Use of Rice Husk Ash as an Adsorbent for the Removal of Zinc from Standard Solution

A DISSERTATION

Submitted in partial fulfilment of the
Requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
ENVIRONMENTAL MANAGEMENT OF RIVER AND LAKES

By
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CANDIDATE DECLARATION

I hereby certify that the work which is being presented in progress report, entitled **"Analysis of Rice Husk Ash as an Adsorbent to remove Zinc from its Synthetic Solution"** in partial fulfilment of the requirement for the award of the degree of **Masters Of Technology** with specialization in **"Environment Management of River and Lakes",** submitted in **DEPARTMENT OF HYDRO AND RENEWABLE ENERGY,Indian Institute of Technology Roorkee** is an authentic record of my own work carried out during the period from May 2018 to May 2019 under the supervision of **Prof. S.K. Singal and Prof. M.P. Sharma,Department of Hydro And Renewable Energy, Indian Institute of Technology Roorkee India**.

I have not submitted the matter embodied in this seminar report for award of any other degree.

Dated:

Place: ROORKEE-247667 **(ANSHUL TYAGI)**

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

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ABSTRACT

In the present study Rice Husk Ash has been used as a fixed bed in Column Adsorption Test to study the removal of Zinc metal from its Standard Solution. Various parameters such as pH, Initial Metal Ion Concentration were studied to find the optimum conditions for maximum efficiency. Temporal analysis was carried out to obtain the breakthrough curve which shows the time at which the bed has been fully utilized and cannot be further utilized. Experimental data obtained from the column study were fitted in two well established column models, Yoon-Nelson Model and Thomas Model to calculate the breakthrough time and adsorption capacity of the adsorbate respectively. Morphological Characteristics of Rice Husk Ash was also studied using the Image obtained from Scanning Electron Microscope and its analysis using ImageJ software. From the study it is concluded that RHA is highly porous and have high specific surface area, and from the results obtained from the tests it was concluded that Rice Husk Ash has high efficiency for the removal of zinc.

KEYWORDS: Rice Husk Ash, Adsorption, Fixed Bed Column, Zinc, Scanning Electron Microscope

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1.1 GENERAL INTRODUCTION

Industrial activities such as mining, electroplating, tanning, metallurgical operation and manufacturing have led to the release of heavy metals into the environment. Unlike the organic pollutants which are bio-degradable,heavy metallike Cadmiumand Zinc are not bio-degradable. These heavy metals have hazardous effects on theenvironment and humanhealt h. A little exposure to these heavy metals even at low concentrations can cause many serious diseases. They start to bio-accumulate in the human body. Therefore, both human health and agriculture are at risk. Hence, the removal of heavy metals from water is to be considered. So for removal of heavy metals adsorption is used. Adsorption is a very efficient process if carried out in a proper way. It is the process by which molecules of a substance, such as a gas or a liquid binds on the surface of another substance such as a solid is called adsorption. Solids that adsorb a component are called the adsorbents and the component adsorbed is called the adsorbate. This process arises due to presence of unbalanced or residual forces at the surface of liquid or solid phase. These forces have tendency to attract and retain the molecular species with which it comes in contact with the surface. This is essentially a surface phenomenon. [12]

Removal of heavy metals is of utmost importance. “Heavy metals” refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration. Their atomic density is said to be greater than 4 g/cm^3, or 5 times greater than water. However, chemical properties are of more concern than density. Most heavy metals are toxic and carcinogenic in nature and represent a serious threat to the human population and the fauna and flora of the receiving water bodies. Hence, the removal of heavy metals from water is to be considered. Some methods have been developed to remove heavy metals from waste water before discharge into the water bodies. These methods include reduction, precipitation, ion exchange reverse osmosis, dialysis and adsorption by coated carbon. But these are not economically suitable for developing countries. Adsorption is the most widely used methods among existing techniques. This has therefore led to the use of agricultural wastes in removal of heavy metals. Agricultural wastes are characterized by ready availability, affordability, Eco friendliness and high uptake capacity for heavy metals due to the presence of functional groups which can bind metals to effect the removal of heavy metal from effluents. Peanut hull (an agricultural waste) was found to be 36 times more efficient compared to granular activated carbon which is the widely used adsorbent.[12][13]

Other agricultural wastes which have been investigated for their metal adsorption property include sugar cane bagasse, soybeans hulls, cotton seed hull, rice bran, rice husk and straw as efficient heavy metal adsorbents.Need for safe and economical methods for the removalof heavy metals from contaminated waters has necessitated the use of Rice Husk. Rice husk because of its reasonable cost & greater availability can be used as an adsorbent in countries like India.

1.2 RICE HUSK ASH

Rice husks (or rice hulls) are the hard protecting coverings of grains of rice. It is an agricultural waste material generated in rice producing countries, especially in Egypt. They are the coatings of seeds, or grains, of rice. The seed is protected by husk during the growing season, since it is formed from hard materials, including silica and lignin. The husk is mostly indigestible to humans. The rice husk is separated from rice by the process of winnowing. It is one of the simplest processes which involve throwing of the mixture into the air so that the wind blows away the lighter husk, while the heavier rice fall back down for recovery. Globally, approximately 600 million tons of rice is produced each year. On average 10-20% of the rice paddy is husk, giving an annual total production of 120 million tons. India being one of the biggest rice producers in the world, not surprisingly, also produces vast amounts of rice husk. Bihar alone is estimated to produce 1.8 billion kilograms of rice husk every year.

In majority of rice producing countries much of the husk produced from processing of rice is either burnt or dumped as waste. Burning of Rice husk (RH) in ambient atmosphere leaves a residue, called rice husk ash. [14]

For every 1000 kgs of paddy milled, about 220 kgs (22 %) of husk is produced, and when this husk is burnt in the boilers, about 55 kgs (25 %) of RHA is generated. Some of the major problems caused by rice husk is its disposal due to less commercial interest and handling and transportation of RH due to its low density. This causes a great damage to land and surrounding area where it is dumped. Hence, commercial use of rice husk and its ash is the alternative solution to disposal problem.

Suitability of RH to be used for different applications depends upon the physical and chemical properties of the husk such as ash content, silica content etc. Apart from its use as fuel, RH finds its use as source raw material for synthesis and development of new phases and compounds. Applications of rice husk in industrial sectors as well as other fields include.

- As a Fuel in Power Plant
- Production of Portland cement
- Fireworks
- Formation of Activated Carbon
- As a source of Silica and Silicon Compounds Porous SiO_2/C composite from RH
- Insulating fire brick using RH
- Other uses RH is used as a raw material for production of xylitol, furfural, ethanol, acetic acid, lingo sulphonic acids

In recent years, attention has been focused on the utilization of unmodified or modified rice husk as a low cost (agricultural by-product) bio-adsorbent for the removal of various heavy metals (such as Pb, Cd, Zn, Ni) and metalloids (As) from both groundwater and surface water. The present study is focused on review of previous and current available information on potential rice husk for the removal of heavy metals and metalloids. Various studies on adsorption of rice husk taking into account the parameters: contact time, adsorbent dose (rice husk), and Initial concentration of heavy metals, pH, and temperature.[15]

1.3 REMOVAL OF HEAVY METALS

The adsorption process of heavy metals from waste water is influenced by various physical and chemical parameters like pH, temperature, initial heavy metal concentration, amount of adsorbent, particle size of adsorbents etc. These parameters determine the overall adsorption through affecting the selectivity and amount of heavy metals removed.

Heavy metals have a huge tendency to bio-accumulate and end up as permanent additions to the environment. Heavy metals include mercury (Hg), lead (Pb), cadmium (Cd), zinc (Zn), arsenic (As), silver (Ag) chromium (Cr), copper (Cu) iron (Fe), and group elements of platinum. Heavy metals like Cu, Zn, Ni, and Ar are known to have toxic effects at very low concentrations as well as very high concentration.

The binding to the surface is usually weak. The fluid that dissolves or suspends the material of interest is bound but compounds with color and those that have taste odor tend to bind strongly. Compounds that contain chromogenic groups (atomic arrangements that vibrate at frequencies in the visible spectrum) very often are strongly adsorbed on activated carbon.

Decolorization is very efficient by adsorption and with negligible loss of other materials.Most commonly used industrial adsorbents are activated carbon, silica gel, and alumina because they present enormous surface areas per unit weight. Adsorption phenomenon provides an excellent method of separation particularly at low concentrations and hence it is recognized as an important mass transfer operation.

Among all the heavy metals above mentioned, our focus will be on Zinc, therefore a brief introduction is preferable. Zinc is a lustrous bluish-white metal. It is found in group IIB of the periodic table. It is brittle and crystalline at ordinary temperatures, but it becomes ductile and malleable when heated between 110°C and 150°C. It is a fairly reactive metal that will combine with oxygen and other non-metals, and will react with dilute acids to release hydrogen. Its uses are quite variable from galvanization of steel to the manufacture of the negative plate in electrical batteries, passing through the preparation of some alloys. As a pigment, zinc is used in plastics, cosmetics, photocopier paper, wallpaper, printing inks etc, whereas in rubber production its role is to act as a catalyst during manufacture and as a heat disperser in the final product. Zinc metal is included in most single tablet, it is believed to possess anti-oxidant properties, which protect against premature aging of the skin and muscles of the body. Zinc is the 23rd most abundant element in the Earth's crust and its concentrations are rising unnaturally, due to addition of zinc through human activities. Most zinc is added during industrial activities, such as mining, coal and waste combustion and steel processing. When it is present in less quantity in human’s body, it affects considerably human’s health. Although humans can handle large extent of zinc, too much of it can still cause eminent health problems. Zinc is widely used in industries such as galvanization,paint, batteries, smelting, fertilizers and pesticides, fossil fuel combustion, pigment, polymer stabilizers, etc, and the wastewater from these industrie is polluted with zinc, due to its presence in large quantities. This wastewater is not purified satisfactory. One of the consequences is that rivers are depositing zinc-polluted sludge on their banks. [16]

1.4 Adsorption

Adsorptionis the process of adhesion of any substance on the surface of another substance. The Substance which gets adsorbed is called adsorbate and the substance on which the adsorbate gets adsorbed is called adsorbent. When a solid surface is exposed to a gas or a liquid, molecules from the gas or the liquid phase starts accumulating at the surface of the solid. This phenomenon of accumulation of molecules of a gas or liquid at a solid surface is called adsorption.

Forces of attraction exist between adsorbate and adsorbent. These forces of attraction can be due to Vander Waal forces of attraction which are weak forces or due to chemical bond which are strong forces of attraction. On the basis of type of forces of attraction existing between adsorbate and adsorbent, adsorption can be classified into two types: Physical Adsorption or Chemical Adsorption.

1.5 Types of ColumnAdsorption methods

In Column Adsorption methods, the Adsorbate is in continuous supply and always remains in contact with the Adsorbent; therefore the concentration of the Adsorbate that comes in contact with Adsorbent always remains constant.[22] There are various methods to bring the adsorbate and adsorbent in contact with each other such as:

- Batch Adsorption method
- Continuous moving bed method
- Continuous fixed bed method
- Continuous fluidize bed method
- Pulsed bed method

Table: 1 Comparative study of all methods of their features is done here

Parameters	**Batch Adsorption**	**Continuous fixed bed**	**Continuous moving bed**	**Continuous fluidize bed**	**Pulsed bed**
Contact Mechanism	In batch Adsorption adsorbate and adsorbent are brought in intimate contact by	In continuous fixed bed adsorbate is allowed to continuously pass down through the adsorbent.	In this method Adsorbent and Adsorbate are in continuous motion	Adsorbate is in contact with fluidized adsorbent beds with adequate or inadequate flow in this method.	In the method the adsorbate is brought in the contact with same adsorbent until

	directly mixing the known weight of both.		where the bed length remains constant but continuous removal and regeneration of bed is done		satisfactory removal is achieved.
Advantages	It is an easy and cheap method Generally used by researchers for analysis of Adsorption behaviour as it is to understand the different parameters affecting Adsorption.	It is also an easy and cheap method It is widely usedin the industrial world as it can handle higher waste water load having higher degree of pollution, it is so achieved as the adsorbate is in continuous supply and fresh waste water remains in	Complicated and very costly method. As adsorbent is substituted continually and new adsorbent is constantly in intimate contact of the adsorbent.	Complicated and very costly method. It is also useful for the industries having greater load and pollution level. Also, applicable to industrial sectors as it enables fast mixing of sorbate and sorbent and also adsorbate flows	Very easy and cheap technique Easy as it is controlled automatically It is beneficial as it requires lesser quantity of adsorbent. Also as soon as the bed is utilised it is reenergised.

		contact with the adsorbent.		continuously with controlled operation and easy handing	
Disadvantage	This method is not used industrially as it can handle mere quantity of waste water having low degree of pollution, So it is not generally used in industries.	The difficulties arise in this method are adsorbate does not pass through the bed uniformly, feed channelling etc Interaction between the adsorbate and adsorbent is pressurised in this method to reduce space and time. So it is difficult to design and optimize the fixed bed.	There is wastage of adsorbent in this method therefore it require higher quantity of adsorbent as compared to others for completeads orption It is vital to continuously regenerate adsorbent and to have an adsorbent storage.	Adsorbent flow is not evaluated with significant deviation from plug flow and bubbling or feed channeling, resulting in inadequate adsorbent contact.	This method is also not useful at industrial level as it is used for low pollution and waste water load.

1.6 LITERATURE REVIEW

Heavy metals such as chromium, cadmium, zinc, lead, mercury and copper in waste water are hazardous to the environment. The term “heavy metal” does not have a rigorous scientific basis or chemical definition. In observation, this group should preferably have been referred to as “toxic elements”.

In view of toxicities associated with these heavy metal ions, their removal from industrial effluents has become one of the thrust areas in modern research. Table 2 shows various literature which have been studied, discussed underneath, their findings have been concluded and gaps have been identified.

Table: 2 Literature Review

S.No	AUTHOR	TOPIC	WORK DONE	GAPS IDENTIFIED
1	Srivastava, 2008	Competitive adsorption of nickel and cadmium metal ions from aqueous solution on Rice Husk Ash	His study deals with the competitive adsorption of cadmium and nickel ions from aqueous solution onto rice husk ash.	All parameters needs to be studied
2	Foo, 2009	Utilization of Rice Husk Ash as novel adsorbent	Study about the state of the art review of the rice milling industry, its background studies, fundamental properties and industrial applications	Study can be done by varying pH conditions
3	Pramada, 2010	Rice Husk as an adsorbent for methylene blue effect of ashing temperature	The possible utilization of Rice Husk Ash as an adsorbent for methylene blue dye from aqueous solutions has been	Study on heavy metals needs to be done

			investigated	
4	Muneer, 2010	Removal of Zn, Pb and Cr in textile waste water using Rice Husk as adsorbent	Biosorption technique has been employed for the treatment of textile processing industrial waste water using rice husk as biosorbent for the metal binding.	Comparitive study of RHA can be done with Activated carbon
5	Nhapi, 2011	Removal of heavy metals from industrial waste water using rice husk	Adsorbent like Carbonized Rice Husk and Activated Rice Husk are investigated as viable materials for treatment of Pb, Cd, Cu and Zn containing industrial wastewater at controlled pH	1. Research needs to be carried out on the competitive effects of these dissolved metals with each other on the adsorption 2. Applicability of these adsorbents to remove these heavy metals at different pH needs further research
6	Trgo et.al, 2011	Application of mathematical empirical models to dynamic removal of lead on natural zeolite clinoptilolite in a fixed bed column	The study examined the applicability of the mathematical empirical models by Adam-Bohart, Wolborska, Thomas and Yoon-Nelson on lead removal from aqueous solution on a fixed bed of natural zeolite.Applicability these models has been evaluated by fitting the experimental breakthrough curves with the curves obtained from the applied	

			model	
7	Gupta, 2012	Rice Husk and its ash as low cost adsorbent in water and waste water treatment	Studies on the adsorptionof various pollutants by rice husk materials are reviewed and the adsorption mechanis , influencing factors, favorable condition, etc. are discussed	1. Study should be carrying out on pilot plant to verify their viability at an industrial scale. 2. Real waste water should be used instead of synthetic solutions 3. The interaction of different adsorbates in solution will play important role on adsorption of other heavy metals.
8	Munaf, 2012	The use of Rice Husk to remove toxic metals from waste water	The ability of rice husk to remove chromium, zinc, copper and cadmium from waste water has been investigated. And several parameters that can affect metals uptake such as particle size, pH, and temperature are discussed.	The high selectivity for the interested adsorbates is most important for the removal of interested adsorbates from large volume of solution.
9	Kumar et.al, 2013	Utilization of Rice Husk and their Ash	Various industrial and domestic application of Rice Husk and Rice Husk Ash are discussed	Can be used as a source of bio ethanol production
10	Hegazi, 2013	Removal of heavy metals from waste water using agricultural	This research studies the utilization of less expensive adsorbents for the elimination of heavy metals from waste water	Rice Husk ability to effectively remove these dyes, surfactants, phenols present in industrial

		waste as adsorbent		effluent should also be done
11	Chauhan, 2015	Rice Husk Ash as a potential for removing of metal ions- A review	This review summarizes some latest development using rice husk and its derivatives for removal of heavy metals	The adsorption is influenced by various parameters like pH, temp., initial metal ion concentration, amount of adsorbate, size of particle, these parameters determine the overall efficiency
12	Biswas et.al, 2015	Continuous Fixed-Bed Column Study and Adsorption Modeling: Removal of Lead Ion from Aqueous Solution by Charcoal Originated from Chemical Carbonization of Rubber Wood Sawdust	The efficiencyof chemically carbonized rubber wood sawdust for the removal of lead ion from the aqueous stream as investigated by column process.	For industrial prospective, series of column should be attached for better adsorption results. Other factors such as column containing multiple adsorbents, numerous adsorbate system and also their appropriate ratio are to be considered.
13	Rouf et.al, 2015	Modeling of Fixed Bed Column Studies for Adsorption of Azo Dye on Chitosan	Removal of diazo dye Brilliant Black BN from aqueous solution was studied by conducting adsorption in fixed bed column using chitosan	

		Impregnated with a Cationic Surfactant	beads impregnated with a cationic surfactant Cetyl Trimethyl Ammonium Bromide.Effect of flow rate, bed height and initial dye concentration were investigated.	
14	Rohacti, 2016	Utilization of Rice Husk as lead adsorbent in blood cockles	Comparison of Rice Husk and Rice Husk Ash in reducing the concentration of lead in blood cockles	Study needs to be done on other heavy metals
15	Diasa et. al, 2018	Cr removal from synthetic and industrial wastewaters by using co-gasification chars of rice waste streams	Blends of rice waste streams were submitted to co-gasification assays. The resulting chars were characterized and used in chromium removal assays from synthetic solution	It is an expensive procedure.
16	Patel, 2019	Fixed-bed column adsorption study: A comprehensive review	Review of fixed bed column studies for removal of various contaminants from synthetic wastewater study of breakthrough curve for designing adsorptive column is interpreted	1. Real industrial waste water from industries like textile, dyeing, electroplating, tanning, paper, etc effluent must be consi dered for the removal of components contributing the COD, BOD, Color and other parameters 2.Regeneration studie

				s and desorption step modeling must be conducted.

1.6.1 MAJOR FINDINGS

From the study it has been found that Rice Husk Ash is a low cost adsorbent having specific surface area of 30-80 m^2/gm, it has also strong affinity and high selectivity towards heavy metals. So it can be used as an adsorbent for the removal of heavy metals from waste water. Many parameters affect the adsorption of heavy metals such as pH, temperature, initial metal ion concentration, adsorbent doze etc which should be properly taken care of during the study.

1.6.2 GAPS IDENTIFIED FROM THE LITERATURE

- Study can be done by varying pH conditions.
- RHA can be used as a source of bioethanol production.
- Study should be carry out on pilot plant to verify their viability at an industrial scale.
- Real wastewater should be used instead of synthetic solution.
- The interaction of different adsorbates in solution will play important role on adsorption of other heavy metals.
- The adsorption is influenced by various parameters like pH, temp, initial metal ion conc, amount of adsorbate, size of particle, these parameters determine the overall efficiency.
- The high selectivity for the interested adsorbate is most important for the removal of interested adsorbate from large volume of solution.
- Research needs to be carried out on the competitive effects of these dissolved heavy metals with each other on the adsorption.
- Rice Husk ability to effectively remove dyes, surfactants, and phenols, present in industrial effluent should also be done.
- Comparative study of RHA can be one with activated carbon.

1.6.3 OBJECTIVES

- To collect the RHA sample.
- To find the Morphological Properties of RHA.

- To study the effect of adsorption of Zinc solution of different concentrationon RHA under the different conditions of pH, metal ion concentration and time.
- Model development for Fixed Bed Column Adsorption.
- To interpret the result.

1.6.4 METHODOLOGY

Methodology adopted will be Fixed Bed Adsorption.

The steps involved are-

- Collection of RHA samples.
- Morphological study of RHA using SEM.
- Preparation of Solution of Zinc metal.
- Study the adsorption on RHA using different metal conc.
- Preparation of models for Adsorption capacity and 50% breakthrough time.
- Analysis of the Results

1.7 Breakthrough Curve

The relation between fixed-bed adsorption and breakthrough curves can be explained by using mass transfer zone or primaryadsorption zone. As per Fig 1, feed water or waste water is supplied through the inlet of the column, Adsorption starts at the upper layers where the adsorbate gets adsorbed on the adsorbent rapidly and effectively during the initial stage of the operation. This can be explained due to the fact that at initial stages all the active sites of adsorption are available for adsorption and adsorption takes place very rapidly at these sites and no adsorbate is passed downed the lower layers and no adsorbate is observed in the effluent in the first stage. So, primary adsorption zone or MTZ is attained near the top or influent end of the column. At this point, concentration of adsorbate (C) is zero in the effluent therefore the ratio of effluent and initial concentration ($C/C0$) is zero. Thereafter, due to the continuous supply of adsorbate the active sites at the upper layer of adsorbent gradually starts to saturate, with feeding the water into the column, which makes the adsorbent less efficient progressively. Thus, the primary sorption zone also travels down to the fresher or un-adsorbed part of adsorbent in the column. Further, as the mass transfer zone moves down the column effluent concentration of adsorbate increases gradually as per points $C1/C0$, $C2/C0$, $C3/C0$ and $C4/C0$. The movement of this zone is mainly increasing with increasing initial concentration compared to linear velocity of the feed water. After some time (*C*s), all the sites of the adsorbent have been completely utilized and after that adsorption does not occur. At this point, the ratio of *C*/*C*0 is 1. In most of the cases of the sorption by column method operation of water and wastewater, breakthrough curves exhibit a characteristic 'S' shape but with varying degree of steepness.[21][22]

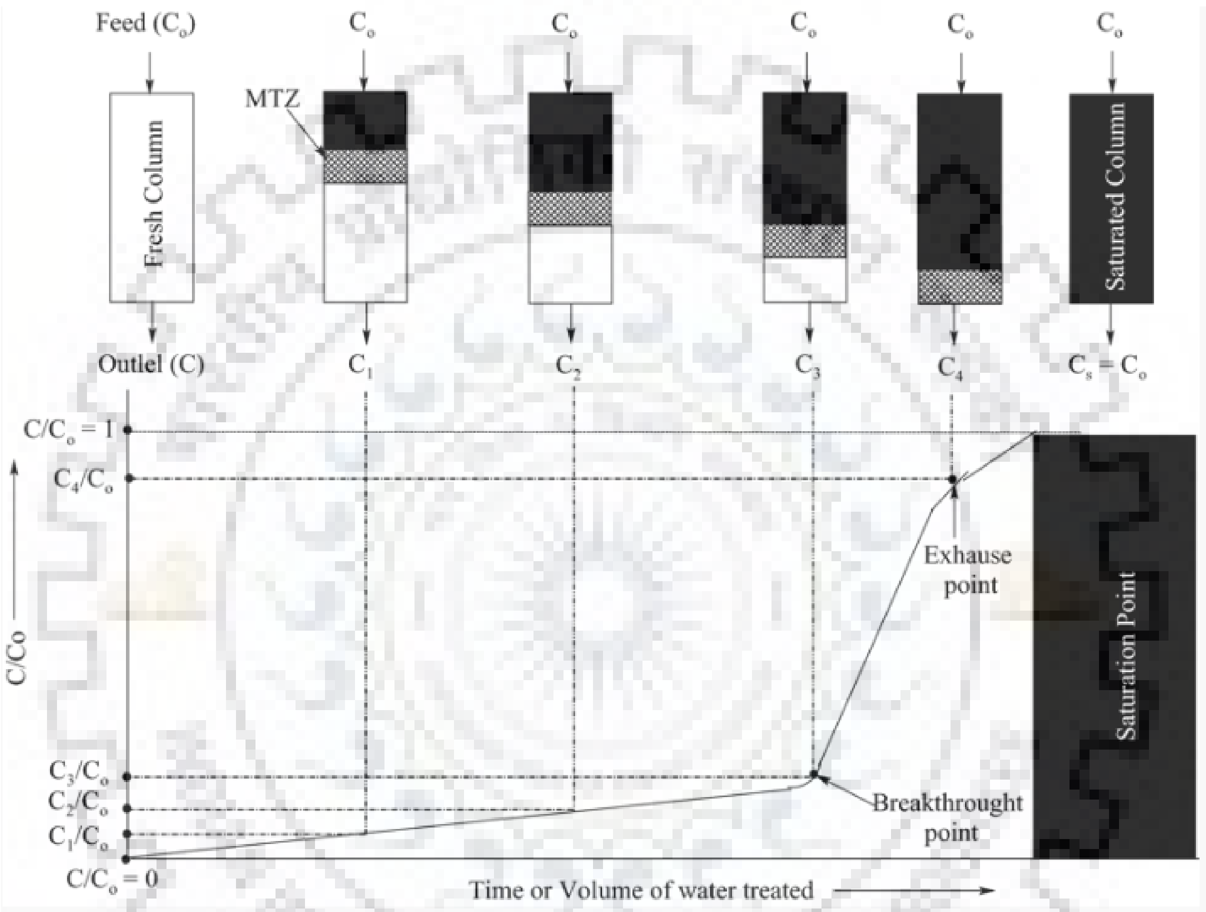

Fig: 1 Shows the relation between Breakthrough curve and Fixed bed Adsorption

Fig 2 shows the breakthrough curve that incorporates a typical S form, breakthrough point is chosen from the breakthrough curve in such a way that at break point concentration the ratio of effluent concentration to influent concentration starts increasing rapidly which generallycommence at lower value of break point concentration (*C*b) and exhaustion point concentration (*C*x) is identified when the same ratio approaches unity. *V*x is the volume of effluent at the exhaustion point and *V*b is the volume of effluent at break point concentration. The primary sorption zone (PSZ) is the portion where active adsorption takes place at a particular time it travels downwards with time. If PSZ is assumed to have a constant length many parameters can be found easily like amount of bed adsorbed, rate of adsorption, these are important parameters which guides a designer to design a Fixed Bed Column.[21][22][23]

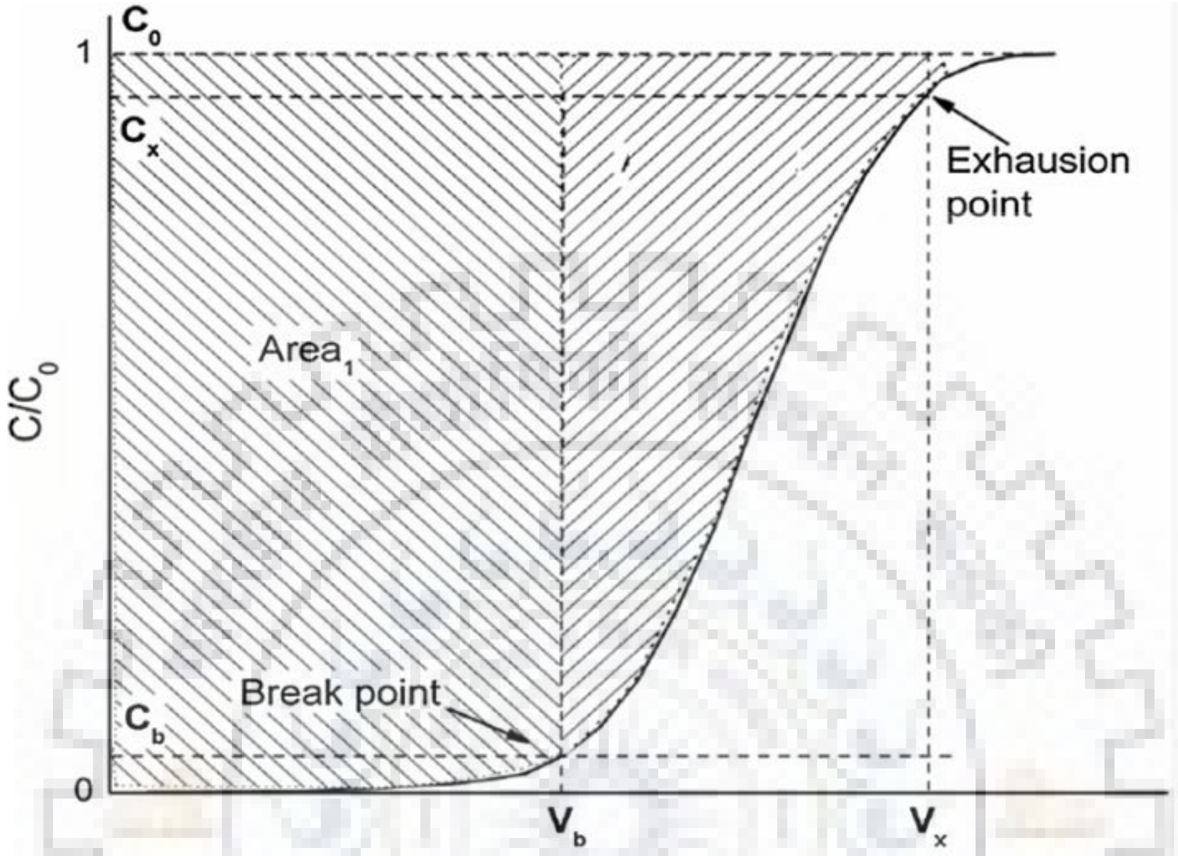

Fig: 2 Breakthrough Curve, showing relation between ratios of effluent concentration to IMC with Volume of fixed bed column

2.1 GENERAL

In the present study, the sample of RHA collected was generated as waste in Ganga Dairy which is situated in Ramzanpur District of Bihar Fig 3, where Rice Husk is used as a fuel to convert milk into milk powder, RH is burnt here at around $400^{O}C$ for about 3 to 4 hours. RHA thus produced was disposed of in nearby open farmlands where it is leached out into the ground water creating ground water pollution which can be seen in Fig 3 where the farmlands on left side of the Dairy have turned blackish and the soil has lost its fertility.

Fig: 3 Location of Ganga Dairy from Google Maps

2.1.1 MATERIAL

The adsorbent material used in the present study is rice husk ash, as it is readily accessible in India and has excellent surface features and contains a large amount of carbon, silica and hydrogen ions, making it an excellent heavy metal adsorbent.

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Fig: 3 Shows RH being burnt in updraught kiln

2.1.2 Standard Solution

In chemistry, a standard solution contains a weighted concentration of any substance. to create a particular quantity, a known solvent weight is dissolved. Standard solutions are used to determine the concentrations of other substances , such as solutions in titrations. The concentrations of standard solutions are normally expressed in units of moles per liter (mol/L, often abbreviated to M for molarity), moles per cubic decimetre (mol/dm3), and kilomoles per cubic metre (kmol/m3) or in terms related to those used in particular titration. A simple standard is obtained by the dilution of a single element or a substance in a soluble solvent with which it reacts.

Standard solutions are also commonly used to determine the concentration of an analyte species. By comparing the absorbance of the sample solution at a specific wavelength to a series of standard solutions at differing known concentrations of the analyte species, the concentration of the sample solution can be found via Beer's Law. Any form of spectroscopy can be used in this way so long as the analyte species has substantial absorbance in the spectra. The standard solution is a reference guide to discover the molarity of unknown species. Titration methods can be used to acquire the concentration of a standard solution. These involve using equipment such as a burette.

Standard solutions of zinc of varying concentration are prepared from the stock solution of Zinc of 1000ppm, Stock solution are concentrated solution of the solute by the use of which standard solution of lower concentration are prepared by diluting a part of stock solution. Benefits of stock solution are it saves preparation time, conserve materials, reduce storage space, and improve theaccuracy with which working lower concentration solutions are prepared. For preparation of the Stock solution of zinc of 1000 ppm, measure 1g of zinc accurately by weighing and dissolve it in 1 liter of 2% nitric acid. To make 2% nitric acid, add 20 ml of nitric acid and add distilled water in volumetric flask to make the volume up to 1liter. From the stock solution different metal ion concentration of 20 ppm, 10 ppm, 5 ppm wasprepared.

2.2 METHODOLOGY

2.2.1 MORPHOLOGICAL ANALYSIS OF RICE HUSK ASH

Morphological analysis of RHA was performed by analyzing the Scanning Electron Microscope Image, The sample of RHA analyzed was directly obtained from the waste site for its Morphological Characteristics,which was burned at 400 ^{O}C in kiln for 4 hours.

Fig 4 shows Scanning electron microscope which works on the principle that when electron beam is generated at top and passed through the column, accelerated down the column and passed through a combination of lens and apertures to produce a focused beam of electrons which strikes the surface of the sample which is covered with a gold film as shown in the fig 5 to produce the image of the surface and magnify it using electromagnetic fields.

Fig: 4 Scanning Electron Microscope

Fig: 5 Sample Preparation for analysing the Morphological Characteristics of RHA

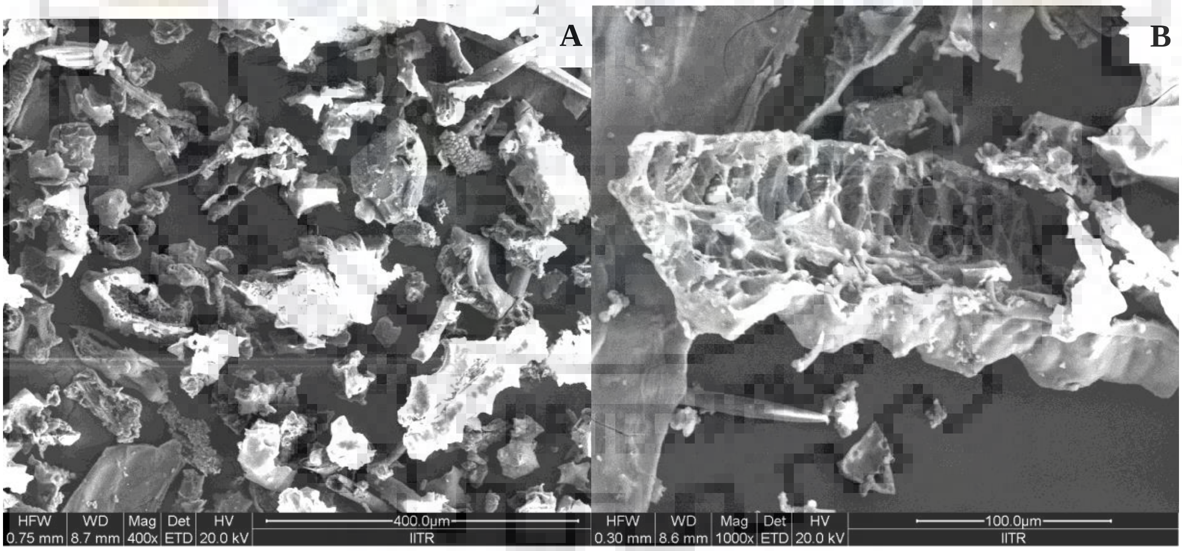
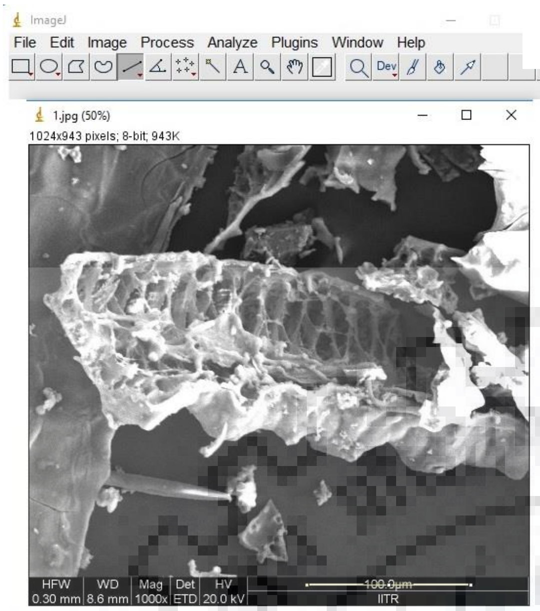


Fig: 6 SEM Images of RHA, Fig A shows Image at 400X magnification, Fig B shows at 1000X

From the SEM images generated it can be infered that RHA is highly porous and irregular in shape and size, which indicates it has high specific surface area.

A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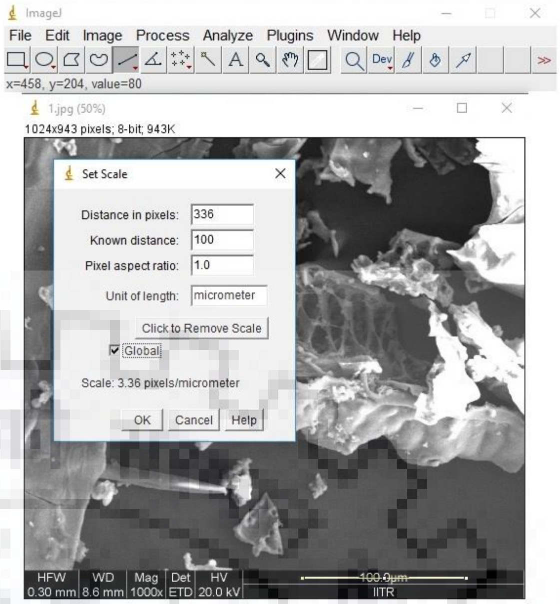
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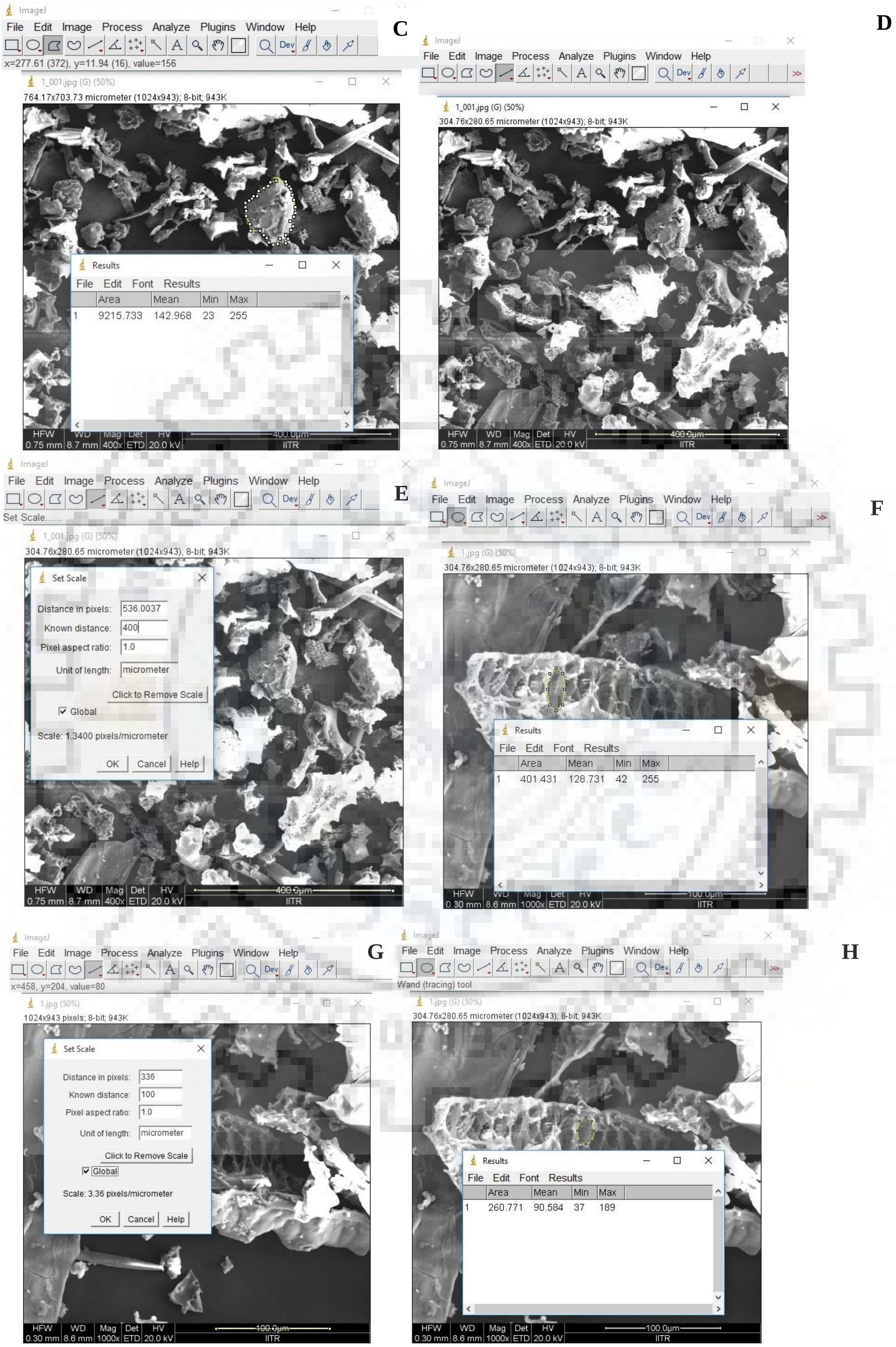

Fig: 7 Shows calculation of pore size and particle size using ImageJ software; A, D shows the magnification of the image; B, E, G shows setting of the scale; C shows the result of particle size; F, H shows the result of pore size

2.2.2Experimental Procedure

Adsorption of heavy metals was performed by constructing a glass column filled with RHA, through which standard solutions of Zinc was passed as shown in Fig 9. RHA was used as the fixed bed material for the column, which acts as adsorbent. A base was created to support the fixed bed in the column above and a stopper to control the flow of solution. Laboratory prepared solutions werethen passed through the column containing RHA with a varying head (maximum head was 0.5m). The solution after passing through column were collected at the bottom of the column. Samples were collected after 4 hours for finding the optimum pH and Initial Metal ion concentration, and for obtaining the time varying removal of zinc the samples were collected at an interval of 10min. The solutions were then tested in a HACH Spectrophotometer for obtaining the residual concentration of the zinc in the solution as well as to find out the adsorptive capacity rice husk for adsorption of zinc metal. All experiments were carried out under room temperature.

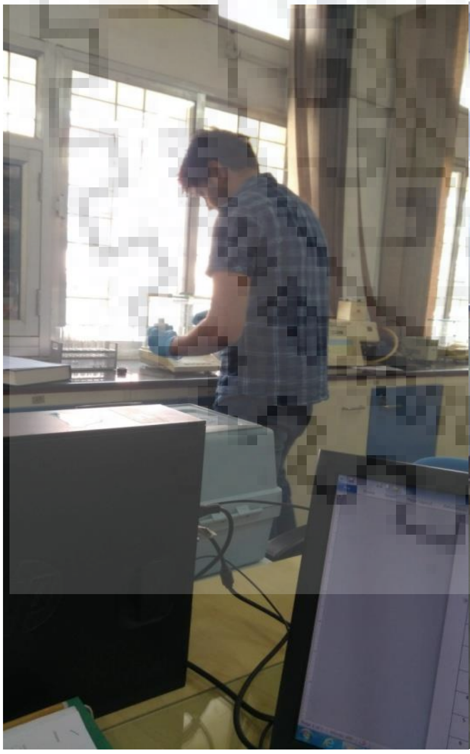

Fig: 8 Preparation of Stock solution of Zinc Sample of standard value of 1000 ppm

Fig: 9 Fixed bed Column

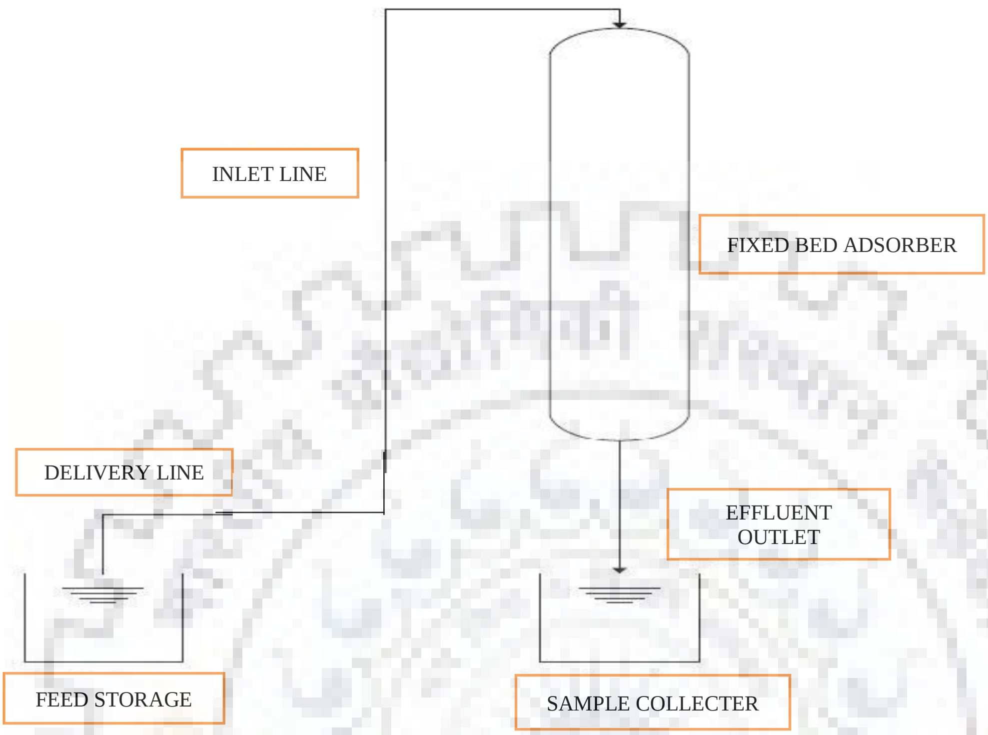

Fig10 Schematics of the Experimental Setup for Fixed Bed Column Test Operation

2.3 Effect of Parameters on Adsorption

2.3.1 Effect of pH

1000 mL of the working solution was put in conical flasks at varying pH. The pH was adjusted in the range 2-6 by the addition of $HNO_3$and NaOH solution depending upon the pH desired; pH of the solution was measured using a pH meter. In the end, a graph will be plotted between % removal efficiency and pH.

2.3.2Effect of initial metal ion concentration

The metal ion concentration effect will be studied in the range of 2-20 mg/L, at optimum pH found out above initial metal ion concentration variation was studied keeping other conditions i.e. adsorbent dose, contact time same as used in other conditions. The residual metal ion concentration was measured and a graph is plotted between % removal efficiency and metal ion concentration.

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2.3.3 Time varying Analysis of Adsorption

The time of contact for the column studies should be in the range of 0-250 minutes. The optimum initial metal ion concentration and pH was used. 2000ml of the working solution was passed through the RHA column and the graph of effluent concentration to influent concentration v/s time is plotted, the plot thus obtained is also known as breakthrough curve.

2.4DATA ANALYSIS

Data obtained from the experiment has been subjected to Yoon Nelson and Thomas Models for calculation of 50% breakthrough time and Adsorptive Capacity of Fixed Bed respectively.

2.4.1 Yoon Nelson Model

Yoon Nelson Model is relatively simple model compared to Thomas's and Adam Bohart's model because it is a single component system.

If 'C' is the amount of solute being adsorbed in the system and 'Ce' is the amount of solute in effluent, then the rate of adsorption can be expressed as

$$-dC/dt=Kyn*(t-T) \qquad ..... (1)$$

Where Kyn is Yoon-Nelson Coefficient (min^{-1})

It is Time of breakthrough

Substituting C=1-Ce and at C=0.5 (Yoon Nelson Model is valid only for 50% breakthrough)

Integrating the above equation yields

$$\ln(C/Co-C) =Kyn*(t-T) \qquad ...... (2)$$

Where It is time when Ce/C=0.5

Model parameters Kyn and T can be calculated as ln(C/Co-C) vs time linearly dependent.

Value of 'T' obtained is known as 50% breakthrough time.

For symmetrical breakthrough curves total breakthrough will occur at 2T.[24]

2.4.2 Thomas Model

Thomas model is the most widely used model, its behaviour is similar to Langmuir model.

Thomas model is

$$C/Co=1/ (1+e^{((Kth)*(q*m/Q-Co*t))}) \quad .....(3)$$

Where Kth is the rate constant (l/mg min)

Co is Initial metal ion concentration

C is metal conc at different time

Q is the flow rate (l/h)

It is time (min)

M is mass of the bed (g)

q is the adsorption capacity

Linearization of the above equation yields

$$\ln ((Co/C)-1) = (Kth*q*m)/Q – (Kth*Co*t) \quad .....(4)$$

From the linear dependency of ln ((Co/C)-1) vs t, model parameters q and Kth can be calculated.

'q' obtained from equation 4 is known as the Adsorption Capacity of the Adsorbent.[24]

CHAPTER 3 RESULT AND DISSCUSION

Fixed Bed Column Adsorption Test were conducted by using standard solution of Zinc of different concentration as adsorbate and using Rice Husk Ash as Adsorbent. Experiments were conducted to find the optimum pH and initial metal ion concentration for finding out the maximum efficiency of Adsorption, Time varying analysis was carried out to obtain the breakthrough curve and breakthrough time. The Results of the Experiment and their Discussions are depicted below.

3.1 Effect Of pH

The pH of the working solution plays an important role in the adsorption process. The experiments were conducted for the zinc concentration of 10 mg/L and the pH was studied in the range 2-6. From the results obtained a graph between %removal vs the pH of the sample was obtained which is shown in Fig 11, from the graph it can be inferred that the % removal efficiency is very low at pH 2. But, as the pH increases, the removal efficiency increases and is found to be maximum i.e. 84% at pH 5 and then again decreases. Thus, pH 5 is chosen as the optimum pH.

Table: 3 Effect of pH on Adsorption

S. No.	pH	Effluent Conc.	% Removal
1	2	7.5	35
2	3	4.2	58
3	4	2.2	78
4	5	1.6	84
5	6	1.9	81

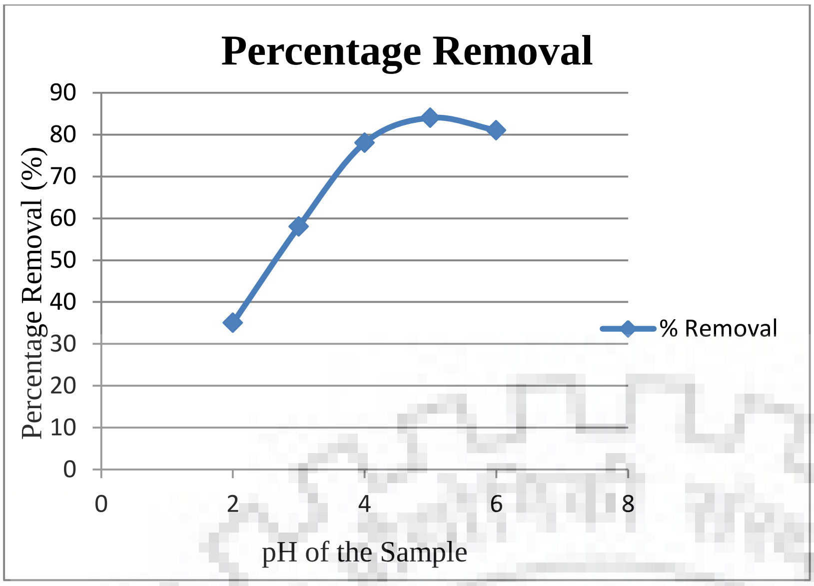

Fig: 11 Effect of pH on Percentage Removal of Zinc

3.2 Effect of Initial Metal Ion Concentration

The effect of metal ion concentration was studied for the metal ion concentration of 2, 4, 6, 8 and 10 ppm. From the results obtained the graph between percentage removal and initial metal ion concentration was made and it was inferred that with increase with initial metal ion concentration, the removal efficiency showed an increasing trend line up to 6ppm and thereafter decreases. The maximum removal of 82% was observed for 6 ppm.

Table 4 Effect of IMC on % Removal

S. NO.	Initial Metal Ion Conc.	Effluent Concentration	% Removal
1	2	0.49	75
2	4	0.844	79
3	6	1.068	82
4	8	1.656	79
5	10	2.22	78

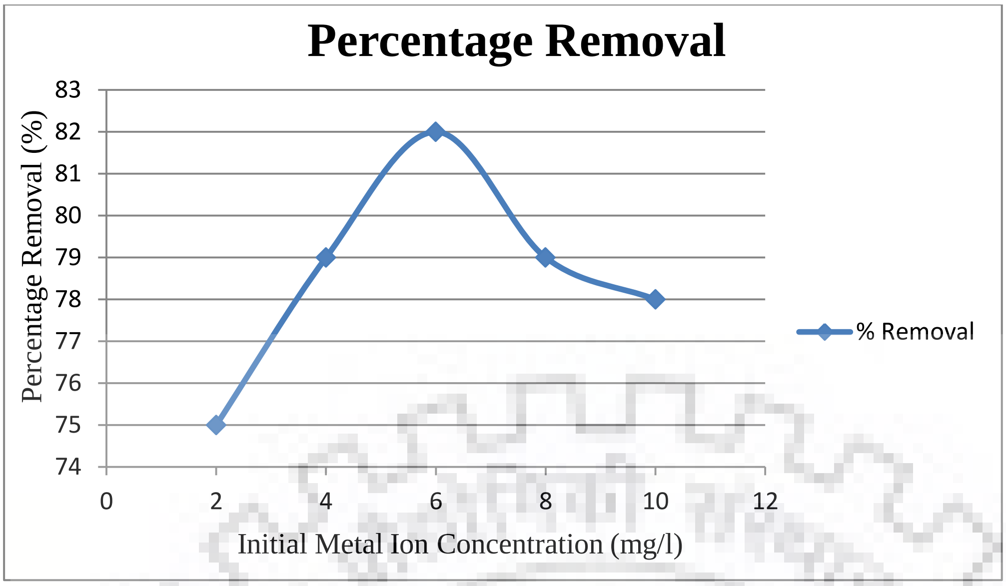

Fig: 12 Effect of Initial Metal Ion Concentration on Percentage Removal of Zinc

3.3 Time Varying Analysis of Adsorption on Fixed bed

The time varying analysis of Adsorption on fixed bed of RHA was carried out varying from 0 to 250 min.

The test was conducted at optimum pH of 5 and optimum initial metal ion concentration of 6ppm. The tread shows that the effluent to initial metal ion concentration increases slowly in the beginning but increases rapidly after 120 min and again slows down after 200 min.

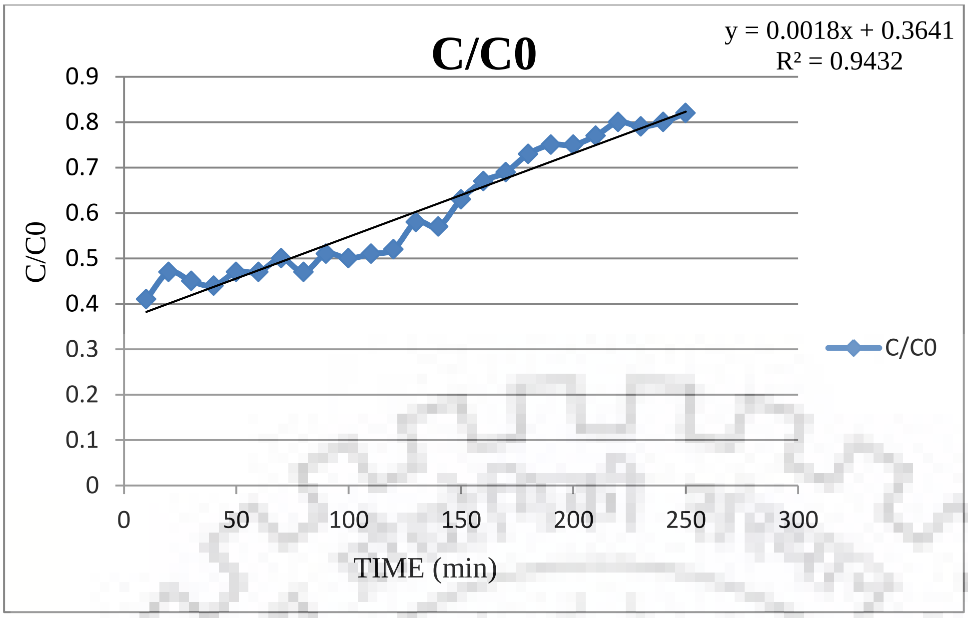

Fig: 13 Breakthrough Curve for Zinc

Breakthrough ... tion of heavy metal with tir ... which shows the time after which the bed has been almost completely utilized, the point after which there is an rapid increase in the curve shows the breakthrough time, after this point it is advised to remove the bed and replace it with new fixed bed.

From the Breakthrough curve of zinc thus obtained the breakthrough time is found out to be around 150 min.

3.4 Yoon Nelson Model

Time required for 50% breakthrough was found on the basis of Yoon Nelson Model, The value of Yoon Nelson coefficient and 50% breakthrough time were found by fitting the Experimental data in the following Equation

$$\ln (C_t / (C_o - C_t)) = K_{yn} * t - T * K_{yn}$$

Ct is effluent conc. (mg/l)

T is 50% breakthrough Time (min)

Table: 5 Calculation for Yoon Nelson Model

Time	Ct (mg/l)	Co-Ct	Ct/(Co-Ct)	ln(Ct/(Co-Ct))
10	2.46	3.56	0.6910	-0.3696
20	2.82	3.18	0.8868	-0.1201
30	2.70	3.30	0.8180	-0.2010
40	2.64	3.36	0.7860	-0.2410
50	2.82	3.18	0.8868	-0.1201
60	2.82	3.18	0.8868	-0.1201
70	2.98	3.02	1.0000	0
80	2.82	3.18	0.8868	-0.1201
90	3.06	2.94	1.0410	0.0402
100	3.00	3.00	1.0000	0
110	3.06	2.94	1.0410	0.0402
120	3.12	2.88	1.0830	0.0800
130	3.48	2.52	1.3810	0.3230
140	3.42	2.58	1.3256	0.2820
150	3.78	2.22	1.7030	0.5320
160	4.02	1.98	2.0300	0.7100
170	4.14	1.86	2.2260	0.8000
180	4.38	1.62	2.7040	0.9950
190	4.50	1.50	3.0000	1.0980
200	4.50	1.50	3.0000	1.0980
210	4.62	1.38	3.3480	1.2083
220	4.80	1.20	4.0000	1.3860
230	4.74	1.26	3.7620	1.3250

240	4.80	1.20	4.0000	1.3860
250	4.92	1.08	4.5500	1.5150

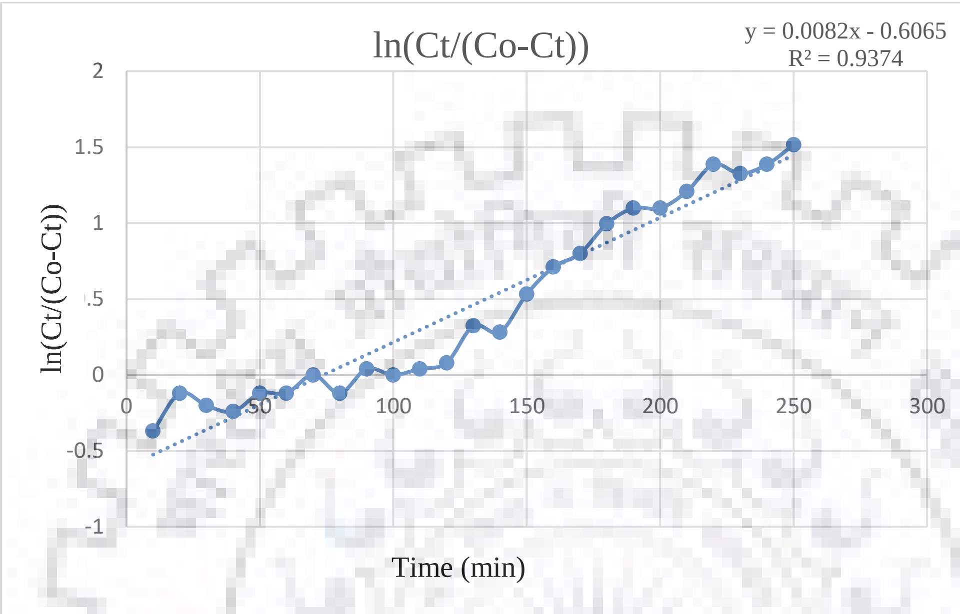

Fig: 14 Yoon Nelson Model

Slope of the Curve = 0.008212

Intercept of the Curve = -0.60651

From the above result Yoon Nelson Coefficient was found to be 0.008212

50% breakthrough timeiscalculated to be 73 min.

3.5 Thomas Model

Thomas model was modelled for obtaining the value Adsorption Capacity and Kinetic Coefficient. Experimental values were fitted in equation and Thomas parameters were obtained

ln((Co/C)-1) = (Kth*q*m)/Q – (Kth*Co*t)

Table: 6 Calculation for Thomas Model

Time (min)	Effluent Conc. (Co) (mg/l)	Co/C-1	ln(Co/C-1)
10	2.46	1.44	0.3646
20	2.82	1.13	0.1220
30	2.70	1.22	0.2000
40	2.64	1.27	0.2400
50	2.82	1.13	0.1220
60	2.82	1.13	0.1220
70	2.98	1.00	0
80	2.82	1.13	0.1220
90	3.06	0.96	-0.0408
100	3.00	1.00	0
110	3.06	1.13	0.1220
120	3.12	0.923	-0.0800
130	3.48	0.724	-0.3230
140	3.42	0.754	-0.2820
150	3.78	0.59	-0.5300
160	4.02	0.49	-0.7100
170	4.14	0.45	-0.8000
180	4.38	0.37	-1.0000
190	4.50	0.37	-1.0000
200	4.50	0.33	-1.1100
210	4.62	0.30	-1.2040
220	4.80	0.25	-1.3860
230	4.74	0.26	-1.3240
240	4.80	0.25	-1.3860
250	4.92	0.22	-1.5140

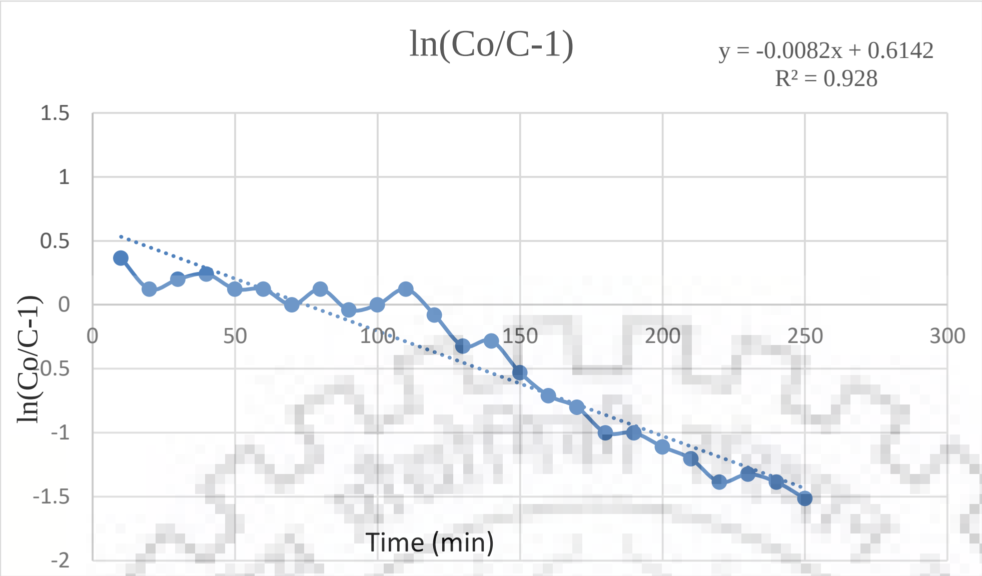

Fig: 15 Thomas Model

Slope of the curve = -0.00819

Intercept of the curve = 0.614192

Kinetic Coefficient calculated is = 1.365 * 10^{-4} L/min/mg

Adsorption Capacity Obtained is = 0.4mg/g

From the above mentioned study on the removal of Zinc from its aqueous solutions using rice husk ashas fixed bed, Column Adsorption study, it may be concluded that

- Column adsorption experiments have shown that adsorption is greatly dependent on process parameters like pH and initial metal ion concentration.
- The optimum conditions for the removal of Zinc as obtained from column studies may be summarised as
  - Optimum pH is 5.
  - Optimum IMC is 6 mg/l.
  - Breakthrough Occurs at Around 150 min.
- From Yoon-Nelson Model
  - Yoon-Nelson Coefficient was found to be 0.008212
  - 50% break through was calculated as 73 min.
- From Thomas Model
  - Kinetic Coefficient is $1.365*10^{-4}$L/min/mg
  - Adsorption Capacity Obtained is 0.4 mg/g
- Fixed Bed Adsorption Data obtained from the experiment can be explained by both Yoon-Nelson and Thomas model, however for removal Zinc by using RHA as an adsorbent Yoon-Nelson model better correlates then Thomas model.
- Morphological Analysis shows that Rice Husk Ash is highly porous and irregular in shape and has high specific surface area.

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