



PROJECT REPORT
ON
REMEDICATION OF Cr (VI) FROM CONTAMINATED
WATER BY ACTVATED CARBON ENTRAPPED IN
CALCIUM ALGINATE BEADS

BY
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SUPERVISED BY
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CERTIFICATION

This is to certify that this project report was written and carried out by MAKANJUOLA JEREMIAH OLAJIDE, a student of the Department of Industrial Chemistry, Federal University Oye-Ekiti, Ekiti State under the supervision of Dr E.G. Olumayede.

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Date

DEDICATION

I dedicate this work first to God, who has made it possible for me to start and finish the research work successfully. I also dedicate this work to my Parents who assisted me financially and also my able lecturers and staff of the Department of Industrial Chemistry, Federal University, Oye-Ekiti.

ACKNOWLEDGEMENT

I am using this opportunity to thank the Almighty God for the breath of life He has given to me, His love, protection and provision throughout my project work. I will forever be thankful for the opportunity He has given unto me.

I also want to acknowledge the efforts of my supervisor, Dr E.G. Olumayede for his outstanding support during the course of my project and for painstakingly going through the report.

I also acknowledge the efforts of my parents, Mr and Mrs Makanjuola for their prayers, encouragement, and financial support up to this level in life. I pray that God Almighty will give them long life to reap the fruits of their labour.

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ABSTRACT

Cr (VI) is a well-known highly toxic metal. This project focuses on the removal of Cr (VI) from contaminated water using activated carbon entrapped in calcium alginate beads. Activated carbon used for this work was prepared from an organic waste material called walnut shell by carbonization using phosphoric acid as an activating agent. 0.5g of activated carbon was added to 10mL of 4% sodium alginate solution. The mixture was promptly dropped into 3.5% aqueous solution of calcium chloride (CaCl_2) using a pump. It was then continuously stirred until homogenous mixture was obtained. Finally the calcium alginate beads formed were hardened and rinsed. Batch experiments were carried out in the laboratory to evaluate the efficacy of activated carbon entrapped in calcium alginate beads for the removal of Cr (VI) from contaminated water. Different masses of entrapped calcium alginate beads (0.5g, 1.0g, & 1.5g) were mixed with contaminated water containing Cr (VI). It was observed that when different masses of entrapped calcium alginate beads were added to the contaminated water, the concentration of Cr (VI) present in it reduced. It was concluded that activated carbon entrapped in calcium alginate beads is effective for removing Cr (VI) in contaminated water.

CHAPTER ONE- INTRODUCTION

1.1 BACKGROUND

Hexavalent chromium Cr (VI) is a potential carcinogen, teratogen, and mutagen and is on the top priority list of toxic pollutants defined by USEPA (USEPA, 1998). Contamination of water with Cr (VI) is a worldwide problem and the remediation of contaminated site has become environmental challenge. Chromium is one of the key contaminants in the wastewaters of industrial dyes and pigments, film and photography, galvanometry and electric, metal cleaning, plating and electroplating, leather and mining (Anwar *et al.*, 1961). While hexavalent and trivalent species of chromium are prevalent in industrial waste solutions, the hexavalent form has been considered more hazardous to public health due to its mutagenic and carcinogenic properties.

Chromium occurs in the environment primarily in two valence states, trivalent chromium Cr (III) and hexavalent chromium Cr (VI). Exposure may occur from natural or industrial sources of chromium. Chromium (III) is much less toxic than chromium (VI). The respiratory tract is also the major target organ for chromium (III) toxicity, similar to chromium (VI). Chromium (III) is an essential element in humans. The body can detoxify some amount of Cr(VI) to Cr (III). The respiratory tract is the major target organ for chromium (VI) toxicity, for acute (short-term) and chronic (long-term) inhalation exposures. Shortness of breath, coughing, and wheezing were reported from a case of acute exposure to chromium (VI), while perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, and other respiratory effects have been noted from chronic exposure (Danielsson *et al.*, 1982). Human studies have clearly established that inhaled chromium (VI) is a human carcinogen, resulting in

an increased risk of lung cancer. Animal studies have shown chromium (VI) to cause lung tumors via inhalation exposure (Danielsson *et al.*, 1982).

1.2 ACUTE EFFECTS OF CHROMIUM (VI)

Chromium (VI) is much more toxic than chromium (III), for both acute and chronic exposures. The respiratory tract is the major target organ for chromium (VI) following inhalation exposure in humans (Bloomfield and Blum, 1928). Shortness of breath, coughing, and wheezing were reported in cases where an individual inhaled very high concentrations of chromium trioxide. Other effects noted from acute inhalation exposure to very high concentrations of chromium (VI) include gastrointestinal and neurological effects, while dermal exposure causes skin burns in humans. Ingestion of high amounts of chromium (VI) causes gastrointestinal effects in humans and animals, including abdominal pain, vomiting, and hemorrhage. Acute animal tests have shown chromium (VI) to have extreme toxicity from inhalation and oral exposure (Davies, 1978).

1.3 CHRONIC EFFECTS OF CHROMIUM (VI)

Chronic inhalation exposure to chromium (VI) in humans results in effects on the respiratory tract, with perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, asthma, and nasal itching and soreness reported (Davies, 1978). Chronic human exposure to high levels of chromium (VI) by inhalation or oral exposure may produce effects on the liver, kidney, gastrointestinal and immune systems, and possibly the blood (Frentzel-Beyme,

1983). Rat studies have shown that, following inhalation exposure, the lung and kidney have the highest tissue levels of chromium. Dermal exposure to chromium (VI) may cause contact dermatitis, sensitivity, and ulceration of the skin.

1.4 STATEMENT OF PROBLEM

The presence of hexavalent chromium in water resulting from rapid industrialization and high anthropogenic activities has posed a threat to man. It is therefore essential to find a cheaper way of removing Cr (VI) from waste water.

1.5 AIM AND OBJECTIVES OF THE PROJECT WORK

- 1) To prepare activated carbon from walnut shell by carbonization using phosphoric acid as an activating agent.
- 2) To entrap activated carbon into calcium alginate beads.
- 3) To remove Cr (VI) from contaminated water using activated carbon entrapped in calcium alginate beads.

CHAPTER TWO- LITERATURE REVIEW

2.1 HISTORY OF ACTIVATED CARBON AND PRESENT DAY

APPLICATIONS

The useful properties of activated carbon have been known since ancient times. This traces back to 1500 BC when Egyptians used charcoal as an adsorbent for medicinal purposes and a purifying agent. Around 420 BC it was observed that Hippocrates dusted wounds with powdered charcoal to remove their odor. Ancient Hindu societies purified their water by filtration through charcoal. In 1773, the Swedish chemist Karl Wilhelm Scheele was the first to observe adsorption of gases on charcoal. A few years later activated carbons began being used in the sugar industry as a decolorizing agent for syrup.

In the early 20th century the first plant to produce activated carbon industrially was built for use in sugar refining industry in Germany. Many other plants emerged in the early 1900's to make activated carbons primarily for decolorization. During World War I activated carbon was used in gas masks for protection against hazardous gases and vapors. Today, activated carbons are used to remove colour from pharmaceutical and food products, as air pollution control devices for industrial and automobile exhaust, for chemical purification, and as electrodes in batteries.

2.2 DEFINITION OF ACTIVATED CARBON

Activated carbon also called activated charcoal, is a form of carbon that has been processed with oxygen to create millions of tiny pores between the carbon atoms. Commercial activated carbons have internal surface area ranging from 500 to 1500 m²/g (Gomez-Serrano *et al.*, 2005).

Activated carbon can be prepared from feed stock with high carbon and low inorganic

content(Gratuito *et al.*, 2008). The most common feed stocks used for the production of activated carbon are wood, coconut shell, bituminous coal, peat etc. The chars obtained from them could be activated easily to produce reasonably high quality activated carbons. During the activation process, the unique internal pore structure is created, which provides the activated carbon its outstanding adsorptive properties. Activated carbons have a number of unique characteristics such as large internal surface area, chemical properties and good accessibility of internal pores. According to IUPAC definitions three groups of pores can be identified.

- I. Macropores (above 50nm diameter)
- II. Mesopores (2-50 nm diameters)
- III. Micropores (Under 2 nm diameter)

Micropores generally contribute to a major part of the internal surface area. Macro and micropores can generally be regarded as the highways into the carbon particle, and are crucial for kinetics. The desirous pore structure of an activated carbon product is attained by combining the right raw material and suitable activation procedure (Hassler, 1974).

2.3 CLASSIFICATION OF ACTIVATED CARBON

Activated carbons are complex products which are difficult to classify on the basis of their behaviour, surface characteristics and preparation methods. The types of activated carbon available in the current market are powder, granular and pellet. It is classified according to its particle sizes and shape, and each type has its specific application (Jagtøyen *et al.*, 1992). However, some broad classification is made for general purpose based on their physical characteristics.

2.3.1 Powdered activated carbon (PAC)

The size of powder activated carbon is less than 100 μ m in size with an average diameter between 15 and 25 μ m (Khalili *et al.*, 2000). Thus, they present a large internal surface with a small diffusion distance. PAC is made up of crushed or ground carbon particles, 95–100% of which will pass through a designated mesh sieve or sieve. Powdered activated carbons are mainly used in liquid phase adsorption and flue gas treatment. In wastewater treatment, the most common use of powdered activated carbon is in the secondary treatment called powdered activated carbon treatment process. PAC is not commonly used in a dedicated vessel, owing to the high head loss that would occur. PAC is generally added directly to other process units, such as raw water intakes, rapid mix basins, clarifiers, and gravity filters (Marsh and Rodriguez-Reinoso, 2006).

2.3.2 Granular activated carbon (GAC)

Granular activated carbon has a relatively larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface (Kim *et al.*, 2001). Diffusion of the adsorbate is thus an important factor. These carbons are therefore preferred for all adsorption of gases and vapours as their rate of diffusion are faster. Granulated carbons are used for water treatment, deodorization and separation of components of flow system. GAC can be either in the granular form or extruded. GAC is designated by sizes such as 8 \times 20, 20 \times 40, or 8 \times 30 for liquid phase applications and 4 \times 6, 4 \times 8 or 4 \times 10 for vapour phase applications (Marsh and Rodriguez-Reinoso, 2006).

2.3.3 Extruded activated carbon (EAC)

Extruded activated carbon combines powdered activated carbon with a binder, which are fused together and extruded into a cylindrical shaped activated carbon block with diameters from 0.8 to 130 mm. These are mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.

2.3.4 Impregnated carbon

Porous carbons containing several types of inorganic impregnate such as iodine, silver, cations such as Al, Mn, Zn, Fe, Li, and Ca have also been prepared for specific application in air pollution control especially in museums and galleries. Due to antimicrobial/antiseptic properties, silver loaded activated carbon is used as an adsorbent for purification of domestic water. Drinking water can be obtained from natural water by treating the natural water with a mixture of activated carbon and $Al_2(OH)_3$, a flocculating agent. Impregnated carbons are also used for the adsorption of H_2S and thiols. Adsorption rates for H_2S as high as 50% by weight have been reported.

2.3.5 Polymer coated carbon

This is a process by which a porous carbon can be coated with a biocompatible polymer to give a smooth and permeable coat without blocking the pores. The resulting carbon is useful for hemoperfusion i.e. a treatment technique in which large volumes of the patient's blood are passed over an adsorbent substance in order to remove toxic substances from the blood.

2.4 METHODS OF PREPARATION OF ACTIVATED CARBON

Most carbonaceous substances can be converted into activated carbon. The final properties of the carbon will depend significantly on the nature of the starting material. A large number of

processes for making activated carbons have been developed over the past century. However, most processes consist of the pyrolysis of the starting material, followed by a stage of controlled oxidation or vice versa. The purpose of the oxidation stage is to activate the carbon.

2.4.1 Pyrolysis

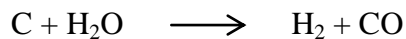
Pyrolysis step (or also called as Carbonization) involves heating the source materials to temperatures ranging between 600 to 900°C in the absence of air (Lartey *et al.*, 1999). This process is to eliminate most of the non-carbon elements such as hydrogen, nitrogen, oxygen and sulphur as volatile gaseous products. Low molecular weight volatiles are first released, followed by light aromatics and finally the hydrogen gas, the resultant product being a fixed carbonaceous char. The residual carbon atoms are grouped into condensed sheets of aromatic ring with a cross-linked structure in a random manner. The mutual arrangement of these aromatic sheets is irregular and leaves free interstices between the sheets, which may be filled with the tarry materials. To remove these tarry materials, activation process is carried out. It also enlarges the diameters of the pores, which were created during the carbonization process and creating new porosity.

2.4.2 Activation

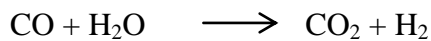
The basic characteristics of a carbon are established during the pyrolysis, and the ensuing oxidation step must be designed to complement the pyrolysis step. During this step, the oxidising agent increasingly erodes the internal surfaces of the carbon, develops an extensive and fine network of pores in the carbon, and changes the atoms lying on the surface to specific chemical forms which may have selective adsorption capabilities. This activation step is done by two methods physical activation or chemical activation (Mozammel *et al.*, 2002).

2.4.3 Physical activation

Physical activation or partial gasification is generally carried out at elevated temperatures between 750 and 1100 C using oxidants such as steam, carbon dioxide, air or mixture of these gases. Chlorine, sulphur vapours, sulphur dioxide, ammonia and a number of other substances having activation effects are rarely used (Malik, 2004). Gasification of the carbonized material with steam and carbon dioxide occurs by the following endothermic reactions:



The reaction of steam with carbon is accompanied by the water gas formation reaction, which is catalyzed by the carbon surface as,



Since the reaction of carbon with steam and with carbon dioxide is both endothermic, external heating is required to drive the reactions and to maintain the reaction temperature. The activation process can be manipulated to produce products of desired characteristics. Activation temperature, steam and CO₂ flow rates control the pore development, which in turn affect pore size distributions and the level of activity of the activated carbon (Marsh *et al.*, 1984).

2.4.4 Chemical activation

Chemical activation is usually carried out by impregnating the raw or pre-carbonized material with an activating agent and pyrolyzed between 400 and 800°C in the absence of oxygen. The most commonly used activating agents are phosphoric acid, hydrochloric acid, sulphuric acid, alkalis namely KOH and NaOH, zinc chloride and alkaline metal compounds. Phosphoric acid and zinc chloride are used for the activation of lignocellulosic materials (Mattson and Mark, 1971). Phosphoric acid is the most preferred activating agent because of its low environmental

impact when compared to zinc chloride. The resultant activated carbon is washed, dried till constant weight is obtained and ground to required size. Activated carbons produced by chemical activation generally exhibit a very open structure and bottle shaped, ideal for the adsorption of large molecules.

2.4.5 Combination of physical and chemical activation

A combination of physical and chemical activation can be used to prepare granular activated carbons with a very high surface area and porosity adequate for certain specific applications such as gasoline vapour control, gas storage, etc. Activated carbons of these types have been reported using lignocellulosic precursors chemically activated with phosphoric acid and zinc chloride and later activated under a flow of carbon dioxide. Uniform, medium-size microporosity and surface areas above 3600 m²/g are obtained with this mixed procedure (Molina-Sabio et al., 1995).

2.5 APPLICATIONS OF ACTIVATED CARBON

Activated carbon is used in gas purification, gold purification, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and respirators, filters in compressed air and many other applications. Recently Activated Carbon filters have gained popularity among recreational users of Cannabis, and other smoking herbs for their use in effectively filtering out "Tar" from the smoke. Some of the applications include:-

2.5.1 Metal finishing field

This is one major industrial application of activated carbon in the metal finishing field. It is very widely employed for purification of electroplating solutions. For example, it is a main purification technique for removing organic impurities from bright nickel plating solutions. A variety of organic chemicals are added to plating solutions for improving their deposit qualities

and for enhancing properties like brightness, smoothness, ductility, etc. Due to passage of direct current and electrolytic reactions of anodic oxidation and cathodic reduction, organic additives generate unwanted break down products in solution.

Their excessive build up can adversely affect the plating quality and physical properties of deposited metal. Activated carbon treatment removes such impurities and restores plating performance to the desired level. Activated carbon, in 50% w/w combination with celite, is used as stationary phase in low pressure chromatographic separation of carbohydrates using ethanol solutions (5–50%) as mobile phase in analytical or preparative protocols.

2.5.2 Environmental field

Here, activated carbon adsorption has numerous applications in removing pollutants from air or water streams both in the field and in industrial processes such as spill clean-up, groundwater remediation, drinking water filtration, air purification, volatile organic compounds capture from painting, dry cleaning, gasoline dispensing operations, and other processes.

2.5.3 Medical application

In medical applications activated carbon is used to treat poisonings and overdoses following oral ingestion. It is thought to bind to poison and prevent its absorption by the gastrointestinal tract. In cases of suspected poisoning, medical personnel administer activated charcoal on the scene or at a hospital's emergency department. Dosing is usually empirical at 1 gram/kg of body mass (for adolescents or adults, gives 50-100g), usually given only once, but depending on the drug taken, it may be given more than once. In rare situations activated charcoal is used in Intensive Care to filter out harmful drugs from the blood stream of poisoned patients. Activated charcoal has become the treatment of choice for many poisonings, and other decontamination methods such as

ipecac-induced emesis or stomach pumping are now used rarely (Srinivasakannan and Zailani, 2003).

2.5.4 Gold recovery

Activated carbon acts as a sponge to aurocyanide and other complex ions in solution. Carbon particles which are much larger than the ore particle size can be mixed with the ore and cyanide solution. When this is applied to gold extraction, the gold cyanide complex is adsorbed onto the carbon until it comes to equilibrium with the gold solution. Since the carbon particles are much larger, they can easily be separated from the slurry by screening using a wire mesh. The gold is then reactivated and returned to the circuit.

2.5.5 Alcohol purification

Activated carbon filters can be used to remove organic impurities from alcohols (vodka and whiskey) that affect colour, taste, and odour increasing its purity.

Some other common uses included corn and cane sugar refining, dry cleaning recovery processes, fat and oil removal, catalyst support, battery electrodes and super-capacitors.

2.5.6 Water purification

Activated carbon water filters have been used in home water purification systems primarily to remove taste and odour. Taste and odour, although undesirable, are generally not considered unhealthy. In recent years, however, activated carbon filters have been used to remove some of the contaminants that have been discovered in water supplies. Activated carbon is most effective at removing organic compounds such as volatile organic compounds, pesticides and benzene. It can also remove some metals, chlorine and radon. As with any treatment system, it cannot remove all possible drinking water contaminants.

Because Activated carbon systems are limited in the types of compounds they can effectively remove, it is essential that the home owner determine which water contaminants are present before using such a system thus results in the need of water analysis (Srinivasakannan and Zailani, 2003).

2.5.7 Activated carbon filters

Home Activated carbon treatment systems are quite simple. The activated carbon is normally packaged in filter cartridges that are inserted into the purification device. Water needing treatment passes through the cartridge contacting the AC on its way to the faucet. AC filters eventually become fouled with contaminants and lose their ability to adsorb pollutants. At this time, they need to be replaced or regenerated.

2.6 A REVIEW ON ACTIVATED CARBON PREPARATION USING CHEMICAL ACTIVATION

The term chemical activation refers to the treatment of the precursor with an activating agent used for restricting tar formation during the thermal step. During thermal treatment, chemical activating agents such as phosphoric acid and zinc chloride among others, provoke carbonization of the precursor by dehydration, depolymerisation and redistribution of biopolymers and cross linking of lignocellulosic materials (Jagtoyen and Derbyshire, 1998).

Production of activated carbon from biological sludge (Martin *et al.*, 2002) and sewage sludge (Rozada *et al.*, 2003) by chemical activation using phosphoric acid at 700°C for 30 min yielded mesoporous network with certain percentage of macropores. Preparation of activated carbon from cork waste using potassium hydroxide at 800 C for 2h yielded surface area of 1415 m² g⁻¹ (Carvalho *et al.*, 2003)

Srinivasakannan *et al.*(2004) carried out a two-stage process for the preparation of activated carbon from rubber wood saw dust. The two-stage process with semi-carbonization up to 200 C for 15 min followed by activation at 400 and 500 C for 30, 45, 60 and 90 min. Phosphoric acid was used as an activating agent with various impregnation ratio (dry wt. of H₃PO₄/dry wt. of rubber wood saw dust) of 1, 1.5, and 2. At the optimal conditions of activation, activated carbon with iodine number and surface area of 1096 mg g⁻¹ and 1496 m² g⁻¹ respectively were obtained.

Corcho *et al.* (2006) prepared activated carbon from vineyard shoot using phosphoric acid as the activating agent. They found the activated carbons porosity was better when the raw material was impregnated and heated at intermediate temperatures. Haimour & Emeish (2006) reported phosphoric acid activated date pit carbon, the iodine number increased with increasing activation temperature. Impregnation increases caused an oscillation in the iodine number.

Senthilkumaar *et al.* (2006a) prepared activated carbon from male flowers of coconut tree and jute fibre using 15% phosphoric acid in the ratio 1:3. They found a porosity of 72.36% and 76.14%, surface area of 328 and 680 m²/g and pHzpc of 6.23 and 4.56 for coconut flower carbon and jute fibre carbon respectively indicating that the fibrous materials gave a higher surface area than the other cellulosic materials. The porosity of the carbon varied based on the activating agent, activated carbon prepared from coconut male flower using phosphoric acid and sulphuric acid (Senthilkumaar et al 2006b) yielded carbons with 72.36% and 65% porosity respectively.

Baccar *et al.* (2009) prepared activated carbon from olive-waste cake using phosphoric acid as a activating agent, carbon preparation parameters such as concentration of the activating agent, impregnation ratio and activation time were optimized. They found the surface area of the sorbent increased rapidly from 716 to 1020 m²/g with an increase of acid concentration from 35

to 65% phosphoric acid, and further increase in the acid concentration (85%) did not show an appreciable increase in the surface area.

Chan *et al.* (2009) prepared activated carbon from bamboo waste scaffolding using phosphoric acid. They found the surface area up to 2500 m²/g of the activated carbon increased with impregnation ratio (2.4) and activation temperature (400 or 600°C).

Lim *et al.* (2010) prepared activated carbon from palm shells by phosphoric acid impregnation. They prepared carbon at low activation temperature (425°C) and activation time (30 min), while varying the impregnation ratio of phosphoric acid from 0.5 to 3. The yield of activated carbon was not vary with the impregnation ratio and was found to be about 50%. The textural characteristics were found to improve with increase in the impregnation ratio, up to 2 and further increase in IR the textural character decreased. The BET surface area of activated carbon corresponding to an impregnation ratio of 3, with an iodine number of 1035 mg/g was found to be 1109m²/g with a pore volume of 0.903cm³/g and an average pore diameter of 3.2 nm. The textural characteristics of activated carbon reveal that the pore size is widely distributed with the contribution of micropores around 50%.

Fabiana *et al.* (2010) prepared activated carbon from piassava fibre using chemical activation with zinc chloride and phosphoric acid and physical activation with carbon dioxide or water vapour. Zinc chloride gave the highest surface area of 1190 m²/g and phosphoric acid activated carbon gave largest pore volume of 0.543 cm³/g. Li *et al.* (2010) reported that activated carbon prepared from *Polygonum orientale* Linn by phosphoric acid activation gave a surface area of 1398 m²/g.

Bhari *et al.* (2012) prepared activated carbon from grape seeds using chemical activation with phosphoric acid. Grape seeds were pre-treated with sulfuric acid to improve its wettability. Microporous activated carbons with some contribution of mesoporosity were obtained. The best results in terms of surface area ($1139 \text{ m}^2/\text{g}$) and mesopore volume ($0.24 \text{ cm}^3/\text{g}$) development were observed for a grape seeds to phosphoric acid ratio of 1:3 and a carbonization temperature of 500°C . They found the activated carbon morphology had an egg shell structure that favored applications in liquid phase.

Mohamad & Paul (2012) studied the pore characteristics of activated carbons obtained from the phosphoric acid activation of cotton stalks. They concluded that the textural characteristics of the derived activated carbons were found to be strongly dependent on the impregnation ratio and activation temperature. The mesopore volume attained a maximum value ($0.61 \text{ cm}^3/\text{g}$) in the case of activated carbons produced at the highest impregnation ratio and activation temperature.

Aghdas *et al.* (2014) revealed the impregnation ratio of the activating agent highly influenced the surface area and the porosity development during activated carbon preparation. They prepared highly microporous activated carbon from *Eucalyptus camaldulensis* wood by chemical activation with H_3PO_4 , ZnCl_2 at different impregnation ratios as well as by pyrolysis, followed by activation with KOH. Varying the H_3PO_4 /biomass ratio from 1.5 to 2.5, the prepared activated carbon displayed BET surface areas in the range of $1875\text{--}2117 \text{ m}^2/\text{g}$ with micropores content of 69–97%. For the ZnCl_2 activated carbon, BET surface areas varied from 1274.8 to $2107.9 \text{ m}^2/\text{g}$ with micropores content of 93–100% for impregnation ratios of 0.75–2.0. The activated carbon obtained by KOH activation had the largest BET surface area of $2594 \text{ m}^2/\text{g}$ and a high micropore of 98%. From the above they found that the activating agent and its concentration strongly influenced the textural characteristics of the eucalyptus wood based activated carbon.

Alicia *et al.* (2014) studied the influence of activation atmosphere used in the chemical activation of almond shell on the carbon characteristics. They found activated carbons prepared at low and intermediate impregnation ratios showed higher yields. This could be attributed to the decomposition of the polymeric structures of the activated carbons during the activation stage that release most elements different from carbon (N, H and O). Activating agent employed permits the dehydration, depolymerization and redistribution of the constituent polymers, and the conversion of aliphatic groups to aromatics, increasing the yield of the activated carbons. Higher impregnation ratios produce a higher elimination of tars of the pores decreasing the yield.

CHAPTER THREE- MATERIALS AND METHODOLOGY

3.1 CHEMICAL REAGENT USED

- 1) Sodium alginate solution
- 2) Calcium chloride solution
- 3) Distilled water
- 4) Phosphoric acid solution

3.2 EQUIPMENT USED

- 1) Glass funnel
- 2) Spatula
- 3) 50mL beaker
- 4) 250mL volumetric flask
- 5) Mortar and pestle
- 6) Muffle furnace
- 7) Walnut shell
- 8) Desiccator
- 9) pHmeter
- 10) Colorimeter

3.3 PRODUCTION OF ACTIVATED CARBON FROM WALNUT SHELL

The walnut shell was first ground using mortar and pestle. After grinding the walnut shell, it was screened using a sieve and dried in an oven at a temperature of 50°C. After drying, 20g of dried crushed walnut shell was soaked in 100mL of H₃PO₄ solution (60% concentration). The mixture

was stirred continuously at room temperature for 2h and left to soak for 12h to allow penetration of phosphoric acid into the dried crushed walnut shell. It was now heated in a furnace at a temperature of 600-800°C for 1 hour. After heating, the carbonated walnut shell was cooled in desiccator for 20 minutes. After cooling it was then washed using hot distilled water until it reaches a pH of 7. After washing, it was dried and heated at constant temperature of 40°C.

3.4 SYNTHESIS OF ACTIVATED CARBON ENTRAPPED IN CALCIUM ALGINATE BEADS

Activated carbon entrapped in calcium alginate beads was prepared by mixing small quantity AC with 10mL of 4% sodium alginate solution. The mixture was promptly dropped into 3.5% aqueous solution of calcium chloride (CaCl₂) using a pump. It was then continuously stirred until homogenous mixture was obtained. Finally the calcium alginate beads formed were hardened and rinsed.

3.5 BATCH EXPERIMENT FOR THE EVALUATION OF THE EFFICACY OF ACTIVATED CARBON ENTRAPPED IN CALCIUM ALGINATE BEADS

Batch experiments were carried out in the laboratory to evaluate the efficacy of activated carbon entrapped in alginate beads for the removal of Cr (VI) from contaminated water. Different masses of activated carbon entrapped in alginate beads (0.5g, 1.0g, & 1.5g) were mixed with contaminated water containing Cr (VI). The initial concentration of Cr(VI) is 100µg/g. The reaction mixture was allowed to react for 60 minutes with continuous shaking. The mixture was

now centrifuged and then the supernatant formed was analyzed for residual Cr (VI) by colorimetric technique.

So in order to study the trend of Cr (VI) removal with contact time, the reaction mixture was taken out at predetermined time interval (15, 30, 45, 60, 75, 90, 105 and 120) and also filtered through filter paper and then analyzed for Cr (VI).

Cr (VI) removal percentage was also calculated using

$$\text{Cr (VI) removal (\%)} = \frac{(C_0 - C)}{C_0} \times 100$$

C and C_0 ($\mu\text{g/g}$) are the final and initial concentration of Cr (VI) present in the contaminated water respectively.

CHAPTER FOUR- RESULT AND DISCUSSION

4.1 RESULT

4.1.1 XRD ANALYSIS RESULT

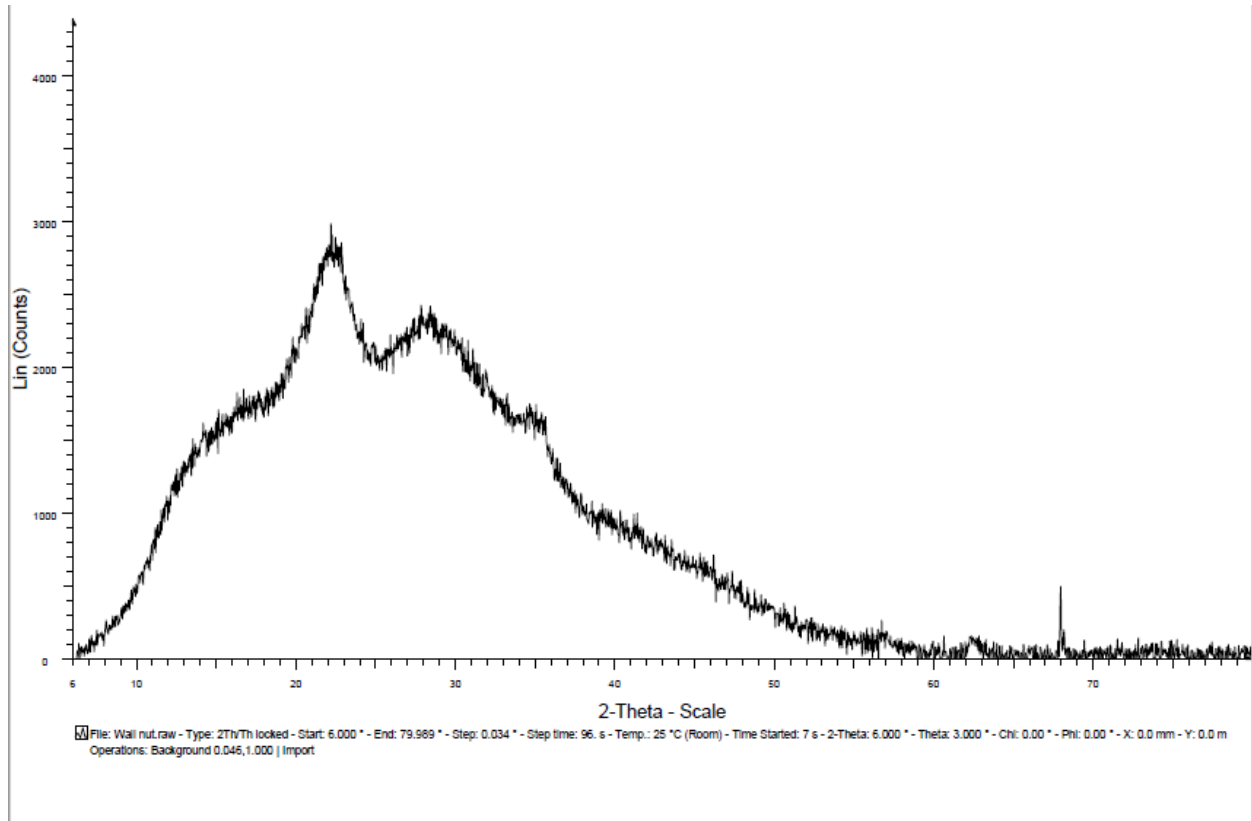


Figure 4.1 presents the XRD spectra of the prepared activated carbon. The result showed that the carbon atoms present in the activated carbon are not orderly arranged. This simply means that the carbon atoms have an amorphous structure.

Table 4.1 presents the data obtained after entrapped calcium alginate beads were used to remove Cr (VI) from contaminated water.

Masses of entrapped calcium alginate beads (g)	Conc of Cr (VI) before the application of entrapped calcium alginate beads($\mu\text{g/g}$)	Conc of Cr (VI) after the application of entrapped calcium alginate beads($\mu\text{g/g}$)
0.5	100	40
1.0	100	20
1.5	100	10

The result above showed that as the dose increases from 0.5 to 1.5g, the Cr (VI) concentration in contaminated water decreases from 40 to 10 $\mu\text{g/g}$.

Table 4.2 presents the data obtained for the contact time of the reaction between 0.5g of entrapped calcium alginate beads and Cr (VI) in contaminated water.

Contact time (min.)	Cr (VI) concentration after the application of 0.5g of entrapped calcium alginate beads (µg/g)
15	52
30	43
45	35
60	30
75	25
90	20
105	18
120	15

The result above showed that as the contact time increases from 15 to 120minutes, the concentration of Cr (VI) in contaminated water decreases from 52 to 15µg/g.

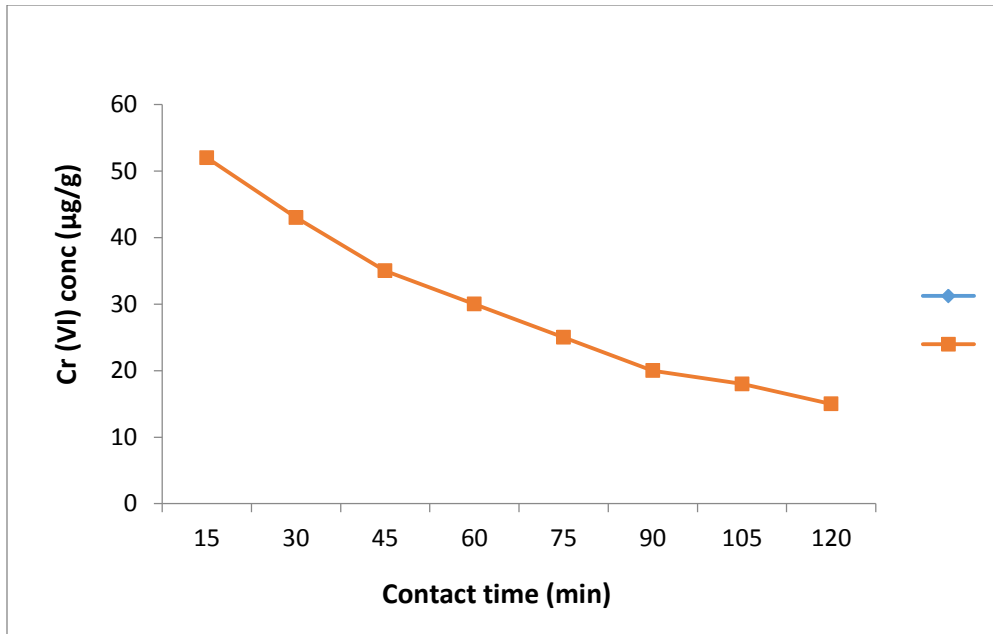


Figure 4.2 presents the graphical representation for the contact time of the reaction between 0.5g of entrapped calcium alginate beads and Cr (VI) in contaminated water. The graph result showed that as the contact time increases, the concentration of Cr (VI) in contaminated water reduces.

Table 4.3 presents the data for the contact time for the reaction between 1.0g of entrapped calcium alginate beads and Cr (VI) in contaminated water

Contact time (min.)	Cr (VI) concentration after the application of 1.0g of entrapped calcium alginate beads (µg/g)
15	25
30	18
45	10
60	8
75	5
90	3
105	1
120	0

. The result above showed that as the contact time increases from 15 to 120 minutes, the concentration of Cr (VI) in contaminated water decreases from 25 to 0µg/g.

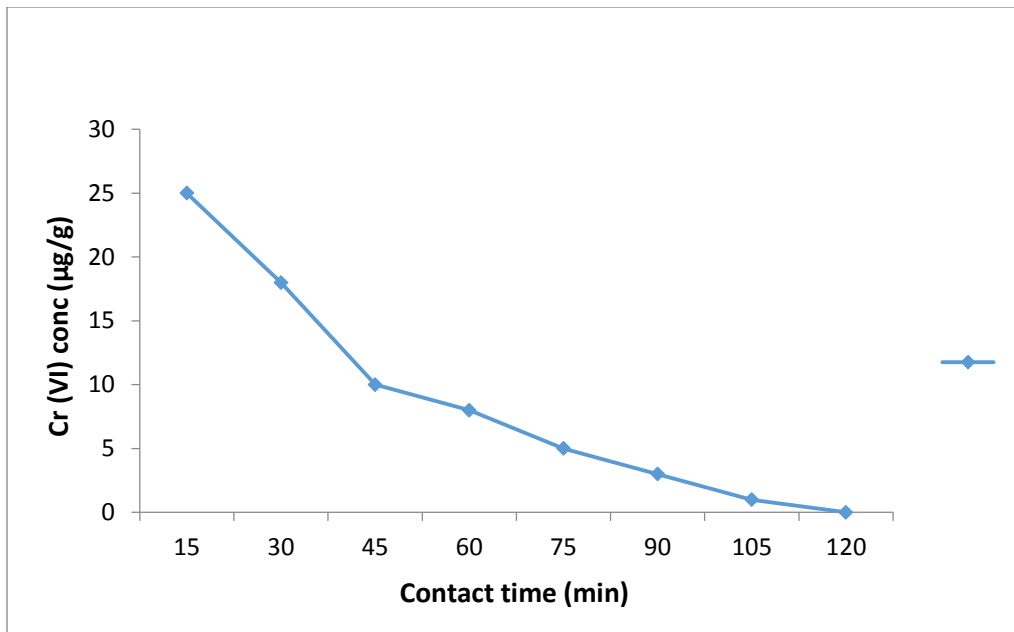


Figure 4.3 presents the graphical representation for the contact time of the reaction between 1.0g of entrapped calcium alginate beads and Cr (VI) in contaminated water. The graph result showed that as the contact time increases, the concentration of Cr (VI) in contaminated water reduces.

Table 4.4 presents the data for the contact time of the reaction between 1.5g of entrapped calcium alginate beads and Cr (VI) in contaminated water.

Contact time (min.)	Cr (VI) concentration after the application of 1.5g of entrapped calcium alginate beads (µg/g)
15	8
30	6
45	4
60	2
75	0
90	0
105	0
120	0

The result above showed that as the contact time increases from 15 to 120 minutes, the concentration of Cr (VI) in contaminated water decreases from 8 to 0µg/g.

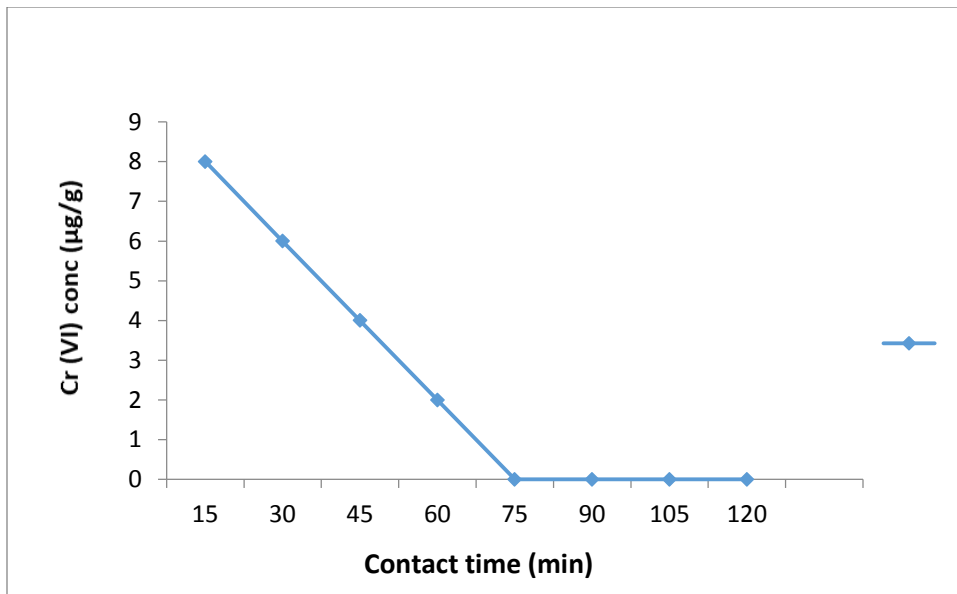


Figure 4.4 presents the graphical representation for the contact time of the reaction between 1.5g of entrapped calcium alginate beads and Cr (VI) in contaminated water. The graph result showed that as the contact time increases, the concentration of Cr (VI) in contaminated water reduces.

$$\text{Cr (VI) removal \%} = \frac{C_0 - C}{C_0} \times 100$$

Table 4.5 presents the data obtained for Cr (VI) removal percentage for different masses of entrapped calcium alginate beads.

Mass of entrapped calcium alginate (g)	Cr (VI) removal percentage after the application of entrapped calcium alginate beads
0.5	60
1.0	80
1.5	90

The result above showed that as the quantity of entrapped calcium alginate beads increases in mass, the Cr (VI) removal percentage also increases.

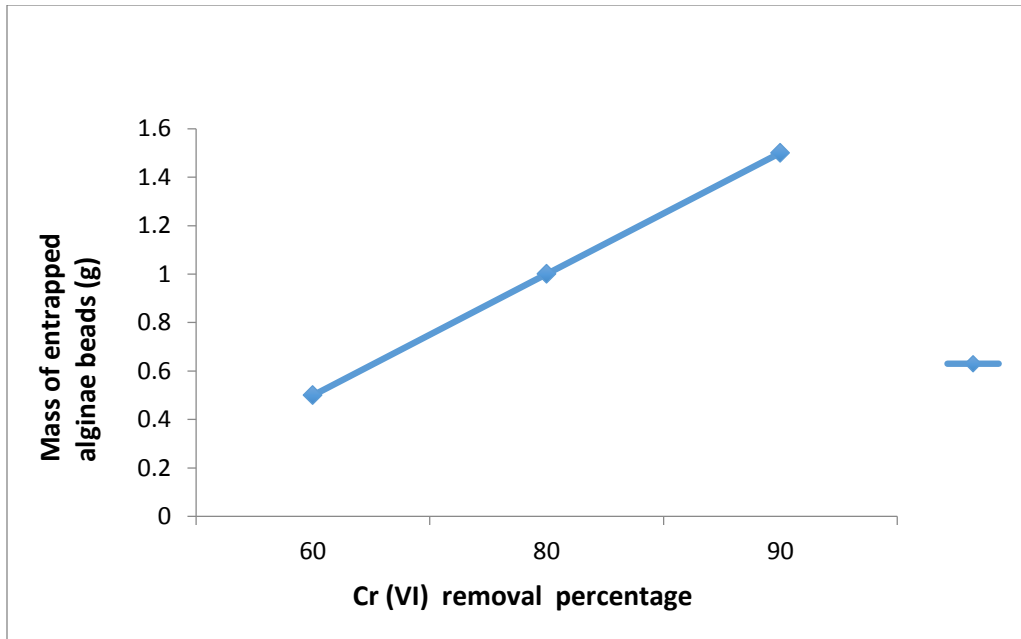


Figure 4.5 presents the graphical representation of data obtained for Cr (VI) removal percentage for different masses of entrapped calcium alginate. The result showed that as the mass increases the Cr (VI) removal percentage also increase

4.2 DISCUSSION

The above XRD analysis result shows that the carbon atoms present in the activated carbon are not orderly arranged. This simply means that the carbon atoms have an amorphous structure. *Table 4.1* above shows the effect of varied doses of activated carbon entrapped in calcium alginate beads on Cr (VI) concentration in contaminated water. It is clear from the *Table 4.1* above that as the dose increases from 0.5 to 1.5g, the Cr (VI) concentration in contaminated water decreases from 40 to 10 μ g/g. This simply means that as the mass of the entrapped calcium alginate beads used increases, the concentration of Cr (VI) in contaminated water reduces.

The length of contact time between activated carbon entrapped in calcium alginate beads and Cr (VI) in contaminated water has an important effect in Cr (VI) removal. *Table 4.2* above shows that as the contact time for reaction time between activated carbon entrapped in calcium alginate beads and Cr (VI) in contaminated water increases from 15 to 120minutes, the concentration of Cr (VI) in contaminated water decreases from 52 to 15 μ g/g. This indicates that as the contact time for the reaction between entrapped calcium alginate beads and Cr (VI) increases, the concentration of Cr (VI) in contaminated water reduces.

Table 4.3 above shows that as the contact time for the reaction between activated carbon entrapped in calcium alginate beads and Cr (VI) in contaminated water increases from 15 to 120 minutes, the concentration of Cr (VI) in contaminated water decreases from 25 to 0 μ g/g. This also indicates that as the contact time for the reaction between entrapped calcium alginate beads and Cr (VI) increases, the concentration of Cr (VI) in contaminated water reduces.

Table 4.4 above shows that as the contact time for the reaction between activated carbon entrapped in calcium alginate beads and Cr (VI) in contaminated water increases from 15 to 120 minutes, the concentration of Cr (VI) in contaminated water decreases from 8 to 0 μ g/g. This also

indicates that as the contact time for the reaction between entrapped calcium alginate beads and Cr (VI) increases, the concentration of Cr (VI) in contaminated water reduces.

The mass of activated carbon entrapped in calcium alginate beads used for the removal of Cr (VI) in contaminated water is very important. This is because it helps determine the percentage of Cr (VI) that will be removed from contaminated water. In the sense that as the mass of entrapped calcium alginate beads used increases, the percentage of Cr (VI) that was removed also increases.

Table 4.5 above shows that as the mass of activated carbon entrapped in calcium alginate increases from 0.5g to 1.5g, the Cr (VI) removal percentage increases from 60% to 90%.

CHAPTER FIVE- CONCLUSION

In the present study, activated carbon was prepared and entrapped in calcium alginate bead. The entrapped calcium alginate bead was applied on Cr (VI) in contaminated water to demonstrate its potential in the remediation of Cr (VI) in contaminated water. According to the result obtained so far, it can be concluded that activated carbon entrapped in calcium alginate bead is effective for removing Cr (VI) from contaminated water.

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