Adsorption Studies on Removal of Chromium from Synthetic Waste Water using Activated Carbon prepared from Rice Husk and Sugarcane Bagasse

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***Abstract* - Activated carbon (AC) was prepared using locally available agricultural wastes like rice husk and sugarcane bagasse. These were used as adsorbents for the removal of Chromium from potassium dichromate solution. Batch mode adsorption studies were carried out by varying contact time, adsorbent dosage and pH. Langmuir and Freundlich adsorption isotherms were applied to model the adsorption data. The adsorption of Chromium was pH dependent and maximum removal was observed in the acidic pH range.**

Index Terms – **Adsorption, Activated carbon, Chromium removal, Sugarcane bagasse, Rice husk.**

I. INTRODUCTION

Activated carbon, also called activated charcoal, is a form of carbon processed to have small, low-volume pores that increase the surface area available for adsorption or chemical reactions. *Activated* is sometimes substituted with *active*.

Due to its high degree of microporosity, just one gram of activated carbon has a surface area in excess of 3,000 m^2 (32,000 sq ft), as determined by gas adsorption. An activation level sufficient for useful application may be attained solely from high surface area; however, further chemical treatment often enhances adsorption properties.

Activated carbon is usually derived from charcoal and is sometimes utilized as biochar. Those derived from coal and coke are referred as activated coal and activated coke respectively.

The environmental pollution due to the development in technology is one of the most important problems of this century. Heavy metals like chromium (Cr), lead (Pb), mercury (Hg), arsenic (As), cadmium (Cd), copper (Cu), aluminium (Al), nickel (Ni), in waste water are hazardous to nature. These metals cannot be decomposed or readily detoxified and have tendency to accumulate in living matter. Besides, heavy metals discharge in the wastewater can be toxic to aquatic life and render natural waters unsuitable for human consumption. The Cr (VI) is toxic to flora and fauna. The limit of Cr (VI) for drinking water is 0.05 mg/L. Hexavalent chromium, which is primarily present in the form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions possess significantly higher levels of toxicity than the other valency states. The industrial and domestic wastewater is responsible for causing severe damage to the environment and adversely affecting the health of the people. Chromium is one of the contaminants, which exists in hexavalent and trivalent forms. Hexavalent form is more toxic trivalent and requires more concerns. Chromium (VI) is highly toxic element in the environment. Chromium emission sources can be broadly classified into two classes, direct and indirect. The direct category basically includes sources that either produce Cr or consume Cr or a Cr compound to manufacture a product. The sources category within the direct category are: Chromites ore refining (60%), Ferrochromium production (71%), Refractoryproduction (3%), Chromium chemical (17-18%), Chromium plating (70%), Leather tanning (90%). The concentration of chromium (VI) in industrial wastewater may be from 10 to 100 mg/dm^3. The treatment of chromium bearing effluents has been reported by several methods such as reduction, precipitation, ion exchange, electrochemical reduction, evaporation, reverse osmosis, and direct precipitation. Most of these methods need high capital cost and recurring expenses such as chemicals, which are not suitable for small scale industries. In view of above, adsorption method is considered to be one of the preferable method for the removal of chromium (VI) or other metal ions from aqueous solution due to its significant advantage such as; low operational cost, widely applicable and creates relatively low sludge[1].

Chromium (Cr) compounds are used in many industries such as textile dying, tanneries and metal electroplating. Chromium can exist mainly as Cr(VI) or Cr(III) in the natural environment. Cr(III) species are less soluble and more stable compare to Cr(IV) species which are highly soluble and mobile in aqueous solutions [2]. Chromium (VI) also has higher mobility than chromium (III) therefore, it has higher potential to contaminate the groundwater. The high risk of chromium (VI) is associated with its high reactivity and its potential carcinogenic properties [3]. Acute exposure to Cr(VI) causes nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhage, and respiratory problems [4]. Inhalation may cause acute toxicity, irritation and ulceration of the nasal septum and respiratory sensitization (asthma) [5]. Ingestion may affect kidney and liver functions. Skin contact may result in systemic poisoning damage or even severe burns, and interference with the healing of cuts or scrapes. If not treated promptly, this may lead to ulceration and severe chronic allergic contact dermatitis. Eye exposure may cause permanent damage.

Recently, various agricultural by-products derived adsorbents like wool, olive cake, sawdust, pine needles, almond shells, cactus leaves, charcoal used tyres, soot, hazelnut shell, coconut shell charcoal, banana peel, seaweed, dead fungal biomass, cyanobacterium, and green alga have been used for the removal of chromium from waste waters [6]. These materials can be used as adsorbents with little processing and available locally in large quantities. The term charcoal generally refers to the carbonaceous residue of wood; cellulose, coconut shells or various industrial wastes left after heating organic matter in the absence of oxygen. This very fine, odorless, tasteless black powder is an adsorbent for many toxic metals, toxins, gases, drugs, fat, and fat-soluble substances without any specific action. Carbon adsorbents, due to their non-polar nature, adsorb selectively non-polar rather than polar substances, but heteroatoms, especially oxygen, have an effect on the adsorbent–adsorbate interactions and in the resulting adsorptive properties [5]. Some methods had been used for removing heavy metals are chemical or electrochemical precipitation [6], cation exchange membranes [7], solvent extraction and filtration [5], chemical precipitation, oxidation/reduction, filtration, ion exchange, membrane separation and adsorption [8]. Adsorption techniques are widely used to remove certain classes of pollutants from wastewater [9]. Adsorption is also considered to be cheap and effective method for the removal of Cr(VI) from waste water [10]. Adsorption is a process by which molecules of a substance, such as a gas or a liquid, collected on the surface of another substance, such as a solid [11].

Adsorption is a unit process that occurs when a vapour or liquid solute collects on the open surface of a solid or a liquid (adsorbent), forming a molecular or atomic layer thick film (the adsorbate). It is different from absorption process, in which a substance moves into the bulk of a liquid or solid to form a perfect solution. The term sorption consists of both processes, while desorption is the only reverse process. Adsorption is useful in most natural systems and is widely used in industries such as activated commercial charcoal, synthetic resins and warm desalination. Activated carbon an inert porous carrier material, is widely used in air and wastewater decontamination since its capability of distributing chemicals on its large hydrophobic internal surface. Activated carbon having high specific porosity, high surface areas are extremely versatile adsorbent of major industrial significance. Pretreatment method can be divided into different categories: physical (milling and grinding), physic-chemical (steam explosion, wet oxidation. etc.), chemical (alkali, dilute acid, oxidizing agents and organic solvents), biological, electrical, or a combination of these. Physical pretreatment is used to increase the accessible surface area and pore size. The chemical activation process has generally been based on the deformation of the raw material with a chemical activator at a specific temperature. Chemical activation by $ZnCl_2$ improves the pore development in the carbon structure and because of the effect of chemicals: the yields of carbon are usually high[12]. Material such as phosphoric acid, magnesium chloride, zinc chloride, potassium hydroxide, and sodium hydroxide can be used as activator but the most commonly used among them are zinc chloride and phosphoric hydroxide. One of the major challenges associated with adsorption using activated carbon is its cost effectiveness. The purpose of this investigation was to prepare activated carbon from low cost waste material (Sugarcane Bagasse and Rice Husk) available in the locally for the removal of chromium (VI) ions from aqueous solution and to find optimum adsorption isotherm. Adsorbent dosage, pH, agitation time, initial chromium (VI) concentration were the parameters investigated in the present study.

The process of Adsorption is usually studied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature. Different adsorption isotherms are Freundlich, Langmuir and BET theory.

Basic Adsorption Isotherm:

In the process of adsorption, adsorbate gets adsorbed on adsorbent.

$$\text{Adsorbate} + \text{Adsorbent} \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} \text{Adsorption}$$

$$A + B \rightleftharpoons AB$$

According to Le-Chatelier principle, the direction of equilibrium would shift in that direction where the stress can be relieved. In case of application of excess of pressure to the equilibrium system, the equilibrium will shift in the direction where the number of molecules decreases. Since number of molecules decreases in forward direction, with the increases in pressure, forward direction of equilibrium will be favored.

From the graph in Fig.1, we can predict that after saturation pressure Ps, adsorption does not occur anymore. This can be explained by the fact that there are limited numbers of vacancies on the surface of the adsorbent. At high pressure a stage is reached when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, Adsorption is independent of pressure.

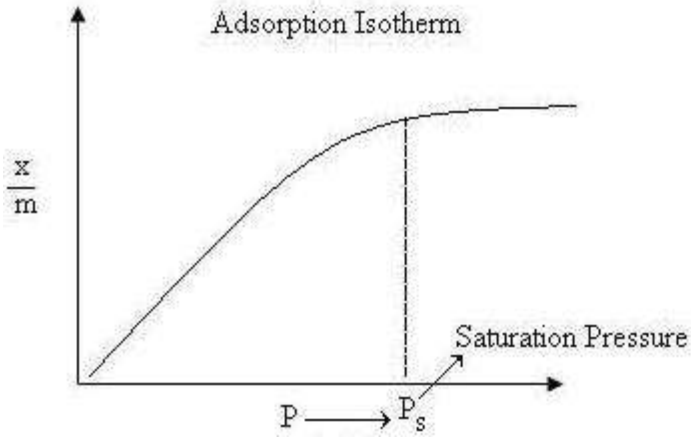


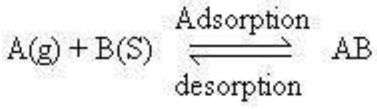
Fig. 1: Basic Adsorption Isotherm

Freundlich Adsorption Isotherm:
In 1909, Freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation or simply Freundlich Isotherm.

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

Where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p and k, n are constants whose values depend upon adsorbent and gas at particular temperature. Though Freundlich Isotherm correctly established the relationship of adsorption with pressure at lower values, it failed to predict value of adsorption at higher pressure.

Langmuir Adsorption Isotherm:
In 1916 Langmuir proposed another Adsorption Isotherm known as Langmuir Adsorption isotherm. This isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.



$$A(g) + B(S) \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} AB$$

Where A(g) is unadsorbed gaseous molecule, B(s) is unoccupied metal surface and AB is Adsorbed gaseous molecule.

Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

$$\theta = \frac{KP}{1+KP}$$

Where θ the number of sites of the surface which are covered with gaseous molecule, P represents pressure and K is the equilibrium constant for distribution of adsorbate between the surface and the gas phase .The basic limitation of Langmuir adsorption equation is that it is valid at low pressure only.

At lower pressure, KP is so small, that factor (1+KP) in denominator can almost be ignored. So Langmuir equation reduces to

$$\theta = KP$$

At high pressure KP is so large, that factor (1+KP) in denominator is nearly equal to KP. So Langmuir equation reduces to

$$\theta = \frac{KP}{KP} = 1$$

The phenomenon of adsorption is essentially an attraction of adsorbate molecules to an adsorbent surface. The preferential concentration of molecules in the proximity of a surface arises because the surface forces of an adsorbent solid are unsaturated. Both repulsive and attractive forces become balanced when adsorption occurs.

Adsorption is nearly always an exothermic process.
There are *2 types* of adsorption process depending on which of these 2 force types plays the bigger role in the process. Adsorption processes can be classified as either physical adsorption (van der Waals adsorption) or chemisorption (activated adsorption) depending on the type of forces between the adsorbate and the adsorbent.

In **physical adsorption**, the individuality of the adsorbate and the adsorbent are preserved. In **chemisorption**, there is a transfer or sharing of electron, or breakage of the adsorbate into atoms or radicals which are bound separately.

Physical adsorption from a gas occurs when the inter-molecular attractive forces between molecules of the solid adsorbent and the gas are greater than those between molecules of the gas itself. In effect, the resulting adsorption is like condensation, which is exothermic and thus is accompanied by the release of heat.

Physical adsorption occurs quickly and may be mono-molecular (unimolecular) layer or monolayer, or 2, 3 or more layers thick (multi-molecular). As physical adsorption takes place, it begins as a monolayer. It can then become multi-layer, and then, if the pores are close to the size of the molecules, more adsorption occurs until the pores are filled with adsorbate. Accordingly, the maximum capacity of a porous adsorbent can be more related to the pore volume than to the surface area.

In contrast, **chemisorption** involves the formation of chemical bonds between the adsorbate and adsorbent is a monolayer, often with a release of heat much larger than the heat of condensation. Chemisorption from a gas generally takes place only at temperatures greater than 200°C, and may be slow and irreversible. Most commercial adsorbents rely on physical adsorption; while catalysis relies on chemisorption.

II. LITERATURE REVIEW

A wide range of physical and chemical processes are available for the removal of Cr(VI) from waste water such as electro-chemical precipitation, ultrafiltration, ion exchange, electro-dialysis, reverse osmosis, chemical precipitation, and adsorption (Jung and Shiau, 2000, Yan and Viraraghavan, 2001, Balel and Kumiawan, 2004, Donati et al., 2003). The major drawbacks with these processes are high cost, toxic sludge generation or incomplete metal removal.

Several commercial activated carbons have been used as received and also after chemical modifications for Cr(VI) adsorption (Balel and Kumiawan, 2004, Barros et al., 2006).

Many reports have appeared on the development of low-cost activated carbon from renewable resources and also how to decontaminate water in an environmentally friendly manner. Agricultural and industrial waste materials have been utilized as activated carbon precursors, by a large number of researchers for the removal of chromium. Feedstocks such as sawdust (Sumathi and Naidu, 2005), nut shells (Agarwal et al., 2006), cactus, olive stone/cake, wood charcoal, oil palm fibre (Dakiky et al., 2002), fruit gum dust (Samantaroy et al., 1997), wheat bran (Dupont and Guillon, 2003), and sugar beet pulp (Atlundogan, 2005) have all been reported in the literature. The removal of Cr(III), by olive stone (Lyubchik et al., 2004) and commercial active carbons was also reported (Hu et al., 2003).

Some basic information about the adsorptive properties of activated carbon prepared from olive stone was presented by Pereira et al., (2006). The results made clear that olive stones, a very abundant agricultural by-product in Mediterranean countries, could be a very adequate feedstock to obtain active carbons with good adsorptive properties and hardness, which could be of interest in future environmental protection programs.

Mr. Sohail Ayub and Syed Iqbal (1998) reviewed the earlier work for the removal of heavy metals using agricultural waste products.

Gupta, Srivastava et al. (1997) used activated carbon developed for fertilizer waste for the removal Hg (II), Cr (VI), Pb (II) and Cu (II).

Singh and Mishra (1992) used saw dust coated with the iron hexamine gel for the removal of certain heavy metals such as Hg (II), Pb (II), Cr (VI), Ni (II), Cd (II) and Cu (II).

Bhalke, Tripati et al. (1999) studied the uptake of heavy metals including fertile uranium and fission products strontium and cesium by using sunflower plant dry powder at pH 2.5, 4.0 and 7.5.

M. Rao et al. (1999) studied the removal of various pollutant from its aqueous waste by adsorption using various low cost adsorbents.

Manju and Anirudhan (1990) investigated the removal of Cr (VI) using coconut fibre pith (CFP).

Raji and Anirudhan (1998) used saw dust charcoal for the removal hexavalent chromium.

Patnaik and Das (1995) used blast furnace flue dust generated in the steel plants for the removal of hexavalent chromium.

Talokar A.Y. (2011) studied removal of chromium from waste water by adsorption using low cost agricultural biomass as adsorbents. The study was aimed at efficiency evaluation of non-conventional low cost adsorbents such as Fly ash powder, Bagasse, W.Straw Dust, SD, and Coconut coir as compared to the powder activated carbon for the removal of chromium from aqueous solution. The efficiency of the adsorbents for the removal of chromium was investigated. The efficiency of adsorbent used is found in the order of PAC>Bagasse>FA>SD>WSD>Coconut coir. The effect of chromium solution PH, contact time, adsorbent dosage, initial chromium concentration and adsorbent mesh size on adsorption were studied in a batch experiment.

Tahiruddin and Ya'akub (2013) investigated the potential of wood charcoal as a low-cost adsorbent for the removal of Cr(VI). The granular adsorbent was made up of charcoal, an agricultural waste from local industries. Surface modification with oxidizing agents such as sulfuric acid and nitric acid, was conducted to improve removal performance. The adsorption of Cr(VI) with wood charcoal was investigated in a batch arrangement using potassium dichromate ($K_2Cr_2O_7$) solution. The results of Cr removal performances was compared. It was proven that adsorbents chemically modified with oxidizing agents demonstrated better Cr(VI) removal capabilities than unmodified adsorbent. The functional group of both modified and unmodified adsorbent had been characterized using Fourier Transform Infra Red Spectrometer (FTIR).

Muthukumaran K. and Beulah S. (2010) prepared chemically activated carbon from *Syzygium jambolanum* nut, an agricultural waste, after activation with ammonium persulphate in the presence of sulphuric acid and then subjected it to thermal activation by dolomite process. It was then successfully used to remove chromium (VI) from wastewater in batch studies by adsorption process. The performance of Chemically Activated High Temperature *Syzygium jambolanum* nut Carbon (CHSJC) was compared with a Commercial Activated Carbon (CAC).

Attia A. A., Khedr S. A. and Elkholy S. A. (2010) produced activated carbon from olive stones which was chemically activated using sulfuric acid, (OS-S), and utilized as an adsorbent for the removal of Cr(VI) from aqueous solution in the concentration range 4-50 mg/L. The equilibrium adsorption data was better fitted to the Langmuir adsorption model. It was concluded that activated carbon produced from olive stones (OSS) has an efficient adsorption capacity compared to (CAC-S) sample.

Aravind J., Sudha G., Kanmani P., Devisri A.J., Dhivyalakshmi S., Raghavprasad M. (2015) used Gooseberry seed (Phyllanthus acidus) as an adsorbent to determine its feasibility for the removal of chromium (VI). Various parameters such as pH, temperature, contact time, initial metal concentration and adsorbent dosage were investigated to determine the biosorption performance. Equilibrium was attained within 60 minutes and maximum removal of 96% was achieved under the optimum conditions at pH 2. The results of the study indicated that gooseberry seed powder can be employed as adsorbent for the effective removal of hexavalent chromium economically.

Shrivastava P.K. and Gupta S. K. (2015) studied Removal of Chromium from Waste Water by Adsorption Method Using Agricultural Waste Materials. Several low cost biomaterials such as rice husk, sugar cane bagasse, Tulsi Leaf &branches, coconut shell & coir and fly ash were tested for removal of chromium. All the experiments were carried out in batch process. The adsorbent, which had highest chromium (VI) removal, was coconut shell.

Maheshwari U and Gupta S (2011) used a waste biodegradable material, that is, neem bark. The neem bark was activated using concentrated sulphuric acid (98 wt%) and was used as an adsorbent for Cr(VI) removal from aqueous solutions.

III. MATERIALS AND METHODS

In order to assess the performance of each adsorbent and to avoid interference by other elements in waste water, the experiments were conducted with aqueous solution of hexavalent chromium in redistilled water. Synthetic samples of various initial chromium concentrations were prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) in water. There are various materials which can be used as an adsorbents [1].

Chemicals

All chemicals $K_2Cr_2O_7$, H_2SO_4, NaOH employed were of reagent grade. Laboratory distilled water was used for preparation of all solutions.

Glasswares

All the glasswares used in the study were of Borosil (A grade). All the glasswares were washed with the double distilled water every time before use.

Preparation of carbon from rice husk

Waste rice husk was collected from a rice mill. The initial colour of the sample was yellow ochre. The husk was then dried at 120°C for 24 hours in a dryer. The colour darkened and the texture became more rough. It was then subjected to crushing in a hammer mill and sieved to obtain uniform particle sizes of 1mm diameter. The powdered raw material was then kept in a muffle furnace for 2 hours at 500°C to form charcoal. The sieved rice husk was transformed to carbon by ignition in the furnace without addition of chemical agent and under atmospheric air. By carbonization, most of the noncarbon elements, hydrogen and oxygen are removed in gaseous form and the remaining carbon atoms are grouped into organized crystallographic formation known as elementary graphitic crystallites.

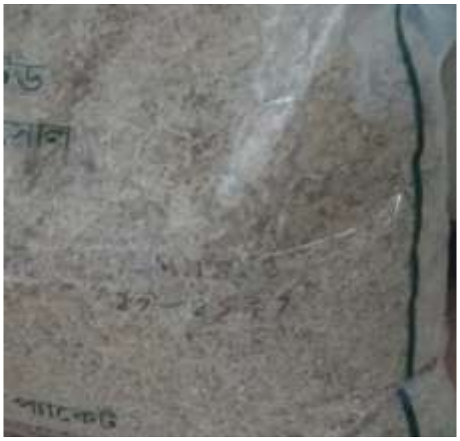


Fig. 2: Rice Husk before drying


Fig. 3: Rice Husk after drying


Fig. 4: Carbon made from Rice Husk

Preparation of carbon from sugarcane bagasse

Waste sugarcane bagasse was collected from a local cane juice seller. It initially was light yellow in colour. The bagasse was then dried at 120°C for 24 hours in a dryer. Having lost moisture it shrunk in size and the colour turned darker. It was then crushed manually to reduce the size and volume and then it was crushed in a hammer mill and finally sieved to get 1 mm diameter particles. The powdered raw material was then kept in a muffle furnace for 2 hours at 500°C to form carbon. The sieved sugarcane bagasse was transformed to carbon by ignition in the furnace without addition of chemical agent and under atmospheric air. By carbonization, most of the noncarbon elements, hydrogen and oxygen are removed in gaseous form and the remaining carbon atoms are grouped into organized crystallographic formation known as elementary graphitic crystallites.


Fig. 5: Sugarcane Bagasse before drying


Fig. 6: Sugarcane Bagasse after drying

Fig. 7: Carbon made from Sugarcane Bagasse

Preparation of Aqueous Solution

Potassium dichromate was used as the source of hexavalent chromium. Stock solution of chromium was prepared by dissolving potassium dichromate crystals in double distilled water. 500mg/l stock solution of Cr(VI) was prepared by dissolving 1.41435g of potassium dichromate crystals in 500ml distilled water and the stock solution was stored in a volumetric flask.

IV. ADSORPTION EXPERIMENT

Effect of contact time

After 0.5g of carbon was put into a flask with 30ml of $K_2Cr_2O_7$ (50ppm), the flask was shaken for different time (30-120 minutes) at constant temperature of 25°C. The residual concentration of $K_2Cr_2O_7$ solution was kept for analysis.

Effect of different dosage

The effect of adsorbent dosage on the adsorption of chromium was investigated by putting different adsorbent dosage (0.1-0.5g) into a 30ml potassium dichromate solution (50ppm). The suspension was shaken at 25°C for 2 hours. The supernatant was kept for further analysis.

Effect of pH

0.5g of adsorbent was added to a series of flasks with 30 ml of potassium dichromate solution (50ppm). The pH of the solution was adjusted from pH 2-8 in gaps of 2 by adding H_2SO_4 and NaOH solutions. The mixture was agitated for 2 hours at 25°C. The supernatant was filtered and kept for further analysis.

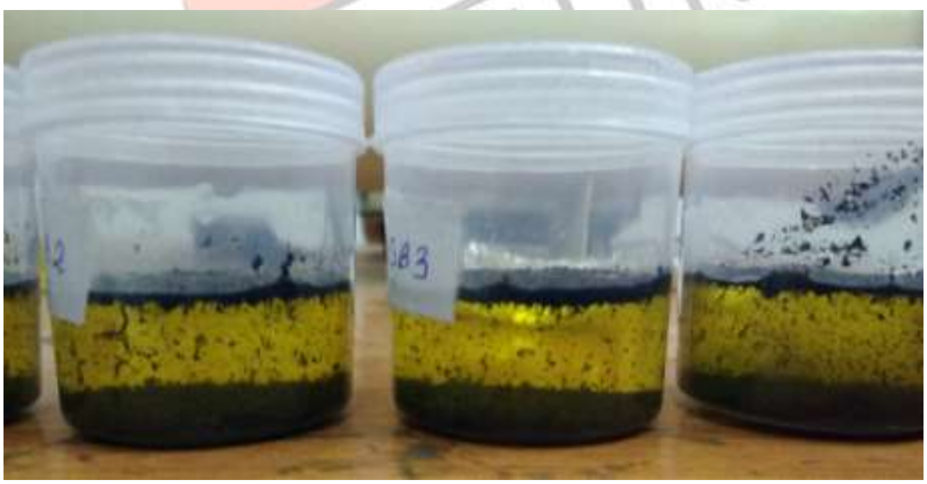


Fig. 8: Adsorbent sample in 50ppm solution (Before Test)

Percentage Removal of Chromium (VI)

The percentage removal of chromium (VI) in solution was calculated by following equation:

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

where, C_0 and C_e are initial and final concentrations (mg/L) of chromium (VI) at a given time.

The amount of adsorption at any time, Q_e was calculated by: $Q_e = \frac{(C_o - C_e) \times V}{m}$

C_0 and C_e are initial and final concentrations (mg/L) of chromium (VI) at a given time. V is the volume of the solution, m is the weight of the adsorbent used (g).

V. RESULTS AND DISCUSSIONS

FTIR Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a technique which is 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. The FTIR analysis method uses infrared light to scan test samples and observe chemical properties. The FTIR test results for carbon prepared from rice husk and sugarcane bagasse samples have been obtained as follows:

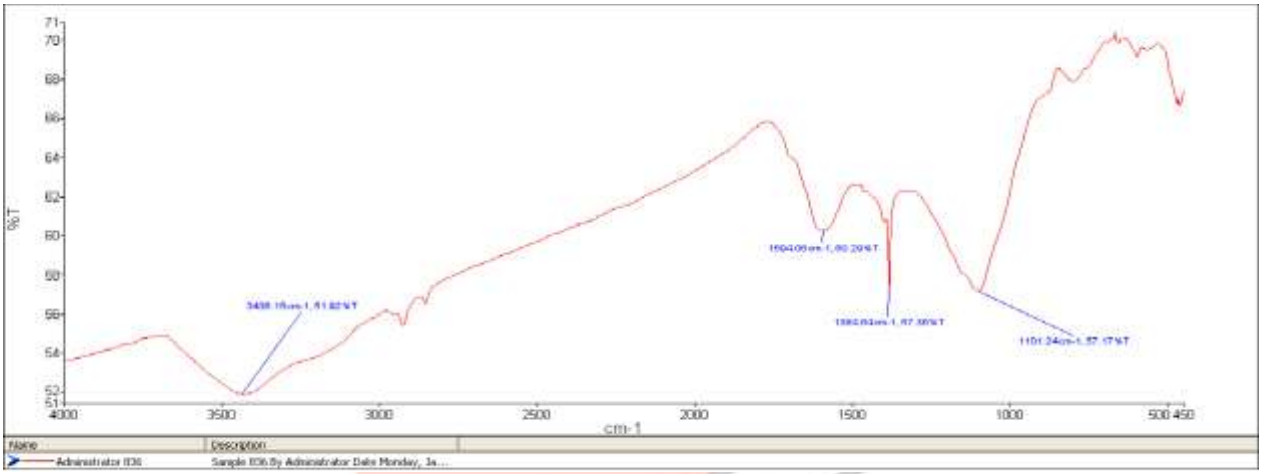


Fig. 9: FTIR Analysis of carbon sample prepared from rice husk

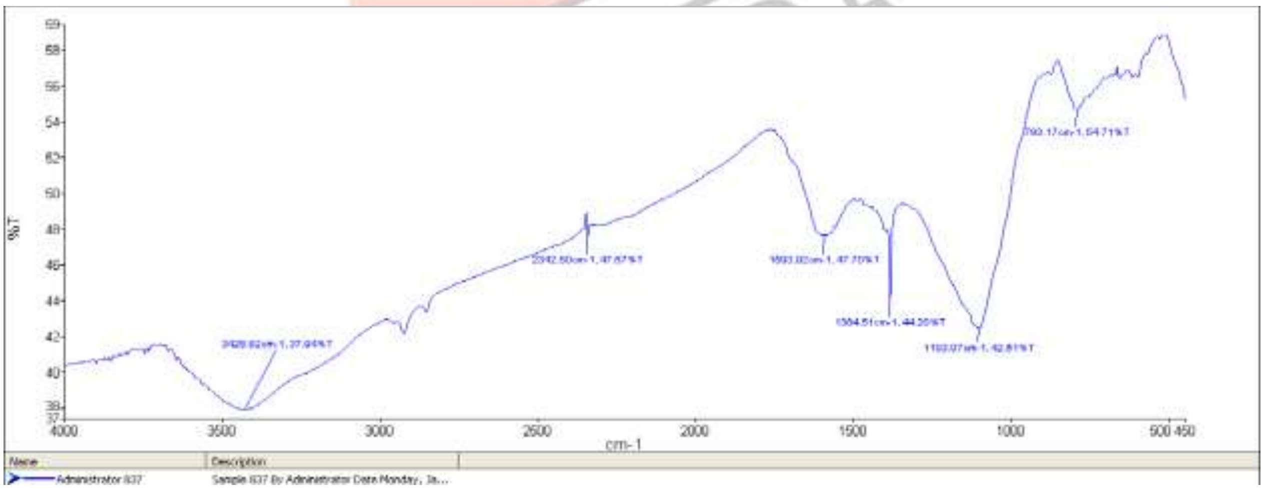


Fig. 10: FTIR Analysis of carbon sample prepared from sugarcane bagasse

XRD Analysis

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of X-rays diffracted at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the distribution of atoms within the lattice. Consequently, the X-ray diffraction pattern is the fingerprint of the periodic atomic arrangements in a given material. The XRD test results for carbon prepared from rice husk and sugarcane bagasse samples have been obtained as follows:

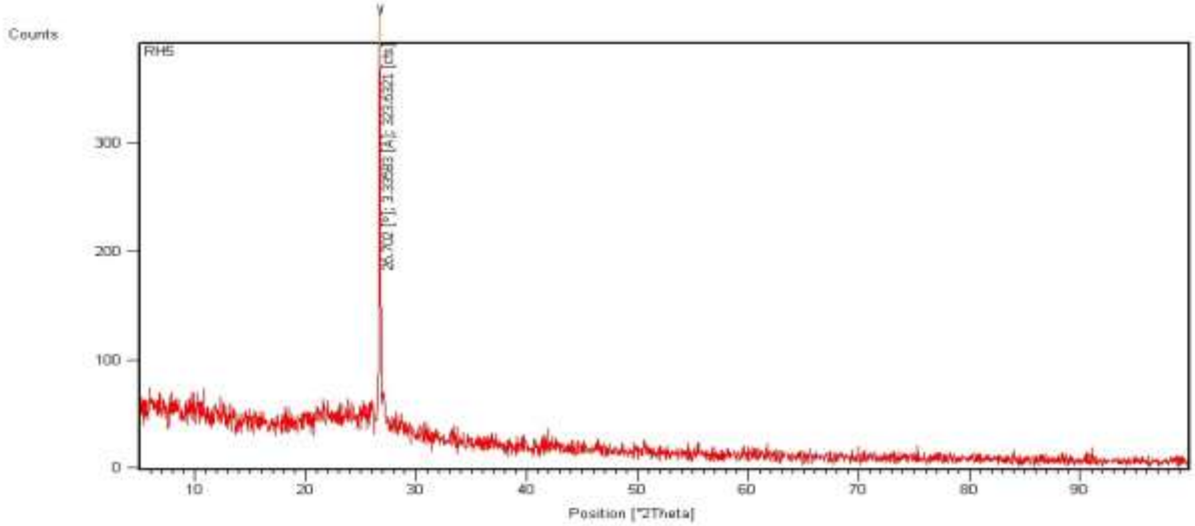


Fig. 11: XRD Analysis of carbon sample prepared from rice husk

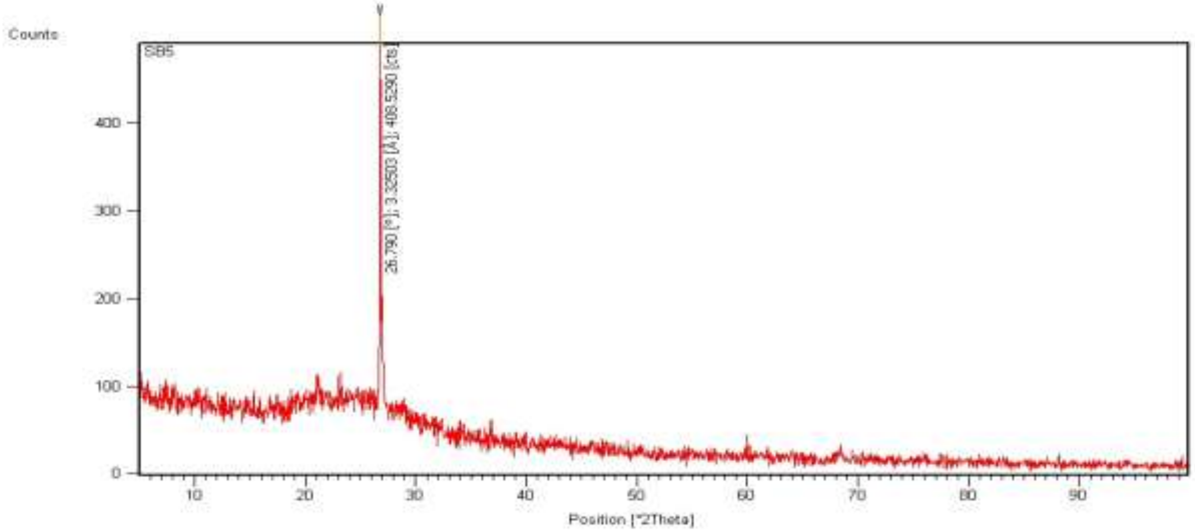


Fig. 12: XRD Analysis of carbon sample prepared from sugarcane bagasse

Standardization

The equipment used for standardization was a Double Beam Spectropotometer 2203 manufactured by Systronics.

Fig. 13: Double Beam Spectrophotometer

The Calibration Curve obtained is as follows:

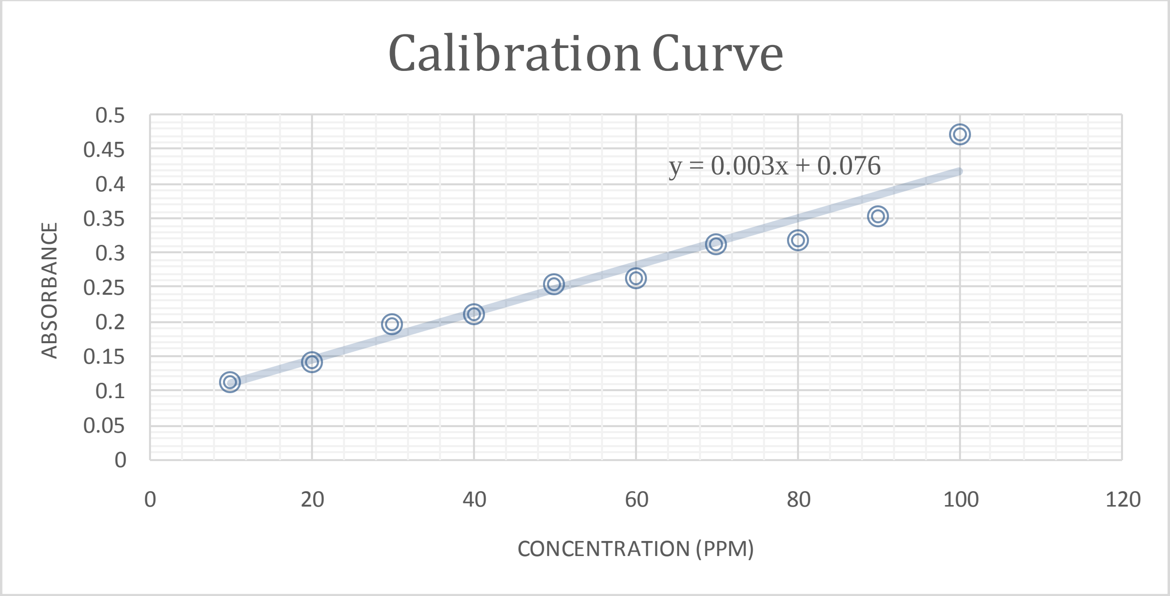


Fig. 14: Calibration Curve

Effect of contact time

The effect of contact time on adsorption was studied at 50ppm initial concentration with varying contact times as shown in Fig. It is obvious that increase in contact time from 30 minutes to 120 minutes enhance significantly the percentage removal of Cr (VI). The initial rapid adsorption gives away a very slow approach to equilibrium. The nature of adsorbent and its available adsorption sites affected the time needed to reach the equilibrium. From the plotted data we can see that the carbon prepared from sugarcane bagasse acted as a more efficient adsorbent than that prepared from rice husk.

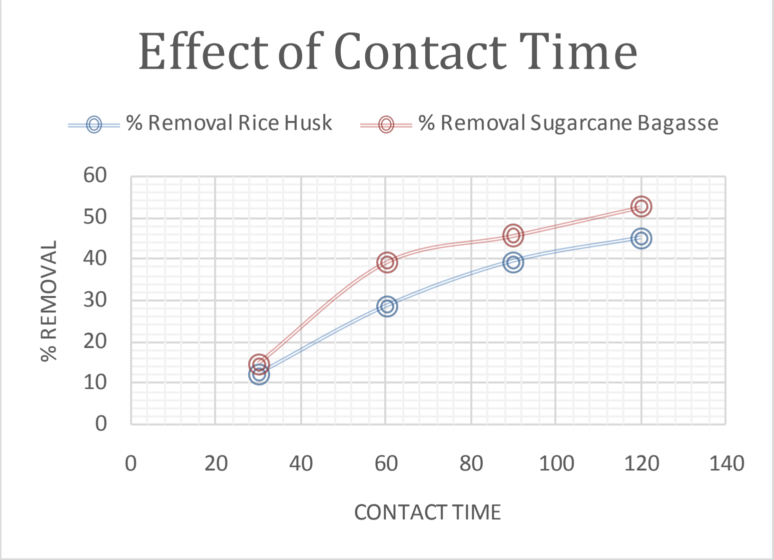


Fig. 15: Effect of Contact Time

Effect of different dosage

The percentage adsorption of Cr6+ ions onto Activated carbon of the agricultural waste materials was studied at different adsorbent doses (0.1, 0.2, 0.3, 0.4, 0.5 grams) at room temperature, Contact time was 120 minutes and initial Cr6+ ions concentration was 50 ppm (Parts Per Million). The result showed that optimum removal was observed with increasing adsorbent dose.

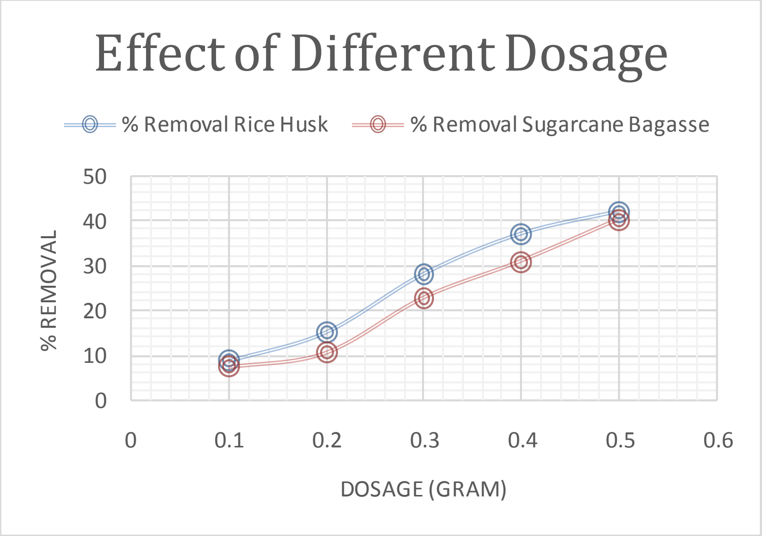


Fig. 16: Effect of Different Dosage

Effect of pH

Rice husk showed maximum adsorption efficiency at a pH of 2 and the efficiency decreased with increasing pH. For sugarcane bagasse, adsorption occured more efficiently at a ph of 6. In this case adsorption efficiency increased from pH 2 to 6 and then decreased as the medium became alkaline. So from the obtained data we can conclude that Chromium removal is enhanced in acidic medium.

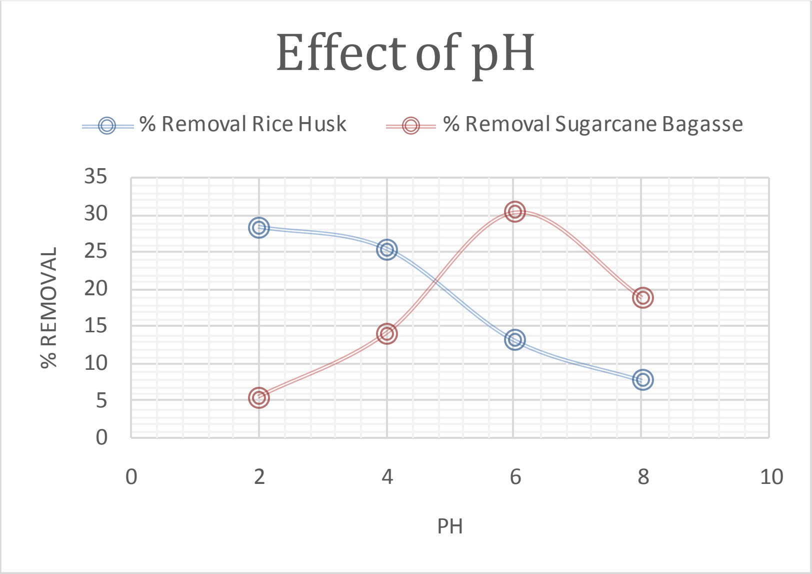


Fig. 17: Effect of pH

Adsorption Isotherm

To examine the relationship between adsorbed (q_e) and the aqueous concentration C_e at equilibrium sorption isotherm models are widely employed. The isotherm results were analyzed using the Langmuir & Freundlich isotherm. The amount of adsorption at equilibrium, q_e (mg/g) was calculated by equation:

$$q_e = (C_o - C_e)\, V/\, W$$

where, C_o and C_e (mg/L) are the liquid-phase concentrations of hexavalent chromium at initial and equilibrium respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used.

Langmuir Isotherm: The Langmuir isotherm model assumes that the uptake of metal ions occur on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions. Langmuir isotherm constants were calculated from the following linearized form:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L}$$

Where $1/Q_m$ and $1/Q_mK_L$ are the slope and intercept of the plot, indicative of maximum adsorption capacity (mg/g) of adsorbent and energy of adsorption respectively, while C_e is the remaining concentration of adsorbate after equilibrium(mg/l) and Q_e is the amount adsorbed at equilibrium(mg/g). The linear plot of C_e/Q_e and C_e show that the experimental data reasonably well fitted the linearized equation of the Langmuir isotherm over the chromium concentration range.

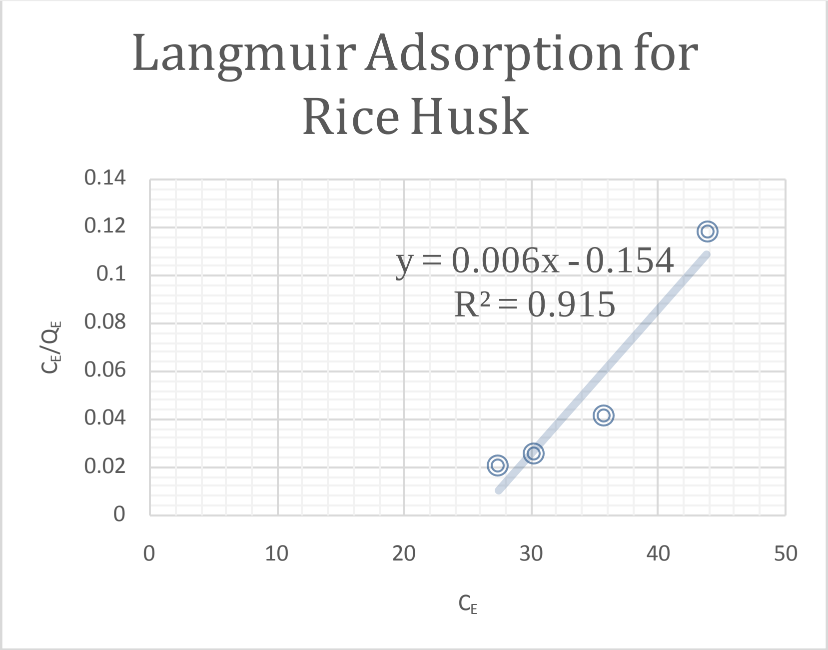


Fig. 18: Langmuir Adsorption Isotherm for Rice Husk

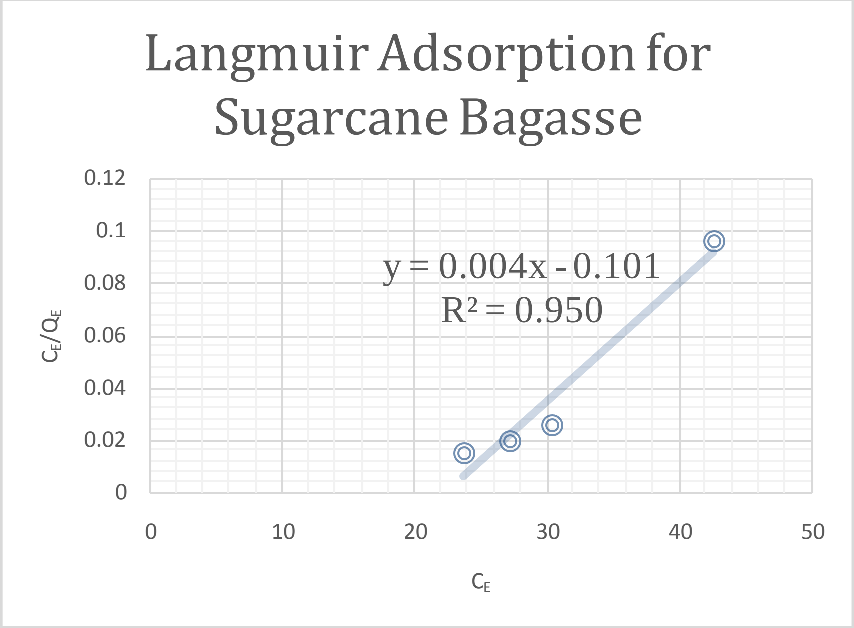


Fig. 19: Langmuir Adsorption Isotherm for Sugarcane Bagasse

Freundlich Isotherm: The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. Freundlich isotherm assumes that the uptakes of metal ions occur on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration .The Freundlich isotherm is expressed as:

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

Where, K_F and n are constants of freundlich isotherm incorporating adsorption capacity (mg/g) and intensity.

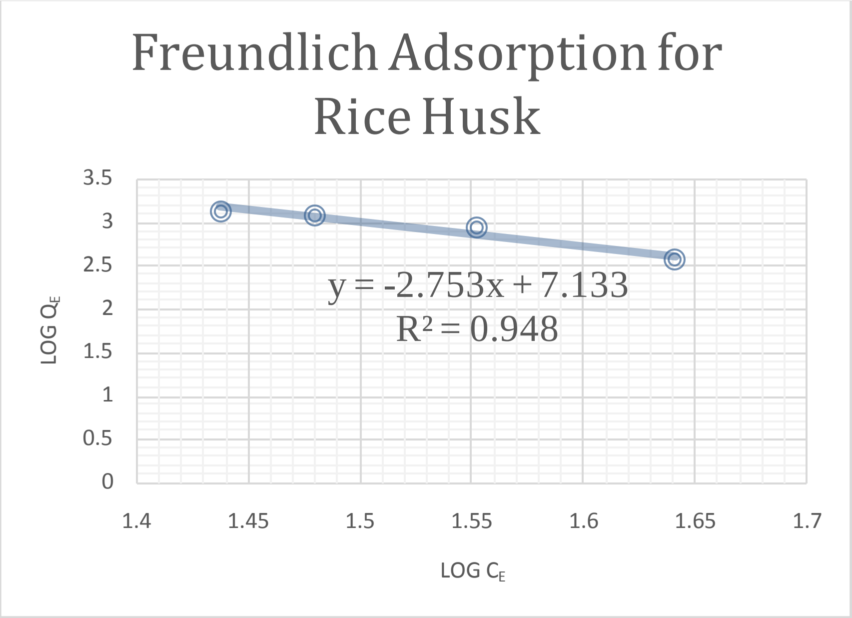


Fig. 20: Freundlich Adsorption Isotherm for Rice Husk

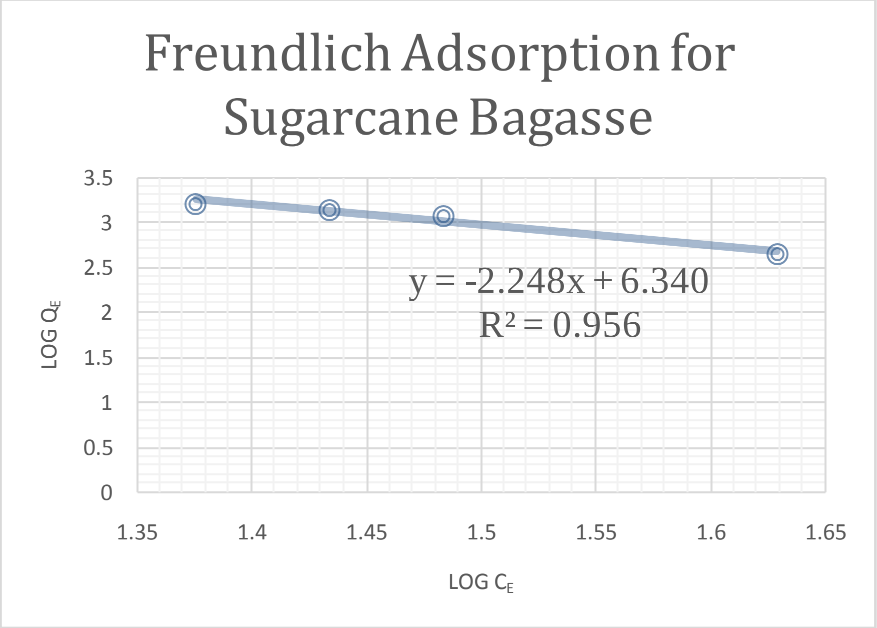


Fig. 21: Freundlich Adsorption Isotherm for Sugarcane Bagasse

VI. CONCLUSION

The study indicated the suitability of the adsorbents used for removal of Chromium from aqueous solution. The activated carbon prepared from sugarcane bagasse and rice husk can be used for the removal of chromium from aqueous solution effectively. The adsorption depends on the contact time of the solution and the adsorbent, dosage of adsorbent and the solution pH. The adsorbent under consideration was not only economical, but also an agricultural waste product. Hence adsorbent prepared from these materials would be useful and economical for treatment of wastewater containing chromium metal. The result of the investigations are quite useful in developing an appropriate technology for designing a wastewater treatment plant for the removal of chromium.

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