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Characteristic Analysis of $ZnCl_2$ Activated *Ricinus Communis* Stem.

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ABSTRACT

An Eco friendly adsorbent is prepared from *Ricinus communis* stem which is impregnated by using $ZnCl_2$.The Raw *Ricinus communis* stem and its activated form are characterized using SEM, EDAX, XRD and FTIR techniques respectively. The physiochemical parameters of the RRCS and ZRCS such as Carbon yield (%), Moisture content, pH, Acidity and Basicity, Zero point charge, Boehm's titration, Iodine Number are carried out. The surface area of ZRCS is 714m^2/g is higher than the surface area of RRCS 413.13 m^2/g and the yield and iodine number of ZRCS are also more than the RRCS. The present investigation concludes that the ZRCS possess good yield, iodine number and surface area when compared to RRCS .So it could be used to treat the wastewater in future.

Keywords: *Ricinus communis* stem, adsorbent, Characterization, impregnation, $ZnCl_2$.

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INTRODUCTION

Industrial and domestic wastewater are responsible for causing damage to the environment. The main sources of water contamination are industrialization, civilization, agricultural activities, and other environmental and global changes [1]. Dyes from the industries undergo chemical as well as biological changes after being released into water resulting in further increase of the chemical oxygen demand and reduction of light penetration as well as visibility [2, 3]. Furthermore, certain dyes and their degradation counterparts are potentially carcinogenic and toxic, and hence, their presence in water becomes a serious threat to aquatic life and human populations [4-8]. The contaminated wastewater may be treated with conventional physical-chemical methods like reverse osmosis, ion exchange, chemical precipitation or lime coagulation and oxidation, the application of these techniques have been restricted due to high energy consumptions or expensive synthetic resins and chemicals[9]. Moreover these methods generate large amount of toxic sludge and ineffective at lower concentrations of dyes [10]. Activated carbon is one of the most widely used factor for the treatment of wastewater because of its high cost , high surface area and regeneration difficulties of activated carbon have augmented the need to explore low cost reusable and biodegradable plant material for the removal of dyes [11]. *Ricinus Communis* is an agricultural waste and its common name is castor bean, in important drought resistance shrub belongs to the family of Euphobiaceae .There are two methods employed for the preparation of AC via, physical and chemical activation. In physical activation the carbonization and activation are carried out separately, but in chemical activation both carbonization and activation takes place simultaneously. The raw material is first impregnated with activating chemical and then carbonized at ambient temperature that varies according to activating chemical used [12]. The development of pores is much higher than raw material in the case of chemical activation [13]. Chemical activation is held in the presence of dehydrating reagents such as KOH, K_2CO_3, NaOH, $ZnCl_2$ and H_3PO_4. The Chemical activation gives higher yield than physical activation at low temperature. $ZnCl_2$ activation results High surface area and high yield [14]. New economical, easily available and highly effective *Ricinus communis* stem powder is activated by using $ZnCl_2$ and characterized systematically. Further it is used to treat the wastewater.

MATERIALS AND METHODS

Preparation of *Ricinus Communis* stem powder (RRCS)

Ricinus communis stems are collected from nearby area of Saravanampatti, washed, air dried and crushed into fine powder in a grinder. The dried and powdered stem is stored in a air tight container and used as an Ecofriendly adsorbent.

Preparation of $ZnCl_2$ activated *Ricinus Communis* stem powder (ZRCS)

RRCS is taken in a beaker containing Zinc Chloride and is thoroughly mixed and agitated for 24 hours in a magnetic stirrer. After this agitation, the whole content is heated in a hot air oven for 4 hours, Then 0.5M HCl is added and the mixture is kept for 24 hours in the room temperature. The obtained slurry is washed with distilled water until the filtrate turning as a colorless one and dried in a hot air oven [15].

CHARACTERIZATION

Physiochemical characterization

The Yield, Moisture content, pH, Determination of surface acidity and Basicity, Zpc and Iodine number are determined for the prepared adsorbents such as RRCS and ZRCS.

Yield

The yield of the RRCS and ZRCS in percentage is calculated by using the formula given below

$$Yield\,(Y) = (M/M_0) \times 100 \qquad (1)$$

Where, M = Mass of the ZRCS (M), M_0= Mass of RRCS

Moisture Content

About 5 g of the RRCS and ZRCS are weighed in a china dish and heated in an oven at 110±2°C for about 5 h. After heating, the dish is cooled in desiccators and weighed. Heating and cooling is repeated at 30 Min interval until the difference between the two consecutive weighing is less than 5 mg. The loss in the weight gives the moisture content.

$$Moisture\ content\ (\%) = [(M - X)/M] \times 100 \qquad (2)$$

Where, M = Mass of the materials before drying (g)
X = Mass of the materials taken after after drying (g)

pH of the Adsorbent

About 200mg of RRCS and ZRCS are weighed and taken in 50 ml beaker. 30 ml of boiled and cooled water, whose pH is adjusted to 7.0, is added and heated to boiling. First 10 ml of the filtrate is rejected. The remaining filtrate is cooled and the pH is determined using the digital pH meter.

Surface acidity and Basicity of the adsorbent

Acidity

To 200 mg of RRCS and ZRCS, 25 ml of 0.5M NaOH solution is added in a conical flask, agitated it for 10 h in a closed flask. Filter it and the filtrate is titrated with 0.5M HCl.

Basicity

To 200 mg of RRCS and ZRCS, 25 ml of 0.5M HCl solution is added in a conical flask, agitated it for 10 h in a closed flask. Filter it and the filtrate is titrated with 0.5M NaOH. Acidity and basicity is expressed in m.mol/g.

Zero Point Charge of the adsorbent

About 200 mg of RRCS and ZRCS are added to a solution of sodium nitrate concentration of 0.01M, whose pH is adjusted with 0.1M NaOH and 0.1M HNO_3 and final pH is measured. The results are plotted with initial pH VsΔpH (ΔpH = Initial pH- final pH). The pH equals to zero, yielded pH_{zpc} of RRCS and ZRCS.

Determination of Iodine value of the adsorbent

Iodine value is calculated for RRCS and ZRCS using Iodimetry titration method. The concentration of Iodine adsorbed by the RRCS and ZRCS at room temperature is calculated as the amount of Iodine adsorbed in milligrams [16].

Conversion Factor(C) =B-A

Where B is the titre value of Blank Solution, A is the titre value of RRCS and ZRCS added solution.

$$\text{Iodine Number} = \frac{\text{Molecular weight of } I_2 \text{ x Normality of } I_2 \text{ x50}}{\text{Weight of RRCS or ZRCS x Blank Reading}} \qquad (3)$$

Determination of surface group (Boehm's Titration)

The RRCS and ZRCS are taken in the 50 ml conical flask and 20 ml of different bases are added. The flask is then sealed and agitated in shaker for 3 days. Filter these solutions separately and 5 ml of each filtrate is titrated with 0.1M HCl using water-ethanol solution of methyl orange as the indicator. The number of basic sites calculated from the amount of HCl reacts with the carbon (Boehm *et al*., 1964) [17].

SURFACE CHARACTERIZATION

Fourier Transform infrared Spectroscopic analysis is carried out on Jasco-460 plus model to obtain the structural information of RRCS and ZRCS. The surface morphology of the RRCS and ZRCS are studied with the scanning electron microscope and Elemental spectra are obtained using JSM 6390 model. X-ray diffraction is carried out by using XRD 6000 model. The SEM observation allows qualitative detection and localization of elements in the RRCS and ZRCS.

RESULT AND DISCUSSION

Physiochemical Characterization of RRCS and ZRCS

The Physiochemical characteristics of RRCS and ZRCS are summarized in the Table 1. This result indicates that yield and iodine number can be correlated with the ability to adsorb low-molecular-weight substances and provides a measure of the surface area or capacity available to small molecules. The higher the yield and iodine value, the higher will be the uptake of the pollutants. From the determined result ZRCS has high Yield and Iodine number than RRCS (85.46 & 77%, 2136.719 & 2858.817mg/g).

The measure of moisture content is reported that if the moisture content of the carbon is more it dilutes the action of carbon and necessitates to utilize some extra load of carbon [18].

RRCS and ZRCS have the surface acidity of 3.375mmoles/gm and 4.35respectively. Basicity of these carbons 4.383mmoles/gm and 4.822mmoles/gm. The Surface Acidity and Basicity of RRCS and ZRCS are confirmed by Boehm titration method. Boehm titrations quantify the basic and oxygenated acidic surface groups on the adsorbent [19]. In Boehm titration NaOH neutralize carboxyl lactone and phenolic groups, Na_2CO_3 neutralizes carboxyl and lactones, and $NaHCO_3$ neutralizes only carboxyl groups respectively and values obtained can be expressed in the milli equivalents per gram.

If the adsorbent has more surface area and bulk density the up taking capacity of the pollutants is high. From result the surface area of ZRCS (714m^2/g) is greater than the surface area of RRCS (383.12m^2/g).The ZRCS reaction increases the existing pores and creates new porosities to increase the specific area and pore volume. This indicates that the ZRCS possesses higher uptake property [20].

The Zpc of an activated carbon is a very important property that determines the pH of the adsorbent. The zero point charges of RRCS and ZRCS are $pH_{zpc=}$5.02 and 4.20 at which the adsorbent surface has net electrical neutrality. Above this pH the adsorbent has positive charge density on its surface which favours the uptake property of pollutants like anions. Below this pH the adsorbent has negative charge density on the surface of RRCS and ZRCS which favours the uptake property of the pollutants like cations.

Table 1. Physiochemical Characterization of RRCS and ZRCS.

Parameters	RRCS	ZRCS
Yield %	77	85.46
Moisture content %	7.13	5.63
Surface area (m^2/g)	413.13	714
Porosity %	58.56	69
pH	5.88	6.06
Surface acidity (mmoles/gm)	3.375	4.35
Surface basicity (mmoles/gm)	4.383	4.822
ZpC	5.02	4.20
Boehm titration (m.eq/gm) NaoH	1.694	1.080
Na_2CO_3	0.6224	1.480
$NaHCO_3$	0.160	1.480
Iodine Number mg/g	2136.719	2858.817

Scanning electron microscopic spectroscopy (SEM)

SEM images RRCS and ZRCS are shown in the Figure 1, which indicates the complex rough surface in the untreated form (Figure1a). Its pores and surface area get increased a lot after $ZnCl_2$ activation (Figure1b)[22].

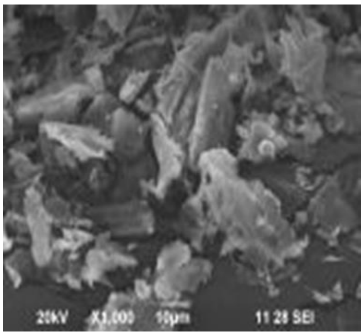

Figure1a. SEM image of RRCS

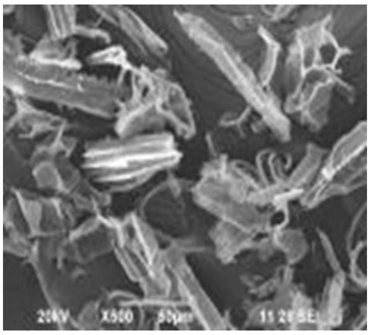

Figure1b. SEM images of ZRCS

Energy Dispersive X-Ray spectroscopy (EDS or EDX) of RRCS and ZRCS are shown in Figure 2a and 2b. The presence of respective ions of RRCS is confirmed in the figure 2a. In the Figure 2b the Zinc sorption has occurred on ZRCS is confirmed by the presence of Zinc [23].

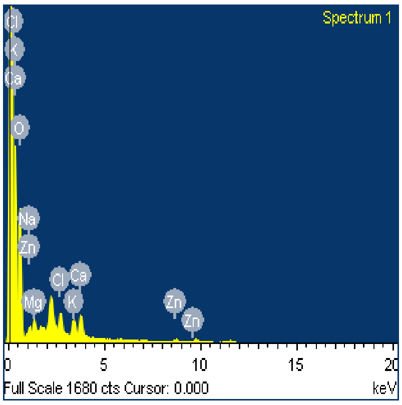

Figure 2a. EDAX image of RRCS

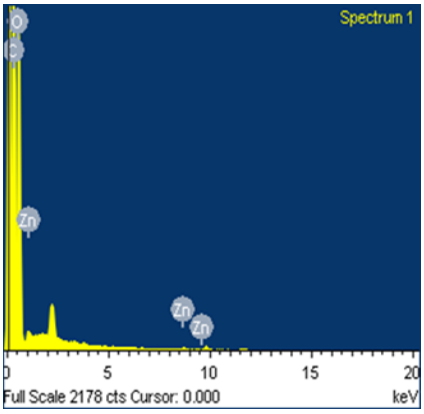

Fig 2b. EDAX images of ZRCS

X-ray refractory diffraction (XRD)

X-ray refractory diffraction (XRD) shows the RRCS and ZRCS are amorphous in nature due to the 2θvalue lies between 20-30˚in both the cases [24]. From the result it is confirmed that the XRD patterns of RRCS is similar to ZRCS. This indicates that the addition of $ZnCl_2$ does not cause any shift in peak position of the RRCS [25]. The broad peaks of ZRCS appeared at around 20-30˚, which was similar to the Crystalline graphite peak. From this we confirmed that the completion of Zinc chloride chemical activation for ZLRC preparation.

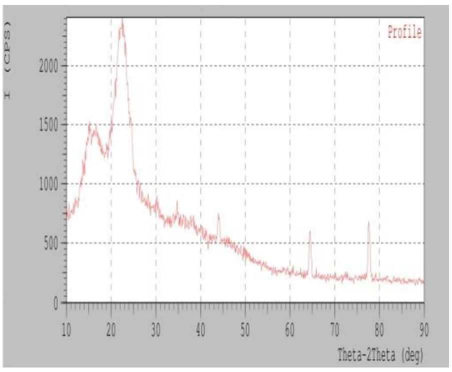

Figure 3a. XRD image of RRCS

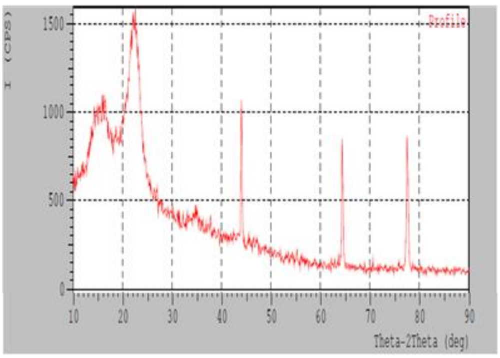

Figure 3b. XRD Image of ZRCS

Fourier Transform infrared Spectroscopic analysis (FTIR)

The aim of using FTIR analysis is used to determine the existence of functional groups, and identification of characteristic peak is based on the studies reported in the literature [26-28]. The FTIR spectrum of RRCS is shown in the figure 4a. RRCS shows that the most predominant peaks is in 3417.04 cm^{-1} which indicates the presence of H_2 bonded OH and the peak at 2925.17 cm^{-1} shows the presence of asymmetric CH stretching. The peak around 1737.94 cm^{-1} shows the presence of C=O stretching. The peak at 1633.78 cm^{-1} shows the presence of NH_2 stretching and the peak at 1511.29 cm^{-1} shows the presence of C=C stretching aromatic skeleton. The peak present at 1380.13 cm^{-1}indicates the presence of methyl group. The band observed at 1249.93 cm^{-1} shows the presence of C-O-C symmetric stretching of ester, ether and epoxides. The peak around 1053.18 cm^{-1} indicates the presence of C-N stretching [29].

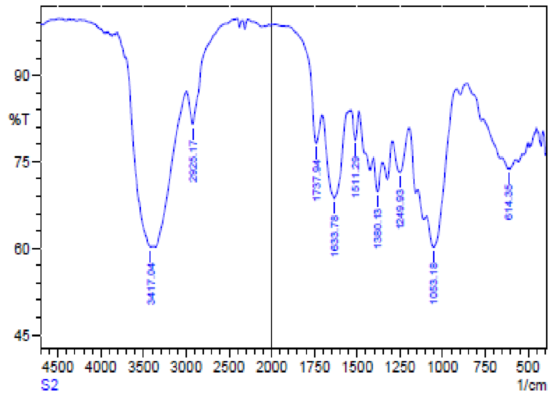

Figure 4a. FTIR spectrum of RRCS

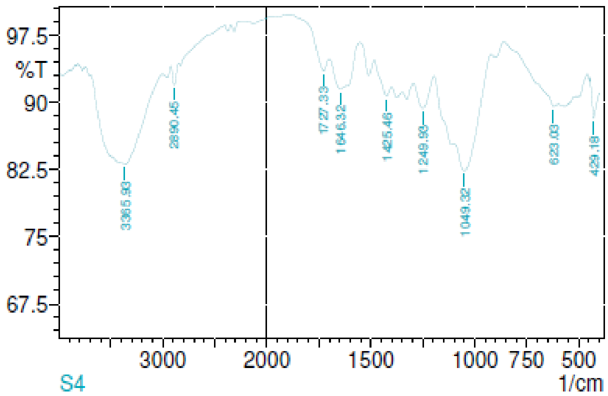

Figure 4b.FTIR spectrum of ZRCS

The FTIR spectrum of ZRCS is shown in the Figure 4b. The intense bent at about 3336.03 cm^{-1} shows the presence of stretching vibration of OH groups. The peak around 2924.21 cm^{-1} is indicating the presence of asymmetric and symmetric vibration modes of methyl and methylene group [30]. The peak at 1736.97 cm^{-1} shows the presence of C= C group. The peak at 1511.29 cm^{-1} indicates the presence of C=C stretching of aromatic skeleton and the peak 1378.20 cm^{-1} shows the presence of C-O stretching. The peak present at 1252.82 cm^{-1} shows the presence of C-C-O-C-C anti symmetric stretching. The peak around1047.39 cm^{-1} indicates the presence of Lignin. The peak at 630.75 cm^{-1} indicates the presence of aromatic heterocyclic molecules [31].

CONCLUSION

This study confirms that the adsorbent prepared from *Ricinus communis* stem, a low cost agricultural waste can be effectively used as a raw material for the preparation of activated carbon using $ZnCl_2$ activation method. From the SEM analysis of ZRCS shows the increasing in pores and surface area compared to RRCS. The higher yield and iodine value will give the higher adsorption ability of the carbons for the treatment of waste water. The XRD results confirm the amorphous nature of the adsorbent. Among RRCS and ZRCS, ZRCS shows the most uptaking capacity of pollutants in the wastewater than in RRCS.

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