International Journal of Chemical Science
Online ISSN: 2523-2843, Print ISSN: 2523-6075
Impact Factor: RJIF 5.22
www.chemicaljournals.com
Volume 2; Issue 3; May 2018; Page No. 13-16

Comparative studies of the effect of $ZnCl_2$-activated pawpaw seeds and H_3PO_4-activated pawpaw seeds adsorbent dosage and pH on the adsorption of malachite green

FS Omeiza[1], SA Egu[2*], LO Abuh[3]
[1] Department of Chemistry, Kogi State College Of Education Ankpa, Nigeria
[2-3] Department of Integrated Sciences, Kogi State College Of Education Ankpa, Nigeria

Abstract
The present study was undertaken to compare the effect of adsorbent dosage and pH on adsorption effectiveness of $ZnCl_2$-activated pawpaw seeds (ZAPS) and H_3PO_4-activated pawpaw Seeds (HAPS) based granulated activated carbon in removing Malachite Green (MG). The capacity of ZAPS and HAPS adsorbents prepared to adsorb MG from aqueous solution at different pH values (2.0-10.0) and adsorbent dosage (0.50-2.50 g) were monitored using batch mode. The effects of agitation time, adsorbent dosage and pH were examined in each case. The findings shows that at different adsorbent dosages and pH values, ZAPS is a better adsorbent than HAPS.

Keywords: adsorbent dosage, pH, adsorption effectiveness, malachite green

Introduction
Adsorbents prepared in the form of activated carbon from low cost and readily available materials have been used previously to adsorb toxic materials from aqueous solutions. It has been pointed out that many dye intermediates are aromatic amine with constituent side groups (Levine, 1991).The enormous available environmental pollutants in the present age is due to urbanization and industrialization which has added significant amount of heavy metals and toxic dyes into natural aquatic and terrestrial ecosystem (Sanyahumbi *et al*., 1998) [10]. The disposal of coloured wastes such as dyes and pigments into receiving water damages the environment as they are toxic to aquatic life (Lee *et al*., 1999) [5]. Hence, adsorption processes can be widely used to remove pollutants from waste water. Recently concern has increased about the long time toxic effects of water containing pollutants such as dyes, toxic metals, and agricultural waste. This is due to the fact that waste water from dyeing processes discharged into the environment exhibit low Biochemical Oxygen Demand (BOD), high Chemical Oxygen Demand (COD), highly coloured and contains high amount of dissolved solid (Rajeshwarisivaraj. *et al*., 2001) [8]. Waste water exhibits a wide range of pH making convectional biological and chemical processes troublesome because these dyes compose of highly coloured polymers which are difficult to decompose biologically (Rajeshwarisivaraj. *et al*., 2001) [8].
Pollution control in textile industries from previous reports has never been intensified as it is today, one option, which has always been adopted till date in attempt to solve pollution problems resulting from textile industries is the “end of pipe” solution (Hazel, 1991) [3] because synthetic dyes are indispensable to these industries. For instance, indigo dye (an azo dye) is the most commonly used and because they are synthetic, natural environment cannot recognise them nor degrade the toxic intermediates which have been found to be carcinogenic (Trevor, 2001) [11]. Therefore, adsorption appears to be the only and best method in this context because a wide range of adsorbents prepared in form of activated carbon exist for the removal of these dyes and toxic metals. A large number of activated carbon have been prepared from different raw materials such as coconut shell, rice husks, nut shell (Pollard *et al*. 1992) [7], cow dung (Kagbu and Ekanem, 2004) [4], cow horn (Oviawe and Ademoroti, 2005) [6], with each having its own limitations and applications. In view of the above tends to expand safe environmental method using ZAPS and HAPS as absorbent to remove malachite from aqueous solution.

Materials and Methods
Sample Collections
Samples of pawpaw seeds were collected from Samaru, Sabo, and Giwa markets in Zaria, Kaduna State. All the samples from the above listed market were mixed and used for the analysis. Malachite Green (MG) sample was obtained from Spinner and Dyer textile industries located at No. 6, independent road, Bompai, Kano State.

Sample Preparation
The pawpaw obtained were cut into pieces and the seeds were collected, washed thoroughly with distilled water; sun dried and powdered into small particle sizes with a mortar and pestle. They were then sieved into different particle sizes.

Procedure for carbonization and activation
Raw Carica papaya (CPS) sample, 2g was weighed into preweighed crucibles and placed in a carbolite furnace at 500°C for 3 minutes to carbonize as shown in the equation 1 (Gimba *et al*., 2004) [1].

$$\text{Raw CPS} \xrightarrow{500^\circ C.\ 3\text{minutes}} C + CO_2 \text{ (Carbonisation)} \quad (1)$$

The carbonised CPS sample, 2g was mixed separately with 2.00 cm^3 of each activating agents (AA) 0.10 M $ZnCl_2$. The samples were heated in a furnace at 750°C for 5 minutes as shown in equation 2. They were cooled in ice cold water, allowed to dry at room temperature and stored in sealed air tight polythene bag (Gimba *et al.*, 2004) [1]. The procedure above was repeated using H_3PO_4 as activating agent(AA). The resulting ZAPS and HAPS activated carbon were stored appropriately

$$\text{Carbonised-CPS} \xrightarrow{\text{AA, 750°C, 5 minutes}} \text{AC} + CO_2 \text{ (Activation)} \quad (2)$$

The above was repeated until substantial amount of activated CPS was obtained. It was allowed to cool in H_2O and dried at room temperature and stored in polythene bags.

Preparation of Malachite Green (MG) Stock Solution

Malachite green, 1g was weighed into a 1000.00 cm^3 volumetric flask containing about 500.00 cm^3 of distilled water. It was made up to mark with distilled water to obtain 1000.00 mg/l stock solution of malachite green (Gimba *et al.*, 2004) [1].

Effect of adsorbent dosage on the removal of MG using CPS samples at various initial dye concentrations

Exactly 0.50 g, 1.00 g, 1.50 g, 2.00 g and 2.50 g each of ZAPS adsorbents were placed into 60.00 ml of 2.00 mg/l, 4.00 mg/l, 6.00 mg/l, 8.00 mg/l and 10.00 mg/l MG solution in a container. They were agitated at predetermined time interval 5 minutes in a Griffin shaker at 12.52 (×g) at room temperature. The samples were withdrawn from the shaker at predetermined time intervals of 5 minutes and repeated until when equilibrium was achieved and no further adsorption was observed. The adsorbate and adsorbent solution were separated by centrifugation at 1,395 (×g). The absorbance was measured with a corning colorimeter and the amount of unadsorbed MG was calculated using the calibration curve for MG. The above procedure was repeated for HAPS adsobents (Rajeshwarisivaraj *et al*., 2001; Gullen *et al*., 2004) [8, 2].

Effect of pH on the removal of MG removal using activated-CPS at various initial dye concentration

Exactly 1.00 g of ZAPS adsorbents was placed into 60.00 ml of 2.00 mg/l, 4.00 mg/l, 6.00 mg/l, 8.00 mg/l and 10.00 mg/l MG solution in a container and studied separately at different pH values of 2.0, 4.0, 6.0, 8.0, and 10.0 adjusted by adding 0.10 M HCl and 0.10 M NaOH as appropriate depending on the required pH. The samples above were agitated at predetermined time interval of 5 minutes in a Griffin shaker at 12.52 (×g) at 29±2°C. The samples were withdrawn from the shaker at predetermined time intervals of 5 minutes and repeated until when equilibrium was achieved and no further adsorption was observed. The adsorbate and adsorbent solution were separated by centrifugation at 1,395 (×g). The absorbance was measured with a corning colorimeter and the amount of unadsorbed MG was calculated using the calibration curve for MG. The above procedure was repeated for HAPS adsorbents (Rajeshwarisivaraj *et al*., 2001; Gullen *et al*., 2004) [8, 2].

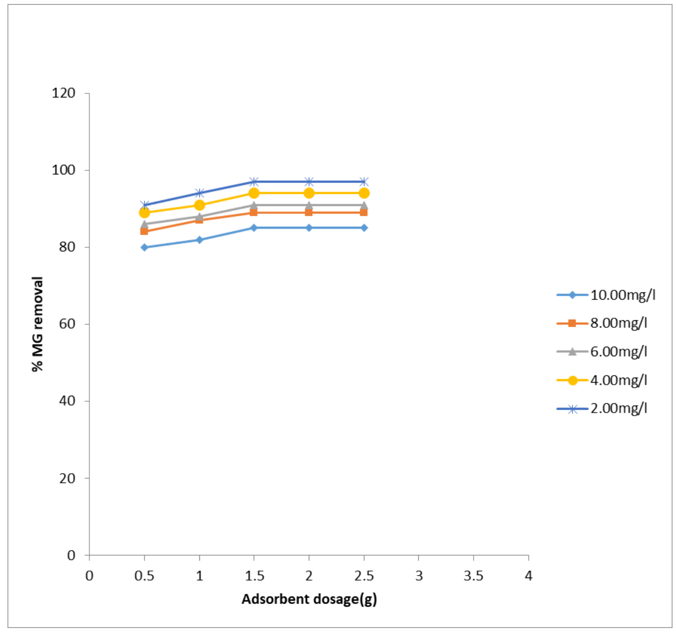

Fig 1: Effect of adsorbent dosage on the removal of MG using HAPS at various initial dye concentrations.

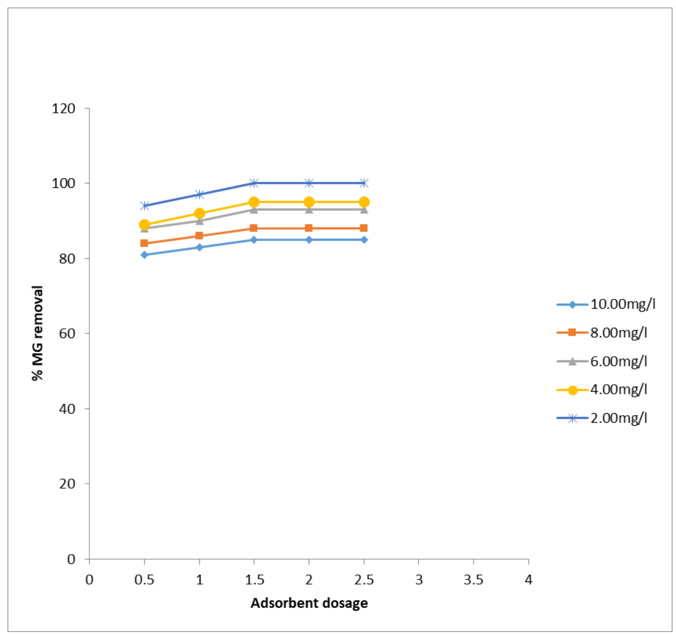

Fig 2: Effect of adsorbent dosage on the removal of MG using ZAPS at various initial dye concentrations.

The effect of adsorbent dosage on MG removal for HAPS was 80 %–91 % as well as 85 %–97 % were observed at dosages of 0.50 and 2.50 g/60.00 ml. however 81 % – 94 %, as well as 85 %–100 % were observed at dosages of 0.50 and 2.50 g/60.00 ml respectively when ZAPS.

The adsorption of MG increased with adsorbent dosage and reaches a constant value after a particular dosage of 2.0g for all the different form of adsorbents studied. This increase in adsorption of MG with adsorbent dosage could be due to the availability more adsorption site. It was also noticed that an optimum dye removal of 1.00 g /60.00 ml for ZAPS is better than that of HAPS. The results indicated that an increase in Adsorbent dosage leads to increase in 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 also be due to the fact 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 and overlapping of adsorption sites as a result of greater number of adsorbent particles. This study is in agreement with reports of Sadhasivam *et al*., (2005) and Gullen *et al*., (2004) [2].

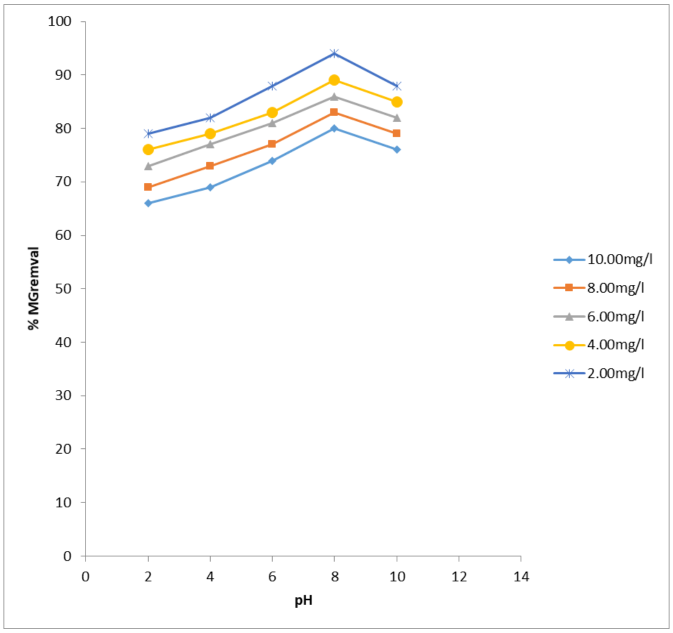

Fig 2: Effect of pH on the removal of MG removal using HAPS at various initial dye concentrations.

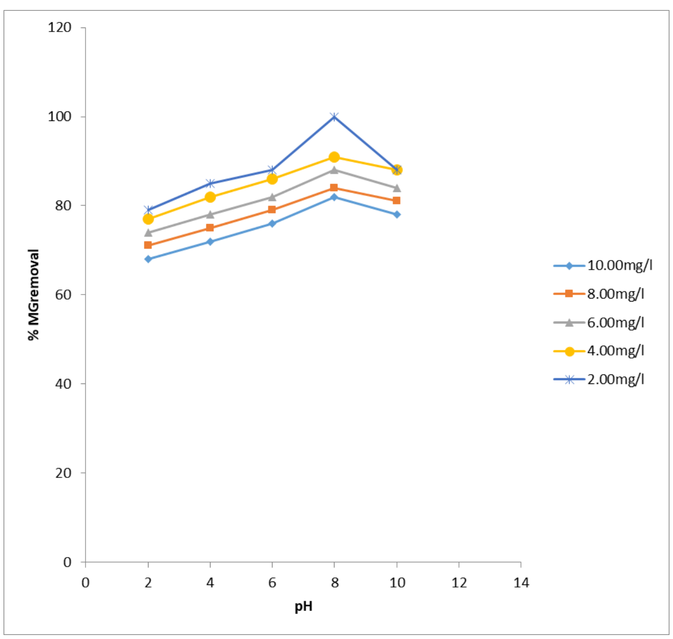

Fig 4: Effect of pH on the removal of MG removal using ZAPS at various initial dye concentrations.

Effect of pH on MG removal

The effect of pH on MG removal when HAPS and ZAPS were used to adsorb MG from aqueous solution was 94 % and 100 % at pH 8.0 respectively. The percentage of MG removed by the adsorbents was highest at pH 8.0 and decreases as from pH 10.0.

The noticed effect of pH on MG adsorption may indicate ion exchange mechanism which influences both the dye molecules and the adsorbents in an aqueous solution because the pH of the MG solution is an important factor in determining the rate of surface reactions. The variation in adsorption capacity in this range was largely due to the influence of the surface adsorption characteristics of the adsorbents and the results of the experiments carried out at different pH values was to determine the optimum pH range for MG adsorption by CPS samples. However, at acidic pH (2-4) the dye adsorption onto adsorbent samples were unfavourable suggesting that pawpaw seed may be negatively charged on its surface and since the initial pH of the dye decreased the number of negatively charged adsorbent sites and increase positively charged sites in which did not favour the adsorption of positively charged dyes due to electrostatic repulsion. Hence, the lower rate of dye adsorption at acidic pH may due to the presences of excess H^+ ions competing with dye cations for adsorption sites. Therefore the ionic exchange, electrostatic repulsion, the organic and structural properties of the MG and adsorbent samples could play a vital role in the adsorption process.

Conclusion

Pawpaw samples are cheap and 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 the findings, it can be concluded that pawpaw seed waste can be used as an adsorbent for Malachite Green (MG) and prepared adsorbents 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, hence, adsorption by ZAPS and HAPS has emerged as an option for developing economical and eco-friendly method.

References

1. Gimba CE, Ocholi O, Nok AJ. Preparation of activated carbons from agricultural wastes: cyanide binding with activated carbon matrix from ground shell. Nigerian Journal of Scientific Research. 2004; 4:106-110.
2. Gullen J, Aroguz AZ, Dalgin D. Adsorption kinetic of azinphosmethyl from aqueous solution onto pyrolyed horse show sea crab shell from atlantic ocean. Bioresource Technology. 2005; 96:1169-1174.
3. Hazel BG. Current problems and future restrictions in dye house operations.Journal of Society of Dyers and Coluorist. 1991; 109:3392-3394.
4. Kagbu JA, Ekanem EJ. The effectiveness of modified cow dung in the removal of chemical burdens from textile effluents. Nigeria Journal of Scientific Research. 2004; 4:25-30.
5. Lee CK, Low KS, Gan PY. Removal of some organic dyes by acid treatment spent bleaching earth. Environment Technology. 1999; 20:99-104.
6. Oviawe AP, Ademoroti CMA. Adsorption of heavy metal ions from aqueous solution using Keratineous substance. Journal of Chemical Society of Nigeria, 2005, 47-50.

7. Pollard SJT, Thompson FE, McConnachie GL. Microporous carbon from marigo oleifa husks for water purification in less developed countries. Water Research. 1992; 29:337-347.
8. Rajeshwarisivaraj S, Sivakumar PS, Subbaram V. Carbon from cassava peel, an agricultural waste as an adsorbent in the removal of dyes and metals from aqueous solution. Bioresources Technology. 2001; 80:233-235.
9. Sadhasivam S, Saritha E, Saritha S, Swaminathan K. Comparison of the efficacy of live and autoclave mycelium of Trichoderma harzianum on the removal of trypan blue. Bulletin of Environmental Contamination and Toxicology. 2005; 7:546-1053.
10. Sanyahumbi D, Duncan JR, Zhou M, Hille R. Removal of lead from solution by the non-viable of the water fern (Azollafilliculoides). Biotechnology Letters. 1998; 20:745-747.
11. Trevor H. Biological treatment of a synthetic dye water and industrial textile wastewater containing azo dye compounds.A M. Sc.Thesis submitted to. Virginia Polytechnic Institute and State University, Virginia, United States America, 2001.