Short communication report

COMPARATIVE STUDIES ON ADSORPTION OF METHYLENE BLUE (MB) BY SAWDUST AND WALNUT SHELLS CARBON COATED WITH ZnO

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The use of charcoal dates backs to the prehistoric discovery of fire, however it was only in 1785 that it was found to decolourise tartanic acid and applied to the refinement of sugar in 1794 (OMRI 2002). The use of natural forms of activated carbon such as charred animal bone in refinement of sugar has been reported as far back as 1845 (OMRI 2002). Rudimentary as it was, charcoal functioned in basically the same manner for water purification then as does activated carbon today; namely, by adsorption of certain types of impurities (Walter 1973). The use of activated carbon in removing pollutants from water has become established and widespread. It is now used in municipal water treatment, pharmaceutical and food industries.

The Textile industry is in the forefront in the use of dyes in its operations (Garg *et al*. 2003) with more than 9,000 types of dyes incorporated in the colour index. Similarly, Kannan & Meenakshisundaram (2001) reported that more than 70000 tons of approximately 10000 different types of dyes and pigments are produced annually world wide, of which 20-30% are wasted in industrial effluents during dyeing and finishing processes in the textiles industries. The discharge of coloured waste is not only damaging the aesthetic nature of receiving streams, but is also toxic to the aquatic life (Kadirvelu *et al*. 2000). As a result of the low biodegradability of dyes, the conventional biological treatment process is not very effective in treating dye wastewater (Garg *et al*. 2003). Some of the physicochemical methods that have been employed to remove dye from wastewater include chemical precipitation, coagulation and oxidation. However these methods are not economical. According to McKay *et al*. (1979) as cited by Kadirvelu *et al.* (2000), adsorption seems to offer the best prospects over the other treatment techniques but it is expensive and difficult to source the materials required to prepare the activated carbon. Several source materials of agricultural origin have been converted to activated carbon in an attempt to reduce the cost of the commercially available ones. This investigation is aimed at examining the capacity and efficiency of dye removal from aqueous solution by activated carbon prepared from walnut shells and sawdust. The effects of initial dye concentration, contact time and carbon dosage are also assessed.

CPAC is a commercial powdered animal charcoal obtained from Fischer Limited while SDZ and WNSZ are sawdust and walnutshell carbon coated with ZnO respectively. The coating and activation was done as described by Abechi (2006). A stock solution of 500 ppm methylene blue was prepared by dissolving. 0.5 g methylene blue (MB) in 1 litre of distilled water. Serial dilutions were made to obtain various lower concentrations. 0.5 g of the WNSZ was agitaged in 50ml of various dye concentrations at varying times. The experiment was repeated with SDZ using 0.5g / 100 ml of the adsobate. The dosage of WNSZ was varied between 0.1 and 0.8 g and shaking was done at the predetermined contact time and optimum initial concentration. The experiment was repeated with SDZ at a dosage range of 0.01-0.2 g at the various initial concentration of the adsobate. The final absorbances of MB solutions were determined colourimetrically.

Contact time effects

The adsorption of MB by WNSZ and SDZ at various contact time is shown in Table 1.

The adsorption characteristics indicated a rapid uptake of the adsorbate. The adsorption rate however decreased to a constant value with increase in contact time. Similar results were reported by Garg *et al.* (2003) and Kardirvelu *et al.* (2000). The contact time for SDZ and WNSZ were observed to be 25 and 50 min respectively. The rate of adsorption was faster for SDZ compared to WNSZ.

Effects of initial concentration of dye

Tables 2 shows that the % dye removed decreased with increase in initial concentration of the dye for both SDZ and WNSZ and this may be due to lack of available active sites required for the high initial concentration of the dye. The % MB removed by SDZ decreased from 100-99.85 % while that of WNSZ fluctuate between 99.70 and 99.97 % and finally decreased to 98.80 %.

Effects of adsorbent dosage

The % MB adsorbed as the carbon dosage increases is shown in table 3. The % MB adsorption increased as the dose of the carbon increased. The % adsorption for SDZ increases from 95.5-97.8 % while that of WNSZ increases from 94.6-98.7 %.

Adsorption Isotherm

The constant parameters of the Freundlich and Langmuir isotherms are presented in Table 4.

The k_f value increases with the total adsorption capacity of the adsorbent whereas n value is a useful index of adsorption efficiency (Ribeiro *et al*. 2001). The 'n' values in the range of 0.26 to 0.55 were observed for the activated carbons, indicating a favourable adsorption process. The adsorption is more favourable when the value of n is smaller (Rozada *et al*. 2003). Ribeiro *et al*. (2001) reported n values ($0.39 \leq n \leq 0.62$) for chlorophylls adsorption and ($0.46 \leq n \leq 0.74$) for carotenoids adsorption onto activated carbons. The k_f values are in the range of 0.15-5.44.

TABLE 1: VARIATION OF % MB ADSORBED WITH CONTACT TIME.

Contact time mins)		5	10	15	20	25	30	40	50	60
% MB adsorbed	WNSZ	-	83.2	-	83.6	-	91.1	95.2	98.8	98.7
	SDZ	99.0	99.3	99.8	99.9	99.9	-	-	-	-

TABLE 2: EFFECT OF INITIAL CONCENTRATION (CI) ON MB ADSORPTION

WNSZ	Ci (ppm)	50	75	100	125	150
	% Removal	99.7	99.6	99.9	99.6	98.8
SDZ	Ci (ppm)	100	150	200	250	400
	% Removal	100	100	100	100	99.8

TABLE 3. EFFECTS OF ADSORBENT DOSAGE ON % MB ADSORBED

SDZ	Dosage (g/100ml)	0.01	0.02	0.05	0.1	0.2
	% MB adsorbed	95.5	95.8	96.0	96.1	97.8
WNSZ	Dosage (g/50ml)	0.1	0.2	0.4	0.6	0.8
	% MB adsorbed	94.6	95.6	97.4	98.3	98.7

TABLE 4: CONSTANT PARAMETERS OF THE ISOTHERMS

Carbon Type	**Langmuir Constants**				**Freundlich Constants**		
	Q_o	B	RL	R^2	K_f	N	R^2
CPAC	50,000,00	0.04	0.07	0.99	0.23	0.26	0.67
SDZ	10,000,00	1.00	0.01	0.94	0.15	0.26	0.67
WNSZ	2,500.00	0.40	0.20	0.98	5.44	0.55	0.54

The Q^o value for the activated carbons shows the order of monolayer adsorption capacities as CPAC>SDZ>WNSZ.

Results from these studies showed that % of dye removed decreases as the initial concentration of dye increases. It further showed a fluctuation in the % of MB removed by SDZ and WNSZ. The fluctuation may be as a result of desorption occurring along side adsorption. It is observed that though increase in initial dye concentration decreased the % adsorption, the actual amount of dye adsorbed increased with increase in the concentration of the dye in solution. This accorded well with the findings of Garg *et al.* (2003).

The effects of adsorbed dosage shows an increase in the % MB adsorbed as the dose of the carbon increased. This is as a result of increased surface area and availability of more adsorption sites. The trend compares with that reported by Selvi *et al.* (2001).

The observed correlation coefficient value R^2, for the two isotherms shows that the experimental data fitted better into the Lagmuir model than the Freundlich model. The K_f values range of 0.15-5.44 obtained in this study is similar to the values reported by Kannan and Meenashisundaram (2001) for Congo red adsorption by bamboo dust, coconutshell, groundnut shell and rice husk. The Q^o and b are the Langmuir constants which are a measure of the monolayer adsorption capacity and surface energy of adsorption respectively. The higher the value of Q^o and b, the more effective in terms of capacity of the adsorbent (Babarinde 2002). The superior performance of the CPAC is expected especially that it is in powdered form and therefore have greater surface area. However the SDZ and WNSZ have capacities values comparable to that reported for other activated carbon of agricultural bye-product origin. In all, the SDZ is a better adsorbent for MB than the WNSZ especially in terms of capacities and efficiency.

The lower n values and higher Q^0 values estimated for CPAC and SDZ indicates a superior performance of these adsorbent for MB adsorption from aqueous solution when compared to the WNSZ. The higher performance of the CPAC over SDZ may not be unconnected with the powdered nature of the CPAC. However, the SDZ and WNSZ are of the same particle size of 125 µm, thus SDZ tends to have greater pore volume and better performance than the WNSZ.

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