DETERMINATION OF SORPTION CAPACITY OF A DESIGNER ADSORBENT FROM RICE HUSK (RH) AND MAIZE COB (MC) FOR ADSORPTION OF DISPERSED AZO DYES (DAD)

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ABSTRACT

This work investigated the sorption of synthesized disperse azo dye from aqueous solution by adsorbent prepared from a composite of rice husk and maize cob. The optimum efficiency of the adsorbent was obtained at a composition of 70% to 30% rice husk/maize cob and at pH value of 2; contacts time of 5 minutes and initial dye concentration of 40 mg/L. The percentage of colour removal increased with increased in initial dye concentration. Rice husk/maize cob composite adsorbent could be a low cost alternative for the treatment of dye effluent. This composite proved to be a better adsorbent for DAD than the individual precursors.

Keywords: Adsorption, disperse azo dye, maize cob, rice husk.

INTRODUCTION

With the rapid development of modern technologies and industries, the environment is more polluted than in the past [1]. Water pollution due to coloured compounds is of utmost concern both in the advanced and developing countries of the world today. There are more than 100,000 commercially available dyes of which 65-70% of dyes produced annually are azo dyes [2].

Dyes are organic substances that absorb light from the electromagnetic spectrum within wavelength of 400- 800 nm and have affinity for the substrate to which they are being applied. Azo dyes are synthetic organic compounds widely used in textile dyeing, paper printing, and other industrial processes such as the manufacturing of pharmaceutical drugs, toys, and food. This class of dyes, which is characterized by the presence of at least one azo bound (-N=N-) being aromatic rings [3]. About 10-15% of the used dyes are discharged into the environment through wastes. These dyes are harmful to the environment, as they are often toxic, carcinogenic, and mutagenic to living organisms, chemically and photo-chemically stable, and non-

biodegradable [4-6]. Azo dyes may degrade to produce carcinogens and toxic products [7] hence, they have to be removed from the effluents before being discharged into the body of waters. Discharge of dyes into water channels makes water unsuitable for domestic, agricultural and industrial purposes. Highly coloured wastes are not only aesthetically displeasing but also significantly affect photosynthetic activity in aquatic life due to reduced light penetration into water and may in consequence distort biological activities of the aquatic life [8].

A number of treatment methods for the removal of dyes from aqueous solutions have been reported, namely; reduction, ion exchange, electrochemical precipitation, evaporation, chemical coagulation, flocculation, chemical oxidation, photochemical degradation, membrane filtration, including aerobic and anaerobic biological degradation, solvent extraction and adsorption with activated charcoal [9-11]. Adsorption is a widely-used process for either separation or purification due to its simplicity and easy operational conditions. In addition, it is amenable to significant cost reduction depending on the source of the adsorbent [12, 13].

Activated carbon is a microcrystalline form of carbon with very high porosity and surface area. Activated carbon has a high volume adsorbing porosity and very strong physical adsorption forces. It's the most common adsorbent used in conventional adsorption plants but is quite expensive. However, adsorbents produced from agro- based wastes are low cost and the performance efficiencies are comparable to the commercial activated carbons.Among the potential adsorbent materials are rice husk and maize cob obtained from agricultural wastes. It is conventional to convert the source agriculture waste to activated carbon to enhance the available surface area and ionic charges.This work studies the sorption capacity of low cost adsorbents prepared from a composite of abundantly available rice husk and maize cob for adsorption of disperse azo dye.

EXPERIMENTALS
Preparation of 200mg/L dispersed azo dye solution

Stock solution of the dispersed azo dye was prepared by dissolving 0.2 g of the azo dye powder in10 ml of dimethyl formaldehyde (DMF) and making up to mark in 1liter volumetric flask with distilled water.

Preparation of rice husk-based adsorbents

Rice husk (RH) was sieved and washed with a stream of distilled water to remove dirt, dust, clay particles and any superficial impurities. This was dried in an oven at 100°C for 20 hours. The dried RH weighed into a 500 ml clean dry beaker was soaked in 10 M H_2SO_4 solutions for 20 hours. The treated rice husk was washed again thoroughly with distilled water and dried [14]. The dried RH was pyrolyzed in an oxygen atmosphere at 180°C for 5 hours with occasional stirring [15]. It was cooled for 30 min. Acid treated rice husk was labeled as RHA. The corn cob collected from local agricultural field in the Faculty of Agricultural Science, Ahmadu Bello University Zaria, Nigeria was washed and dried, and subsequently ground using laboratory pestle and mortal. The ground powder was sieved and treated with 10M H_2SO_4 solution at room temperature for 20 hours and washed with distilled water to remove excess H_2SO_4. It was dried using hot air oven at 100°C for 5 hours. The treated maize cob was labeled as MC. The corn cob adsorbents were stored in a desiccator.

Batch Studies

All the batch experiments were carried out in duplicate and the results given are the averages. A control (without sorbent) was simultaneously carried out to ascertain that the sorption was by sorbent and not by the wall of the container. The batch sorption experiment was carried out in a 250 ml conical flask by mixing 20 ml of 40 mg/L of the standard working solutions of the dispersed azo dye solution with 0.2 g of the mixture of the sorbents (70% RH and 30% MC). The mixture was then stirred thoroughly at room temperature (27 ± 2 ^{0}C) and at constant speed of 150rpm for 20 min using a magnetic stirrer. After the equilibrium time, the mixture was filtered immediately using a vacuum pump aided filtration set-up and Whitman filter paper. The absorbance of the filtrate was measured using UV/Visible-spectrophotometer (Helios γ) at λ_{max} = 592 nm of the azo dye and pH = 2. The equilibrium concentration was evaluated from the calibration curve and the percentage of the dye adsorbed was consequently calculated from Equation 1.

$$\text{Dye removal (\%)} = \frac{C_o - C_e}{C_o} x100 \qquad\qquad 1$$

where *Co* and *Ce* are initial and equilibrium dye concentrations, respectively.

The amount of dye adsorbed per unit weight of adsorbent at equilibrium (qe) was calculated as:

$$q_e = (C_o - C_e)\frac{V}{W}$$
<div align="right">2</div>

Where V is the volume of experimental solution (L) and W is the mass of the adsorbent (g) used.

RESULTS AND DISCUSSION

Effect of Contact Time on Dye Removal

The results of experiment on contact time shows that percentage of dye removal increases with increasing contact time and optimum time was obtained at 5 minutes as shown in Figure 1. Thereafter, there was no significant change in adsorption. Similar trend has been observed in literature [16]. The rapid adsorption is due to the availability of positively charged surface of rice husk/maize cob composite adsorbent for adsorption of dispersed azo dye in the solution at pH 2.
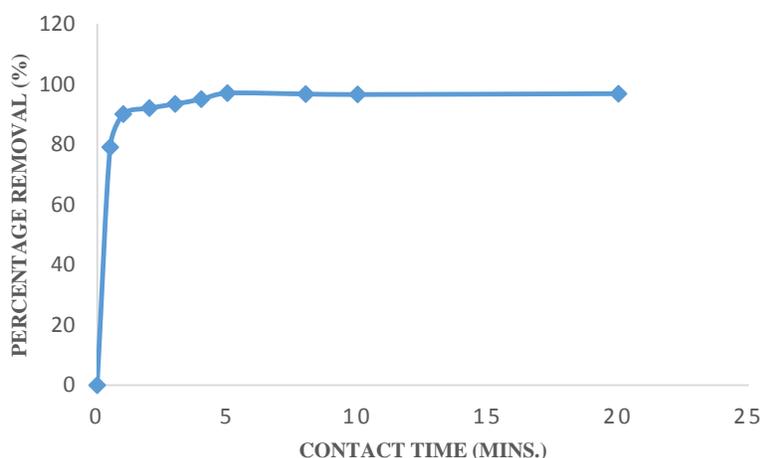

Figure1: Effect of contact time on dye removal

Effect of pH on Dye Removal

Figure 2 presents the result of the effect of pH on dye removal. The maximum pH of adsorption onto the mixed RHA/MC adsorbent was 2. It has been reported that Acid Green 1 dye had its maximum adsorption onto activated carbon at same pH 2[17]. The result shows that as pH value increases (from 2 to 10), the percentage of the dye removed decreases. This indicates that protonation of the dye solution increases the capacity of the adsorbent to remove the dye. The positive charge of the surface of the activated carbon increases, this causes an increase of the electrostatic attraction between the dye and the surface of the adsorbent.
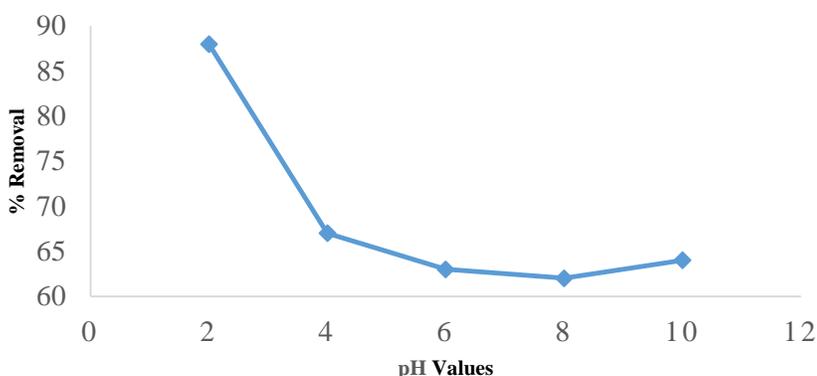
Figure 2: Effect of pH on dye removal

Effect of Adsorbents Composition on Dye Removal

Figure 3 shows the effect of the adsorbent composition on the percentage of dye removed. It was observed that as the maize cob composition in the composite varied from 0 to 100%, the percentage dye removed increased to about 95% at 30 wt% MC and started to decline thereafter. Hence 30 % maize cob (MC) in rice husk (RH) gave the highest percentage of dye removal.
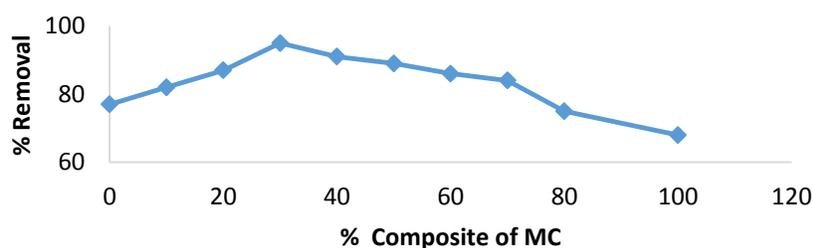

Figure 3: Effect of the adsorbent composite composition on dye removal

Effect of Initial Dye Concentration on Dye Removal

The falling trend in percentage dye removal observed in Figure 4 indicates that at lower concentration, the ratio of the initial number of dye molecules to the available surface area was low. Subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentration the available sites of adsorption become fewer and hence the percentage removal of dye is dependent upon initial concentrations. Hence, the percentage removal decreases as concentration increases.
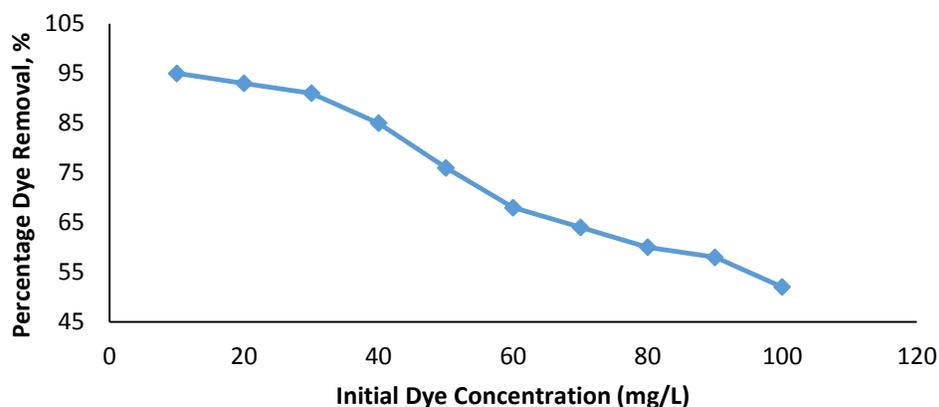
Figure 4: Effect of Initial Dye Concentration on Percentage Dye Removal

Adsorption Isotherms

The Langmuir and Freundlich isotherms were both used to describe observed sorption phenomena of the dye. The Langmuir isotherm applies to adsorption on completely homogenous surfaces with negligible interaction between adsorbed molecules. For a single solute, it is given by

$$\frac{x}{m} = \frac{VmKCe}{1 + KCe} \qquad 3$$

Where Ce is the equilibrium concentration of the solution, x/m is the amount adsorbed per unit mass of adsorbent (q_e), m is the mass of the sorbent, Vm is the monolayer capacity, and K is an equilibrium constant that is related to the heat of adsorption by equation. However, the linear form of the equation is given as:

$$\frac{Ce}{qe} = \frac{1}{KVm} + \frac{Ce}{Vm} \qquad 4$$

A linear plot from Eq. (4) for adsorption dye is shown in Fig. 5 and the values Vm and K, for the isotherms of the dye under study are shown in Table 1.
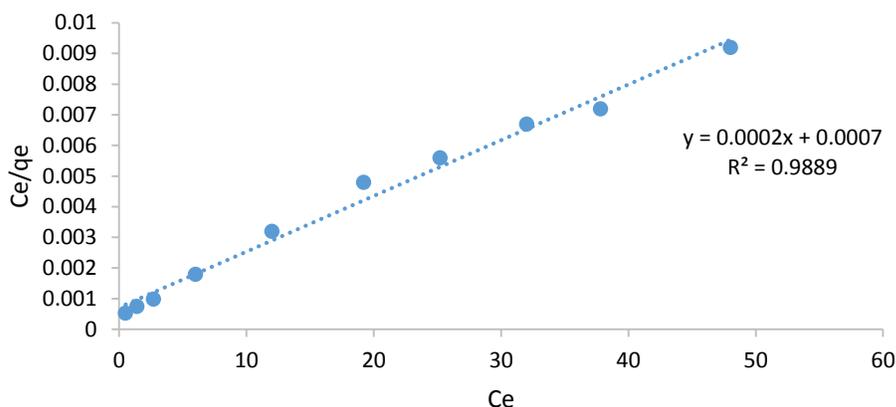
Fig. 5. Linear Langmuir isotherm for dye adsorption on adsorbent
Adsorbent dose: 0.2 g/L; temperature: 27°C; pH = 2.0; contct time: 20 min.

Table 1: The constant parameters of Langmuir and Freudlich isotherm models

Langmuir	V_m (mg/g)	5,000
	K	0.286
	R^2	0.988
Freudlich	I/n	0.336
	K_f	3.195
	R^2	0.934

The Freundlich model, which is an empirical model used to describe adsorption in aqueous systems, was also used to explain the observed phenomena of dye adsorption on RHA/MC materials. The Freundlich isotherm is shown as the following equation.

$$\frac{x}{m} = Kf = Ce^{1/n} \qquad\qquad 5$$

The linear form of the equation is given as:

$$\log(qe) = \log Kf + \frac{1}{n} log Ce \qquad\qquad 6$$

K_f is the measure of sorption capacity, $1/n$ is sorption intensity and other parameters have been defined as in Eq. (4). A plot of log (qe) against log Ce gives a straight line, the slope and intercept of which correspond to $1/n$ and log K_f, respectively. Freundlich plots for DAD adsorptions on RHA/MC material is shown in Fig. 6. The Freundlich constants values are shown in Table 1. In the current study, the 1/n value was 0.336 for activated carbon, indicating that activated carbon has a high degree of heterogeneity. A value of 1/n ranging from 0 to 1 is a

measure of the adsorption density or surface heterogeneity and becomes more heterogeneous when the value approaches zero [18].
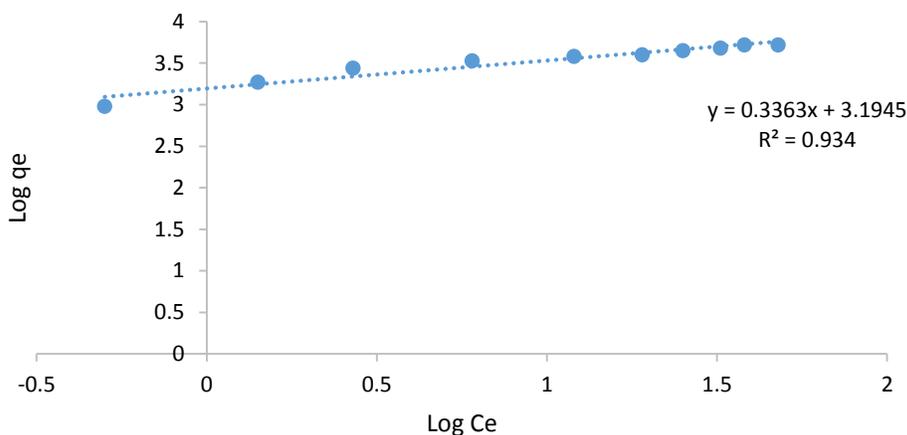

Fig. 6. Linear Freundlich isotherm for dye adsorption on adsorbent
Adsorbent dose: 0.2 g/L; temperature: 27°C; pH = 2.0; contact time: 20 min.

The correlation coefficient for both Langmuir and Freundlich models were 0.988 and 0.934 respectively (Table 1). The high linearity indicates the validity of the two models to describe the adsorption characteristics of the dye onto the RHA/MC material. Table 1 also shows a very high adsorption capacity for the uptake of the dye by the material (5,000 mg/g). The Langmuir adsorption capacity of waste cotton activated carbon for Acid Red 94 and Acid Blue 45 were reported as 370.475 and 434.78 mg/g respectively [19] while Al-Azabil *et al*. [20] reported Langmuir adsorption capacity of orange peel powder for methylene blue as 25.87. These values are far lower than the value obtained in these studies.Comparison of the capacity of the adsorbent under investigation with commercial activated carbon reported in literature as shown in Table 2 shows clearly the RHC/MC adsorbent is far better than the commercially available activated carbon [2]. It can be deduced that the mixed precursor is an excellent material for adsorption of DAD.

Table 2: Adsorption Capacities of Various Commercial Activated Carbon for a typical Dye (Methylene Blue)

Commercial activated carbon	Adsorbents Adsorption capacity (mg/g)
Commercial activated carbon	980.3
Activated carbon from New Zealand coal	588
Filtrasorb 400	476
Activated carbon	400
Peat	324
Coal	323.68
Filtrsorb 400	299
Norit	276
Picacarb	246
Filtrasorb 300	240
Coal	230
Commercial activated carbon	200
Bituminous Coal	176
Charcoal	62.7

CONCLUSION

A batch system was applied to study the adsorption of a disperse azo dye from aqueous solution by adsorbent obtained from rice husk/maize cob composite. The percentage of dye removed increased with increasing contact time, decreased with increasing pH and initial dye concentration. Optimum contact time for equilibrium to be achieved was found to be 5 min at a pH of 2. At initial dye concentration of 40 mg/L and composite dosage of 0.20 g, 30/70% MC/RHA was found to be the optimum composition to achieve maximum sorption of DAD. Rice husk/maize cob composite adsorbent could be a low cost alternative for the treatment of dye effluent. This composite proved to be a better adsorbent for DAD than the individual precursors.

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