Thermodynamic Study of Congo red Dye Adsorption Using Rice Husk Activated Carbon

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Abstract: - **This work investigated the applicability of activated carbon prepared from local rice husk as adsorbent for effective removal of Congo red dye from aqueous solution. The study considered an agro based waste material which otherwise could be disposed, is employed and its efficiency in the removal of dye substance from contaminated wastewater was tested. The adsorbent was characterized using FTIR spectroscopy. The effects of physical parameters such as carbon content, moisture and pH values, bulk density and operational parameters which include, dye concentration, adsorbent dosage, contact time were investigated with respect to dye removing efficiency. The result showed that efficiency of dye adsorption on the adsorbent range from 34.30 to 83.35% within temperature values of 35 to 65^{oC}.The results further indicated that, adsorption efficiency of the dye increases as contact time changed from 5 to 90 minutes, then became constant.**

Key words: **adsorbate, bulk density, FTIR Spectroscopy, micropore and peaks**

I. INTRODUCTION

Nowadays, industrial technology has developed rapidly to accommodate the fast increasing population's demand. The discharge of effluents that contained colored material from leather, food, paper, textile, and cosmetics, pharmaceutical and plastic industries into the environment poses serious problems to different forms of life (kornwipha *et al.,* 2014).The effluents of serious concern are those of dye industries which have various environmental issues some of which include inhibiting sunlight penetration into water deceasing photosynthesis, high chemical oxygen demand as well as stagnant growth of microorganisms (*Forgacs et al.,* 2004; Singh *et al.,* 2013). Therefore, contaminated dye in wastewater needs removal before release into natural stream. The release of dyes into the environment has become a serious concern due to impacting color to water bodies and toxicity of these dyes and their bio-transformation products (Kar *et al.*, 2009). Some dyes such as Congo red and methylene blue from textiles, printing and dyeing industries have complex molecular structure and are usually persistent against biodegradation, it becomes difficult to remove them by natural aquatic environment. Dye materials are known to absorb the oxygen in water. Removal of toxic dyes from the environment is a serious challenge. A removal process has to be effective, simple and less expensive. The methods suggested to remove dyes from wastewaters are biological and physico-chemical processes. Some common methods of decolorizing synthetic dyes include; adsorption, coagulation, membrane filtration, flocculation, ion exchange, oxidation as well as microbiological or enzymatic decomposition (Bhavnagar and Sillanpaa, 2010; Gupta *et al*., 2012; Mahmoud *et al*., 2017). Adsorption is receiving more attention among other technologies due to its simplicity, ease of operation, low energy requirements, effective and reliable for dye removal (Silva *et al.*, 2012; Djilani *et al*., 2015). Its major advantages in the control of water pollution are, less cost, simple design, free from generating toxic materials, as well as easy and safe recovery of both adsorbent and adsorbate materials. Activated carbon is very efficient and most frequently used adsorbent for the efficient removal of water-soluble dyes. It has gained acceptance as adsorbent in wastewater treatment which allow the adsorption of both cationic and anionic pollutants in effluent (Namasivayam and Kavitha, 2002; Mittal *et al*., 2010; Lafi *et al.,* 2018). The use of agricultural wastes and lignocellulose materials as activated carbon precursors have been receiving attention due to their inexpensive, abundance with simple application, high efficiency and renewability, thus encouraging researchers to focus on the activated carbon preparation from agricultural materials (Zhou *et al*., 2012; Orkun *et al*., 2012). Various materials proposed as adsorbents such as wheat straw, orange peel, papaya seed, peanut hull, hardwood sawdust, bagasse pith, coffee waste, Neem leaf powder and rice husk (Garg *et al*., 2003;Gong *et al*.,2005; Kornwipha *et al*., 2014). Physical and chemical activations are common methods for producing activated carbons. Physical activation is achieved by pyrolysis of the carbonaceous materials at a very high temperature in the presence of oxidizing gas such as air and steam (Gonzalez et al., 2009; and Sugumaran et al., 2012). Chemical activation involves the use of activating agents like $ZnCl_2$, KOH, K_2CO_3 or H_3PO_4 to prepare activated carbon (Cruz *et al*., 2012; Lafi *et al*., 2018).This research work investigate the potential applicability of local rice husk as activated carbon (RiHuAC) for the effective removal of Congo red dyes from aqueous solution. The effect of parameters such as initial dye concentration, pH, contact time, adsorbent dosage and temperature were studied. The characteristics of the prepared RiHuAC were analyzed via Fourier transform infrared spectroscopy (FTIR) and carbon content.

II. MATERIALS AND METHODS

Preparation of activated rice husk

The rice husk was acquired as a solid waste free of charge from a local miller in Nguru town, Yobe; Nigeria. The collected materials were washed thoroughly with distilled water to remove soil and other adhering dirt. The rice husk was dried in an oven at 105°C for 24 h, which was ground and made to pass through different sieve sizes to obtain a uniform size particle. The portion with a size of 600--1200µm was used for activated carbon production.

Exactly 80.0g rice husk and 80.0g Zinc Chloride were mixed to obtain a 1:1 ratio by weight. Enough distilled water was added to wet the mixture, which was mixed well, allowed to stand for 24 hour at ambient temperature. The resultant mixture was dried in hot air oven at 105°C overnight and carbonized for 1½ h at 450°C in a muffle furnace and allowed to cool inside the furnace. The carbonized sample was washed with distilled water continually to obtain a pH in the range 6.8—7.0. This was oven dried at 105°C and was kept in an airtight moisture free container for further analysis. The procedure adopted for adsorbent preparation and activation were carried out as per standard procedure reported by (Reddy *et al*., 2012 and Amor *et al.,* 2018).

Table 1: Physico-Chemical Properties of the Prepared Rice Husk Activated Carbon

Parameters	Values
Bulk density (Kg/M^3)	0.745
pH	6.75
Ash (%)	5.16
Moisture (%)	5.28
Carbon (%) Volatile matter (%)	40.45 54.65

The activated carbon yield which is defined as the ratio of final weight ($\mathbf{W_2}$) of the prepared product after washing and drying to the weight of dried precursor ($\mathbf{W_1}$) initially used for the preparation was calculated using the following equation:

$$RiHuAC\ (\%) = \frac{W2}{W1}\ X\ 100 \ldots\ldots\ldots.. (1)$$

Where W_2 and W_1 stand for the weight of final activated carbon (g) and the weight of dried rice husk used respectively.

Materials required

All the reagents used for this research were of analytical grades. These are potassium dichromate ($K_2Cr_2O_7$), ferrous ammonium sulphate ($Fe(NH_3)SO_4$), phosphoric acid (H_3PO_4),sulfuric acid (H_2SO_4), zinc chloride ($ZnCl_2$), diphenylamine ($C_6H_5NHH_5C_6$) hydrochloric acid (HCl) sodium hydroxide (NaOH) and Congo red dye. The analytical instruments used include; UV, visible spectrophotometer, muffle furnace, oven, electric weighing balance, pH meter, sieves and some other routine laboratory apparatus. Congo red dye used for this study was procured from Kemlite laboratory, India (MW = 696.68g/mol., λ_{max} = 497nm). Figure 1; below shows the chemical structure of Congo red dye. During experimental work, 500mg/l of the stock solution was prepared by adding 500mg of CR dye in 1L of distilled water and the other concentrations were prepared by diluting this stock solution using the following formula: $M_1V_1 = M_2V_2$, where M_1, M_2 and V_1, V_2 are the initial and final concentrations and volumes respectively.

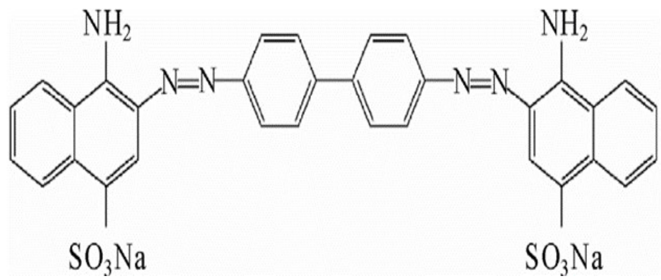

Fig.1.0 Chemical structure of Congo red (CR) dye

Batch Adsorption Studies

Batch adsorption studies was conducted using procedure adopted by Bhahacharyya and Sharma (2004). Features of the prepared RiHuAC were analyzed using Fourier transform infrared spectrophotometer (Buck Scientific, M 530), carbon content was determined using titrimetric method as adopted by McLeod, 1973. Bulk density and pH were determined using methods described in ASTM (1999). Ash and moisture contents were analyzed by the methods described in AOAC (1995).

Dye removal efficiency was expressed as the percentage ratio of decolorized dye concentration to that of the initial concentration as presented in the formula:

$$\text{Dye removal (\% CR)} = \frac{(Ci-Cf)}{Ci} \text{ x } 100\ldots\ldots\ldots\ldots\ldots\ldots\ldots.....(2)$$

The amount of CR dye removed per unit weight of adsorbent at time t, q_1 (mg/g) were calculated by:

$$q_1 = \left\{\frac{(Ci-Cf)}{M}\right\} V \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(3)$$

V is the volume of CR dye solution in adsorption process (L) and M is the mass of rice husk activated carbon (g).

III. RESULTS AND DISCUSSION

Moisture content is related to freshness and stability of substances. It affects physical and chemical structures by diluting the carbon and increasing its weight during treatment process. Thus, the lower the moisture in the activated carbon the better. Moisture content of packed activated carbon is usually less than 5%, but may increase during transport and storage processes (Zhou *et al., 2001)*. The moisture content value is found to be 5.28%. Low moisture content indicates that the activated carbon can be stored for long time. When it is above 10% according to Solener *et al.,* (2008) it may affect the condition of the carbon after long-term storage.

The pH value of 6.75 was recorded for the adsorbent which is near neutral. This value close to 7.0 is an indication that the rice husk activated carbon can be used for the treatment of Congo red dye. The pH range of 6 – 8 is acceptable for the activated carbon (Okiemmen *et al.,* 2008).

The Fourier transform infrared spectroscopy of $RiHuAC$ was presented in Figure 1, which shows the spectrum of the adsorbent after adsorption. The FTIR study was carried out to identify functional groups present in the adsorbent ranging from 1000 to 4000 cm^{-1}. The spectra after adsorption revealed the presence of prominent peaks at 1400 cm^{-1}, 1570—1670 cm^{-1}, 1700—1600cm^{-1}, 1700—17500 cm^{-1}, 2900—3000cm^{-1} and 3658 cm^{-1} which indicates the presence of C=C, C=O, aromatic carbon rings, alkene and ether compound`s presence. The spectra also shows the presence of C-H stretch from alkanes and O-H stretch bond which lead to formation of hydroxyl groups as phenols or alcohols (Rahman *et al.,* 2015 and Gedam *et al.,* 2019).

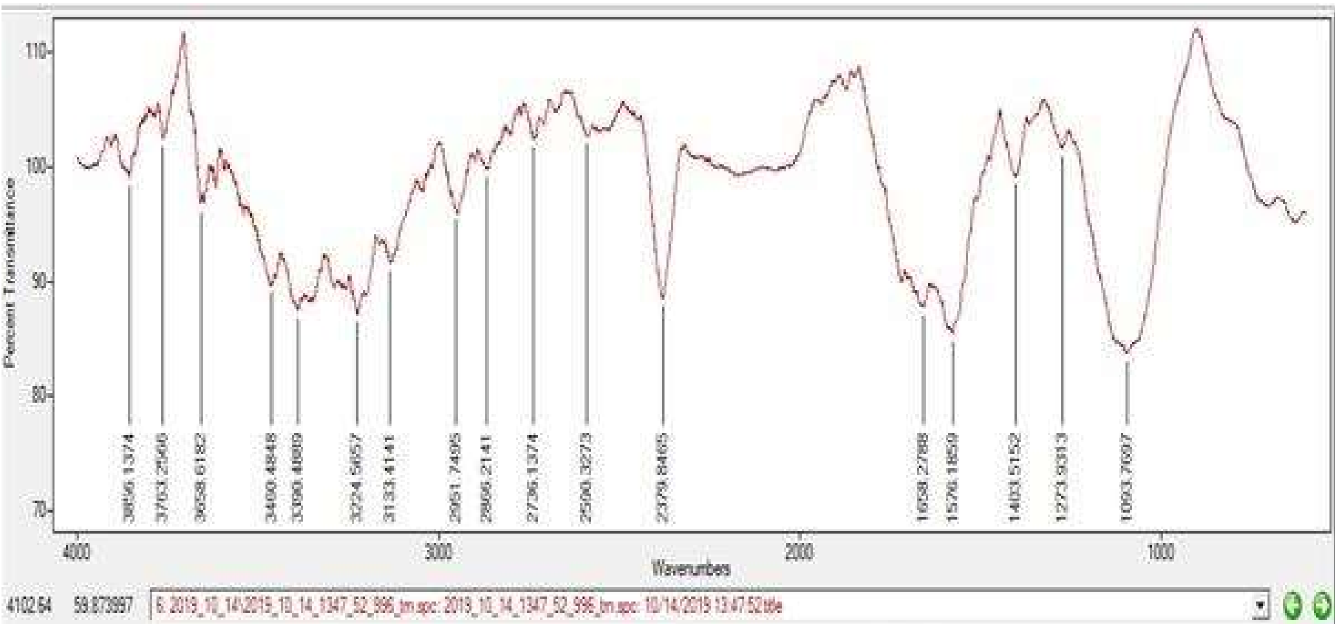

Figure 1: Fourier transform infrared spectroscopy spectrum of rice husk adsorbent after adsorption

Carbon content value found to be 40.45%. High carbon content implies that the amount of activated carbon produced by the rice husk is of high quality and relatively optimum for use in industrial waste purification. Activated carbon products can be characterized by its activity and physical properties (Dawood and Sen, 2012). Activity properties include pore size distribution that defines the available pore volume of a carbon over three pore size regions: the micropore, mesopore, and macropore regions. Pore size distribution properties are key indicators of a carbon material`s potential performance for removing contaminants from water. The molecules encountered in gas phase are generally smaller than those in aqueous solutions application; thus, a gas phase carbon has the majority of its pores concentrated in the micropore region (Rhaman *et al.,* 2015). Micropores are created during activation process and are responsible for the large surface area of activated carbons.

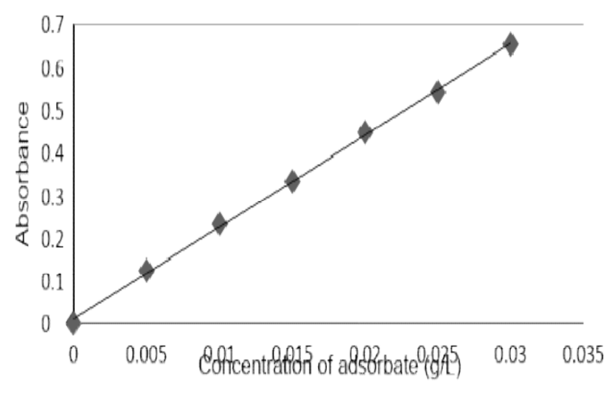

Figure 2: Calibration Curve for Standard Solutions of CR dye

Bulk density (apparent density) which is the density of the carbon at maximum packing efficiency. Bulk density considers both the solids and the pore space in carbon materials and was found to be 1.46 (g/ml) which suggests that the activated carbon is denser than water. Bulk density is an important variable in the design of adsorption column. It determines the mass of carbon which can be contained in a filter by a given solids capacity and the amount of treated liquid that can be retained by the filter cake (Okiemmen et al., 2008). The lower the bulk density value the high liquor volume it will filter before the available cake space is filled up. This property would facilitate easy separation of the carbon from its mixture with adsorbate solution upon which it acts (Kyas, 2013).

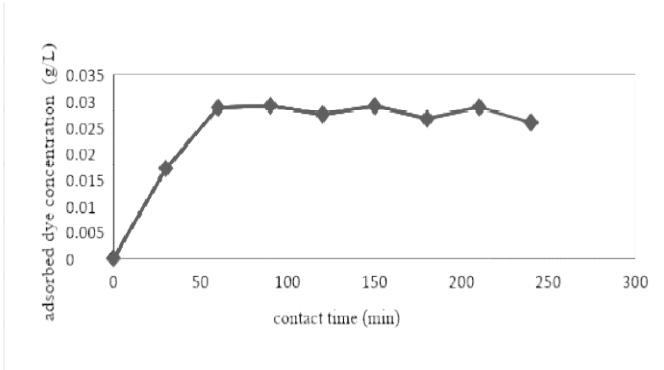

Figure 3: Effect of contact time on adsorbed dye

Effect of contact time evaluation of Congo red dye adsorption on activated rice husk was shown in Fig.3. The result showed that, adsorption efficiency of Congo red dye increased as the contact time changed from 5 to 90 min and became constant, then the curve drops down and then surge upward till it reaches 150mins and equilibrium was attained. Adsorption of Congo red dye on the activated rice husk increases from 33.30% to 83.35% as indicated from the curve. This increase was further shown in fig.4.0. When temperature was increased from 35^{oC} to 65^{oC}.This suggest that the adsorption process is endothermic and increases with increase in temperature. Due to increased temperature, mobility of the adsorbate increases with an increase in some active sites for adsorption on the adsorbent (Salleh *et al.,* 2011 and Gedam *et al.,* 2019) After 150 mins, the vacant adsorption sites on the adsorbent were all occupied by the dye, thus slowing down the rate at which it is adsorbed.

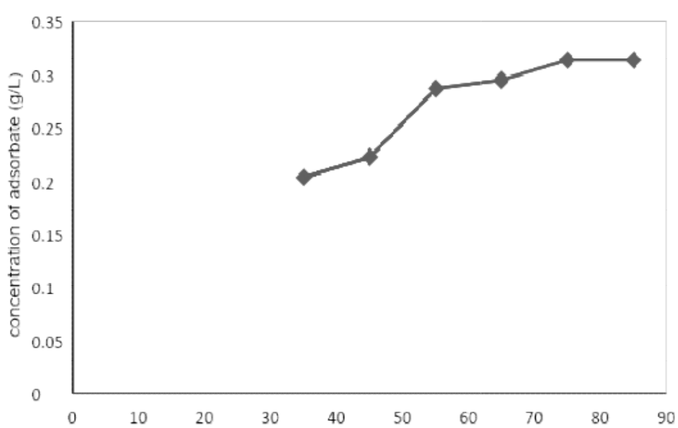

Figure 4: Effect of temperature on CR adsorption onto the adsorbent

Figure 4, shows the relationship between adsorption of Congo red dye on rice husk activated charcoal and temperature. The result indicated that removal of CR dye by the adsorbent increases with increase in temperature. Adsorption of dye increased slowly with temperature elevation from 35 to 65^{oC}, its rate then shows a marked increase in pace from 65 to 75^{o}C, then slows down from 75 to 85^{o}C. This trend may be attributed to the endothermic nature of adsorption process; where increase in temperature increases the rate of adsorption. On the other hand, increasing temperature may produce a swelling effect within the internal structure of the adsorbent, so that large dye molecules can penetrate further (Bao and Zhang, 2012).

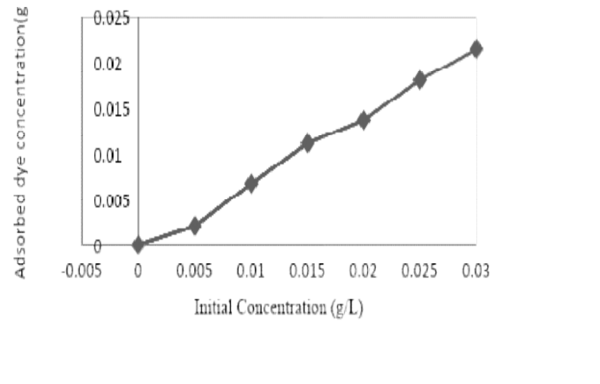

Figure 5: Variation of adsorbent dose with adsorbate

Plot of adsorbed dye initial concentration against varied dye concentrations was shown in Fig.5.The result indicates that adsorption of Congo red dye increased with increasing initial concentration with minimum rate from 0.005 to 0.010g/L. The rate increases rapidly and uniformly for the subsequent initial concentrations (0.010-0.030g/L). At higher initial concentration of the dye, the ratio of the number of dye molecules to available active adsorption sites is large thereby increasing the rate of interaction between the adsorbate and the adsorbent. This rate decreases with decrease in initial dye concentration, which results to small molecule to active site ratio, and hence low interaction.

IV. CONCLUSION

The study indicated that, rice husk activated carbon an agro-based waste was converted to useful adsorbent which was employed for the removal of Congo red dye an aqueous industrial effluent. The work further showed that the percent removal of adsorbate increases with increasing adsorbent dosage to a certain initial concentration level and subsequently decreases. The percentage removal of the dye was found to increase with temperature initially, but as the heat content increases; the process showed no further significant uptake of the adsorbate. It can be said that, under optimized conditions ofs temperature, concentration, contact time and adsorbent/adsorbate dosage, local rice husk activated charcoal would be economically feasible and effective for the removal of congo red dye from wastewater and hence its application as an adsorbent.

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