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Author(s) : F.S.Omeiza, P.A.Ekwumemgbo, J.A.Kagbu, K.O.Israel

MS Title: Adsorption kinetics of malachite green from aqueous solution onto carica papaya seed

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Adsorption kinetics of malachite green from aqueous solution onto carica papaya seed

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ABSTRACT

Carica papaya seed (CPS) waste was used as an adsorbent for the removal of malachite green and was studied in batch mode the effect of agitation time and initial dye concentration, adsorbent dosage and pH were examined. The study revealed that the amount of dye adsorbed (mgg^{-1}) increased with increase in agitation time and reached equilibrium after 35 minute. for dye concentration of 2.00-10.00 mg/l. the adsorbent dosage of 1.00 g/60.00 ml and pH 8.0 were found to be the optimum for maximum for maximum dye removal. The batch mode adsorption followed both the Langmuir and Freundlich isotherms. The pseudo first and second order kinetics model provided the best correlation of the equilibrium data. The adsorption kinetics of malachite green showed that the pseudo first order kinetic model provided the best correlation of the equilibrium data. This study implies that it is possible to develop a dye removal system using carica papaya seed, which occur as a waste in the environment.
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KEYWORDS

Carica papaya seed (CPS);
Malachite green;
Rate kinetics;
Desorption studies;
Gravity (xg).

INTRODUCTION

The preparation of low cost adsorbent for industrial effluent purification has recently been reviewed by[1]. For example a wide range agricultural by-products have successfully been converted into activating carbon includes coconut shell, rice husk, maize cob etc. activated carbon prepared from various locally available materials have been employed in adsorption processes for the treatment of waste water and even for the purification of water in less developed countries[1]. In the present investigation, the possibility of using Carica papaya seed waste for the removal of Malachite Green from an aqueous solution was accessed. Batch mode experimental parameters such as agitation time and initial dye concentration, adsorbent dosage and pH were determined. Adsorption isotherms and rate kinetics were applied to the batch mode equilibrium adsorption data.

EXPERIMENTAL

Material

The samples of carica papaya were carbonized and activated by 2- step method[2]. 2.00 g of raw CPS samples was weighed into reweighed crucibles and placed in a carbolite furnace at 500°C for 3minute to carbonize as shown below

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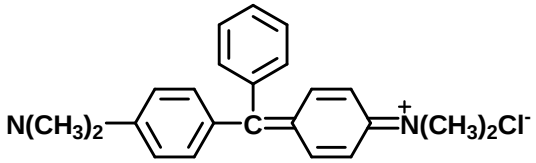
$$\text{Raw-CPS} \xrightarrow[\Delta]{\text{500 C, 3 minutes}} \text{C + CO2 (Carbonization)}$$

2.00 g of carbonized CPS samples were mixed, Separately with 2.00 cm^3 of Activating Agents (AA) (i.e 0.1M H_3PO_4)

The samples were heated in a furnace at 750°C for 5minutes after they were cooled with ice cold water and allowed to dry at room temperature. They were stored in sealed air tight polythene bag

$$\text{Carbonized-CPS} \xrightarrow[\Delta]{\text{AA, 750 C, 5 minutes}} \text{AC + CO2 (Activation)}$$

The above was repeated until substantial amount of activated CPS was obtained. It was allowed to cool in H_2O and allowed to dry at room temperature and stored in polythene bags. The dye used in this study was malachite green and It has a molecular formula of $C_{23}H_{25}CIN_2$ with a molar mass of 364.911g/mol. Its maximum absorbance was 620nm



Structure of malachite green

A stock solution of 1000.00 mg/l malachite green was prepared by dissolving 1.00g of malachite green in 1000.00 cm^3 volumetric flask containing about 500cm^3 of distilled water. It was made to mark with distilled water to obtain 1000mg/l stock solution of malachite green. Dye concentrations were estimated using CORNING colorimeter. All chemicals used were of analytical grade

Methods

Batch mode of studying adsorption kinetics

The prepared adsorbent was tested for the removal of malachite green using a batch mode process. In these studies, various parameters such as initial dye concentration and agitation time, adsorbent dosage and pH were determined for maximum dye removal. The effects of agitation time and initial concentration were tested by adding 1.00g of adsorbent to 60ml of dye solution of various concentration (2.00 mg/l -10.00 mg/l) and agitating in a shaker at predetermined time intervals at 29±2°C. The samples were withdrawn from the shaker at predetermined time internals and the adsorbate and adsorbent were separated by centrifugation at 1395 (x g). The absorbance of the supernatant solution was taken. The study was carried out with different adsorbent dosages. 0.50, 1.00, 1.50, 2.00 and 2.50 g/60.00 ml at a predetermined equilibrium time of 35minutes. In order to find out the optimum pH for maximum dye removal efficiency, the experiments were conducted at different pH values ranging from 2.0 to 10.0 with optimum adsorbent dosage of 1.00 g for 35 minutes at 29±2°C. the Langmuir plots were obtained using the equilibrium time curves data (i.e the adsorbent dosage was fixed while the adsorbate concentration was varied). Freundlich plots were obtained from the equilibrium data of the adsorbent dose effect (i.e the adsorbate concentration was fixed while the adsorbent dosage was varied). Kinetic studies were also carried out with different initial concentration of malachite green while maintaining the adsorbent dosage at constant level. Control experiments were carried out in the absence of the adsorbent in order to find out whether there was any adsorption on the container walls[3].

Desorption studies

For the desorption experiments, the adsorbate-laden adsorbent from batch process for H_3PO_4 activated-CPS for various initial dye concentrations (2.00-10.00 mg/l) was washed gently with distilled water to remove the unadsorbed dye. The washed samples were resuspended in flasks containing 60.00 ml of 0.10 M NaOH and agitated in a shaker at 12.52 (xg) for different time intervals to determine the equilibrium time for maximum dye desorption. Once the equilibrium time for desorption was fixed, the dye- laden adsorbent was suspended in the flasks containing 60.00 ml of various concentration of NaOH (0.10-0.50 M) and agitated for the predetermined equilibrium time to determine the optimum NaOH concentration for maximum desorption. The desorbed dye concentration was determined in the supernatant using corning colorimeter.

RESULTS AND DISCUSSION

Effect of initial dye concentration and agitation time on dye removal

This studies revealed that the percentage dye removal decreases with an increase in the initial dye concentra-

tion and the amount of dye uptake increased with an increase in contact time but remained constant once an equilibrium was achieved when H_3PO_4 activated – CPS, as shown in Figure 1. However, the percentage dye removal at equilibrium time decreases from 94 % –85 % for H_3PO_4 activated – CPS, for the dye concentrations of 2.00–10.00 mg/l. It was clear that the percentage dye removal was dependent on the initial dye concentration and the equilibrium time for the adsorbent was 35 minutes at all the dye concentrations studied. The effect of agitation time on dye uptake was a single, smooth and continuous curve leading to saturation, suggesting the possible monolayer coverage of dye on the surface of the adsorbent. This studies agreed with reports of[4-6]

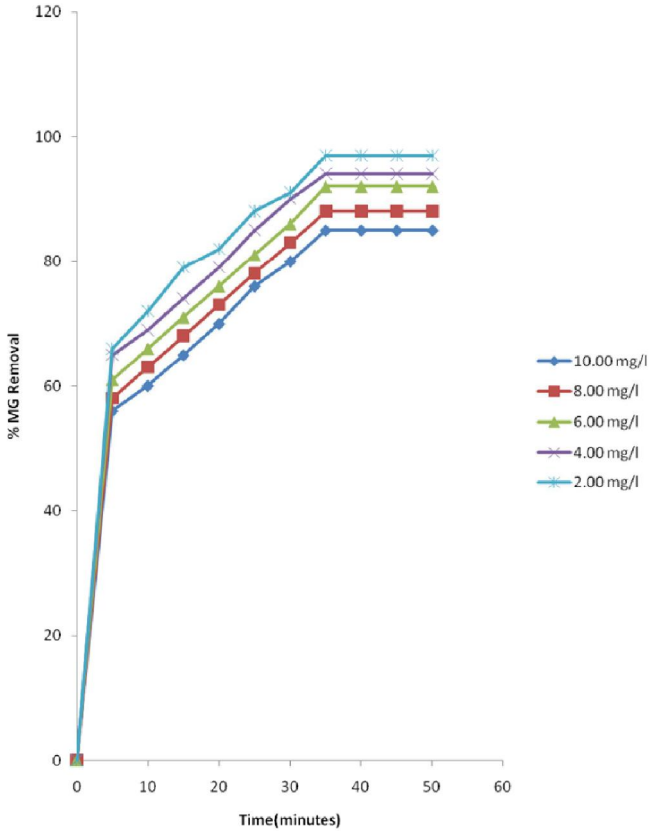


Figure 1 : Effect agitation time and initial dye concentrations on MG removal using H_3PO_4 activated-CPS samples, pH 8.0 and adsorbent dosage of 1.00 g and temperature of 29±2°C.

Effect of adsorbent dosage on dye removal

The effect of adsorbent dosage on dye removal was studied for H_3PO_4 activated–CPS, Figure 2. However the minimum and maximum dye removal of 80 %–91 %, and 85 %–97 % were observed at dosages of 0.50 and 2.50g/60.00 ml respectively when H_3PO_4 activated-CPS was used for the adsorption of MG and It was also noticed that an optimum dye removal of 82%–94% was observed at adsorbent dosage of 1.00 g/60.00 ml for H_3PO_4 activated-CPS. The result indicated that an increase in adsorbent dosage increase the percentage dye removal which either reached a constant value or revealed a very low rate of removal after a particular dosage level. The reason for the above may be that the rate of adsorption increased with an increase in adsorbent dosage which may be due to the availability of more binding sites at higher adsorbent dosage. This study is in agreement with reports of[3,4]. An adsorbent dosage of 1.0.00 g/60.00 ml was used for further studies.

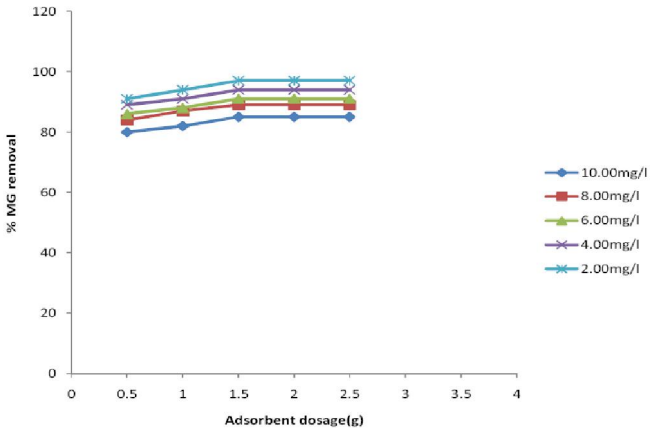


Figure 2 : Effect of adsorbent dosage on the removal of MG using H_3PO_4 activated -CPS at pH 8.0, and temperature 29±2°C

Effect of pH

The initial pH of dye solution influences both the dye molecules and the CPS in an aqueous solution. Furthermore, the variation in pH (2-10) did not cause any degeneration of the biosorbent as shown on Figure 3. H_3PO_4 activated-CPS, shows that a maximum dye adsorption of 94% was observed at pH 8.0 but at acidic pH (2-4) the dye adsorption unto CPS was unfavourable. This suggests that CPS may be negatively charged on its surface and since the initial pH of the dye decreased the number of negatively charged adsorbent sites and positively charged sites increased which did not favour the adsorption of positively charged dyes due to electrostatic repulsion. However the lower rate of dye adsorption at acidic pH is also due to the presences of excess of H^+ ions competing with dye cations for adsorption sites. Therefore the ionic exchange and electrostatic repulsion and t he organic and structural properties of the dye and CPS could play a vital role in the adsorption process.

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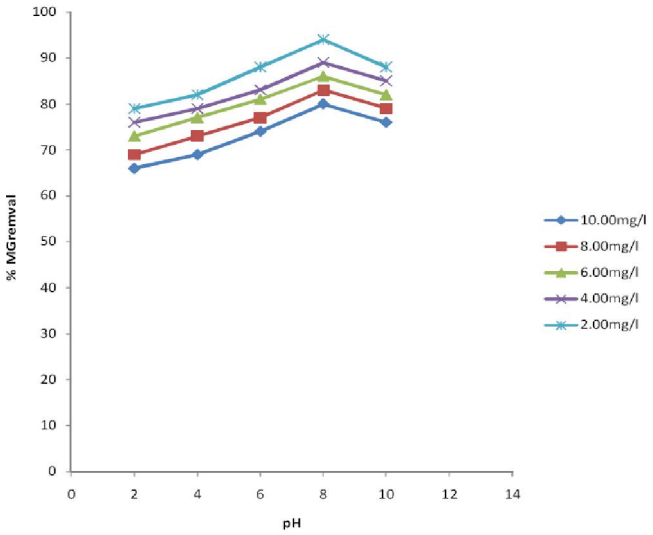


Figure 3 : Effect of pH on the removal of MG using H_3PO_4 activated-CPS at temperature of 29±2?C and adsorbent dosage of 1.00g

Determination of adsorption isotherms

A comparison of calculated and experimental results for dye removal onto CPS is shown TABLES 1, 2 for H_3PO_4 activated – CPS,. All the tables shows that for the pseudo-second-other model, the rate constant (k_2) decreases with an increase in initial dye concentration. The correlation values (R^2) of the pseudo-second order model for Malachite Green were much higher than those for pseudo first order. However the sorption capacity (q_e) for the pseudo-first-order equation was slightly more reasonable than that of the pseudo-second-order when compared to experimental q_e values in (TABLE 1) This suggests that the adsorbent system studied belongs to the pseudo- first-order kinetic model based on the assumption that the rate limiting step may be chemical or chemisorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate. Similar phenomena have been observed in biosorption of RB 2, RY2 and Remazol Black B dyes on biomass[7,8] and exploitation of trichoderma harianum mycelial to adsorb Rhodamine 6G[4]. The adsorption capacity(Q_O) calculated from Langmuir isotherm was 9.85 for

TABLE 1 : Comparison of the first- and second-order adsorption rate constants of calculated qe values with experimental qe values for different initial concentration using H_3PO_4 activated-CPS

Dye concentration (mg/l)	qe(exp) (mgg^{-1})	First-order kinetic model			Second-order kinetic model		
		K_{ad} ($lmin^{-1}$)	qe(cal) (mgg^{-1})	R^2	K_2 (gmg^1min^{-1})	qe(cal) (mgg^{-1})	R^2
2	1.94	0.318	0.920	0.966	2.089	0.480	0.989
4	3.75	0.359	2.010	0.922	1.271	0.830	0.987
6	5.51	0.306	3.090	0.952	0.720	1.290	0.984
8	7.02	0.576	6.460	0.852	0.592	1.570	0.983
10	8.53	0.327	7.890	0.942	0.004	1.890	0.982

TABLE 2 : Langmuir and Freundlich constants for the removal of malachite green (MG) using H_3PO_4 activated-CPS

Dye concentration (mg/l)	Q_O (mgg^{-1})	B (lmg^{-1})	R^2	K_f [mgg^{-1}] (Lmg^{-n})	n	R^2
2				7.798	1.680	0.781
4				33.806	0.457	0.871
6	30.303	0.327	0.984	15.066	0.352	0.906
8				5.957	0.310	0.911
10				0.948	0.255	0.900

H_3PO_4 activated – CPS.

Desorption studies

The desorption process allows the recovery of dye from waste water and regeneration of the adsorbent, which minimize cost of treatment. In the present study NaOH was used for the desorption of malachite green from H_3PO_4 activated-CPS because the dye has increase solubility in water with higher pH and thus the dye was eluted from CPS.[9] used HCl and ethanol for the desorption of methyl violet, basic fushin from aspergillus niger. The equilibrium time required for the desorption of various dye concentration(2.00-10.00 mg/l) was found to be 90 minutes as shown in figure 4. It was noted that at equilibrium time, the minimum desorption rate for H_3PO_4 activated–CPS was 30%-40% and maximum 53 %-61 %. The desorption studies results showed that an increase in NaOH concentration from 0.1M-0.5M caused an increase dye desorption from 30 %-61 % H_3PO_4 activated–CPS. The desorption profile indicates that the adsorbent can be recycled. Similar results were obtained by[8,11]

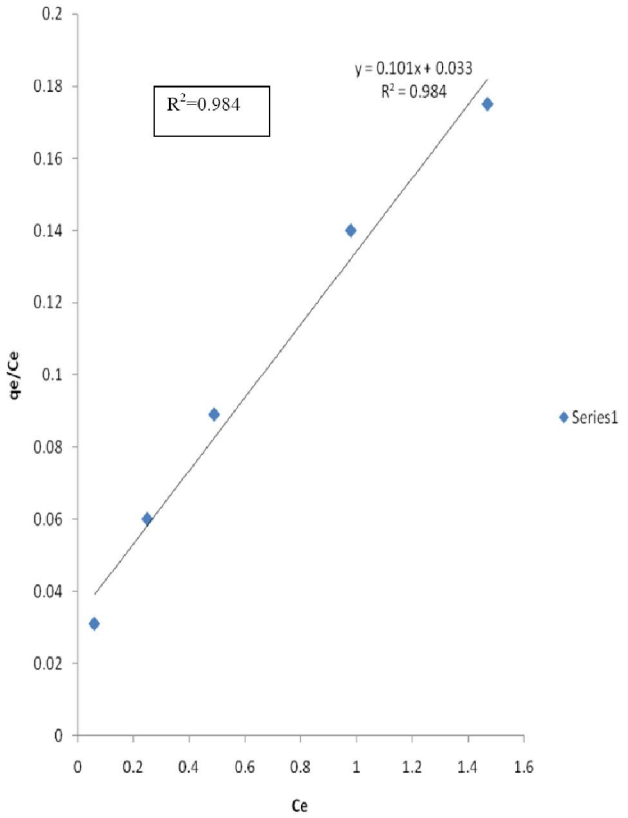


Figure 4 : Langmuir isotherm for H_3PO_4 activated carbon

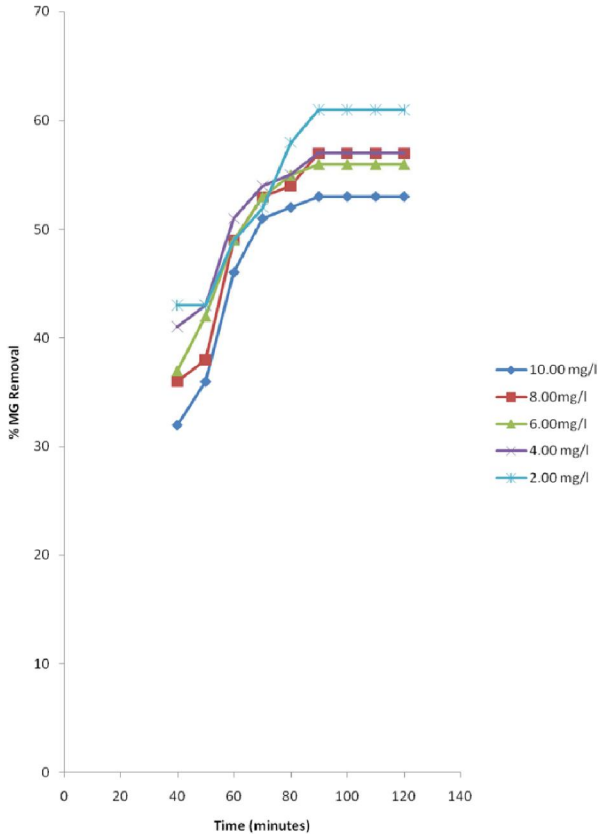


Figure 5 : Desorption profile for H_3PO_4 activated-CPS

CONCLUSION

From the observations,results, and discussions, it can be seen that carica papaya seed samples are cheap, good alternative sources for AC production and the 2-step method of preparation with suitable AA and activation time can be employed for industrial production. However from our studies, it can be concluded that Carica Papaya Seed waste can be used as an adsorbent for decolouration of Malachite Green and has maximum dye removal capacity at lower dye concentration. The adsorption process was highly dependent on agitation time and initial dye concentraion, adsorbent dosage and pH. The adsorption capacities based on the Langmuir (Q_O) and Freundlich (k_f) isotherms were found to be 33.806 to 0.908 for H_3PO_4 activated-CPS. Based on adsorption rate kinetic studies. The pseudo first-order rate kinetics provided the best correlation of experimental data and the sudies assume that the chemisorption mechanism may be the rate controlling step. At this juction, adsorption by carica papaya seed has emerge as an option for developing an economical and eco-friendly method for traeting dye wastewaters.

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