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Preparation and Characterization of Activated Carbon Derived From Rice Husk by NaOH Activation

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Abstract: **Rice husk is treated as waste and disposed at power plant sites, and leads to a serious environmental problem. Therefore, it is important to treat rice husk before disposing. So, rice husk is used as precursors to produce activated carbon. This work deals with the preparation and characterization of activated carbon from agricultural waste for the adsorption of methyl orange in an aqueous solution. The removal of methyl orange onto AC's from aqueous solution was investigated by using parameters such as pH, and binding forces. A spectrophotometer was used for measuring the extent of adsorption. The extent of dye removal decreased with increasing adsorbent dosage and also decreased with pH increasing absorbance. Optimum pH value for dye adsorption was determined to be 2.0, strong pH-dependence of methyl orange adsorption onto AC's together with FT-IR results indicate to the possible involvement of physical forces such as hydrogen bonding, and electrostatic force of attraction in the adsorption process. In addition, the adsorption data of methyl orange by AC's were applied to SEM analysis. The results indicate that AC's could be employed as low-cost alternative adsorbents in the removal of methyl orange from aqueous solution.**

Keywords: **Activated Carbon (AC), Rice Husk, pH, UV- Vis, SEM, FT-IR.**

1. INTRODUCTION

Normally, rice husk is treated as waste and disposed at power plant sites, and leads to a serious environmental problem. Therefore, it is important to make full use of the husk. Recently, rice husk is used as precursors to produce activated carbon (AC). With porous structure, high surface area and low cost, AC has attracted considerable attention and has been widely used as catalyst carriers (catalytic support), adsorbent to adsorb metal ions and organic molecules **(Liou *et al.*, 2009).** The properties of activated carbons depend on the activation process and the nature of the source materials. Moreover, in both physical and chemical activation processes, knowledge of different variables is very important in developing the porosity of the carbon **(Lozano- Castello *et al.*, 2001).** The excellent ability and economic promising of the activated carbons prepared from bamboos, plum, kernels, and corn cobs for adsorption of dyes and phenols from aqueous solutions have been recently presented **(Wu *et al.*, 1999).** In recent years, special emphasis on the preparation of activated carbons from several agricultural by-products has been given due to the growing interest in low cost activated carbons for application concerning treatment of wastewater. Researchers have studied the production of activated carbon from palm-tree cobs **(Avom *et al.*, 1997)**, plum kernels **(Wu *et al.*, 1999),** cassava peel **(Rajeshwarisivaraj *et al.*, 2001),** bagasse **(Tsai *et al.*, 2001),** jute fibre **(Senthilkumar *et al.*, 2005),** coconut husk **(Tan *et al.*, 2008),** rattan sawdust **(Hameed *et al.*, 2007),** seed shells **(Thinakaran *et al.*, 2008),** cocoa shell **(Theivarasu *et al.*, 2011)** and Eucalyptus globules Bark **(Kannan *et al.*, 2012).** The advantage of using agricultural by-products as raw materials for manufacturing activated carbon is that these raw materials are renewable and potentially less expensive to produce. Azo dye and nitrated polycyclic aromatic hydrocarbon are two groups of chemicals that are abundant in environment. They cause severe contamination in river and ground water in the vicinity of dyeing industries **(Riu *et el.*, 1998).** The most commonly used adsorbent for color removal is activated carbon, because of its capability for efficiently adsorbing a broad range of different types of adsorbate **(Hameed *et al.*, 2007).** At present, there is a growing interest in using low-cost and non-conventional alternative materials instead of traditional adsorbents **(Barka *et al.*, 2011**).

2. METHOD AND MATERIALS

Preparation of Activated Carbon:

Activated carbon was prepared from rice husk (which is supposed to be an agricultural waste also it is not consumed by any animal) by going through the following steps. First, rice husk was washed with water to remove the dirt particle or particles which is soluble in water and filtered off the contaminant present in the rice husk now then the wet rice husk was subjected for drying in at 110˚C for 12hour. Then, the dried rice husk was grounded and sieved to the average particle size of 1.0 mm. After, grinding to the desired size of particle it was subjected to the cabonization process at 400˚C for 8hour, so that the organic substance was converted into carbon containing residue which was carbon(char-coal). The prepared carbon was impregnated with solid NaOH (weight ratio is 1:3) in order to activate and subjected for drying at 120˚C for 12hour. Then, the impregnated activated carbon is heated nearly at 400˚C for 20minute in nitrogen atmosphere. Thereafter the temperature was raised to the predetermined range of (650-800)˚C and maintained for 60minute to obtain the required material. Finally, the activated product was grounded for once more and neutralized by 0.1N HCl solution and washed off several times with hot distilled water to constant pH(6.6-7.0). The washed activated carbon sample was dried at 120˚C for 24hour and stored in a dessicator in order to prevent from moisture.

Adsorbate Used:

Methyl orange used in this study has a molecular formula of $\mathbf{C_{14}H_{14}N_3NaO_3S}$ and molecular weight of **327.33 g/mol**. The maximum wavelength of absorption of this dye is **550nm**. The prepared activated carbon pores sites are cationic in nature (surface is +vely charged) and then anionic dye was loaded on it. It gets adsorbed on it very strongly because methyl orange dye was an anionic dye (or azo dye). Due to electrostatic force of attraction between activated carbon (having pores site +ve due to presence of Na^+ ion) and methyl orange dye (due to its anionic -N=N-). Also Methyl orange was a pH indicator frequently used in titrations because of its clear and distinct color change. Because it changes colour at the pH of a mid strength acid, it is usually used in titrations for acids. Unlike a universal indicator, methyl orange does not have a full spectrum of color change, but has a sharper end point. Further adsorbate methyl orange of **50 ppm** of concentration was loaded on activated carbon and then characterization of loaded and unloaded (pure) activated carbon was done.

Characterization of Activated Carbon:

FT-IR (fourier transform Infrared) Analysis: Principles of FT-IR spectrophotometry is it relies on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule. The frequency ranges were measured as wave numbers typically over the range 4000 – 600 cm^{-1}. The sample of activated carbon with loaded(adsorbed) methyl orange and without unloaded methyl orange is mixed with KBr and its pellete is formed for both sample of activated carbon and then a fourier transform infrared spectrum was recorded for the activated carbon (pure) without loaded dye and with a loaded dye

pH Analysis: second, characterization of loaded (with dye) and unloaded(without dye) activated carbon was pH analysis. Effect of pH on the removal methyl orange dye was studied. The adsorption of this anionic dye onto the adsorbent surface was primarily influenced by the surface charge on the adsorbent, which in turn was influenced by the pH of the solution

SEM (Scanning Electron Microscopy) Analysis: Principle of SEM is essentially a high magnifying microscope, which uses a focussed scanned electron beam to produce images of the sample, both top-down and, with the necessary sample preparation, cross-sections. The primary electron beam interacts with the sample. Scanning Electron Microscope (SEM) studies provide useful information regarding the textural/morphological characteristics of the dye loaded and dye unloaded activated carbon.

3. RESULTS AND DISCUSSIONS

After preparing activated carbon different characterization was done and the following results were obtained.

FT-IR Analysis:

When the activated carbon was subjected to FT-IR spectroscopy then the following peak was observed.

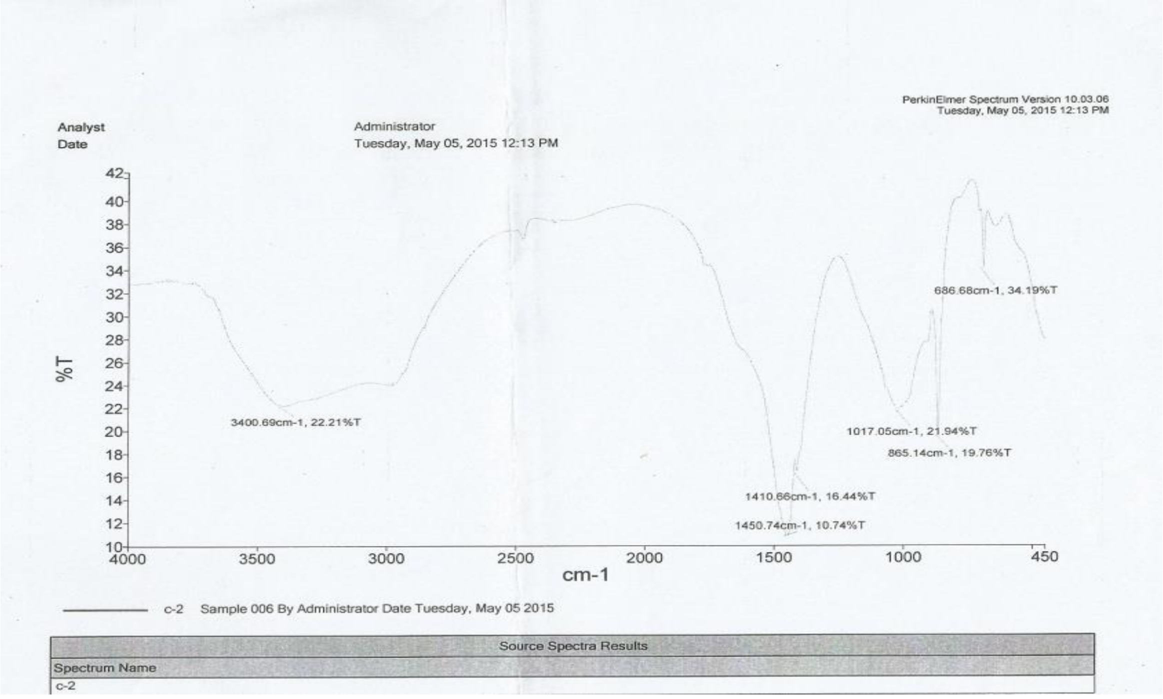

Figure 3.1 Spectral plot for unloaded (without dye) activated carbon.

And, when the activated carbon loaded with dye was subjected to FT-IR spectroscopy then, the following peak was obtained.

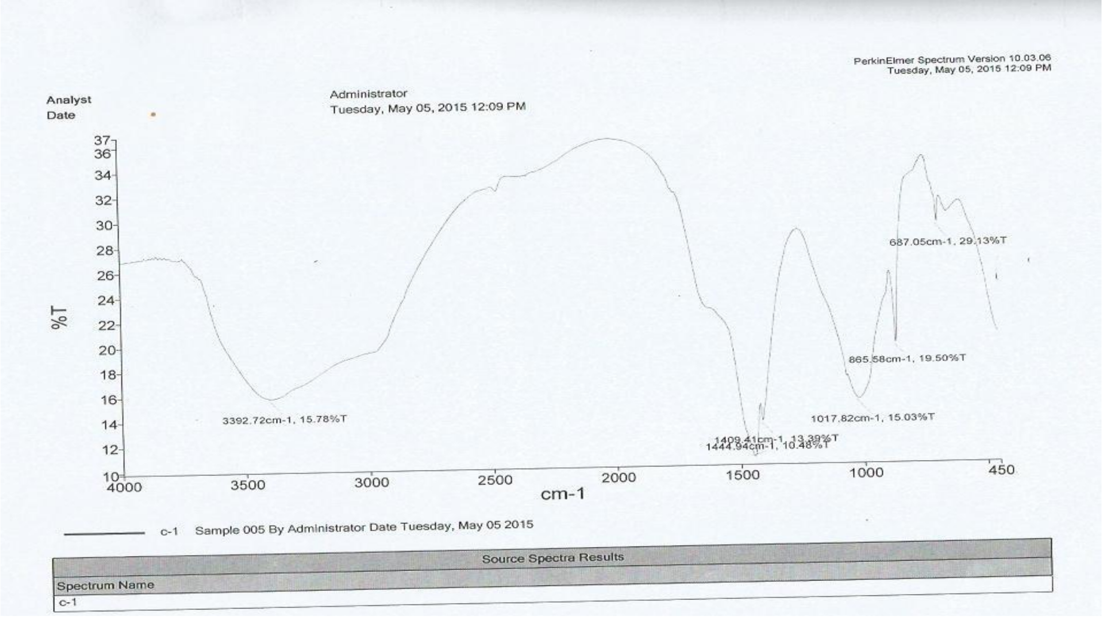

Fig. 3.2 Spectral plot of loaded (with dye) activated carbon.

Discussion for FT-IR analysis:

Table 3.1. FT-IR spectroscopic characteristics frequencies of activated carbon before and after adsorption of dye

S.No.	Adsorbents Stretching	Peaks before adsorption of dye (cm^{-1})	Peaks after adsorption of dye (cm^{-1})	Transmittance % before loading dye	Transmittance % after loading dye
1	-OH	3400.69	3392.72	22.21	15.78
2	C=O	1450.74	1444.94	10.74	10.48
3	S=O	1017.05	1017.82	21.94	15.03
4	C-S	865.14	865.58	19.76	19.50
5	Ar-H	686.68	687.05	34.19	29.13

The slight shifting of FT-IR absorption spectra in the low cost activated carbon was recorded when the same was get loaded with the methyl orange dye. FT-IR spectra of pure activated carbon contains several peaks at 686.68 cm^{-1}, 865.14 cm^{-1}, 1017.05 cm^{-1}, 1410.66 cm^{-1}, 1450.74 cm^{-1} and 3400.69 cm^{-1} . The peaks recorded for methyl orange loaded activated were 687.05 cm^{-1}, 865.58 cm^{-1} , 1017.82 cm^{-1}, 1409.41 cm^{-1},1444.94 cm^{-1}, and 3392.72cm^{-1}. **(Saravanan *et al.*, 2012).**

These changes in the absorption spectra and transmittance percentage confirmed the participation of the functional group present at the surface of activated carbon (C=O, – CS, -OH, S=O and Ar-H). The shifting of absorption peaks confirms the interaction between surface sites of activated carbon and SO_3^{2-},–N=N- group of methyl orange (similar results were reported by **Shahul *et al.*, 2013**; **Saravanan *et al.*, 2012**).

i). –OH stretching:

The absorption peaks obtained for –OH group present on the surface of activated carbon was 3400.69 cm^{-1} which shifted to 3392.72 cm^{-1}. The lowering of vibrational frequency and increase in intensity shows the increase in –OH bond length. This change in bond length is due to formation of H-Bond between –OH group present at the surface of activated carbon and –N=N-, SO_3^{2-}, of methyl orange **(Cazetta *et al.*, 2011).**

(ii) C=O stretching:

The presence of 1450.74cm^{-1} peak for unloaded activated carbon indicates that activated carbon may contain carbonyl group (aldehyde, ketone, carboxylic acid, acid halides, ester, amides etc.). and the peaks obtained for loaded activated carbon was 1444.94 cm^{-1}. This lowering of absorption frequency indicates the decrease in bond length -C=O (carbonyl group) which is due to coupling of carbonyl group of activated carbon with the functional present in methyl orange **(Cazetta *et al.*, 2011).**

(iii) S=O stretching:

The peaks obtained for unloaded and loaded activated carbon was at 1017.05 cm^{-1} and 1017.82 cm^{-1} respectively. It indicates the formation of H-Bond and enolization of S=O group present at the surface of activated carbon **(Cazetta *et al.*, 2011).**

(iv) C-S stretching:

The peaks recorded for C-S stretching frequency for unloaded and loaded activated carbon was 865.14 cm^{-1} and 865.58 cm^{-1} respectively.

(v) Ar-H stretching:

The peaks recorded for unloaded and loaded activated carbon at 686.68 cm^{-1} and 687.05 cm^{-1} respectively, which signifies that arene are 1,3and5 substituted along with medium intensity. **(Cazetta *et al.*, 2011).**

There was no real shift in absorption peaks but the intensity becomes lower after absorption, this is indicated as a physical adsorption.

Effect of pH on the adsorption of methyl orange:

In general, initial pH value may enhance or depress the uptake of solute. pH of adsorption medium influences not only the surface charge of adsorbent, the degree of ionization of the material present in the solution and the dissociation of functional groups on the active sites of the adsorbent, but also the solution dye chemistry. Adsorption of methyl orange dye by activated carbon was found to be dependent on pH of the solution, which increased with the decrease in pH.

Table 3.2 Absorbance of methyl orange at different pH.

S.No	**λ = 550nm**	
	pH	Absorbance
1	1	0.074
2	**2**	**0.102**
3	3	0.083

From the above observation it has been concluded that the surface of the activated carbon contains different functional group in which adsorption was higher because even at lower pH, an excess H+ ion balances the anionic charge of the dye. The excess anionic part of the methyl orange gets attracted to the cationic adsorption surface and thereby enhances adsorption. With increase in solution pH due to the reduction of H+ ion more anionic dyes can be adsorbed on the cationic surface of the adsorbent.

At pH 2 the UV absorption of solution was found to be 0.102, and maximum absorption is at pH 2 **(**similar results were reported by **Kavitha *et al.*, 2008; Shahul *et al.*, 2013; Alzaydien *et al.*, 2015).**

Adsorption mechanism for methyl orange may be as follows:

Methyl orange was dissolved in an aqueous solution after which the sulfonate groups of methyl orange dye ,($R\text{-}SO_3Na$) become dissociated and converted into anionic dye ions.

$$\mathbf{R\text{-}SO_3Na + H_2O \longrightarrow R\text{-}SO_3^- + Na^+}$$

The adsorption process was taking place due to electrostatic attraction between the adsorbent surface which was cationic and the methyl orange which was anionic in nature

$$\textbf{Cationic surface of activated carbon} + \mathbf{RSO_3^-} \longrightarrow \textbf{strong electrostatic binding}$$

However, the adsorption weakened with increasing the pH value of methyl orange solution. The decrease of methyl orange adsorption can be explained by the competition of the abundant presence of H^+. **(Huang *et. al.*, 2013).**

The maximum removal for methyl orange was observed at pH 2, when the surface was positively charged with excess proton in solution. (**Kavitha *et al.*, 2008**).

Assay of SEM Analysis:

When the activated carbon without loading dye was subjected to scanning electron microscopy then the following picture was obtained.

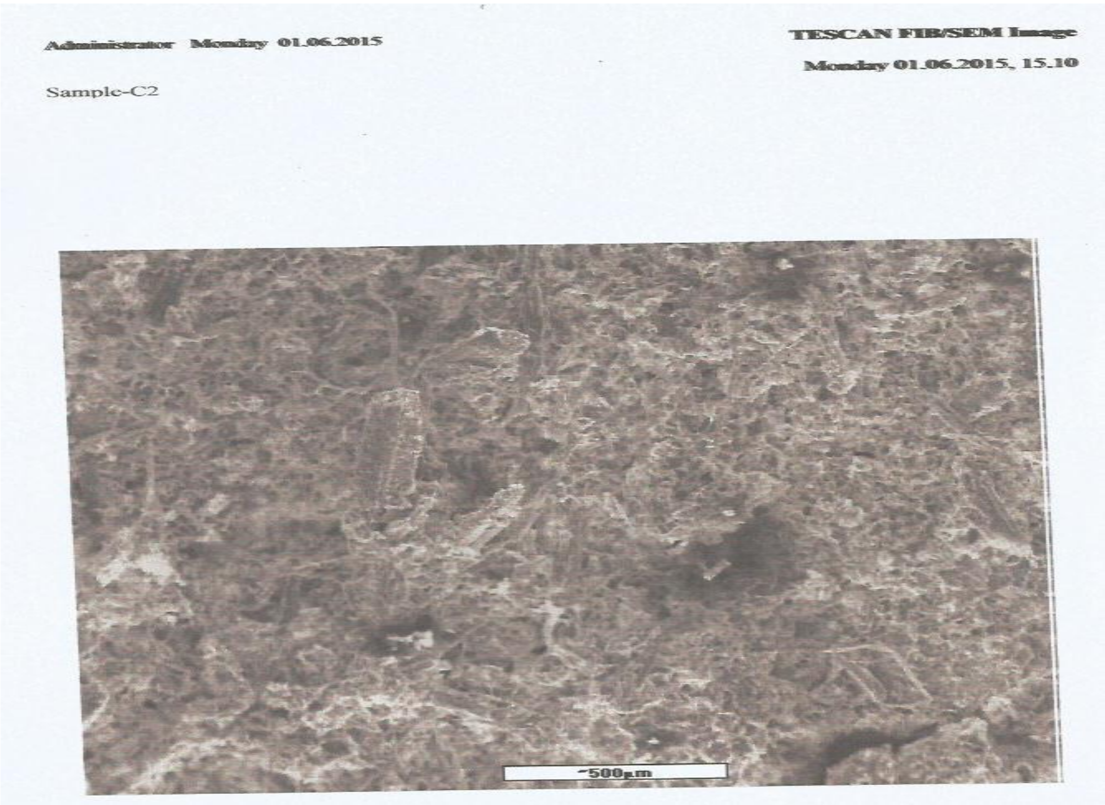

Fig.3.3 SEM image of unloaded activated carbon

And, when the activated carbon with loaded dye was subjected to scanning electron microscopy following was obtained.

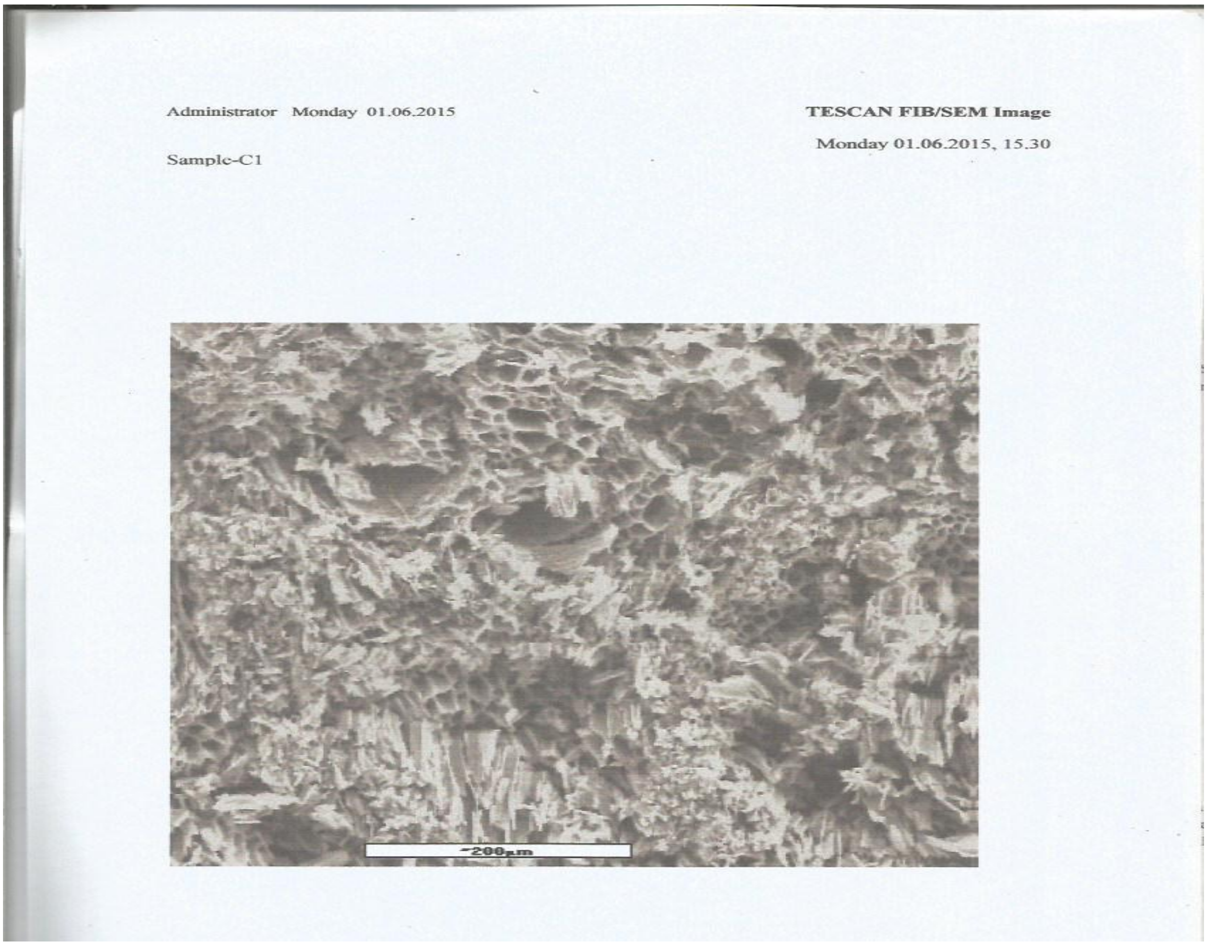

Fig.3.4 SEM image of unloaded activated carbon

Discussion for SEM Analysis:

SEM micrograph showed that the adsorbents surface was irregular, rough and highly porous, indicating the possibility of its good adsorption properties. In the SEM image of activated carbon absorbed Methyl orange, the layer of adsorbed dye are clearly visible. After dye adsorption, a significant change is observed in the structure of the adsorbent. The adsorbent appears to have a rough surface and pores containing new shiny particles after adsorption.

Also, SEM image clears that the pore size of adsorbent decreases on loading the methyl orange. The micrographs presented in (Fig. 4.3 and 4.4) show clearly the dye-loaded adsorbent coated by dye molecules over the whole surface at natural pH conditions. The dye molecules seem to have formed a void-free film masking the reliefs of particles and porosity of the aggregates. (Similar reported by **Lata *et al.*, 2008; Sarkar *et al.*, 2014).**

4. CONCLUSION

Activated carbon from rice husk was successfully synthesized and chemically activated by using NaOH as activating agent. Before and after activation it had been treated at different temperature ranging between 400- 600 ˚C for several times. And the work showed that activated carbon prepared from rice husk has suitable adsorption capacity with regards to the removal of methyl orange (anionic and azo dye) from its aqueous solution of 50 ppm. The adsorption capacity of activated carbon was considerably affected by its surface functional groups and surface charge as well as by pH and strong pH-dependence of methyl orange adsorption onto activated carbon together with FT-IR results indicated to the possible involvement of physical forces such as hydrogen bonding, vander waals and covalent chemical bonds in the adsorption process. Adsorbed amount of methyl orange dye decreases with increasing pH. It can be concluded that the activated carbon is an efficient adsorbent for the removal of methyl orange dye from aqueous solution which is cleared from the SEM picture of unloaded and loaded activated carbon which shows decrease in pore size when methyl orange dye was adsorbed onto activated carbon.

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