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Optimum conditions for the removal of colour from waste water by mango seed shell based activated carbon

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Abstract

Activated carbons (AC) were produced from seed shells of two (2) varieties of mango (Local & Dausha varieties), by varying the impregnation ratio of the shells (impregnation ratios of 1:2 and 1:3 were used) with $ZnCl_2$ before carbonization. Their performance was evaluated through batch studies for the purpose of obtaining optimum conditions for the removal of colour (methylene blue) from wastewater. Contact time, stirring rate, adsorbent dose, initial methylene blue (MB) concentration, particle size and pH were used as variables. Results obtained revealed the optimum carbon dose of 400mg (4g/l) and 600mg (6g/l) for Local and Dausha varieties respectively, stirring rate of 98 rpm and pH value of 3. MB removal decreased with increase in initial MB concentration for all the 4 activated carbons studied. All the carbons achieved at least 97.7% removal at initial MB concentration of 87 Pt-Co units and hence this was adopted as the optimum initial MB concentration. In general, Local $Zncl_2$ with the impregnation ratio of 1:2 performed better as an adsorbent due to its higher surface area and porosity of 1667.8m^2/g and 69% respectively. Also Local 1:2 achieved 100% removal of MB in 30 minutes, while Dausha 1:2 achieved 100% removal in 40. Local 1:3 and Dausha 1:3 achieved 94.3% and 92% respectively within 40 minutes period. Because at least 90% MB removal was attained within 40 minutes by all the carbons and it was chosen as the optimum contact time.

Keywords: Activated carbon, mango seed shells, Adsorption, colour, optimum conditions

Introduction

An adsorbent is a material of natural or synthetic origin sometimes used in environmental application. The most common adsorbent is activated carbon, which is widely used for the adsorption of pollutants from gaseous and liquid phases (Elizalde- Gonzalez & Hernandez-Montoya, 2007). The high cost of activated carbon has simulated interest in examining the feasibility of using cheaper raw materials. Agricultural wastes/ by products are considered important precursors for production of activated carbon (AC) not just because of their low cost but because they are renewable. Besides, it is a way of recycling agricultural wastes which could otherwise constitute environmental pollution, especially as it relates to solid waste management.

Many attempts on the use of agricultural wastes/by products as adsorbents in water treatment have been made. Ogedengbe *et al*. (1985) used carbonized and activated palm kernel shells for household filters. Ochonogor *et al*. (2000) studied the adsorption of phosphate by *Terminalia catappa* based activated carbon. Agunwamba *et al*. (2002a, 2002b) studied the adsorption of lead and phosphates from water using maize cob based activated carbon. Gurses *et al*. (2006) produced and applied activated carbon from *Rosa canina* in the removal of dye from wastewater. Aloko and Adebayo (2007) produced and characterized activated carbon from rice husk and corn-cobs and used it to remove phosphates from water.

Bansode (2002) used granulated activated carbon (GAC) prepared from pecan and almond shells to remove some VOCs, COD, Cu^{2+} and Zn^{2+} from municipal waste water. The results showed efficient adsorbability of benzene and other halogenated aliphatic compounds. Namasivayam *et al*. (2007) prepared AC from jatropha husk and used it for the removal of anions, heavy metals, organics and dyes from water.

However, scanty information is available on the use of mango seed shells as adsorbent, though the potential for its use has been recognised by some researchers (Ajmal *et al*., 1998; Kumar & Kumaran, 2005; Elizalde-Gonzalez & Hernandez-Montoya, 2007). More so, the optimum conditions for removal of colour from aqueous solution using mango seed shell based AC has not been reported. There is a considerable need for the removal of colour from wastewater/effluents. The discharge of dye-bearing wastewater into natural streams and rivers from textile, paper, carpet, leather, distillery and printing industries pose severe pollution problems (Gurses *et al*., 2006). Various processes tried so far for the removal of colour from water are aerobic and anaerobic microbial degradation, chemical oxidation, membrane separation, dilution, electrochemical treatment, adsorption etc. However, most of these methods have high operational and maintenance cost, low removal efficiencies, lack of selectivity and other limitations. Adsorption by AC is of interest because of the large surface area they present for pollutants removal.

It is therefore the purpose of this research to investigate the optimum conditions (with respect to pH, carbon dose, initial adsorbate concentration, particle size

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and contact time) for the removal of methylene blue (MB) from simulated wastewater.

Materials and methods

Two varieties of mango (*Magnifera indica*); Dausha, an improved variety and chu-kpev, a local variety (herein after referred to as Local) were used as the precursors for the production of activated carbons. The mango seeds were sourced from Gboko, Ushongu and Makurdi LGAs of Benue State, air dried and broken to free the shells. The shells were then thoroughly washed with water to remove any dirt, air dried and cut into sizes of 2-4cm for chemical activation.

The shells were impregnated with $ZnCl_2$ solution in the ratios of 1:2 and 1:3 for both varieties. That is one part of anhydrous $ZnCl_2$ to 2 parts of specified mango variety seed shell by weight. In all, four (4) variations of the activated carbons were prepared, two for each variety. The activated shells were then carbonized in a muffle furnace at 500^0C for 60 minutes to produce activated carbons. Specifically, the activated carbons produced were Dausha 1:2, Dausha 1:3, Local 1:2 and Local 1:3. Dausha 1:2 refers to Dausha shells impregnated in the ratio 1:2 of anhydrous $ZnCl_2$ to Dausha shells. The same nomenclature was used for the other carbons.

Adsorption studies

All the chemicals used were analytical grade. Wastewater was simulated by mixing desired concentrations of methylene blue (MB) in 100ml of water contained in 500ml beakers. Thus, adsorption studies were conducted with pH, contact time, stirring rate, initial concentration of adsorbate and adsorbent dose as variables. The adsorption efficiency of the test carbons for methylene blue (MB) removal was used as criterion for determining optimum conditions.

To investigate the effect of adsorbent dose, 100ml of test samples of pH 7 and initial adsorbate (MB) concentration of 87pt-Co units were mixed using a flocculator (ESF 12/10 model) in 500ml beakers. Specified adsorbent (activated mango seed shell) doses of 100mg, 200mg, 400mg, 600mg, 800mg and 1000mg were added to each beaker respectively and stirred at 98 rpm using electrically operated paddles for one hour. This corresponds to 1g/l, 2g/l, 4g/l, 6g/l, 8g/l and 10g/l respectively. At the end of the stirring period, the beakers were removed slowly from the jar test platform and the contents allowed to settle for 5 minutes and then filtered through no. 42 filter paper. The filtrates were then separately analyzed for residual concentrations of MB according to standard methods as specified in HACH Model DR/2000 Spectrophotometer operator's manual. The above procedure was repeated for other initial MB concentrations of 126 pt-Co units, 181pt-Co units, 240 pt-Co units and 262 pt-Co units. The carbon particle size range used was 150-850 µm.

Studies on the effect of stirring rate on the adsorption of MB were conducted by varying speeds of 98 rpm, 192 rpm and 260 rpm at the optimum adsorbent doses of 400mg and 600mg for local and dausha varieties respectively. The other test conditions remained same as in the effect of adsorbent dose. Studies on the effect of initial adsorbate concentration were conducted by adjusting initial concentration of the adsorbate via dilution of the test samples. In all, five variations of the initial adsorbate concentration were investigated. The optimum stirring rate and absorbent doses were adopted in this study, other test conditions being same as in the effect of adsorbent dose.

The effect of contact time of up to 2 hours on adsorption was studied at the optimum stirring rate, initial adsorbate concentration and adsorbent dose. The experimental procedure was the same as in the effect of adsorbent dose except that the beakers were removed from the batch apparatus in the course of the experiment at specified intervals of 5 min, 10 min, 20 min, 30 min, 40 min and 60min and analyzed for residual concentrations of methylene blue (MB). The effect of pH was investigated at the optimum stirring rate, initial adsorbate concentration, contact time and adsorbent dose. Other test conditions remained same as in the effect of adsorbent dose. pH was maintained at the desired values of 3, 5, 7, 9, and 11 by adding NaOH or HCl as the case may be.

In order to evaluate the influence of carbon particle size for a constant weight on the removal of MB from wastewater, sieve analysis was carried out on the activated carbons for determination of particle sizes. Five particle sizes of 850µm, 600µm, 425µm, 300µm and 150µm were investigated using the optimum values of contact time, stirring rate, absorbent dose, initial concentration of adsorbate and pH, while the other test conditions remained the same as in the effect of adsorbent dose.

Results and discussion

Effect of Adsorbent Dose: The result for variation of % removal of MB with adsorbent doses of 100mg, 200mg, 400mg, 600mg, 800mg, and 1000mg at initial MB concentration of 87 Pt-Co units for the various carbons is presented in Fig.1. The figure revealed that an increase in the quantity of adsorbent results in a corresponding increase in the amount of MB removed. This increase in removal efficiency with simultaneous increase in adsorbent dose is due to the increase in surface area and hence more sites were available for adsorption of MB. Also 400mg of local 1:2 and local 1:3 were enough to achieve 100% and at least 98% removal of MB from wastewater respectively. On the other hand 600mg of Dausha 1:3 and Dausha 1:2 were required to remove 100% and 97.7% of colour respectively. It is clear from these observations that the local variety is a better adsorbent with respect to MB removal compared to Dausha as indicated by the less quantity of local variety based carbons required to achieve the same level of treatment. Thus 400mg of local and 600mg of Dausha were respectively chosen as the optimum carbon dose for further studies. The efficiency of the carbons was in the order Local 1:2 > Local 1:3 > Dausha 1:2 > Dausha1:3. It is also obvious from Fig.1 that impregnation ratio has effect on the efficiency of the activated carbon, with Local 1: 2 been the most efficient. These observations confirm the hypothesis that surface area affects adsorption positively (Bansode, 2002).

Fig. 1. ***MB Removal as a Function of adsorbent dose***

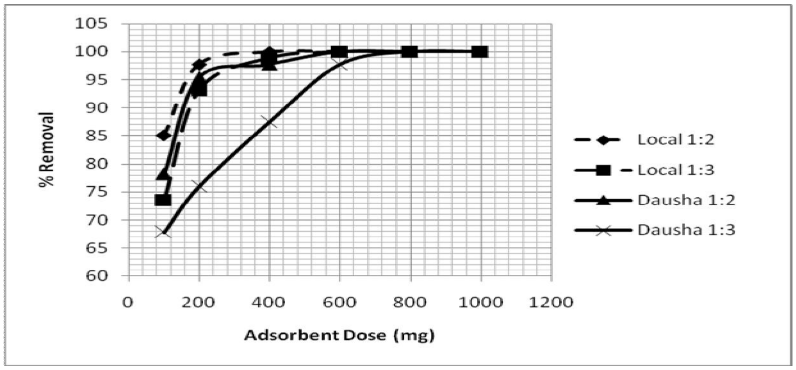


Fig. 2. MB Removal as a function of stirring rate

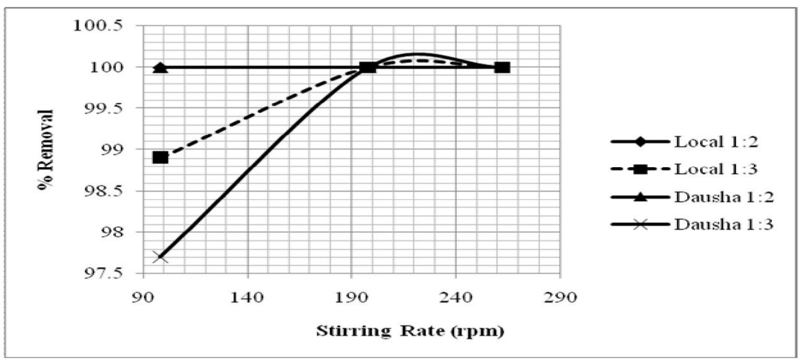


Fig.3. MB Removal as a function of Initial MB concentration

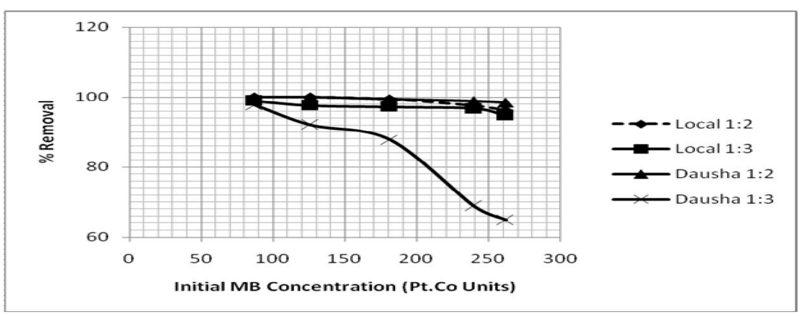
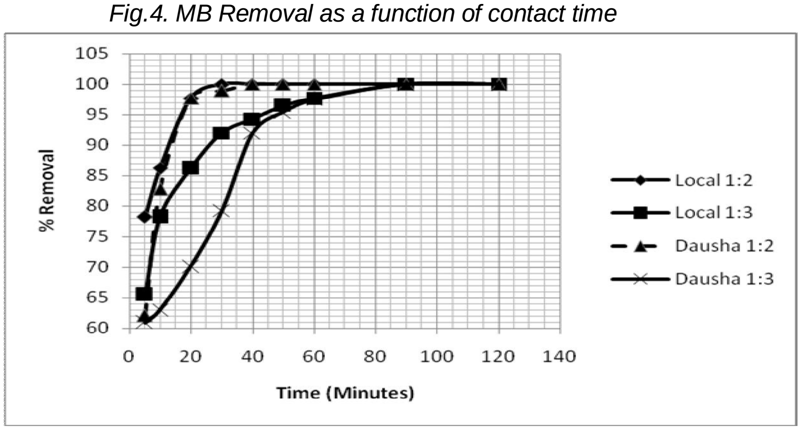


Fig.4. MB Removal as a function of contact time



Effect of stirring rate

The influence of stirring rate on the extent of MB adsorption is shown in Fig. 2. The figure reveals that MB removal is a function of stirring rate. It increases with the rate of stirring (see Dausha 1:3 and Local 1:3). In general there was less significant MB removal after applying 98 rpm and hence this speed was chosen as the optimum for further studies.

Effect of initial MB concentration

Studies on the effect of the initial adsorbate concentration were conducted by varying MB concentration from 87 Pt- Co units to 262 Pt- Co units. Carbon dose was 400mg and 600mg for Local and Dausha based carbons respectively. The initial pH was maintained at 7 and a stirring rate of 98rpm. Fig.3 indicates that Dausha1:3 consistently trailed behind the other activated carbons for all the initial MB concentrations investigated in terms of % removal. It is obvious from the figure that % removal decreased with increased in initial MB concentration.

All the carbons under study achieved at least 97.7 % removal at initial concentration of 87 Pt-Co units hence was chosen as the optimum initial concentration for further studies. This is probably due to the fact that for a fixed adsorbent dose, the total available adsorption sites are limited, thereby adsorbing almost the same amount of MB, a decrease in percentage of removal corresponding to an increase initial MB concentration was observed. Tembhurkar and Dongre, (2006) observed a similar trend for fluoride removal by some commercially available carbons.

Effect of contact time

Fig.4 shows the effect of contact time on the removal efficiency of MB by the 4 activated carbons. The studies were conducted by varying time from 5 to 120 minutes at the optimum carbon dose of 600mg and 400mg for Dausha and Local varieties respectively, stirring rate of 98rpm, initial MB concentrations of 87 Pt-Co units and pH of 7. As seen from Fig.4, 30 minutes is sufficient to achieve 100% MB removal efficiency for Local 1:2 while Dausha 1:2 require 40 minutes to achieve the same level of treatment; while Local 1:3 and Dausha 1:3 achieved 94.3% and 92% respectively within 40 minutes period. Because at least 90% MB removal was attained within 40 minutes by all the carbons, it was chosen as the optimum contact time for further studies.

Fig. 5. MB removal as a function of pH

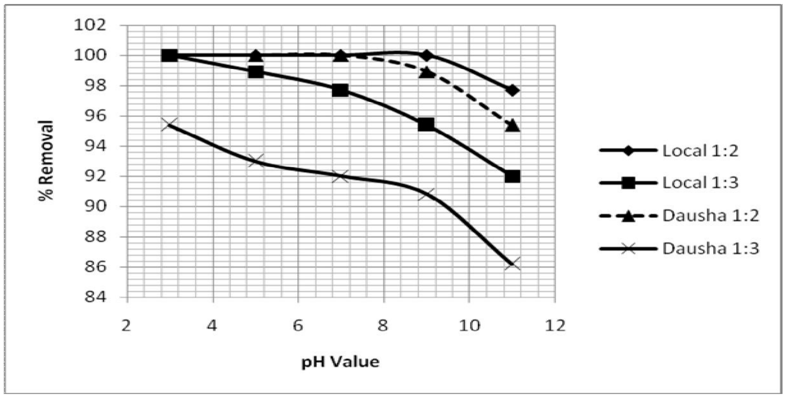
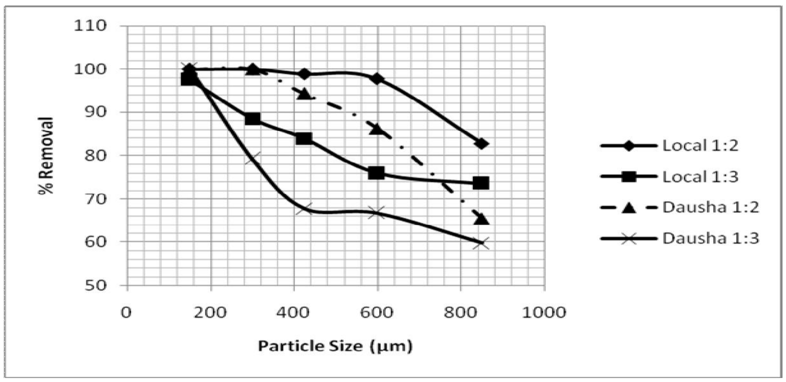


Fig.6. MB removal as a function of carbon particle size



In general, the removal efficiency increased with time and attained equilibrium in 40 minutes for Local 1:2 and Dausha 1:2, while it took 90 minutes to attain equilibrium for Local 1:3 and Dausha 1:3 at the same initial concentration of 87 pt co units. These observations indicate that Local 1:2 would require less residence time for complete removal of MB compared to the other activated carbon.

Effect of pH: Fig.5 presents the effect of initial pH on the removal of MB by the four activated carbons. It is evident from the figure that % removal efficiency decreased with increase in pH value. This implies that MB removal is pH dependant and is better at lower pH values (acidic-neutral pH). Considering Local 1:2 for instance, MB removal was 100% for pH range 3-9, but falls to 97.7 % at pH 11. The same trend was observed for the other carbons. Tembhurkar and Dongre (2006) reported that one of the reasons for better adsorption at low pH values may be attributed to the large number of H^+ present at these pH values which in turn neutralizes the negatively charged OH^- ions on adsorbed surfaces thereby reducing hindrance to the diffusion of MB molecules. Because the difference in % removal between pH 3 and pH 7 was not significant (≤ 3.4% for all activated carbons) the original solution pH of 7 was maintained for further studies.

Effect of Particle Size: The effect of particle size on the removal of MB is depicted in Fig 6. There is a general decrease in MB removal with increase in particle size. This is due to the decrease in surface area for adsorption as carbon diameter increases. Another explanation for this is the increase in the diffusion path occasioned by the larger diameter of particles. Diameter 150-300µm achieved 100% removal with local 1:2 and Dausha 1:2. The optimum conditions for the adsorption of MB from wastewater for the various carbons are summarised in Table 1.

Summary and conclusion

Activated carbons were produced from 2 varieties of mango seed shells by impregnation of the shells with $ZnCl_2$ before carbonisation and their performance evaluated through laboratory batch studies for the purpose of obtaining the optimum conditions for the removal of MB from wastewater. The results obtained revealed that Local 1:2 is a better adsorbent compared to Local 1:3, Dausha 1:2 and Dausha 1:3, given the highest % removal efficiencies for tests performed. The optimum carbon dose of Local 1:2 and Local 1:3 is 400mg while that of Dausha 1:2 and Dausha 1:3 is 600mg. This implies that less quantities of Local variety based AC are required to achieve about the same level of treatment as Dausha based AC. MB removal decreased with increase in initial MB concentrations for all the 4 activated carbons studied. In general all the carbons achieved at least 97.7% removal at initial MB concentration of 87 Pt-Co units and this was adopted as the optimum initial MB concentration.

Contact time of 30 minutes was sufficient for 100% removal of MB by Local 1:2 while Dausha 1:2 require 40 minutes to achieve 100% removal. This further confirms that Local 1:2 is more efficient in MB removal. The other carbons Dausha 1:3 and Local 1:3 trailed behind with 94.3% and 92% MB removal respectively. Therefore 40 minutes was adopted as the optimum contact time for MB removal. The optimum pH for MB removal was found to be 3. In general removal efficiencies were higher at acidic- slightly alkaline pH values (3-9). In terms of particle sizes, diameter 150µm carbon gave highest removal efficiencies for all the experimental carbons. Particle size range 150-425µm was adopted as the optimum particle size range. The optimum stirring rate of 98rpm was selected because the difference in removal efficiencies between

Table 1. Optimum conditions for adsorption of MB from wastewater

Variable	Optimum conditions			
	Dausha 1:2	Dausha 1:3	Local1:2	Local1:3
Adsorbent dose (mg)	600	600	400	400
Initial MB (Pt-Co unit)	87	87	87	87
Initial pH	3-7	3-7	3-7	3-7
Contact time (minutes)	40	40	30	40
Stirring rate (rpm)	98	98	98	98
Particle size (µm)	150-425	150-425	150-425	150-425

198rpm and 262rpm was not significant. It was therefore concluded that mango seed shells can be used for the removal of colour from wastewater. The most efficient carbon been that produced from Local with impregnation ratio of 1:2.

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