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DYE ADSORPTION WITH SUGARCANE BAGASSE AND CORN COB

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Abstract-The use of agricultural waste and ecofriendly adsorbents has been examined as a better alternative for expensive adsorbents used in dye removal from wastewater. Adsorbents prepared from sugarcane bagasse (SCB) and corn cob (CC) agro-waste were successfully used to remove dye from an aqueous solution. This study investigates the potential use of SCB and CC for the removal of methylene blue dye from simulated wastewater. The adsorbents were used to adsorb methylene blue at varying dye concentration, adsorbent dosage, pH and contact time. The adsorption efficiency of the adsorbents was in the order of SCB>CC. The adsorption equilibrium process was described well with the Langmuir and Freudlich isotherm model.

Keywords: Dye adsorption, sugarcane bagasse, corncob, agricultural waste, methylene blue.

INTRODUCTION

Water is so essential to life. But currently, there is a global challenge of water shortage. The United Nations Development Programme (UNDP), stated in its reports that World water use during the 20th century grew six times. This is more than twice the rate of the population increase in the period. In this current century fresh water is anticipated to become as valuable as the oil of the last centuries. This is because it is estimated that by 2025, as much as two-thirds of the world's population, presently 7.4 billion, could be under conditions of water stress (Jamsaid *et al.*, 2017; Osuide, 2017). To mitigate for the problem of water shortage due to population growth there is the need to explore the possibilities of decontaminating wastewater for their reuse.

Wastewater could be generated from agricultural, industrial and domestic activities which result to the release of water with high level of contaminants so detrimental to the environment and living creature. The textile industry is an intensive producer of wastewater. Different dyes and contaminant are present in the wastewater generated through the production of fabrics and yarns (Fatoye, 2019, Filhoa *et al.* 2007). The discharge of these compounds into the environment is unfavourable, not only for aesthetic reasons, but also because many synthetic dyes and their breakdown products are toxic and mutagenic for life forms (Suteu *et al.*, 2008). A reliable wastewater treatment is extremely important before the discharge of this effluent from the production of textile. Common technique that has been developed include; precipitation, coagulation, flocculation, reverse osmosis, ultrafiltration, ion exchange, electrochemical treatment and adsorption (Gupta and Babu, 2009; Kanawade, 2014). But, some of these methods are very expensive, less effective and with varying degree of side effects.

Adsorption is considered the most economic and effective method for removal of dye and decolourization of textile mill effluent. This is a surface phenomenon in which there is the accumulation of a substance (giving higher concentration of molecular species) on the surface of another substance as compared to that in the bulk. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate. When biological materials like plants are used it is termed bioadsorption. In this process there is a passive physico-chemical interaction between the charged surface groups of biological material and ions in solution (Ramahali and Mahlangu, 2010).

The advantages of this process when compared to the conventional water treatment methods include low operating costs, minimization of the volume of chemical and/or biological sludge to be handled and high efficiency in detoxifying effluents. Activated carbon is mostly used for this purpose. But, due to its high production cost, alternative and cheap sorbents from agricultural waste materials are being considered. These adsorbents are cost effective, readily available, biodegradable and have been found to be most effective in treating textile wastewater (Adegoke and Bello 2015; Elettat, 2018; Gardazi, 2014).

Common example of these alternative adsorbents from agricultural wastes include sugarcane bagasse, corn cob, cotton linter, coconut shell, silk cotton husk, banana peel, mango peel, orange mesocap and rice husk (Arami *et al.*, 2005; Fahim *et al.*, 2013; Farnane *et al.*, 2017; Onigbinde *et al.*, 2016). This work therefore aims at using sugarcane bagasse (SCB) and corn cob (CC) to replace activated carbon for the removal of dye in simulated wastewater.

Adsorption Isotherms

The equilibrium data were evaluated using adsorption isotherms. Equilibrium isotherm equations are used to describe experimental sorption data. Among several models that have been published in literature, Langmuir and Freundlich are the most frequently used models. The equation parameters

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and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into the sorption mechanism, surface properties and affinity of the sorbent.

Freundlich isotherm

In 1906, Freundlich presented the earliest known sorption isotherm equation. This empirical model can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption (Dawodu and Akpomie, 2014) and is expressed by Equations 1 and 2.

$$q_e = K_f C_e^{1/n} \qquad (1)$$

Where, K_f is adsorption capacity, C_e concentration of the sorbate at equilibrium, (mg/L), n adsorption intensity and q_e is the amount of sorbate per unit mass of biosorbent (mg/g).

The linearized Freundlich equation is shown in Equation 2.

$$Log\ q_e = log\ k_f + {}^{1}/_{n}\ log\ C_e \qquad (2)$$

A plot of log q_e versus log C_e is a straight line with slope, $^1/n$ and intercept, log k_f.

Langmuir isotherm

Langmuir developed a theoretical equilibrium isotherm relating the amount of gas `sorbed on a surface to the pressure of the gas. The Langmuir model is probably the best known and most widely applied sorption isotherm. It has produced good agreement with a wide variety of experimental data and may be represented as in Equation 3. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many monolayer adsorption processes (Sanna, 2014). The linearized Langmuir can be used as expressed in Equation 4.

$$q_e = \frac{q_m b C_e}{1 + bC_e} \qquad (3)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \qquad (4)$$

Where, C_e is the concentration of the sorbate at equilibrium (mg/L), q_e is the amount of sorbate per unit mass of biosorbent (mg/g), q_m is a constant representing the strength with which the solute is

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bound to the substrate (L/mg) and *b* is the adsorption capacity of the substrate (gram solute/gram adsorbent). Plotting against C_e, a straight line graph with slope and intercept are obtained.

MATERIALS AND METHOD

MATERIALS

Raw materials used in this study are sugarcane bagasse(SCB) and corncob(CC) which were obtained from Ibadan in Oyo State and Ekiti in Ekiti State respectively.

METHODS

Preparation of Adsorbents

The sugarcane bagasse was prepared by crushing the sugarcane in a mortar, and then the sucrose was squeezed out. The sugarcane bagasse was then soaked in water (for three days). It was sun dried for four days, pulverized, sieved using a standard sieve of 600micron and stored in a polyethylene bag.

Corn cobs also were sundried, pulverized, sieved using a standard sieve of 600micron and stored in a polyethylene bag.

Evaluation of the Physicochemical Properties of Sugarcane Bagasse and Corn Cob

The following physicochemical analysis was carried out on the raw SCB and CC using standard methods: ash content, moisture content, pH, bulk density, water retention value, colour, form and percentage yield (AOAC, 2007; Ekebafe *et al*., 2012).

Preparation of Dye Standards (Absorbate)

Methylene blue (MB) basic dye was used for the purpose of this study without further purification. The stock dye solution was prepared by dissolving 1 g of MB in 1000 ml distilled water. The experimental solutions were obtained by diluting the stock dye solution with distilled water to give each appropriate concentration of the experimental solutions. The pH of the experimental solution was adjusted by the addition of either dilute 0.1 M NaOH or 0.1 M HCl solutions.

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Adsorption Study

Adsorption measurements were determined by batch experiments of known amount of the adsorbent in 25 ml of aqueous dye solution (methylene blue) of known concentration. The mixture was shaken for 30 minutes at room temperature. Then, the residual dye concentration in the reaction mixture was determined at 665nm using an ultra-visible spectrophotometer. Sorption experiments were performed by varying the pH (5, 6, 7, 8 and 9), contact time (30, 60, 90, 120 and 150 minutes), adsorbent dose (0.1, 0.2, 0.3, 0.4 and 0.5g) and MB concentration (50, 100, 150, 200 and 250mg/l). The percentage color removal and sorption capacity, *qe* (mg/g) were expressed as:

$$\text{Colour Removal } (\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad (5)$$

$$q_e = \frac{(C_o - C_e)V}{W} \qquad (6)$$

Where C_e is the concentration after adsorption, C_o is initial concentration (mg/L), W is the amount of adsorbent and V is the volume of the solution.

The equilibrium data were evaluated using adsorption isotherms.

RESULTS AND DISCUSSION

RESULTS

Physicochemical properties of the raw sugarcane bagasse and corn cob

Table 1: Physicochemical properties of the raw SCB and CC.

Physicochemical parameters	**Raw SCB**	**Raw CC**
Ph	5.04	5.21
Moisture content (%)	10.1	7.6
Ash content (%)	1.42	2.8
Bulk density (mg/l)	0.0459	0.217
Water retention g/g	807.23	330.50
Colour	Cream	Brownish white
Form	Powder	Powder

Adsorption isotherm

Table 2: Langmuir and Freundlich isotherm constants obtained

	Langmuir			Freundlich		
Adsorbents	q_m	K	R^2	N	K_f	R^2
SCB	5.08	-11.78	0.880	-1.16	40.27	0.736
CC	-2.92	-1.37	0.825	0.20	0.0045	0.902

Comparism of the adsorption study for sugarcane bagasse and corn cob

Table 3: Optimum adsorption conditions for the two adsorbents

Condition	**Sugarcane bagasse**	**Corn cob**
Dosage (g)	0.3	0.4
Time (mins)	30	180
MB Conc.(mg/L)	250	200
pH	7	5

DISCUSSION

Physicochemical properties of the raw sugarcane bagasse and corn cob

The determination of the physicochemical properties of any agricultural waste intended to be used for adsorption is very essential. It is needed to determine the suitability of the material for the sorption process. The pH values of the two adsorbents used in this work is close to the acceptable range for most applications. The activated carbon generated from Dika nut seed shell used for metal adsorption in a past work was of pH 5.8 (Ewansiha et al, 2014). The pH determination is important because adsorption process is pH dependent and extreme pH values are capable of inducing undesirable physical or chemical effect. The moisture content was higher for SCB compared to CC. However, the ash content was higher in CC and this directly affected the bulk density of CC making it higher than SCB.

Effect of different variables on the adsorption process

Four conditions were varied; adsorbent dose, dye-adsorbent contact time, dye concentration and pH. The comparative results of the optimization of these conditions for both adsorbents are presented in Figures 1 to 4.

Effect of amount of adsorbent (dosage)

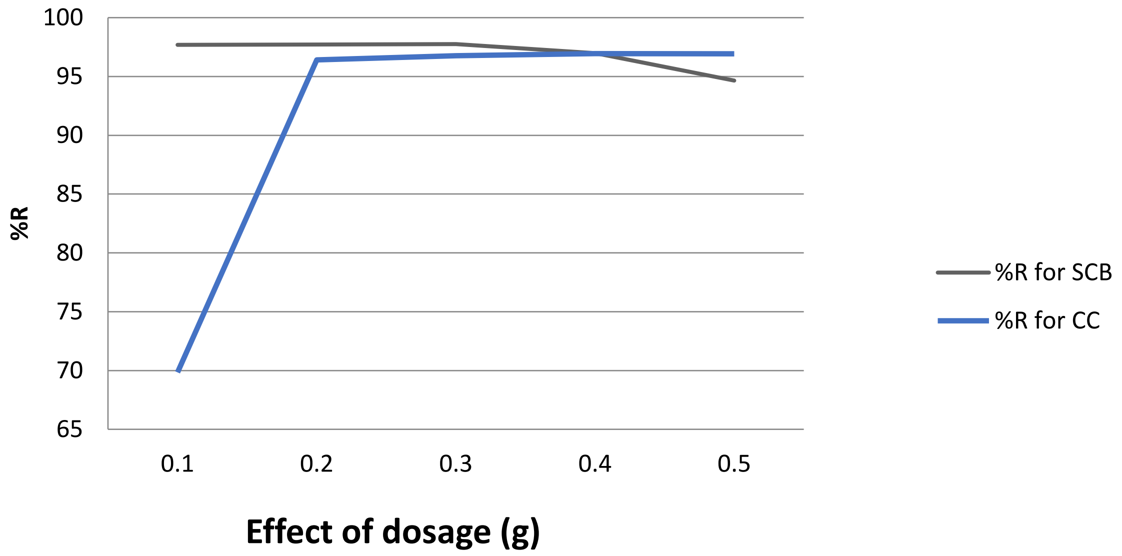

Fig. 1: Effect of SCB and CC dose on MB adsorption

The availability and accessibility of adsorption site is controlled by adsorbent dosage. The effect of adsorbent dose on MB adsorption was investigated. The percentage dye removal increased as both SCB and CC dosage increases as seen in Figure 1. This trend is comparable to the results of Pankaj and Harleen (2011) and Farnane (2017). The percentage dye removal with SCB increased to a point and decreased from 97.75% to 94.65% and for the CC, it increased from 69.84% to 96.94% and then decreased to 96.92 as the adsorbent dosage increased from 0.1g to 0.5g at 150mg/L concentration of the dye. This result revealed that larger surface area was made for increased mass of CC adsorbent which led to increase in the total number of sites available for methylene blue adsorption until an optimum point was reached. From the Figure 1 shown above 0.3g of SCB indicates the optimum adsorbent dose while 0.4g was the optimum adsorbent dose for CC.

Effect of dye-adsorbent contact time (duration)

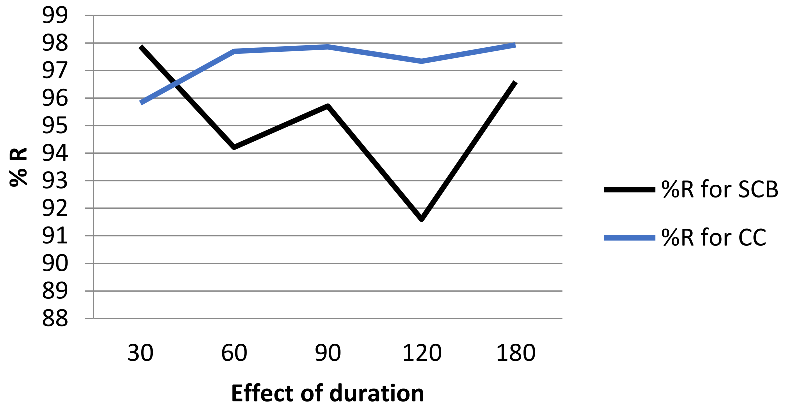

Fig. 2: Effect of duration on MB adsorption with SCB and CC

The effect of time on reaction rate is a very important factor in any reaction. Effect of contact time on dye adsorption was studied and the results are shown in Fig, 2. At 30mins the effectiveness of dye removal was high using SCB while the higher effectiveness of dye removal using CC was achieved at 180mins. Percentage dye removal increased as the contact time for CC increases and then become constant and percentage dye removal decreased as SCB contact time increases up to 60 mins and later increased . With increase of duration it is expected that adsorption increase due to increased interaction between the adsorbent and the adsorbate until a point when the pores and reaction sites are blocked, slowing down the adsorption (Pankaj and Harleen, 2011; Tchuifon *et al.*, 2016).

Effect of dye concentration

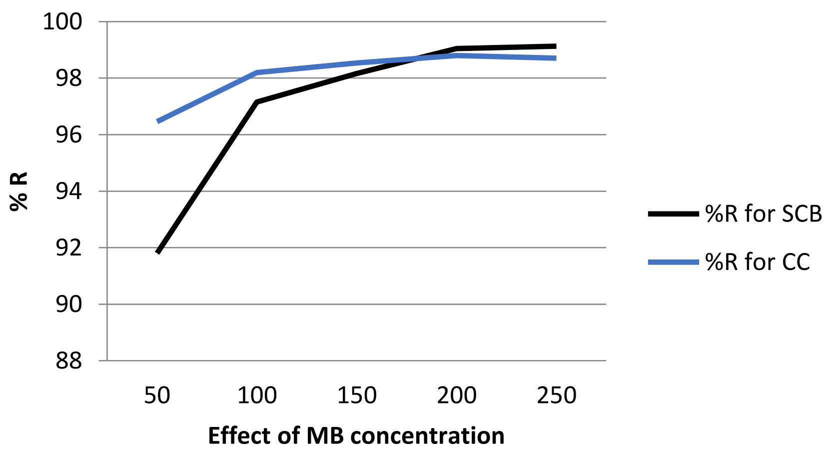

Fig. 3: Effect of MB concentration on the adsorption with SCB and CC

The effect of concentration on adsorption was examined and results shown in Figure 3. There is an increase in percentage dye removal for both SCB and CC as the concentration of the dye increases. At 250mg/L and 200mg/l concentration, both SCB and CC have the highest effective dye removal respectively. Increase in concentration of the adsorbate led to increase in competition of adsorbate molecules for few available binding sites on the surface of the adsorbent hence increase in the amount of dye removed. This result is comparable with the work of Pankaj and Harleen (2011).

Effect of pH

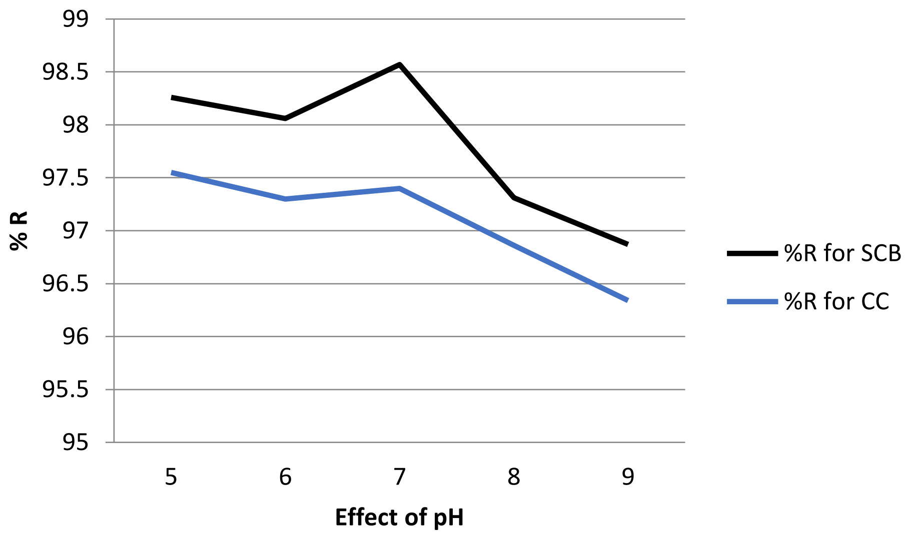

Fig. 4: Effect of pH on MB adsorption with SCB and CC

The initial pH is reported as a critical parameter in adsorption process because it affects the surface charge of the adsorbent and the degree of ionization and specification of the adsorbate (Igwe and Abia, 2007). The effect of dye pH on adsorption was examined and the results shown in Figure 4. These results showed that the pH of dye solution significantly affect its adsorption. At a neutral pH, high level removal of dye using SCB was observed while at pH5 effective removal of dye was observed for CC. The optimal percentage dye removal was achieved at pH7 for SCB and pH5 for CC. This variation may be due to the unique influence of pH on the nature of the adsorbent types (Suteu, *et al*. 2011).

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Adsorption Isotherm

The Langmuir isotherm represents the equilibrium distribution of methylene dye between the solid and the liquid phase. Langmuir describes the adsorption in homogenous phases while Freundlich described adsorption in heterogenous surface. From the linearized form of their equations, their isotherm constants can be graphically deduced.

A comparism of the coefficient of regression (R^2) for both isotherm is shown in Table 6. The value of the Langmuir constants q_m, K and the Freundlich constant K_f and n calculated from the lines of best fit are also shown. Methylene blue dye adsorption best fit into Freundlich isotherm for CC while for SCB the adsorption best fit into Langmuir isotherm.

CONCLUSION

This research work has established the possibility of using agricultural waste from SCB and CC as cheap bioadsorbent for dye adsorption. However, raw SCB gave a better adsorption capacity when compared with CC. From this experiment it is clear that the adsorption of methylene blue dye onto the adsorbents (SCB and CC) is influenced by amount of adsorbents, contact time, dye concentration and pH value. For higher removal of dye from simulated wastewater, adsorbent dose for SCB of 0.3g and CC of 0.4g gave optimum adsorption. The uptake of methylene dye for CC increased with increase in contact time. The optimal time were obtained at 30mins for SCB and 180mins for CC. Also, adsorption was higher at pH 7 for SCB and pH 5 for CC. From the commonly less utilized agricultural waste like sugarcane bagasse and corn cob it has been established from this study that inexpensive, readily available and eco-friendly bioadsorbent with high adsorption efficiency can be generated. Hence, they can be used to substitute other expensive adsorbents. More importantly, the results of this research have established the possibility of using bioadsorption process for the treatment of textile industrial effluents.

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