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ADSORPTION OF CATION DYE USING ACTIVATED CARBON DERIVED FROM GOLDEN SHOWERSEED POD (*CASSIA FISTULA*)

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Abstract

This study investigated the use of Golden shower seed pod (cassia fistula) as an adsorbent for the removal of cationic dye in a batch system. The raw material was Carbonized at 600^{o}C for one hour to obtain a purely carbonized material; then impregnated with NaOH of 0.1M and allowed to stay for 24 hours to obtain the desired GS-AC activated carbon. The adsorbent was characterized using scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and energy-dispersive X-ray fluorescence (EDXRF) elemental composition analysis. The effects of adsorbent dosage and contact time on the adsorption process were studied in a batch system. The results revealed that, there was good enhancements in pores of the adsorbent GS-AC due to the chemical impregnation. The FTIR spectra showed the presence C-H, NH_2, C-O, and S=O functional groups indicating a favourable surface for adsorption. Batch studies indicated that, the methylene blue uptake decreased with increase in the GS-AC dosage. The amount of Methylene blue adsorbed onto GS-AC increased with time and subsequently remained constant at some point in time with maximum uptake at 500 mg/l. Thus, adsorption capacity of methylene blue increased with longer contact time, indicating a stronger interaction between the adsorbent and the dye. Based on the findings, Golden shower seed pod (cassia fistula) impregnated with NaOH can be used as an alternative and suitable material for cationic dye removal from liquid phase.

Keywords: *Adsorption, cationic dye, Methylene blue, NaOH, Golden Shower Seed Pod*

1.0 Introduction

The discharge of dye-containing wastewater from various industries poses a significant environmental challenge due to its adverse effects on water quality and aquatic life. One of the commonly used dyes in industries is methylene blue, which is toxic and non-biodegradable in nature (Wang *et al*; 2021). The presence of cationic dye (methylene blue) in wastewater poses a significant environmental challenge due to the detrimental effects of dye pollution on ecosystems and human health. Existing treatment methods for dye removal often involve expensive and complex processes, leading to high operational costs and limited efficiency (Wang et al., 2005; Baccar et al., 2010; Dural et al., 2011; Kyzas et al., 2012). Adsorption has emerged as a promising technique for the removal of dye pollutants from wastewater due to its simplicity and ease of applicability. Several research have been conducted for the removal of dye pollutants using various low-cost adsorbents (Ouachtak *et al*; 2021). Golden shower seed pod is one such adsorbent that has attracted attention due to its abundant availability as a waste Golden shower seed pods are abundantly available agricultural waste with the potential to be a cost-effective and eco-friendly solution for dye adsorption. However, their efficacy and suitability as an adsorbent have not been extensively explored. This study focuses on investigating the potential of golden shower seed pods as an adsorbent for the removal of cataionic dye from wastewater. Moreover, the characterization and influence of various kinetic parameters on the adsorption process will also be investigated.

2.0 Materials and Methods

2.1 Precursor Preparation:

The golden shower seed pods were obtained from Faculty of agriculture university of

Maiduguri campus. The seed pods were cleaned by removing any visible impurities or debris. They were later rinsed with distilled water to remove any surface contaminants. The seed pods were dried at a suitable temperature (50-60°C) until a constant weight was achieved. The pod was Grind into fine particles to obtain a uniform size fraction for subsequent experiments.

2.2 Adsorbent Preparation:

The carbonization was carried out at temperature of 600^{o}C for one hour to obtain a purely carbonized material and was impregnated with 0.1M NaOH (≥99%, BDH limited England). The impregnated material was allowed to stay for 24 hours for the purpose of development of pores and active site on the material, the activated material was later washed several times to achieve neutrality with distilled water. The material was later dried in an oven at 105^{o}C and was later stored in a polyethylene bag for further usage, this was designated as GS-AC.

2.3 Batch Adsorption Experiment:

A 100ppm stock solution of methylene blue was prepared in distilled water. A series of working solutions with different initial concentrations of methylene blue by diluting the stock solution with distilled water was prepared. In individual containers, a fixed volume of the prepared working solution of 50 ml were poured and mixed with the desired amount of GS-AC. The containers are placed on a shaker for a uniform agitation at a constant speed and temperature for a predetermined contact time. After the adsorption period, the adsorbent is separated from the solution using a filtration method. The methylene blue concentration was analysed using a UV Visible spectrophotometer. The amount of adsorption at equilibrium was obtained using equation 1

$$q_e = \frac{(C_o - C_e)V}{w} \quad \text{.....(1)}$$

Where q_e, C_o, and C_e (mg/L) are the equilibrium adsorption capacity, initial and equilibrium concentrations respectively, V is the solution volume (mL) and W is the adsorbent mass used (g).

2.4 Characterization of the Adsorbent:

The Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Fluorescence (EDXRF) of GS-AC before and after adsorption were determined using Phenom Prox, manufactured by phenom World Eindhoven, Netherlands to ascertain the morphology and elemental composition. The SEM images were obtained when the electron beam on the samples interacts with the atoms of the sample showing signals relating to the surface micrograph and composition of the adsorbent. While a Digi lab Fourier Transform Infrared spectrophotometer (Model Excalibur FTS2000) was used to verify the organic structure of GS-AC before and after adsorption by passing an IR signal through the organic compound causes the functional groups to vibrate at specific frequencies. The obtained FTIR spectra are in the range of relevant wave numbers (4000-400 cm^{-1}).

3.0 Results and Discussion

3.1 Characterization of Adsorbents

The GS-AC adsorbent was characterized to understand the surface morphology and the functional groups present on the adsorbent before and after adsorption. The SEM micrographs of GS-AC before and after methylene blue adsorption are shown in Fig. 1 (a) and (b). It is clear that there are good enhancements in pores on the surface before the adsorption process, this is as a result of the high temperature carbonization and base impregnation. Surface is rough because of its heterogeneous pores and cavities, which are suitable to accommodate large MB molecules on its surface (Ilnicka*et al*., 2020). Whereas the dye-loaded adsorbent (Fig. 1(b)) is different unlike the precursor. After adsorption, the surface structure was found to be filled with dye molecules indicating a saturated surface. Furthermore, the Energy Dispersive X-ray Fluorescence (EDXRF) analysis reveals the presence of elemental composition of the prepared adsorbent. The elements present on the surface of the GS-AC

before and after adsorption are presented in Table 1. The registered elements are common inorganic constituents in biomass such as such as Magnesium Oxide, Silicone Dioxide, Calcium Oxide, Ferric Oxide, Titanium dioxide among other compounds.

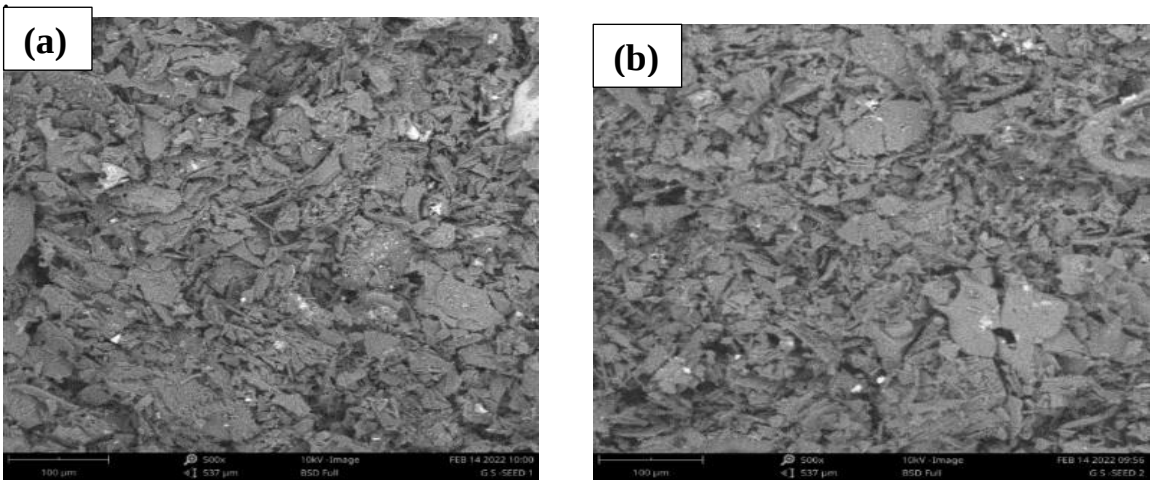

Plate 1: SEM images of GS-AC (a) Before Adsorption (b) After Adsorption

Table 1: Elemental composition of GS-AC before and after adsorption

	Elemental composition (%)									
Adsorbent	**Fe_2O_3**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**K_2O**	**CaO**	**MnO**	**SnO_2**
Before adsorption	0.342	0.54	0.486	0.588	2.875	0.300	1.489	6.907	0.175	1.366
After adsorption	0.432	1.12	0.725	0.874	2.896	0.782	0.979	6.749	0.165	1.306

The adsorptive capacity of an adsorbent depend on the amount and chemical reactivity of surface functional groups (Wang *et al*., 2020). The infrared spectra were analysed to observe these groups present in the GS-AC before and after adsorption. The FTIR spectra of GS-AC before and after adsorption are shown in Figure 1(a) and (b). As shown in Figure 1a, the peak observed at 745 cm^{-1} indicates the presence of the aromatics (C-H) stretch. The band at 868 cm^{-1} can be attributed to the C–H bond stretch (Kadiri *et al*., 2018; Xu *et al*., 2013). The band at 1032 cm^{-1} can be attributed to the C-O bond stretch (Xu *et al*., 2013; Cheraghi *et al*., 2015). The band at 1162 cm−1 is associated with C-O stretch. The peak at 1364 cm^{-1} is associated with S=O. The strong peak at 1561 cm^{-1} can be attributed to the NH_2 amine. The additional bands at 2370 cm^{-1}, 2914 cm^{-1} and 3034 cm^{-1} are attributed to P-H, C-H stretch and OH group respectively. After adsorption, the functional groups either shifted to different frequencies or, in some cases, disappeared possibly due to saturated surfaces by methylene blue molecules. The new peaks that at 1379 cm^{-1}, 1591 cm^{-1}, 2344 cm^{-1}, 2922 and 3045 cm^{-1} were attributed to CH_2 and CH_3 stretching vibrations, C-O stretch, Si-H plane and C-H stretch respectively (De Sales *et al*., 2015; Pereira *et a*l, 2018). The C-

O stretch justify the fact that oxygen containing functional groups contribute to the adsorption potential of activated carbon using interactions such as hydrogen bonds and π–π interaction (Wang *et al*., 2020).

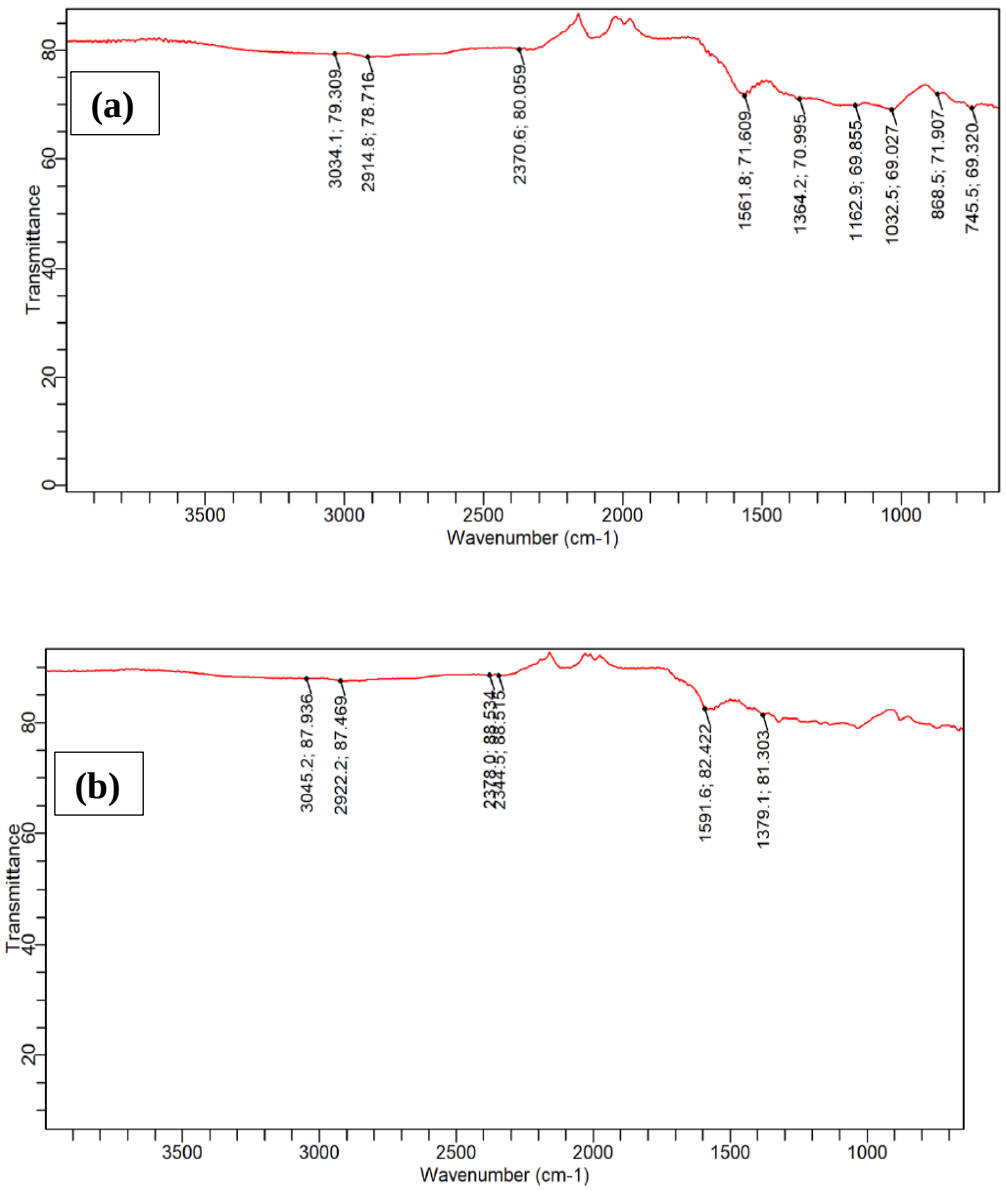

Figure 1: FTIR spectra of GS-AC (a) Before Adsorption (b) After Adsorption

4.0 Effects of operating parameters on adsorption of methylene blue

4.1 Effect of contact time and initial concentration

In the adsorption process, the contact time is an important parameter for the adsorbent to provide the necessary interaction with the adsorbate. Figure 2 shows the effect of the contact time on Methylene blue uptake of GS-AC at 30 °C. It was observed that, equilibrium was achieved rapidly at lower initial concentration (100 and 200mg/L). However, at higher initial concentration (300-500mg/L), longer contact time was required to attain equilibrium. Furthermore, there was a drastic drop in the adsorption capacity of GS-AC at a higher contact time due to faster saturation of active sites. It can be observed in Figure 2, that after the first 40 min, there are still available active sites on blue adsorbed onto GS-AC increased with time and subsequently remained constant at some point in time with maximum uptake at 500 mg/l. However, beyoung this time, the uptake of Methylene blue decreased due to saturated active sites. The initial dye concentration provides the necessary driving force to overcome the resistances to the mass transfer of methylene blue between the aqueous and solid phases (Srivastava *et al*., the adsorbent to further continue with adsorption process up 60 to 80 min. It is observed that between 60 min and 80 min, there was no significant difference in the methylene blue uptake, this situation is understood due to the saturation of the adsorbent's active sites (Egbosiuba *et al*., 2020). While after that time the adsorbent begin to experience a drop in adsorption capacity. Further increase in contact time did not show significant change in equilibrium adsorption. Therefore, a contact time of 80 min was used for other subsequent kinetic parameter studies.

Figure 2 shows the time dependant interaction and methylene blue adsorption of GS-AC at different concentrations (100–500 mg/l) and 30ºC. The adsorption capacity GS-AC was highly dependent on the initial concentrations. The amount of Methylene 2016). The decrease in adsorption with increase in sample concentration could be explained on the basis that methylene blue removal depended on the availability of the binding sites. A similar phenomenon was observed for the adsorption of methylene dye onto banana stalk waste (Hameed *et al.,* 2018), pomelo (*C. grandis*) peel (Hameed *et al.,* 2018) and castor seed shell (Oladoja *et al.,* 201

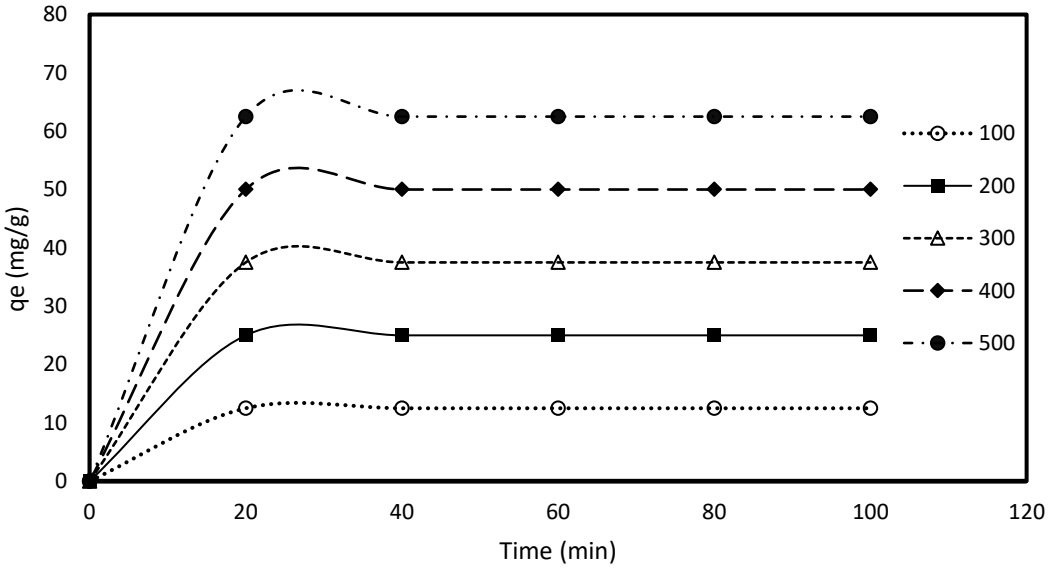

Figure 2: Effect of contact time and initial concentration on removal of Methylene blue onto GS-AC at 30°C

4.2 Effect of adsorbent dosage

The effect of dosage on methylene blue uptake is shown in Fig. 3. It is observed that the methylene blue uptake decreased with increase in the GS-AC dosage Furthermore, the amount of methylene blue adsorbed at equilibrium increases to 50 mg g^{-1} at 0.1 g dosage at the beginning and then it decreases from 50 to 4.9 mg g^{-1} with increasing of the amount of GS-AC dosage from 0.1 to 1 g. This behaviour explains that the increase in dosage of the adsorbent has no any contributory effect on the methylene blue adsorption because the increase in the dosage has a little or no effect on the removal of methylene blue in the solution and this is due to the fact that the active sites on the adsorbent at 0.1 g is sufficient enough to adsorb a quite number of adsorbents in the methylene blue solution. Pathania *et al*., 2017 reported similar findings on the adsorption of methylene blue by activated carbon derived from Ficuscarica.

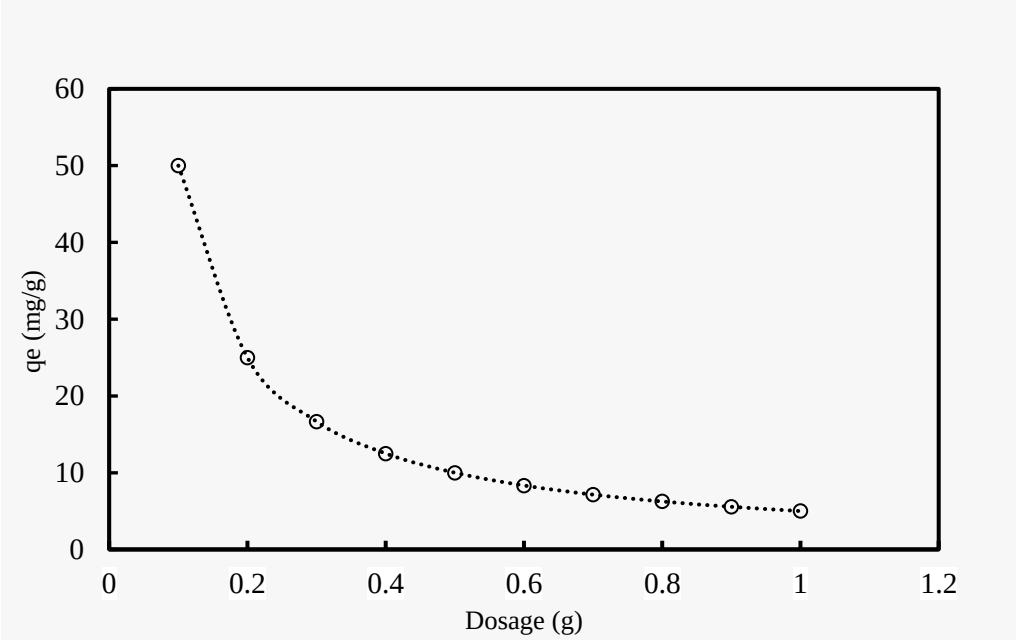

Figure 3: Effect of adsorbent dosage on removal of Methylene blue onto GS-AC at 30°C

5.0 Conclusion

This study explored the potentials of using Golden shower seed pod (cassia fistula) as an adsorbent for the removal of methylene blue. The GS-AC was prepared by carbonisation and subsequent impregnation with NaOH. The GS-AC showed relatively good surface morphology and presence of common inorganic constituents of biomass such as Magnesium Oxide, Silicone dioxide, Calcium Oxide, Ferric Oxide, Titanium dioxide among other compounds favourable for adoption. In addition, several functional groups either shifted to different frequencies or disappeared after adsorption. The presence of C-H, NH_2, C-O, and S=O functional groups on the adsorbent surface indicated their participation in the adsorption mechanism. It is observed that the methylene blue uptake decreased with increase in the GS-AC dosage. The amount of Methylene blue adsorbed onto GS-AC increased with time and subsequently remained constant at some point in time with maximum uptake at 500 mg/l. Thus, an adsorbent dosage of 0.2 g, a contact time of 80 minutes, and an initial dye concentration of 500 mg/L were the optimum conditions for efficient adsorption of Methylene blue onto GS-AC. The present findings suggest that GS-AC may be used as

an effective adsorbent for the removal of dye effluents.

List of acronym

GS-AC	Golden shower seed pod
NaOH	Sodium Hydroxide
C_e	Equilibrium liquid phase concentration, mg/l.
C_o	Initial concentration of ad sorbate in solution, mg /l .
C_t	Equilibrium liquid phase concentration after time t, mg /l.
q_e	Equilibrium adsorption capacity, mg /g.
t	Time, min.
V	Volume of the solution, l.
W	Weight of adsorbent (g)
EDXRF	Energy Dispersive X-ray Analysis.
FTIR	Fourier Transform Infrared Spectroscopy.
AAS	Atomic Adsorption Spectrophotometer.
SEM	Scanning electron microscopy.

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