

a well-known efficient technique and also a highly reported method of dye removal from aqueous solution [7]. It is also reported to be environmentally friendly [8]. The adsorption process shows high efficiency in the removal of dye from aqueous solution, this causes the transfer of synthetic dyes from wastewater to the solid phase of the adsorbent, thereby reducing their content in the effluent wastewater [9]. Various adsorbents produced from different materials have been employed to remove dyes from contaminated water bodies [10].

The amount of solute such as dye molecules adsorbed per unit mass of adsorbent such as MEAC is measured as a function of the equilibrium concentration of the solute (dye molecule) in the bulk solution of dye at a constant temperature by adsorption isotherm. The adsorption mechanism, rate constant and equilibrium adsorption capacity are predicted by adsorption kinetics. Understanding the adsorption kinetics and mass transfer processes in any adsorption system is crucial in the of adsorption treatment systems design.

Mango seed endocarp was employed in the present study to produce activated adsorbent. The choice of mango seed endocarp was informed by a genuine need toward abating the continued environmental pollution problems associated with the consumption of mango fruit yearly in Nigeria. The MEAC was the choice adsorbent employed for the treatment of textile effluent containing dye mixtures such as rhodamine B, safranin, methylene blue and malachite green. The MEAC efficiency in the removal of the HD mixtures was determined by applying Scanning Electron Microscopy (SEM), proximate analysis, BET analysis, bulk density, and Fourier Transform Infrared Spectroscopy (FTIR). The pH of dye, adsorbent dosage, solution temperature and initial concentration were the factors considered. Some adsorption isotherm and adsorption kinetic models were employed to fit the experimental data generated.

Materials and Methods

Material collection and preparation

The mango seeds were fetched from a waste dump at Eke-Awka market in Anambra state Nigeria. The chemicals used were purchased from the chemical and reagent stores at Bridge head market Onitsha, Anambra state, Nigeria and are of analytical grades. The mango seeds collected were washed thoroughly in clean running water and thereafter sun dried. The endocarp was separated from the seed and was dried at 105°C in a convective hot air dryer. The dried endocarp was later carbonized in a muffle furnace at 500°C for 2 hours, crushed with a mortar, and stored in airtight container for further use.

Activation and particle size classification

The essence of chemical activation of the adsorbent is to increase the number of active sites in the adsorbent as well as increase the degree of its porosity. This was achieved by mixing a 1:1 ratio of 60% Orthophosphoric acid (H_3PO_4) with respect to the carbonized endocarp of the mango seed. The mixture was stirred evenly and transferred to an earthen pot and sealed properly with aluminum foil to prevent entrance of air. The mixture was thereafter allowed to stand for thirty minutes prior to been put in the oven and heated for four hours at 250°C. The resultant adsorbent was allowed to cool to room temperature. The adsorbent produced was washed several times with warm distilled, followed by cold distilled water until a pH of 7.0 was attained. The resultant activated carbon was subsequently dried in a hot air dryer set at 105°C for two hours. The resultant Mango seed Activated Carbon (MEAC) was separated into different sizes using mechanical shaker and stored in an airtight container for use.

Proximate analysis

Standard established methods of proximate analysis were employed to determine some proximate composition of the sample. Such analysis includes ash content moisture content bulk density, volatile matter and fixed carbon content of the adsorbent [11-14].

Instrumental analysis of the adsorbents

The MEAC particles of uniform particle size (150 μm) were characterized using Shimadzu FTIR-8400S spectrophotometer to identify the functional groups present. Also, the surface morphology of MEAC was determined using SEM machine of model JSM6400. The BET surface area of MEAC was done by employing NOVAVin equipment of 11.03 versions.

Preparation of effluent

The simulated textile dye effluent (hybrid dye) was prepared by mixing malachite green, safranin, methylene blue and

Rhodamine B dyes in equal ration. 1 g each of the dyes was measures into a 1000 mL volumetric flask in order to prepare 1 g/L concentration of the simulated HD effluent. Thereafter, 200 mL of distilled water was added to the solution which was shaking properly to produce a homogenous solution and thereafter made up to 1000 mark. Serial dilution of different HD concentrations was prepared from the stock solution.

Batch adsorption study

The HD uptake from the aqueous solution using MEAC adsorbent was investigated in this report. The influence of solution pH, initial conc. of HD, dosage of adsorbent and solution temperatures was the factors under study. The dosage of MEAC considered was 0.5 g, 1.0 g, 1.5 g, 2.0 g and 2.5 g. The HD concentrations used were 50 mg/L, 100 mg/L, 200 mg/L, 300 mg/L and 500 mg/L, the solution temperatures used were 30°C, 35°C, 40°C, 50°C and 60°C. Furthermore, the pH of the solution studied where 2.0-12.0 at 2.0 intervals, while keeping the particle size constant at 150 µm. Five different 250 mL conical flask containing 50 ml of HD effluent each was set up and 0.5 g, 1.0 g, 1.5 g, 2.0 g and 2.5 g of MEAC was measured into it respectively. 0.1 N HCl or 0.1 N NaOH was used to adjust the pH of the solution to 4.0, followed by constant agitation of the mixture using a magnetic stirrer set at room temperature (30°C). At time of 5, 10, 20, 30, 40, 50, 60, 70, 80, 100, 120 min test samples were drawn from the flasks into sample bottles. The samples collected were allowed to cool before been analyzed by UV-VIS spectrophotometer at 525 nm to obtain the absorbance of the supernatant. A calibration curve was done to evaluate the HD concentration. The removal percentage of the HD at equilibrium state was determined by employing equation 1 [15,16].

$$RE = \frac{C_0 - C_e}{C_0} \quad (1)$$

Equally, equilibrium amount of HD q_e and the amount adsorbed at time t , q_t , were calculated by employing equations 2 and 3. [17].

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (2)$$

$$q_t = \frac{(C_0 - C_t)V}{w} \quad (3)$$

The whole procedure was repeated for the influence of solution pH, temperature of solution, and initial concentration of HD effluent. The adsorbate (HD) and the adsorbent (MEAC) interactions were evaluated by the application of 3 equilibrium isotherm models, namely; Freundlich, Langmuir and Temkin models. The information on the pathways and reaction mechanisms of the reaction as it relates to the rate of the adsorption of HD with the MEAC in the solution was analyzed by the kinetic study. Kinetic study on the adsorption of HD by MEAC adsorbent was done with the help of Elovich, Pseudo First Order (PFO), Intra Particle Diffusion (IPD) and Pseudo Second Order (PSO) models. The isotherm and kinetics equations as well as the plots made are presented in Table 1.

TABLE 1. List of equilibrium isotherm studied.

Adsorption models	Type	Expression	Plot made	Equation no
Isotherm	Langmuir	$\frac{1}{q_e} = \left(\frac{1}{K_L q_{max}}\right) \frac{1}{C_e} + \frac{1}{q_{max}}$	$\frac{1}{q_e}$ Vs. $\frac{1}{C_e}$	(4)
	Freudlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$\ln q_e$ Vs. $\ln C_e$	(5)
	Temkin	$q_e = \left(\frac{RT}{b_T}\right) \ln A_T + \frac{RT}{b_T} \ln C_e$	q_e Vs. $\ln C_e$	(6)
Kinetics	PFO	$\ln(q_e - q_t) = \ln q_e - K_1 t$	$\ln(q_e - q_t)$ Vs. t	(7)

PSO	$\frac{t}{q_t} = \frac{1}{K_2^2 q_e^2} + \frac{t}{q_e}$	$\frac{t}{q_t}$ Vs. t	(8)
Elovich	$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \frac{1}{\beta} \text{Int}$	q_t Vs. t	(9)
Intra particle diffusion	$q_t = K_d t^{1/2} + C$	q_t Vs. $t^{1/2}$	(10)

Where, q_e is the HD ion concentration C_e is the HD concentration in the effluent solution at equilibrium, K_L is the Langmuir isotherm const. q_{max} is the maximum adsorption capacity K_F and n are the Freundlich isotherm constant A_T is the Temkin isotherm equilibrium binding constant b_T is the Temkin isotherm constant T is the temp of the solution, R is the gas constant is the adsorption capacity of HD at time, t ; K_1 is the pseudo 1st order rate constant K_2 is the pseudo 2nd order rate constant α and β are the Elovich constant.

Results and Discussion

Surface area and proximate analysis

The BET surface area pore diameters of MEAC obtained from the sample were 452.436 m²/g, 892.216 m²/g and 687.894 m²/g for before activation, after activation and after adsorption, respectively. The MEAC had specific surface area of 452.436 m²/g before activation and was enhanced by activation to 892.216 m²/g. The BET surface area was reduced from 892.216 m²/g to 687.894 m²/g after adsorption. Activation treatment given to the adsorbent opened up more pores spaces in the adsorbent and consequently increased its surface area. After adsorption, the surface area reduced as the HD molecules had taken up some of the actives sites on the MEAC. The MEAC has micro pores of less than 2 nm and are classified as micro pore.

However, the proximate analysis results are shown in Table 2. The bulk density obtained was 0.7685 g/ml as shown in table. The sample contains 56.88 of fixed carbon which signify that the sample used is a good adsorbent material with high carbon content.

TABLE 2. Analysis of the proximate composition of MEAC.

Properties	Value
Bulk density (g/ml)	0.7685
Moisture content (%)	7.081
Volatile matter (%)	15.058
Ash content (%)	21.044
Fixed carbon (%)	56.88

Scanning electron micrograph

The SEM images of MEAC adsorbent done before activation of adsorbent, after activation of adsorbent and after the adsorbent has been used for adsorption are shown in Figure 1a-c. Figure 1a reveals that the pore surfaces of MEAC adsorbent before the adsorbent activation were not well established. The absence of pronounced surface morphology in MEAC before it was activated impedes the penetration of HD molecules into the internals of the adsorbent. Figure 1b shows the formations of several well-developed pores on the MEAC owing to the effects of agent of activation acid at high temperature which usually results to the volatile compounds volatilization. This confirmed that orthophosphoric acid used in the activation resulted in the formation of well-developed pores on the adsorbent surfaces. The essential properties of a good and effective adsorbent is a well-developed porous surfaces coupled with an enhanced surface area. Figure 1c revealed marked closure in the interstitial spaces observed in the MEAC before activation. This could be due to adsorbed HD that filled some of the void spaces present in unused adsorbents. The activation produced a structural defect in the carbonized mango seed endocarp by promoting pore development which enhances the rate of adsorption as well as the capacity of the system.

