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KINETIC AND ISOTHERM STUDIES OF MALACHITE GREEN AND CONGO RED ADSORPTION FROM AQUEOUS SOLUTION BY CORN STALK BIO-WASTE MATERIAL

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ABSTRACT
This study shows that corn stalk (CS) is an effective adsorbent for malachite green (MG) and Congo red (CR) dyes. MG and CR sorption behavior onto the corn stalk adsorbent was investigated in this study. Basic condition was favorable for MG and CR adsorption to the adsorbent. The pseudo second order equation well described MG and CR adsorption onto the CS adsorbent, hence chemisorptions was the main rate limiting step. The Freundlich Isotherm could describe the sorption data for the dyes. The adsorption of MG and CR on CS was confirmed by FTIR and SEM study, as it showed the change in characterization before and after adsorption, Present investigation and comparison with other reported adsorbents concluded that, CS may be applied as a low-cost attractive option for removal of MG and CR from aqueous solution.
Keywords:* *Adsorption, Corn Stalk, Malachite Green, Congo Red, Isotherms and Kinetic.

INTRODUCTION

Dye is an organic compound that has an ability to impart specific color to the substance to which it is being applied. There is a variety of dyes like; acid dyes, basic dyes, azo dyes, mordant dyes, plastic dyes, *etc*. The main applications of the dyes have been associated with industries like textiles, leather, food, dyeing, cosmetics, *etc* (Yousefi *et al*, 2011). The effluents from these industries contain dyes as main pollutants (Kaur 2014; Walker, *et al,* 2003*)*. Due to their chemical structure, these dyes interfere in the photosynthetic activity of plants since it resists solar radiation penetration, thereby affecting the ecosystem and highly toxic (Syed and Shabudeen, 2011). Consequently, there is a Considerable need for the removal of dyes from water effluents prior to their discharge in to receiving water (Dogan *et al* 2000). A number of methods such as; physical and chemical methods, which include adsorption, electrocoagulation, electrochemical and biodegradation, have been used for the removal of dyes from the effluents. Among all these methods, adsorption has been found to be most effective for the removal of dyes from effluents (Etim, *et al,* 2013, Uddin *et al,* 2009). Adsorption method provides a direct and economically cheap route for the efficient removal of dyes from effluents.

Malachite green dye is a synthetic compound used for dyeing different materials such as silk, wool, cotton and paper. Congo red [1-napthalenesulfonic acid, 3,3′-(4,4′-biphenylene bis (azo)) bis (4-amino-) disodium salt] is a benzidine-based anionic diazo dye, which is known to be toxic and carcinogenic. The waste water containing dye is difficult to treat due to their complex nature and relative stability from degradation (Syed and Shabudeen, 2011). During the past three decades, several physical, chemical and biological decolourization processes have been reported. These include; Coagulation, Flocculation, Biodegradation, Adsorption, Membrane separations, Ion exchange e t c. However, these methods have several disadvantages such as incomplete removal, high reagent and energy requirements and generation of toxic sludge or other waste products that requires proper disposal and further treatment. These methods are uneconomical and unviable. Amongst the numerous techniques of dye removal, adsorption is the best results and cheapest (Crini 2006). The most efficient technique for the removal of dyes from wastewater is adsorption on activated carbon. However, the cost implication of activated carbon has necessitated the need for low cost adsorbents. The use of biomass as low cost adsorbent for the removal of dyes from wastewaters has received increased interest (Benaissa, 2010, Crini *et al.,* 2007).

Corn is major staple cereal in Nigeria and therefore produces large volume of waste either as stalk or cereal husk. The stalk can be used as suitable adsorbent for dye removal from industrial effluents, since the conventional methods are expensive and unavailable.

The present work is focused on the removal of malachite green and Congo red dyes from aqueous solution by using corn stalk as adsorbent. Similarly, from the data obtained the adsorption isotherms and the kinetic processes were also explored.

MATERIALS AND METHODS

Sample Collection and Preparation

Fresh Corn stalk samples were collected from a local Corn/Maize Mill in Rimi Local Government Area, Katsina State. The stalks were washed thoroughly with tap water followed by distilled water. They were sun-dried followed by oven-drying at 65°C for 24 hours. The dried stalk was pounded with a mortar and sieved to mesh size of 106µm and stored in a plastic container labeled as CS (Corn stalk) for further analysis.

Preparation of Adsorbates

The analytical grade Adsorbates (Malachite Green and Congo Red) were obtained from the laboratory without any further treatment. Approximately 1g of each adsorbate was dissolved in a litre volumetric flask and made up to the mark with distilled water to make 1000mg/L stock solution. The Congo Red solution was labeled as CR and Malachite Green as MG. Subsequent preparations were made from the stock solution.

Adsorption experiment

The adsorption of malachite green and congo red onto the adsorbent was investigated in batch experiments. Various parameters such as contact time, adsorbent dose, pH, and initial concentration were examined. The experiment was carried out using rotary shaker at the speed of 300 rpm. The known quantity of adsorbent was mixed with 100 ml of each of MG and CR dye solutions separately. At the end of each experiment, the filtrate was removed from the adsorbent solution and filtered using whatman No. 1 filter paper. The percentage removal and adsorption capacity were calculated from the relations:

$$\%\,removal = \frac{C_0 - C_e}{C_0} x\ 100,$$

$$q_e = \frac{(C_0 - C_e)V}{m}.$$

Where C_o and C_e are the concentrations (mg/L) of the dyes, initially and at equilibrium time, respectively, m is the weight of the adsorbent (g), q_e is the amount of the dye adsorbed (mg/g) while V is the volume of the solution in litre (Ibrahim *et al*, 2006; Wang and Chen, 2010).

RESULTS AND DISCUSSION

Effect of contact time

About 50ml of 40mg/L for each MG and CR solution was placed in 250ml Erlenmeyer flask followed by determination of its initial absorbance using a UV/VIS spectrophotometer (Turner Model SP-850). 0.4g Corn stalk (particle size >106<1000µm), was then added in to the Erlenmeyer flask placed on an orbital shaker which was preset at 300 rpm. Absorbance was measured at interval of time (15, 30, 45, 60….120 minutes). Each experiment was perfomed in triplicate for accuracy. The result is shown in Figure 1(a) which indicated a steady rise in percentage removal for the first forty five minutes. Subsequent increase in the time of agitation showed a decrease in the percentage removal. These could be attributed to deposition of dye molecules on the available adsorption sites on adsorbent material (Vimonses, *et al.*, 2009). The amount of the dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the dye being adsorbed onto the adsorbent. The percentage removal was 80.3 and 76.5 for MG and CR respectively.

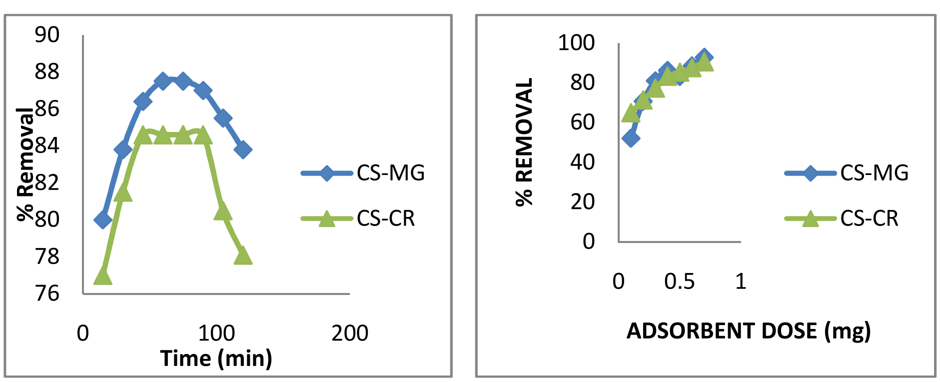


Figure 1. Effect of (a) time and (b) adsorbent dose on the percentage removal of MG and CR dyes

Effect of adsorbent dose

The effect of adsorbent dosage on bio-sorption experiment was studied by varying the amount of adsorbent (particle size >106<1000µm) from 0.1- 0.7g at a pH 7 and equilibrium time of 60 and 45 min for MG and CR respectively.

Similar procedure as earlier stated was followed by varying the amount of adsorbate for each set of experiment. Figure 1(b) shows the result. There was steady increase in adsorption of both dyes, with increase in adsorbent dose. This was evident from the fact that, increase in adsorbent dose increases the number of active sites for adsorption of the dyes.

Effect of initial dye concentration and pH of the adsorbets

The effect of initial concentration of MG and CR was determined by agitation of different solutions of MG and CR(40, 80, 120, 160 and 200 mg/L) containing fixed amount of adsorbent (0.4 g) at room temperature and equilibrium time of 60 and 45 min for MG and CR respectively. Figure 2(a) shows the result. There was initial rise in adsorption with increase in adsorbate concentration, until it reached 100 mg/L when it remained unchanged; this was due to availability of large number of vacant sites at the initial stage. As the time proceeded there was accumulation of dye particles in the vacant sites leading to decrease in adsorption rate. The effect of pH on the adsorption of MG and CR was evaluated by adding 0.4 g of adsorbent into flasks containing 50 ml of 40 mg L^{-1} at different initial pH (2-14). It was found that optimum removal of the dyes was at pH 6.5-7.0 (90%) for CS-MG and 4.0 – 5.0 for CS-CR (84.7%).

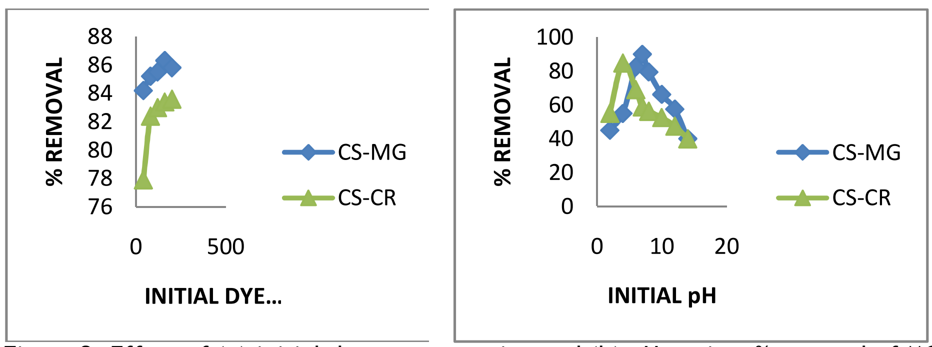


Figure 2. Effect of (a) initial dye concentration and (b) pH against % removal of MG and CR dyes.

Kinetic studies

Kinetic models were used to fit the experimental data. The kinetics of malachite green and congo red adsorption processes were investigated using the pseudo-first order and pseudo-second order kinetic models as shown in Table 1.

Table 1; shows kinetic studies

Adsorbent-Dye Interactions	pseudo fisrt order kinetic				pseudo second order kinetic			
	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	K_1 min^{-1}	R^2	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	K_2 $gmin^{-1}mg^{-1}$	R^2
CS-MG	4.375	2.2646	0.0944	0.912	4.375	4.5050	0.1128	0.999
CS-CR	4.228	2.4604	0.1198	0.824	4.228	4.4053	0.1074	0.999

Table 2; shows the Isotherm studies

Adsorbent-Dye Interactions	Langamuir Isotherm				Freundlich Isotherm		
	q_m (mg/g)	K_L(L/mg)	R^2	R_L	K_F (mg/g)	n (g/L)	R^2
CS-MG	4.092	0.2585	0.952	0.7891	0.5623	0.9107	0.998
CS-CR	3.329	0.1533	0.991	1.9596	0.2655	0.7911	0.990

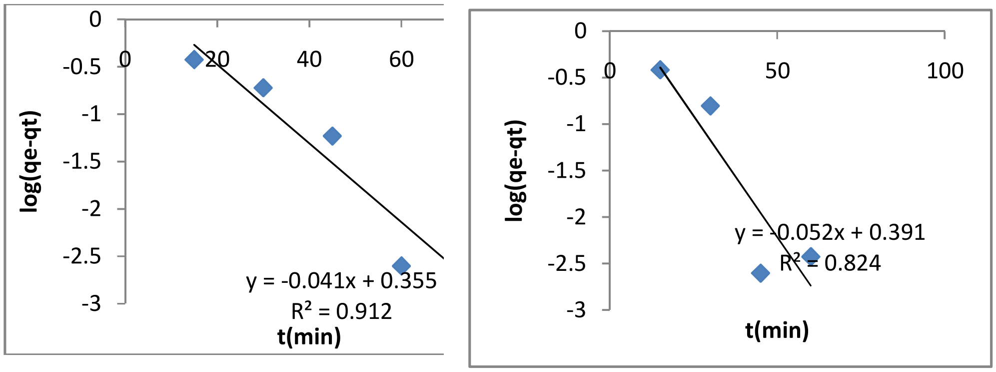


Figure 3: pseudo first order model (a) CS-MG and (b) CS-CR

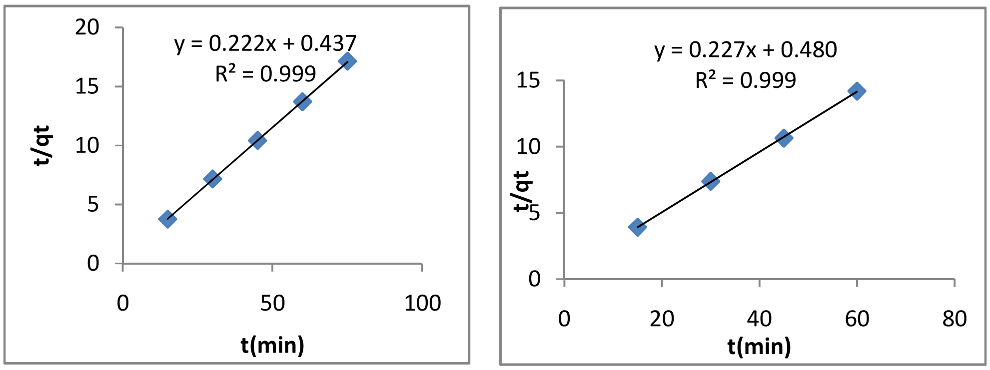


Figure 4: pseudo second order model (a) CS-CR and (b) CS-MG

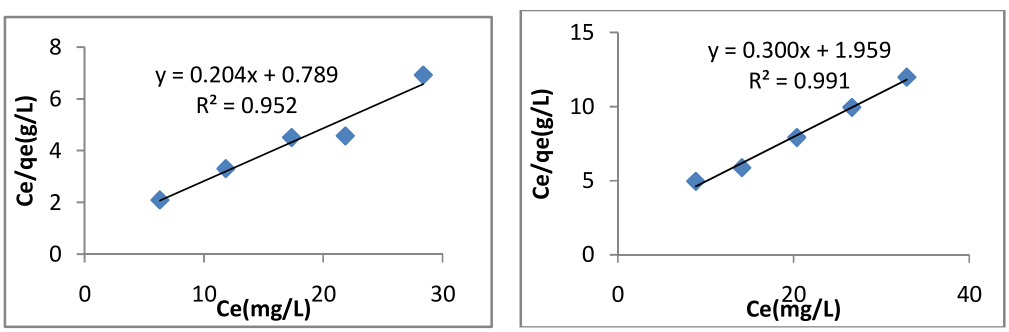


Figure 5: Langmuir isotherm (a) CS-CR and (b) CS-MG

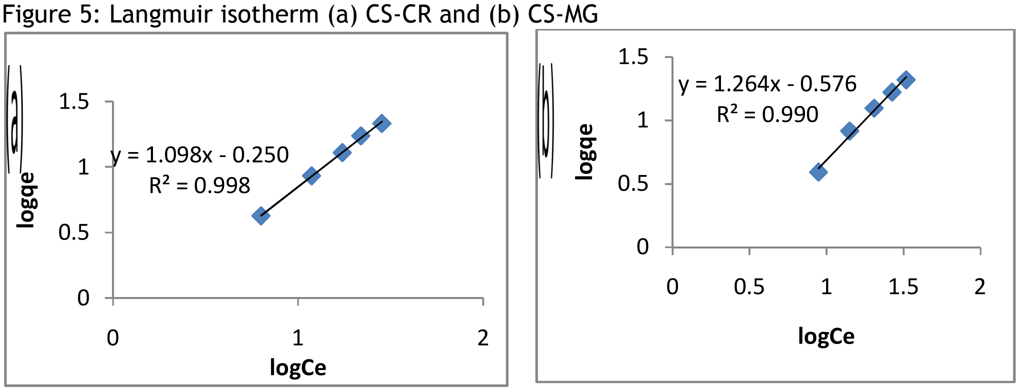
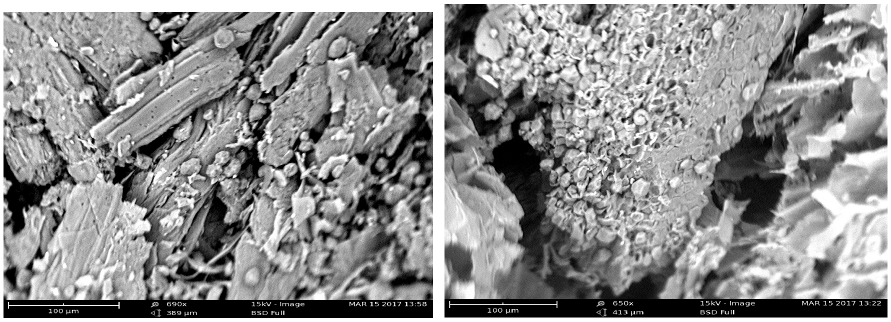


Figure 6: Freundlich isotherm (a) CS-CR and (b) CS-MG

Scanning electron microscopy (SEM) analysis
The SEM characterization of CS, before and after adsorption showed complete change in surface texture. Before adsorption there was rough surface morphology as observed (Fig. 7a), while after adsorption of dye on the CS layer the surface of adsorbent indicated smooth morphology with tiny pores as observed in Fig. 7(b). These changes in the morphologies were in good agreement with the literature for various materials (Saha et al., 2010).



(a) (b)

Figure 7: SEM of CS (a) before adsorption and (b)CS-CR after adsorption

FTIR ANALYSIS
The FTIR spectrum of the CS (Fig. 8a and 8b) before dyes adsorption has shown the various functional groups with respect to their peak value, characterizing the complexity and heterogeneity of the surfaces (Giwa *et al*., 2013). Peak at 3320 cm^{-1} indicates the presence of –OH before adsorption, a slight shift was observed after adsorption to 3286 and 3283 cm^{-1} for MG and CR adsorption respectively. The peak values at 1738, 1607, 1238, and 1078 cm^{-1} confirm the functional groups C-O stretch, C=C, C-C, and C–H bending, respectively. The peak at 1659 and 1588 cm^{-1} corresponds to C=C aromatic stretching and peak at 1369 cm^{-1} was due to C–C aromatic stretching while 1160 cm^{-1} was due to C–N stretching for MG adsorption. Fig. 6(b) shows the FTIR spectrum of CR dye absorbed on CS, where the peaks were slightly shifted towards higher side with values 1607, 1514, 1238, and 1026cm^{-1}.On the basis of the FTIR one can confirm the adsorption of dyes on CS.

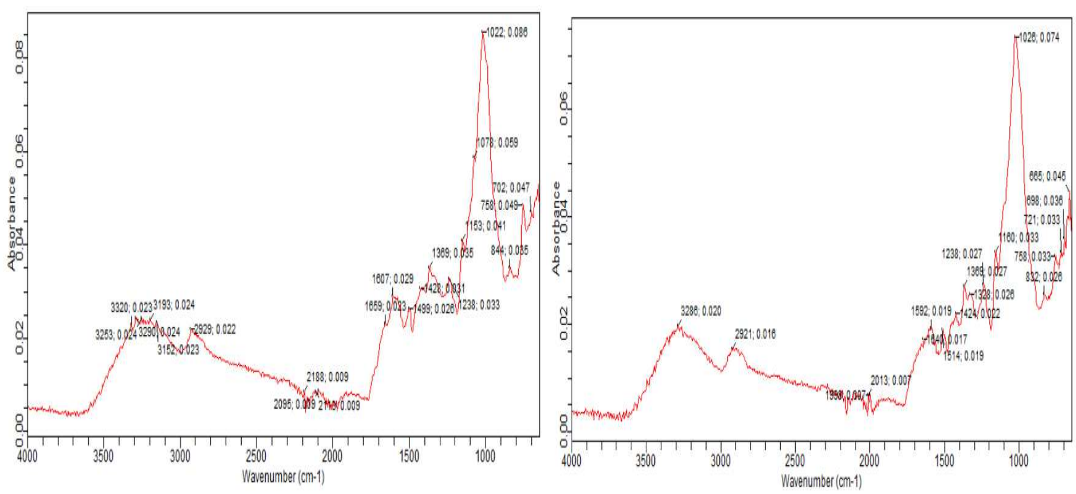


FIGURE 8: FTIR OF (a) CS and (b) CS-MG

CONCLUSION
This study has shown the potential of corn stalk (CS) as eco-friendly material for treatment of wastewater. Equilibrium adsorption capacities for both MB and CR showed an increase in percentage removal with increase in initial dye concentration, contact time. However, the rate of dye adsorption became constant at equilibrium. Adsorption process was found to be electrostatic as evidenced from dependence on pH. Maximum adsorption for MG dye was attained at neutral pH (6.3 to 7.0) while adsorption of CR dye reached its maximum at pH 5.0.

The equilibrium data for MG fits well to the Freundlich isotherm model as evidenced by high regression coefficient values (*R2* >0.998). On the other hand equilibrium adsorption data for CR also fitted the Freundlich model (*R2*>0.990). This indicated that, both MG and CR adsorptions occurred by multilayer formation on the adsorbent surfaces. The shifting of peaks in FTIR spectrum confirmed the MG and CR dyes adsorption onto CS. The SEM result also revealed variation in the surface morphology of the adsorbents before and after, thus reflecting successful removal of the dye molecules from the waste water.

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