Evaluation of Adsorption Efficiency of Zirconium Impregnated Granular Activated Carbon for the Removal of Heavy Metal Ions Pb^{2+} and Cd^{2+}

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Master of Science in PHARMACEUTICAL CHEMISTRY

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<u>CERTIFICATE</u>

This is to certify that the project report entitled "Evaluation of Adsorption Efficiency of Zirconium Impregnated Granular Activated Carbon for the Removal of Heavy Metal Ions Pb^{2+} and Cd^{2+}" is bonafide work carried out by **SANIYA E SANTHOSH** M.Sc Pharmaceutical Chemistry student, under the supervision and guidance of **Prof. Dr. V. SIVANANDAN ACHARI**, Dean and Professor, School of Environmental Studies, Cochin University of Science and Technology, Kerala under co-guidance of Dr. Sindhu Joseph, Assistant Professor, Department of Chemistry, BHARATA MATA COLLEGE, THRIKKAKARA in partial fulfillment of award of the degree of Master of science in pharmaceutical chemistry at BHARATA MATA COLLEGE, THRIKKAKARA affiliated to Mahatma Gandhi University, Kottayam, during the period 2020-2022.

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This is to certify that the dissertation entitled "**Evaluation of Adsorption Efficiency of Zirconium Impregnated Granular Activated Carbon for the Removal of Heavy Metal Ions Pb^{2+} and Cd^{2+}**" submitted to Mahatma Gandhi University, Kottayam, in partial fulfillment of the requirement for the degree of Master of Science in Environment Science and Management is an authentic record of original work done by Ms. Saniya E Santhosh (Reg No: 200011011986) M.Sc. student, Department Chemistry Bharata Mata College, Thrikkakara, under my guidance in the School of Environmental Studies, Cochin University of Science and Technology, kochi -682022 during the period from 6th May 2022 to 31st July 2022. The results embodied in the dissertation work have not been submitted to any other Institution or University for the award of any Degree

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DECLARATION

I **SANIYA E SANTHOSH** hereby declare that this project report entitled "**Evaluation of Adsorption Efficiency of Zirconium Impregnated Granular Activated Carbon for the Removal of Heavy Metal Ions Pb^{2+} and Cd^{2+}**", is recorded of bonafied work carried out at the School ofEnvironmental Studies, Cochin University of Science and Technology, under the supervision and guidance of **Prof. Dr. V. SIVANANDAN ACHARI**, Dean and Professor, School of Environmental Studies, Cochin University of Science and Technology, Kerala and co-guidance of Dr. Sindhu Joseph, Assistant Professor, Department of Chemistry, BHARATA MATA COLLEGE, THRIKKAKARA and the same has not been submitted elsewhere for any degree or diploma earlier.

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ABSTRACT

Surface modification of activated carbon using metal, metal oxides, nano particles, and chemical reagents greatly affect the development of surface porosity, surface area and adsorption affinity. In this regard, zirconium as zirconyl chloride is being identified as activation agent to improve porosity of coconut shell based GAC. Zirconium (Zr^{4+}) is an important material because of its use in different fields of chemistry (ceramics, fuel cells, biomaterials, thermal barrier coatings and catalysis). This research work mainly discusses the preparation, adsorption kinetics, and adsorption isotherm studies of Zr^{4+} modified coconut shell carbons. There are four different types of granular activated carbons prepared by chemical activation at different Zr^{4+} / C ratios (Zr/C ratios of 0.002,0.008, 0.015,0.022) and at activation temperature of 1073K. Surface functional group of prepared carbon was analyzed by using FTIR and results showed that there is no additional functional group is noted by changing the impregnation ratio of Zr^{4+} in GAC. Adsorption efficiency towards heavy metal ion is determined by using Pb^{2+} and Cd^{2+} as adsorbates. The ability of zirconium impregnated activated carbon (GACZR) to adsorb Pb^{2+} and Cd^{2+} from an aqueous solution has been investigated through batch experiments. The adsorption of lead and cadmium onto GACZR series carbons has been found to depend on adsorbent contact time and impregnation ratio. The adsorption of Pb^{2+} on GACZR series was rapid during the first 60 min and the equilibrium attained within 360 min. While, the adsorption of cadmium (II) ions onto GACZR rapid for the first 120 min and equilibrium was nearly reached after 240 min. The experiments were carried out at natural solution pH. Equilibrium data fitted will with Langmuir and Freundlich model with maximum adsorption capacity of 59.81mg of Pb/g and 28.12939mg of Cd/g. The kinetic processes of Pb^{2+} and Cd^{2+} adsorption on GACZR series were described by applying pseudo-first-order and pseudo-second-order kinetic models. The kinetic data for the adsorption process obeyed a pseudo-second-order kinetic model, suggests that the adsorption process is chemisorption. The GACZR series investigated in this study showed sufficient potential for the removal of Pb^{2+} and Cd^{2+} from aqueous solution than the basic carbon GAC.

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INTRODUCTION

1.1 General Introduction

Drugs and pharmaceutical industries uses various chemical ingredients, hence their industrial discharges may contain organics and heavy metal ions as pollutants. Removal of these organic pollutants, heavy metals and pathogens are very important to control their release into environment. The prominent among them are zinc, nickel, lead, cadmium, cobalt, copper, iron, chromium, arsenic, manganese and mercury. Adsorption has proven to be economical and efficient method for the treatment of the pollutants. Several adsorbents such as activated carbon, silica, and graphene can be used in the purification of water. Activated carbon (AC) is a processed form of carbon-based materials consisting of microscale pores with high surface area, broad surface reactivity, diverse pore size distribution and chemical as well as thermal stability. The activated carbons have been generally used in various separation techniques of solid–liquid interface pollutants, gaseous pollutants, pharmaceutical waste, catalytic materials, and elimination of industrials pollutants (*Pu et al; 2019*)

Enhancement of the adsorptive capacity of activated carbon has been achieved either by different surface functional groups modification or by impregnation of metals with appropriate chemical or physical treatments or both. Metal impregnation or oxidative functionalization has been carried out, after the activation process by treating with appropriate chemicals in liquid or gaseous phases. These impregnation and oxidation processes have a higher influence on the modification of AC, as it enhances the number of active sites of the surface (*Achari et al; 2021*).

Usually, carbon surface modification has been carried out using different transition metals and organometallic compounds of various elements such as Al, Zn, Fe, Ag, and Ti. The utility of different transition metal is well-known in the field of water treatment as these metals do not leach out into water owing to their high positive character. Among different transition elements, zirconium is more superior over other elements in terms of efficiency, cost and toxicity. Literature also suggested the zirconium(IV) application, in the form of metal salts, does not exhibit any toxic effect on the aquatic environment (*sonal et al; 2018*). Hence, the present study mainly focuses on the pioneer use of zirconium oxychloride salt as an impregnated material on activated carbon to develop a novel adsorbent for the removal of Pb^{2+} from aqueous solution.

1.2. Adsorption

The term adsorption, first introduced by kayser in 1881, it is the phenomenon of accumulation of large number of molecular species at the surface of liquid or solid phase in comparison to the bulk. The adsorbent is the term used for the solid onto which adsorption takes place and adsorbate is the compound retained by adsorbent and the remaining atoms or molecules that are ready to be adsorbed in the system are called the adsorptive *(Gregg et al; 1982).*

The phenomenon of adsorption- the accumulation of concentration at a surface- is essentially an attraction of adsorbate molecules to an adsorbent surface. Interaction between adsorbate and adsorbent consist of molecular forces embracing permanent dipole, induced dipole, quadrupole electrostatic effect, otherwise known as van der waal' s forces

1.2.1. Types of adsorption

The two types of adsorption are physical adsorption or physi-sorption (van der Waals adsorption) and chemi-sorption (activated adsorption)

1.2.1.1. Physisorption

Physisorption is the adsorption in which the molecular interactions between the adsorbate molecules and the adsorbent are primarily governed by relatively weak van der Waals forces. Physisorption is also known as physical adsorption and it is an exothermic process. Its adsorption enthalpy is low, nearly 20 to 40 kJ /mol. Physisorption depends on the surface area of the adsorbent *(Roop et al; 2005)*.

Physisorption is not site specific, implying that it can take place on an entire surface of solid and with any molecule. Once the surface of the solid is covered by the first layer of adsorbate molecules, another layer can forms on the top of that, reffered as multilayer adsorption.

1.2.1.2. Chemisorption

Chemisorption involves exchange or sharing of electrons between the adsorbate molecules and the surface of the adsorbent resulting in a chemical reaction. Or involves the valence forces of the kind found in the formation of chemical contaminants**.** Chemisorption has irreversible

nature and it also favours high pressure. Due to chemical bonding, enthalpy of adsorption of chemisorption is high nearly 80 to 240 kJ/mol. Chemisorption depends on the surface area.

Chemisorption takes place in monolayer only in site specific and involves stronger forces than van der waal's forces due to the formation of chemical bonds *(Roop et al; 2005)*.

1.2.2. Types of adsorbents

Major types of adsorbents in use are: activated alumina, silica gel, activated carbon, molecular sieve carbon, molecular sieve zeolites and polymeric adsorbents *(*Grégorio *et al;2008).* Most adsorbents are manufactured (such as activated carbons), but a few, such as some zeolites, occur naturally. Each material has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces.

1.3. Activated carbon

Activated carbons are carbonaceous materials that an internal surface area of more than $400m^2g^{-1}$. Activated carbon in its broadest sense includes a wide range of processed amorphous carbon based material it is not truly an amorphous material but has a microcrystalline structure. Activated carbons have a highly developed porosity and an extended inter particulate surface area *(Roop et al; 2005)*.

1.3.1 Different types of activated carbon

Powdered activated carbon(PAC): PAC particles have typically a particle size less than 100 m. Its application involves industrial and muncipal waste treatment, food industry, and in pharmaceutical field.

Granular activated carbon(GAC): GAC particles have a mean particle size in the range of 1-5mm. It is used for both liquid and gas phase applications. GAC has more advantage over PAC that can be regenerated, has low pressure drop, high apparent density, high hardness.

1.3.2. Structure of activated carbon

The high adsorptive capacities of activated carbons are highly related to porous characteristics such as surface area, pore volume, and pore size distribution. The porous structure formed during the carbonization process is developed further during the activation process, when the

spaces between the elementary crystallites are cleared of tar and other carbonaceous material. The activation process enhances the volume and enlarges the diameters of the pores.

Activated carbons are associated with pores starting from less than a nanometer to several thousand nanometers. The International Union of Pure and Applied Chemistry (IUPAC) classified the pores into three groups based on their width. Width is the distance between the walls of a slit-shaped pore or the radius of a cylindrical pore. Pore sizes in adsorbents may be distributed throughout the solid. Pore sizes are classified generally into 3 ranges: macropores have "diamaters" in excess of 50 nm, mesopores (also known as transitional pores) have "diameters" in the range 2 – 50 nm, and micropores have "diameters" which are smaller than 2 nm.
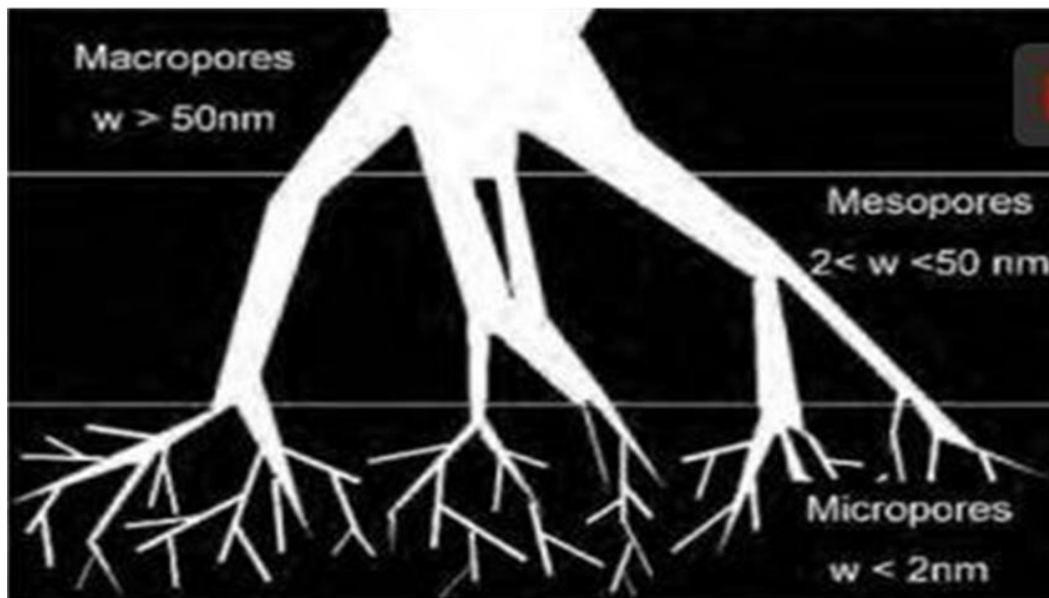
Figure 1.1 : Graphical representation of pore structure on activated carbon

1.3.2.1 Crystalline structure

During carbonization, microcrystalline structure of activated carbon develops. Activated carbon structure is different from that of graphite with respect to the interlayer spacing. In graphite interlayer spacing is 0.335 nm and in activated carbon is 0.34 to 0.35 nm. Activated carbons are classified into two types, based on graphitizing ability, these are graphitizing and non-graphitizing carbons. In graphitizing carbon, it contains number of graphene layers oriented parallel to each other. The carbon obtained was delicate due to the weak cross linking

between the neighbor microcrystallites and had a less developed porous structure. The non-graphitizing carbons are hard due to strong cross linking between crystallites show well developed micro pores structure (Franklin 1951, Jenkins and kawamura 1976). The formation of non-graphitizing structure with strong crosslinks is promoted by the presence of associated oxygen or by an insufficiency of hydrogen in the original raw material *(Spagnoli et al;2017).*
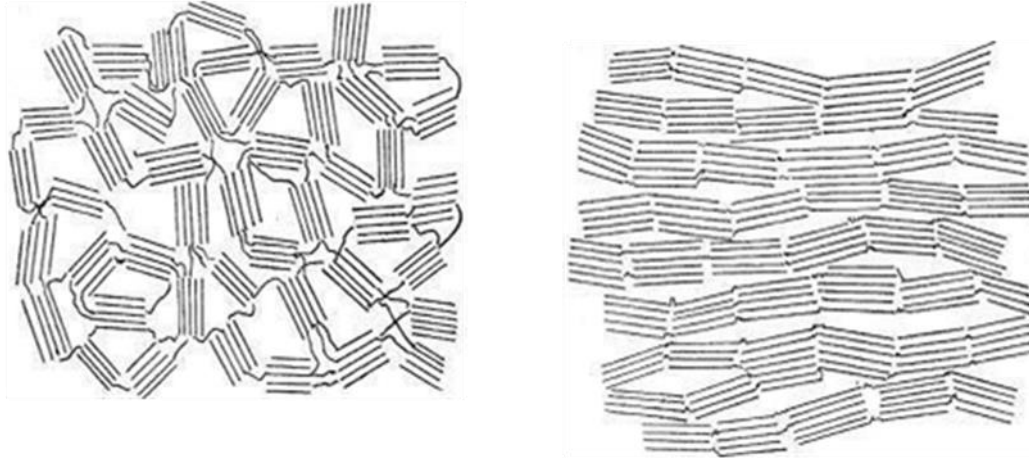
Figure 1.2 : Schematic illustration of structure of activated carbon ;(a) graphitizing carbon and (b) non-graphitizing carbon

1.3.2.2. Chemical structure

Activated carbon has porous and crystalline structure, with this it also has chemical structure. Though the adsorption capacity of activated carbon is determined by its porous structure but is strongly influenced by a relatively small amount of chemically bonded heteroatoms (mainly oxygen and hydrogen) *(Bansal et al., 1988).* The variation in the arrangement of electron clouds in the carbon skeleton result in the creation of unpaired electrons and incompletely saturated valencies which influences the adsorption properties of active carbons, mainly for polar compounds.

1.4. Adsorption isotherms

Adsorption isotherms are commonly used to reflect performance of adsorbents in adsorption processes. To examine the relationship between the metal uptake (q_e) and concentration of metal ions (C_e) at equilibrium, adsorption isotherm model are widely used for fitting data.

1.4.1 Types of adsorption isotherms

Five different types of adsorption isotherms and their characteristics are explained below:
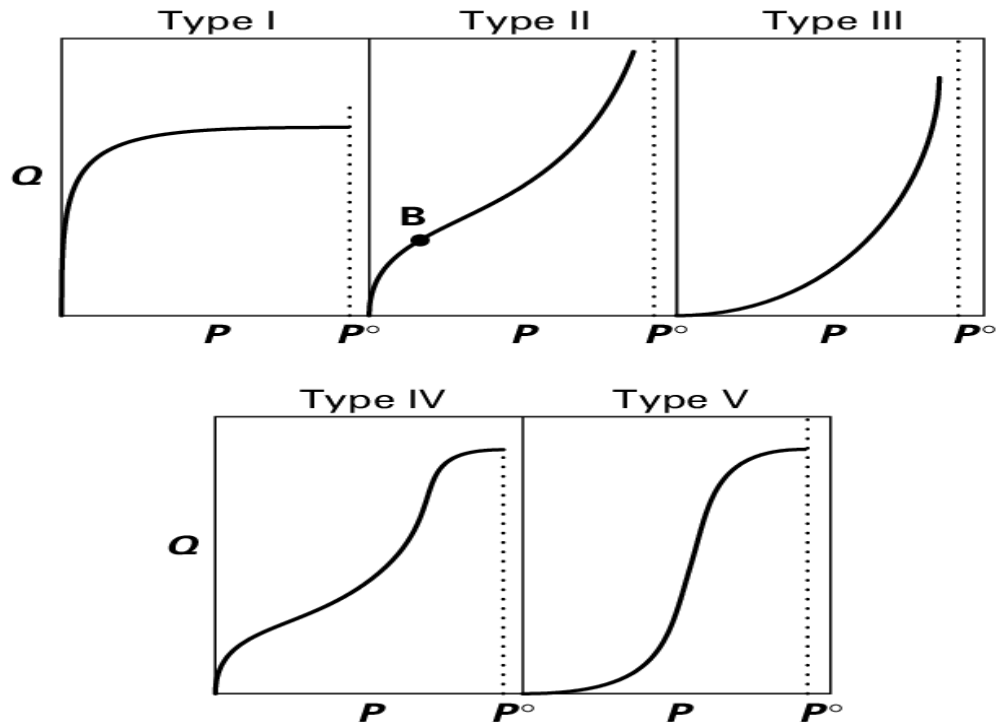
Figure 1.3 : IUPAC classification of Adsorption Isotherms

1.4.1.1 Type 1

- Type one graph depicts Monolayer adsorption
- This graph can be easily explained using Langmuir Adsorption Isotherm.

1.4.1.2. Type 2

- Type two Adsorption Isotherm shows large deviation from Langmuir model of adsorption.
- The intermediate flat region in the isotherm corresponds to monolayer formation.

1.4.1.3. Type 3

- Type three Adsorption Isotherm also shows large deviation from Langmuir model.

1.4.1.4. Type 4

- At lower pressure region of graph is quite similar to Type two. This explains formation of monolayer followed by multilayer.

1.4.1.5 Type 5

- Explanation of Type five graph is similar to type four.

1.4.2. Adsorption Isotherm Models

1.4.2.1. The Langmuir Isotherm Model

In 1932, the Langmuir adsorption model was proposed by Irving Langmuir and the main assumptions of this isotherm model are the following *(Irving Langmuir; 1918):*

o Adsorption occurs at specific binding sites that are localized on the surface of the adsorbent.
o All adsorption sites on the surface of the adsorbent are identical.
o The surface of the adsorbent is covered with a monolayer of adsorbed molecules.
o There is no interaction between the adsorbed molecules on the adsorbent surface.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e$$

Where C_e (mg/l) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, K_L (dm^3/g) and a_L (dm^3/mg) are the Langmuir constants.

By plotting $\frac{C_e}{q_e}$ vs Ce , a straight line is obtained whose slope $= a_L/K_L$ and intercept $1/K_L$ where a_L/K_L is the monolayer volume and from the slope a_L can be calculated. The favouratability of a Langmuir adsorption process can be determined by dimensionless constant separation factor R_L.

$$R_L = \frac{1}{1 + a_L C_0}$$

Where R_L is a dimensionless constant separation factor.

1.4.2.2. Freundlich isotherm

The Freundlich isotherm model is used for the description of the multilayer and heterogeneous adsorption of molecules to the adsorbent surface and non-linear energy adsorption from solution phase. Equation here is an exponential equation which assumes that as the adsorbate solution concentration increases, the concentration of adsorbate on the adsorbent surface increases.

The Freundlinch adsorption isotherm equation is given by,

$$q_e = k_F c_e^{\frac{1}{n}}$$

$$log q_e = log K_F + \frac{1}{n} log C_e$$

A plot of $log q_e$ vs $log\ C_e$ gives a straight line whose intercept is $log K_F$ and slope is $1/n$ from that the values of n and K_F can be calculated.

q_e – Amount of adsorbed from solution per uint mass of adsorbent (mg/g or m mol/g)

C_e – residual concentration of adsorbate at the equilibrium (mg/l or m mol/l)

K_F is the adsorption capacity constant for multi-layer coverage (mg/g)

n is the intensity of adsorption constant.

1.5. Review of literature

Kadirvelu, (et al; 2003) was conducted a study on activated carbon prepared from coirpith, an agricultural solid waste by-product, has been used for the adsorption of Cd(II) from aqueous solution. Parameters such as the agitation time, metal ion concentration, adsorbent dose and pH were studied. The results show that adsorption data fit well with the Langmuir and Freundlich isotherm models. It was observed that adsorption capacity (Q_0) calculated from the Langmuir isotherm was 93.4 mg Cd(II)/g at an initial pH of 5.0 at 30 °for the particle size 250–500 μm. The percent removal increased with pH from 2 to 4 and remained constant up to pH 10. Desorption studies was performed with dilute hydrochloric acid. Quantitative recovery of the metal ion was also possible. The mechanism of adsorption seems to be an ion exchange.

Jusoh (et al; 2007) was carried out a study to examine the potential and effectiveness of granular activated carbon (GAC) to remove heavy metals, particularly cadmium (Cd) and lead (Pb) through adsorption from the prepared solutions respectively. A fixed bed column test was conducted to simulate the actual condition of adsorption in a continuous manner in a filtration process. Different flow rates were used to evaluate their effects on the column performance where different breakthrough curves was obtained. The Adam-Bohart breakthrough curve equation was used to predict the breakthrough curve and to obtain the adsorption capacity of cadmium and lead on GAC. The results showed that the Adam-Bohart equation fitted the experimental data well and cadmium and lead can be successfully removed by granular activated carbon (GAC) through the column test.

Bernard (et al; 2013) was conducted a study on activated carbon produced from coconut shell (ACS) as an adsorbent to remove Cu^{2+}, Fe^{2+}, Zn^{2+} and Pb^{2+} ions from electroplating industrial wastewater. The activated carbon produced was chemically activated with zinc chloride. Batch adsorption experiment was conducted to examine the effects of adsorbent dosage, contact time, pH and stirring rate on adsorption of Cu^{2+}, Fe^{2+}, Zn^{2+} and Pb^{2+} from the wastewater. The obtained results showed that, the adsorption of the metal ions was adsorbent dosage, contact time, pH and stirring rate dependent. The optimum adsorbent dosage, stirring rate and pH, were found to be at 1g, 350 rpm and pH 6 respectively. Kinetic studies showed that pseudo-second-order reaction model best described the adsorption process. The study also showed that activated carbon prepared from coconut shell can be efficiently used as low cost alternative for removal of metal ions.

Moreno (et al;2011) was synthesised activated carbon from coconut shells and used for the removal of metal ions (manganese, iron, nickel and copper) from aqueous solutions. Two different adsorption models was used for analysing the data. Adsorption capacities was determined: copper ions exhibited the greatest adsorption on activated carbon obtained from coconut shells because of their size and pH conditions. Adsorption capacity varied as a function of the pH. Adsorption isotherms from aqueous solutions of heavy metals on ACCS were determined and was found to be consistent with Langmuir's adsorption model. Adsorbent quantity and immersion enthalpy also were studied. The results was compared with other adsorbents used in a prior study.

A study was conducted by Tangjuank (et al;2009) on activated carbon prepared from cashew nut shells using potassium hydroxide activation at 850°C in N_2 and CO_2 atmosphere was used

as an adsorbent for the removal of chromium ions from aqueous solutions. The adsorption of Cr(III) ions on activated carbon was studied. The effect of experimental parameters such as, pH of initial concentration of Cr(III) solutions, contact time, dosage of adsorbent and initial concentration of Cr(III) solutions was investigated. The Freundlich and Langmuir isotherm fitted well to data of Cr(III) adsorption. Cr(III) uptake capacity was 13.93 mg/g which was calculated from the Langmuir isotherm.

V.A Smith (et al;2021) tested for removal of Cr (VI) onto the surface activated carbons prepared from cashew nut shells and modified by grafting polyethylenimine. The removal efficiency of carbons without and with polyethylenimine decreased with an increase in pH, with maximum efficiency found at pH 2. The average maximum adsorption capacities of carbons were calculated to be 340 ± 20 mg/g and 320 ± 20 mg/g for unmodified and modified carbons, respectively. Surface characterization of carbons revealed that C–O functionalities are actively involved in both polyethylenimine grafting and Cr (VI) removal. Moreover, lactone groups and amides, formed by polyethylenimine grafting, seemingly undergo acid hydrolysis with formation of phenol and carboxylic groups. Considering that Cr (III) is the only form of chromium found on the surface of both carbons, the reduction mechanism is deduced as the predominant one. Here Cr (VI), majorly present as $HCrO_4^-$, is attracted to the positively charged carbon surface, reduced to Cr (III) by phenol groups, and adsorbed inside the pores. The mechanism of Cr (VI) removal appears to be similar for unmodified and modified carbons, where the smaller adsorption capacity of the latter one can be related to steric hindrance and pore inaccessibility

G. Alagumuthu (et al, 2010) was conducted a study on Zirconium impregnated cashew nut shell for the adsorption of fluoride from aqueous solution. The results show that zirconium impregnated cashew shell carbon have great potential for the removal of fluoride ions. 80.33% of removal has been identified in 3mg/l of 100ml fluoride using 1.5mg dosage of adsorbent. The result shows that adsorption isotherm most fitted for Langmuir isotherm mode. The kinetic data showed that the sorption process follows pseudo-second order equation. The sorption process was complex, both at the boundary of liquid film and intra-particle diffusion contributed to the rate- determining step. The regeneration of the adsorbent is possible 96.2% of 2.5% sodium hydroxide in 180 min.

Thang (et al;2021) study focused on evaluating the influences of variable factors, such as activation temperature and time, on the properties of the activated carbon obtained from cashew

nut shell (CNS). Methylene blue (MB) adsorption was applied to understand the adsorption mechanism of the products. The results show that increasing the activation temperature led to a rise in the adsorption capacity of the activated carbon within the temperature range of 800 to 850 °C. Otherwise, the values were reduced when the temperature was greater than 850 °C and this was related to the thermal decomposition of carbon. The adsorption capacity also increased when the activation time was changed from 30 min to 50 min. However, in the activation time range from 50 to 70 min, there was a reduction of the adsorption capacity of CNS-based activated carbon. The results also show that the MB adsorption of the activated carbon occurred with one-site-occupancy in the first layer and then layer-by-layer adsorption formation.

In 2007 Spagnoli (et al;2007) prepared activated carbon from cashew nut shells by chemical activation with zinc chloride. Cashew nut oil was extracted from the shells, followed by various ratios of impregnation at 400 °C. The structural features of the carbons were characterized by nitrogen adsorption and scanning electron microscopy. The surface chemistry was studied by Fourier transform infrared spectroscopy and potentiometric titration. The sample activated at the ratio of 1.5:1 (zinc chloride/shells) showed the highest surface area, pore volume, and the amount of basic surface groups. Equilibrium adsorption data had the best fit to Langmuir equation for all the activated carbons. The highest maximum adsorption capacity was found for the sample with 1.5:1 ratio. The linear correlation was found between the adsorption capacity and the surface area, the adsorption capacity and the volume of pores with diameter of 1.6–2 nm, and the adsorption capacity and the amount of basic groups. Methylene blue molecules are likely attracted to the carbon surface by dipole-dipole interactions between nitrogen in methylene blue and phenolic groups of carbon. Finally, the effect of carbonization temperature on adsorption capacity was studied, and the carbonization temperature of 500 °C resulted in the best adsorption capacity value for methylene blue, 476 mg/g.

Kumar (et al;2007) investigated the removal of Congo red (CR) dye from an aqueous solution where Cashew nut shell (CNS) - a novel, low cost adsorbent prepared from agricultural waste has been utilized as the adsorbent. The effect of pH, adsorbent dose, initial dye concentration, time and temperature on adsorption was studied. The results indicate that CNS can be employed as a low cost alternative compared to other commercial adsorbents. The experimental data were analyzed by Langmuir, Freundlich, Redlich–Peterson, Koble–Corrigan, Sips, Toth, Temkin and Dubinin–Radushkevich adsorption isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined using MATLAB 7.1.

Thermodynamic parameters such as ΔG^o, ΔH^o and ΔS^o have also been evaluated and it has been found that the sorption process was feasible, spontaneous and exothermic in nature. Pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to fit the experimental data. Kinetic parameters, rate constants, equilibrium sorption capacities and related correlation coefficients, for each kinetic model were calculated and discussed. It was shown that the adsorption of CR could be described by the pseudo-second-order equation, suggesting that the adsorption process is a presumably chemisorption.

Chapter 2

AIM AND OBJECTIVE

The aim and objective of this project work is to prepare and evaluate the efficiency of Zr^{2+} modified activated granular carbon (GACZR series) for the removal of metal ions (Pb^{2+} and Cd^{2+}) from aqueous solutions. Commercial activated carbon (GAC) was used as a reference to compare the maximum adsorption capacity. The effect of operating variables such as contact time, and initial metal ion concentration on the percentage removal of metal ions (Pb^{2+} and Cd^{2+}) by these adsorbents is investigated. In order to understand the adsorption nature, equilibrium isotherm and kinetic parameters were evaluated and discussed in detail.

Chapter 3

METHODOLOGY

3.1. Carbon

The basic carbon is procured from a nearby carbon manufacturing industry Indo-German carbon Limited, Binanipuram, Cochin, Kerala, India [particle size (US mesh) 12x40, lodine No.1100 mg/g, apparent density 0.50 g/cc, moisture 5%, ash 4%) is used throughout the study as the starting material. It is represented as GAC.

3.1.1. Washing of carbon

100 grams of carbon is washed with distilled water for 3 times. After washing with distilled water 0.05N NaOH and 0.05 N HCl is used separately for washing to remove acid and alkali impurities. The carbon is again washed with distilled water until the carbon pH obtained near the neutral value. The washed carbon collected and dried in hot air at 110°C. The dried carbon is designated GAC.

3.2. Preparation of GACZR - impregnation of zirconium

Different weights of zirconyl chloride ($ZrOCl_2.8H_2O$) noted as the impregnation ratio 0.0685 0.265,0.5238 and 0.785 (Zr/C ratios of 0.002,0.008, 0.015,0.022) were used in each 10 g of carbon for surface loading. Impregnation was done by mixing the GAC and activating agent of $ZrOCl_2.8H_20$ at 85°C for 2 hours with a magnetic stirrer. After stirring sample were placed in a water bath for about 5-6 hours and finally dried in an air oven at 383K. The prepared sample again activated with steam at 1073K and represented as GACZR series with respect to their Zr/C ratio such as GACZR $_{0.002}$, GACZR $_{0.008}$, GACZR $_{0.015}$ and GACZR $_{0.022.}$

3.3. Surface characterisation by FTIR

Surface functional group present in the surface of prepared carbon samples were analysed by FTIR (FTIR spectrometer model: NICOLET IS5, Brand: Thermo Fisher)

3.4. Batch Adsorption Experiment

Batch adsorption experiment were performed by contacting 250 mg of the activated samples with 25 mL of the aqueous solution of Pb^{2+} and Cd^{2+} concentrations 50 mg/l of natural solution pH. The experiment was performed in a mechanical shaker at controlled temperature

$(25 \pm 2 \, °C)$ for the time ranging between 10 and 480 min. At the end of the predetermined time, the suspension was filtered using Whatman filter paper to make it carbon free. The remaining concentration of Pb^{2+} and Cd^{2+} in each sample after adsorption was determined by Perkin Elmer (Pinaccle 900H) Atomic Absorption Spectrophotometer (AAS).

3.4. Adsorption isotherms study

Adsorption isotherm studies of heavy metal ions Pb^{2+} and Cd^{2+} were performed by using batch technique in a water bath shaker at constant temperature at 30^0C. A stock solution of Pb^{2+} and Cd^{2+} was prepared by water bath shaker by dissolving the required amount of $Pb(NO_3)_2$ and $Cd(NO_3)_2$ millipore water. The stock solution was diluted wath Millipore water to obtain desired concentration, ranging from 10mg/L to 100mg/L (10,25,50,75 and 100mg/L).

The experiments were performed in a water bath shaker for a period of 6 hour and 4 hour for lead and cadmium respectively using 100 ml Erlenmeyer flasks containing 25 ml of Pb^{2+} and Cd^{2+} concentrations and adsorbent dose of 0.025 g. After predetermined time interval, solution is filtered using Whatman no.1 filter paper and analysed by using Atomic Adsorption Spectrometer.

3.5. Instrumentation

1) Electronic Weighing Balance: Sartorius model was used for accurate weighing

2) Air oven: LABLINE oven used for drying the sample

Figure 3.1 : Air oven: LABLINE oven

3) Muffle Furnace: Tempsen model LMT-512 SP muffle furnace was used for heat treatment steps. The temperature range varied between 20⁰C and 1200⁰C with accuracy of 5⁰C

Figure 3.2 : Muffle Tempsen model LMT-512 SP muffle furnace

4) Temperature controlled water bath shaker: HEXATECH Model Water shaker are used in the batch Experiments

Figure 3.3 : Temperature controlled water bath shaker : HEXATECH Model Water shaker

5) Atomic absorption spectrometer (pinnacle 900H, Perkin Elmer): Used for the analysis of Pb^{2+} and Cd^{2+}

Figure 3.4 : Pinnacle 900H Atomic Absorption Spectrometer

Chapter 4

RESULTS AND DISCUSSION

4.1 Characterisation of Activated Carbons

4.1.1. FTIR Study

The FTIR spectrum of activated carbon samples without heavy metal ions loaded were presented within 500-4000 cm^{-1} as shown in Figures 4.1. It is clearly noted that there are a number of adsorption peaks present in the samples that indicating different functional groups including water, acid, amide, alkane, alcohol, and alkene etc. (Giri et al; 2012).
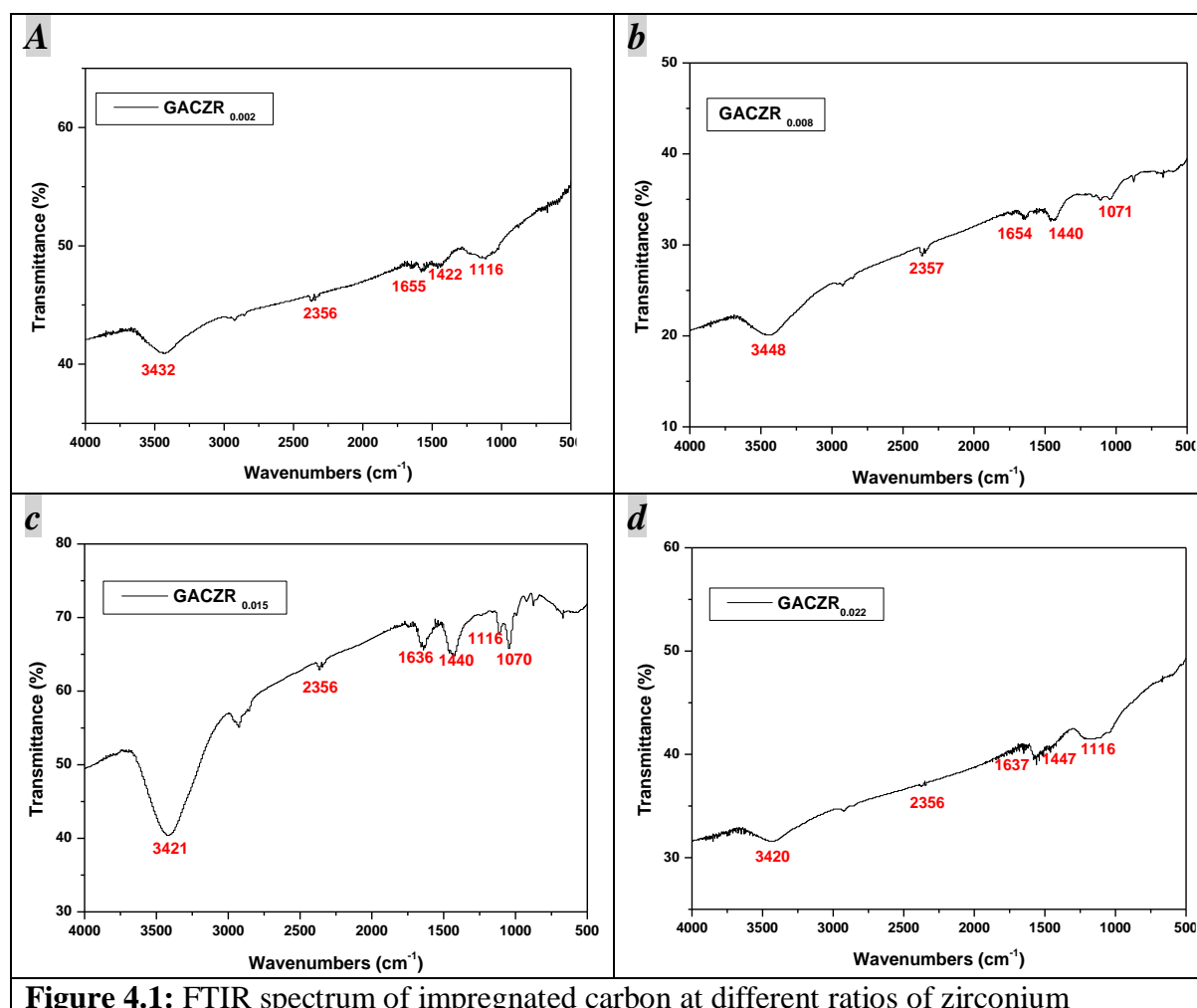

Figure 4.1: FTIR spectrum of impregnated carbon at different ratios of zirconium

It gives prominent peaks around at 3420 cm^{-1} due to adsorbed water molecule, 2910 cm^{-1} due to O-H stretching vibration and 1623 cm^{-1} due to quinine structure. The presence of the peaks

around 1620 and 1660 cm^{-1} suggests the presence of carbonyls C=O groups coming from the stretching of the C=C bond. The lines observed around 1450-1500 cm^{-1} could correspond to the vibrations in the plane of the aromatic rings. The peak 1070 cm^{-1} and 1100 cm^{-1} due to –C-OH stretching vibration characteristic respectively of primary and secondary alcohols. The FTIR spectra indicate the presence of oxygen containing surface functional groups such as hydroxyl groups, carboxyl groups, carbonyl groups in the activated carbon sample.

4.2 Solid -Liquid Adsorption Isotherm Study

Basic carbon (GAC) and its Zr^{4+} impregnated form (Zr/C ratios of 0.002,0.008, 0.015,0.022) are prepared and the relationship between contact time and adsorption isotherm are studied using lead and cadmium as absorbate. The pseudo-first-order and pseudo-second-order kinetic models were applied to model the kinetics of lead and cadmium adsorption onto prepared carbons. Langmuir and Freundlich isotherms equations are used for applying the adsorption data to optimize the design of specific adsorbent/adsorbate system.

4.2.1. Effect of Contact Time on the Adsorption of Lead (Pb^{2+})

Contact time is one of the effective factors in batch adsorption process. The relationship between contact time and lead sorption onto GAC and GACZR series carbons at initial lead concentrations of 50 ppm is shown in the Figure 4.2.
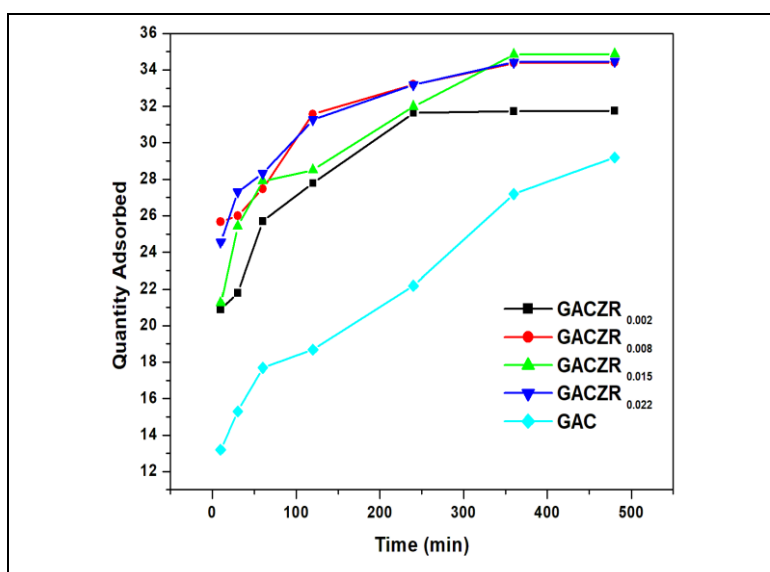

Figure 4.2: Effect of Contact Time on the adsorption of Pb^{2+}

As it is shown, adsorption rate initially increased rapidly, and the optimal removal efficiency was reached within about 1 hr for any initial concentration. The uptake of Pb^{2+} occurred in two stages i.e. an initial rapid uptake followed by subsequent slow uptake. The stages of sorption of lead on activated carbon might be controlled by the diffusion process from bulk to the surface or the heterogeneous nature of the adsorbent *(Ndi et al;2013)*. The adsorption process appeared to proceed rapidly when the numbers of available sites are much larger than the number of Pb^{2+} species to be adsorbed *(Panda et al;2017)*.

The required contact time increased with increase in lead adsorption. There was no significant change in equilibrium concentration after 6 hr, the adsorption phase reached to equilibrium. Therefore, the contact time is decided 360 min for all experiments.

4.2.3 Adsorption Kinetics for the adsorption of lead on GACZR series

In order to investigate the controlling mechanism of adsorption processes the pseudo-first-order and pseudo-second-order kinetic models were applied.

The pseudo-first-order rate equation, given as (Lagergren 1898):

$$\ln(q_e - q_t) = ln q_e - K_1 t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$
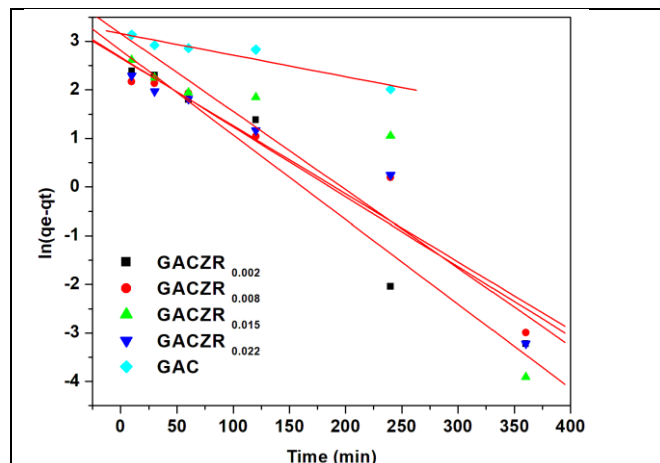

Figure 4.3: Pseudo First order Kinetic model for the adsorption of Pb^{2+} on GACZR series (C$_0$=50 ppm, time= 6 hr)

where q_t is the adsorption capacity at time t (mg/g) and k_1 (min^{-1}) is the pseudo-first order rate constant of the adsorption.

The application of the pseudo-first-order model to the experimental data is shown in Figure 4.2 from which the values of q_e and K_1 were determined from the intercepts and slopes of the plots (Table 4.1). The calculated values of q_e from the pseudo-first-order model were compared with those determined experimentally.

Table 4.1: Pseudo First order Kinetic Parameter for the adsorption of Pb^{2+} on GACZR series					
Sample	**K_1*10^3 (min^{-1})**	**lnq_e**	**q_e (cal) (mg/g)**	**q_e (exp) (mg/g)**	**R**
GACZR 0.002	17.41	2.81	16.69	31.77	0.9828
GACZR 0.008	13.98	2.66	14.28	34.42	0.9655
GACZR 0.015	16.09	3.16	23.64	34.86	0.9031
GACZR 0.022	14.05	2.58	13.25	34.46	0.9514
GAC	33.33	3.08	21.68	29.19	0.9893

The correlation coefficients (R^2) for the pseudo-first order kinetic model are very low. Moreover, a large difference of equilibrium adsorption capacity (q_e) between the experiment and calculation was observed (Table 4.1), it indicates that adsorption data not fitted to pseudo first-order kinetic model.

The pseudo-secon d-order equation is expressed as (Ho and McKay 1999)

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

Figure 4.4: Pseudo Second order Kinetic model for the adsorption of Pb^{2+} on n GACZR series
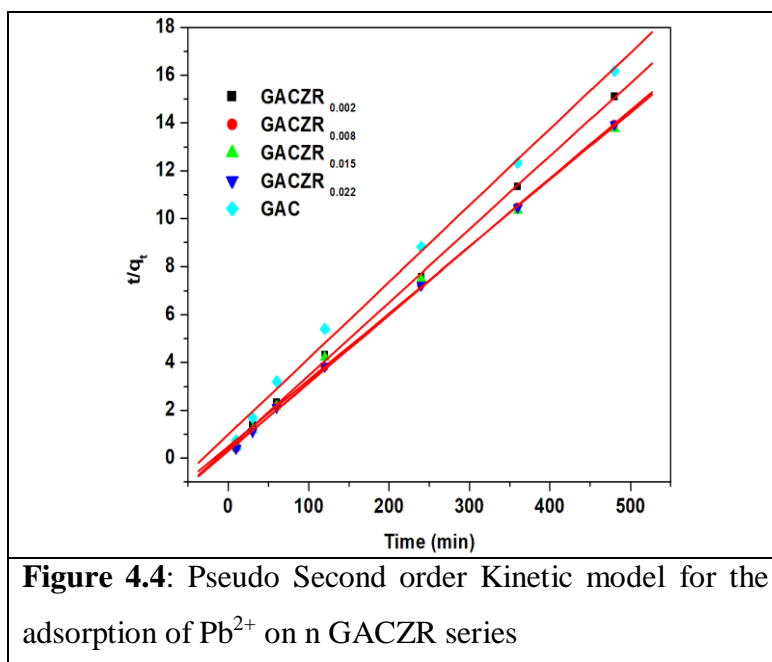
The application of the pseudo-second order model to the experimental data is shown in Figure 4.4 from which the values of q_e, and K_2 were determined from the intercepts and slopes of the plots (Table 4.2). The R^2 values (0.999) indicate that the pseudo-second order model provides a reasonable fit to the experimental data. Experimental q_e is well agreement with calculated q_e obtained from pseudo second order kinetics.
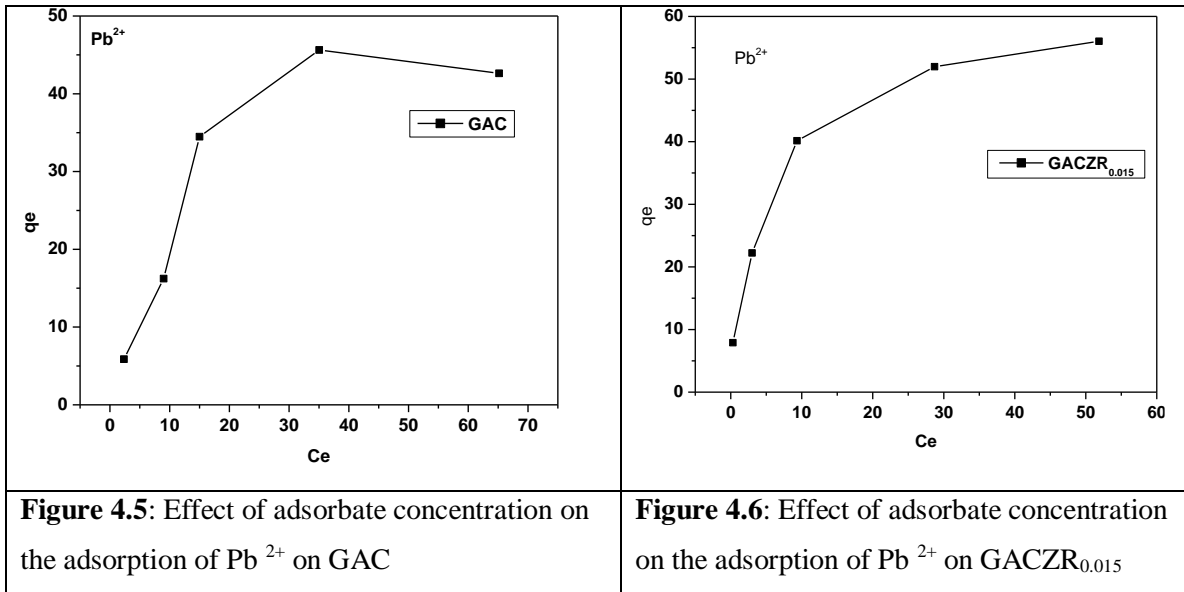
Table 4.2: Pseudo Second order Kinetic Parameter for the adsorption of Pb^{2+} on GACZR series

Sample	$\dfrac{1}{q_e}$	q_e (cal) (mg/g)	q_e (exp) (mg/g)	$\dfrac{1}{K_2 q_e^2}$	K_2*10^4 (gmg^{-1}min^{-1})	R
GACZR 0.06855	0.0305	32.74	31.77	0.4073	22.9	0.9996
GACZR 0.2656	0.0284	35.17	34.42	0.3158	25.59	0.9997
GACZR 0.52387	0.0279	35.83	34.86	0.4762	16.36	0.9987
GACZR 0.7826	0.0285	35.07	34.46	0.2798	29.05	0.9997
GAC	0.0327	30.58	29.19	0.8670	12.30	0.9961

If the adsorption system follows a pseudo-second order kinetics, then the rate limiting step may be chemical adsorption involving valency forces through sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces, and ion exchange *(Ho et al; 2006)*.

4.2.4. Effect of Concentration for the adsorption of Pb^{2+} on Zirconium incorporated carbon

As seen from Figure 4.5 and 4.6 the removal efficiencies for Pb(II) on GAC and $GACZR_{0.015}$ increased with increasing metal ion concentrations. The removal efficiency also varied from one adsorbent to another. The lead adsorption efficiencies on the $GACZR_{0.015}$ is higher than the other GAC adsorbents.

| **Figure 4.5**: Effect of adsorbate concentration on the adsorption of Pb $^{2+}$ on GAC | **Figure 4.6**: Effect of adsorbate concentration on the adsorption of Pb $^{2+}$ on $GACZR_{0.015}$ |

4.2.4.1 Langmuir Isotherm

The Langmuir Isotherm model assumes that adsorption occurs on a homogeneous surface by monolayer coverage and no subsequent interaction between adsorbed species.

The Equation (Xu et al. 2012) is as follows

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(3)$$

The linear plot of C_e/q_e verses C_e was made for the Langmuir isotherm (Figure 4.7 and 4.8). The R values (goodness fit criterion) were computed using linear regression for the isotherms. The results obtained show that for the two types of adsorbent materials, Langmuir isotherms are best suited for adsorption of Pb $^{2+}$ on GACZR $_{0.015}$
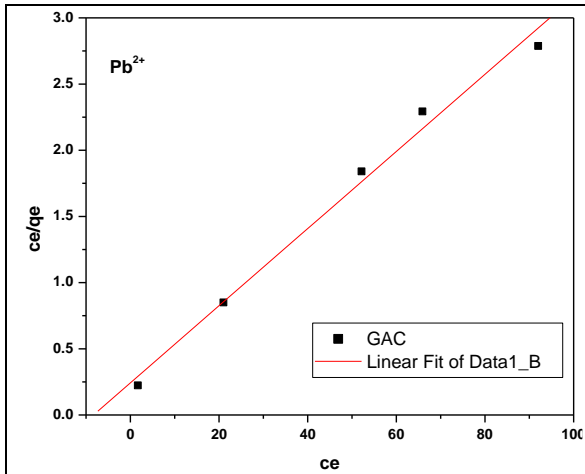
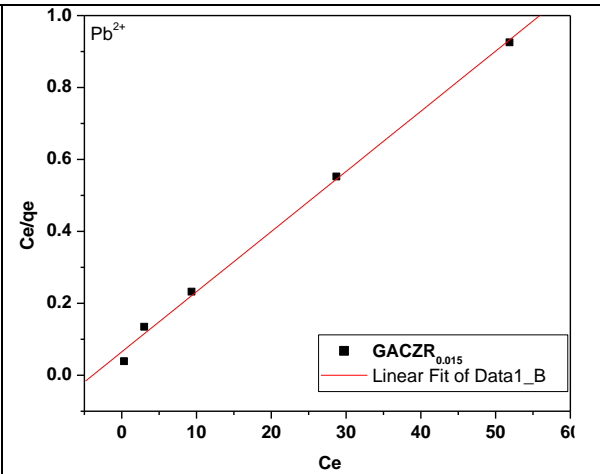| **Figure 4.7:** Langmuir isotherm of Pb^{2+} ions adsorption on GAC | **Figure 4.8:** Langmuir isotherm of Pb^{2+} ions adsorption on GACZR$_{0.015}$ |

The results obtained showed that GACZR$_{0.015}$ can adsorb 59.81 mg/g of Pb^{2+} ions from aqueous solutions comparable to that of GAC (34.32mg/g). These results show that Zirconium impregnated granular activated carbons made from agricultural waste (coconut shell) can be used with greater effectiveness for Pb^{2+} removal from pharmaceutical wastewater.

Table 4.3: Langmuir isotherm parameter for the adsorption of Pb^{2+}

Sample	$\dfrac{a_L}{K_L}$	V_m ($\dfrac{K_L}{a_L}$) (mg/g)	$\dfrac{1}{K_L}$	K_L (Lg^{-1})	a_L (Lg^{-1})	R
GACZR$_{0.015}$	0.0167	59.81	0.0651	15.36	0.2568	0.9985
GAC	0.02914	34.32	0.2427	4.12	0.1200	0.9948

4.2.4.2 Freundlich Isotherm

The Freundlich model is an empirical model based on multilayer adsorption on heterogeneous surfaces. The equation is commonly described as

$$\log q_e = log K_F + \frac{1}{n}\log C_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

The plot of log C$_e$ verses log q$_e$ gives the Freundlich parameters K$_F$ and n values. The n value in Freundlich equation was found to be 2.53 for GACZR$_{0.015}$ and 1.57 for GAC this indicates

the favorable adsorption of lead (II) onto these adsorbents. Compared to Langmuir isotherm, Freundlich isotherm is not well fitted to the adsorption data as the value of R^2 is $\cong 0.98$ and 0.94 respectively.
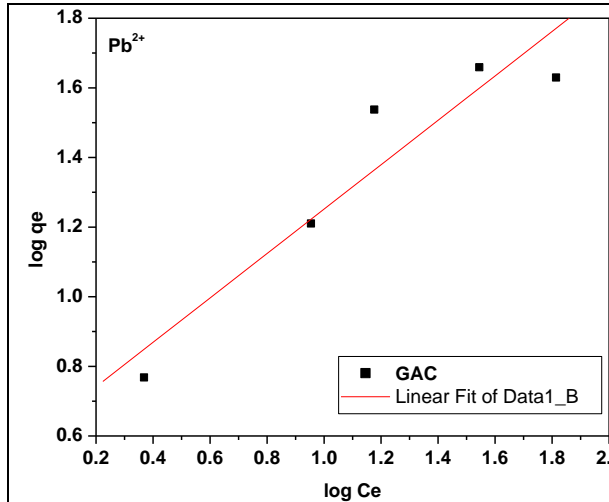
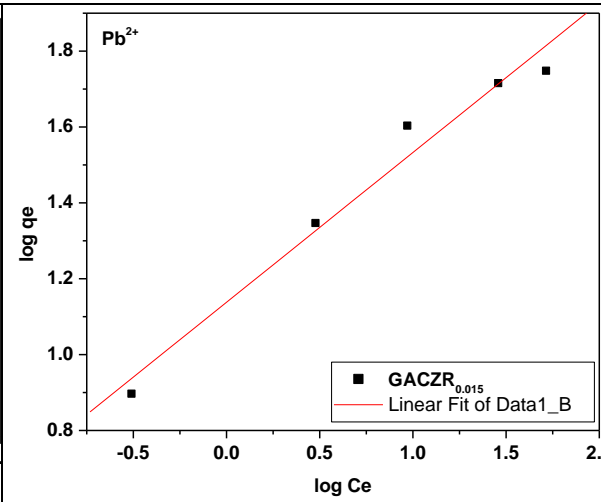|	
Figure 4.9: Freundlich isotherm of Pb $^{2+}$ ions adsorption on GAC	**Figure 4.10:** Freundlich isotherm of Pb $^{2+}$ ions adsorption on GACZR$_{0.015}$

The relatively low correlation of the Freundlich equation over the Langmuir equation proves that the adsorption process is mainly monolayer.

Table 4.4: Freundlich isotherm parameter for the adsorption of Pb^{2+}

Sample	$\dfrac{1}{n}$	n	$logK_F$	K_F (Lg^{-1})	R
GACZR$_{0.015}$	0.3947	2.53	1.14	13.74	0.9866
GAC	0.6378	1.57	0.6138	4.11	0.9453

The coefficient K_F is a parameter that reflects the amount of the active adsorption site whereas 1/n is a characteristic coefficient related to energy or intensity of adsorption *(Makene et al;2014).* As seen in Table, GACZR$_{0.015}$ is having large values of K_F compared to GAC.

4.2.5. Effect of Contact Time on the Adsorption of Cadmium (Cd^{2+})

The relationship between contact time and cadmium sorption onto GAC and GACZR$_{0.015}$ carbons at   initial cadmium concentrations of 50 ppm is shown in the Figure 4.11 and 4.12.

The effect of contact time on efficiency of cadmium (II) adsorption on $GACZR_{0.015}$ and GAC was investigated to study the rate of cadmium (II) removal and the results are shown in Figure 4.11 and 4.12. The data obtained from the adsorption of cadmium (II) ions onto the $GACZR_{0.015}$ showed that the adsorption increases with increase in contact time. The adsorption of cadmium (II) ions onto these was rapid for the first 120 min and equilibrium was nearly reached after 240 min.
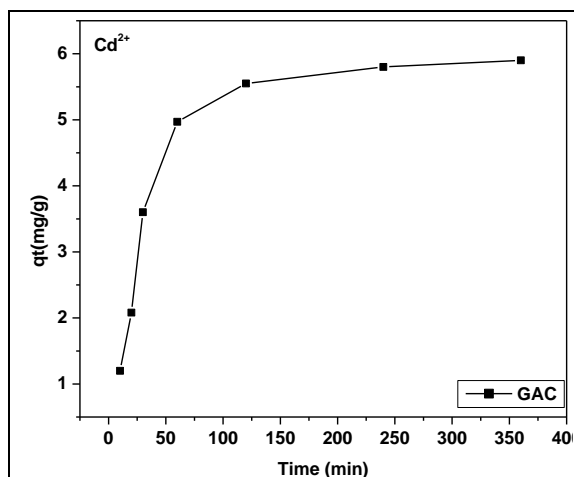

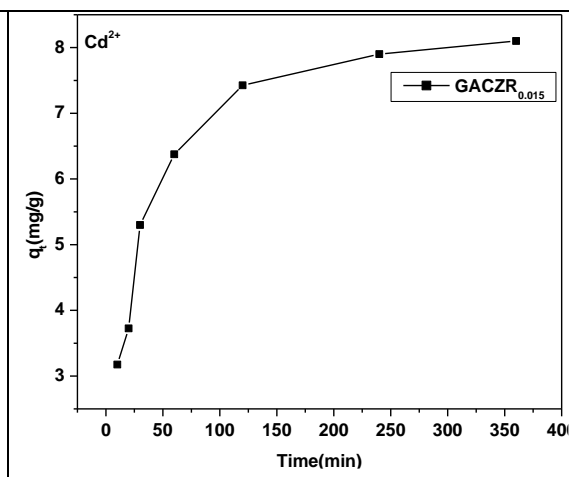| **Figure 4.11:** Effect of time on the adsorption of Cd^{2+} on GAC (C_0= 50 ppm)	**Figure 4.12**. Effect of time on the adsorption of Cd^{2+} on $GACZR_{0.015}$ (C_0= 50 ppm)

The metal uptake by the sorbent surface will be rapid initially and slow down as the competition for the decreasing availability of active sites intensifies by the metal ions remaining in the solution.

4.2.6. Adsorption Kinetics for the adsorption of Cd^{2+}

The kinetics study is required to find out the mechanism and rate determining step of a chemical reaction. Experiments were performed to find the required time for Cd (II) adsorption onto $GACZR_{0.015}$ and GAC.

4.2.6.1. Pseudo first order kinetics

Linear fit of ln (q_e-q_t) vs.time, gives the value of rate constant K_1 (min-1) and q_e from slope and intercept respectively.
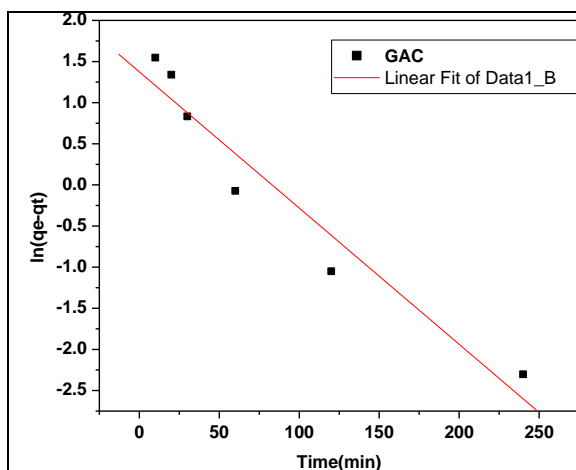
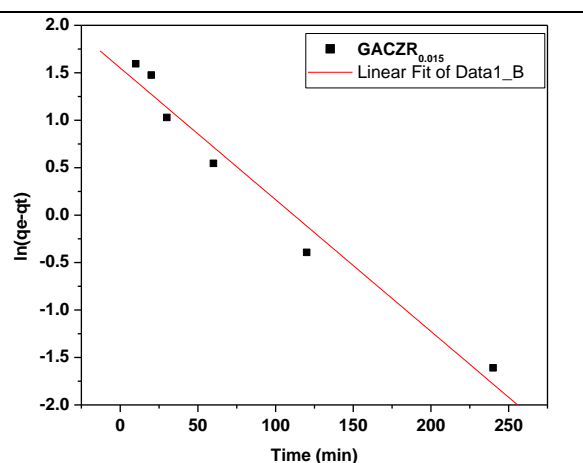| **Figure 4.13:** The pseudo-first-order kinetic model fitting for the adsorption of Cd^{2+} on GAC	**Figure 4.14:** The pseudo-first-order kinetic model for the adsorption of Cd^{2+} on GACZR$_{0.015}$

The results from the Table 4.5 indicating that the obtained R^2 -values were found to be low and also the difference between the calculated q_e and experimental q_e values were high. Therefore, the adsorption of metal ions onto these adsorbents is not following a pseudo-first-order kinetic model.

Table 4.5: Pseudo First order Kinetic Parameter for the adsorption of Cd^{2+} on GAC and GACZR$_{0.015}$

Sample	$K_1 * 10^3$ (min^{-1})	$\ln q_e$	q_e (cal) (mg/g)	q_e (exp) (mg/g)	R
GACZR $_{0.015}$	13.89	1.55	4.72	8.1	0.9854
GAC	16.56	1.37	3.95	5.9	0.9689

4.2.6.2. Pseudo second order kinetics

Plot of t/q_t verses t give linear relationship indicate the applicability of pseudo second order kinetics. The rate constant K_2 (g mg^{-1}min^{-1}) and equilibrium adsorption capacity q_e were calculated from the slop and intercept of the linear plot of t (time) vs t/q_t. The results show that the second order model is applicable to describe the adsorption kinetics of Cd (II)) onto GACZR$_{0.015}$ and GAC.
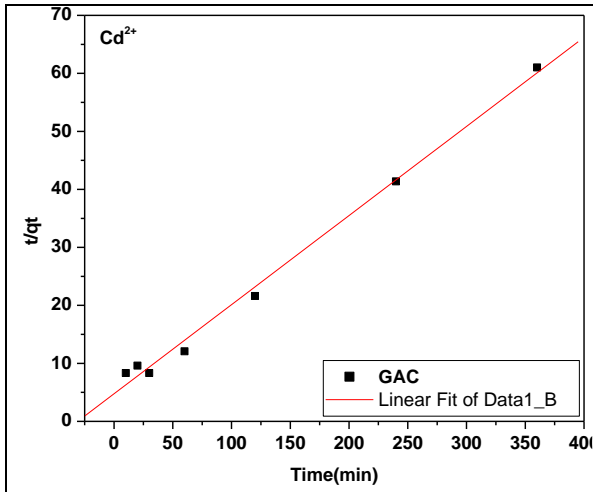
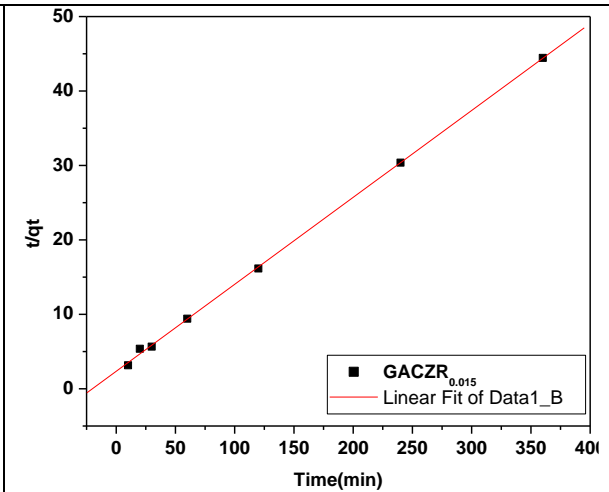| **Figure 4.15**: The pseudo-second-order kinetic model fitting for the adsorption of Cd^{2+} on GAC | **Figure 4.16:** The pseudo-second-order kinetic model fitting for the adsorption of Cd^{2+} on $GACZR_{0.015}$ |

The pseudo-second-order equation is expressed as (Ho and McKay 1999)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$$

From Table 4.6, obtained R -values for the pseudo-second-order kinetic model were found to be high (>0.99), which indicates the applicability of the pseudo-second-order kinetic model to better describe the adsorption of metal ions onto the $GACZR_{0.015}$ and GAC. The calculated q_e values were found to be close to the experimental q_e values.

Table 4.6: Pseudo Second order Kinetic Parameter for the adsorption of Cd^{2+} on GAC and $GACZR_{0.015}$

Sample	$\dfrac{1}{q_e}$	q_e (cal) (mg/g)	q_e (exp) (mg/g)	$\dfrac{1}{k_2 q_e^2}$	$K_2 * 10^3$	R
$GACZR_{0.015}$	0.1168	8.56	8.1	2.36	49.50	0.9998
GAC	0.1537	6.51	5.9	4.76	32.27	0.9969

4.2.7. Equilibrium Adsorption Isotherm Study for the adsorption of Cd^{2+}

The analysis of the adsorption isotherms data by fitting them into different isotherm models is an important step to find the suitable model that can be used for design process.
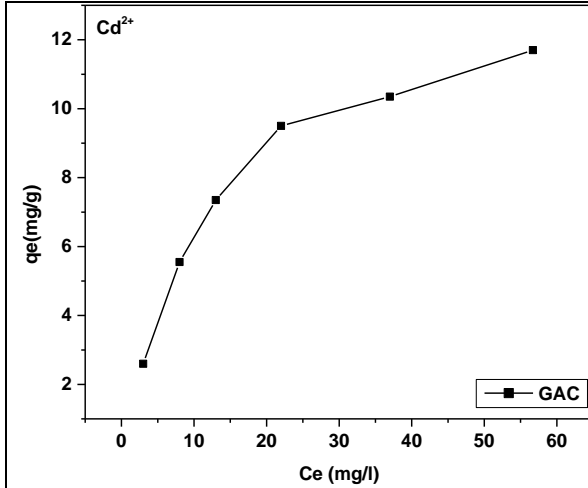

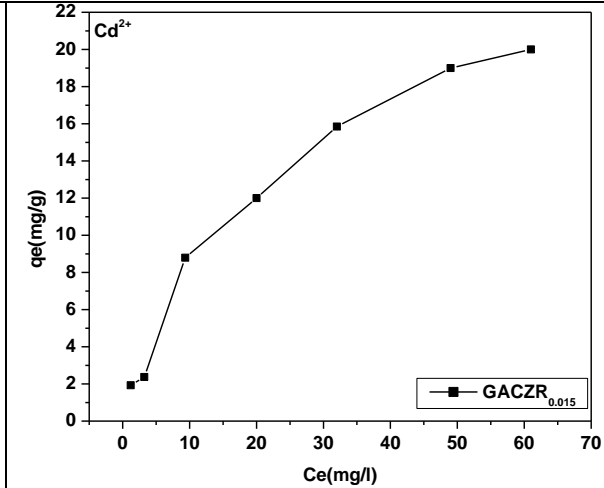| **Figure 4.17**: Effect of adsorbate concentration on the adsorption of Cd^{2+} on GAC | **Figure 4.18:** Effect of adsorbate concentration on the adsorption of Cd^{2+} on GACZR $_{0.015}$ |

4.2.7.1. Langmuir Isotherm

A linear plot of (C_e/q_e) against Ce was employed to give the values of q_m (from slope) and K_L (from intercept). They are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively.
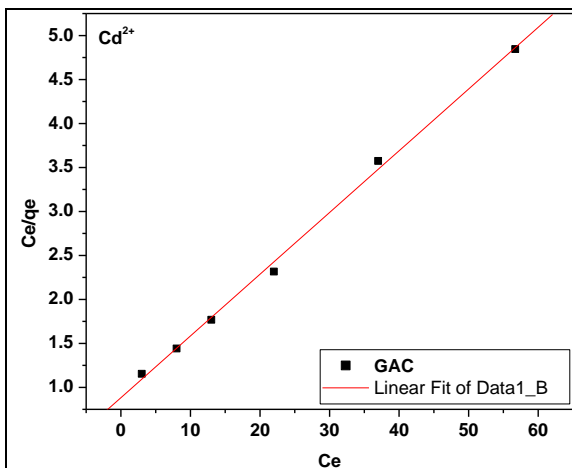
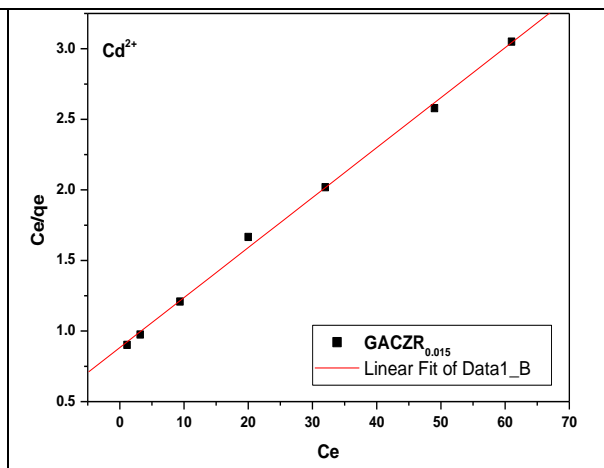| **Figure 4.19**: Langmuir isotherm of Cd^{2+} ions adsorption on GAC | **Figure 4.20:** Langmuir isotherm of Cd^{2+} ions adsorption on GACZR$_{0.015}$ |

The recommended isotherm equation for different adsorbent is selected on the basis of values of R^2. The linear equation of isotherm having more values of R^2 which is closer to 1.0 is the

most effective fitting isotherm. The results obtained show that for the two types of adsorbent materials Langmuir isotherms are best suited for adsorption of Cd^{2+} and the maximum monolayer adsorption capacity was found to be for GAC.

Table 4.7: Langmuir isotherm parameter for the adsorption of Cd^{2+}						
Sample	$\frac{a_L}{k_L}$	$Vm\ (\frac{k_L}{a_L})$ (mg/g)	$\frac{1}{k_L}$	K_L (Lg^{-1})	a_L	R
GACZR$_{0.015}$	0.0354	28.25	0.8831	1.13	0.04	0.999
GAC	0.0702	14.24	0.8827	1.13	0.0793	0.9987

4.2.7.2. Freundlich Isotherm

The plot of log C_e verses log q_e gives the Freundlich parameters K_F and n values. The n value in Freundlich equation was found to be 1.53 for GACZR and 1.98 for GAC this indicates the favorable adsorption of cadmium (II) onto these adsorbents. Compared to Langmuir isotherm, Freundlich isotherm is not well fitted to the adsorption data as the value of R^2 is $\cong$ 0.97.
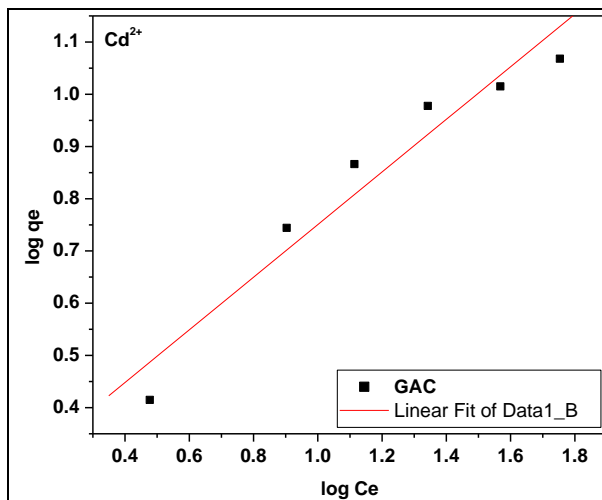

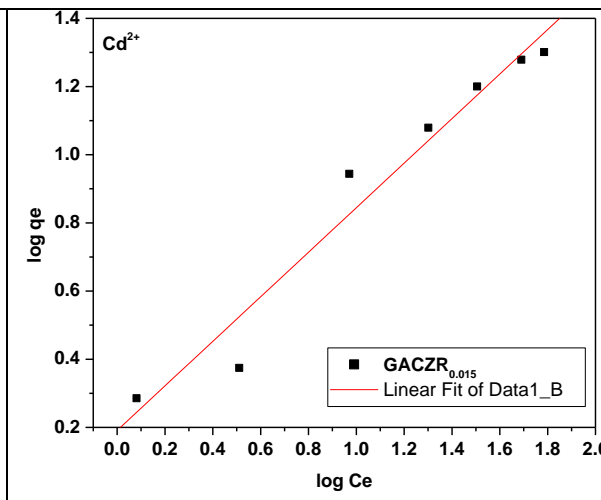| **Figure 4.21:** Freundlich isotherm of Cd $^{2+}$ ions adsorption on GAC | **Figure 4.22:** Freundlich isotherm of Cd $^{2+}$ ions adsorption on GACZR$_{0.015}$ |

4.2.7.2.1. Freundlich isotherm parameter for the adsorption of Cd^{2+}

Sample	$\dfrac{1}{n}$	n	$logK_F$	K_F (Lg^{-1})	R
GACZR$_{0.015}$	0.6534	1.53	0.1911	1.5528	0.9795
GAC	0.5037	1.98	0.2468	1.7652	0.9691

Table 4.8: Freundlich isotherm parameter for the adsorption of Cd^{2+}

The Freundlich equation is also suitable for a highly heterogeneous surface. Higher the K_F value, greater the adsorption intensity. Therefore, the K_F values which is slightly higher for the GAC confirms that the adsorption capacity of the GAC was greater than that of GACZR$_{0.015}$. The values of 1/n, less than unity is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentration and vice versa.

CONCLUSION

The present investigation shows that Zirconium impregnated carbon is an effective adsorbent for the removal of Pb^{2+} and Cd^{2+} from aqueous solutions. The removal capacity and efficiency were controlled by adsorbent dosage, agitation time, and metal ion concentration. The uptake of Pb^{2+} and Cd^{2+} occurred in two stages i.e. an initial rapid uptake followed by subsequent slow uptake. The stages of sorption of lead and cadmium on activated carbon might be controlled by the diffusion process from bulk to the surface or the heterogeneous nature of the adsorbent. From the kinetics studies it is observed that the adsorption of Pb^{2+} and Cd^{2+} is very rapid in the initial stage and decreases upon approaching equilibrium. The kinetics of Pb^{2+} and Cd^{2+} ions adsorption obeys the pseudo-second-order model, which suggests chemisorption as the rate-limiting step in the adsorption process. It indicates chemical adsorption comprises electron exchange between heavy metal ions and activated carbon. The experimental data were found to be fitted well with the Freundlich and Langmuir isotherm models. Langmuir isotherm model exhibited a superior fitting than the Freundlich model due to the higher values of correlation coefficient (R^2), which means that the adsorption of metal ions (Cd^{2+} and Pb^{2+}) occurred as monolayer on the adsorbent surface. The isotherms offered that the capacity of adsorption for Pb^{2+} was found to be higher than cadmium. The maximum sorption capacities of the Pb^{2+} and Cd^{2+} ions on $GACZR_{0.015}$ is detected as 59.81and 28.12 (mg/g), respectively. This results also reveal that activated carbon modified with zirconium is an efficient adsorbent for the adsorptive removal of heavy metal ions from aqueous solutions.

FUTURE ASPECTS

Experimental results of zirconium-based carbon shows that it can be used as a future adsorbent for removal of Heavy metal ions.

REFERENCE

(1)   Achari, V. S.; Lopez, R. M.; Rajalakshmi, A. S.; Jayasree, S.; Shibin, O. M.; John, D.; Sekkar, V. Microporous Carbon with Highly Dispersed Nano-Lanthanum Oxide (La2O3) for Enhanced Adsorption of Methylene Blue. *Sep. Purif. Technol.* **2021**, *279*, 119626. https://doi.org/10.1016/j.seppur.2021.119626.

(2)   Achari, V. S.; Rajalakshmi, A. S.; Jayasree, S.; Lopez, R. M. Adsorption of P-Nitrophenol from Aqueous Solutions by Zr4+activated Carbon: Adsorption Isotherm Studies. *Indian J. Chem. Technol.* **2018**, *25* (2), 158–169.

(3)   Achari, V. S.; Rajalakshmi, A. S.; Jayasree, S.; Lopez, R. M. Surface Area and Porosity Development on Granular Activated Carbon by Zirconium: Adsorption Isotherm Studies. *J. Appl. Res. Technol.* **2018**, *16* (3), 211–228. https://doi.org/10.22201/ICAT.16656423.0.16.3.719.

(4)   Achari, V. S.; Lopez, R. M.; Rajalekshmi, A. S.; Jayasree, S.; Ravindran, B.; Sekkar, V. Scavanging Nitrophenol from Aquatic Effluents with Triethyl Amine Catalyzed Ambient Pressure Dried Carbon Aerogel. *J. Environ. Chem. Eng.* **2020**, *8* (2), 103670. https://doi.org/10.1016/j.jece.2020.103670.

(5)   Alagumuthu, G.; Rajan, M. Equilibrium and kinetics of adsorption of fluoride onto zirconium impregnated cashew nut shell carbon, *Chem Eng J*. **2010**, 158(3):451- 457.

(6)   Atkins, P. W., Physical Chemistry. 5th Edition, Oxford. Oxford University Press **1995**.

(7)   Bernard, E.; Jimoh, A.; Odigure, J. Heavy metals removal from industrial wastewater by activated carbon prepared from coconut shell, *Res J Chem Sci*. 2231, 606X.

(8)   Grégorio, Crini.; Eric.; Lichtfouse, Lee.; Wilson, NM-C. Adsorption-Oriented Processes Using Conventional and Non-Conventional Adsorbents for Wastewater Treatment. Vol 17. France; **2018**. https://doi.org/10.1007/s10311-018-0786-8.

(9)   Ho, Y. S.; McKay, G. The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Research* **2000**, 34 (3), 735-742.

(10)   Ho, Y.S. Review of second-order models for adsorption systems, *J Hazard Mater*. **2006**, 136(3):681-689.

(11)   Irving, Langmuir. The adsorption of gases on plane surface of glass, mica and Platinum, *J Am Chem Soc Chem*. **1918**, 40(9):1361-1403

(12)   Jusoh, A.; Shiung, L. S.; Noor, M. J. M. M. A simulation study of the removal efficiency of granular activated carbon on cadmium and lead, *Desalination*. **2007**, 206(1-3), 9-16.

(13)   Kadirvelu, K.; Namasivayam, C. Activated carbon from coconut coirpith as metal adsorbent: adsorption of Cd (II) from aqueous solution, *Advances in Environmental Research*. **2003**, *7*(2), 471-478**.**

(14)   Kumar, P. S.; Ramalingam, S.; Senthamarai, C.; Niranjanaa, M.; Vijayalakshmi, P.; Sivanesan, S. (2010). Adsorption of dye from aqueous solution by cashew nut shell: studies on equilibrium isotherm, kinetics and thermodynamics of interactions, *Desalination*. **2010**, 261(1-2), 52-60.

(15)   Lagergren, S., About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens. Handlingar*, Band **1898**, 24, 1-39.

(16)   Makene2 JEGM and JSM, 1Department. Removal of lead(ii) ions from aqueous solutions using cashew nut shell liquid-templated thiol-silica materials, *Bull Chem Soc Ethiop*. **2014**, 3(28):363-372.

(17)   Moreno-Piraján, J. C.; Garcia-Cuello, V. S.; Giraldo, L. The removal and kinetic study of Mn, Fe, Ni and Cu ions from wastewater onto activated carbon from coconut shells, *Adsorption*. **2011**, 17(3), 505-514.

(18)   Ndi, Nsami. J.; Ketcha, M.; Badcam, J. The adsorption efficiency of chemically preparedactivated carbon from cola nut shells by ZnCl2 on methylene blue, *J Chem*. **2013**, 2013:1-8.

(19)   Panda, H.; Tiadi, N.; Mohanty, M.; Mohanty, C.R. Studies on adsorption behavior of an industrial waste for removal of chromium from aqueous solution, *South African J Chem Eng*. **2017**, 23:132-138.

(20)   Pu, W.; Song, Z.; Yan, J.; Xu, H.; Ji, H.; Yuan, S.; Li, H. Preparation of oxygen-deficient 2D WO3x nanoplates and their adsorption behaviors for organic pollutants: equilibrium and kinetics modeling, *J. Mater. Sci.* **2019**, 54(19), 12463–12475.

(21)   Roop, Chand.; Bansal, M.G. London: Taylor and Francis, *Activated Carbon Adsorption*, **2005**.

(22)   Smith, V. A.; Rivera, J. F.; Bello, R.; Rodríguez-Aguado, E.; Elshaer, M. R.; Wodzinski, R. L.; Bashkova, S. The Role of Surface Chemistry and Polyethylenimine Grafting in the Removal of Cr (VI) by Activated Carbons from Cashew Nut Shells. **2021**, C, 7(1), 27.

(23)   Sonal, S.; Singh, A.; and Mishra B. K. Decolorization of reactive dye Remazol Brilliant Blue R by zirconium oxychloride as a novel coagulant: optimization through response surface methodology, *Water Sci. Technol*. **2018**, 78(2), 379–389.

(24)   Spagnoli, A. A.; Giannakoudakis, D. A.; Bashkova, S. Adsorption of methylene blue on cashew nut shell based carbons activated with zinc chloride: The role of surface and structural parameters, *Journal of Molecular Liquids.* **2017**, 229, 465-471.

(25)   Tangjuank, S.; Insuk, N.; Udeye, V.; Tontrakoon, J. (2009). Chromium (III) sorption from aqueous solutions using activated carbon prepared from cashew nut shells, *International Journal of Physical Sciences*.**2009**, 4(8), 412-417.

(26)   Thang, N. H.; Khang, D. S.; Hai, T. D.; Nga, D. T.; Tuan, P. D. Methylene blue adsorption mechanism of activated carbon synthesised from cashew nut shells, *RSC advances*. **2021**, 11(43), 26563-26570.