3^-+OH^-}$ ...(16)

Increasing the pH caused the acidic dissociation of surface functional groups of these solids providing a negatively charged surface on the surface which inhibited the sorption of As(III) and As(V) as because of the strong repulsive forces operated between the solid surface and sorbing oxyanions of As(III) and As(V) (Tiwari and Lee, 2012). Moreover, at higher pH i.e., above the $\mathrm{pH_{pzc,}}$ there was a strong competition between the $\mathrm{OH^-}$ ions and the anion species of As(III) and As(V), which greatly caused the decrease of As(III) and As(V) sorption by these solids surfaces (Li *et al.,* 2000).

Table 15(a): Effect of pH in the removal of As(III) by AC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.27	9.88	3.87	2.40	60.83
3.56	9.88	4.92	1.98	50.20
4.78	9.88	5.77	1.64	41.60
5.43	9.88	6.81	1.23	31.07
6.39	9.88	7.23	1.06	26.82
7.54	9.88	7.64	0.90	22.67
8.42	9.88	8.32	0.62	15.79
9.27	9.88	8.99	0.36	9.01
10.01	9.88	9.36	0.21	5.26

Table 15(b): Effect of pH in the removal of As(III) by MCAC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.85	9.88	2.78	2.84	71.86
3.92	9.88	3.94	2.38	60.12
5.27	9.88	4.86	2.01	50.81
6.39	9.88	5.75	1.65	41.80
6.98	9.88	6.83	1.22	30.87
8.01	9.88	7.24	1.06	26.72
8.92	9.88	7.56	0.93	23.48
9.84	9.88	8.04	0.74	18.62
10.37	9.88	8.87	0.40	10.22

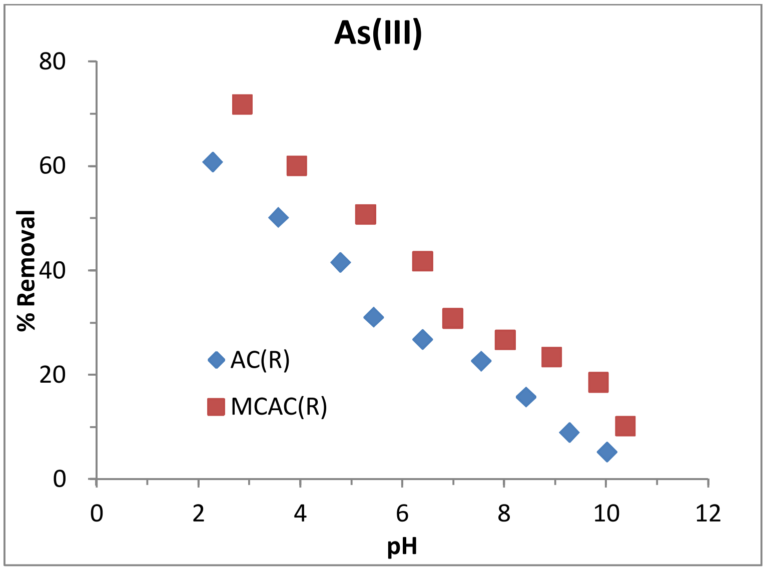

Figure 14(a): Effect of pH in the removal of As(III) by AC(R) and MCAC(R)

Initial sorptive concentration: ~10 mg/L; Temperature: 25±1 ^{0}C

Table 15(c): Effect of pH in the removal of As(III) by AC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.34	9.88	4.02	2.34	59.31
3.48	9.88	4.96	1.97	49.80
4.80	9.88	5.93	1.58	39.98
5.64	9.88	7.07	1.12	28.44
6.61	9.88	7.35	1.01	25.61
7.62	9.88	7.82	0.82	20.85
8.59	9.88	8.34	0.62	15.59
9.46	9.88	9.17	0.28	7.19
10.07	9.88	9.50	0.15	3.85

Table 15(d): Effect of pH in the removal of As(III) by MCAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.88	9.88	2.82	2.82	71.46
3.93	9.88	4.17	2.28	57.79
5.41	9.88	5.06	1.93	48.79
6.57	9.88	5.83	1.62	40.99
7.05	9.88	7.05	1.13	28.64
8.24	9.88	7.31	1.03	26.01
8.97	9.88	7.98	0.76	19.23
9.86	9.88	8.45	0.57	14.47
10.39	9.88	9.04	0.34	8.50

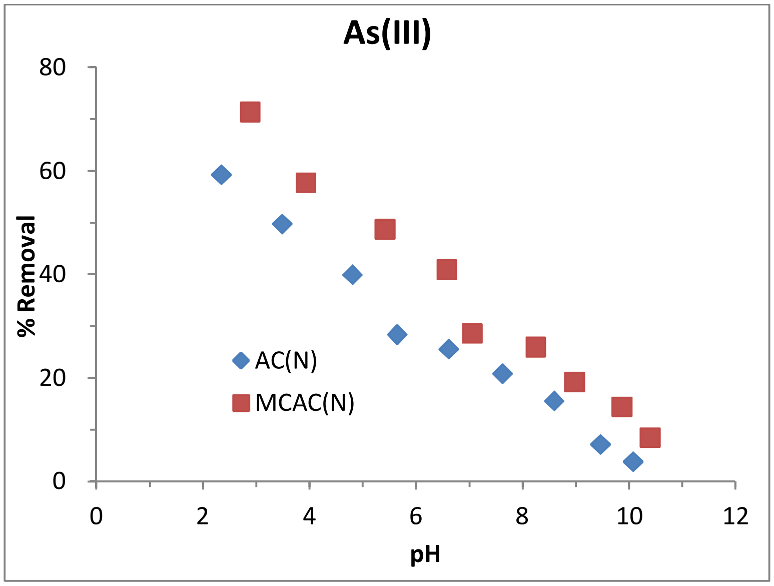

Figure 14(b): Effect of pH in the removal of As(III) by AC(N) and MCAC(N)
Initial sorptive concentration: ~10 mg/L; Temperature: 25±1 ^{0}C

Table 16(a): Effect of pH in the removal of As(V) by AC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.18	9.75	3.64	2.44	62.67
3.39	9.75	4.76	1.99	51.18
4.67	9.75	5.42	1.73	44.41
5.47	9.75	6.64	1.24	31.90
6.28	9.75	7.04	1.08	27.79
7.38	9.75	7.57	0.87	22.36
8.29	9.75	7.92	0.73	18.77
9.34	9.75	8.74	0.40	10.36
10.20	9.75	9.10	0.26	6.67

Table 16(b): Effect of pH in the removal of As(V) by MCAC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.59	9.75	2.32	2.97	76.21
4.02	9.75	3.74	2.40	61.64
4.96	9.75	4.68	2.02	52.00
6.04	9.75	5.27	1.79	45.95
7.12	9.75	6.15	1.44	36.92
7.85	9.75	6.83	1.16	29.95
8.67	9.75	7.01	1.09	28.10
9.72	9.75	7.66	0.83	21.44
10.32	9.75	8.42	0.53	13.64

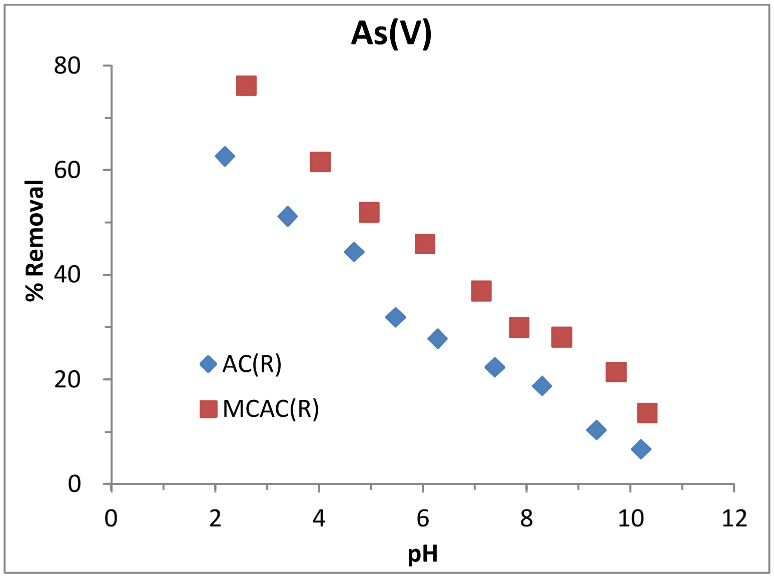

Figure 15(a): Effect of pH in the removal of As(V) by AC(R) and MCAC(R)

Initial sorptive concentration: ~10 mg/L; Temperature: 25±1 ^{0}C

Table 16(c): Effect of pH in the removal of As(V) by AC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.31	9.75	3.85	2.36	60.51
3.45	9.75	4.81	1.97	50.67
4.69	9.75	5.53	1.68	43.28
5.72	9.75	6.68	1.23	31.49
6.65	9.75	7.19	1.02	26.26
7.43	9.75	7.79	0.78	20.10
8.37	9.75	8.02	0.69	17.74
9.39	9.75	8.87	0.35	9.03
10.18	9.75	9.22	0.21	5.44

Table 16(d): Effect of pH in the removal of As(V) by MCAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
2.78	9.75	2.55	2.88	73.85
3.97	9.75	3.91	2.33	59.90
5.26	9.75	4.82	1.97	50.56
6.51	9.75	5.64	1.64	42.15
7.08	9.75	6.47	1.31	33.64
7.96	9.75	7.12	1.05	26.97
8.79	9.75	7.18	1.03	26.36
9.88	9.75	7.96	0.72	18.36
10.43	9.75	8.69	0.42	10.87

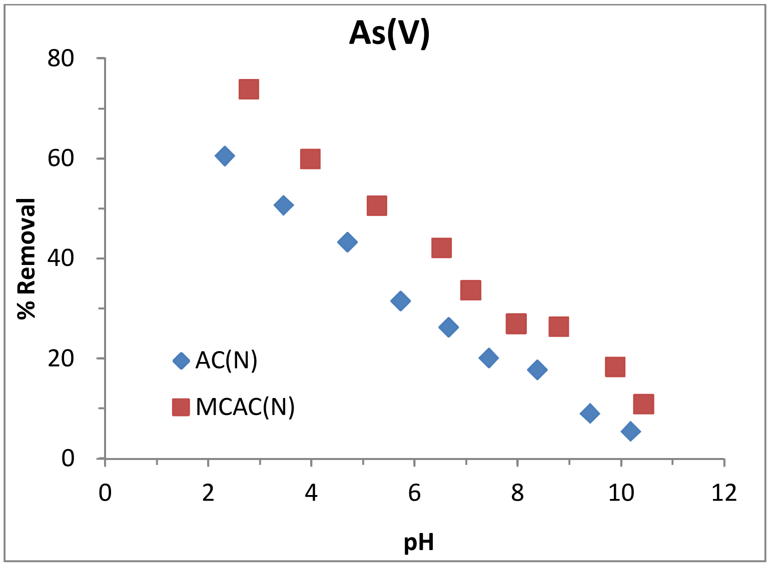

Figure 15(b): Effect of pH in the removal of As(V) by AC(N) and MCAC(N)

Initial sorptive concentration: ~10 mg/L; Temperature: 25±1 ^{0}C

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3.3.2. Effect of initial sorptive concentration

3.3.2.1. Cadmium (II)

The effect of sorptive concentration for Cd(II) was carried out by varying the initial Cd(II) concentration from 1.0 mg/L to 25.0 mg/L and at a constant pH 5.0. The equilibrium stage sorption data obtained for Cd(II) was plotted between the percent removal against the initial bulk sorptive concentration (mg/L) and results are returned in Table 17(a-f) and Figure 16(a) and 16(b), respectively for rice hulls and *areca* nut waste based materials. At low sorptive concentrations, an enhanced percentage of adsorption was observed which was gradually decreased with increasing initial sorptive concentration. This may be explicable with the fact that at low concentration of metal ions, relatively large number of active sites is available onto the solid surface for lesser number of sorbing ions. Whereas on increasing the sorptive concentrations for the same solid dose, relatively lesser number of active sites is available which results in less percent removal of the metal ions (Mishra *et al.*, 2004; Tiwari *et al.*, 1999). On the other hand, increasing the sorptive concentration from 1.0 to 25.0 mg/L of Cd(II) caused an apparent increase in amount of Cd(II) uptake by the solids used.

Table 17(a): Effect of initial concentration in the removal of Cd(II) by AC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
5.0	1.40	0.46	0.38	67.43
5.0	3.40	1.84	0.62	45.88
5.0	5.20	3.15	0.82	39.42
5.0	10.05	7.25	1.12	27.86
5.0	14.50	10.69	1.52	26.28
5.0	18.90	13.58	2.13	28.15

Table 17(b): Effect of initial concentration in the removal of Cd(II) by MCAC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
5.0	0.97	0.00	0.39	100.00
5.0	3.42	0.94	0.99	72.51
5.0	6.05	2.41	1.46	60.17
5.0	10.08	5.88	1.68	41.67
5.0	14.77	7.70	2.83	47.87
5.0	20.12	11.61	3.40	42.30

Table 17(c): Effect of initial concentration in the removal of Cd(II) by ICAC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
5.0	0.97	0.00	0.39	100.00
5.0	3.42	0.19	1.29	94.44
5.0	6.05	1.60	1.78	73.55
5.0	10.08	5.13	1.98	49.11
5.0	14.77	7.02	3.10	52.47
5.0	20.12	11.48	3.46	42.94

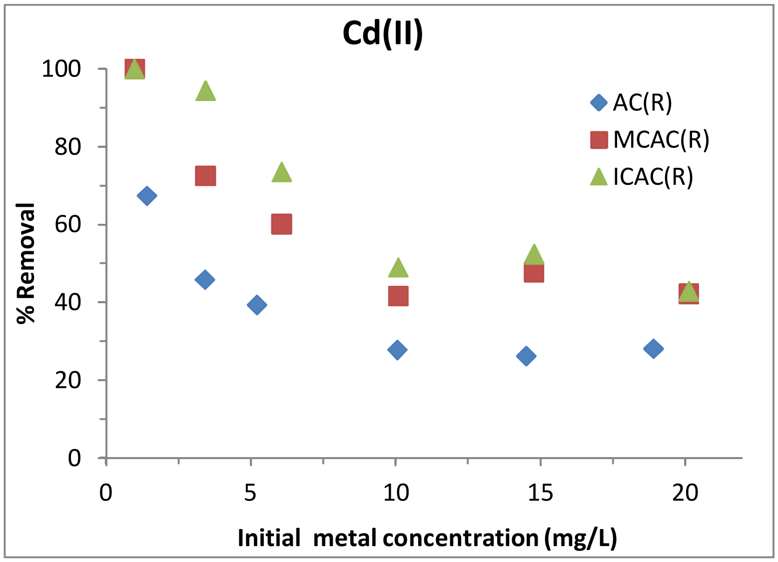

Figure 16(a): Effect of initial sorptive concentration in the removal of Cd(II) by AC(R), MCAC(R) and ICAC(R) at pH= 5.0, Temperature: 25±1 ^{0}C

Table 17(d): Effect of initial concentration in the removal of Cd(II) by AC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
5.0	1.4	0.48	0.37	65.71
5.0	3.4	1.87	0.61	45.00
5.0	5.2	3.32	0.75	36.15
5.0	10.05	7.3	1.10	27.36
5.0	14.5	10.93	1.43	24.62
5.0	18.9	14.43	1.79	23.65

Table 17(e): Effect of initial concentration in the removal of Cd(II) by MCAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
5.0	0.97	0.00	0.39	100.00
5.0	3.42	1.57	0.74	54.09
5.0	6.05	3.46	1.04	42.81
5.0	10.08	6.10	1.59	39.48
5.0	14.77	9.38	2.16	36.49
5.0	20.12	12.39	3.09	38.42

Table 17(f): Effect of initial concentration in the removal of Cd(II) by ICAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
5.0	0.97	0.00	0.39	100.00
5.0	3.42	1.20	0.89	64.91
5.0	6.05	2.39	1.46	60.50
5.0	10.08	5.40	1.87	46.43
5.0	14.77	9.08	2.28	38.52
5.0	20.12	14.06	2.42	30.12

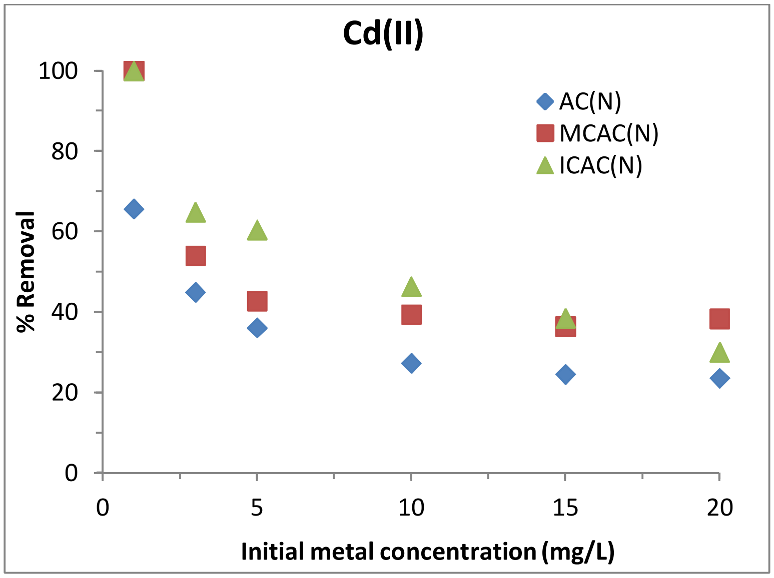

Figure 16(b): Effect of initial sorptive concentration in the removal of Cd(II) by AC(N), MCAC(N) and ICAC(N) at pH= 5.0, Temperature: 25±1 ^{0}C

3.3.2.2. Copper (II)

The concentration dependence data for the Cu(II) was studied varying the Cu(II) concentration from 1.0 to 15.0 mg/L at a constant pH 4.0. The results obtained were presented with the percent removal of Cu(II) as a function of sorptive concentration and returned in the Tables18(a-f) also in the Figures17(a) and 17(b), respectively for rice hulls and *areca* nut waste samples. Results clearly demonstrated that increasing the sorptive concentration from 1.0 to 15.0 mg/L caused an apparent increase in amount of Cu(II) adsorbed whereas for the similar increase in sorptive concentration caused to decrease in percent uptake of Cu(II).

Table 18(a): Effect of initial concentration in the removal of Cu(II) by AC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
4.0	0.80	0.21	0.24	73.75
4.0	3.12	1.90	0.49	39.10
4.0	5.15	3.77	0.55	26.79
4.0	8.21	6.71	0.60	18.27
4.0	9.91	8.51	0.56	14.13
4.0	14.15	12.44	0.68	12.08

Table 18(b): Effect of initial concentration in the removal of Cu(II) by MCAC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
4.0	0.80	0.12	0.27	85.00
4.0	3.12	1.55	0.63	50.32
4.0	5.15	3.10	0.82	39.80
4.0	8.21	6.06	0.86	26.18
4.0	9.91	7.79	0.85	21.39
4.0	14.15	11.87	0.91	16.11

Table 18(c): Effect of initial concentration in the removal of Cu(II) by ICAC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
4.0	1.45	0.14	0.52	89.79
4.0	3.59	0.85	1.093	76.24
4.0	6.16	2.83	1.33	53.96
4.0	11.74	7.73	1.60	34.17
4.0	18.78	12.93	2.34	31.17
4.0	25.60	18.26	2.93	28.67

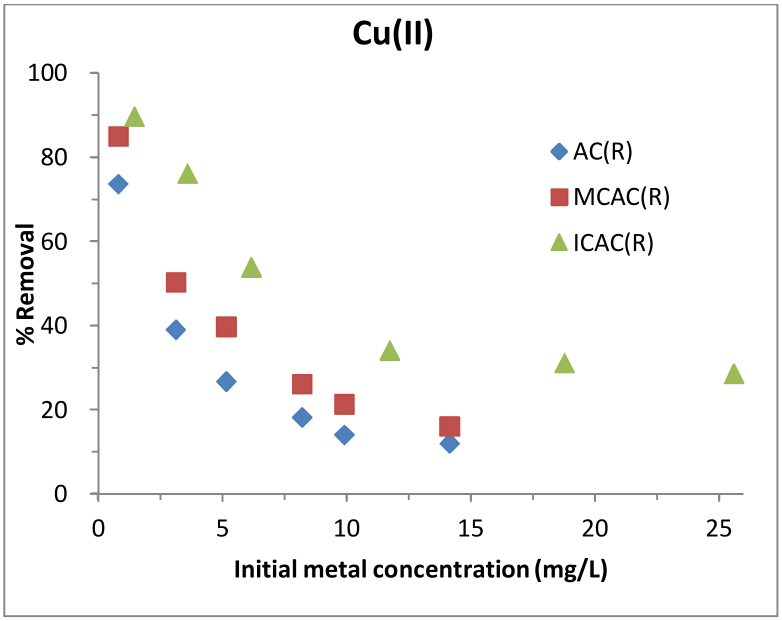

Figure 17(a): Effect of initial sorptive concentration in the removal of Cu(II) by using AC(R), MCAC(R) and ICAC(R) at pH= 4.0, Temperature: 25±1 ^{0}C

Table 18(d): Effect of initial concentration in the removal of Cu(II) by AC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
4.0	0.80	0.27	0.21	66.25
4.0	3.12	2.06	0.42	33.97
4.0	5.15	3.81	0.53	26.02
4.0	8.21	7.15	0.42	12.91
4.0	9.91	8.73	0.47	11.90
4.0	14.15	12.83	0.53	9.33

Table 18(e): Effect of initial concentration in the removal of Cu(II) by MCAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
4.0	0.80	0.14	0.26	82.50
4.0	3.12	1.62	0.60	48.07
4.0	5.15	3.38	0.71	34.37
4.0	8.21	6.18	0.81	24.72
4.0	9.91	8.08	0.73	18.46
4.0	14.15	11.95	0.88	15.55

Table 18(f): Effect of initial concentration in the removal of Cu(II) by ICAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
4.0	1.45	0.15	0.52	89.79
4.0	3.59	0.85	1.09	76.24
4.0	6.16	2.84	1.33	53.96
4.0	11.74	7.73	1.60	34.17
4.0	18.78	12.93	2.34	31.17
4.0	25.60	18.26	2.94	28.67

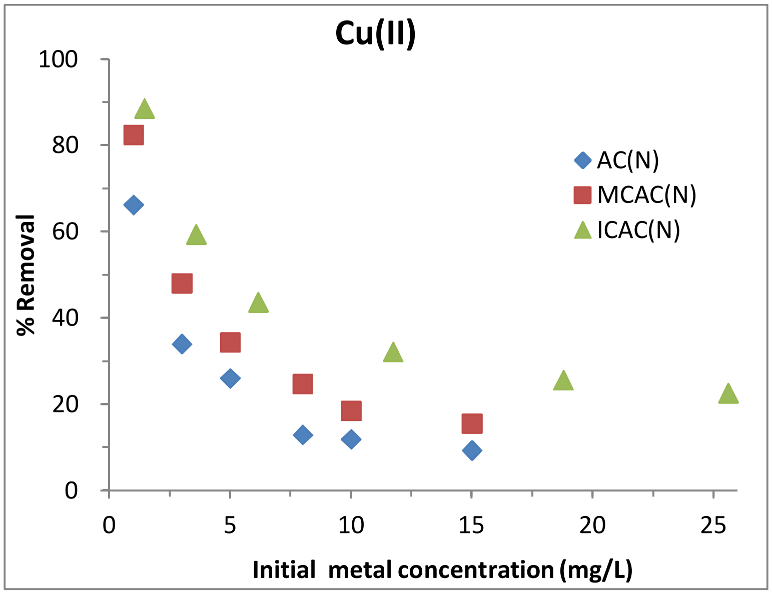

Figure 17(b): Effect of initial sorptive concentration in the removal of Cu(II) by AC(N), MCAC(N)and ICAC(N) at pH=4.0; Temperature: 25±1 ^{0}C

3.3.2.3. Lead (II)

The sorptive concentration dependence data for Pb(II) was obtained varying the Pb(II) initial concentration from 2.0 mg/L to 20.0 mg/L at constant pH 5.0 and at temperature 25±1^{0}C. The percentage removal of Pb(II) at various initial concentration along with the amount adsorbed were returned in Table 19(a-f) and presented graphically in Figures18(a) and 18(b). The concentration dependence data clearly revealed that increasing the Pb(II) from 2.0 to 20.0 mg/L caused an apparent increase in amount adsorbed using these solids however, the percent removal was decreased for the similar increase in Pb(II) concentration. Interestingly, in case of ICAC solid very high percent uptake of Pb(II) was almost unaffected with such an increase in concentration i.e., 2.0 to 20.0 mg/L. This suggested very high affinity of surface active sites for Pb(II) also indicated the potential applicability of the material in the remediation of lead contaminated water even at higher concentration levels (Dang *et al*., 2009).

Table 19(a): Effect of initial concentration in the removal of Pb(II) by AC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
5.0	2.06	0.68	0.55	66.99
5.0	3.14	1.18	0.78	62.42
5.0	5.50	2.27	1.29	58.73
5.0	8.13	3.53	1.84	56.58
5.0	13.30	5.92	2.92	55.15
5.0	16.16	8.80	2.94	45.54

Table 19(b): Effect of initial concentration in the removal of Pb(II) by MCAC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
5.0	2.06	0.37	0.67	82.04
5.0	3.14	0.77	0.95	75.48
5.0	5.50	1.51	1.59	72.54
5.0	8.13	2.41	2.28	70.35
5.0	13.30	5.34	3.14	58.86
5.0	16.16	7.87	3.32	51.29

Table 19(c): Effect of initial concentration in the removal of Pb(II) by ICAC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
5.0	0.93	0.13	0.32	86.02
5.0	3.17	0.26	1.16	91.80
5.0	4.96	0.33	1.85	93.35
5.0	10.28	0.59	3.88	94.26
5.0	16.06	1.11	5.98	93.09
5.0	20.14	1.5	7.46	92.55

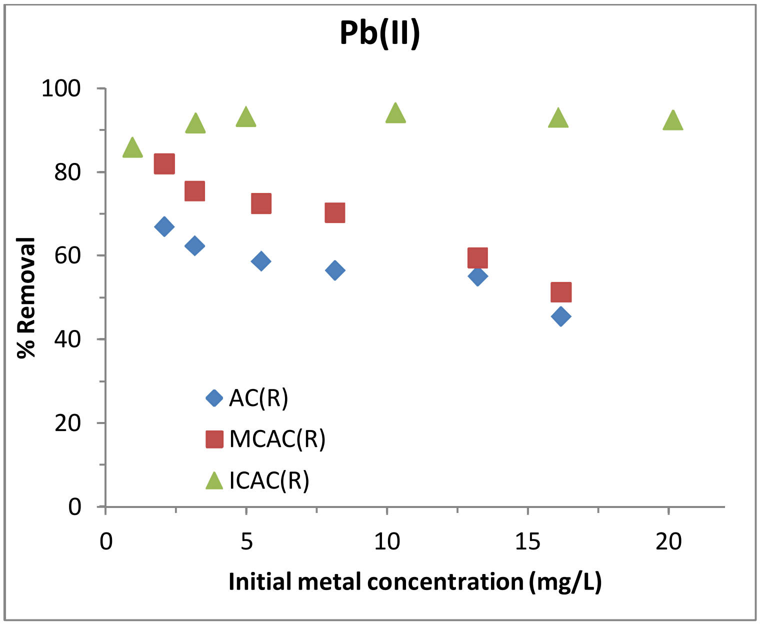

Figure 18(a): Effect of initial sorptive concentration in the removal of Pb(II) by AC(R), MCAC(R)and ICAC(R) at pH=5.0 and Temperature: 25±1 ^{0}C

Table 19(d): Effect of initial concentration in the removal of Pb(II) by AC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
5.0	2.06	0.75	0.52	63.59
5.0	3.14	1.33	0.72	57.64
5.0	5.50	2.43	1.22	55.82
5.0	8.13	3.82	1.72	53.01
5.0	13.30	6.79	2.56	48.56
5.0	16.16	9.26	2.76	42.69

Table 19(e): Effect of initial concentration in the removal of Pb(II) by MCAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
5.0	2.06	0.46	0.64	77.66
5.0	3.14	1.06	0.83	66.24
5.0	5.50	1.87	1.45	66.00
5.0	8.13	2.94	2.08	63.84
5.0	13.30	6.66	2.62	49.54
5.0	16.16	8.19	3.19	49.32

Table 19(f): Effect of initial concentration in the removal of Pb(II) by ICAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
5.0	0.93	0.16	0.31	82.80
5.0	3.17	0.36	1.12	88.64
5.0	4.96	0.55	1.76	88.91
5.0	10.28	0.69	3.84	93.29
5.0	16.06	0.8	6.10	95.02
5.0	20.14	1.85	7.32	90.81

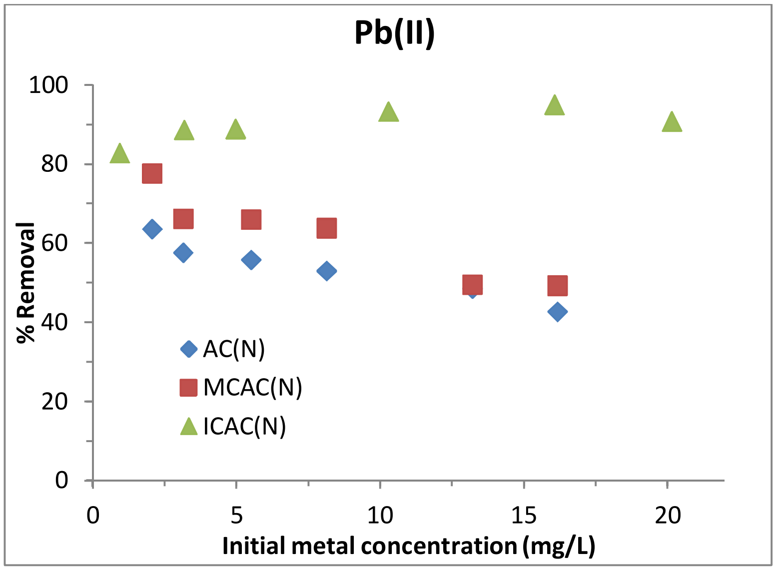

Figure 18(b): Effect of initial sorptive concentration in the removal of Pb(II) byAC(N), MCAC(N) and ICAC(N) at pH=5.0 and Temperature: 25±1 ^{0}C

3.3.2.4. Arsenic (III) and Arsenic (V)

Similar to other metal ions studied, the concentration dependence data was collected varying the initial concentration of As(III)/or As(V) from 1.0 mg/L to 10.0 mg/L at 25±1^{0}C and at pH~4.5. The equilibrium stage sorption data was collected and presented the percent uptake of arsenic as a function of arsenic initial concentrations graphically in Figures 19 (a & b) and 20 (a & b) respectively, for the As(III) and As(V) solids. Moreover, the amount adsorbed along with the percent removal of arsenic data with the change in sorptive concentration was compiled and returned in the Tables 20(a-d) and 21(a-d), respectively for the As(III) and As(V). It is evident from the data that an enhanced percent uptake of arsenic was occurred at lower sorptive concentrations which was gradually decreased with increase in initial sorptive concentration. Moreover, it is evident that increasing the initial sorptive concentration from 1.0

mg/L -10.0 mg/L of As(III) and As(V) caused to increase in amount adsorbed of As(III) or As(V) by these solids. Results are in a line to the previous findings (Tiwari and Lee, 2012) .

Table 20(a): Effect of initial concentration in the removal of As(III) by AC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
4.5	1.05	0.45	0.24	57.14
4.5	2.10	1.23	0.35	41.42
4.5	5.09	3.45	0.66	32.22
4.5	10.19	7.76	0.97	23.85

Table 20(b): Effect of initial concentration in the removal of As(III) by MCAC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
4.5	1.05	0.23	0.33	78.09
4.5	2.10	0.85	0.50	59.52
4.5	5.09	2.47	1.05	51.47
4.5	10.19	6.96	1.29	31.70

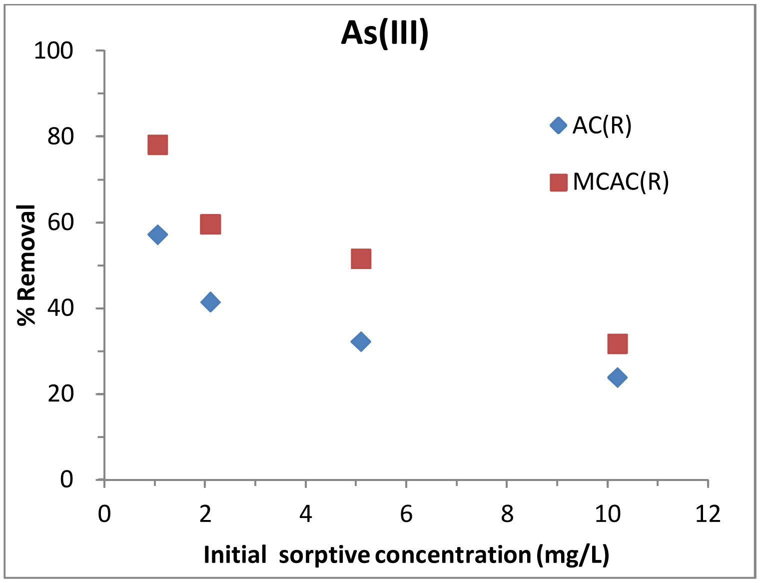

Figure 19(a): Effect of initial sorptive concentration in the removal of As(III) by AC(R) and MCAC(R) at pH=4.5 and Temperature: 25±1 ^{0}C

Table 20(c): Effect of initial concentration in the removal of As(III) by AC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
4.5	1.05	0.63	0.17	40.00
4.5	2.10	1.44	0.26	31.43
4.5	5.09	4.12	0.39	19.06
4.5	10.19	8.54	0.66	16.19

Table 20(d): Effect of initial concentration in the removal of As(III) by MCAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
4.5	1.05	0.43	0.25	59.05
4.5	2.10	1.36	0.30	35.24
4.5	5.09	3.71	0.55	27.11
4.5	10.19	7.86	0.93	22.87

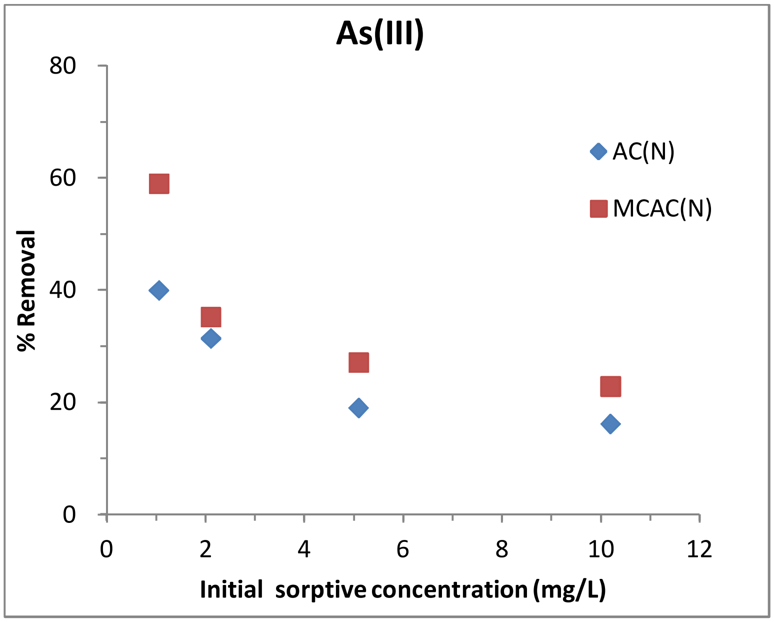

Figure 19(b): Effect of initial sorptive concentration in the removal of As (III) by AC(N), and MCAC(N) at pH=4.5 and Temperature: 25±1 ^{0}C

Table 21(a): Effect of initial concentration in the removal of As(V) by using AC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
4.5	1.10	0.38	0.29	65.45
4.5	2.26	1.45	0.32	35.84
4.5	5.54	3.74	0.72	32.45
4.5	10.46	7.89	1.03	24.57

Table 21(b): Effect of initial concentration for the removal of As(V) by MCAC(R)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
4.5	1.10	0.18	0.37	83.64
4.5	2.26	0.65	0.64	71.24
4.5	5.54	1.56	1.59	69.05
4.5	10.46	6.89	1.43	34.13

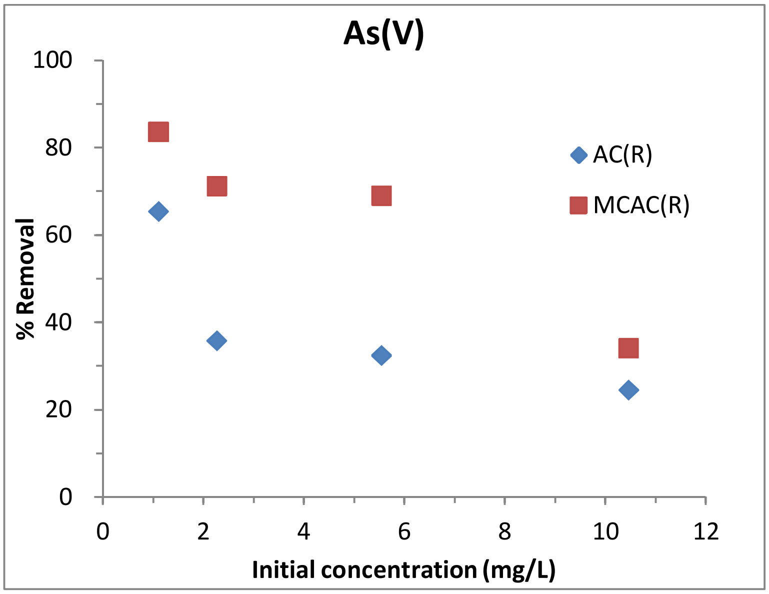

Figure 20(a): Effect of initial sorptive concentration in the removal of As(V) by AC(R) and MCAC(R) at pH=4.5 and Temperature: 25±1 ^{0}C

Table 21(c): Effect of initial concentration for the removal of As(V) by AC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
4.5	1.10	0.53	0.23	51.82
4.5	2.26	1.59	0.27	29.65
4.5	5.54	3.97	0.63	28.34
4.5	10.46	8.17	0.92	21.89

Table 20(d): Effect of initial concentration in the removal of As(V) by MCAC(N)

pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
4.5	1.10	0.37	0.29	66.36
4.5	2.26	1.33	0.37	41.15
4.5	5.54	3.36	0.87	33.33
4.5	10.46	7.64	1.13	26.96

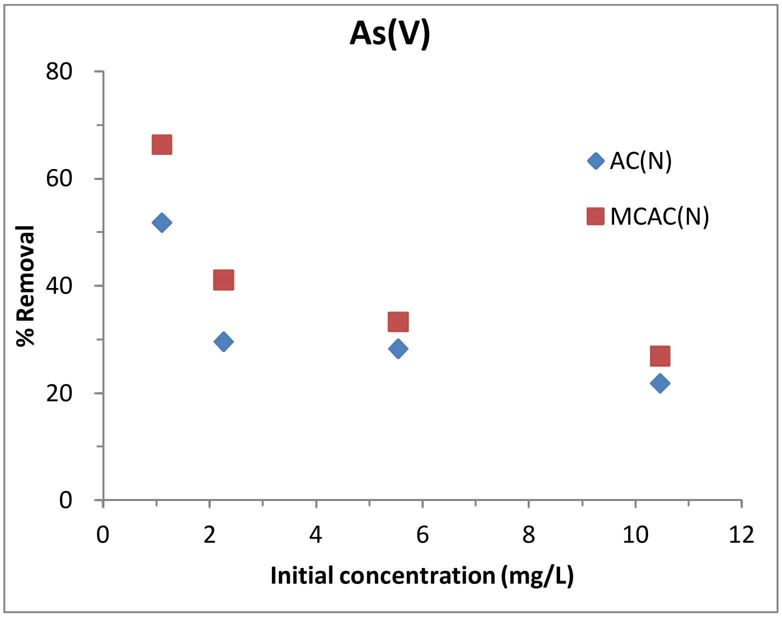

Figure 20(b): Effect of initial sorptive concentration in the removal of As (V) by AC(N), and MCAC(N) at pH=4.5 and Temperature: 25±1 ^{0}C

3.3.3. Effect of contact time

3.3.3.1. Cadmium (II)

The time dependence adsorption studies are an important parameter deducing the kinetics of the adsorption as well to provide a plausible mechanism involved at solid solution interface. Keeping in view, the sorption of Cd(II) by these solids was studied varying the time between 0- 24 hrs keeping the initial Cd(II) concentration 10.0 mg/L and pH 5.0 as constant. The time dependence sorption data collected is returned in the Tables 22(a-f) and Figures 21(a) and 21(b). It was observed that the uptake of Cd(II) by these solids was very fast during initial period of contact time and most of the Cd(II) ions were adsorbed within *Ca* 60 minutes of contact.. This could be explicable with the fact that the surface coverage was low at the initial stage of contact and sorptive ions occupy the active surface sites rapidly and in a random manner, as a result, the percent adsorption increased rapidly during initial period (Mishra and Tiwari, 2002). At latter stages, the surface coverage was increased which caused to slow down the sorption of Cd(II). Finally, after a lapse of *Ca* 180 -300 minutes an apparent saturation was achieved for these systems.

Table 22(a): Effect of contact time in the removal of Cd(II) by AC(R)

Time (Minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
10	5.0	8.93	6.93	0.80	22.40
30	5.0	8.93	6.73	0.88	24.61
60	5.0	8.93	6.63	0.92	25.72
120	5.0	8.93	6.56	0.95	26.46
180	5.0	8.93	6.41	1.01	28.19
300	5.0	8.93	6.23	1.08	30.16
1440	5.0	8.93	6.18	1.10	30.80

Table 22(b): Effect of contact time in the removal of Cd(II) by MCAC(R)

Time (Minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
10	5.0	10.13	7.64	0.99	24.58
30	5.0	10.13	5.92	1.68	41.56
60	5.0	10.13	5.29	1.94	47.78
120	5.0	10.13	5.14	1.99	49.26
180	5.0	10.13	5.03	2.04	50.35
300	5.0	10.13	5.15	1.99	49.16
1440	5.0	10.13	5.04	2.04	50.25

Table 22(c): Effect of contact time in the removal of Cd(II) by ICAC(R)

Time (Minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
10	5.0	10.19	7.23	1.18	29.05
30	5.0	10.19	5.39	1.92	47.11
60	5.0	10.19	4.29	2.36	57.90
120	5.0	10.19	3.63	2.62	64.38
180	5.0	10.19	3.59	2.64	64.77
300	5.0	10.19	3.52	2.67	65.46
1440	5.0	10.19	3.57	2.65	64.97

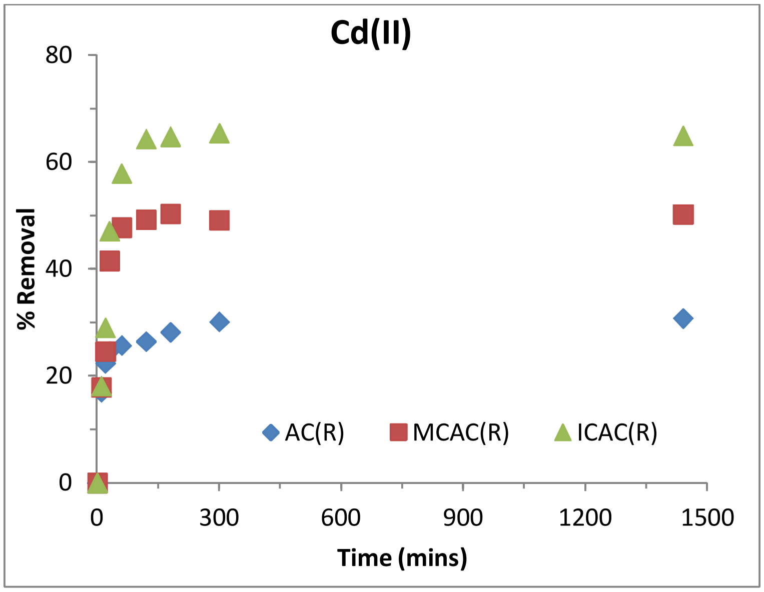

Figure 21(a): Effect of contact time in the removal of Cd(II) by AC(R), MCAC(R) and ICAC(R) at pH 5.0; Initial Cd(II) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

Table 22(d): Effect of contact time in the removal of Cd(II) by AC(N)

Time (Minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
10	5.0	9.06	7.41	0.66	18.17
30	5.0	9.06	7.17	0.76	20.84
60	5.0	9.06	7.15	0.76	21.08
120	5.0	9.06	6.97	0.83	23.02
180	5.0	9.06	6.83	0.89	24.60
300	5.0	9.06	6.79	0.90	24.97
1440	5.0	9.06	6.72	0.93	25.77

Table 22(e): Effect of contact time in the removal of Cd(II) by MCAC(N)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
10	5.0	10.62	9.23	0.56	13.09
30	5.0	10.62	8.56	0.82	19.40
60	5.0	10.62	7.97	1.06	24.95
120	5.0	10.62	6.56	1.62	38.23
180	5.0	10.62	6.32	1.72	40.49
300	5.0	10.62	6.19	1.77	41.71
1440	5.0	10.62	6.05	1.83	43.03

Table 22(f): Effect of contact time in the removal of Cd(II) by ICAC(N)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
10	5.0	10.73	8.89	0.74	17.15
30	5.0	10.73	6.74	1.59	37.19
60	5.0	10.73	6.15	1.83	42.68
120	5.0	10.73	4.12	2.64	61.60
180	5.0	10.73	3.98	2.70	62.91
300	5.0	10.73	3.92	2.72	63.47
1440	5.0	10.73	3.83	2.76	64.31

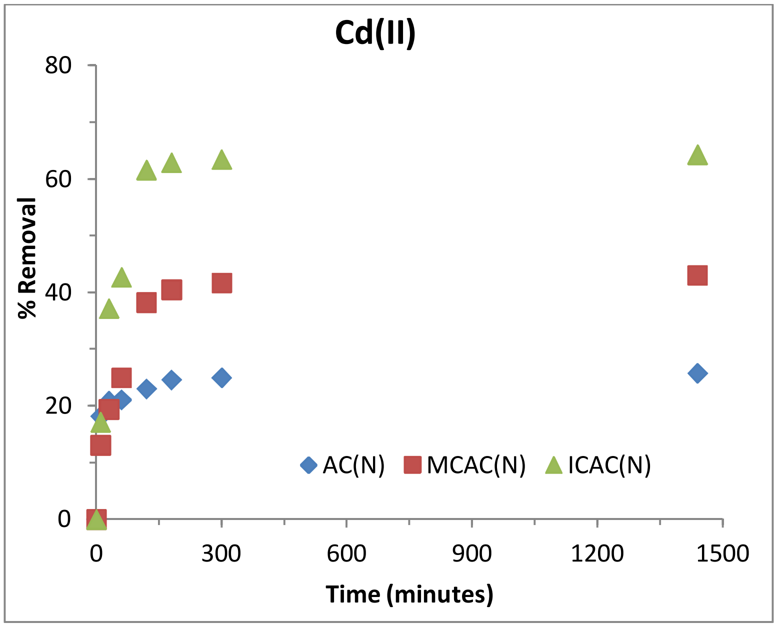

Figure 21(b): Effect of contact time in the removal of Cd(II) by AC(N), MCAC(N) and ICAC(N) at pH 5.0; Initial Cd(II) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

3.3.3.2. Copper (II)

Similarly, the removal of Cu(II) as a function of time was studied by varying the contact time from 0 min to 24 hours at a fixed Cu(II) concentration of 10.0 mg/L and at a constant pH 4.0 by employing the ACs, MCACs and ICACs samples. The amount adsorbed along with the percent adsorbed is calculated are returned in the Tables 23(a-f). Moreover, the percent removal of Cu(II) as a function of contact time is also presented graphically in Figures 22(a) and 22(b), respectively for the rice hulls and *areca* nut based solids. These figures show that the uptake of Cu(II) was slightly slow but a gradual increase was occurred and an apparent equilibrium was attained within *Ca* 480 minutes of contact time. This could be explained with the fact that sorption of Cu(II) was conducted at slightly low pH, i.e., pH 4.0 where these solids possessed with some net positive charge. Therefore, Cu^{2+} ions could experience less attractive forces towards the surface. Hence, there could be a competition with H^+ ions and Cu^{2+} ions which ultimately retarded the uptake of Cu(II) as well caused an slow uptake of Cu(II) by these solids (Xu *et al.*, 2008)

Table 23(a): Effect of contact time in the removal of Cu(II) by AC(R)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	4.0	9.93	9.71	0.88	2.21
10	4.0	9.93	9.58	0.14	3.52
30	4.0	9.93	9.52	0.16	4.12
60	4.0	9.93	9.09	0.33	8.46
120	4.0	9.93	9.06	0.35	8.76
180	4.0	9.93	8.97	0.38	9.66
300	4.0	9.93	8.76	0.47	11.78
420	4.0	9.93	7.99	0.77	19.54
480	4.0	9.93	7.83	0.84	21.15
1440	4.0	9.93	7.86	0.83	20.84

Table 23(b): Effect of contact time in the removal of Cu(II) by MCAC(R)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	4.0	10.12	9.63	0.19	4.84
10	4.0	10.12	9.30	0.33	8.10
30	4.0	10.12	8.93	0.47	11.76
60	4.0	10.12	8.87	0.50	12.35
120	4.0	10.12	8.54	0.63	15.61
180	4.0	10.12	8.29	0.73	18.08
300	4.0	10.12	8.11	0.80	19.86
420	4.0	10.12	7.57	1.02	25.20
480	4.0	10.12	7.37	1.10	27.17
1440	4.0	10.12	7.35	1.11	27.37

Table 23(c): Effect of contact time in the removal of Cu(II) by ICAC(R)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	4.0	9.71	8.45	0.50	12.94
10	4.0	9.71	8.09	0.65	16.61
30	4.0	9.71	7.90	0.72	18.63
60	4.0	9.71	7.54	0.87	22.37
120	4.0	9.71	6.71	1.20	30.88
180	4.0	9.71	6.48	1.29	33.31
300	4.0	9.71	5.90	1.52	39.23
420	4.0	9.71	5.59	1.65	42.39
1440	4.0	9.71	5.61	1.64	42.27

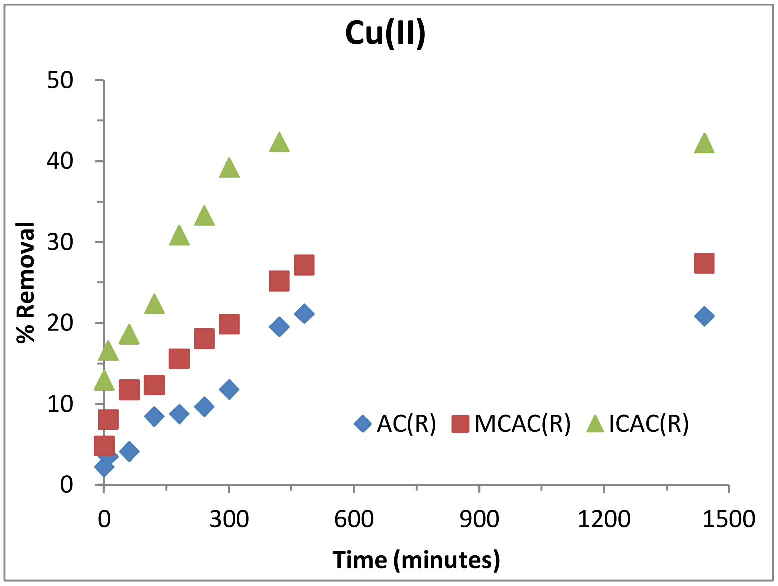

Figure 22(a): Effect of contact time in the removal of Cu(II) by AC(R), MCAC(R) and ICAC(R) at pH 4.0; Initial Cu(II) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

Table 23(d): Effect of contact time in the removal of Cu(II) by AC(N)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	4.0	10.04	9.74	0.12	2.99
10	4.0	10.04	9.72	0.13	3.19
30	4.0	10.04	9.54	0.20	4.98
60	4.0	10.04	9.35	0.27	6.87
120	4.0	10.04	9.27	0.31	7.67
180	4.0	10.04	9.12	0.37	9.16
300	4.0	10.04	8.98	0.42	10.56
420	4.0	10.04	8.44	0.64	15.94
480	4.0	10.04	8.31	0.69	17.23
1440	4.0	10.04	8.29	0.70	17.43

Table 23(e): Effect of contact time in the removal of Cu(II) by MCAC(N)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	4.0	10.02	9.69	0.13	3.29
10	4.0	10.02	9.55	0.18	4.69
30	4.0	10.02	9.15	0.35	8.68
60	4.0	10.02	9.02	0.40	9.98
120	4.0	10.02	8.92	0.44	10.98
180	4.0	10.02	9.89	0.45	11.28
300	4.0	10.02	8.64	0.55	13.77
420	4.0	10.02	7.93	0.84	20.86
480	4.0	10.02	7.83	0.88	21.86
1440	4.0	10.02	7.79	0.89	22.26

Table 23(f): Effect of contact time in the removal of Cu(II) by ICAC(N)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	4.0	10.03	9.37	0.26	6.53
10	4.0	10.03	9.21	0.33	8.16
30	4.0	10.03	9.00	0.41	10.23
60	4.0	10.03	8.56	0.59	14.65
120	4.0	10.03	7.79	0.89	22.24
180	4.0	10.03	7.25	1.11	27.64
300	4.0	10.03	6.37	1.46	36.41
420	4.0	10.03	6.13	1.56	38.92
1440	4.0	10.03	5.58	1.78	44.35

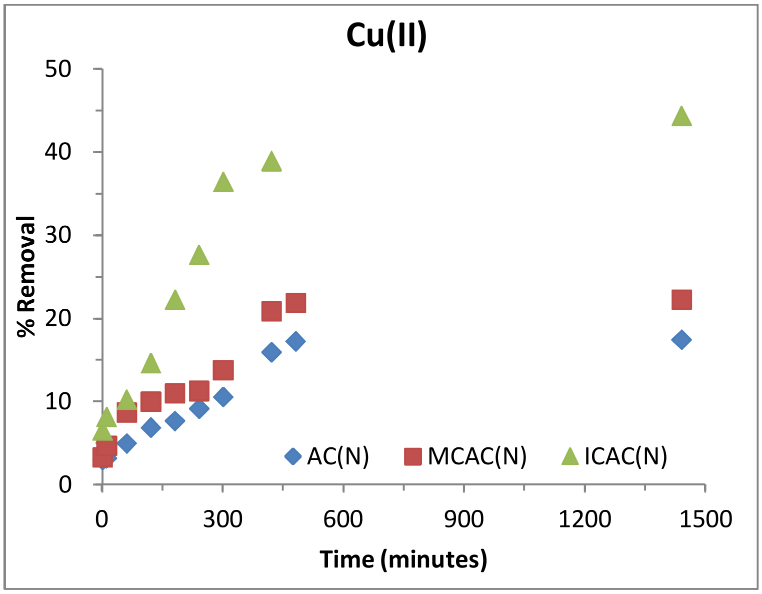

Figure 22(b): Effect of contact time in the removal of Cu(II) by AC(N), MCAC(N) and ICAC(N) at pH 4.0; Initial Cu(II) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

3.3.3.3. Lead (II)

The removal of Pb(II) as a function of time was also studied by varying the contact time from 0 min to 24 hours at a metal concentration of ~10.0 mg/L and at constant pH 5.0. The amount adsorbed and percent uptake of Pb(II) as a function of contact time is given in the Tables 24(a-f) for these systems studied. Further, the percent uptake of Pb(II) by these solids as a function of time is presented graphically in Figures 23(a) and 23(b), respectively for rice hulls and *areca* nut waste based materials. Results clearly demonstrated that a very fast initial rise of adsorption was slowed down in the latter stages of contact time and achieved almost a constant adsorption after *Ca* 300-400 minutes of contact time. Moreover, the maximum adsorption was taken place within initial few minutes of contact i.e., within 60~90 minutes of contact. The time dependence data was further utilized to discuss the kinetics of sorption using the pseudo-first order and pseudo-second order equations.

Table 24(a): Effect of contact time in the removal of Pb(II) by AC(R)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	5.0	9.67	7.89	0.71	18.41
10	5.0	9.67	7.64	0.81	20.99
20	5.0	9.67	7.52	0.86	22.23
30	5.0	9.67	7.31	0.94	24.41
60	5.0	9.67	6.82	1.14	29.47
120	5.0	9.67	6.38	1.32	34.02
180	5.0	9.67	6.10	1.43	36.92
300	5.0	9.67	6.03	1.46	37.64
1440	5.0	9.67	5.96	1.48	38.37

Table 24(b): Effect of contact time in the removal of Pb(II) by MCAC(R)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	5.0	9.61	7.69	0.77	19.98
10	5.0	9.61	7.27	0.94	24.35
20	5.0	9.61	7.14	0.99	25.70
30	5.0	9.61	6.45	1.26	32.88
60	5.0	9.61	6.19	1.37	35.59
120	5.0	9.61	4.40	2.08	54.21
180	5.0	9.61	4.16	2.18	56.71
300	5.0	9.61	3.65	2.38	62.02
1440	5.0	9.61	3.62	2.40	62.33

Table 24(c): Effect of contact time in the removal of Pb(II) by ICAC(R)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
10	5.0	9.59	6.5	1.24	32.22
20	5.0	9.59	5.29	1.72	44.84
30	5.0	9.59	5.08	1.80	47.03
60	5.0	9.59	3.47	2.45	63.82
120	5.0	9.59	3.26	2.53	66.01
180	5.0	9.59	2.68	2.76	72.05
300	5.0	9.59	1.12	3.39	88.32
420	5.0	9.59	0.42	3.67	95.62
1440	5.0	9.59	0.64	3.58	93.33

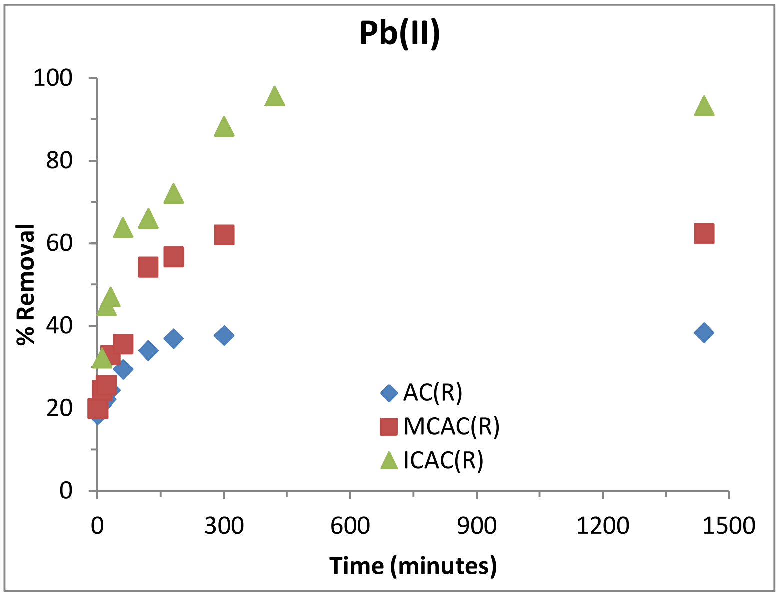

Figure 23(a): Effect of contact time in the removal of Pb(II) by AC(R), MCAC(R) and ICAC(R) at pH 5.0;Initial Pb(II) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

Table 24(d): Effect of contact time in the removal of Pb(II) by AC(N)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	5.0	9.70	7.87	0.73	19.98
10	5.0	9.70	7.74	0.78	21.30
20	5.0	9.70	7.64	0.82	22.39
30	5.0	9.70	7.30	0.96	26.09
60	5.0	9.70	7.16	1.02	27.61
120	5.0	9.70	7.05	1.06	28.80
180	5.0	9.70	6.78	1.17	31.74
300	5.0	9.70	6.62	1.23	33.48
1440	5.0	9.70	6.58	1.25	33.91

Table 24(e): Effect of contact time in the removal of Pb(II) by MCAC(N)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	5.0	9.63	7.84	0.72	18.59
10	5.0	9.63	6.79	1.14	29.49
20	5.0	9.63	6.65	1.19	30.94
30	5.0	9.63	6.53	1.24	32.19
60	5.0	9.63	6.33	1.32	34.27
120	5.0	9.63	5.85	1.51	39.25
180	5.0	9.63	5.37	1.70	44.24
300	5.0	9.63	5.23	1.76	45.69
1440	5.0	9.63	5.18	1.78	46.21

Table 24(f): Effect of contact time in the removal of Pb(II) by ICAC(N)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
10	5.0	6.4	9.75	1.34	34.36
20	5.0	6.18	9.75	1.43	36.62
30	5.0	5.56	9.75	1.68	42.97
60	5.0	4.49	9.75	2.10	53.95
120	5.0	4.17	9.75	2.23	57.23
180	5.0	3.56	9.75	2.48	63.49
300	5.0	2.06	9.75	3.08	78.87
420	5.0	1.54	9.75	3.28	84.21
1440	5.0	0.84	9.75	3.56	91.38

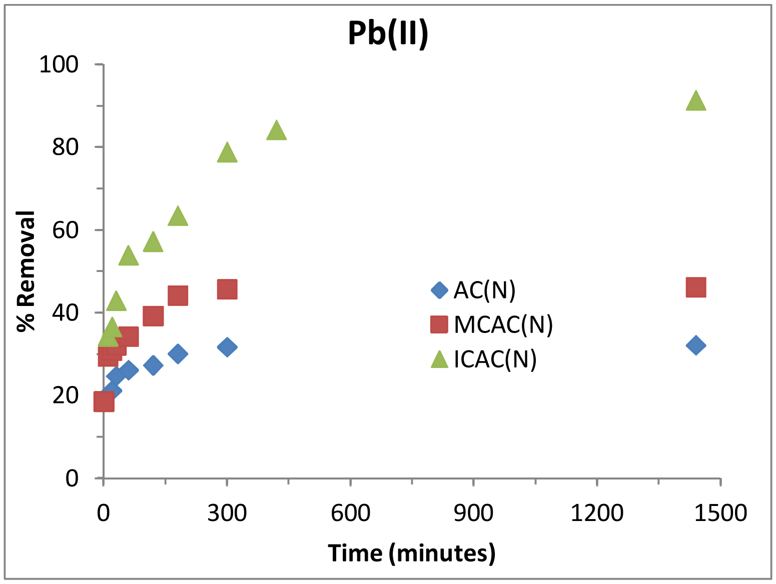

Figure 23(b): Effect of contact time in the removal of Pb(II) by AC(N), MCAC(N) and ICAC(N) at pH 5.0; Initial Pb(II) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

3.3.3.4. Arsenic (III) and Arsenic (V)

Studies were also conducted in the removal of As(III) and As(V) as a function of time using ACs, MCACs and ICACs solids while keeping the initial arsenic concentration ~10.0 mg/L and pH ~4.5 as constant. The time dependence sorption data obtained for As(III) and As(V) by these solids are returned in Tables 25(a-d) and Table 26(a-d), respectively for As(III) and As(V). Moreover, the percent sorption as a function of time is presented graphically in Figures 24(a, b) and Figures 25(a,b), respectively for As(III) and As(V). The result showed that the uptake of these ions by the utilized solids was very fast during initial period of contact. Moreover, maximum amount of arsenic was sorbed during initial period of contact i.e., Ca 180 minutes of contact. It was explicable with the fact that the surface coverage was low at the initial stage of contact and sorptive ions occupy the active surface site rapidly in a random manner, as a result, the percent adsorption increased rapidly during initial period. At latter stages, the surface coverage was enhanced causing to slow down of the percent uptake of arsenic by these solids (Mishra and Tiwari, 2002).

Table 25(a): Effect of contact time in the removal of As(III) by AC(R)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	4.5	9.95	9.66	0.12	2.91
10	4.5	9.95	9.54	0.16	4.12
20	4.5	9.95	9.15	0.32	8.04
30	4.5	9.95	9.04	0.36	9.15
60	4.5	9.95	8.73	0.49	12.26
120	4.5	9.95	8.00	0.78	19.60
180	4.5	9.95	7.16	1.12	28.04
1440	4.5	9.95	6.76	1.28	32.06

Table 25(b): Effect of contact time in the removal of As(III) by MCAC(R)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	4.5	9.95	9.54	0.16	4.12
10	4.5	9.95	9.25	0.28	7.04
20	4.5	9.95	8.89	0.42	10.65
30	4.5	9.95	8.65	0.52	13.05
60	4.5	9.95	8.51	0.58	14.47
120	4.5	9.95	7.87	0.83	20.90
180	4.5	9.95	6.99	1.18	29.75
1440	4.5	9.95	6.08	1.55	38.89

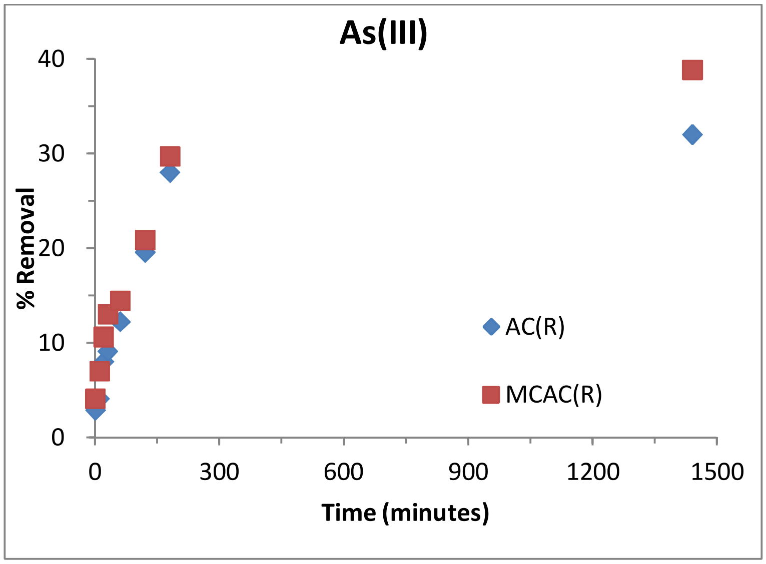

Figure 24(a): Effect of contact time in the removal of As(III) by AC(R) and MCAC(R) at pH: 4.5; Initial As(III) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

Table 25(c): Effect of contact time in the removal of As(III) by AC(N)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	4.5	9.95	9.79	0.06	1.61
10	4.5	9.95	9.72	0.09	2.31
20	4.5	9.95	9.66	0.12	2.91
30	4.5	9.95	9.54	0.16	4.12
60	4.5	9.95	9.21	0.30	7.44
120	4.5	9.95	9.05	0.36	9.05
180	4.5	9.95	8.27	0.67	16.88
1440	4.5	9.95	7.85	0.84	21.11

Table 25(d):: Effect of contact time in the removal of As(III) by MCAC(N)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	4.5	9.95	9.78	0.07	1.71
10	4.5	9.95	9.65	0.12	3.02
20	4.5	9.95	9.58	0.15	3.72
30	4.5	9.95	9.35	0.24	6.03
60	4.5	9.95	9.05	0.36	9.05
120	4.5	9.95	8.56	0.56	13.97
180	4.5	9.95	8.01	0.78	19.50
1440	4.5	9.95	7.14	1.12	28.24

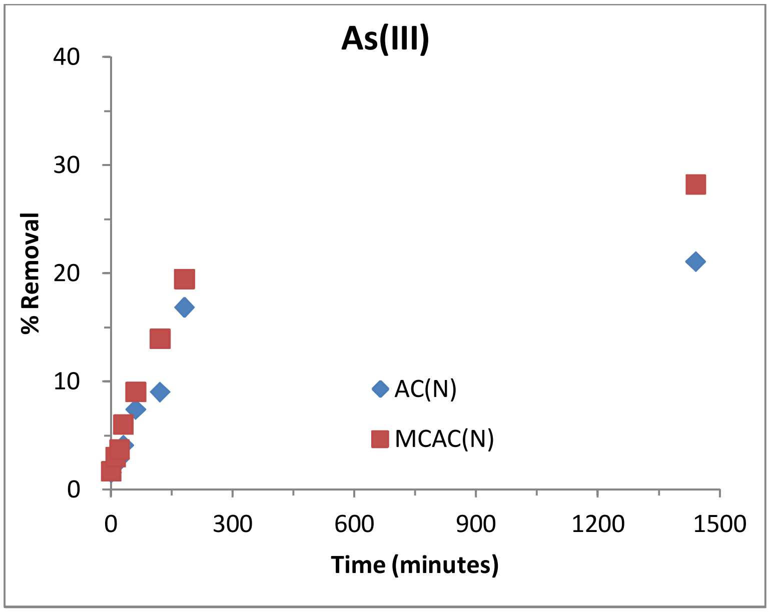

Figure 24(b): Effect of contact time in the removal of As(III) by AC(N) and MCAC(N) at pH 4.5; Initial As(III) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

Table 26(a): Effect of contact time in the removal of As(V) by AC(R)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	4.5	9.45	8.36	0.44	11.53
10	4.5	9.45	8.22	0.49	13.02
20	4.5	9.45	7.80	0.66	17.46
30	4.5	9.45	7.72	0.69	18.31
60	4.5	9.45	7.70	0.70	18.52
120	4.5	9.45	7.66	0.72	18.94
180	4.5	9.45	7.40	0.82	21.69
1440	4.5	9.45	6.46	1.19	31.64

Table 26(b): Effect of contact time in the removal of As(V) by MCAC(R)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	4.5	9.45	8.89	0.22	5.93
10	4.5	9.45	8.76	0.34	7.30
20	4.5	9.45	8.68	0.28	8.15
30	4.5	9.45	8.6	0.31	8.99
60	4.5	9.45	8.09	0.54	14.39
120	4.5	9.45	7.92	0.61	16.19
180	4.5	9.45	7.33	0.85	22.43
1440	4.5	9.45	5.62	1.53	40.53

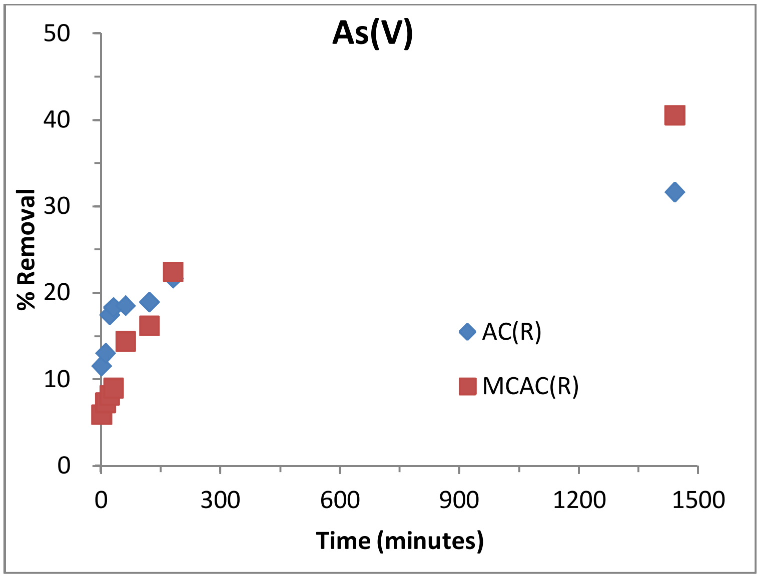

Figure 25(a): Effect of contact time in the removal of As(V) by AC(R) and MCAC(R) at pH 5.0; Initial As(V) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

Table 26(c): Effect of contact time in the removal of As(V) by AC(N)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	4.5	9.45	9.36	0.04	0.95
10	4.5	9.45	8.92	0.21	5.61
20	4.5	9.45	8.82	0.25	6.67
30	4.5	9.45	8.74	0.28	7.51
60	4.5	9.45	8.44	0.40	10.69
120	4.5	9.45	8.22	0.49	13.02
180	4.5	9.45	7.84	0.64	17.04
1440	4.5	9.45	6.86	1.04	27.41

Table 26(d): Effect of contact time in the removal of As(V) by MCAC(N)

Time (minutes)	pH	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0	4.5	9.45	9.38	0.03	0.74
10	4.5	9.45	9.22	0.09	2.43
20	4.5	9.45	9.07	0.15	4.02
30	4.5	9.45	8.81	0.26	6.77
60	4.5	9.45	7.79	0.66	17.57
120	4.5	9.45	7.26	0.87	23.17
180	4.5	9.45	6.57	1.15	30.48
1440	4.5	9.45	5.89	1.42	37.67

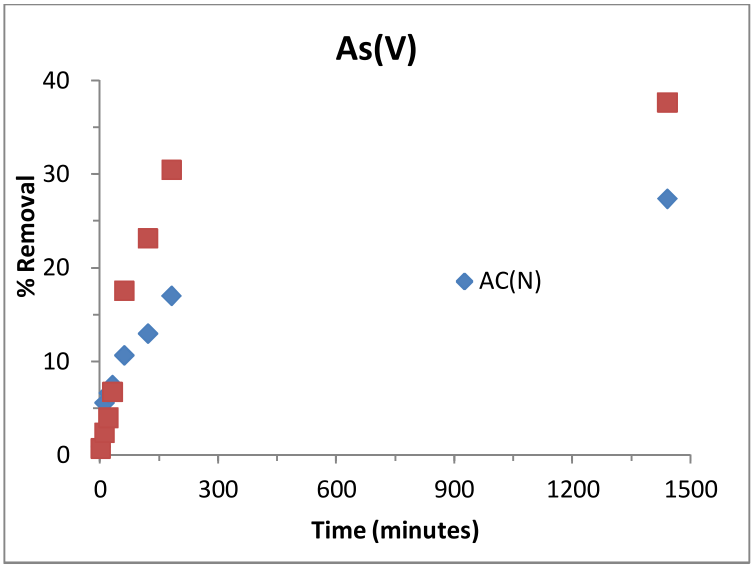

Figure 25(b): Effect of contact time in the removal of As(V) by AC(N) and MCAC(N) at pH 4.5; Initial As(V) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

3.3.4. Kinetic modelling of the adsorption

The data obtained for the effects of contact time were further utilized to study the adsorption kinetics hence, to estimate the rate of sorption. These results could enable to understand the sorption mechanism involved at solution-solid interfaces (Wu *et al*., 2001). The two known kinetic models, *viz.*, pseudo-first-order kinetic model and pseudo-second-order kinetic model in its linear form (equation 4 and 5) were applied for the kinetic studies.

3.3.4.1. Pseudo-first order kinetic model

The pseudo first order kinetic model was employed to its linear form (equation 4).The pseudo-first-order constant k_1 was obtained from the slope of the plots drawn between $log\ (q_e - q_t)$ versus t in (*cf* Figure 26(a-j)). All these figures show that the kinetic data is fitted not extremely well since the R^2 values are obtained a little less. However, the sorption capacities (q_o) of these materials i.e., ACs, MCACs and ICACs, the pseudo-first-order rate constants of sorption process (k_1) along with the regression coefficients (R^2) were estimated and returned in Tables 27(a-e). The sorption capacities calculated from the kinetic data. The higher sorption capacities obtained for these solids towards the studies heavy metal ions indicated the potential affinity of the materials towards these ions *viz*., Cd(II), Cu(II), Pb(II) and As(III) and As(V). Comparatively, the ICACs showed the higher sorption capacity comparing to the ACs and MCACs materials. Moreover, the removal capacity obtained for Pb(II) is significantly high comparing to other sorbing species. Several factors such as ionic charge, ionic radii and electrode potential, perhaps, accounted for varied metal removal capacity assessed for different solids (Sekhar *et al.,*2004). The similar results were also reported previously, different solid sorbent materials possessed, relatively, higher Langmuir sorption capacity for Pb(II) comparing to other heavy metals toxic ions as studied under the same experimental conditions (Ofomaja *et al.,* 2010; Tiwari *et al.,* 2007; Quek *et al.,* 1998). Further, since the data is not fitted reasonably well to the pseudo-first-order kinetic model, therefore the modelling for the pseudo-second-order model is studied.

Table 27(a): Values of q_e, k_1 and R^2 obtained for the sorption of Cd(II) onto the solids using pseudo-first order kinetic model

Materials	Cd(II)		
	k_1 (min^{-1})	q_e(mg/g)	R^2
AC(R)	8.98x 10^{-3}	0.387	0.943
MCAC(R)	10.59 x 10^{-3}	0.547	0.574
ICAC(R)	33.39x 10^{-3}	2.291	0.979
AC(N)	7.83x 10^{-3}	0.251	0.943
MCAC(N)	11.51x 10^{-3}	1.246	0.937
ICAC(N)	14.74x 10^{-3}	1.592	0.877

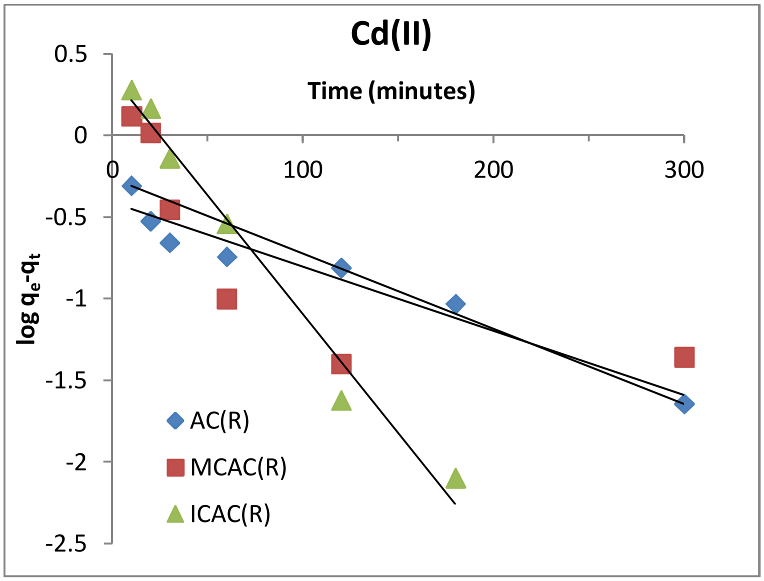

Figure 26(a): Plots of *log* ($q_e - q_t$) versus *t* for the sorption of Cd(II) by AC(R), MCAC(R) and ICAC(R)

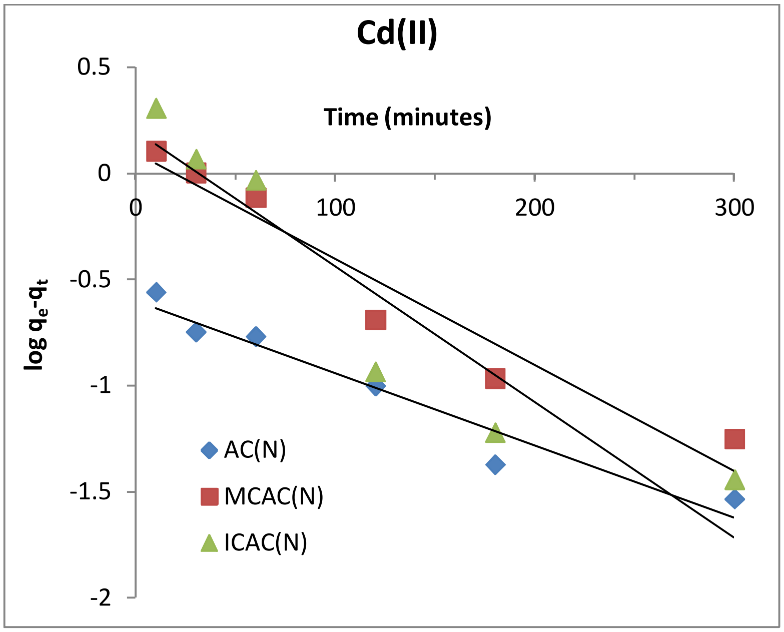

Figure 26(b): Plots of *log* $(q_e - q_t)$ versus t for the sorption of Cd(II) by AC(N), MCAC(N) and ICAC(N)

Table 27(b): Values of q_e, k_1 and R^2 obtained for the sorption of Cu(II) onto the solids using pseudo-first order kinetic model

Materials	Cu(II)		
	k_1 (min^{-1})	q_e(mg/g)	R^2
AC(R)	1.0 x10^{-3}	1.146	0.953
MCAC(R)	1.5 x10^{-3}	1.073	0.976
ICAC(R)	7.3 x10^{-3}	1.189	0.993
AC(N)	1.0 x10^{-3}	1.265	0.993
MCAC(N)	1.0 x10^{-3}	1.169	0.924
ICAC(N)	4.8 x10^{-3}	1.588	0.994

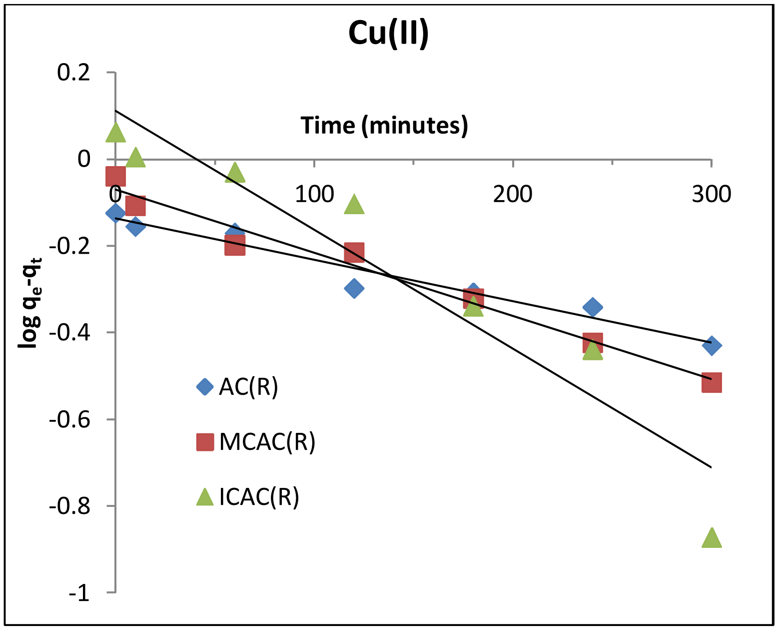

Figure 26(c): Plots of *log* (q_e-q_t) versus *t* for the sorption of Cu(II) by AC(R), MCAC(R) and ICAC(R)

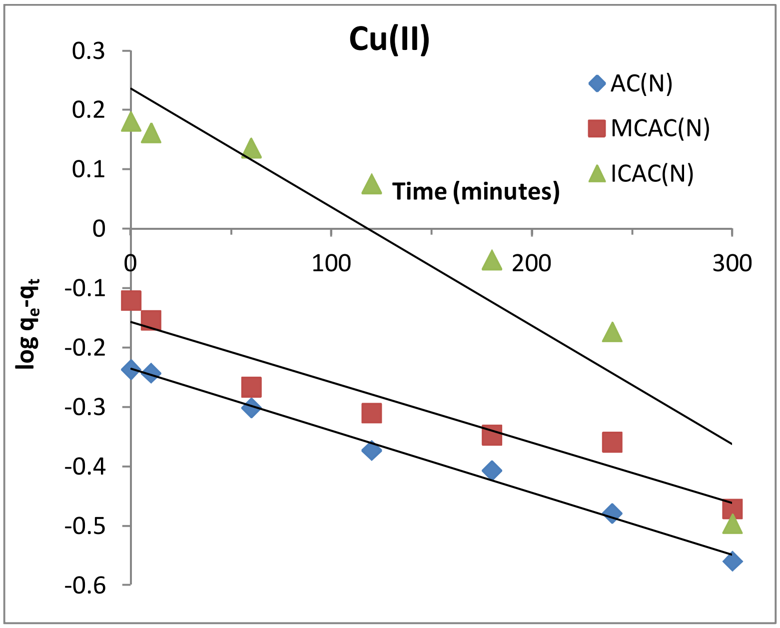

Figure 26(d): Plots of *log* (q_e-q_t) versus *t* for the sorption of Cu(II) by AC(N), MCAC(N) and ICAC(N)

Table 27(c): Values of q_e, k_1 and R^2 obtained for the sorption of Pb(II) onto the solids using pseudo-first order kinetic model

	Pb(II)		
Materials	k_1 (min^{-1})	q_e(mg/g)	R^2
AC(R)	5.1 x10^{-3}	1.150	0.973
MCAC(R)	6.8 x10^{-3}	1.350	0.965
ICAC(R)	6.6 x10^{-3}	2.321	0.949
AC(N)	4.8 x10^{-3}	1.341	0.976
MCAC(N)	5.4 x10^{-3}	1.060	0.979
ICAC(N)	5.1 x10^{-3}	2.281	0.986

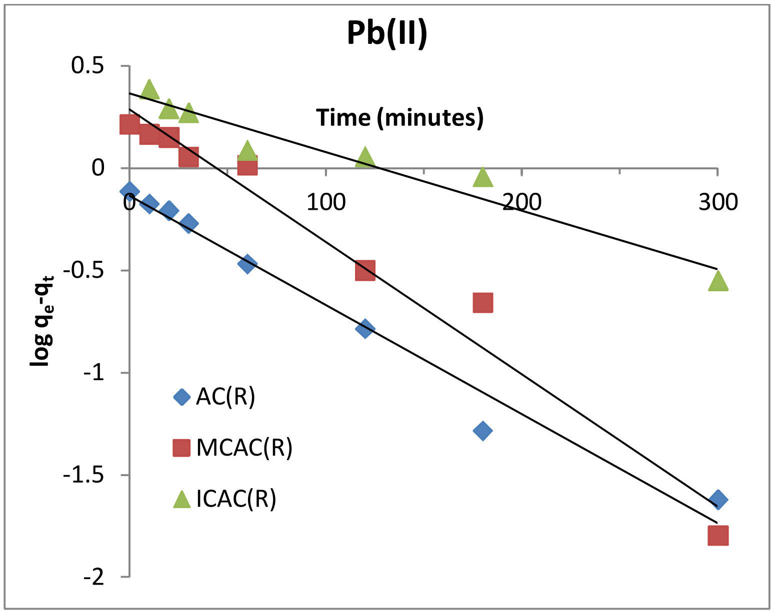

Figure 26(e): Plots of *log* (q_e-q_t) versus *t* for the sorption of Pb(II) by AC(R), MCAC(R) and ICAC(R)

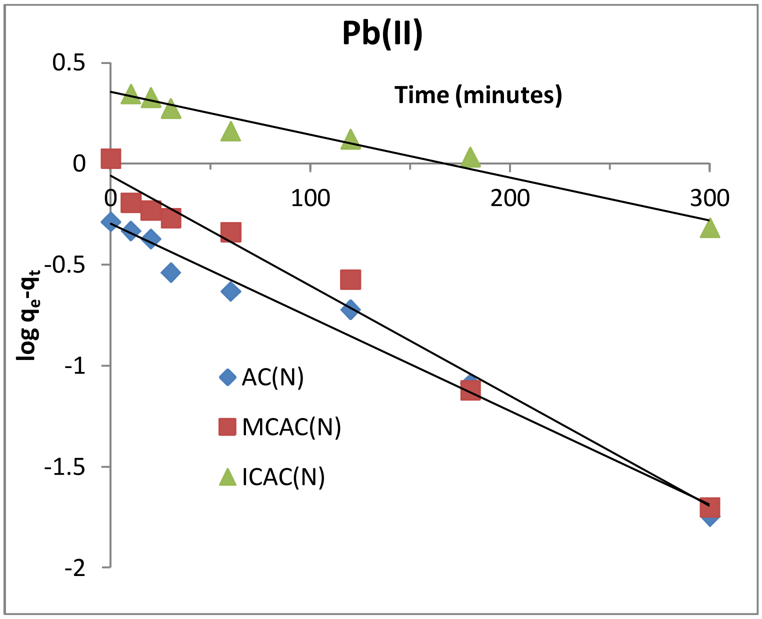

Figure 26(f): Plots of *log* $(q_e - q_t)$ versus t for the sorption of Pb(II) by AC(N), MCAC(N) and ICAC(N)

Table 27(d): Values of q_e, k_1 and R^2 obtained for the sorption of As(III) onto the solids using pseudo-first order kinetic model

	As(III)		
Materials	k_1 (min^{-1})	q_e(mg/g)	R^2
AC(R)	4.4x 10^{-3}	1.106	0.942
MCAC(R)	2.9x 10^{-3}	1.142	0.954
AC(N)	3.3 x 10^{-3}	1.075	0.891
MCAC(N)	2.6x 10^{-3}	1.033	0.989

Table 27(e): Values of q_e, k_1 and R^2 obtained for the sorption of As(V) onto the solids using pseudo-first order kinetic model

	As(V)		
Materials	k_1 (min^{-1})	q_e(mg/g)	R^2
AC(R)	1.3x 10^{-3}	1.208	0.733
MCAC(R)	1.5x 10^{-3}	1.120	0.952
AC(N)	2.0x 10^{-3}	1.052	0.957
MCAC(N)	3.9x 10^{-3}	1.178	0.985

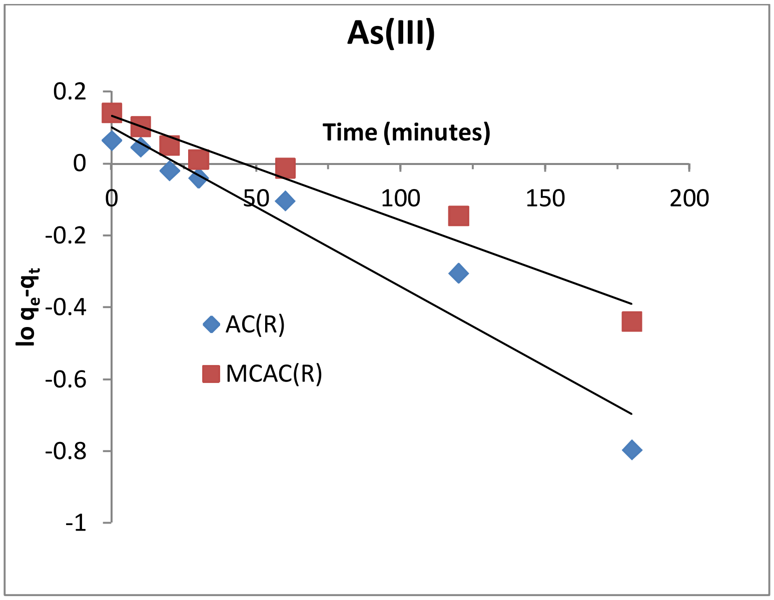

Figure 26(g): Plots of *log* (q_e-q_t) versus t for the sorption of As(III) by AC(R) and MCAC(R)

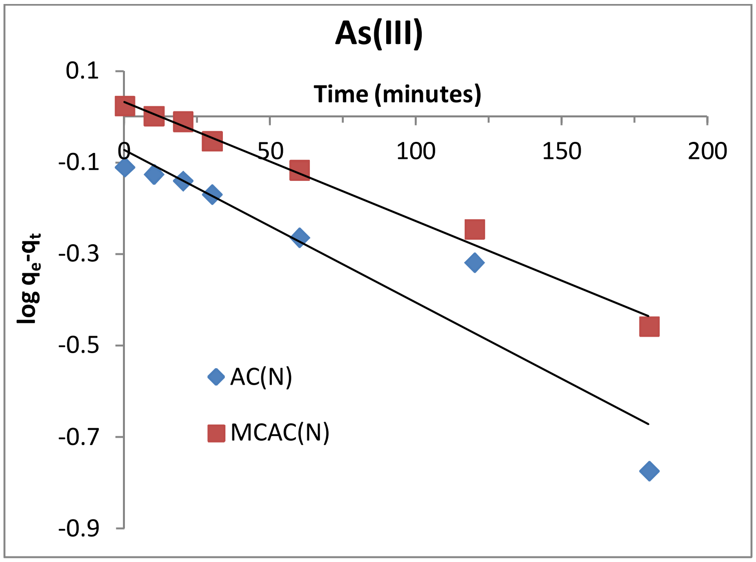

Figure 26(h): Plot of *log* (q_e-q_t) versus t for the sorption ofAs(III) by AC(N)and MCAC(N)

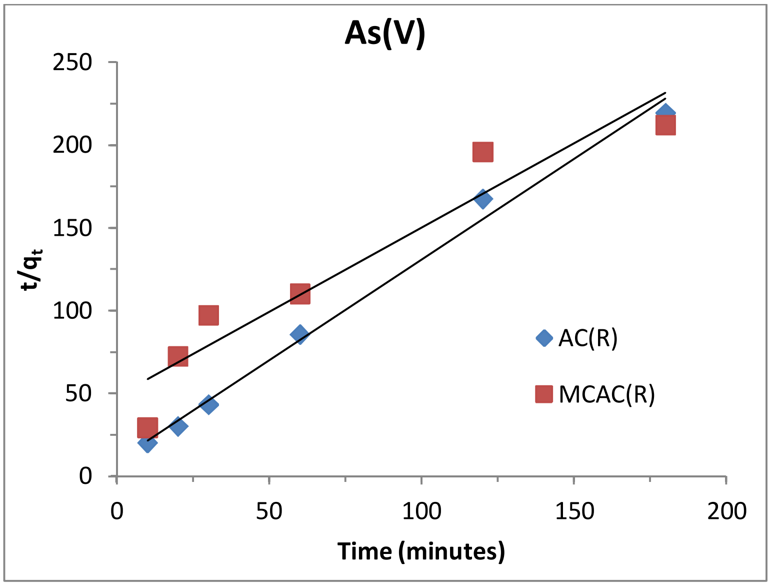

Figure 26(i): Plots of *log* $(q_e - q_t)$ versus *t* for the sorption of As(V) by AC(R) and MCAC(R)

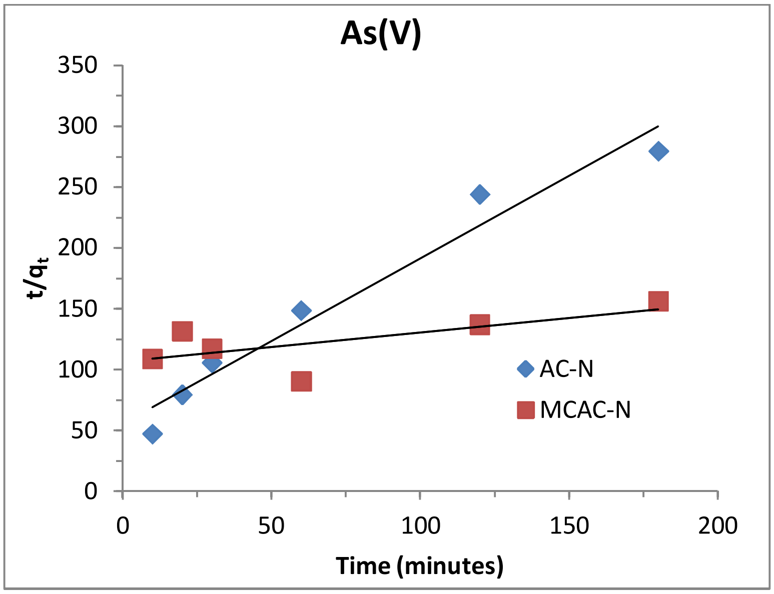

Figure 26(j): Plots of *log* $(q_e - q_t)$ versus *t* for the sorption of As(V) by AC(R) and MCAC(R)

3.3.4.2. Pseudo-second-order kinetic model

Similarly, the pseudo-second order kinetic equation (equation 5) was employed to its linear form as to assess the suitability of the model in the sorption kinetics; studied for these systems. The plots between $\frac{t}{q_t}$ against t in were plotted and presented graphically in Figures 27(a-j). Further, the pseudo-second-order rate constant k_2, the sorption capacity of the solids employed q_e along with the R^2 values were estimated for all the studied metal ions and returned in Tables 28(a-e). It was observed that reasonably a good fitting of kinetic data obtained for pseudo-second-order rate kinetics. Further, the sorption capacity of these solids as obtained by the pseudo-second order model showed that these solids possessed very high removal capacity for all these sorbing ions. Moreover, the results further supported the potentiality of these solids towards the removal of Cd(II), Cu(II), Pb(II) and As(III) and As(V) from the aqueous solutions. Among these ions, Pb(II) was removed at higher extent comparing to other pollutant ions which is in a line to the previous observations obtained by adsorption isotherm studies. Further, the applicability of pseudo-second-order kinetic model indicated again that ‘chemisorption’ could be a predominant uptake process onto the solid surfaces which involved with valence forces through sharing or exchange of electrons between the sorbent surface and the sorbate ions (Ho and McKay, 2000). Similarly, a pseudo-second order rate kinetics was discussed in the sorption of divalent metal ions *viz.*, Cu(II), Pb(II) and Ni(II) on to *sphagnum* moss peat at various initial metal ion concentrations. The values of pseudo second order rate constants were decreased with increasing the concentration of metal solutions. The values of k_2 was found in between 8.97 $\times 10^{-3}$ to 1.67 $\times 10^{-1}$ g/mg/min (Ho et al., 2000). Kinetic study in the uptake of Cu(II) and Pb(II) from aqueous solutions using manganese oxide coated zeolite in batch mode operations showed that the values of k_2 was decreased from 1.83 to 0.561 g/mmol/min for

Cu(II) and from 0.325 to 0.123 g/mmol/min for Pb(II) for increasing the initial concentration from 0.103 to 0.598 mmol/L for Cu(II) and from 0.289 to 0.732 mmol/L for Pb(II), respectively. These studies enabled that the predominant sorption process was chemisorptive in nature (Zou *et al*., 2006).

Table 28(a): Values of q_e, k_2 and R^2 obtained for the sorption of Cd(II) onto the solids using pseudo-second-order kinetic model

Materials	Cd(II)		
	k_2 (g/mg/min)	q_e (mg/g)	R^2
AC(R)	8.83×10^{-2}	1.093	0.997
MCAC(R)	3.71×10^{-2}	2.102	0.995
ICAC(R)	1.27×10^{-2}	3.089	0.989
AC(N)	12.88×10^{-2}	0.925	0.998
MCAC(N)	1.32×10^{-2}	2.016	0.990
ICAC(N)	1.13×10^{-2}	3.043	0.994

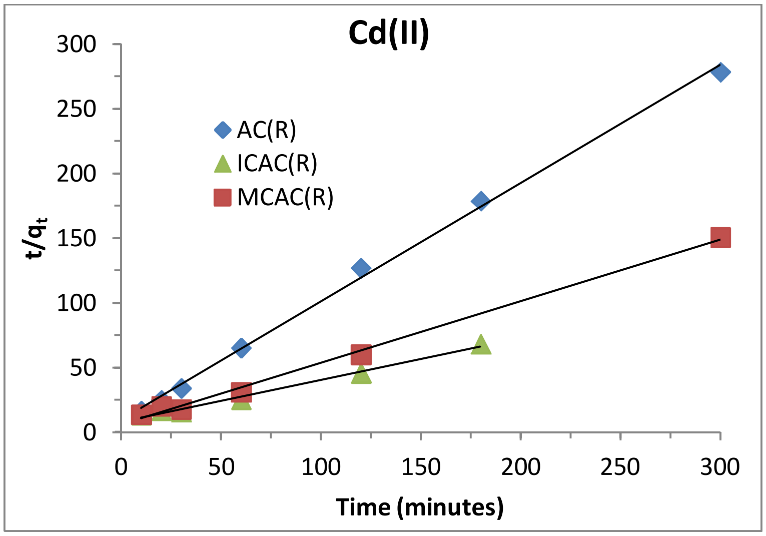

Figure 27(a): Plots of $\frac{t}{q_t}$ against *t* for the sorption of Cd(II) by AC(R), MCAC(R) and ICAC(R)

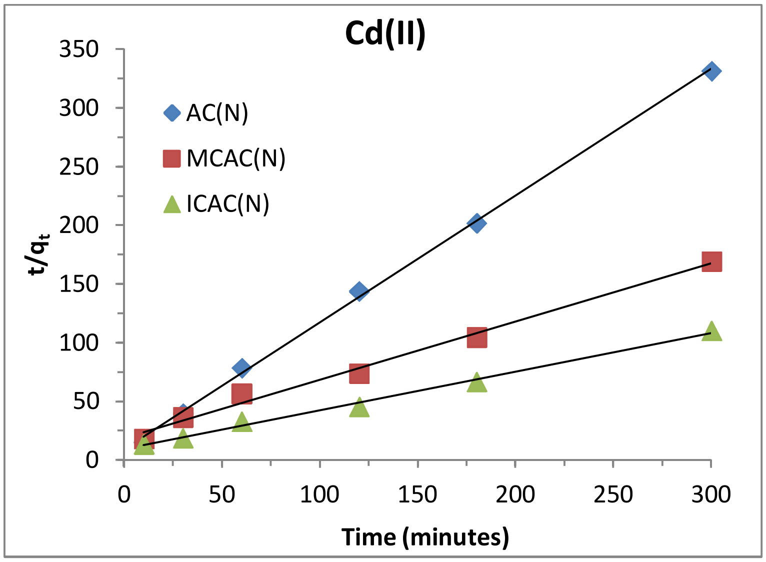

Figure 27(b): Plots of $\frac{t}{q_t}$ against t for the sorption of Cd(II) by using AC(N), MCAC(N) and ICAC(N)

Table 28(b): Values of q_e, k_2 and R^2 obtained for the sorption of Cu(II) onto the solids using pseudo-second-order kinetic model

Materials	Cu(II)		
	k_2 (g/mg/min)	q_e (mg/g)	R^2
AC(R)	44.0×10^{-3}	0.481	0.982
MCAC(R)	42.1×10^{-3}	0.807	0.968
ICAC(R)	12.2×10^{-3}	1.770	0.990
AC(N)	60.7×10^{-3}	0.427	0.934
MCAC(N)	82.0×10^{-3}	0.532	0.947
ICAC(N)	4.75×10^{-3}	1.926	0.971

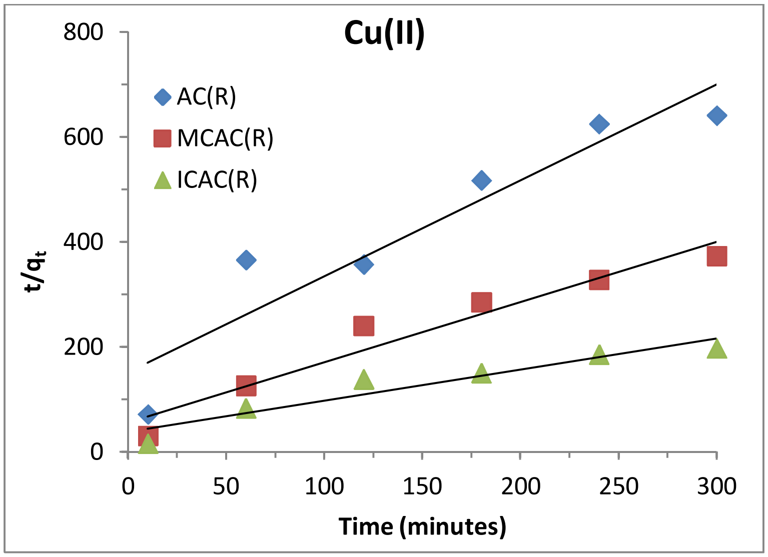

Figure 27(c): Plots of $\frac{t}{q_t}$ against t for the sorption of Cu(II) by AC(R), MCAC(R) and ICAC(R)

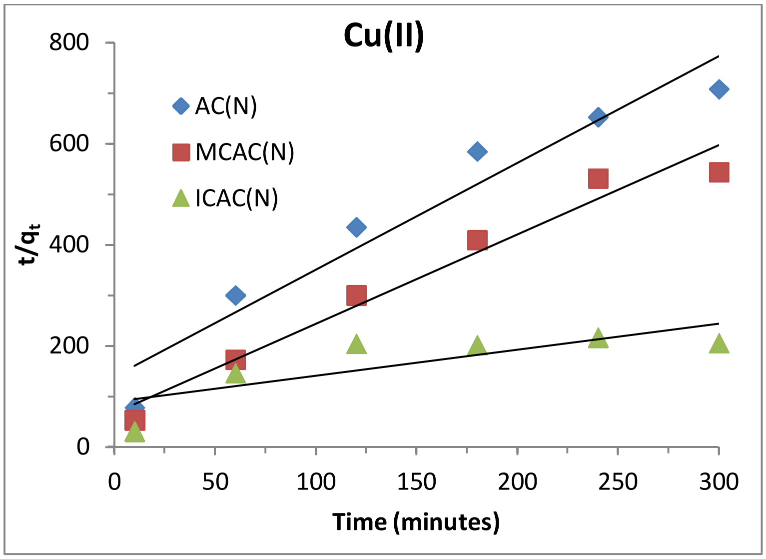

Figure 27(d): Plots of $\frac{t}{q_t}$ against t for the sorption of Cu(II) by AC(N), MCAC(N) and ICAC(N)

Table 28(c): Values of q_e, k_2 and R^2 obtained for the sorption of Pb(II) onto the solids using pseudo-second-order kinetic model

Materials	Pb(II)		
	k_2 (g/mg/min)	q_e (mg/g)	R^2
AC(R)	55.3×10^{-3}	1.502	0.996
MCAC(R)	16.0×10^{-3}	2.518	0.981
ICAC(R)	10.0×10^{-3}	3.507	0.983
AC(N)	89.4×10^{-3}	1.241	0.996
MCAC(N)	51.2×10^{-3}	1.791	0.994
ICAC(N)	7.67×10^{-3}	3.439	0.983

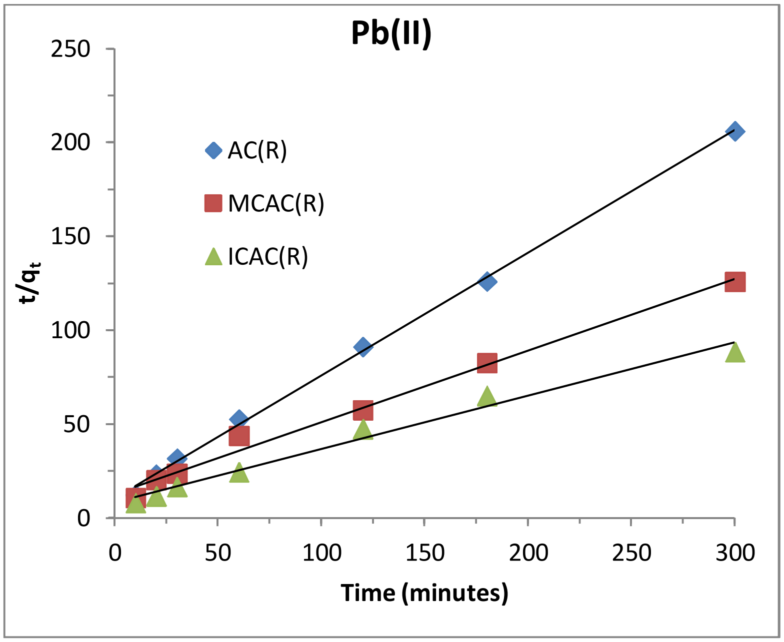

Figure 27(e): Plots of $\frac{t}{q_t}$ against *t* for the sorption of Pb(II) by AC(R), MCAC(R) and ICAC(R)

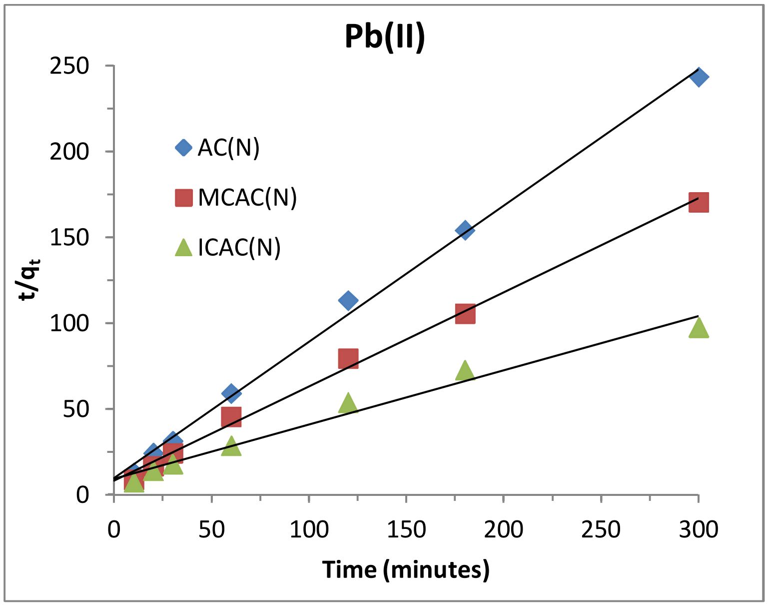

Figure 27(f): Plots of $\frac{t}{q_t}$ against *t* for the sorption of Pb(II) by AC(N), MCAC(N) and ICAC(N)

Table 28(d): Values of q_e, k_2 and R^2 obtained for the sorption of As(III) onto the solids using pseudo-second-order kinetic model

Materials	As(III)		
	k_2 (g/mg/min)	q_e (mg/g)	R^2
AC(R)	6.29 x10^{-3}	1.585	0.882
MCAC(R)	20.2 x10^{-3}	0.973	0.934
AC(N)	6.49 x10^{-3}	1.035	0.674
MCAC(N)	7.45 x10^{-3}	0.913	0.860

Table 28(e): Values of q_e, k_2 and R^2 obtained for the sorption of As(V) onto the solids using pseudo-second-order kinetic model

Materials	As(V)		
	k_2 (g/mg/min)	q_e (mg/g)	R^2
AC(R)	0.332	0.736	0.992
MCAC(R)	0.213	0.984	0.912
AC(N)	0.155	0.823	0.959

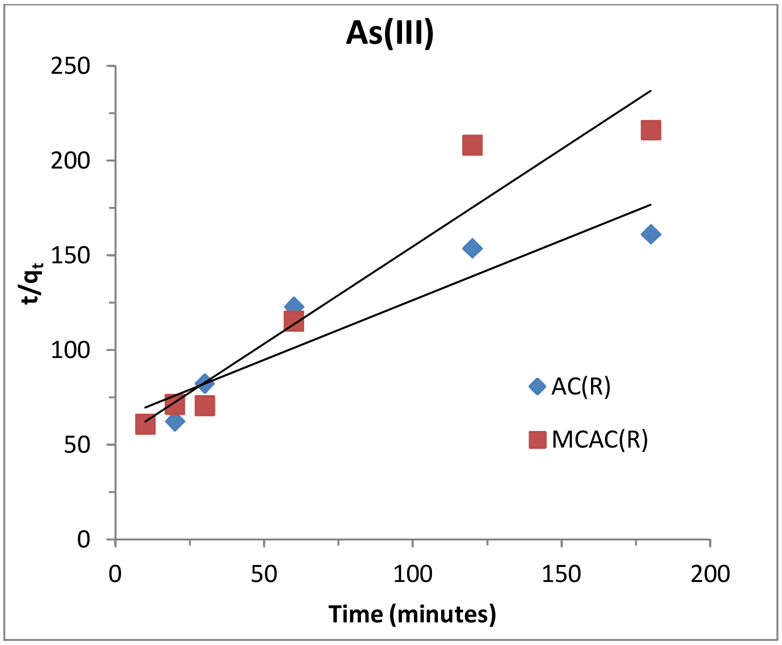

Figure 27(g): Plots of $\frac{t}{q_t}$ against t for the sorption of As(III) by AC(R) and MCAC(R)

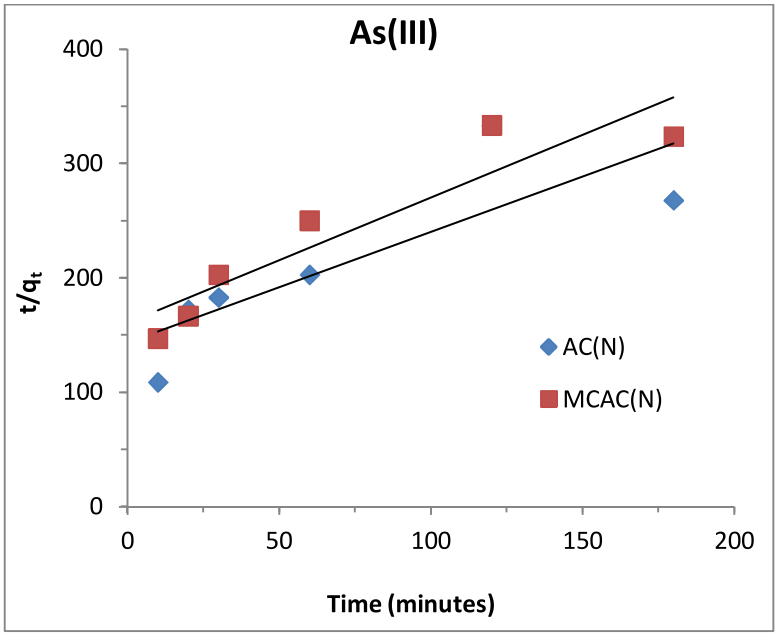

Figure 27(h): Plots of $\frac{t}{q_t}$ against t for the sorption of As(III) by AC(N) and MCAC(N)

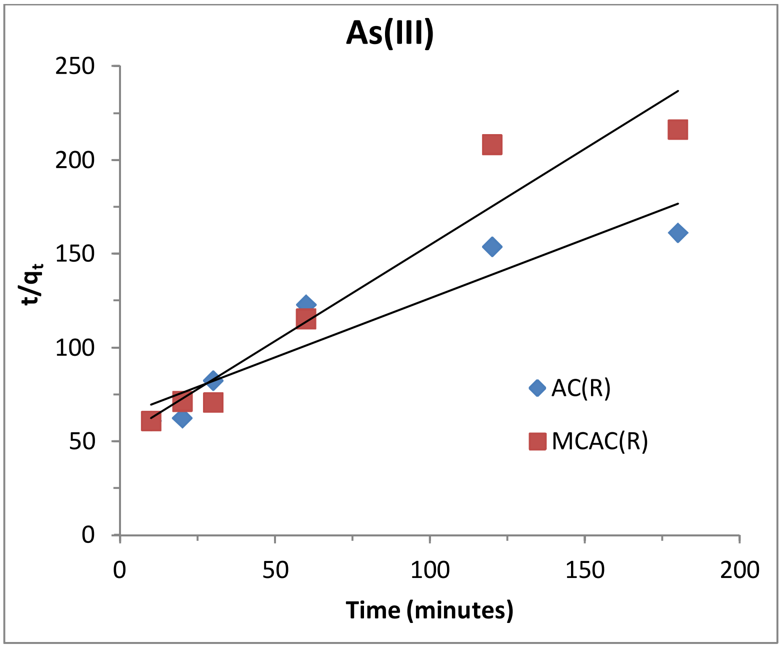

Figure 27(i): Plots of $\frac{t}{q_t}$ against t for the sorption of As(III) by AC(R) and MCAC(R)

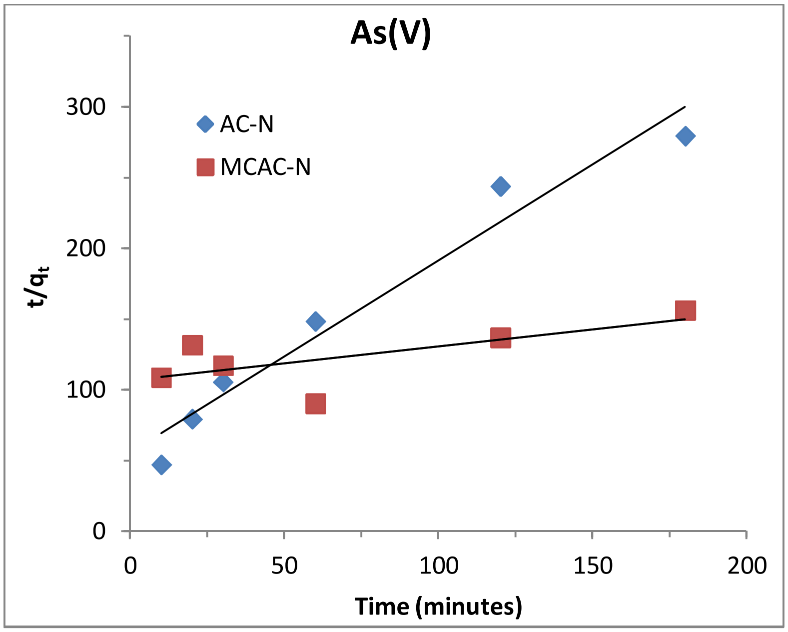

Figure 27(j): Plots of $\frac{t}{q_t}$ against t for the sorption of As(III) by AC(N) and MCAC(N)

3.3.5. Effect of background electrolytes concentration

3.3.5.1. Cadmium (II)

The background electrolyte concentration is an important parameter revealing the nature of binding of the sorptive ions onto the solid surface. It demonstrates that the specific adsorption is not significantly affected with the change in background electrolyte concentrations whereas the non-specific adsorption is greatly affected with the change in background electrolyte concentration (Lee *et al.,* 2012). Therefore, keeping in view, the background electrolyte concentration dependence adsorption data was collected by increasing the $NaNO_3$ concentrations from 0.001to 1.0 mol/L as background electrolytes. The initial Cd(II) concentration 10.0 mg/L, pH 4.5 and temperature 25±1 ^{0}C were kept constant. The results obtained were returned with percent removal versus background electrolyte concentration in Figure 28 (a-b). It was observed that 1000 times increase in the background electrolyte concentration decreased the percent removal of Cd(II) only by 6.34%, 4.93%, and 10.07%,respectively to AC(R), MCAC(R)and ICAC(R) and 7.84%, 3.52%, 6.71% for the solids AC(N), MCAC(N) and ICAC(N), respectively. The insignificant decrease in percent removal of Cd(II) even by 1000 times increase in background electrolyte concentrations; strongly suggested the Cd(II) ions were sorbed specifically onto the solid surface and forming predominantly an 'inner sphere complexes' (Payne and Abdel-Fattah, 2005; Schmidt *et al.,* 2008). The similar observations were reported previously where the copper ion was forming an 'inner sphere complex' with sawdust, the study was supported reasonably well with the theoretical modelling as well (Zhao *et al.,* 2012b).

Table 29(a): Effect of background electrolyte concentrations in the removal of Cd(II) by AC(R)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	9.94	6.78	1.26	31.79
0.01	9.94	6.85	1.24	31.09
0.1	9.94	7.25	1.08	27.06
1.0	9.94	7.41	1.01	25.45

Table 29(b): Effect of background electrolyte concentrations in the removal of Cd(II) by MCAC(R)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	9.94	6.56	1.35	34.00
0.01	9.94	6.68	1.30	32.80
0.1	9.94	6.92	1.21	30.38
1.0	9.94	7.05	1.16	29.07

Table 29(c): Effect of background electrolyte concentrations in the removal of Cd(II) by ICAC(R)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	11.32	5.87	2.18	48.14
0.01	11.32	6.01	2.12	46.91
0.1	11.32	6.86	1.78	39.40
1.0	11.32	7.01	1.72	38.07

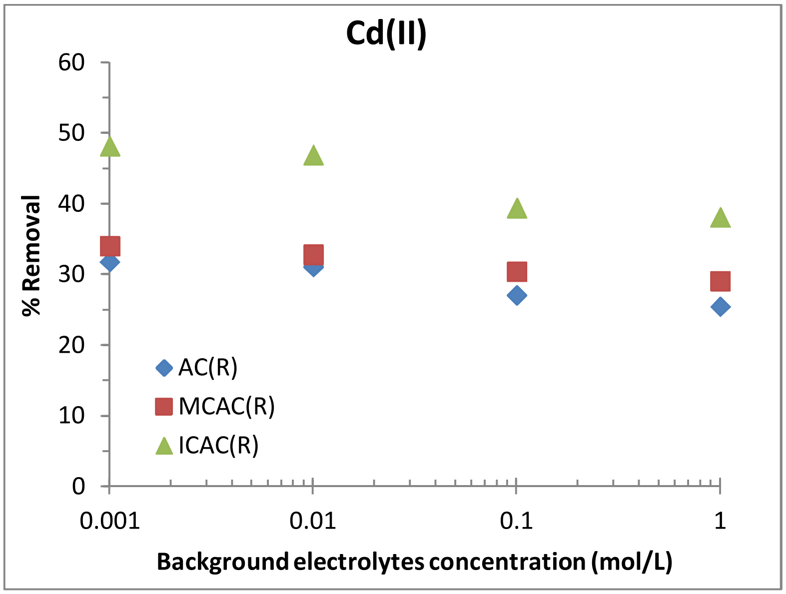

Figure 28(a): Effect of background electrolyte concentrations in the removal of Cd(II) by AC(R), MACAC(R)and ICAC(R) at pH 4.5; initial Cd(II)concentration: ~10 mg/L; Temperature: 25±1 ^{0}C

Table 29(d): Effect of background electrolyte concentrations in the removal of Cd(II) by AC(N)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	9.94	7.04	1.16	29.18
0.01	9.94	7.18	1.10	27.77
0.1	9.94	7.63	0.92	23.24
1.0	9.94	7.82	0.85	21.33

Table 29(e): Effect of background electrolyte concentrations in the removal of Cd(II) by MCAC(N)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	9.94	6.75	1.28	32.09
0.01	9.94	6.79	1.26	31.69
0.1	9.94	7.06	1.15	28.97
1.0	9.94	7.10	1.14	28.57

Table 29(f): Effect of background electrolyte concentrations in the removal of Cd(II) by ICAC(N)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	11.32	6.20	2.05	45.23
0.01	11.32	6.84	1.79	39.58
0.1	11.32	6.60	1.89	41.70
1.0	11.32	6.96	1.74	38.52

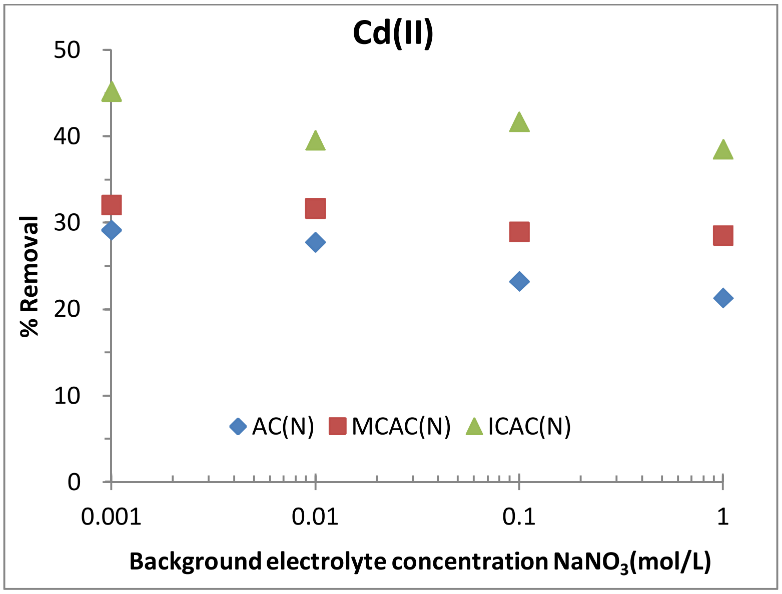

Figure 28(b): Effect of background electrolyte concentrations in the removal of Cd(II) by AC(N), MACAC(N)and ICAC(N)at pH 4.5; initial Cd(II) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

3.3.5.2. Copper(II)

The removal of Cu(II) was studied in the presence of various concentrations of strong electrolytes by employing the ACs, MCACs and ICACs solids. The background electrolyte concentration was increased from 0.001 mol/L to 1.0 mol/L keeping the Cu(II) concentration ~10 mg/L and pH 4.0 as constant. The results obtained were given in the Table 30(a-f) and Figure 29(a, b). The closure scrutiny of the data showed that increasing the concentration of $NaNO_3$ by 1000 times caused to decrease the adsorption of Cu(II) maximum by 6.13 %, 4.91%, 12.51%, respectively for AC(R), MCAC(R) and ICAC(R) and 5.42%, 6.34%, 13.96 % for AC-N, MCAC-N, and ICAC-N, respectively. Further, these results suggesting the formation of an 'inner sphere complexes' on the solid surfaces in the removal processes of Cu(II) from the aqueous solution. In other words Cu(II) is bound onto the surface with strong chemical forces (Tiwari *et al.,* 2007) . The other studies also reported that the removal percentage of Cu(II),by saw dust solid, was decreased insignificantly i.e., from 71.20 % and 49.70 % with increasing the concentration of NaCl concentrations from 0.001-0.1 mol/L, respectively using saw dust (Larous *et al.,* 2005). The Cu(II) was specifically adsorbed by iron oxide nano-particles immobilized sand whereas other metals such as Pb(II) and Cd(II) were less specifically adsorbed by the same materials as reported elsewhere (Lee *et al.,* 2012).

Table 30(a): Effect of background electrolyte concentrations in the removal of Cu(II) by AC(R)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	9.78	6.34	1.38	35.17
0.01	9.78	6.52	1.30	33.33
0.1	9.78	6.85	1.17	29.96
1.0	9.78	6.94	1.14	29.04

Table 30(b): Effect of background electrolyte concentrations in the removal of Cu(II) by MCAC(R)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	9.78	4.45	2.13	54.50
0.01	9.78	4.62	2.06	52.76
0.1	9.78	4.86	1.97	50.31
1.0	9.78	4.93	1.94	49.59

Table 30(c): Effect of background electrolyte concentrations in the removal of Cu(II) by ICAC(R)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	9.84	2.51	2.93	74.49
0.01	9.84	2.86	2.79	70.84
0.1	9.84	3.35	2.59	65.90
1.0	9.84	3.74	2.44	61.98

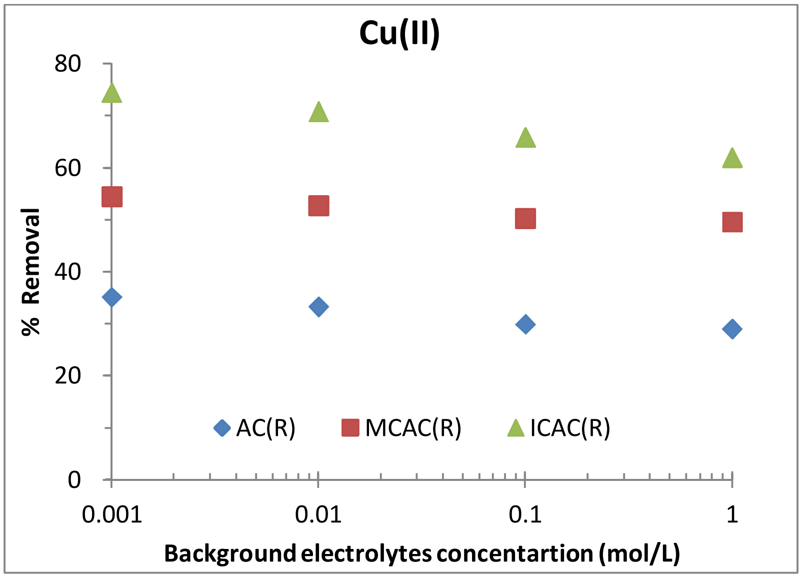

Figure 29(a): Effect of background electrolyte concentrations in the removal of Cu(II) by AC(R), MACAC(R)and ICAC(R)at pH 4.0; initial Cu(II) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

Table 30(d): Effect of background electrolyte concentrations in the removal of Cu(II) by AC(N)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	9.78	6.48	1.32	33.74
0.01	9.78	6.67	1.24	31.80
0.1	9.78	6.92	1.14	29.24
1.0	9.78	7.01	1.11	28.32

Table 30(e): Effect of background electrolyte concentrations in the removal of Cu(II) by MCAC(N)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	9.78	4.49	2.12	54.09
0.01	9.78	4.73	2.02	51.64
0.1	9.78	5.00	1.91	48.88
1.0	9.78	5.11	1.87	47.75

Table 30(f): Effect of background electrolyte concentrations in the removal of Cu(II) by ICAC(N)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	9.84	3.11	2.69	68.40
0.01	9.84	3.56	2.51	63.79
0.1	9.84	3.52	2.53	64.24
1.0	9.84	4.48	2.14	54.44

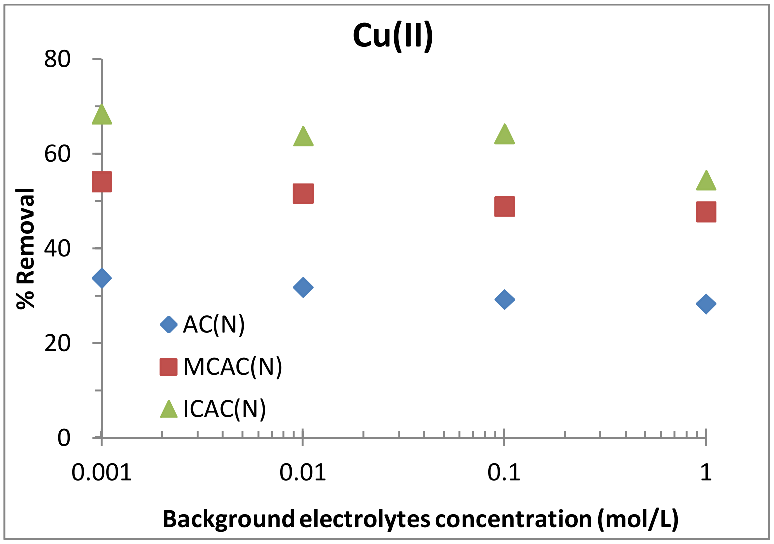

Figure 29(b): Effect of background electrolyte concentrations in the removal of Cu(II) by AC(N), MACAC(N)and ICAC(N)at pH 4.0; initial Cu(II) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

3.3.5.3. Lead (II)

The background electrolyte concentrations was increased from 0.001 mol/L to 1.0 mol/L $NaNO_3$ in the sorption of Pb(II) keeping the initial Pb(II) concentration ~10 mg/L and solution pH 4.0 as constants. The results obtained were returned in Tables 31(a-f) and plotted as percent removal versus background electrolyte concentration in Figures 30(a, b). It was observed that 1000 times increase in the background electrolytes concentration caused to decrease the percent removal of Pb(II) maximum by 3.84%, 5.72% and 10.09% for AC(R), MCAC(R) and ICAC(R), respectively and 4.65%, 8.19% and 1.60% AC-N, MCAC-N and ICAC-N respectively. These results strongly pointed that Pb(II) ions are specifically sorbed on to the surface of the solid and predominantly bound by a strong chemical forces resulting in the formation of 'inner sphere complexes'. Studies on Pb(II) removal by activated carbons obtained from *Polygonum oreintale* in presence of $NaNO_3$ and $Mg(NO_3)_2$ was conducted. It was observed that increasing the concentration of $NaNO_3$ or $Mg(NO_3)_2$ caused to decrease the removal of Pb(II). These results suggested that the sorbing ions were formed an 'outer sphere surface complexes' at the solid surface (Wang *et al.*, 2010). On studying the adsorption of Pb(II) by MX-80 bentonite in presence of $LiNO_3$, $NaNO_3$, KNO_3 suggested that the adsorption was strongly dependent to the ionic strength (Xu *et al.,* 2008).

Table 31(a): Effect of background electrolyte concentrations in the removal of Pb(II) by AC(R)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	9.89	6.07	1.53	38.62
0.01	9.89	6.14	1.50	37.92
0.1	9.89	6.33	1.42	36.00
1.0	9.89	6.45	1.38	34.78

Table 31(b): Effect of background electrolyte concentrations in the removal of Pb(II) by MCAC(R)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	9.89	4.15	2.30	58.04
0.01	9.89	4.27	2.25	56.83
0.1	9.89	4.43	2.18	55.21
1.0	9.89	4.71	2.07	52.38

Table 31(c): Effect of background electrolyte concentrations in the removal of Pb(II) by ICAC(R)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	10.01	1.26	3.50	87.41
0.01	10.01	1.06	3.58	89.41
0.1	10.01	1.36	3.46	86.41
1.0	10.01	2.27	3.10	77.32

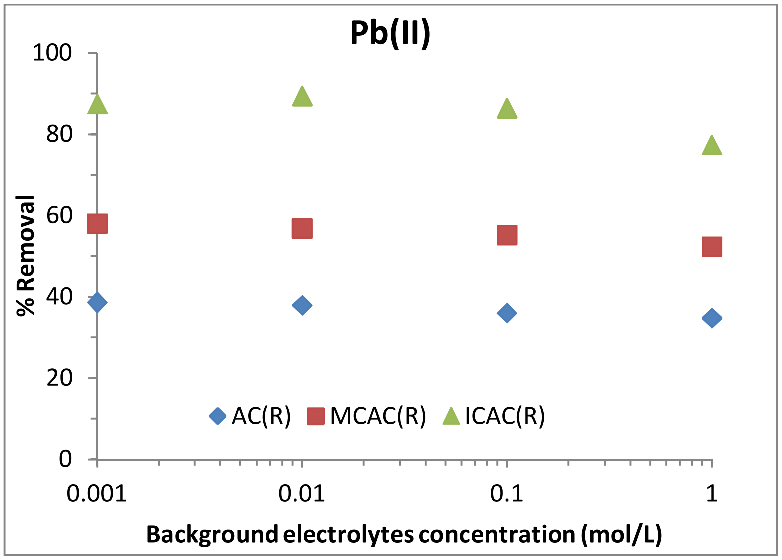

Figure 30(a): Effect of background electrolyte concentrations in the removal of Pb(II) by AC(R), MACAC(R)and ICAC(R)at pH 4.0; Initial Pb(II) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

Table 31(d): Effect of background electrolyte concentrations in the removal of Pb(II) by AC(N)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	9.89	6.32	1.43	36.10
0.01	9.89	6.46	1.37	34.68
0.1	9.89	6.52	1.35	34.07
1.0	9.89	6.78	1.24	31.45

Table 31(e): Effect of background electrolyte concentrations in the removal of Pb(II) by MCAC(N)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	9.89	4.41	2.19	55.41
0.01	9.89	4.69	2.08	52.58
0.1	9.89	4.92	1.99	50.25
1.0	9.89	5.22	1.87	47.22

Table 31(f): Effect of background electrolyte concentrations in the removal of Pb(II) by ICAC(N)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	10.01	0.59	3.77	94.11
0.01	10.01	0.45	3.82	95.50
0.1	10.01	0.54	3.79	94.61
1.0	10.01	0.75	3.70	92.51

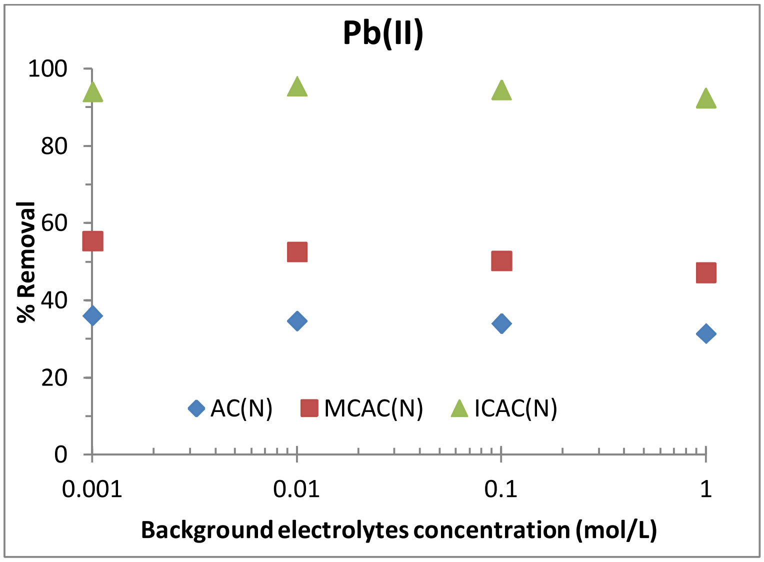

Figure 30(b): Effect of background electrolyte concentrations in the removal of Pb(II) by AC(N), MCAC(N)and ICAC(N) at pH 4.0; initial Pb(II) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

3.3.5.4. Arsenic (III) and Arsenic (V)

The study was further extended to observe the background electrolyte concentrations in the removal of As(III) or As(V) by the solids employed i.e., ACs, MCACs and ICACs. The background electrolyte concentration was increased from 0.001 to 1.0 mol/L of $NaNO_3$ (1000 times)at pH 4.5 keeping the initial concentration of As(III) or As(V) ~10 mg/L as constant. The results obtained were shown in Table 32(a-d) and Figure 31(a, b) for As(III) and Table 33(a-d) and Figure 32(a, b) for As(V). These results clearly indicated that with increasing 1000 times background electrolyte concentration the uptake of As(III) and As(V) were suppressed slightly the uptake of As(III) or As(V) by these solids. The maximum percent decrease in the removal of As(III) and As(V) in presence of $NaNO_3$was occurred with MCAC(R) i.e., by 17.12 %only. Similar to metal cations *viz.,* Cd(II), Cu(II) and Pb(II), these results clearly inferred that As(III) and As(V) were also specifically adsorbed and the sorbing ions were predominantly bound with the strong chemical forces and formed an 'inner sphere complexes' onto the surface of these solid materials (Tiwari and Lee, 2012). The removal of As(III) and As(V) was assesses in presence of various electrolyte concentrations such as NaCl, Na_2SO_4, $NaNO_3$, NaH_2PO_4. It was observed that the presence of NaCl, Na_2SO_4 and $NaNO_3$even up to 50.0 mmol/L, showed almost no detrimental effect on the adsorption capacity of As(III) and As(V) by employing the magnetic γ-Fe_2O_3 nano particles. But, the presence of NaH_2PO_4 was caused to decrease significantly the uptake of As(III) and As(V) by the same magnetic material (Lin *et al.,* 2012). The adsorption of As(III) and As(V) onto the surface of hydrous cerium oxide nano particles was studied as a function of ionic strength using the various concentrations of NaCl (i.e., from 0.01 to 0.1 mol/L) at pH 7.0. It was observed that the adsorption of As(III) was decreased with increasing the NaCl concentrations, however, the adsorption of As(V) was distinctively increased with increasing the ionic strength (Li *et al.,* 2012).

Table 32(a): Effect of background electrolyte concentrations in the removal of As(III) by AC(R)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	10.34	7.54	1.12	27.08
0.01	9.76	7.59	0.87	26.60
0.1	9.50	7.54	0.78	27.08
1.0	9.34	7.73	0.64	25.24

Table 32(b): Effect of background electrolyte concentrations in the removal of As(III) by MCAC(R)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	10.34	6.28	1.62	39.26
0.01	9.76	6.31	1.38	38.97
0.1	9.50	7.15	0.94	30.85
1.0	9.34	8.02	0.53	22.44

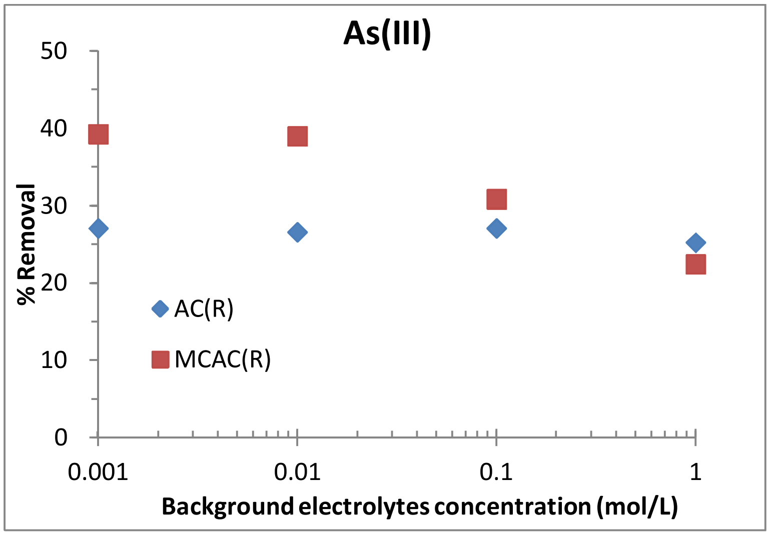

Figure 21(a): Effect of background electrolyte concentrations in the removal of As(III) by AC(R) and MACAC(R)at pH 4.5; initial As(III) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

Table 32(c): Effect of background electrolyte concentrations in the removal of As(III) by AC(N)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	10.34	7.01	1.33	32.21
0.01	9.76	6.91	1.14	33.17
0.1	9.50	7.29	0.88	29.50
1.0	9.34	7.47	0.64	27.76

Table 32(d): Effect of background electrolyte concentrations in the removal of As(III) by MCAC(N)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	10.34	6.19	1.66	40.13
0.01	9.76	6.05	1.48	41.48
0.1	9.50	6.90	1.04	33.27
1.0	9.34	7.69	0.66	25.63

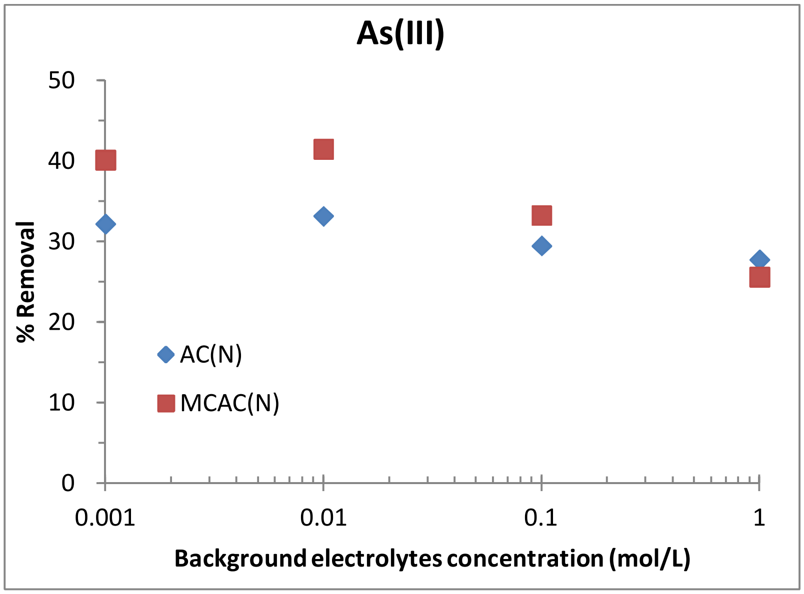

Figure 31(b): Effect of background electrolyte concentrations in the removal of As(III) by AC(N) and MCAC(N) at pH 4.5; initial As(III) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

Table 33(a): Effect of background electrolyte concentrations in the removal of As(V) by AC(R)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	10.16	6.03	1.65	40.65
0.01	10.04	6.42	1.44	36.06
0.1	9.88	6.81	1.22	31.07
1.0	9.94	7.15	1.12	28.07

Table 33(b): Effect of background electrolyte concentrations in the removal of As(V) by MCAC(R)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	10.16	5.86	1.72	42.32
0.01	10.04	5.92	1.65	41.03
0.1	9.88	6.27	1.44	36.53
1.0	9.94	6.89	1.22	30.68

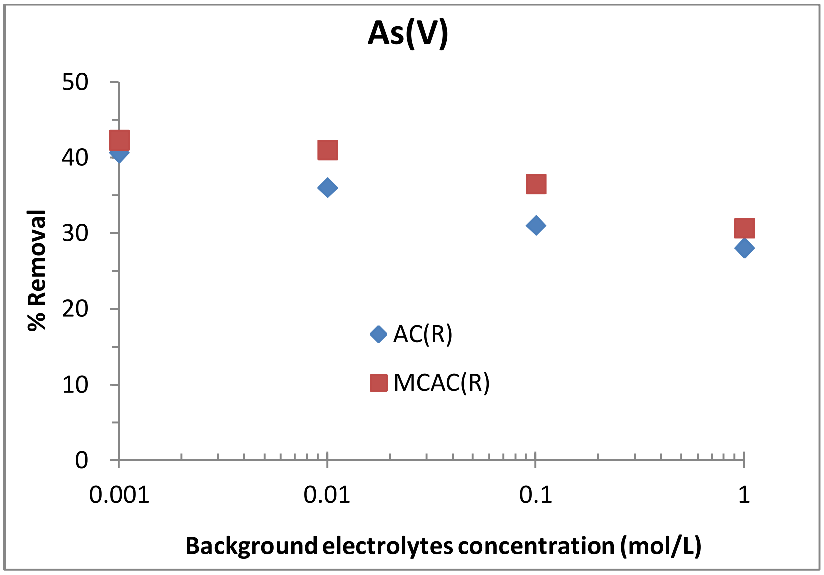

Figure 32(a): Effect of background electrolyte concentrations in the removal of As(V) by AC(R) and MACAC(R)at pH 4.5; initial As(V) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

Table 33(c): Effect of background electrolyte concentrations in the removal of As(V) by AC(N)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	10.16	5.97	1.67	41.24
0.01	10.04	6.08	1.58	39.44
0.1	9.88	6.56	1.33	33.60
1.0	9.94	6.94	1.20	30.18

Table 33(d): Effect of background electrolyte concentrations in the removal of As(V) by MCAC(N)

$NaNO_3$ concentration (mol/L)	Initial concentration (mg/L)	Final concentration (mg/L)	Amount adsorbed (mg/g)	% Removal
0.001	10.16	5.49	1.87	45.96
0.01	10.04	6.00	1.62	40.24
0.1	9.88	6.05	1.53	38.76
1.0	9.94	6.64	1.32	33.19

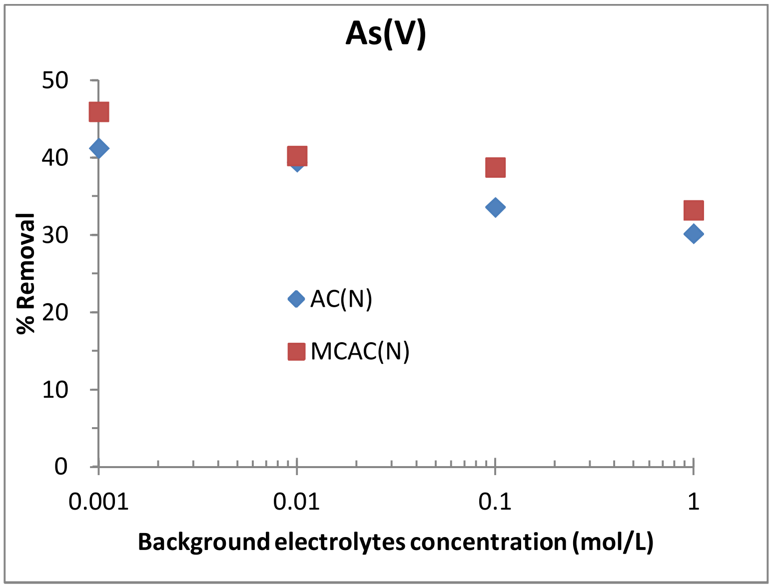

Figure 32(b): Effect of background electrolyte concentrations in the removal of As(V) by AC(N) and MCAC(N) at pH 4.5 and initial As(V) concentration : ~10 mg/L; Temperature: 25±1 ^{0}C

3.3.6. Adsorption isotherm studies

The equilibrium stage sorption data obtained for varied sorptive concentration at constant pH and temperature is further utilized to deduce the adsorption isotherms particularly the Langmuir and Freundlich adsorption isotherms.

3.3.6.1. Langmuir adsorption isotherm

The linearized Langmuir adsorption model in its usual form (equation 2) has been utilized in the adsorption modelling. The concentration dependence sorption data was fitted to the equation (2) and the two unknown parameters viz., the maximum monolayer capacity (q_0) and the Langmuir constant 'b' was estimated for the studied metal cations. It was observed that the equilibrium stage sorption data obtained for these metal ions were reasonably fitted well to the Langmuir adsorption models as shown in Figure 33(a-j) since relatively high R^2 values were obtained. Further, the Langmuir constants i.e., monolayer adsorption capacity (q_o), Langmuir constant (b) along with the regression coefficient (R^2) values obtained for the adsorption of Cd(II), Cu(II), Pb(II) and As(III) and As(III) onto the employed solids were obtained and returned in Tables 34(a-e). The applicability of Langmuir adsorption isotherm pointed that the surface active sites were distributed evenly onto the surface. The results obtained for modified AC showed significantly higher Langmuir monolayer capacity compared to the bare activated carbons. This pointed the greater applicability of the ACs carbons modified with manganese or iron oxide in the remediation of aquatic environment contaminated with these heavy metal toxic ions. Further, Langmuir constant 'b' which reflected the strength and affinity of the solids towards the sorbing species (Gupta *et al.*, 2005), it also related to an equilibrium constant of the uptake process as: M(II)/or As(III)/or As(V) + Solid surface → M(II)/or As(III)/or As(V)…..Solid (surface adsorption complex). It was also observed that the sorption data for the Pb(II) onto ICAC(R) and ICAC(N) was not fitted well Langmuir adsorption isotherms. This is due to, relatively, very high percent uptake of lead(II) was occurred and this was almost independent of concentration range (ranging 1.0 to 20.0 ppm). Since, no proper data fitting was obtained for this system, therefore the Langmuir constants were not evaluated.

Table 34(a): Langmuir monolayer adsorption capacity (q_o), Langmuir constants (*b)* and R^2 values estimated for the adsorption of Cd(II)) onto the different samples of AC, MCAC and ICAC

	Cd(II)		
Materials	q_o (mg/g)	*b* (L/g)	R^2
AC(R)	2.493	0.185	0.807
MCAC(R)	3.582	0.392	0.779
ICAC(R)	3.442	0.947	0.906
AC(N)	2.135	0.213	0.901
MCAC(N)	2.639	0.290	0.655
ICAC(N)	2.874	0.388	0.986

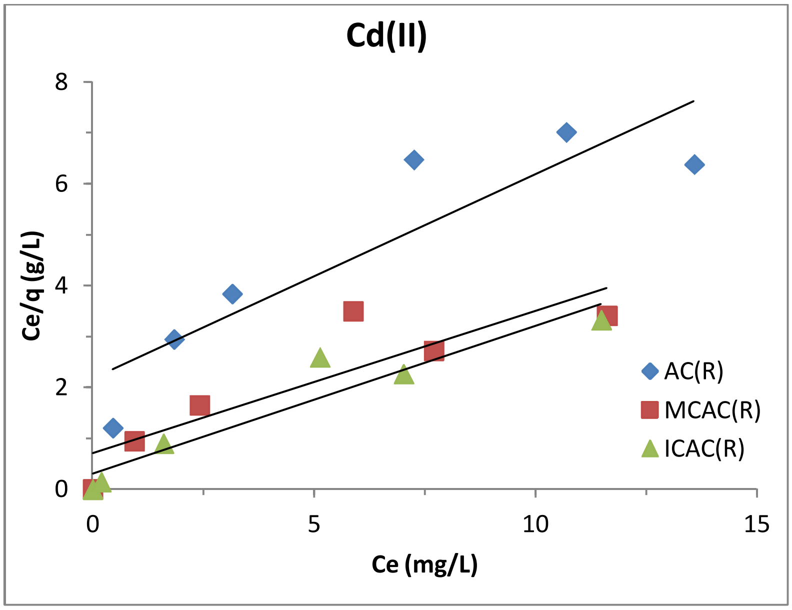

Figure 33(a): Langmuir adsorption isotherm in the removal of Cd(II) by AC(R), MCAC(R) and ICAC(R)

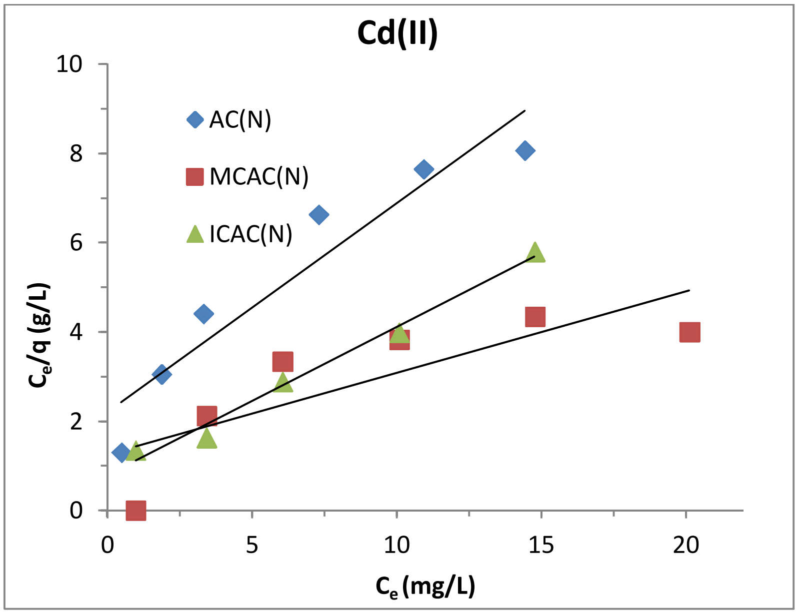

Figure 33(b): Langmuir adsorption isotherm in the removal of Cd(II) by AC(N), MCAC(N)and ICAC(N)

Table 34(b): Langmuir monolayer adsorption capacity (q_o), Langmuir constants (b) and R^2 values estimated for the adsorption of Cu(II)) onto the different samples of AC, MCAC and ICAC

Materials	Cu(II)		
	q_o (mg/g)	b (L/g)	R^2
AC(R)	0.684	1.223	0.981
MCAC(R)	0.938	1.870	0.998
ICAC(R)	3.003	0.363	0.902
AC(N)	0.521	1.899	0.979
MCAC(N)	0.887	1.386	0.984
ICAC(N)	2.475	0.327	0.949

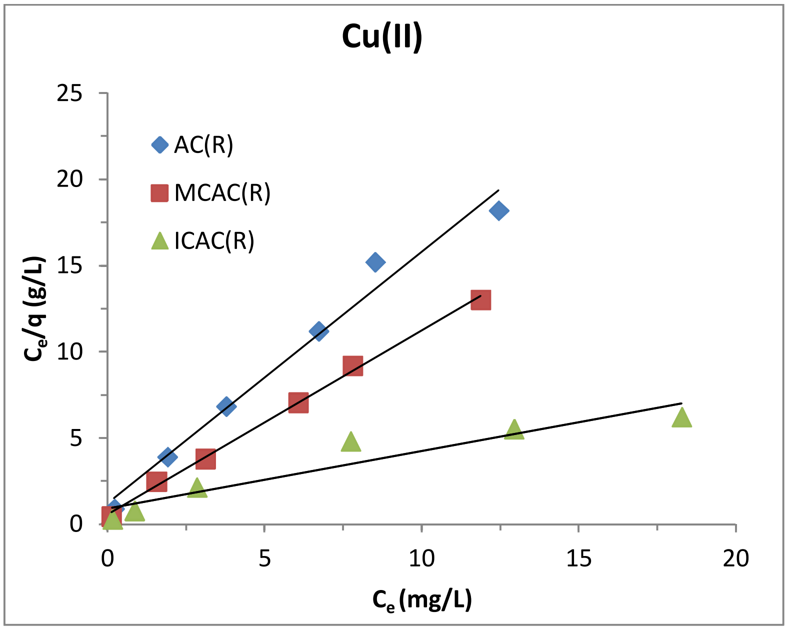

Figure33(c): Langmuir adsorption isotherm in the removal of Cu(II) by AC(R), MCAC(R) and ICAC(R)

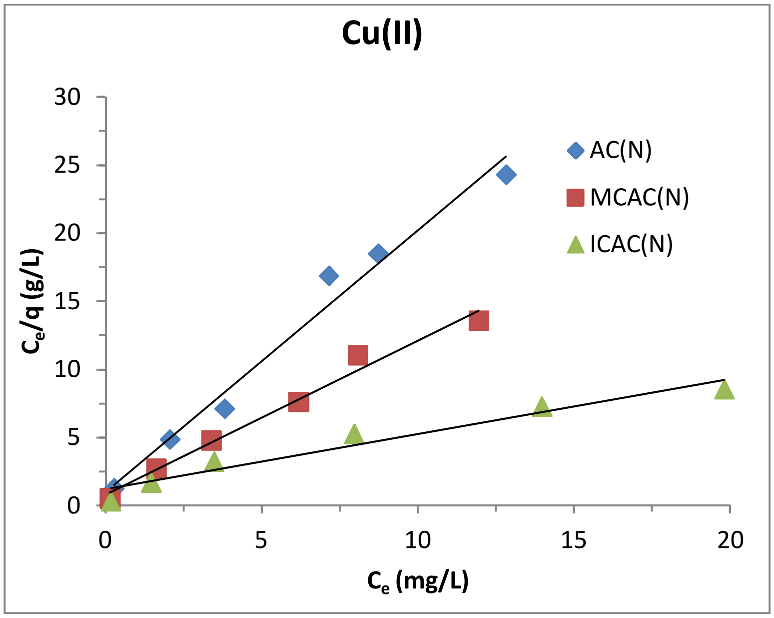

Figure 33(d): Langmuir adsorption isotherm in the removal of Cu(II) by AC(N), MCAC(N)and ICAC(N)

Table 34(c): Langmuir monolayer adsorption capacity (q_o), Langmuir constants (b)and R^2 values estimated for the adsorption of Pb(II)) onto the different samples of AC, MCAC and ICAC

Materials	Pb(II)		
	q_o (mg/g)	b (L/g)	R^2
AC(R)	5.348	0.155	0.928
MCAC(R)	2.843	0.381	0.878
AC(N)	5.000	0.140	0.969
MCAC(N)	4.318	0.283	0.947

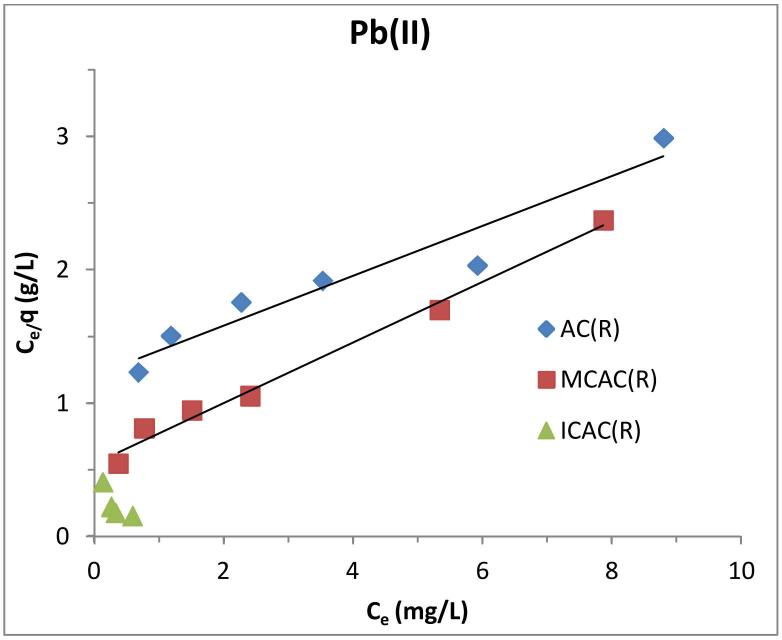

Figure 33(e): Langmuir adsorption isotherm in the removal of Pb(II) by AC(R), MCAC(R) and ICAC(R)

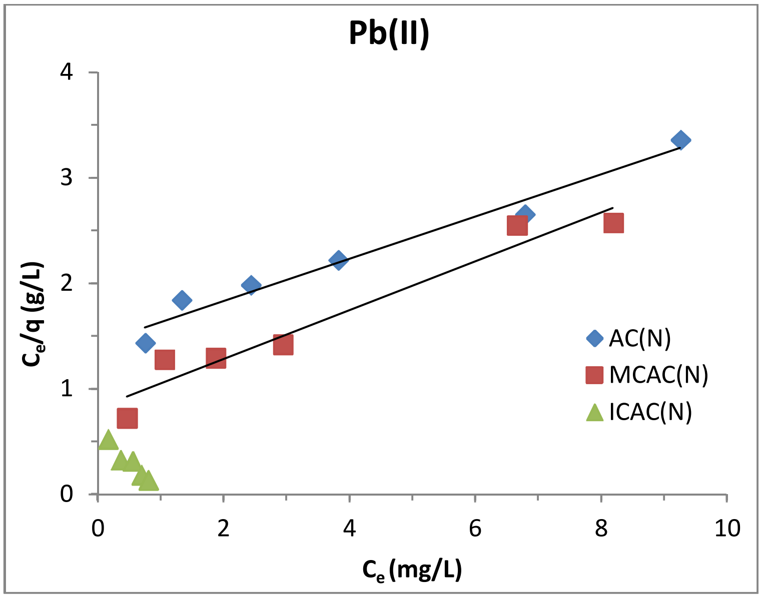

Figure 33(f): Langmuir adsorption isotherm in the removal of Pb(II) by AC(N), MCAC(N)and ICAC(N)

Table 34(d): Langmuir monolayer adsorption capacity (q_o), Langmuir constants (b) and R^2 values estimated for the adsorption of As(III) onto the different samples of AC, MCAC and ICAC

Materials	As(III)		
	q_o (mg/g)	b (L/g)	R^2
AC(R)	1.28	0.362	0.961
MCAC(R)	1.52	0.819	0.985
AC(N)	0.87	0.290	0.904
MCAC(N)	1.24	0.298	0.848

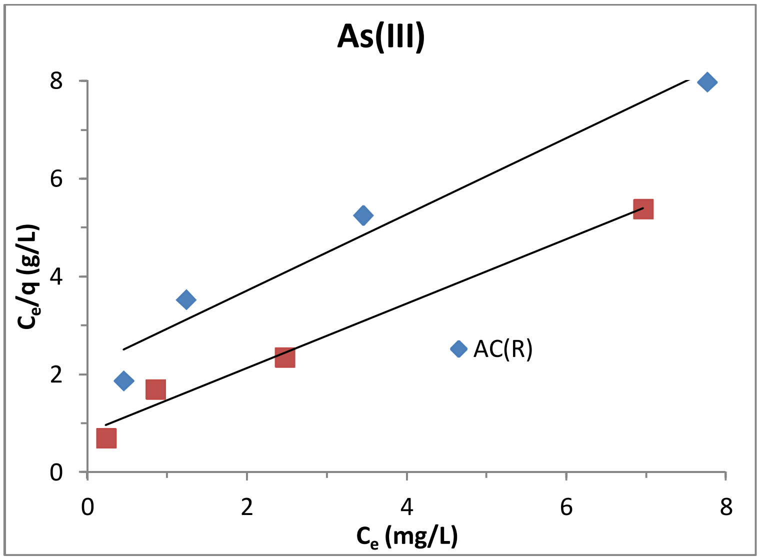

Figure 33(g): Langmuir adsorption isotherm in the removal of As(III) by AC(R) and MCAC(R)

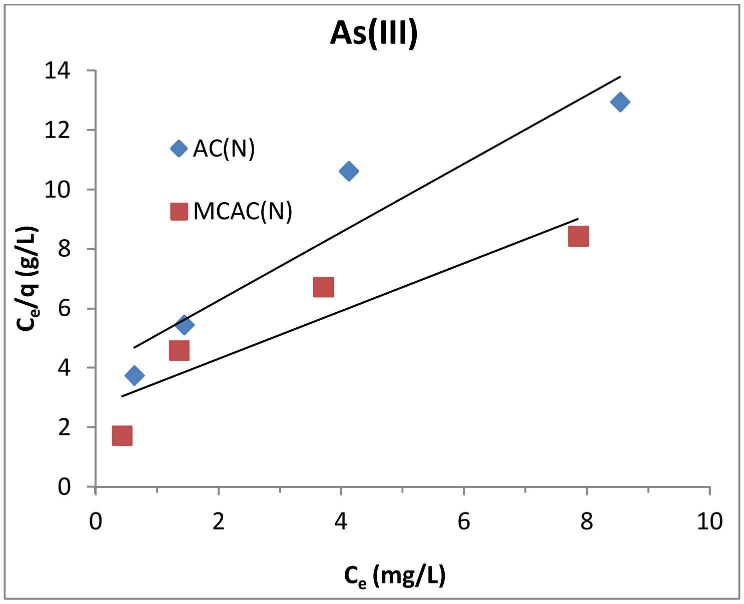

Figure 33(h): Langmuir adsorption isotherm in the removal of As(III)) by AC(N)and MCAC(N)

Table 34(e): Langmuir monolayer adsorption capacity (q_o), Langmuir constants (*b)* and R^2 values estimated for the adsorption of As(V)) onto the different samples of AC, MCAC and ICAC

	As(V)		
Materials	q_o (mg/g)	*b* (L/g)	R^2
AC(R)	1.37	0.328	0.855
MCAC(R)	1.55	1.946	0.983
AC(N)	1.39	0.218	0.811
MCAC(N)	1.50	0.379	0.906

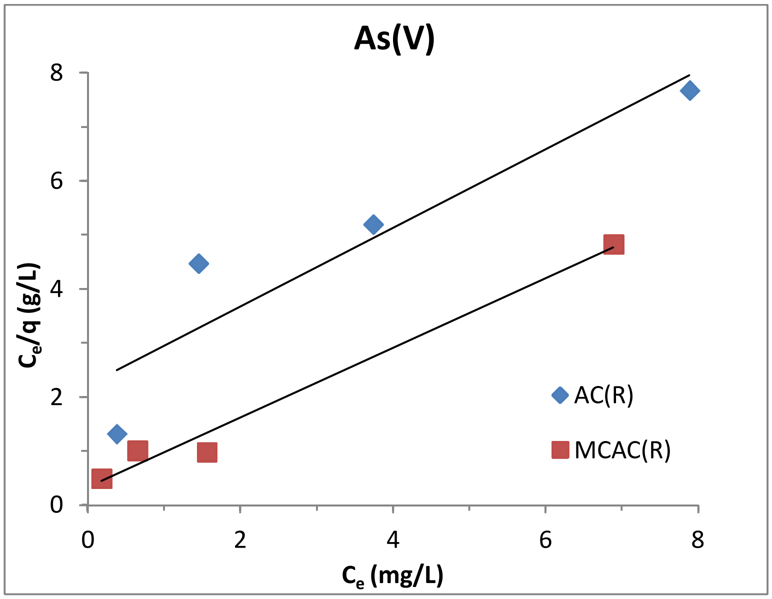

Figure 33(i): Langmuir adsorption isotherm in the removal of As(V) by AC(R) and MCAC(R)

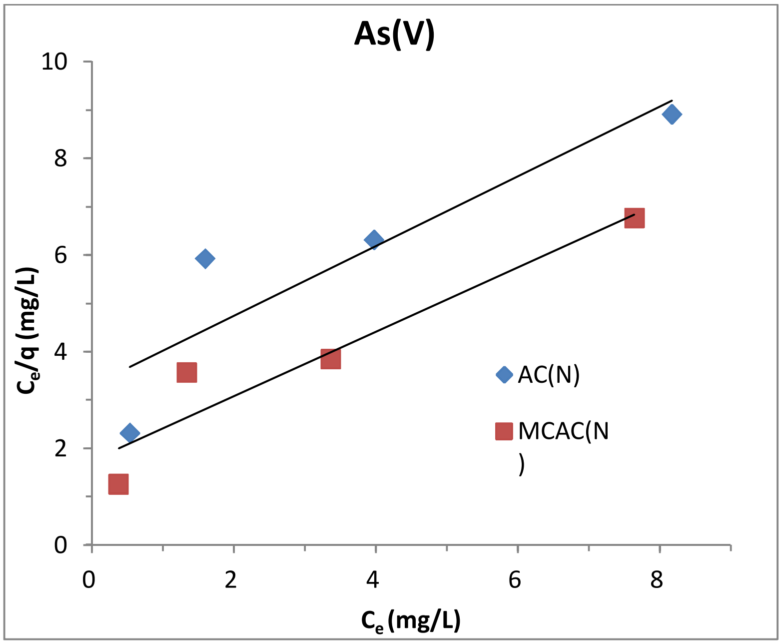

Figure 33(j): Langmuir adsorption isotherm in the removal of As(V) by AC(N) and MCAC(N)

3.3.6.2. Freundlich adsorption isotherm

Further, the concentration dependence data obtained at equilibrium between solid and solution interfaces were utilized in the adsorption isotherm modelling studies as to fit it in the liberalized Freundlich adsorption model (equation 3). The concentration dependence data obtained for systems studied were fitted reasonably well to the linearized form of the Freundlich equation (equation 3) (*cf* Figures 34(a-j) since relatively high value of R^2 was obtained. Therefore, using the fitted lines, the Freundlich constants were estimated and returned in Table 35(a-e). The higher values of R^2 obtained for these studied systems indicated fairly a good applicability of Freundlich adsorption isotherms. It was observed that the estimated Freundlich constant (1/n), which demonstrated the adsorption intensity, always found to be a fractional value(i.e., $0 < 1/n < 1$) for the systems studied, except the systems Pb(II)-ICAC(R) and Pb(II)-ICAC(N), systems. The fractional values of ‘1/n’ pointed it towards the heterogeneous surface structure of these solid materials with an exponential distribution of surface active sites. Also the applicability of Freundlich adsorption isotherm indicated that the sorption on an energetically heterogeneous solid surface on which the sorbed species were interacted laterally and the sorption were occurred with strong chemical forces. Therefore, it may underline that the sorption of these heavy metal toxic ions were of ‘chemisorptive’ in nature which is in a line to the other studies conducted i.e., the effect of background electrolyte concentration (Tiwari and Lee, 2012; Lee *et al.,* 2012).

On the other hand, the sorption capacities (K_f) of these solids were estimated for the sorption of Cd(II), Cu(II), Pb(II), As(III) and As(V) were estimated and already included in the Tables 33(a-e). The closure scrutiny of the tables indicated that the capacities of the iron or manganese modified samples possessed with relatively higher sorption capacities comparing to its respective bare activated carbons. This is pointed the better suitability of these modified materials in the water remediation studies. Moreover, comparing the MCAC and ICAC materials, the ICAC materials showed significantly higher sorption capacities for all these studied metal ions. This could be explained based on the stability of the impregnation. It was observed that iron immobilization was perfectly good within the pH region 3.0-10.0 whereas, manganese was slightly desorbed within the pH region 3-6 (vide Figure 7(b)). Possibly, this could cause in lesser sorption capacities of these sorbing ions. Further, it was observed that a marked difference in sorption capacity was obtained as estimated by two different models i.e., Freundlich and Langmuir models, perhaps, this could be explained with the fact that the two models were developed based on the different basic assumptions which significantly affecting in estimating the sorption capacities (Freundlich, 1906; Langmuir, 1918)

Table 35(a): Freundlich constants along with R^2 values obtained for the adsorption of Cd(II) using different samples of AC, MIAC and ICAC

Materials	Cd(II)		
	1/n	K_f(mg/g)	R^2
AC(R)	0.479	0.500	0.960
MCAC(R)	0.208	0.697	0.868
ICAC(R)	0.176	1.856	0.956
AC(N)	0.454	0.477	0.982
MCAC(R)	0.199	1.132	0.755
ICAC(N)	0.398	1.088	0.948

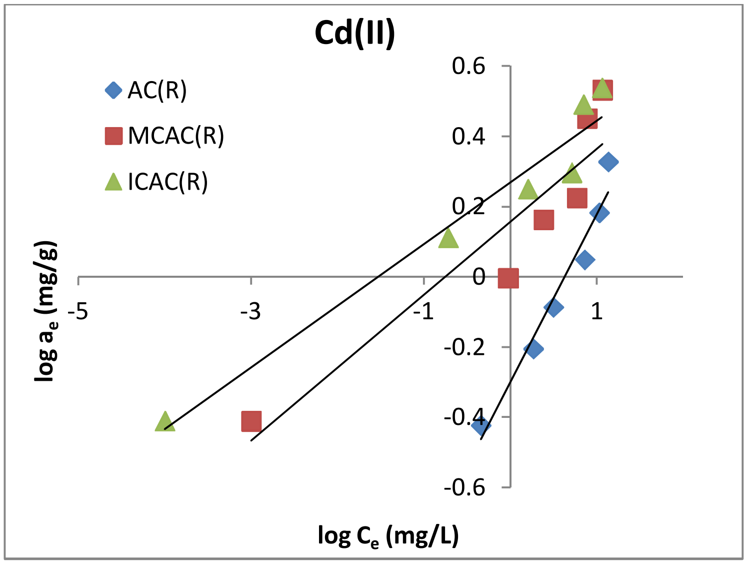

Figure 34(a): Freundlich adsorption isotherm in the removal of Cd(II) by AC(R) MCAC(R) and ICAC(R)

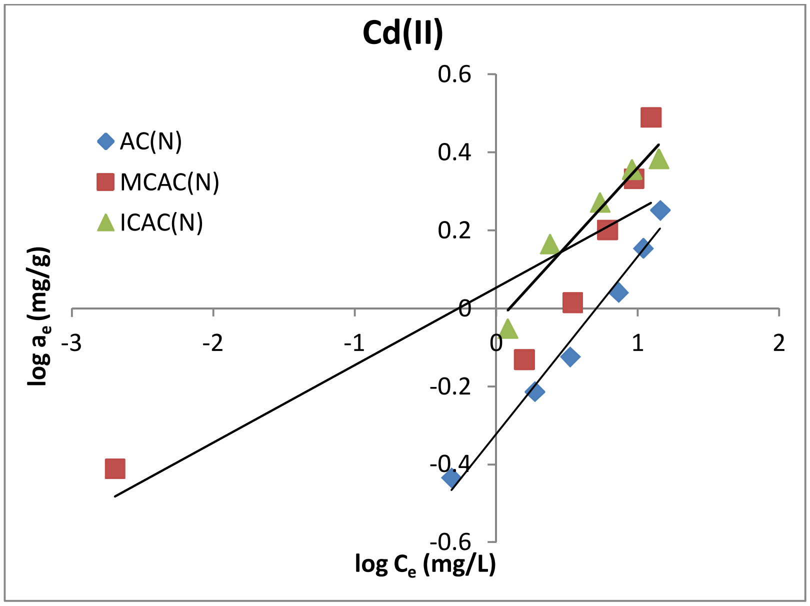

Figure 34(b): Freundlich adsorption isotherm in the removal of Cd(II) by AC(N), MCAC(N) and ICAC(N)

Table 35(b): Freundlich constants along with R^2 values obtained for the adsorption of Cu(II) using different samples of AC, MIAC and ICAC

Materials	Cu(II)		
	$1/n$	K_f(mg/g)	R^2
AC(R)	0.248	0.370	0.949
MCAC(R)	0.270	0.519	0.954
ICAC(R)	0.325	1.002	0.957
AC(N)	0.220	0.315	0.809
MCAC(N)	0.265	0.475	0.958
ICAC(N)	0.310	1.217	0.973

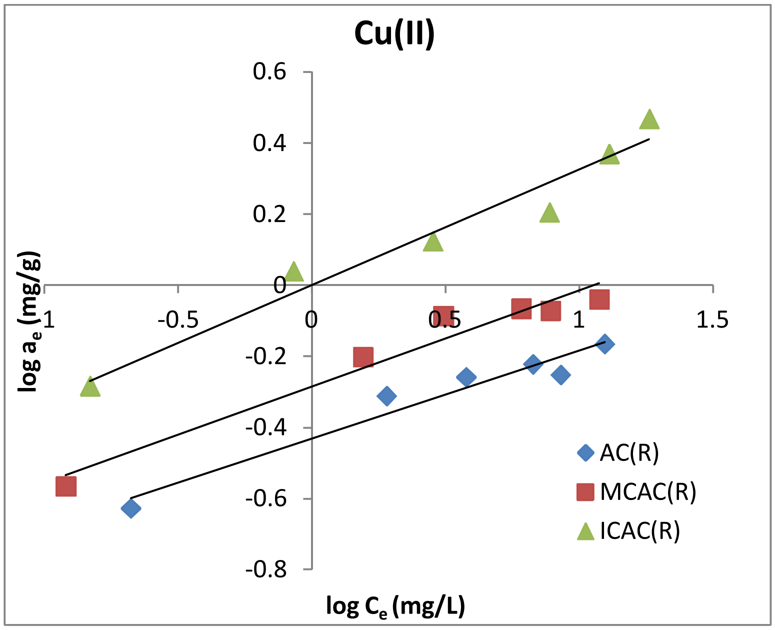

Figure 34(c): Freundlich adsorption isotherms in the removal of Cu(II) by AC(R), MCAC(R) and ICAC(R)

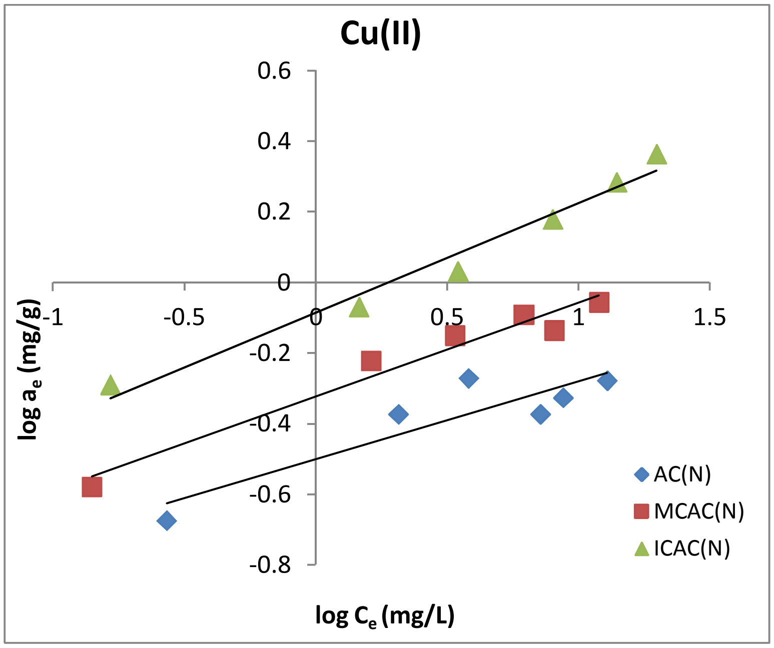

Figure 34(d): Freundlich adsorption isotherm in the removal of Cu(II) by AC(N), MCAC(N) and ICAC(N)

Table 35(c): Freundlich constants along with R^2 values obtained for the adsorption of Pb(II) using different samples of AC, MIAC and ICAC

Materials	Pb(II)		
	$1/n$	K_f(mg/g)	R^2
AC(R)	0.704	0.727	0.983
MCAC(R)	0.554	1.202	0.974
ICAC(R)	1.247	5.662	0.953
AC(N)	0.699	0.636	0.991
MCAC(N)	0.574	0.957	0.968
ICAC(N)	1.392	4.808	0.908

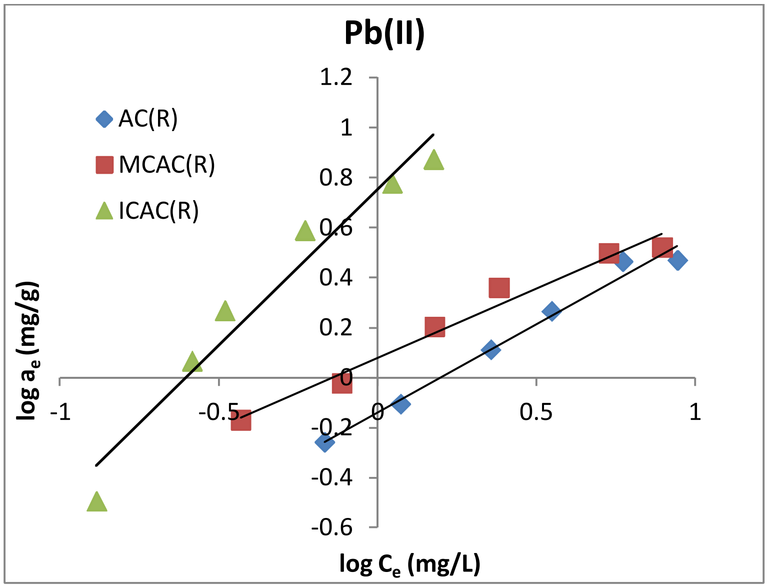

Figure 34(e): Freundlich adsorption isotherm for the removal of Cu(II) by using AC-R, MCAC-R and ICAC-R.

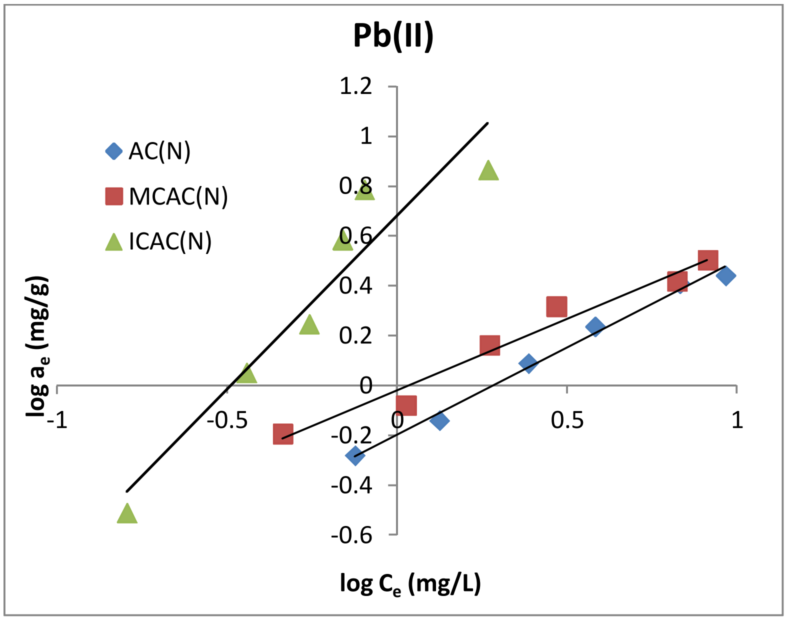

Figure 34(f): Freundlich adsorption isotherm for the removal of Cu(II) by AC(N), MCAC(N) and ICAC(N)

Table 35(d): Freundlich constants along with R^2 values obtained for the adsorption of As(III) using different samples of AC, and MCAC

Materials	As(III)		
	1/n	K_f(mg/g)	R^2
AC(R)	0.342	0.504	0.990
MCAC(R)	0.603	0.429	0.962
AC(N)	0.211	0.501	0.984
MCAC(N)	0.317	0.462	0.924

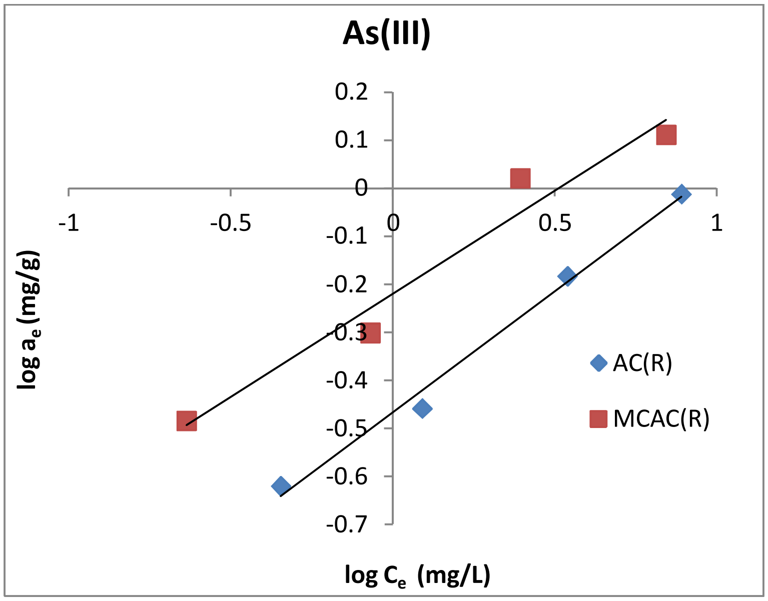

Figure 34(g): Freundlich adsorption isotherm in the removal of As(III) by AC(R) and MCAC(R)

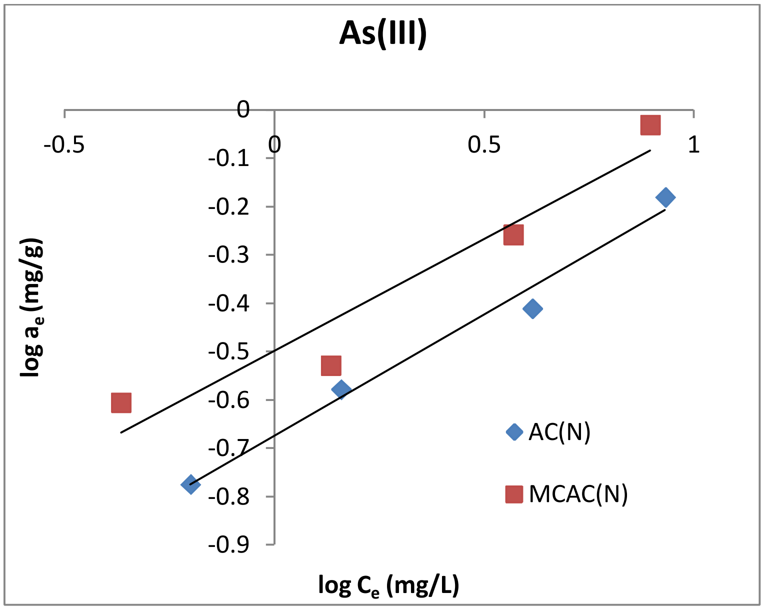

Figure 34(h): Freundlich adsorption isotherm in the removal of As(III) by AC(N) and MCAC(N)

Table 35(e): Freundlich constants along with R^2 values obtained for the adsorption of As(V) using different samples of AC and MCAC

Materials	As(V)		
	1/n	K_f(mg/g)	R^2
AC(R)	0.376	0.442	0.880
MCAC(R)	0.837	0.402	0.792
AC(N)	0.276	0.541	0.916
MCAC(N)	0.421	0.481	0.920

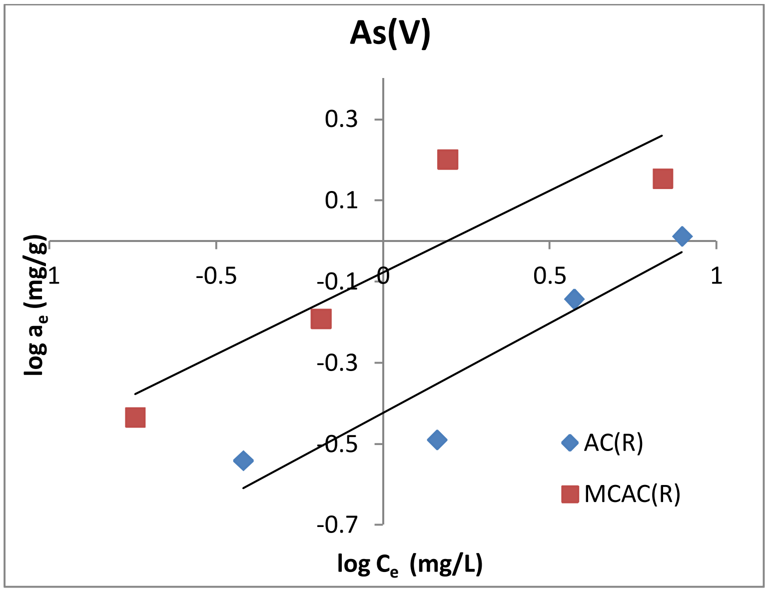

Figure 34(i): Freundlich adsorption isotherm in the removal of As(V) by AC(R) and MCAC(R)

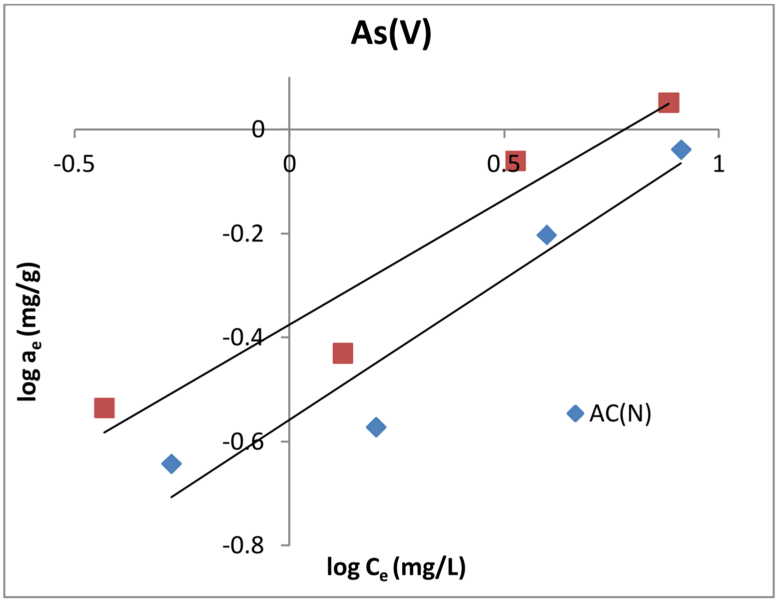

Figure 34(j): Freundlich adsorption isotherm in the removal of As(V) by AC(N) and MCAC(N)

3.4. COLUMN REACTOR STUDIES

The breakthrough data were obtained to examine the applicability of ACs, MCACs and ICACs in the removal of Cd(II), Cu(II) and Pb(II) under the dynamic conditions. The experimental set up was arranged as described previously (vide Chapter 2, Section 2.3).

3.4.1. Cadmium (II)

The column conditions were maintained as influent concentration of Cd(II): 10.0 mg/L pH 5.0 and the flow rate 1.0 mL/min. The column data was obtained and the breakthrough curves were drawn between the C_e/C_o and throughput volume (V). Results were presented graphically in Figure 35(a) and 35(b), respectively for the rice hulls and *areca* nut waste based solids. The figures clearly indicated that a complete breakthrough for Cd(II) was obtained at the throughput volume of 0.38L, 0.42L and 0.38L, respectively of AC(R),MCAC(R) and ICAC(R) and 0.30L, 0.43L, 0.39L for AC(N), MCAC(N)and ICAC(N), respectively. These results inferred that these solid materials showed fairly good affinity towards the Cd(II) sorption. Hence, there could be an enhanced loading capacity of Cd(II) even under the dynamic conditions as well. The breakthrough data was further utilized to optimize the loading capacity of these solids under the dynamic conditions using the Thomas equation to its non-linear form (Thomas, 1944). The least square fitting of the breakthrough data is reasonably well fitted to the Thomas equation hence, the Thomas constants i.e., the loading capacity of column and Thomas rate constants were obtained and returned in Table 36. The marked difference in loading capacity was occurred for the modified activated carbon samples comparing to the bare activated carbons suggested the comparable use of these modified solids in the removal/attenuation of Cd(II) from contaminated wastewater. These results were in a line to the findings of batch reactor operations and the previous reports in which the Thomas equations were fitted well to demonstrate the loading capacity of different sorbents (Lee *et al.,* 2012; Singh *et al.,* 2012).

Table 36: Thomas constants for the removal of Cd(II) from aqueous solutions by different solid samples.

Materials	Cd(II)		
	q_0 (mg/g)	K_T (L/min/mg)	*Least square sum*
AC(R)	2.036	$2.27\text{x } 10^{-3}$	$8.0\text{x}10^{-2}$
MCAC(R)	2.197	$2.91\text{x } 10^{-3}$	$5.8\text{x}10^{-2}$
ICAC(R)	2.723	$3.47\text{x } 10^{-3}$	$2.9\text{x}10^{-2}$
AC(N)	1.524	$3.18\text{x } 10^{-3}$	$5.8\text{x}10^{-2}$
MCAC(N)	2.124	$2.56\text{x } 10^{-3}$	$1.2\text{x}10^{-2}$
ICAC(N)	2.265	$2.59 \text{ x } 10^{-3}$	$1.4\text{x}10^{-1}$

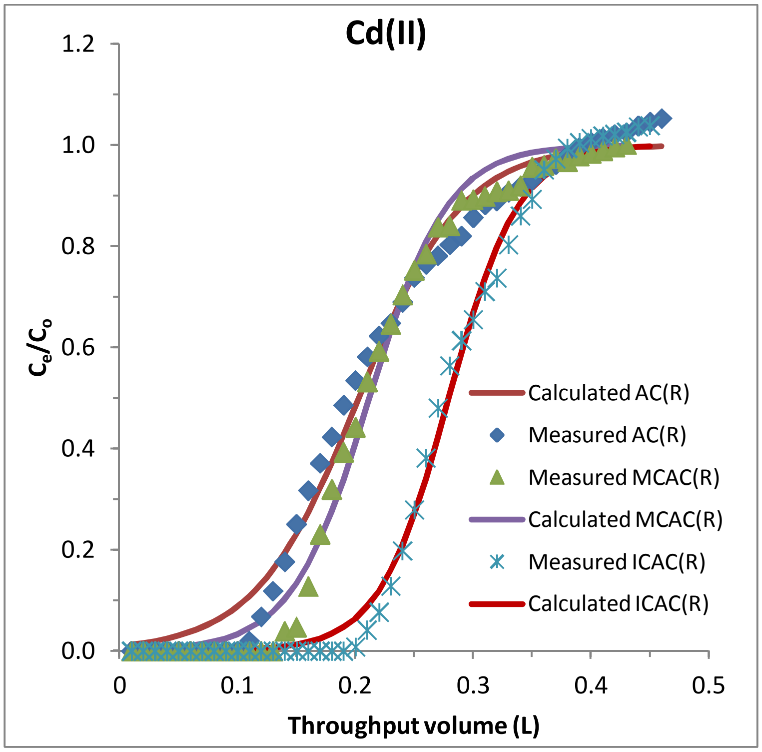

Figure 35(a): Breakthrough curves in the removal of Cd(II) by AC(R), MCAC(R) and ICAC(R)[pH: 5.0;InfluentCd(II) concentration: 10 mg/L; Flow rate: 1.0 mL/min]

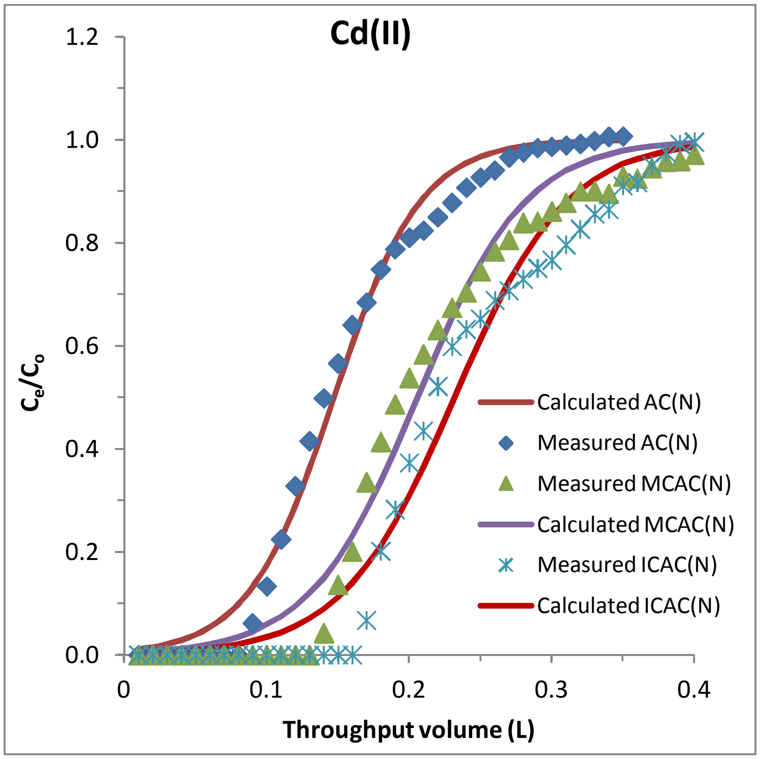

Figure 35(b): Breakthrough curves in the removal of Cd(II) by AC(N), MCAC(N) and ICAC(N)[pH: 5.0; Influent Cd(II) concentration: ~10 mg/L; Flow rate: 1.0 mL/min]

3.4.2. Copper (II)

Similarly, the removal of Cu(II) under dynamic conditions was performed by keeping the initial sorptive concentrations at 10.0 mg/L and pH 4.0 as constant. The complete breakthrough was obtained at the throughput volume 0.13 L, 0.15 L and 0.16 L, respectively for AC(R), MCAC(R) and ICAC(R) and 0.14 L, 0.15 L and 0.22 L for AC(N), MCAC(N)and ICAC(N), respectively (*cf* Figures36(a) and 36(b)). The difference in breakthrough volume obtained for the manganese immobilized activated carbon samples and bare activated carbons was less pronounced comparing to other systems as well other metal ions studied for these solids as well. However, the complete removal of Cu(II) until 0.13-0.22 L conferred that these materials possessed significantly high loading capacity for Cu(II) even under the dynamic conditions. The data obtained were further utilized to obtain the adsorption capacity (***q_o***) by using Thomas equation (equation 9). The non-linear fitting was performed as to obtain the Thomas constants and the results were thereby in Figure 36(a) and 36(b) and the calculated values were returned in Table 37. The low values of the least square sum reflected better applicability of the Thomas fitting (Lee *et al.,* 2012). The other studies reported for the removal of Cu(II) by using expanding rice husk under fixed bed column experiments indicated that the loading capacity was found to be 4.357 mg/g and 5.838 mg/g for the influent Cu(II) concentrations of 9.73 mg/L and 26.95 mg/L, respectively at the flow rate of 10 mL/min and solid dose of 10 g. It was further observed that the flow rate, metal concentration and bed height were affected greatly the loading capacity of Cu(II) (Luo *et al.,* 2011). The breakthrough curves obtained by column experiments in the removal of Cu(II) by sericite clay was well explained with the Thomas equation and the loading capacity was found to be 0.607 mg/g under the conditions: flow rate 9.0 x10^{-4} L/min, influent Cu(II) concentration 20.49 mg/L and dose of sericite 1g (Tiwari *et al.,* 2007). Therefore, it was concluded that reasonably a high loading capacity for Cu(II) was observed under the dynamic conditions using the materials *viz.,* ACs, MCACs and ICACs.

Table 37: Thomas constants for the removal of Cu(II) from aqueous solutions by different samples.

Materials	Cu(II)		
	q_0 (mg/g)	K_T (L/min/mg)	*Least square sum*
AC(R)	2.316	1.80x10^{-3}	2.80x10^{-1}
MCAC(R)	2.449	2.23x10^{-3}	2.10x10^{-1}
ICAC(R)	2.746	2.97 x10^{-3}	2.9x10^{-2}
AC(N)	2.506	1.76x10^{-3}	1.50x10^{-1}
MCAC(N)	2.535	1.72x10^{-3}	3.20x10^{-1}
ICAC(N)	3.057	2.42x10^{-3}	1.1x10-1

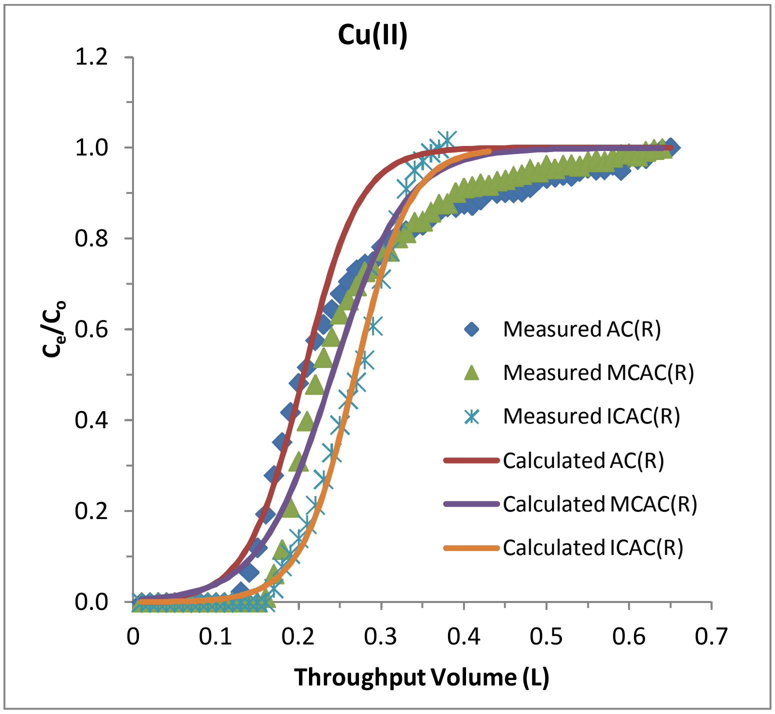

Figure 36(a): Breakthrough curves in the removal of Cu(II) by AC(R), MCAC(R) and ICAC(R)[pH: 4.0; Influent Cu(II) concentration: 10 mg/L; Flow rate: 1.0 mL/min]

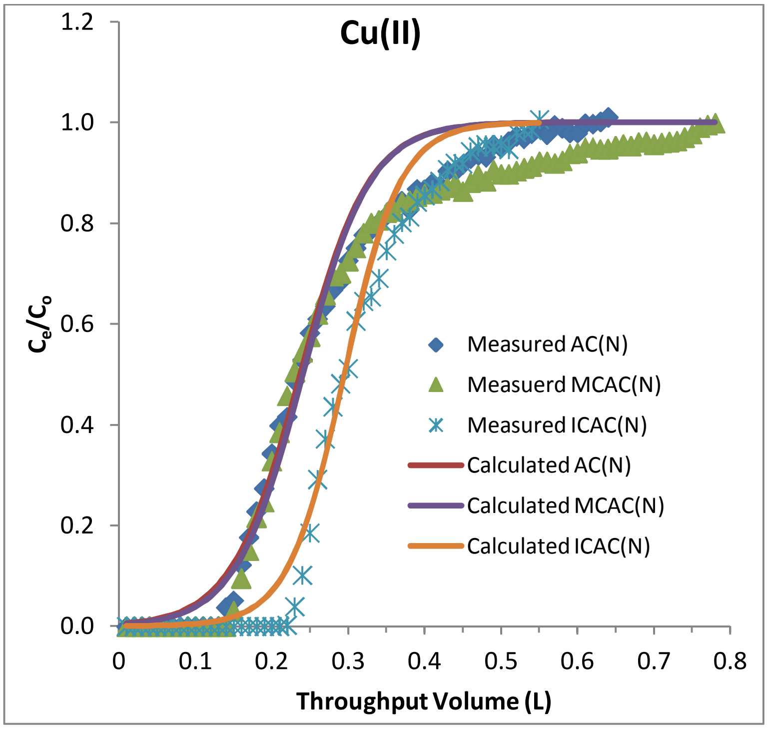

Figure 36(b): Breakthrough curves in the removal of Cu(II) by AC(N), MCAC(N) and ICAC(N) [pH: 4.0; Influent Cu(II) concentration: ~10 mg/L; Flow rate: 1.0 mL/min]

3.4.3. Lead (II)

The breakthrough data for the removal of Pb(II) were obtained by keeping initial sorptive concentration at 10.0 mg/L having a constant pH 4.0.The complete breakthrough was obtained at the throughput volume of0.50 L, 0.57 L and 0.52 L, respectively for AC(R), MCAC(R) and ICAC(R) and 0.40 L, 0.44 L and 0.42 L for AC(N), MCAC(N)and ICAC(), respectively (*cf* Figure 37(a) and 37(b)). The high value of the breakthrough volume indicated the potential use of these solids in the removal of Pb(II) even under the dynamic conditions. The breakthrough data obtained were further utilized to optimize the loading capacity of the columns under the specified column conditions using the Thomas equation (Equation 9). A non-linear regression was conducted using the Thomas and it was observed that good fitting was obtained since a low value of the least square sum obtained for these systems. Further, the Thomas constants i.e., loading capacity (q_0) and Thomas rate constant (K_T) were estimated and returned in the Table 38. The obtained data clearly indicated that very high loading capacity was achieved even under the dynamic conditions showing an enhanced use of these solid materials for removal/attenuation of Pb(II) ions from aqueous solutions. Comparatively, the materials showed very high loading capacity for Pb(II) comparing to other metals ions studied i.e., Cu(II) and Pb(II).These results are in a line to previous data obtained by batch reactor experiment. The other fixed bed column studies performed by employing different solids such as macro fungus *Pycnoporus sanguineus,* sericite and iron-oxide nanoparticles immobilized sand were also reported higher loading capacity for Pb(II) comparing to other heavy metal toxic ions (Zulfadhly *et al.,* 2001; Tiwari *et al.,* 2007; Lee *et al.,* 2012).

Table 38: Thomas constants for the removal of Pb(II) from aqueous solutions by different samples

Materials	Pb(II)		
	q_0 (mg/g)	K_T (L/min/mg)	*Least square sum*
AC(R)	5.960	1.92x10^{-3}	1.80x10^{-1}
MCAC(R)	6.242	3.39x10^{-3}	5.80x10^{-2}
ICAC(R)	6.957	2.03 x10^{-3}	1.40x10^{-2}
AC(N)	4.932	2.26x10^{-3}	3.30x10^{-2}
MCAC(N)	5.346	1.71x10^{-3}	1.30x10^{-1}
ICAC(N)	6.505	1.58 x10^{-3}	3.50x10^{-2}

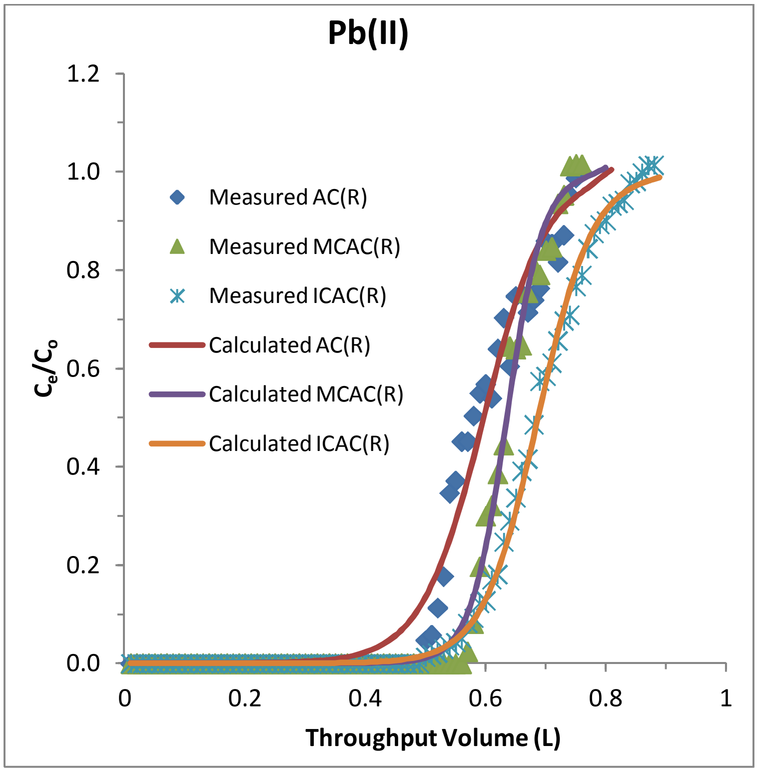

Figure 37(a): Breakthrough curves in the removal of Pb(II) by AC(R), MCAC(R) and ICAC(R) [pH: 4.0; Influent Pb(II) concentration: ~10 mg/L; Flow rate: 1.0 mL/min]

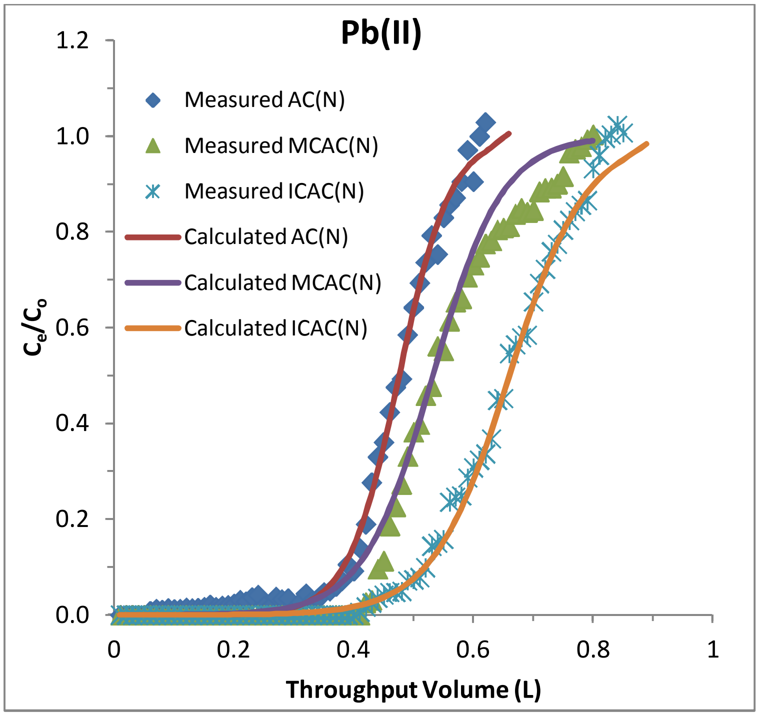

Figure 37(b): Breakthrough curves in the removal of Pb(II) by AC(N), MCAC(N) and ICAC(N) [pH: 4.0; Influent Pb(II) concentration: ~10 mg/L; Flow rate: 1.0 mL/min]

4. CONCLUSIONS

The agricultural by-product/waste *viz*., rice hulls and *areca* nut waste were fully exploited to obtain the activated carbons in an attempt to obtain cost effective and environmentally benign materials. Further, the large specific surface area of ACs was utilized to impregnate it with minimal dose of manganese or iron as to obtain the manganese and iron-oxide impregnated activated carbons. The surface morphology and elemental composition of the ACs along with MCACs and ICACs were obtained by SEM-EDX analysis. Surface morphology of AC samples showed very porous surface structure of these solids and the pores are very unevenly distributed on the surface. The surface structure of ACs was greatly changed with the impregnation of manganese or iron, manganese dioxide or iron oxide particles were significantly aggregated on the surface as well as within pores of the ACs. The particles are predominantly small in size and unevenly distributed on the surface of the AC samples. The particles are partly clustered at places onto the surface. Moreover, a distinct additional peak of manganese and iron were obtained by MCAC and ICAC in the EDX analytical data. The functional groups present in the solid samples were characterized by using FT-IR analysis. The carbon samples could possess various functional groups *viz*., aliphatic, aromatic, cyclic since the IR bands were observed at around 1480 cm^{-1} and regions around 1110 cm^{-1} for both the ACs. Predominant and broad peak appeared at around 3470-3495 cm^{-1}were ascribed to the stretching vibrations of –OH groups (carboxyl, alcohol or phenols) and the peaks at 2800-2900 cm^{-1} was indicated to the existence of aldehyde groups. The peak at around 450- 475 cm^{-1} was assigned as the stretching vibrations of Fe-O obtained for the ICACs samples. And peaks at around 840 cm^{-1} inferred to the υ_s vibrations of Si-O-Si or δ-Fe-OH vibrations predominant in the rice hulls activated carbon samples. The content of iron or manganese onto the surface of AC was perhaps caused for distinct diffraction peaks in the XRD pattern. Sharp peak at the 2θ value of 39 which was an indicative of *akaganeite* (β-FeOOH) and a weak diffraction peak at the 2θ value of 32.5 in case of MCAC(R) were possibly, due to the presence of Mn_3O_4 mineral phase. The specific surface areas of these solids i.e., ACs, MCACs and ICACs samples were determined by using the BET analyser and the results showed that the activated carbon obtained from rice hulls and *areca* nut waste was possessed with very high specific surface area. The specific surface area of AC(R), MCAC(R) and ICAC(R) were found to be 322.14 m^2/g, 315.82 m^2/g, 303.79 m^2/g, respectively and the solid materials obtained from *areca* nut waste, the specific surface area were found to be 379.77 m^2/g, 371.04 m^2/g, and 370.88 m^2/g, respectively for AC(N), MCAC(N) and ICAC(N). The specific surface area of ACs was slightly decreased in presence of iron or manganese oxides since the iron or manganese oxides occupied the pores and spaces of the ACs. The stability tests were performed in the wide range of pH i.e., between pH 2.0 to 10.0 for MCAC and ICAC samples. It was observed that the impregnation of manganese was quite stable within the pH region 3.5 to 10.0 since no significant manganese was leached into the bulk solution in this pH region. Whereas, the ICACs were fairly stable within the pH region 3.0-10.0 as almost a negligible amount of iron was leached out into the bulk solution. These results suggest the possibility of employing these materials over a wide pH range in the wastewater treatments and enhanced its suitability for the purpose described. The pH_{pzc} were obtained for these solid samples by simple acid base titrations at constant ionic strength and temperatures. The pH_{pzc} were found to 6.6, 6.5, 6.1, 6.7, 6.5, 6.2 respectively for the solids AC(R), MCAC(R), ICAC(R), AC(N), MCAC(N) and ICAC(N). The pH_{pzc} in presence of iron or manganese oxide was caused to decrease slightly comparing to their respective AC samples.

The speciation studies were conducted by using the MINEQL geochemical computer simulation program for Cd(II), Cu(II), Pb(II) and As(III) and As(V). A complete speciation studies were carried out in a wide range of pH i.e., pH 2.0 to 10.0 using known equilibrium constants. The results obtained with speciation studies enabled to understand the sorption studies or to deduce the mechanism involved at solid/solution interface.

The batch reactor data obtained for various physico-chemical parametric studies showed that an increase in pH greatly favoured the uptake of Cu(II), Cd(II) and Pb(II) with almost 100% removal at higher pH values was occurred whereas the uptake of As(III) and As(V) was significantly decreased with increasing the pH of sorprtive solution. An increase in sorptive concentration showed marked decrease in percent uptake for all the sorptive ions except Pb(II) removal by using both ICAC-R and ICAC-N, which was almost unaffected for such increase in sorptive concentrations. The equilibrium state sorption data was reasonably fitted well to the Langmuir and Freundlich adsorption isotherms and hence, the removal capacity was estimated for these solids towards the pollutants employed. The kinetic data showed that a fast initial uptake was occurred and most of the ions i.e., Cd(II), Cu(II), Pb(II) and As(III) and As(V) were adsorbed within the initial contact time of 60-90 minutes and an apparent equilibrium in sorption was achieved within 180 minutes of contact time for Cd(II), 420- 480 minutes for Cu(II) and 300-420 minutes for Pb(II). The data is fitted well to the pseudo-first-order and pseudo-second-order rate equations. However, the pseudo-second order rate laws were fitted well comparing to the pseudo-first order rate law. The applicability of pseudo-second-order rate equations further conferred the chemisorption as the predominant process involved with valency forces through sharing or exchange of electrons between the sorbent and the sorbate. Further, the 1000 times increase in background electrolyte concentrations $NaNO_3$, i.e., increasing the electrolyte concentration from 0.001 mol/L to 1.0 mol/L, caused insignificant decrease in Cd(II), Cu(II), Pb(II) and As(III) and As(V) uptake by these solids which inferred that sorbing ions/species were sorbed specifically and forming an ‘inner-sphere’ complexes on to the solid surface.

The column reactor operations revealed that relatively high breakthrough volume was obtained for the Cu(II), Cd(II) and Pb(II) and the breakthrough data was reasonably fitted well to the Thomas equation. Therefore, the loading capacities were estimated by using Thomas equation. The results inferred that these solid materials i.e., AC(R), AC(N), MCAC(R), MCAC(N), ICAC(R) and ICAC(N) showed fairly good affinity towards the Cu(II), Cd(II) and Pb(II) sorption and hence, there was an enhanced loading capacity of Cu(II), Cd(II) and Pb(II) even under the dynamic conditions. Comparatively, in a line with the batch reactor experiment, the loading capacities were in the order Pb(II)> Cu(II)>Cd(II) for all these solid materials employed.

From the overall present investigation, it can be concluded that activated carbon precursor to rice husk and *areca* nut waste along with immobilized manganese/iron activated carbon were found to be an alternative sortive materials for the removal of heavy metal toxic ions *viz*., Cd(II), Cu(II), Pb(II) and As(III) and As(V) from aqueous solutions. Surface modifications of activated carbon(AC) by immobilizing manganese/ iron as small or nano-sized particles onto the surface of AC caused to enhance the uptake of Cd(II), Cu(II), Pb(II) and As(III) and As(V) from aqueous solutions. The input laboratory data obtained with the batch and column reactor operations using the modified materials could have an enhanced application and may likely to be employed in the treatment of waste waters at the larger scale or even at the pilot plant level in order to enable the practical applicability of these materials.

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Lists of Publications

(A) Journals:

1. **Lalhmunsiama**, Diwakar Tiwari, Seung-Mok Lee. Activated carbon and manganese coated activated carbon precursor to dead biomass in the remediation of arsenic contaminated water. ***Environmental Engineering Research,*** **17(S1) (2012): S41-S48**.
2. **Lalhmunsiama**, Seung-Mok Lee, Diwakar Tiwari. Manganese oxide immobilized activated carbons in the remediation of aqueous wastes contaminated with copper(II) and lead(II). ***Chemical Engineering Journal***, **225 (2013): 128-137.**
3. Seung-Mok Lee, **Lalhmunsiama**, Sang-Il Choi, Diwakar Tiwari. Manganese and iron oxide immobilized activated carbons precursor to dead biomasses in the remediation of cadmium contaminated waters. ***Environmental Science Pollution Research,*** **(2013), DOI 10.1007/s11356-013-1609-x.**
4. **Lalhmunsiama**, Seung Mok Lee, Diwakar Tiwari, 2013. Application of sericite in the remediation of wastewater contaminated with cadmium (II): Batch and column reactor studies. ***Science and Technology Journal,*** **1(1)(2013): 14-21.**

(B) Conferences/Symposiums:

1. **Lalhmunsiama**, Diwakar Tiwari, Seung-Mok Lee, (2011). Activated carbon and manganese coated activated carbon precursor to dead biomass in the remediation of arsenic contaminated water. *Proceedings of International conference on Advances in Environmental Chemistry (AEC-2011),* 16-19 November, 2011, Department of Chemistry, Mizoram University, Aizawl, Mizoram, India.
2. **Lalhmunsiama**, Diwakar Tiwari, Seung-Mok Lee. Manganese oxide immobilized activated carbon in the remediation of water contaminated with cadmium (II). *Proceedings of Korean society of environmental engineers Conference, 2012.* 22-24, August, 2012, Changwon, Korea.
3. **Lalhmunsiama**, Diwakar Tiwari, Seung-Mok Lee. Manganese oxide immobilized activated carbon precursor to agriculture by-product in the remediation of lead (II)

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4. **Lalhmunsiama**, Diwakar Tiwari, Seung-Mok Lee. Activated carbon and metal oxide modified activated carbon precursor to agriculture by-product in the treatment of wastewater contaminated with copper (II). *2013 Water Korea organized by Korean society of water and wastewater and Korean society of water environment*, 21-22 March, 2013, Daegu, Korea.
5. Desireddy Harikishore Kumar Reddy, **Lalhmunsiama**, Diwakar Tiwari, Hee-Jeong Choi and Seung-Mok Lee, (2012). Attenuation of Radioactive Sr(II) from Water Environment Using sericite clay. ***2012 International Conference on Environment, Chemistry and Biology***, 29-31 November, 2012, Hongkong, China.
6. Diwakar Tiwari, **Lalhmunsiama**, Seung-Mok Lee. Physico-Chemical Studies in the Removal of Cd(II) and Mn(II) from Aqueous Solutions using Sericite. *Proceedings of Global Engineering, Science and Technology Conference,* 1-2 April, 2013, Dubai, UAE.
7. **Lalhmunsiama**, Seung-Mok Lee, Diwakar Tiwari. Iron oxide modified activated carbons for the treatment of aqueous solutions contaminated with lead (II) : Batch and column reactor studies. *Proceedings of Asia Pacific Conference on Sustainable Energy and Environmental Technologies (APCSEET-2013).* 5-8 July, 2013, Narita, Japan.
8. **Lalhmunsiama,** Diwakar Tiwari. Removal behaviour of heavy metal toxic ions Cu(II) and Cr(VI) from aqueous solutions by using dead biomass. *National seminar cum training programme on Green and Environmental Chemistry*, Department of Chemistry, Mizoram University, 30th March, 2011.