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Sequestration of Methylene Blue and Malachite Green from Aqueous Solution using Areca Husk Carbon

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Abstract: In the present study adsorption capacity of Agro-waste materials of Areca Husk carbon (AHC) was explored for the Sequestration of cationic dye methylene blue (MB) and malachite green (MG) from water. The structural morphology and functional groups present were investigated by scanning electron microscope (SEM) and Fourier transform infrared (FTIR) spectroscopy. The factors affecting the rate processes involved in the uptake of the dye for adsorbent dosage, contact time, initial dye concentration, and pH are studied at ambient temperature. Equilibrium data were analyzed using Langmuir, Freundlich and Temkin isotherm models. Kinetic data were studied using pseudo-first and pseudo-second order kinetic models and the mechanism of adsorption was described by intraparticle diffusion model. **Key words**: AHC, MB, MG, Kinetics, Isotherm.

Introduction

Many manufacturing industries such as paper, plastics, cosmetics, textile and food use dyes for colouring their products. The discharge of effluents from these industries contain large amount of dyes, not only damage the aesthetic nature of receiving water bodies, but also may be toxic to aquatic life. Methylene Blue (MB) and malachite green (MG) is cationic dyes, have wide applications which include coloring paper, dyeing cottons, wools, silk, leather and coating for paper stock. Although methylene blue is not strongly hazardous, it can cause some harmful effects, such as Nausea, stomach upset, diarrhea, vomiting or bladder irritation may occur. It also causes the urine, stools and possibly skin to turn green-blue in colour, high fever, severe nausea and vomiting, abdominal pain, headache, chest pain, dizziness, profuse sweating, heart beat increase, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans¹. Though the external use of MG as an antiseptic, antibacterial and anti protozoan agent is well known but its oral consumption is toxic, hazardous and carcinogenic due to presence of nitrogen². Contact to malachite green with skin and eye causes irritation with redness and pain. Therefore, the treatment of effluents containing such dyes is of great interest due to its harmful impacts on receiving waters. The present study is investigated to develop a low cost effective method of treatment of basic dye by using areca husk is an agricultural waste material a hard protecting covering of areca nut obtained from the threshing of the areca palm and constitutes 650 million tons of areca nut produced annually in the world. Areca husk has found several applications in household, industries and even in the treatment of cationic dyes which is facing solid waste disposal problem is effectively and efficiently converted into an activated carbon and it is utilized to study the effectiveness of the uptake of color from aqueous solutions. The dye uptake from textile effluent was attempted and the wastewater management studies were planned and executed. Industrial wastewater treatment from manufacturing chemical industries was analyzed and the chemical properties of synthetic process and methodologies were formulated.

Materials and Methods

Preparation of activated carbon adsorbent

One part by weight of each powdered raw material was chemically activated by treating with two parts by weight of concentrated sulphuric acid with constant stirring and was kept for 24 hours in a hot air oven at 75°C, the carbonized material was washed well with plenty of water several times to remove excess acid, surface adhered particles, water soluble materials dried at 200°C in hot air oven for 24 hours. Then it was taken in an iron vessel in muffle furnace and the temperature was gradually raised to 550°C for an hour, ground well by using ball mill and kept in air tight containers for further use.

Analysis of Cationic dye

The concentration of cationic dye in the supernatant solution before and after adsorption was determined using a double beam UV spectrophotometer (Shimadzu, Japan) at a wave length of 665 and 559 nm for MB and MG. It was found that the supernatant from the activated carbon did not exhibit any absorbance at this wavelength and also that the calibration curve was very reproducible and linear over the concentration range used in this work.

Batch equilibrium studies

Batch experiments were carried out by shaking 100 ml of dye solution with 150 mg of adsorbent in a glass stopper conical flask at a temperature at 30°C at the rate of 120 rpm. The temperature was controlled at 30°C. Agitation was provided at 120 rpm. The initial and equilibrium dye concentration were determined by absorbance measurement using spectrophotometer. It was then computed to dye concentration using standard calibration curve. The amount of adsorption at equilibrium, $q_e(mg L^{-1})$ was calculated using following equation, the solution pH was used without adjusting.

$$qe = \frac{(Co - Ce)}{W}V$$
(1)

where C_0 and C_e (mg L⁻¹) are the liquid-phase concentrations of dye at initial and equilibrium respectively. V is the volume of the solution (1), and W is the mass of dry adsorbent used (g).

Results and Discussion

SEM morphology



Figure1. SEM image of Fresh AHC

Surface morphology of adsorbents was analysed by scanning electron microscopy which showed a clear view of the grains of the materials used as adsorbent in this study. Typical SEM with EDAX photographs are shown in Figure 1. From figure 1 shows energy dispersive analysis (EDAX) has been used by many researchers for the characterization of adsorbent as well as the elucidation of the probable mechanism of adsorption. It indicates the presence of carbon, oxygen in addition to trace amount of sodium, aluminium, silicon, sulphur, chloride, potassium and calcium species. It reveals that the AHC has a rough and uneven surface with more porous and caves like structure. Figure 2 and 3 shows the morphology of the loaded adsorbent. It shows that the dye has densely and homogeneously adhered to the surface of the carrier as a result

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of either natural into the porous AHC material due to physical adsorption by electrostatic forces or to covalent bonding between the AHC and dye molecules .The uniform distribution is an important criterion for the proper adsorption MB on the whole surface area of the AHC.



Figure2. SEM image of MB loaded AHC



Figure3. SEM image of MG loaded AHC

Determination of functional group





The FT-IR spectrum of AHC was detected in the range of 4000 to 400 cm⁻¹ was presented in Figure 4. The band observed at 3425.58 cm⁻¹ was assigned to a v(O-H) stretching vibration. The absorption band at 2854.65 and 2924.09 cm⁻¹ can be attributed to the stretching vibrations of v(C-H) bonds in alkane and alkyl groups where carbon is bonded with hydrogen bonds. Adsorption bands at 2337.72 and 2376.30 cm⁻¹ were

corresponds to v(N-H) stretching. The band at 1573.91 and 1581.63 cm⁻¹ shows the asymmetric v (-COO-) stretching. The band at 1450.47 and 1458.18 cm⁻¹ may be attributed to the aromatic v(C=C) stretching vibration. At 1111.00 and 1095.57 cm⁻¹, the band is highly intense v(C-O) and is related to the v(C-O) stretching vibration of the bonds in ester, ether, or phenol groups. The band corresponding to 802.39 cm⁻¹ in the fingerprint area indicates a mono substituted aromatic structure. The weak absorption band at 678.94 cm⁻¹ corresponds to the v(O-H) vibration in the benzene ring. The band at 462.92 and 594.08 cm⁻¹ which were associated with the inplane and out-of-plane aromatic ring deformation vibrations common that is quite common for activated carbon.

Effect of adsorbent dosage



Figure5. Effect of adsorbent dosage on the uptake of MB &MG

Adsorbent dose is an important parameter influencing adsorption process since it determines the adsorption capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. The effect of AHC dose of uptake of MB and MG was studied in the range of 50 -250 mg. Figure 5 showed that the % uptake of dye increased from 69% to 100 %, 71% to 100% for AHC-MB and AHC-MG systems, respectively, as adsorbent dose increased from 50 to 250 mg. Such a trend is attributed to an increase in the adsorptive surface area and the availability of more binding sites. Further increase in adsorbent dose, did not show a significant increase in % uptake of dye, therefore, 150 mg L⁻¹ adsorbent dose was chosen for both AHC-MB and AHC-MG respectively.

Effect of contact time



Figure6. Effect of contact time on the uptake of MB &MG

The effect of contact time on adsorption of MB and MG onto AHC was studied at 10 mg L^{-1} . From Figure 6, it can be seen that the rate of adsorption was very rapid at initial period of contact time. Thereafter, it decreased gradually with time until adsorption was reached at the equilibrium point. This trend of adsorption kinetics was due to the adsorption of dye on the exterior surface of adsorbent at the initial period of contact time. When the adsorption on the exterior surface reached saturation point, the dye diffused into the pores of the adsorbent and was absorbed by the interior surface of the adsorbent. The equilibrium time for AHC-MB and

AHC-MG, systems was 120 min and 150 min respectively, thereafter, no further adsorption occurred with prolonged time.

Effect of Initial dye concentration



Figure7. Effect of initial dye concentration on the uptake of MB



Figure8. Effect of initial dye concentration on the uptake of MG

A given mass of adsorbent can adsorb only a fixed amount of adsorbate. So the initial concentration of adsorbate solution is very important. The effect of initial MB and MG dye concentrations for their uptake by MB and MG were shown in Figure 7 and 8. From the figure, it is evident that a higher percentage of dye was removed with decrease in initial dye concentration for all the dyes. However, the amount of dye adsorbed per unit adsorbent mass increased with increase in initial dye concentration due to the decrease in resistance to the uptake of the dye from solution. Uptake of MB were found to be 100%, 93%, 88% and 80%, for 5-20 mg L⁻¹ dye concentration respectively at 120 min equilibrium time and MG were found to be 100%, 94%, 90% and 100%, for 5-20 mg L⁻¹ dye concentration respectively at 150 min equilibrium time.

Effect of pH



Figure9. Effect of pH on the uptake of MB &MG

It is an important parameter for the adsorption of MB and MG from aqueous solutions that affects the form and quantity of dye, adsorbent surface sites in water, and the interaction between AHC and the functional groups on the adsorbent surface. Influence of pH on the adsorption of MB and MG onto AHC were evaluated by using initial dye concentration of 10 mg L^{-1} at the pH range of 2–12, and the results are illustrated in Figure 9. The amount of dye uptake was found to be increased from 86 to 100 and 93 to 100 of AHC-MB and AHC-MG systems to increase in pH. When pH was increased, electrostatic repulsion between MB and MG onto adsorbent surface sites and the competing effect of hydronium ions were decreased, So MB and MG uptake was increased. The optimum pH was established at 7.0 for MB uptake and 9.0 for MG uptake.

Kinetic studies

In order to investigate the adsorption processes of MB and MG onto AHC, three kinetic models were used including pseudo-first order, pseudo-second order and intra-particle diffusion models.



Figure10. Pseudo first order kinetics for the adsorption of MB &MG

Pseudo-first-order model

The linear form of pseudo-first order model was described by the following equation³

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}$$

Where q_t is the amount of adsorbate adsorbed at time t (mg g⁻¹), qe is the adsorption capacity in equilibrium (mg g⁻¹), k_1 is the rate constant of pseudo-first-order model (min⁻¹), and t is the time (min). After definite integration by applying the initial conditions $q_t = 0$ at t=0 and $q_t=q_t$ at t=t, the equ. (2) becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$
 (3)

Table 1: Adsorption kinetic Parameters for the adsorption of MB and MG onto AHC

Model	Parameters	Dyes	
		MB	MG
Pseudo- first order	$q_{e}(mg g^{-1})$	6.51	6.67
	q_{cal} (mg g ⁻¹)	5.65	7.65
	$k_1(min^{-1})$	0.010	0.005
	\mathbb{R}^2	0.9608	0.9923
Pseudo-second order	$q_{cal}(mg g^{-1})$	0.61	0.54
	$k_2(g mg^{-1}min^{-1})$	0.124	0.127
	h (mg g ⁻¹ min ⁻¹)	0.04	1.49
	\mathbb{R}^2	0.9581	0.9930
Intra-Particle diffusion	k_{int} (mg g ⁻¹ min ^{-0.5})	0.84	0.52
	C	0.60	0.85
	R^2	0.9493	0.9608

Values of adsorption rate constant (k_1) for MB and MG adsorption onto AHC were determined from the plot of $log(q_e-q_t)$ vs t. These values presented in Table 1 indicate that the adsorption rate was very fast at the beginning of adsorption and that rate of uptake of MB and MG is faster on AHC. k_1 value of 0.0107 min⁻¹ and 0.0051 min⁻¹ for AHC-MB and AHC-MG respectively. The equilibrium adsorption capacities were 6.51 and 6.67 mg g⁻¹ respectively. The calculated equilibrium adsorption capacities were 5.65 and 7.65 mg g⁻¹. The calculated and experimental results reveal that, the pseudo-first order model provided a better approximation to the experimental kinetic data than the pseudo-second order model for adsorption of MB and MG from aqueous solution.

Pseudo-second order model

The pseudo-second order adsorption kinetics ⁴ can be written as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

Where k_2 is the rate constant of adsorption (g mg⁻¹ min⁻¹), q_e and qt are the amount of dye adsorbed at equilibrium and at time t. (mg g⁻¹). The values of k_2 and q_{cal} were calculated from the intercepts and slopes of the plots of t/qt vs. t (Figure 11) were presented in Table 1. The calculated q_e values computed from pseudo-second order equation not showed good agreement with experimental values, indicating that AHC-MB and AHC-MG adsorption does not follow Pseudo second order kinetic model.



Figure11. Pseudo second order kinetics for the adsorption of MB &MG

Intra-particle diffusion model

To identify the importance of pore diffusion in the adsorption process, mathematical expression of intra-particle diffusion model⁵ was used

 $qt = K_{int}t^{0.5} + C$



(5)

Figure12. Intra particle diffusion plots for the adsorption of MB &MG

where k_{int} is the intraparticle diffusion constant (mg g⁻¹min^{-0.5}) and the intercept (C) reflects the boundary layer effect. The values of k_{int} were calculated from slope of the plot of q_t vs. $t^{0.5}$ (Figure 12) and are presented in Table 1. From figure 11 showed the involvement of two steps in adsorption process, first one

representing adsorption of dyes on the surface of adsorbent and second one described diffusion of dyes to adsorption site. Surface adsorption mechanism was dominant in first 5 min of contact time, there after diffusion became a rate-limiting process. The values of C were higher for MG dye revealed more surface adsorption of AHC-MG than AHC-MB. Rates of diffusion were higher in AHC. From results it can be concluded that both surface adsorption and intra-particle diffusion mechanism was followed by all the two adsorption systems.

Equilibrium studies

For the equilibrium study of adsorption of MB and MG onto AHC the experiments were conducted at different initial dye concentrations (20–100 mg L^{-1}).

Langmuir isotherm

Langmuir isotherm model is based on assumption that a saturated monolayer of adsorbate molecules is present on the adsorbent surface, the adsorption energy is constant and there is no migration of adsorbate molecules in the surface plane when maximum adsorption capacity occurs. The linear transformation of the Langmuir equation⁶ is given by



Figure13. Langmuir adsorption isotherm for the adsorption of MB &MG

where q_e is the adsorption density (mg g⁻¹) of MB and MG a equilibrium, Ce is the equilibrium concentration (mg L⁻¹) of MB and MG in solution, Q_0 is the monolayer adsorption capacity (mg g⁻¹) and b is the Langmuir constant (L mg⁻¹) related to the free energy of adsorption. The values of Q_0 and b were calculated from the slope and intercepts of the linear plots of $1/q_e$ vs. $1/C_e$ (Figure 13) and are given in Table 2. The linearity of plots revealed that the adsorption followed Langmuir isotherm model. The maximum monolayer adsorption capacity of AHC-MB and AHC-MG systems was found to be 46.33 mg g⁻¹ and 59.21 mg g⁻¹, respectively.

Table2: Adsorption Isothern	n Parameters for the adsor	rption of MB and MG onto AHC
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N 11	Parameters	Dyes	
Model		MB	MG
	$q_0 (mg g^{-1})$	46.33	59.21
Langmuir	R _L	0.34	0.08
	$b(L mg^{-1})$	0.2270	0.2027
	R^2	0.9931	0.9943
	$k_f (mg g^{-1})$	13.21	8.18
Freundlich	n	2.56	0.00
	\mathbb{R}^2	0.9784	0.9839
	А	2.99	0.66
Tomkin	В	10.26	14.25
Геткіп	b	243.09	175.05
	R^2	0.9784	0.9839

Freundlich isotherm



Figure14. Freundlich adsorption isotherm for the adsorption of MB &MG

The Freundlich equation is used to determining the applicability of heterogeneous surface energy in the adsorption process⁷. The empirical Freundlich equation is expressed as:

$$\ln qe = \ln KF + \frac{1}{n} \ln Ce$$
(7)

Where k_f is measure of adsorption capacity (mg g⁻¹) and n is adsorption intensity. 1/n values indicate the type of isotherm to be irreversible (1/n = 0), favorable (0 < 1/n < 1), unfavorable (1/n > 1). The plots of ln q_e vs ln C_e showed good linearity (R² = 0.9784 & 0.9839).The values of K_f and n given in the Table 2. Values of n lies 1 to 10 indicate an effective adsorption. It also indicates degree of favorability of adsorption. The Freundlich adsorption capacity of AHC-MB and AHC-MG systems was found to be 13.21 mg g⁻¹ and 8.18 mg g⁻¹, respectively. Higher value of k_f indicates higher affinity for MB and MG adsorption. From the results it was clearly observed that both models were well suited for adsorption of MB and MG onto AHC.

Temkin isotherm





Temkin isotherm model predicts a uniform distribution of binding energies over the population of surface binding adsorption⁸. Linear form of Temkin equation is expressed as:

$q_e = B \ln A + B \ln C_e$

(8)

Where B = RT/b, b is the Temkin constant related to heat of sorption $q_e (mg g^{-1})$ and $C_e (mg L^{-1})$ are the amount of adsorbed dye per unit weight of adsorbent and unabsorbed dye concentration in solution at equilibrium, respectively. Therefore, a plot of $q_e v_s \ln C_e$ enables one to determine the constants A and B⁹. From Table 2, the maximum binding energy of AHC-MB and AHC-MG systems was found to be 2.99 Jg⁻¹ and 0.66 Jg⁻¹ which is uniformly distributed. The value for heat of adsorption for AHC-MB and AHC-MG systems was found to be 10.26 J mg⁻¹ and 14.25 J mg⁻¹. The correlation coefficient of 0.9784 and 0.9850 obtained showed that adsorption of MB and MG also followed the Temkin model.

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Conclusion

In this study, AHC was successfully used for the uptake of MB and MG dye from aqueous solution pH 7 and 9 were found to be optimum for MB and MG uptake. The equilibrium of adsorption of MB and MG onto AHC was suitably described by the Langmuir, Freundlich and Temkin isotherm model. The process of adsorption was best described by the pseudo-first order kinetics and intra-particle diffusion model. The dye uptake process was found to be controlled by both surface and pore diffusion, with surface diffusion at the earlier stages followed by pore diffusion at later stages. Finding indicated that the waste materials of Areca husk could be used as a potential adsorbent for the uptake of MB and MG from aqueous solution and is an inexpensive material for treating industrial wastewater.

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