

**SYNTHESIS, CHARACTERIZATION AND ADSORPTION ACTIVITY
OF ZIRCONIUM OXIDE DOPED ACTIVATED CARBON IN DYE
REMOVAL FROM AQUEOUS SOLUTION.**

**Submitted in partial fulfilment of the requirements for the award of
Bachelor of Science Degree in Chemistry**

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TAMILNADU.

MARCH 2021



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DEPARTMENT OF CHEMISTRY **BONAFIDE CERTIFICATE**

This is to certify that this Project Report is the bonafide work of R.Niranjana (38030009) and A.Vishwapriya (38030019) who carried out the project entitled “SYNTHESIS, CHARACTERIZATION AND ADSORPTION ACTIVITY OF ZIRCONIUM OXIDE DOPED ACTIVATED CARBON IN DYE REMOVAL FROM AQUEOUS SOLUTION” under my supervision from December 2020 to April 2021.

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We **R. NIRANJANA** and **A. VISHWAPRIYA**, hereby declare that the Project Report entitled “**SYNTHESIS, CHARACTERIZATION AND ADSORPTION ACTIVITY OF ZIRCONIUM OXIDE DOPED ACTIVATED CARBON IN DYE REMOVAL FROM AQUEOUS SOLUTION**” done by us under the guidance of **Dr. T. Krithiga MSc., M. Phil., Ph.D.**, Associate Professor Department of Chemistry, Sathyabama Institute of Science and Technology is submitted in partial fulfilment of the requirements for the award of Bachelor of Science degree in Chemistry.

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ACKNOWLEDGEMENT

We are pleased to acknowledge my sincere thanks to Board of Management of SATHYABAMA for their kind encouragement in doing this project and for completing it successfully. I am grateful to them.

We convey my thanks to **Dr. J. Karthikeyan**, Head of the Department, Department of Chemistry for providing me necessary support and details at the right time during the progressive reviews.

We would like to express my sincere and deep sense of gratitude to my Project Guide, **Dr. T. Krithiga** for her valuable guidance, suggestions and constant encouragement which paved way for the successful completion of my project work.

We wish to express my thanks to all Teaching and Non-teaching staff members of the Department of Chemistry who were helpful in many ways for the completion of the project.

We take this opportunity to thank my family members and friends for their constant encouragement without which this assignment would not be possible.

R.NIRANJANA

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ABSTRACT

Activated Carbon was prepared from domestic food waste (leftover cooked rice). The rice was sun dried until free of any moisture and carbonization was done by pyrolysis between 400° - 600°C and the carbon was chemically activated by pyrolysis between 500° - 600°C with NaOH. This activated carbon was doped with zirconium oxide by chemical doping with Zirconyl chloride octahydrate. The zirconium oxide doped activated carbon was characterized by FTIR and SEM. The activated carbon was found to have a highly porous structure and larger surface area than activated carbon prepared by conventional methods. The FTIR confirms the presence of $\text{Zr} - \text{O} - \text{C}$ adsorbent peak. The SEM image reveals the porous nature of the zirconium oxide doped activated carbon. The adsorption activity of the prepared zirconium oxide doped activated carbon was tested by methyl orange dye removal from the aqueous solution. The adsorbent showed 85% removal capacity and the adsorption obeys Freundlich isotherm.

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LIST OF ABBREVIATIONS

MCR	- Multicomponent Reaction
FTIR	- Fourier Transform Infrared Spectroscopy
SEM	- Scanning Electron Microscope
CNT	- Carbon Nanotube
AC	- Activated Carbon

CHAPTER 1

INTRODUCTION

1.1 CARBON

On the periodic table, it is the first (row 2) of six elements in group 14 that have a common composition of their outer shell of electrons. It is nonmetallic and tetravalent-making four electrons available to form covalent chemical bonds. There are three naturally occurring isotopes, while C12 and C13 are stable, however C14 is radioactive, with a half-life of around 5730 years decay. Carbon is one of the few elements that have been identified since antiquity. Carbon is the 15th most abundant element in the earth's atmosphere, which by mass after hydrogen, helium which oxygen is the fourth most abundant element in the universe. It is available in all types of carbon-based life, and in the human body carbon is the second richest component by mass (about 18.5%) after oxygen. This bounty, together with the extraordinary assorted variety of natural mixes and their bizarre polymer-framing capacity at the temperatures generally experienced on earth, make this component the concoction premise of all known life.

The most widely recognized oxidation condition of carbon in inorganic mixes is +4, while +2 is found in carbon monoxide and change metal carbonyl buildings. The biggest wellsprings of inorganic carbon are limestone, dolomite and carbon dioxide, yet noteworthy amounts happen in natural stores. Carbon shapes countless mixes portrayed to date which thusly are a minor part of such exacerbates that are hypothetically conceivable under standard conditions.[<https://www.rsc.org/periodic-table/element/6/carbon>]

1.2 HISTORY OF CARBON:

The English name carbon originates from the Latin, carbon for coal and charcoal, whence additionally comes the French carbon, which means charcoal. In German, Dutch and Danish, the names for carbon are Kohlenstoff, koolstof and Kulstof individually, all truly significance coal-substance.

In 1722, Rone Antoine Ferchault de Reaumur showed that iron was changed into steel through the assimilation of some substance, presently known to be carbon.

In 1772, Antoine Lavoisier demonstrated that precious stones are a type of carbon; when he consumed tests of charcoal and jewel and found that neither delivered any water and that both discharged a similar measure of carbon dioxide per gram.

1.3 OCCURENCE OF CARBON:

Carbon is surrounding us and is in us. It makes up around 20% of the human body as a feature of DNA, fats and proteins. It's found in mixes in our air, similar to carbon dioxide (CO_2) and methane (CH_4). It's found in the exacerbates that make up the petroleum derivatives that power our vehicles and urban communities. Since carbon particles can orchestrate themselves in a few particular manners, materials produced using no one but carbon can take on a few distinct structures (or allotropes). Two natural types of unadulterated carbon are graphite and jewel. In any case, researchers have all the more as of late found new types of unadulterated carbon, for example, fullerenes (or buckyballs) and carbon nanotubes (CNTs). Every allotrope has drastically various properties

.[\[https://www.rsc.org/periodic-table/element/6/carbon\]](https://www.rsc.org/periodic-table/element/6/carbon)

1.3.1 Graphite:

Financially suitable normal stores of graphite happen in numerous pieces of the world, yet the most significant sources monetarily are in China, India, Brazil and North Korea. Graphite stores are of changeable beginning, found in relationship with quartz, mica and feldspars in schists, gneisses and transformed sandstones and limestone as focal points or veins, here and there of a meter or more in thickness. Stores of graphite in Borrowdale, Cumberland, England were from the start of adequate size and immaculateness that, until the nineteenth century, pencils were made essentially by sawing squares of normal graphite into strips before encasing the strips in wood. Today, littler stores of graphite are gotten by smashing the parent rock and gliding the lighter graphite out on water.

1.3.2 Diamond:

The soonest wellsprings of pearl precious stones were India and Borneo, where they were found in waterway alluvium. Every well-known precious stone of times long past were Indian jewels, including the Great Mogul, the Orlov, the Koh-I-noor, and the Regent or Pitt. Different celebrated jewels are the Hope (blue), Dresden (green), and Tiffany (yellow). In the mid eighteenth century, stores like those in India were found in Brazil, for the most part of carbonados. Notable South African jewel mines are the Dutoitspan, Bultfontein, De Beers, Kimberley, Jagersfontein, and Premier. Russia, Botswana, Congo (Kinshasa), Australia, and South Africa are currently the world's significant jewel creating countries; other significant nations incorporate Canada, Angola, Namibia, Ghana, and Brazil.

1.4 DIFFERENT FORMS OF CARBON

1.4.1 Graphite

Graphite is extremely delicate and slippery. Thus, it is utilized in pencils and as oil in modern hardware. Graphite's delicate quality and dangerous emerges from the manner in which the carbon molecules are orchestrated on the nanoscale. Graphite comprises of sheets of carbon iotas. In these sheets, the carbon iotas are orchestrated in a hexagonal, or honeycomb, design. Every carbon iota is unequivocally attached to its three neighbouring carbon particles. These hexagonal sheets at that point seem to stack upon one another to make the general structure of graphite. The holding between the sheets is a lot more vulnerable than the holding between the molecules in the planes. Graphite conducts power. The terminal in a typical dry cell battery is made of graphite. [Arfin,Tanvir et al, 2018]

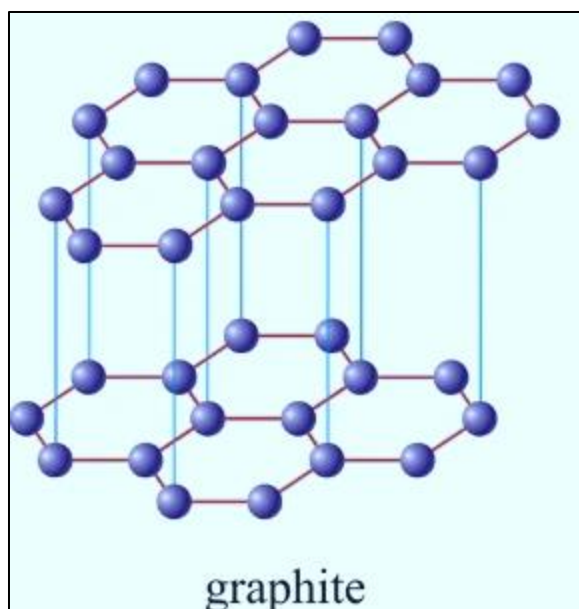


Fig. 1.1: Structure of Graphite

1.4.2 Diamond

Diamonds are the hardest material found in nature. A Diamond ring can scratch glass effectively, and the teeth of some observed cutting edges contain small jewels to assist them with bettering slice through solid, blocks and wood. Jewel's hardness (and its different properties) originates from its nanostructure – the way that the carbon molecules are masterminded on the nanoscale. Every carbon atoms are firmly clung to four neighbouring carbon molecules, in a three-dimensional course of action. This 3-dimensional course of action called a tetrahedron, (alongside the quality of the bonds between the carbons) makes the structure extremely inflexible and hard. In addition to these two familiar forms of carbon, scientists have recently discovered other forms of carbon: fullerenes and carbon nanotubes (CNTs). [Arfin,Tanviretal, 2018]

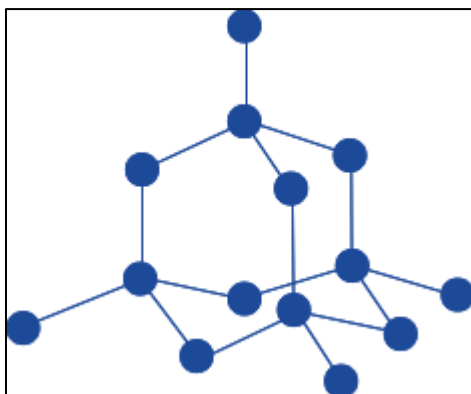


Fig. 1.2: Structure of Diamond

1.4.3 Fullerenes:

A buckminsterfullerene particle, otherwise called fullerene or "buckyball," contains 60 carbon atoms orchestrated to frame an empty circle. It has the structure of a shortened icosahedron. Its sub-atomic recipe is C_{60} . Every carbon molecule in the circle is attached to its three neighboring carbons. The atoms are masterminded to frame a blend of hexagons and pentagons. This equivalent example of hexagons and pentagons can be seen when taking a gander at a soccer ball.

The buckminsterfullerene atom was named after a draftsman, Robert Buckminster Fuller, who was answerable for the first geodesomes. The buckyball was first found in 1985, by Richard Smalley, Robert Curl and Harold Kroto. They found it during an examination where a laserwarmed graphite until it vanished. The rest of the residue contained a little division of buckyballs. In 1996 Smalley, Curl and Kroto won the Nobel Prize in Chemistry for their disclosure. The 'cage like' nature of the bucky ball makes it attractive as a container or trap for other atoms or molecules. It has also been proposed as a possible HIV inhibitor or a lubricant. [Birkett P.R., 2001]

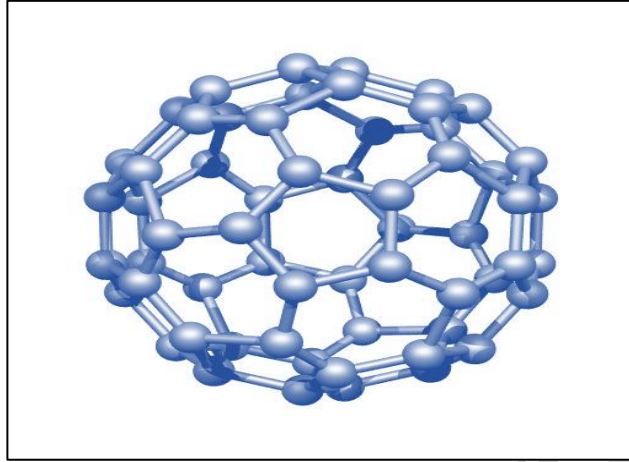


Fig. 1.3: Structure of Fullerene

1.4.4 Carbon Nanotubes (CNTs):

Carbon nanotubes (CNTs) are an all the more as of late found type of carbon. It is advantageous to think about a CNT as a sheet of graphite (likewise called a graphene sheet) moved up to frame a cylinder. Be that as it may, this isn't the way CNTs are shaped. CNTs were found unintentionally by Sujiomlijima in 1991. While making buckyballs, Iijima saw long, needlelike structures (the CNTs) blended in with the buckyballs. CNTs are additionally delegated single-walled (SWNT) or multi-walled (MWNT). SWNTs take after a solitary graphene sheet moved up, while MWNT is comprised of a few SWNTs settled inside one another. There are three sorts of nanotubes: easy chair, crisscross and chiral. The three structures are portrayed by the direction of the hexagonal examples inside the graphene sheets. In spite of the fact that the auxiliary contrasts in the three kinds of CNTs are unpretentious, they offer ascent to altogether different properties. [Arfin, Tanviretal, 2018]

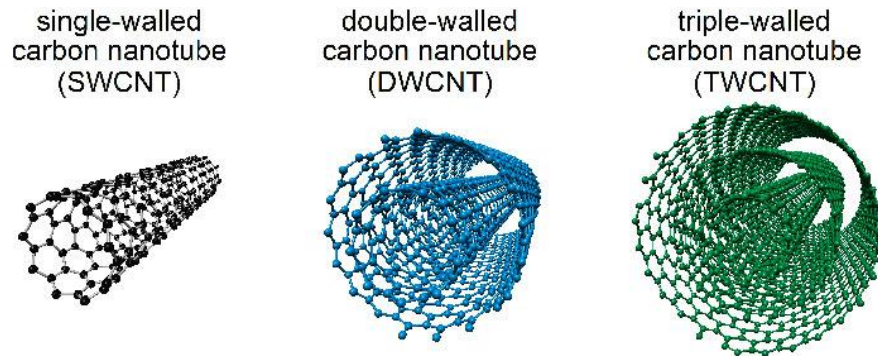


Fig. 1.4: Structure of Types of Carbon nanotubes

1.5 APPLICATION OF CARBON:

Pencil leads for mechanical pencils and sticks of the vine and compacted charcoal are made of graphite. Fabrics of woven carbon filaments, silicon carbide single gem, tungsten carbide end plants are hardly any utilizations of carbon. There are other numerous uses of carbon, for example, carbon blacks in the printing ink, paint, paper and plastic enterprises. Minor sums are utilized in the production of dry cells and carbon brushes, and as protection.

1.6 ACTIVATED CARBON:

Activated carbon, additionally generally known as actuated charcoal or initiated coal is a type of carbon which has been handled to make it incredibly permeable and in this way to have a huge surface zone accessible for adsorption or compound responses. The word dynamic is some of the time utilized instead of actuated. Because of such high level of micro porosity, only 1 gram of initiated carbon has a surface zone more than 500 m (around one-tenth the size of an American football field), as ordinarily dictated by nitrogen gas adsorption. Adequate enactment for valuable applications may come exclusively from the high surface territory, however further substance treatment by and large upgrades the adsorbing properties of the material. Activated carbon is most regularly gotten from charcoal.[Ceyhan, A.A et al, 2013]

1.6.1 Preparation of Activated Carbon:

Activated carbon is nothing but carbon produced from carbonaceous source materials like nutshells, peat, wood, coir, lignite, coal and petroleum pitch. It can be produced by any one of the following described processes:

1.6.1.1. Physical Activation:

By this procedure, the precursor is formed into enacted carbons utilizing gases. This is commonly done by utilizing one or a mix of the accompanying procedures. Physical actuation includes two stages, to be specific carbonization of the carbonaceous antecedent in a dormant air and ensuing initiation of the subsequent scorch within the sight of carbon gasification reactants (vaporous, for example, carbon dioxide, steam or air or an appropriate blend of the previously mentioned vaporous enacting operators. In the technique for physical enactment, the response included is between the carbon iota and the oxidizing gas. [Ahmadpour, A. et al, 1997] [Ahsaine, H.A. et al, 2018]

1.6.1.2 Carbonization:

Material having appreciable carbon content is pyrolysed at temperature ranging between 600–900 °C, in the absence of oxygen (usually in inert atmosphere with gases like argon or nitrogen). [Özdemir, M et al, 2011]

1.6.1.3 Activation/Oxidation:

In this process raw material or carbonized material is exposed to oxidizing atmosphere (carbon monoxide, oxygen, or steam) at temperatures above 250 °C, usually in the temperature range of 600–1200 °C.

1.6.1.4 Chemical activation:

Prior to carbonization, the crude material can be impregnated with specific synthetic compounds. The synthetic should be normally a corrosive, solid base, or a salt (phosphoric corrosive, potassium hydroxide, sodium hydroxide, zincs chloride, separately). After impregnation, the crude material should be carbonized at lower temperatures (450 – 900 °C). It is accepted that the carbonization/initiation step continues at the same time with the concoction enactment. It requires some investment and much

vitality for delivering micro porous activated carbon through physical enactment strategies. Likewise, another natural disadvantage of this technique is that a lot of inward carbon mass is dispensed with to get all around created pore structure. Synthetic enactment is favored over physical initiation inferable from the lower temperatures and shorter time required for actuating material. [Ahsaine, H.A. et al, 2018]

1.6.2 Activated Carbon Micropores:

The micro pores structure a meshwork structure inside the activated carbon. The micro pore dividers have a huge surface territory (500 – 2500 m²/g) and different substrates can be adsorbed on a superficial level. Most activated carbon comprises of 90% or more carbon. Some portion of the carbon is in mixes with oxygen and hydrogen. Debris content is a segment that is unconventional to the crude material and contains Na, Si, K, Ca, and Fe. All around purged activated carbon is utilized for nourishment added substances and clinical employments. [Shu J et al, 2017]

1.6.3 Pore Formation of Activated Carbon:

Activated carbon has miniaturized scale pores (breadth: 10 – 200 Å) made by responding with actuation gas and concoction specialists at high temperatures utilizing a carbon substrate, for example, coal and coconut shells. During this response if carbon iotas were to be expelled from the inside of beginning pores shaped because of devolatilization during carbonization growth of opened small scale pores and the opening up of the shut miniaturized scale pores happens.[Yagmur, E. et al, 2008]

1.6.4 Raw Materials for Different Forms of Activated Carbon:

1.6.4.1 Powdered activated carbon:

Sawdust, Hard wood chips, wood charcoal (carbon from sawdust), Grass ash (peat) etc...

1.6.4.2 Granulated activated carbon:

Charcoal, Coconut shell charcoal, Coal (lignite, brown coal, bituminous coal, anthracite coal, etc.), Oil, carbon, Phenolic resin etc...

1.6.4.3 Fibrous activated carbon:

Rayon, Acrylonitrile, Coal, tar pitch, Petroleum pitch, Phenolic resin, etc.

1.6.5 Properties of Activated Carbon:

Portrayal for activated carbon is significant so as to characterize initiated carbon for explicit employments. Essentially, activated carbon portrayed by physical properties and compound properties. Suzuki M., (1994) referenced that the attributes of initiated carbon rely upon the physical and synthetic properties of the crude materials just as the actuation strategy utilized. Physical properties of initiated carbon, for example, debris substance and dampness substance can influence the utilization of granular enacted carbon and render them either reasonable or unacceptable for explicit applications. While the particular surface territory of activated carbon and surface science is named concoction properties. Besides, the permeable structure of activated carbon additionally can be described by different strategies, for example, adsorption of gases (N₂, Ar, Kr, and CO₂) or fumes (benzene, water), scanning electron microscopy (SEM) and so forth. [Sircar, S.etal, 1996]

1.6.5.1 Moisture Content:

Activated carbon is by and large evaluated on a dampness free premise, albeit once in a while some dampness content is specified, e.g., 3, 8, 10% , except if bundled in sealed shut holders, some activated carbons when putting away under moist conditions will adsorb impressive dampness over a time of a month. They may adsorb as much as 25 to 30% dampness and still seem dry. For some reasons, this dampness content doesn't influence the adsorptive force; however, clearly, it weakens the carbon. In this manner, the extra weight of damp carbon is expected to give the necessary dry weight.

1.6.5.2 Ash Content:

Ash is the inorganic buildup staying after the water and natural issue have been evacuated by warming within the sight of oxidizing operators. It is finished by the proximate examination technique which gives the debris content in rate content regularly under 10% for activated carbon.

1.6.5.3 Surface area:

For the most part, the bigger the particular surface territory of the Activated carbon, the better is its adsorption execution. The most generally utilized business Active carbons have a particular surface zone of the request for 600-1200 m²/g. The pore volume restrains the size of the atoms that can be adsorbed while the surface zone confines the measure of material which can be adsorbed, accepting a reasonable sub-atomic size. The adsorptive limit of adsorbent is identified with its inward surface region and pore volume. The particular surface zone (m²/g) of permeable carbon is most generally decided from gas adsorption estimation utilizing the Brunauer-Emmett-Teller (BET) hypothesis (Hu and Srinivasan, 1999). The most normally utilized strategy to portray these auxiliary parts of the porosity depends on the translation of adsorption isotherm (e.g., N₂ at 77K). Nitrogen at its breaking point of 77K is the suggested adsorptive, in spite of the fact that argon at 77K is likewise utilized.

1.6.6 Application of Activated Carbon:

Uses of Activated carbon are tremendous. Its significant use is for fuel fume outflow control canisters in a vehicle. Activated carbon can go about as a channel material in air cleaning channels for expulsion of gases and fumes in the modern condition [Sircar, S. et al, 1996]. Particularly impregnated grades are utilized in cigarette channels to retain a portion of the unsafe segments of tobacco. It is likewise utilized as the impetus or bearer of chemically dynamic substances or supports. Overwhelming metal particles, for example, mercury, lead and cadmium in drinking waters are extremely risky even in follow sum and adsorption strategy for evacuating these particles can be basic for water and wastewater debased by substantial harmful metal particles [Zhao, D. et al, 2016]. For instance lead, cadmium, mercuric particles all are extremely poisonous and cancer-causing. Lead is additionally a combined metabolic toxin, going about as a mutagen when adsorbed in exorbitant sums. These particles can't be expelled from water with great physical or synthetic medicines totally. Enacted carbon can be utilized for evacuation of noxious substantial metal particles from watery arrangements. Adsorption, for this situation, is because of the surface complex development between the metal particles and the acidic surface capacity gathering of initiated carbon [Ariyadejwanich, P. et al,

2003]. The expulsion productivity is impacted by different factors, for example, arrangement focus, arrangement pH, ionic quality, nature of adsorbate, adsorbent change system, physical properties (surface territory, porosity), and the synthetic idea of activated carbon[Loredo-Cancino, M. et al, 2013].

Activated carbon materials described by high explicit surface zone and tunable porosity discover utility in numerous crucial advancements to be specific vitality stockpiling (super capacitors, batteries, and hydrogen sorption), vitality transformation (power modules, sun oriented cells), sensors, natural assurance (control SO_x and NO_x outflows from fuel ignition in autos), creation of fine and mass synthetics and catalysis, and so on [Yasin, A.S. et al, 2019].

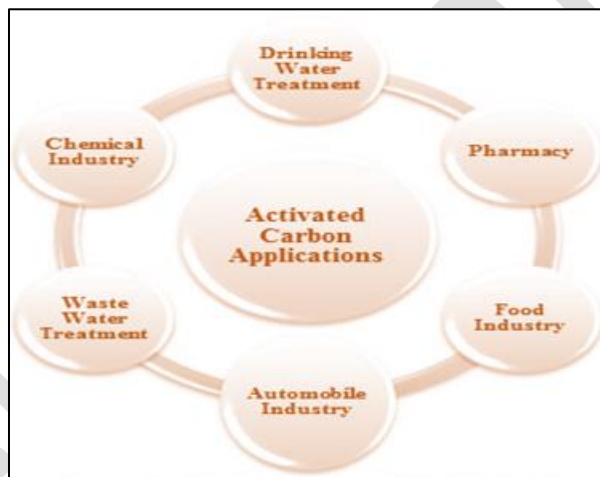


Fig. 1.5: Applications of Activated Carbon

1.6.7 Chemical Structure of Activated Carbon:

The essential concoction structure of Activated carbon is firmly identified with the structure of unadulterated graphite. The graphite precious stone is made out of layers of intertwined hexagons held by powerless Van Der Waals powers. The layers are held via carbon-carbon bonds. Activated carbon is a disordered type of graphite, because of polluting influences and the technique for planning (actuation process). Initiated carbon is set up via a cautious controlled oxidation procedure to build up a permeable carbon structure. The pore structure created in the Activated carbon, and in this manner the last

properties of the Activated carbon, chiefly rely upon the crude material and the creation procedure. The blemished structure brings about a high level of porosity and over an expansive scope of pore sizes from obvious breaks and cleft to holes and voids of sub-atomic measurements [Rodríguez-Reinoso, Francisco, 2002]. (<https://ars.els-cdn.com/content/image/1-s2.0-S1387181117306224-fx1.jpg>)

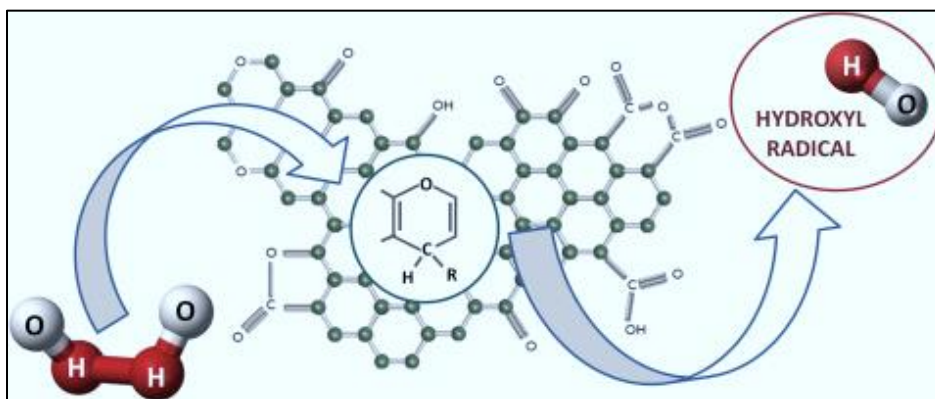


Fig. 1.6: Chemical Structure of Activated Carbon

1.7 ZIRCONIUM DOPED ACTIVATED CARBON:

The Zirconium oxide doped activated carbon was prepared by infusion of 20% wt. of, Zirconyl chloride octahydrate on the prepared activated carbon after six hours of stirring under a magnetic stirrer. It was then washed 4-5 times using hot distilled water and one time using diluted hydrochloric acid. The infused activated carbon was then ground into a fine powder using a mortar and pestle. It was then dried in a hot air oven at 70°C for 12 hours.

1.8 ADSORPTION STUDIES:

Adsorption is the bond of particles, particles or atoms from a gas, fluid or broke up strong to a surface. This makes a layer of the adsorbate on the boundary of the adsorbent. This cycle varies from assimilation, in which a liquid (the absorbate) is disintegrated by or pervades a fluid or strong (the retentive), respectively. Adsorption is a surface marvel, while ingestion includes the entire volume of the material, despite the fact that adsorption

does frequently go before absorption. The term sorption incorporates the two cycles, while desorption is the opposite of it.

Adsorption of proteins is critical when a material is in contact with blood or body liquids. On account of blood, egg whites, which is to a great extent overwhelming, is for the most part adsorbed first, and afterward improvements happen for other minor proteins as per surface proclivity against mass law choice (Vroman impact). Adsorbed atoms are those that are impervious to washing with a similar dissolvable medium on account of adsorption from arrangements. The washing conditions would thus be able to adjust the estimation results, especially when the collaboration energy is low.

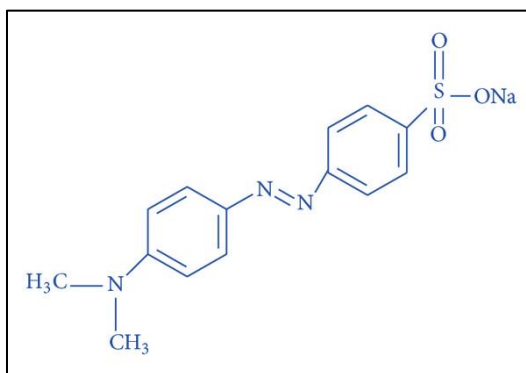
Like surface pressure, adsorption is a result of surface energy. In a mass material, all the holding prerequisites (be they ionic, covalent or metallic) of the constituent atoms of the material are filled by different particles in the material. Notwithstanding, atoms on the outside of the adsorbent are not completely encircled by other adsorbent particles and in this manner can pull in adsorbates. The specific idea of the holding relies upon the subtleties of the species in investigation, the adsorption is physisorption or chemisorption. It might likewise happen because of electrostatic attraction.

Adsorption is available in numerous characteristics, physical, organic and substance frameworks and is generally utilized in modern applications, for example, heterogeneous catalysts, enacted charcoal, catching and utilizing waste warmth to give cold water to cooling and other cycle prerequisites (adsorption chillers), engineered pitches, expanding capacity limit of carbide-inferred carbons and water sanitization. Adsorption, particle trade and chromatography are sorption measures in which certain adsorbates are specifically moved from the liquid stage to the outside of insoluble, inflexible particles suspended in a vessel or stuffed in a section. Drug industry applications, which use adsorption as a way to draw out neurological openness to explicit medications or parts thereof are lesser known.

Different sorts of engineered colors are found in emanating wastewaters from an assortment of enterprises like material, cowhide, plastic, food preparing, makeup, paper, printing, drug and color producing. Colors normally have a manufactured starting point

and complex substance structure which make them truly stable to light and oxidation and hard to biodegrade [Ofomaja et al, 2008]. As perilous toxins, they present biological dangers and are harmful to oceanic life whenever released straightforwardly into accepting waters. They might be mutagenic and cancer-causing and can cause an extreme wellbeing danger to individuals, like brokenness of kidney, regenerative framework, liver, cerebrum and focal sensory system, and accordingly ought to be treated prior to releasing into the getting waterway [Aksu, 2005]. A few physical, synthetic and natural treatment methods have been applied to eliminate colors from wastewater, like photochemical corruption, organic debasement, coagulation, substance oxidation, switch assimilation, buoyancy and adsorption. Among those strategies, adsorption on initiated carbons is generally utilized attributable to its high proficiency and capacity to isolate a wide scope of substance compounds, effortlessness of plan and financial plausibility.

Methyl orange (MO) is one of the notable acidic/anionic colors, and has been broadly utilized in material, printing, paper, food and drug businesses and examination laboratories. Additionally, it is quite possibly the most widely recognized cationic passing on materials for wood, silk and cotton. The design of MO is appeared in structure, despite the fact that MO is not exceptionally dangerous, it can cause some destructive impacts. Intense openness to MO can cause expanded pulse, spewing, stun, cyanosis, jaundice, quadriplegia, and tissue rot in humans. Thus, expulsion of MO from wastewater as well as interaction gushing is vital because of their possible harmfulness to human and climate. MO for the reasons expressed above were chosen in this investigation as the model dye which will be removed from the aqueous solution.



The primary target of the current work is to report adsorption of an anionic dye (MO) over zirconium doped activated carbon in light of the fact that the expulsion of anionic dye is promptly accomplished. The adsorption can be seen much by a correlation between the adsorbate and adsorbent. The other industrially accessible activated carbons including CS-AC (Coconut Shell-Based Activated Carbon), C-AC (Coal-Based Activated Carbon), NS-AC (Nut Shell Based Activated Carbon), and W-AC (Wood Based Activated Carbon) were done in literature.

CHAPTER 2

LITERATURE SURVEY

Activated carbon has been prepared from many raw materials such as agricultural waste, wood, peat, lignite, coal, etc. by various methods. A few related works have been given below along with the emerging uses of activated carbon in various fields.

Emine Yagmuret al prepared activated carbon by chemical activation of waste tea with phosphoric acid with and without microwave treatment. The waste tea activated carbon was characterized for surface area and pore volume and found that microwaving reasonably increased micropores surface area than that of conventional activated carbon.

Jatinder Kumar Ratan et al chose rice husk, corncob and wheat straw from rural agricultural waste as a precursor for activated carbon to be used as a layer in water purification. The thus formed activated carbon was characterized using Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Energy-dispersive-X-ray Spectroscopy (EDS), and BET surface area analyser, proximate and ultimate analysis.

Since 2016 there has been a special interest in activated carbon fiber derived from regenerated cellulose (viscose rayon) and polyacrylonitrile fiber (PAN). In case of viscose rayon to reduce the weight loss during pyrolysis it is infused with a Lewis acid such as ammonium or aluminium chloride. [F Rodriguez-Reinoso et al 2016]

According to Hakan Demiral et al activated carbon prepared from bagasse which was chemically activated using phosphoric acid was used to remove copper(2) from aqueous solutions. The activated carbon thus produced was characterized by Scanning Electron Microscope (SEM), Boehm titration and N₂ adsorption.

Ana lei Cuckierman shows the environmental applications and development of activated carbon cloths as a superior adsorbing material than the powdered or granular form of activated carbon. Activated carbon cloths possess faster adsorption kinetics, higher

efficiency and higher capacity for adsorption due to greater surface area and pore volume in ACC's compared to its counterparts.

H. AitAhsaneet al demonstrated the adsorption of methyl Orange (MO) and crystal violet(CV) into activated carbon(AC)/Zirconium oxide composite prepared from almond shell as adsorbent following full activated carbon characterization by FTIR spectroscopy, scanning electron microscopy (SEM) and BET surface analyser.

Sathiyabama

CHAPTER 3

AIM & SCOPE

3.1 AIM

To prepare activated carbon by using domestic food waste (leftover cooked rice) and use it as a catalyst in the synthesis of Zirconium dioxide activated doped carbon in dye removal from aqueous solution.

3.2 SCOPE

- ❖ Collection of leftover cooked rice from domestic sources.
- ❖ Drying of food waste by sun drying.
- ❖ Preparation of raw carbon from dried food waste.
- ❖ Preparation of activated carbon by using raw carbon as precursor by chemical activation method.
- ❖ Zirconium oxide doping of activated carbon using Zirconyl chloride octahydrate to prepare zirconium oxide doped activated carbon.
- ❖ Characterization of activated carbon and zirconium oxide doped activated carbon by FTIR and SEM analysis.
- ❖ Adsorption studies of zirconium oxide doped activated carbon in methyl orange.
- ❖ Application: Dye removal (using methyl orange) and optimization.

CHAPTER 4

MATERIALS AND METHODS

4.1 MATERIALS

Materials used in this process are waste food product (cooked rice leftovers from domestic sources), Sodium hydroxide, Zirconyl chloride octahydrate, Methyl orange dye. All chemicals were bought from Merck chemicals and used as such.

4.2 CHARACTERIZATION TECHNIQUES

4.2.1 FTIR (Fourier Transform Infrared Spectroscopy):

FTIR is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high spectral-resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time. Spectroscopy is the study of interaction of electromagnetic waves (EM) with matter. The surface functional groups of the samples were qualitatively analysed by FTIR spectroscopy (Bruker FTIR) and recorded in the range of 4000 – 600 cm^{-1} . For this purpose, the samples were mixed with potassium bromide and made into pellets for analysis.

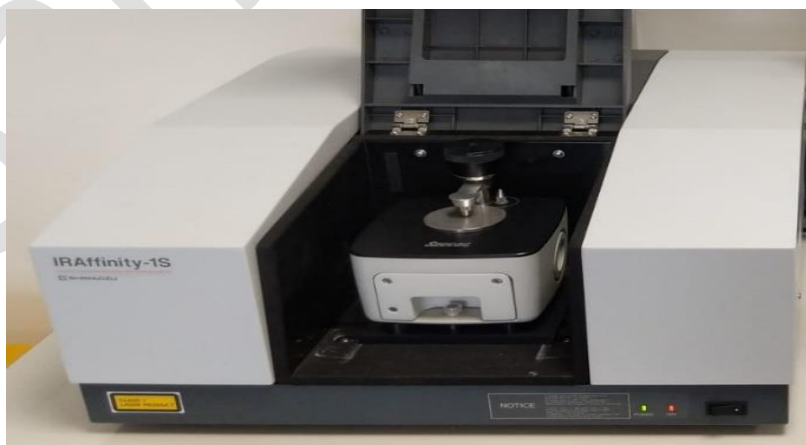


Fig. 4.1: Fourier Transform Infrared Spectrometer

4.2.2 SEM (Scanning Electron Microscopy):

The scanning electron microscopy is vital sorts of portrayal procedure and it utilizes an engaged electron bar and to check strong example from the optical to the Nano scale run. In these kinds of portrayal procedures, auxiliary electrons are transmitted from the example and it gathered to make a region guide of the optional discharge. The force of auxiliary outflow is relies upon neighbourhood morphology. In SEM examination systems electron bar goes through the thin example since it is exceptionally arranged thin example are upheld on the TEM matrix. In this strategies picture appeared fluorescent screen and picture is a two dimensional projection of test. They give three dimensional pictures and it has 0.4 nm in size. The SEM depends on dispersed electrons and dissipated electrons in SEM strategies created picture of the example after magnifying instrument gather and checks dissipated electrons. It offers 2 million greatest dimension of amplification. The scanning electron microscopy is utilized to decide the outer morphology (surface), concoction arrangement, and crystalline structure of the nanomaterial tests. In SEM examination systems the zones territory from around 1 cm to 5 microns in width can be imaged in a filtering mode utilizing unsurprising SEM methods and having amplification run from spatial goals of 50 nm to 100 nm. The different frequencies are utilized for the goals of tests and it gives different morphological shapes pole, package and bloom to the concerned nanomaterial. The gadget and capacity of the SEM is fundamentally the same as the electron test micro analyser (EPMA) and noteworthy covers in ability exist between the two instruments.



Fig. 4.2: Scanning Electron Microscope (SEM)

4.3 SYNTHESIS OF ZIRCONIUM OXIDE DOPED ACTIVATED CARBON

4.3.1 Preparation of Activated Carbon

Leftover cooked rice from domestic organic waste was used as a precursor for the production of activated carbon. The precursor was washed several times with distilled water. The precursor was dried in sunlight for 2 to 3 days until moisture was removed. The precursor was then pyrolysed in a muffle furnace inside a china crucible at 400-500°C. This led to the production of fine carbon powder which is the raw carbon.

4.3.2 Doping with Zirconium oxide

This raw carbon was then activated by chemical activation method in a muffle furnace with NaOH in a crucible at 400-500°C. The activated carbon was then washed 4-5 times using hot distilled water and one time using diluted hydrochloric acid to remove any traces of NaOH. The activated carbon was then ground into a fine powder using a mortar and pestle. It was then dried in a hot air oven at 80°C for an hour.

4.3.3 Adsorption Studies (methyl orange):

The adsorption ability of the synthesized adsorbent in the removal of methyl orange from the aqueous solution was determined for different time period. A known quantity of the zirconium oxide doped activated carbon sample (0.5g) was taken in 25 ml of methyl orange solution (50 ppm) and shaken at a constant speed of 120 rpm in a rotatory shaker at room temperature. The samples of the aqueous methyl orange dye solution after treatment were taken at regular time intervals (10 – 60 min) and centrifuged. The absorbance of the centrifugate solution was measured at 665 nm using a spectrophotometer. The percentage removal of methyl orange by the zirconium oxide doped activated carbons is calculated by

$$\% \text{ Removal} = \frac{(C_0 - C_e)}{C_0} \times 100$$

where C_0 and C_e are the initial and equilibrium concentration (mgL^{-1}) respectively. The adsorption capacity (q_e and q_t) at equilibrium and time t was determined by :

$$q_e = \frac{(C_0 - C_e)V}{M}$$

$$q_t = \frac{(C_0 - C_t)V}{M}$$

where V is the volume of the solution (L) and M is the mass of the adsorbent (g).

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 SPECTRAL DATA FOR ZIRCONIUM OXIDE DOPED ACTIVATED CARBON

5.1.1 SEM (Scanning Electron Microscopy):

The SEM images of activated carbon samples are shown in Figure 5.1 SEM analysis was carried out to show the pore structure of the activated samples. As observed in the micrographs, chemical activation followed by pyrolysis was useful in developing the pore structure on the surface of the activated carbon. The SEM images showed the heterogeneous porous nature of the activated carbon samples. The highly porous surface indicates the relatively high surface area. The SEM image of zirconium oxide doped activated carbon sample is shown in Fig. 5.2. It also shows the layered structure of Doped activated carbon. The pore size has decreased from the pore size of activated carbon, hence doping has done successfully. The ZrO_2 particles are found agglomerated on the surface of the activated carbon. The deposition of ZrO_2 particles is also found even in the pores of the activated carbon.

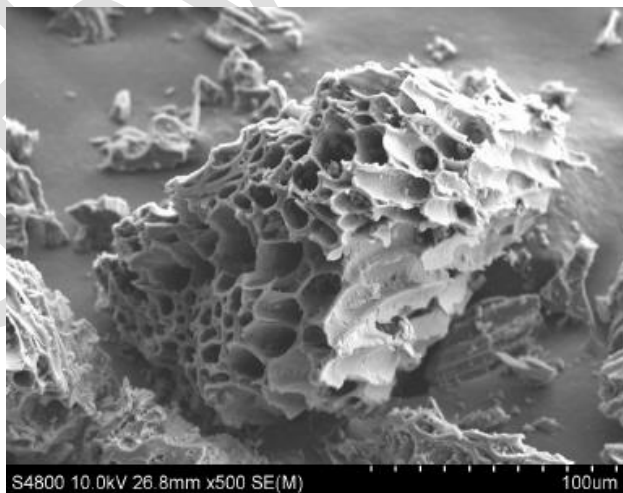


Fig. 5.1: SEM Image for activated carbon

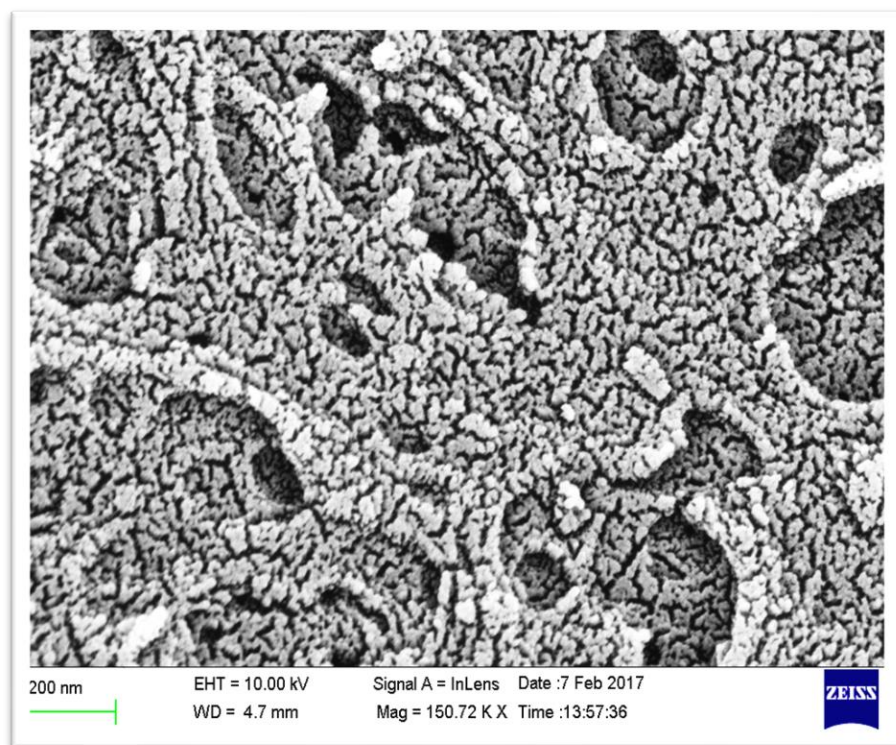


Fig. 5.2: SEM Image for zirconium oxide doped activated carbon

5.1.2 FTIR data for Zirconium oxide doped activated carbon

The FT-IR spectra and data obtained is shown in the Fig. 5.3 and Table 5.1. The absorption peak at 1383.01 cm^{-1} corresponds to the vibrational frequency of $\text{Zr} - \text{O} - \text{C}$ bond which confirms the doping of Zirconium to activated carbon. The common absorption peaks at 3400 cm^{-1} and 2500 cm^{-1} and 1160 cm^{-1} are showing low intense peak due to the doping of Zr with activated carbon

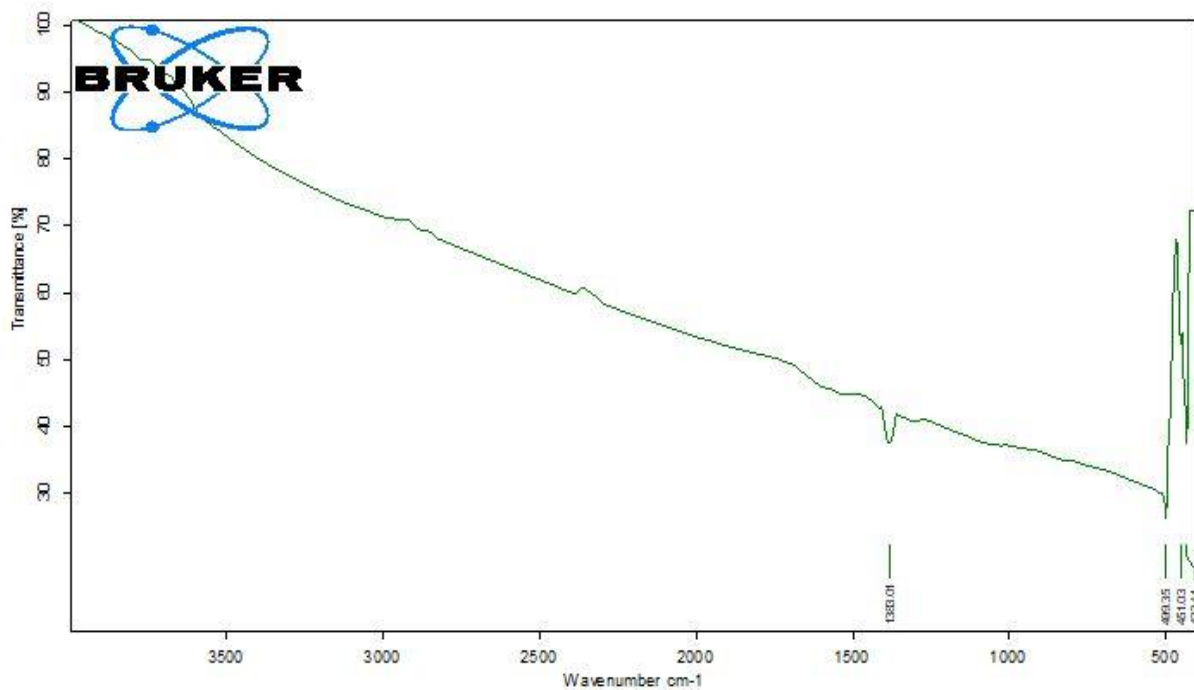


Fig. 5.3: FTIR Image for Zirconium oxide doped Activated Carbon

Table 5.1: Spectral Data for Zirconium Doped Activated Carbon

Vibrational Frequency Identification	Functional Group
1383.01 cm-1	Zr – O – C STRETCHING
499.35 cm-1	C – H STRETCHING
451.03 cm-1	C – H STRETCHING
433.31 cm-1	C – H STRETCHING

5.2 ADSORPTION ISOTHERM

Freundlich isotherm was used to examine the adsorption of methyl orange on the zirconium oxide doped activated carbon. The Freundlich isotherm is generally represented by

$$q_e = k_f C_e^{1/n}$$

$$q_e = \frac{(C_o - C_e)}{M} = k_f C_e^{1/n}$$

where q_e is the adsorption capacity (mg g^{-1}), C_o and C_e are the initial and equilibrium concentration (mg L^{-1}) respectively, k_f and n are Freundlich constants related to the adsorption capacity respectively and M is the mass of adsorbent (g). The logarithmically the Freundlich isotherm is represented as

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e$$

The graph plotted between the $\ln q_e$ versus $\ln C_e$ for the adsorption of methyl orange on the zirconium oxide doped activated carbon is shown in Figure 5.4. k_f and n were determined from the slope and intercept of the linear plot. The Freundlich adsorption isotherm parameters for adsorption of methyl orange dye from the aqueous solution using the adsorbent is shown the Table 5.2. The Freundlich isotherm was proved to be better fit from the regression coefficient. This indicated the heterogeneity of the zirconium oxide doped activated carbon adsorbent surface. Figure 5.5 shows the effect of time on stream for the removal of methyl orange by using the zirconium oxide doped activated carbon sample.

Table 5.2 Parameters of Freundlich adsorption isotherm for the adsorption of methyl orange dye from aqueous solution

S.No	C _i (mg/L)	C _e (mg/L)	1/C _e	log C _e	ln C _e	q _e (mg/g)	1/q _e	ln q _e
1	10	2.4	0.4167	0.38021124	0.87546874	3.8	0.26315789	1.335
2	20	5.1	0.1961	0.70757018	1.62924054	7.45	0.13422819	2.0082
3	30	14.6	0.0685	1.16435286	2.68102153	7.7	0.12987013	2.0412
4	40	18.2	0.0549	1.26007139	2.90142159	10.9	0.09174312	2.3888
5	50	24.5	0.0408	1.38916608	3.19867312	12.75	0.07843137	2.5455

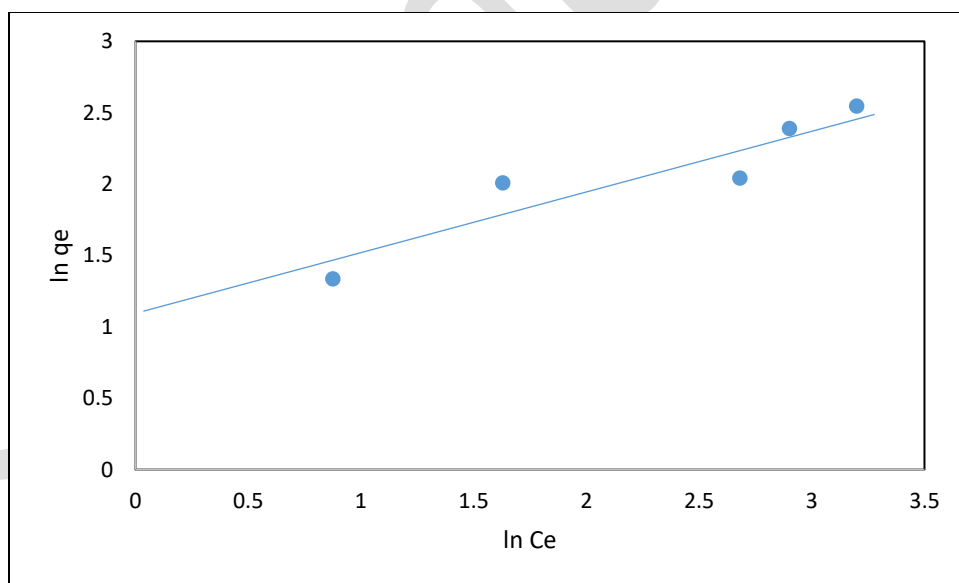


Fig. 5.4: Freundlich adsorption isotherm for adsorption of methyl orange dye from aqueous solution

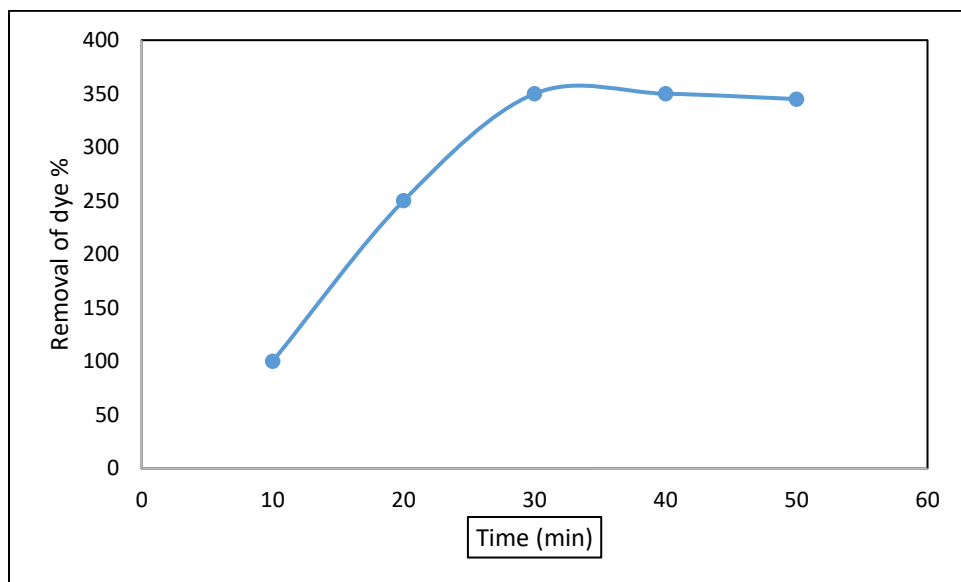


Fig. 5.5: Effect of time on stream for adsorption of methyl orange dye from aqueous solution

CHAPTER 6

CONCLUSION

The zirconium oxide doped activated carbon was prepared effectively from cooked food waste by using NaOH chemical activation method. The synthesized adsorbent material is cheap, environmentally friendly, very efficient for the adsorption of dyes. The activation method has improved the adsorption activity due to the high porosity, thus these materials can be utilized as low-cost adsorbents. The characterization results show the nature and stability of the porous adsorbent. SEM analysis shows the porous nature of the adsorbent. The adsorption of methyl orange dye was done to estimate the adsorption nature of the adsorbent. Methyl orange adsorption was found to obey the Freundlich adsorption isotherm. This investigation showed that the zirconium oxide doped activated carbon synthesized from the food waste can be efficiently used as efficient and less expensive adsorbent material for the adsorption of methyl orange dye from aqueous solution.

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