



EFFICACY OF SUGARCANE BAGASSE AND RICE HUSK ADSORBENT FOR TREATMENT OF HEAVY METALS FROM PETROLEUM REFINERY EFFLUENT

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Heavy metals are being extremely released into the environment due to poor waste management resulting from industrialization and urbanization. Discharging wastewater contaminated with heavy metals poses a significant risk to human health and the surrounding ecosystem. Heavy metals are characterized by their non-biodegradable nature and potential carcinogenic properties. Activated carbons (ACs), which are carbon-based nano-porous adsorbents, are widely utilized in the removal of heavy metals because of their extensive surface area. In this study, active carbon materials were prepared using rice husk and sugarcane precursor by applying physical-chemical activation methods. To examine the sequestering of heavy metals (cadmium, chromium, copper, lead, nickel, and zinc) in a refinery effluent, a batch adsorption technique was adopted, and the process parameters were investigated at different temperatures and impregnation ratio. Scanning Electron Microscope (SEM) and Fourier-Transform Infrared Spectroscopy (FTIR) were used to determine the surface morphology and functional group while X-Ray Diffraction analysis (XRD) was used for the study of the crystallographic property of the activated carbon adsorbent. Both Rice Husk and Bagasse showed promising capacity for multiple adsorption of heavy metals. Freundlich and Langmuir's models were applied to study the sorption behavior. Although, process parameters play a vital role in the activation of the adsorbent, rice husk, and sugar bagasse have a strong potential for heavy metal adsorption. The hierarchy of performance effectiveness of rice husk was $Cr > Pb > Cu > Cd > Zn > Ni$ according to the Langmuir model with Chromium (Cr) having the highest performance with a coefficient of correlation R^2 of 0.9512 and the least Nickel (Ni) having R^2 of 0.6156. While Sugarcane bagasse fitted well to the Freundlich model with the efficacy of removal in the order $Pb > Cu > Cd > Ni > Cr > Zn$ with Lead (Pb) having the highest efficacy of removal with R^2 of 0.957 and the least was Zinc (Zn) with R^2 of 0.211 respectively.

1.0 Introduction

The persistent contamination of water and the environment by heavy metals in a dynamic proportion presents a significant concern. The emergence of these metals from myriad technological and anthropogenic genesis into aquatic systems poses a substantial threat to the well-being and sustainability of various forms of life. Heavy metals are the most common pollutants present in industrial effluents. Their discharge into the environment causes serious environmental problems. Among the hazardous heavy metals, lead, cadmium and copper have received much attention due to their harmful, carcinogenic, and non-biodegradable (Duan et al., 2020) and toxic effects at low concentrations (Aboli et al., 2020). In drinking water,

concentrations of 0.005 mg/L for Pb (II), 0.001 mg/L for Cd (II) and 0.1 mg/L for Cu (II) can cause illness in humans and can even be fatal (Bohli et al., 2015). These ions have damaging effects on humans as they can penetrate via soil or water (Waziri et al., 2016). Lead is released bodies from various industries including oil refineries (Meitei and Prasad, 2013), plastic, paint, cable, steel, and dyes. Nickel is another toxic heavy metal ion heavily used in industries such as mining, oil industry and plating, it poses a potential threat for diseases such as lung and bone cancer while acute nickel poisoning causes headache, nausea, weakness, dry coughs, and pain in the chest (Fu and Wang, 2011) A demanding research trend in environmental science and technology is the improvement of water pollution control and aquatic purification. The demand for efficient, convenient, and cost-effective technology for decontaminating groundwater and surface water without endangering public health remains critical (Luo et al., 2016).

Several researchers in the past decades have shown interest in treating heavy metal ions from effluent before their eventual discharge into natural streams and other water bodies (Deng et al., 2011). Interestingly, there are many methods used for wastewater treatment which include membrane and biological processes, sedimentation, floatation, coagulation, lime precipitation, ion exchange, and electrochemical methods (Gupta, 2015). These methods have been applied for metal ions removal from effluents with some of the techniques having their pros and cons since incomplete metal removal, generates toxic sludge, has high cost, and continuous input of chemicals (Kaur et al., 2016). For instance, in the electrochemical process, most of the metal ions are possible to be removed but it has high operational and capital cost (Anglada et al., 2009) In chemical precipitation, there is the advantage of low cost but it has high sludge quantity thereby creating disposal problems. Similarly, flocculation and coagulation have the advantage of less sludge generation but it has a high cost of chemical consumption (Guimarães et al., 2016), ions exchange offers the benefit of regeneration of material but it is limited by its high cost implication (Kaur et al., 2016). However, the most economical, effective, and efficient method of metal ions removal from wastewater is adsorption (Kulbir et al., 2018). The readily employed sorbent is activated carbon but it has a high cost and needs chelating agents (for metal-containing effluents) to improve its performance, hence exacerbating the cost (Singh and Waziri, 2019). Due to the cost of activated carbon, a more cost-effective and reliable adsorption treatment method is usually applied (Chew et al., 2023).

The world produces a large amount of agricultural waste discarded indiscriminately every year, resulting in a huge waste of resources. The rational application of agricultural waste can not only reduce environmental pressure, but also create economic value, so it is necessary to develop new ways of recycling agricultural waste (Sadh et al., 2018). Agricultural waste refers to the waste generated from agricultural production, livestock breeding, agricultural and side-line products processing, and life activities of rural residents, mainly including residues in farmland and orchard, livestock manure, and residues in agricultural and side-line products and domestic waste. These wastes not only contain 65% to 90% carbon, hydrogen, and oxygen, but also are rich in nitrogen, phosphorus, potassium, calcium, magnesium, sulphur, as well as trace elements. It is essential to pay attention to the extensive use of agricultural waste for sustainable development. Agricultural waste is usually the first choice to prepare biomass-derived activated carbon, attributing to its high specific surface area, high stability, excellent adsorption properties, simple production process and low price (Wang et al., 2023). The major byproduct of the rice milling industry is the rice husk. It contains a large amount of lignocellulosic biomass and ash. The ash is about 99 percent silica. Millions of tons of rice are produced annually by developing countries. Rice plant is about 20 percent rice husk which constitutes a huge disposal challenge as the volume increases annually (Dhaliwal et al., 2011; Kalderis et al., 2008). About 80% of the sugar produced is obtained from sugar cane making it the second largest crop. The extracted juice is adopted as the primary source of sucrose, while the fermented juice has been used for the manufacture of bio-ethanol (Bian et al., 2013). Consequently, it has been faced with the challenge of a large fibrous byproduct, bagasse, which is about 30% of the entire plant (Ijaola et al., 2014).

In this paper, KOH and NaOH treated rice husk and sugarcane bagasse activated carbon are respectively produce for treatment of heavy metals from refinery effluent. Batch adsorption studies was carried out and effect of temperature and impregnation ratio on AC yield, removal efficiency and the treatment mechanisms were studied.

2.0 Materials and methods

2.1 Materials

Rice husk and sugarcane bagasse were the precursors utilized for the activated carbon production. They were obtained from open market (street vendors) in Barara-Ambala, Haryana, India. Waste water sample was obtained from Indian Oil and Petroleum Company Ltd. (IOCL), Panipat, Haryana, India. Potassium hydroxide (KOH), sodium hydroxide (NaOH) and other chemicals were used analytical reagent (AR) grade.

2.2 Methods

2.2.1 Preparation of Activated Carbon

The materials was collected, sun dried, crushed and grinded manually using pestle and mortar into fine powder, the samples was further Sieved through 1.0 to 1.5 mm sieve size to obtain a uniform Precursor of about 500 g was weighed and then placed in a muffle furnace and then carbonized.

The precursor was then pyrolyzed at 300 - 400°C for 1 hour, distillate formed while carbonization was collected to prevent air pollution. The pyrolyzed precursor (charcoal or char) was allowed to cool prior to transferring into a crucible. It was thereafter grounded into powder by using pestle and mortar and sieved through of 0.150mm sieve-size to get uniform particles. Precursor of about 100 g Potassium hydroxide KOH (rice husk) and Sodium hydroxide NaOH (bagasse) (Owabor and Iyaomolere, 2013). 100g was transferred into a beaker mixed with 50% ZnCl₂, 1N NaOH, 1N KOH, at different impregnation ratio (1.0, 1.5, 2.0) until thoroughly mixed. Thereafter, the paste was then poured into a container, dried at 105°C overnight and thereafter placed into the muffle furnace and heated at different temperatures of 500°C, 550°C and 600°C for 1 hour to enhance the surface area of the sample and make it a better adsorbent. After it has cooled, it was then washed with mineral free water and the residual filtrate was ensured neutral pH. Further, it was oven-dried at 105°C overnight. Subsequently the adsorbent was stored in an airtight polyethylene bag and later used (Kannan and Veemaraj, 2009)

2.2.2 Yield

Activated carbon (AC) yield was computed on chemical-free nature basis and is regarded as an indication of the process accuracy of the activation. Yield is represented as percentage weight of activated carbon by weight of dried adsorbent.

$$\text{(Yield (\%))} = \frac{\text{weight of activated carbon}}{\text{weight of raw material}} \times 100 \quad (1)$$

2.2.3 Bulk density

A 25 ml glass cylinder filled to a particular volume with powder AC was placed in oven overnight at 80°C. The vessel was then compacted. Bulk density is expressed as gml⁻¹:

$$\frac{\text{(Weight of dry material (g))}}{\text{(Volume of Packed dry materials (ml))}} \times 100 \quad (2)$$

2.2.4 Microscopy

The surface morphology of the prepared adsorbents was studied using scanning electron microscope (JEO-JSM-5910, JEOL Ltd., Japan).

2.2.5 Iodine number

Iodine number (IN) can be used to determine the relative porosity of the activated carbon. It is micro pore indication of the AC (up to 2 nm). ASTM D4607-94 method was used in this study. Iodine number can be defined as the milligrams of iodine adsorbed by 1.0 g of carbon when the iodine concentration of the filtrate is 0.02 N (0.02 mol. /L).

2.2.6 Chemical Oxygen Demand (COD)

An indirect method that is usually employed for expressing the amount of organic content in waste water is chemical oxygen demand. It is an important water quality indicator, expressed in milligrams per liter (mg/L) which shows mass of oxygen consumed per liter of solution. The experiment was done according IS: 3025 (Part 58) – Reaffirmed 2006.

2.2.7 Total Dissolved and Suspended Solids

Materials which are totally dissolved in water are termed as total dissolved solids. It can be filtered. It can also be defined as remaining part of solids after evaporation of filterable sample. While suspended solids are ones which cannot be dissolved as well as filtered. It is carried out according to IS: 3025 (Part 16 & 17).

2.3 Batch equilibrium studies

Basically the test was conducted on rice husk and sugarcane bagasse to compare their effectiveness in the treatment of oil refinery wastewater. A known quantity of each adsorbent (1g) was transferred into Erlenmeyer flasks of volume 250 mL, containing 100 mL of domestic effluent thereafter put in a shaking incubator at 120rpm for 3hrs at 25°C.

Batch adsorption studies were conducted by adding certain amount of activated carbon (rice husk and sugarcane bagasse) 1g into 250 mL Erlenmeyer flasks containing 100 mL of different impregnation ratio and temperature. The conical flasks then were placed in a shaking incubator at 120 rpm for 3 h. There after the effluent was filtered with a filter paper and the residual filtrate was analyzed. The amount of sorption at time t and the percentage removal were calculated according to previous study (Fathy et al., 2012).

2.4 Adsorption models

The capacity of adsorbent to treat heavy metal pollution up to a certain level is studied with the help of adsorption model. When there is a contact for a particular time between the carbon sorbent and the pollutant, a stage is arrived when the maximum amount of pollutant is adsorbed and the remainder is known. In an equilibrium conditions for any given process, the mass balance equation employed for the calculation of the materials adsorbed is given as Eqn (3).

$$\frac{X}{M} = (C_0 - C_e) \frac{V}{M} \quad (3)$$

where X/M (is milligram of pollutant by gram adsorbent) is the mass of contaminant by the mass of adsorbent, C_0 is the initial concentration of pollutant, C_e is the pollutant concentration after equilibrium, V is the volume of solution to which the adsorbent mass is applied, and M is adsorbent mass.

Langmuir or Freundlich models has been used for the study of many mechanism (Selvaraju & Bakar, 2017).

Langmuir isotherm is represented by Eqn (4).

$$\frac{X}{M} = \frac{K_L C_e}{1 + a_L C_e} \quad (4)$$

Where K_L and a_L are model's constants. Linear regression is used for the determination of K_L and a_L values. The linear equation for Langmuir model is given by Eqn (5):

$$\frac{1}{\frac{X}{M}} = \frac{1}{KLCe} + aL / KL \quad (5)$$

The general Freundlich equation is:

$$\frac{X}{M} = \frac{1}{KLCe} + \frac{aL}{KL} \quad (6)$$

Linear equation for Freundlich model is given by:

$$\ln \frac{X}{M} = \ln K_F + \frac{1}{n} \ln Ce \quad (7)$$

Where n and K_F are affinity and adsorption capacity, respectively.

Langmuir and Freundlich models are employed batch adsorption systems where equilibrium is provided enough time between the pollutant in solution and the pollutant adsorbed. In this way most of the contaminants are trapped on the carbon sorbent.

3.0 Results and discussion

The activated carbon was produced successfully, however, analysis of the data and tests conducted comprising adsorption process by batch method and sample analysis before and after adsorption in the wastewater stream are discussed below.

The properties of the activated carbon produced have been checked by various methods to understand the intrinsic qualities of the precursor towards heavy metals removal as presented in Table 1. The different heavy metal content of the oil refinery effluent use in this study is presented in Table 2.

Table 1. Activated carbon characterization

S/N	Parameters	Rice Husk	Sugarcane Bagasse
1	Bulk density (g/cm ³)	0.400	0.333
2	Yield (%)	77.10	84.44
3	IN (mg/g)	1312	1128
4	Ash Content (%)	22.90	15.56
5	Moisture Content (%)	<1	<1
6	Particle Size (µm)	>150	>150

Table 2. Heavy Metals in oil refinery effluent.

S/N	Parameter	Value
1	Cadmium	0.015
2	Chromium	0.210
3	Copper	0.740
4	Lead	0.030
5	Nickel	0.304
6	Zinc	1.130

The wastewater treatment for various heavy metals at temperature of 600°C with various impregnation ratios using Rice husk and Sugarcane bagasse activated carbon are given in the Table 3. The various impregnation ratios 1, 1.5 and 2 of the rice husk activated carbon is denoted as RH 1, RH 1.5 and RH 2 respectively. Similarly, for sugarcane bagasse activated carbon it is denoted as SB 1, SB 1.5 and SB 2. Accordingly, the corresponding activated carbon produced at temperature of 550°C is presented in Table 4 and that produced at 550°C is provided in Table 5.

Table 3. Heavy metal effluent characteristics after treatment (600°C)

S/N	Parameter	Rice Husk			Sugarcane Bagasse		
		RH 1	RH 1.5	RH 2	SB 1	SB 1.5	SB 2
1	Cadmium (Cd)	0.0009	0.0003	0.00015	0.0012	0.0007	0.00
2	Chromium (Cr)	0.0315	0.0252	0.0210	0.0399	0.0294	0.021
3	Copper (Cu)	0.074	0.052	0.030	0.089	0.067	0.044
4	Lead (Pb)	0.0027	0.0012	0.0003	0.0015	0.0006	0.00
5	Nickel (Ni)	0.058	0.043	0.031	0.055	0.040	0.031
6	Zinc (Zn)	0.147	0.113	0.091	0.102	0.079	0.045

Table 4. Heavy metal effluent characteristics after treatment (550°C)

S/N	Parameters	Rice Husk			Sugarcane Bagasse		
		RH 1	RH 1.5	RH 2	SB 1	SB 1.5	SB 2
1	Cadmium (Cd)	0.0021	0.0017	0.00075	0.0023	0.0018	0.0014
2	Chromium (Cr)	0.0462	0.0420	0.0357	0.0525	0.0462	0.0357
3	Copper (Cu)	0.148	0.104	0.089	0.133	0.118	0.096
4	Lead (Pb)	0.0045	0.0039	0.0030	0.0030	0.0027	0.0018
5	Nickel (Ni)	0.097	0.091	0.076	0.082	0.067	0.058
6	Zinc (Zn)	0.237	0.192	0.124	0.226	0.181	0.136

Table 5. Heavy metal effluent characteristics after treatment (500°C)

S/N	Parameter	Rice Husk			Sugarcane Bagasse		
		RH 1	RH 1.5	RH 2	SB 1	SB 1.5	SB 2
1	Cadmium (Cd)	0.0021	0.0017	0.00075	0.0023	0.0018	0.0014
2	Chromium (Cr)	0.0462	0.0420	0.0357	0.0525	0.0462	0.0357
3	Copper (Cu)	0.148	0.104	0.089	0.133	0.118	0.096
4	Lead (Pb)	0.0045	0.0039	0.0030	0.0030	0.0027	0.0018
5	Nickel (Ni)	0.097	0.091	0.076	0.082	0.067	0.058
6	Zinc (Zn)	0.237	0.192	0.124	0.226	0.181	0.136

3.1 Temperature effect on yield of activated carbon.

The overall efficiency of activated carbon production process can be determined by two important parameters, these are: carbonization and activation temperature. Many researchers have studied the effect of activation temperatures on yield. Thomas et al. studied the adsorption KOH and H₃PO₄ impregnated jack fruit AC for removal of Ni in aqueous solution and showed that as the carbonization temperature increases the yield decreases. Conversely as the impregnation ratio increases the yield of the AC increases (Thomas et al., 2017). Owabor and Iyaomelere (2013) evaluated the influence of salt treatment on the structure of pyrolyzed periwinkle shell and reported that as the temperature increase the yield of the AC decreases while the increase in impregnation ratio increase the yield up to a certain optimum level after which further increase in IR led to the decrease in the yield of the AC.

The effect of temperature on rice husk AC is presented in Figure 1a, it shows that as the temperature increases the yield decrease. At temperatures 500°C, 550°C and 600°C for IR 1, the corresponding yield are 91.11, 90.58 and 88.64 while for IR 1.5 is 89.49, 88.72 and 85.58 and IR 2 recorded 87.78, 87.1 and 84.53 respectively. Furthermore, the effect of temperature on the yield of bagasse shown in Figure 1b follows similar pattern, the yield at temperature of 500°C, 550°C and 600°C for IR 1 is 90.13, 89.76 and 86.32, and IR 1.5 is 88.47, 87.33 and 84.29 while IR 2 is 87.88, 86.19 and 83.54 respectively. This phenomena is due to volatilization of

carbon burn off as the temperature increases. Similar results has been reported by others scholar. Njewa et al. (2022) studied the Synthesis and Characterization of Activated Carbons Prepared from Agro-Wastes by Chemical Activation and observed that the increase in temperature decrease the yield in the actinvarted carbon. Zakaria et al. (2021) reported on effect of impregnation ratio and activation temperature on the yield and adsorption performance of mangrove based activated carbon. They observed that as the temperature is increase 300°C to 500°C the yield decreased from 45% to 38%.

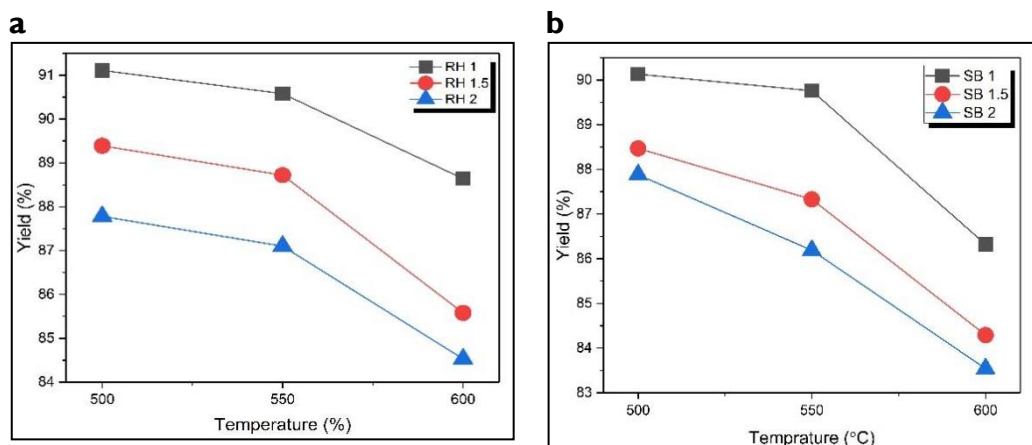


Figure 1 (a) Temperature effect on yield of rice Husk (b) Temperature effect on yield of sugarcane

3.2 Impregnation ratio effect on yield of activated carbon

The weight ratio between the precursor material and the activation agent is known as the impregnation ratio. The effectiveness and efficiency of the chemical activation process are largely dependent on this ratio. Researchers have identified impregnation ratio is one of the most important factors that affects the activation mechanism and the qualities of the activated material (Yahya et al., 2015).

The effect of impregnation on the yield of the rice husk and sugarcane bagasse is presented in Figure 2a and Figure 2b.

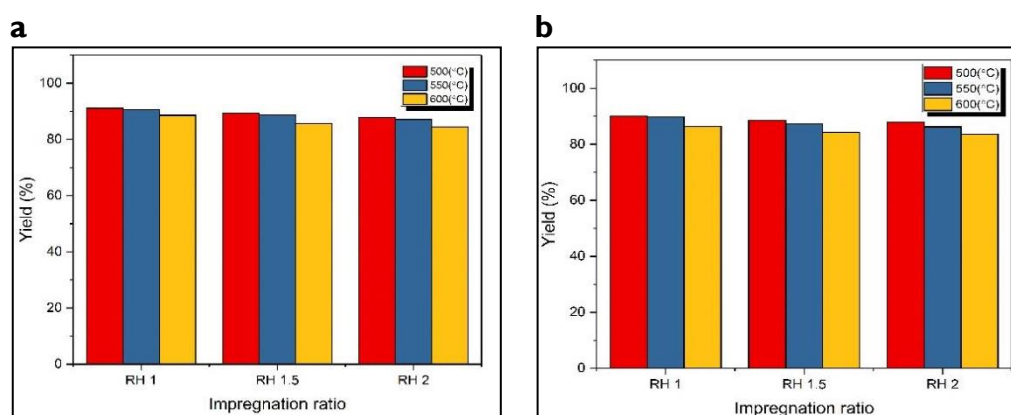


Figure 2 (a) Impregnation ratio effect on yield of rice Husk (b) Impregnation ratio effect on yield of sugarcane

Rice Husk activated carbon produced varied in behavior to other activated carbons. In this case the RHAC yield decrease with increase in impregnation ratio. However, the difference between the ratios are very minimal, this can be as result of pore formation. The yield performance as depicted in Table 2(a), shows that for impregnation ratio one (IR 1) the corresponding yield for carbonization temperatures of 500°C, 550°C and 600°C are 91.11%, 90.58% and 88.64%.

While for IR 1.5, the yield is 89.39% at 500°C, 88.72% at 550°C and 85.58% 600. For the final carbonization temperature of 600°C the yield are 87.78%, 87.1% and 84.53% for IR 1, IR 1.5 and IR 2 respectively. Similarly, the yield of Sugarcane Bagasse activated carbon reduced with increased impregnation ratio as shown in Table 2(b) which can mainly be due to evolution of volatile material. For IR 1, IR 1.5 and IR 2, the yield are respectively 90.13%, 88.47% and 87.88% at temperature of 500°C, and at the same for 550°C, the yield are 89.75%, 87.33% and 86.19%. Similarly for 600°C the yield for IR 1, IR 1.5 and IR 2 are 86.32%, 84.29% and 83.54%.

3.3 Morphology of adsorbent

The surface morphology of the activated carbon was examined using a scanning electron microscope (SEM) at x3000, x4000, x5000 and x10,000 magnifications. This is to enable detail and compressive assessment of the precursor at the various magnifications.

The morphology of the rice husk activated carbon was determined using a scanning electron microscope. SEM images shown in fig 3(a-d) provides detailed information and reactions that took place on the surface of the activated carbon microstructure (Dada et al., 2022). It can be seen from the images obtained, the RHAC surface having heterogeneous and irregular, which also contains undulating layer of outer covering that is referred to as the vascular bundle structure containing SiO₂ (Wazir et al., 2020) as reveled in Figure 3(a) and (b). At higher magnification as shown in Figure 3(c) and (d) rough and coarse surfaces with different cracks and crevices can be observed which reveal the presence of developed pores that emerge as a of the physical and chemical activation (El Nemr et al., 2022). These highly developed pore structure is having imperative effect on the process of adsorption and to affirm the presence of meso and macro-pores which are potential site for the sorption and transportation of metal ions in aqueous solution (Dada et al., 2022).

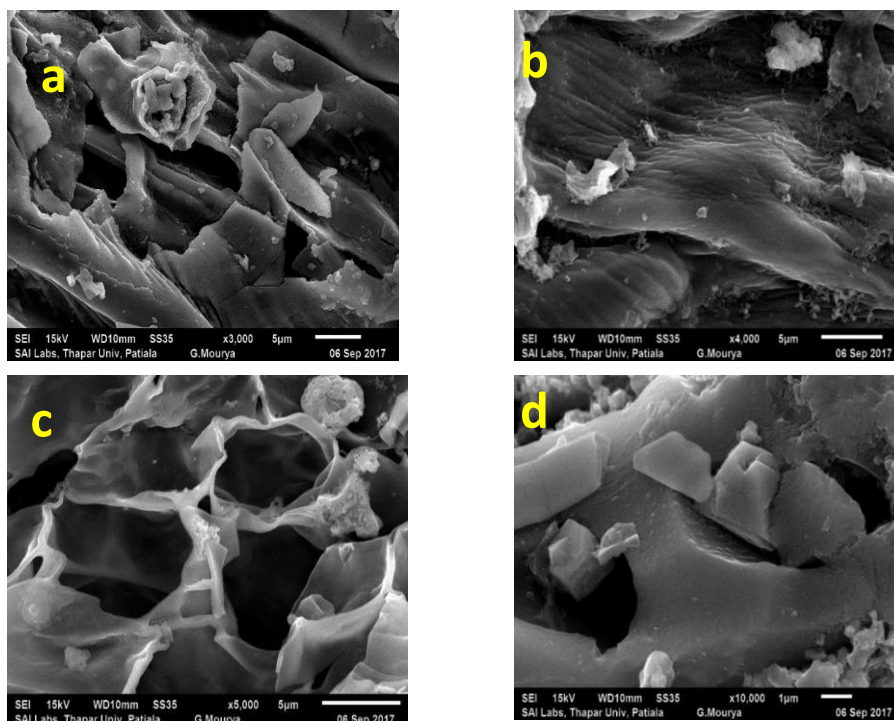


Figure 3: SEM images for rice husk carbon (a) magnification x3000 (b) magnification x4000 (c) magnification x5000 (d) magnification x10,000

Similarly, the SEM sugarcane bagasse activated carbon shown in Figure 4(a-d) comprises relatively smooth surface with cravices that have emerge as result of the activation process. During the thermal activation and preparation of the adsorbent, volatile organic compounds are evolved, this gives rise to the pore network of the sugarcane bagasse. Other literatures have reported identical result. Raut et al. (2023) studied the synthesis and characterization of

raw bagasse, and activated carbon using chemical additive where the developed pore are visibly relative not equal (Raut et al., 2023).

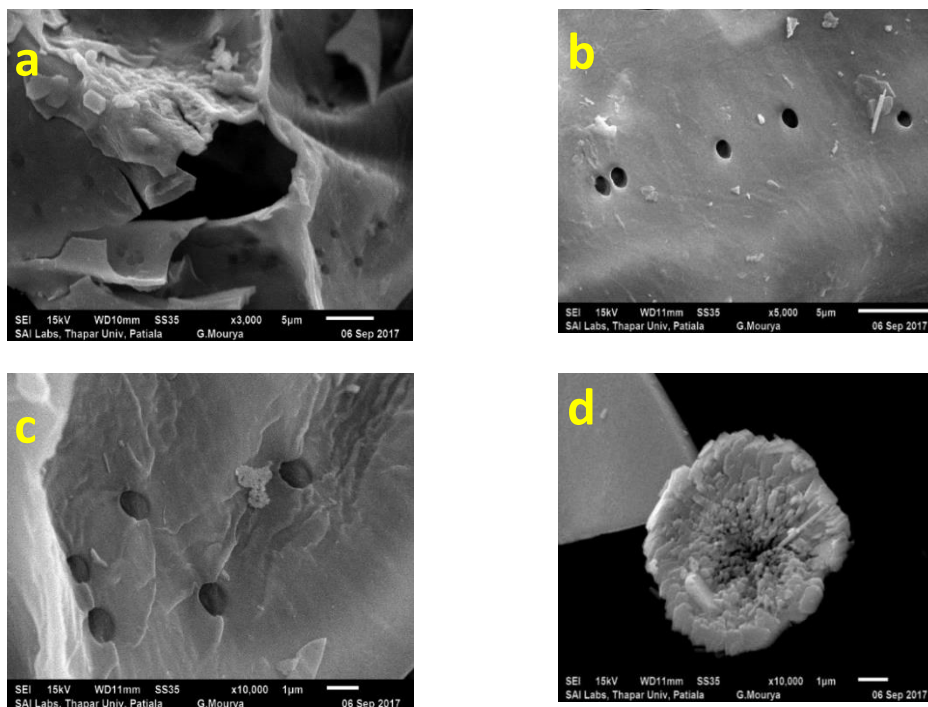


Figure 4: SEM images for sugarcane bagasse Activated Carbon (a) magnification x3000 (b) magnification x4000 (c) magnification x5000 (d) magnification x10,000

3.4 X-ray diffraction spectroscopy (XRD)

In order to determine the level of amorphous nature or crystallinity of an activated carbon, x-ray diffraction becomes indispensable. The X-ray diffractometer Ultima IV, Rigaku (Japan) was used for the study working at a current of 40 mA and voltage of 40 kV. The variation of the diffraction angle (2θ) ranges between 10° to 80° .

X-ray scattering is an analytical method that reveals details about the crystallographic structure, chemical makeup, and physical characteristics of materials. It operates by assessing the intensity of X-rays that are deflected by a sample, taking into account the angles of incidence and scattering, as well as polarization and the wavelength or energy of the X-rays (Raut et al., 2023). The XRD diffractogram of rice husk and sugarcane bagasse are shown in Figure 4(a) and Figure 4(b).

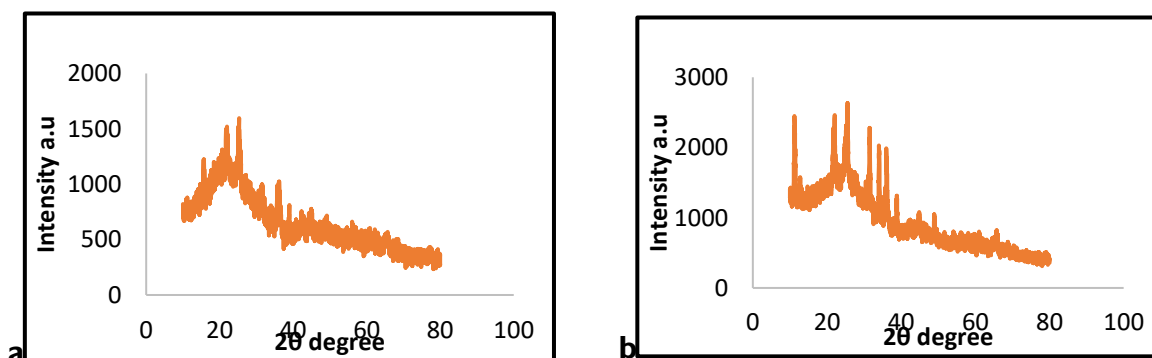


Figure 5: XRD spectra (a) rice husk activated carbon (b) sugarcane bagasse activated carbon

The XRD diffractogram obtained from rice husk activated carbon as shown from Fig. 5(a), displaying irregular pattern with two sharp peaks observed around $2\theta=21^\circ$, $2\theta=25^\circ$ and $2\theta=36^\circ$ which are indication of the presence of a microcrystalline cellulose. Choi et al. (2018) have

reported similar findings in structural characterization of cellulose obtained from extraction wastes of graviola (*Annona muricata*) leaves. However, the rest of the diffractogram does not show any visible peak, this posits the adsorbent as an amorphous in nature there by making a better adsorbent due to large surface area and pore volume (Abdul Khalil et al., 2013; Gurung et al., 2023).

The sugarcane bagasse activated carbon was tested for its crystallinity as represented by the diffractogram pattern shown in Figure 4(b). It can be seen from the spectra that there exist sharp peaks at $2\theta=11^\circ$, $2\theta=22^\circ$ and $2\theta=25^\circ$, and also between $2\theta=30^\circ - 40^\circ$. This signifies that the spectra constitute the presence of ordered arrangement of atom and hence microcrystalline arrangement (Namasivayam and Kavitha, 2006). Although, the well-defined arrangement giving insight as crystalline structure apparently collapses across the diffractogram showing the formation of an amorphous properties of the sugarcane bagasse activated carbon.

4.1 Heavy Metals Adsorption

In the adsorption isotherm, the amount of adsorbate that can be absorbed by the adsorbent is a function of the adsorbate concentration and temperature. The characteristics of the adsorbate include solubility, molecular structure, molecular weight, polarity, and hydrocarbon saturation. The equation that is often used to describe experimental isotherm data was developed by Freundlich, Langmuir, and others (Budhiari and Sumantri, 2021).

The Langmuir adsorption isotherm is based on monolayer, uniform, and finite adsorption site assumptions, therefore a saturation value is reached beyond which no further adsorption takes place. It also assumes that there is no interaction between the molecules adsorbed on neighbouring sites (Belhachemi and Addoun, 2011). The Langmuir equation which is valid for monolayer adsorption onto a surface with a finite number of identical sites is given by Equation (2) above. Freundlich isotherm is an empirical equation for multilayer, heterogeneous adsorption sites. The Freundlich equation is given by equation (4).

Simultaneous adsorption of heavy metals in petroleum refinery effluent using rice husk activated carbon. The obtained data was examined by the R^2 coefficient derived from the linear plots of the isotherm models presented in Figure 6 for rice husk and Figure 7 for sugarcane bagasse.

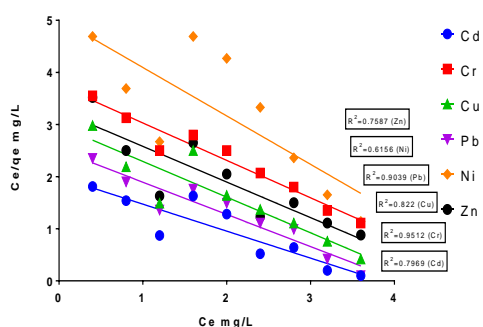


Figure 6: Heavy metal adsorption of rice husk activated carbon.

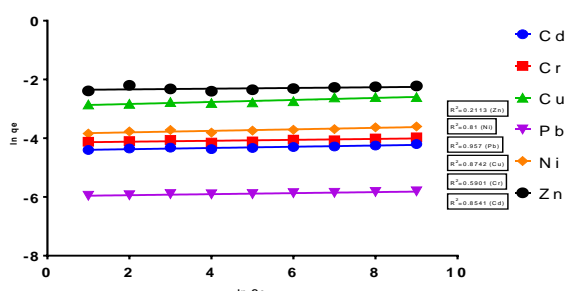


Figure 7: Heavy metal adsorption of sugarcane bagasse activated carbon

The findings in Table 6, shows that the simultaneous adsorption of heavy metals from petroleum refinery is fitted well for both Langmuir and Freundlich models. Cadmium recorded R^2 0.7969 and 0.8343 for Langmuir and Freundlich isotherms, chromium has 0.9512 and 0.936, copper exhibited an R^2 of 0.822 and 0.8093 while lead manifested 0.9039 and 0.6156, and lastly zinc revealed 0.7586 and 0.6726 respectively. This shows that the adsorption of the heavy metals on the surface of the rice husk activated carbon is consistent (Denga et al., 2023).

Furthermore, the separation factor K_L , which was used to assess the favorability of the adsorption, is less than 1, indicating good adsorption of the heavy metals (Mashile et al., 2020)

Table 6: Adsorption isotherm models and their constant for rice husk activated carbon

Heavy metals	Langmuir			Freundlich		
	R ²	Q _{max}	K _L	R ²	K _f	N
Cadmium	0.7969	3.147	-0.7516	0.8343	242.7	0.01193
Chromium	0.9512	4.646	-0.8632	0.936	145.4	0.01801
Copper	0.822	3.568	-0.9687	0.8093	89.64	0.01283
Lead	0.9039	3.527	-0.798	0.9099	213.7	0.01593
Nickel	0.6156	3.887	-1.585	0.6259	81.77	0.00896
Zinc	0.7586	3.75	-1.028	0.6726	73.02	0.00803

On the other hand, the concurrent adsorption of heavy metals using sugarcane bagasse activated carbon is presented in Figure 7. The obtained values were also analyzed based on the R² coefficient obtained in the Langmuir and Freundlich models as revealed in Table 7.

The R² coefficient for cadmium ion obtained from Langmuir and Freundlich models are 0.8676 and 0.8541, chromium 0.5696 and 0.5901, copper 0.8733 and 0.8742, and lead 0.9378 and 0.957. The other metal ions are nickel which recorded R² coefficient of 0.7949 and 0.81, and zinc having 0.2005 and 0.2113 for Langmuir and Freundlich isotherm respectively. Analogous to the rice husk adsorbent, sugarcane bagasse performs well in the tested models, although it fits well with the Freundlich adsorption model as shown in Table 7.

Table 7: Adsorption isotherm models and their constants for sugarcane bagasse activated carbon

Heavy metals	Langmuir			Freundlich		
	R ²	Q _{max}	K _L	R ²	K _f	N
Cadmium	0.8676	3.44	-0.7769	0.8541	156.1	0.01314
Chromium	0.5696	4.654	-0.8573	0.5901	152.4	0.00404
Copper	0.8733	2.989	-1.281	0.8742	64.11	0.0128
Lead	0.9378	3.276	-0.5961	0.957	287.8	0.01419
Nickel	0.7949	4.249	-1.125	0.81	106.2	0.01456
Zinc	0.2005	3.156	-0.941	0.2113	75.3	-0.00872

4.0 Conclusion

The simultaneous adsorption of six heavy metals usually found in refinery wastewater using rice husk and sugarcane bagasse was studied. The experimental data obtained for rice husk shows competitive adsorption and is fitted to both Langmuir and Freundlich models. The order of strength of the sorption was Cr>Pb>Cu>Cd>Zn>Ni. The data obtained for sugarcane bagasse fitted well into the Freundlich model, the order of adsorption preference was Pb>Cu>Cd>Ni>Cr>Zn. The investigated process parameter reveals that the impregnation ratio and temperature affect the sorption capacities of activated carbon. Rice husk and sugarcane bagasse as shown from the batch experiment conducted can be effectively used for the treatment of heavy metal from refinery and other industrial effluents.

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