Utilization of Agro-Waste in the Elimination of Dyes from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Studies

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Abstract. The prospective of maize cob powder (MCP) as an effective adsorbent for the removal of malachite green (MG) and congo red (CR) dyes from aqueous solution was investigated. The presence of functional groups and pores on maize cob powder were confirmed by FTIR and SEM analysis. Batch adsorption studies were conducted and various parameters such as contact time, adsorbent dosage, initial dye concentration, pH and temperature were examined to observe their effects in the dyes adsorption process. The optimum conditions for the adsorption of MG and CR onto the adsorbent (MCP) was found to be: contact time (60mins), pH (10.0) and temperature (303 K), adsorbent dose (1 g) for an initial MG dye concentration of 50 mg/L and contact time (80mins), pH (2.0) and temperature (343K) for an initial CR dye concentration of 50 mg/L and adsorbent dose 1.0 g respectively. The experimental equilibrium adsorption data fitted best and well to the Freundlich isotherm model for CR dye adsorption and Langmuir Isotherm for MG adsorption. The maximum adsorption capacity was found to be 13.02 mg/g and 9.41 mg/g for the adsorption of MG and CR dyes respectively. The kinetic data conformed to the pseudo-second-order kinetic model. Thermodynamic quantities such as Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were evaluated and the negative values of ΔG^0 , ΔH^0 and ΔS^0 obtained indicated the spontaneous and exothermic nature of the MG adsorption process while positive enthalpy (ΔH^0) indicated an endothermic nature of CR adsorption process.

Introduction

Our earth is the only planet in the whole universe accredited with life in abundance. One of the principal factors, which support life in our mother-planet, is water. But, anthropogenic activities have caused a great harm to the quality of our lifeline, i.e. water. Because of rapid exhaustion of the freshwater resources, there exists some crisis [1]. Colour is considered as the first pollutant to be identified in waste water and it is mostly caused by effluents discharged from dyeing industries such as paper, rubber, leather, cosmetics, textile, pharmaceuticals, plastics and food industries [2]. This discharged coloured (dye) effluent can seriously hinder the penetration of light and disturb the biological processes occurring in many water bodies. More so, the natural degradation of these dye compounds, when released into the environment, usually yields highly toxic and carcinogenic products [3-5].

Malachite green (Basic green) is an N-methylateddiaminotriphenylmethane dye most widely used for colouring purpose among all other dyes of its category [6]. It is an extensively used biocide in the aquaculture industry worldwide. It is also used as a food colouring agent, food additive, a medical disinfectant as well as a dye in silk, wool, cotton, paper, etc industries [7-8]. However there are several reports describing its carcinogenic and hazardous effects [9]. Congo red (CR) is a benzidine-based anionic bisazo dye known to metabolize to benzidine, a known human carcinogen

[10]. Congo red (CR) is toxic to animals and plants and thus its introduction to water stream is of potential health, environmental, and ecological concern [11].

Removal of these dyestuffs from wastewater using various physio-chemical and biological techniques such as filtration, precipitation, coagulation, aerobic and anaerobic decolouration, ozone treatment etc. are all complex and expensive techniques which limits their commercial application. Adsorption appears to be one of the best techniques because of its simplicity of design and cost effectiveness [12-13].

The use of activated carbon is, by far, one of the oldest and most employed adsorbents for the removal of many dyes from solutions because of its high surface area and porous nature [14]. However, the continuous use of commercially available activated carbon is limited by its high cost. This has led researchers into studying the efficacy of relatively cheaper and readily available unconventional adsorbents obtained from plant materials to function as effective adsorbents for dyes elimination [15-18].

Maize is largely produced in Africa especially Nigeria and its cobs are left in the environment during processing and after consumption. The availability of corn cobs as waste material is vast in Nigeria. The objective of this study is to investigate the possibility of maize cob powder as an alternative adsorbent in removing of Malachite green and Congo red dyes from aqueous solution. Characterizations of maize cob powder were done by SEM and FTIR analysis. The influence of contact time, adsorbent dose, initial dye concentration, pH and temperature were evaluated. Adsorption isotherms, kinetics, mechanism and thermodynamic parameters were also evaluated and reported.

Literature Review

Raw corn cob was investigated as potential adsorbents for the removal of methylene blue, MB dye by Enenebeaku, Okorocho and Akalezi [19] via batch method. Optimum conditions for the various adsorption parameters examined showed contact time (30 mins), pH (10.0) and temperature (343 K) for an initial MB dye concentration of 100 mg/L and adsorbent dose 1.0 g. It was seen that as the amount of adsorbent increased, the percentage of dye removal increased consequently. The experimental equilibrium adsorption data fitted best to the Freundlich and Halsey isotherm models, while the kinetic data conformed to the pseudo-second-order kinetic model. The maximum adsorption capacity was found to be 18.28 mg/g. Okorocho *et al.* [20] investigated the adsorption of Pb^{2+} and Cu^{2+} ions by raw corn cobs. Adsorption increases with increasing adsorbent dosage for the two metal ions. Pseudo-second order kinetic model provided an appropriate representation of the metal ions adsorption, while the experimental equilibrium adsorption data fitted best to Langmuir isotherm model.

The removal of Malachite green (MG) from aqueous solution was examined by Malik *et al.* [21] using groundnut shell, an agricultural solid waste as an adsorbent. The experimental results indicated that at a dose of 0.5 g/L and initial concentration of 100 mg/L, groundnut shell powder activated carbon showed 94.5% removal of the dye in 30 minutes equilibrium time, while commercially available powdered activated carbon removed 96% of the dye in 15 minutes. The equilibrium data fitted best to the Freundlich isotherm model. The Adsorption of Congo red (CR) dye from aqueous solution using dried roots of *Eichhornia crassipes* was studied by Wanyonyi *et al.* [22]. Batch experiments were carried out for adsorption kinetics and isotherms. Experimental results obtained showed that adsorption process was highly reliant on contact time, adsorbent dosage, initial dye concentration and particle size. The adsorption equilibrium for Congo red dye by *E. crassipes* (roots) was reached within 90 minutes and adsorption efficiency of 96% was achieved. The adsorption kinetics followed a pseudo-second-order kinetic model while Freundlich isotherm model was best applicable for obtaining the equilibrium parameters.

Experimental

Preparation of MCP adsorbent

The maize cobs were obtained from Ihiagwa market and its environs in Owerri west local government area of Imo state, Nigeria. The collected cobs were severally washed with tap water and double distilled water, cut into small pieces thereafter, stored at 50° C until moisture content was stably insignificant. The dried maize cob were then crushed, sieved to pass through 150 µm mesh size, collected into air-tight containers and kept in air-tight desiccators to be used as adsorbent and labelled MCP.

Preparation of dye solution

Stock solution of malachite green and congo red dyes solution were prepared by dissolving 1 g of each commercially available dye (Fluka grade) in 1 L of distilled water to obtain a stock concentration of 1000 mg/L. Experimental dye solutions of desired concentrations were prepared by appropriate dilution of stock solution.

Batch Adsorption Studies

Batch adsorption experiments were conducted to investigate the effects of contact time, adsorbent dose, initial concentration, pH and temperature for MG and CR adsorption on the adsorbent (MCP) with solutions of different initial concentration of MG and CR ranging from 25 mg/L to 130 mg/L. The adsorbents dose of 1.0 g was added to 100 ml of 50 mg/L dye solutions. The temperature was controlled at 27° C. The series of conical flasks were shaken on a rotary shaker at a constant speed of 100 rpm. Samples were withdrawn for spectrophotometer analysis at predetermined duration of contact time ranging from 10 to 120 minutes. The equilibrium dye concentrations (C_e) were then measured and the amount of dyes adsorbed per unit weight of the adsorbents at equilibrium (q_e) were determined by

$$q_e = (C_0 - C_e) \frac{V}{W} \quad (1)$$

Where W is the mass of adsorbent (g), V is the volume of solution (L), C_0 is the initial concentration of dye (mg/L), C_e is the equilibrium dye concentration (mg/L) and q_e is the amount of dye adsorbed at equilibrium (mg/g).

$$\text{Dye removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where C_0 and C_e are initial and equilibrium (final) dye concentrations, respectively.

Results and Discussion

Effect of Contact time

The plot for the variation of the percentage removal of MG and CR dyes at different contact times is provided in Fig. 1. It was observed that the sorption of MG and CR dyes by MCP was rapid at the first 20 minutes and increased slowly in the later stages until optimum adsorption (equilibrium time) at 60 minutes and 80 minutes for MG and CR dyes respectively. Nevertheless, the percentage removal of the dyes sharply dropped slightly after equilibrium time. The result shows that increasing contact time favours the prolonged interaction between the MG and CR dye molecules and the MCP surface and subsequent permeation into the adsorbent pores until saturation is attained at 60 and 80 minutes respectively. Nevertheless, the sharp loss of adsorbed MG and CR dye molecules, with contact time beyond their respective equilibrium times (60 & 80 mins) indicates that the dislodged dye molecules were weakly held during saturation. This is feasible for the

formation a secondary adsorption layer (held with weak bond) on a primarily adsorbed dye layer (having stronger attachment with the MCP substrate) [23].

Fig. 1: Effect of contact time on the percentage removal of MG and CR dyes onto MCP

Effect of Adsorbent Dosage

The variation plot for the effect of adsorbent dosage on the percentage removal MG and CR dyes onto MCP is provided in Fig. 2. The percentage removal of MG and CR dyes increased from 81.88 % to 98.12% and from 83.51% to 97.48% respectively indicating increase in removal efficiency of the dyes with increase in adsorbent dosage. This observation can be attributed to the fact that the number of active sites on MCP surface increased with the increase in the dosage of MCP which led to increase in the MG and CR dyes removal [24].

Fig. 2: Effect of adsorbent dosage on the percentage removal of MG and CR dyes onto MCP

Effect of Initial dyes Concentration

The variation of amount of MG and CR dyes adsorbed, q_e , for different initial dye concentration in the presence of 1 g MCP adsorbent and after 60 and 80 minutes contact time respectively at 27° C.

The result obviously shows that the q_e value for MG and CR steadily increased from 2.34 mg/g to 10.58 mg/g and from 2.14 to 11.47 mg/g respectively in the presence of 25 mg/L to 130mg/L of the dyes. Such trend has also been reported for the adsorption of many dyes on several other adsorbents [25, 26]. This can be understood from the fact that increasing the initial dye concentration for a fixed adsorbent dose promotes a concentration gradient that continuously overcomes the resistance to the mass transfer of the dye from solution to the MCP surface. Thus, the adsorption of MG and CR dyes and subsequent permeation into the pores of the adsorbent, are both facilitated with increasing dye concentration.

Fig. 3: Effect of Initial Concentration on the amount of MG and CR dyes adsorbed onto MCP

Effect of pH

It can be observed from Fig. 4 that the percentage removal of MG dyes by MCP increased from 91.06 % to 97.76 % respectively with increase in pH from 2 to 10. Optimum sorption was obtained at pH of 10. The increase in percentage removal and adsorption capacity with increase in pH can be attributed to the fact that at low pH values of the solution, the presence of excess hydrogen ion in the solution competes with the cationic groups of the MG dye for the adsorption sites on the adsorbent surface. While at high pH values, the positive charges (H^+) at the solution interphase decreases and the adsorbent surface is more negatively charged, thus enhancing attraction of more amounts of the cations of the MG dye [27].

The adsorption capacity and percentage removal of CR dyes by MCP decreased from 99.45 % to 88.66 % respectively as pH increased from 2 to 10. Optimum sorption was obtained at pH of 2. The decrease in percentage removal and adsorption capacity with increase in pH can be attributed to the fact that at high pH values of the solution, the presence of excess hydroxyl ion in the solution competes with the anionic groups of the CR dye for the adsorption sites on the adsorbent surface. While at low pH values, the negative charges in the solution decreases and the adsorbent surface is more positively charged, thus enhancing attraction of more amounts of the anions of the CR dye [28].

Fig. 4: Effect of pH on the adsorption of MG and CR dyes onto MCP

Effect of Temperature

The influence of temperature on the removal of efficiency of MG and CR dyes by MCP is illustrated in Fig. 5. The percentage removal decreased from 95.88 % to 85.18 % for MG onto MCP. While it increased from 84.82% to 99.4% for CR onto MCP as temperature increased from 30 to 70⁰ C. The decrease in adsorption efficiency with increase in temperature for MG onto MCP can be attributed mainly to the fact that as the temperature increases, the physical bonding between the MG dye and the active sites of MCP weakened. In addition, the MG solubility also increased which caused the interaction between the MG molecules and solvent to become stronger than that between MG and MCP adsorbent. Therefore, MG dye became more difficult to adsorb [29]. While the increase in adsorption efficiency with increase in temperature for CR onto MCP can be attributed to increase in both the mobility of the CR dye molecules and the number of active sites for the adsorption; hence the adsorption is an endothermic process [30].

Fig. 5: Effect of temperature on the adsorption of MG and CR dyes onto MCP

Adsorption Isotherms

To comprehend the nature of the interaction involving the elimination of MG and CR dyes by effect of the MCP adsorbent, the experimental data was analyzed according to the linear form of the Langmuir and Freundlich isotherm models. The Langmuir isotherm can be represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_l} + \frac{C_e}{q_m} \quad (3)$$

Where q_e (mg/g) is the amount of dye adsorbed at equilibrium, q_m (mg/g), the amount of dye adsorbed when saturation is attained, C_e is the equilibrium dye concentration (mg/L) and K_l is Langmuir constant related to the binding strength of dye onto the adsorbent.

The linearized form of Freundlich equation is expressed as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

Where K_f and n are the Freundlich constants that represent adsorption capacity and intensity (strength) of adsorption respectively.

Fig. 6: Langmuir isotherm plot for adsorption of MG and CR onto MCP

Fig. 7: Freundlich isotherm plot for adsorption of MG and CR onto MCP

Figure 6 and 7 show the Langmuir and Freundlich model plot for the adsorption of MG and CR dyes onto MCP respectively. The isotherm parameters and R^2 values are summarized in Table 1. It is evident from the plot in (Fig. 6) and the values of correlation coefficient (R^2) (Table 1) that the Langmuir plot was adequate in describing the adsorption process of MG onto MCP, but was inadequate in describing the adsorption of CR onto MCP. Hence such MG adsorption occurred mainly on the homogenous surfaces of MCP. Figure 7 further evidence the adequacy of Freundlich model to describe the adsorption of CR onto MCP. Hence such CR adsorptions mainly occurred on the heterogeneous surface of MCP.

Table 1: Isotherm Parameters and values of correlation coefficient for MG and CR adsorption

Langmuir Isotherm Model				Freundlich Model		
Dyes	Qmax (mg/g)	K_L	R^2	n	K_F (mg/g)(L/mg) ^{1/n}	R^2
MG	13.02	0.168	0.982	1.98	2.363	0.866
CR	-1037.7	0.001	0.333	1.02	9.41	0.973

Adsorption kinetics

The pseudo-first-order and pseudo-second-order kinetic models were applied to study the adsorption kinetics. The pseudo-first-order rate constant (k_1) and q_e determined from the model are presented in Table 2. It was observed that the relationship between the dye solution diffusivity, $\ln(q_e - q_t)$ against t was non-linear (figure not shown). It is also observed that the calculated q_e values did not agree with the experimental q_e since the calculated q_e values were neither equal nor reasonably close to the experimental q_e values (Table 2). Therefore, pseudo-first-order model was inadequate in representing the adsorption of MG and CR onto MCP.

Furthermore, Figure 8 shows the pseudo-second-order kinetic models plot for the adsorption of MG and CR onto MCP. The pseudo-second-order rate constant k_2 , and q_e determined from the model are presented in Table 2. It was observed from Table 4.18 that there are good agreement between the calculated q_e values and the experimental q_e values i.e. q_e (cal.) and q_e (exp.) for the adsorption of

MG and CR by MCP. In addition, highly linear plots with high values of correlation coefficient were also observed from Fig.8 for the adsorption of MG and CR dyes by MCP. It is therefore evident that Pseudo-second-order is the best fit kinetic model in describing the adsorption processes. Similar results were obtained by other researchers [31, 32].

Fig.8: Pseudo second order plot for adsorption of MG and CR onto MCP

Table 2: Pseudo-first and second order kinetic model parameters for MG and CR onto MCP

Dyes	Pseudo-First Order Model				Pseudo-Second Order Model			
	q_e (exp) (mg/g)	k_1 (g.mg ⁻¹ min ⁻¹)	q_e (cal) (mg/g)	R^2	h (mg.g ⁻¹ min ⁻¹)	K_2 (g.mg ⁻¹ min ⁻¹)	q_e (cal) (mg/g)	R^2
MG	4.81	0.0094	0.043	0.062	4.440	0.2117	4.58	0.999
CR	4.89	0.0031	0.086	0.189	3.411	0.1662	4.53	0.996

Adsorption Thermodynamics

The thermodynamic parameters such as change in Gibb's free energy (ΔG^0), change in enthalpy (ΔH^0) and change in entropy (ΔS^0) for the adsorption of the dyes onto MCP have been determined using the following equations:

The Gibb's free energy, ΔG , equation is expressed as follows:

$$\Delta G = -RT \ln K_{ads} \quad (5)$$

The equilibrium constants (K_{ads}) were calculated according to the following equation:

$$K_{ads} = \frac{\text{Dye concentration on the solid (adsorbent) at equilibrium } (q_e^m)}{\text{Dye concentration in solution at equilibrium } (C_e)} \quad (6)$$

The Van't Hoff equation is expressed as follows:

$$\ln K_{ads} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (7)$$

Where R is gas constant, T is absolute temperature in Kelvin, ΔS and ΔH^0 are entropy and enthalpy respectively. The plot of $\ln K_{ads}$ versus $1/T$ gives a linear relationship, which allows the computation of ΔH and ΔS values from the slope and intercept respectively.

Table 3: Thermodynamic data for MG dye onto MCP

T (K)	k_c	$\ln k_c$	ΔG (KJ/mol)	ΔH (KJ/mol.K)	ΔS (J/mol)
303	23.28571	3.14784	-7929	-32.888	-82.14
313	19.73171	2.982227	-7760		
323	9.119048	2.210365	-5935		
333	6.20339	1.825096	-5052		
343	5.746032	1.748509	-4986.		

Table 4: Thermodynamic data for CR dye onto MCP

T (K)	k_c	$\ln k_c$	ΔG (KJ/mol)	ΔH (KJ/mol.K)	ΔS (J/mol)
303	5.588448	1.720702	-4334	68.051	236.94
313	10.06061	2.308627	-6007		
323	15.89815	2.766203	-7428		
333	41.44186	3.724291	-1031		
343	164.9091	5.105394	-1455		

Negative ΔG^0 values obtained at all temperatures (Table 3 & 4) indicate the feasibility and the spontaneous nature of MG and CR dyes adsorption onto MCP.

The negative ΔH^0 value confirms the exothermic nature of the adsorption of MG onto MCP. While the positive value of ΔH^0 indicates the endothermic nature of CR adsorption onto MCP.

The negative value of ΔS^0 reveals decreased randomness at the solid/solution interfaces and suggests the adsorption MG dye adsorption onto MCP was enthalpy driven [33]. While the positive value of ΔS suggest increased randomness at the solid/solution interphase for the adsorption of CR onto MCP [34].

Adsorbent Characterization

The FTIR spectral of maize cobs powder, MCP were obtained using KBr pellets within the spectral range of 4000-500 cm^{-1} and as shown in Fig. 9. The peaks at 526.58 cm^{-1} represent the carbon halogen (C-X) bond. Peaks at 1039.67 and 1190.12 cm^{-1} are due to C-O stretch from alcohol and C-N from aliphatic amine. Peaks at 1511.28 cm^{-1} show N-O symmetric from nitro compounds. C=C stretch is responsible for the peak at 1654.01 cm^{-1} . Sharp peaks at 2265.47 cm^{-1} represents C $\equiv$ C stretch from alkyne. C N stretch from nitriles is responsible for the peak at 2376.38 cm^{-1} . The peaks at 3257.88 cm^{-1} , 3529.85 cm^{-1} and 3742.03 cm^{-1} are due to O-H stretching (from alcohols and carboxylic acids) and N-H symmetric and asymmetric stretch from amines and amides respectively. O-H from adsorbed water on the surface is responsible for the peak as 3857.76 cm^{-1} .

Furthermore, Fig. 10 shows the SEM images of maize cob powder. It can be observed from 2500 magnifications that MCP surface shows very irregular surfaces with ridges. On further magnification (10000) as indicated the surface shows presence of pores.

FTIR- 8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER **Fig. 9:** FTIR spectra of maize cob powder (MCP) **Fig 10:** SEM images of maize cob powder at 2500x & 10000x respectively**Conclusion**

The adsorption of MG and CR dyes onto MCP powder was found to be influenced by contact time, adsorbent dose, initial concentration, temperature and initial pH of the solution. The optimum adsorption of MG and CR dyes was found at pH 10 and 2 respectively. Temperature had strong influence on the adsorption processes. The kinetic studies revealed that the adsorption of MG and CR dyes onto CPP followed the pseudo-second-order kinetic model. The study on equilibrium sorption revealed that Langmuir isotherm model gave the best fit for MG adsorption while Freundlich isotherm model gave the best fit to the experimental data of CR adsorption onto the MCP adsorbent. The calculated thermodynamic parameters indicated a spontaneous and exothermic nature of the adsorption of MG dyes and endothermic nature for adsorption of CR dyes onto maize cobs powder. We conclude that maize cob powder MCP, can be effectively used as an inexpensive and efficient adsorbent without any pre-treatment or modification for the removal of Malachite green and Congo red dyes from aqueous solutions and effluents.

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