SORPTION OF METHELENE BLUE FROM AQUEOUS SOLUTION USING CARBON AND CHEMICALLY MODIFIED CARBON FROM PERIWINKLE SHELL

ABSTRACT

Carbonized periwinkle shell was modified by two types of activation: alkaline modification with 1 M NaOH and 1 M HNO_3*. The three carbon samples thus produced were tested for the removal of methylene blue from solution. This test was carried out to provide a cheap and readily available sorbent. Chemical treatment of the sample was aimed at increasing surface functional groups. The alkaline modified sample introduced more hydroxyl group to the sample, while the* HNO_3 *modified produced less OH group. The amount of adsorbate removed was shown to be pH dependent with the three samples performing best at higher pH values of 9. Optimum adsorption was achieved at an adsorbent dose of 2g. The isotherm data obeyed the Langmuir model and first order kinetics. The maximum removal of dye at 2g of adsorbent dosage for 2hrs was 56.8% and 34.4% for the alkaline, unmodified and acid samples.*

1.0 INTRODUCTION

The Federal Government of Nigeria has a new policy of encouraging local industries in the manufacture of products within the country instead of importation. In this regard a ban was imposed on the importation of some products. Chief amongst them is textile product. The policy is geared into strengthening the local economy, but inevitably as with many industrial activities pollution becomes a significant factor. Many industries uses dyes and pigments to colour their products, a number of these becomes constituents of the industries waste; which could be hazardous to the environment if not adequately managed [1].

Textile and refining industries produce effluents of wide varieties, amongst which are various inorganic compounds, polymers and heavy metals such as Cr, Ni, Cu these chemical substances are present in textile effluents as coloured compounds, dissolved or suspended solids. Since decolorization of textile effluents does not occur when treated aerobically by municipal sewage systems, adsorption on solid surfaces incorporated to such systems will improve the efficiency of treatment [2]. Among the dye classification, the basic and diazo direct dyes are known to have the highest rates of toxicity (LD_{50} values are found to be greater than 2×10^{23} mg/kg). The removal of basic dyes such as methylene blue by adsorption by low cost adsorbents have been studied by many researchers [3],[4].

2.0 MATERIAL AND METHOD

2.1 WITH NITRIC ACID

The dried activated carbon was soaked I a beaker with 1M dilute nitric acid solution. The oxidation was carried out for 24 hrs. the oxidized carbon was washed with distilled water to remove residual acid and was sun dried for 4 hrs. the same method was used for alkaline activation.

2.2 DETERMINATION OF SURFACE FUNCTIONAL GROUP BY INFRARED

The spectra of the carbon samples were recorded using KBr disc in conjunction with a Pekin-Elmer infrared spectrophotometer. KBr disc were prepared by mixing a given sample of KBr crystals, the resulting mixture being ground to a fine powder and heated for 1 hr at 373K. Finally, the mixture was pressed into a KBr disc under vacuum conditions and used as such for IR studies.

2.3 CALIBRATION EXPERIMENT

Concentration of 0ppm, 2ppm, 4ppm, 8ppm, 10ppm were prepared from the stock solution. The absorbencies were taken without adding the carbon, absorbance was taken at 665 nm.

2.4 POINT ZERO CHARGE

50ml 0,01M sodium chloride was placed in a closed flask. The pH was adjusted to values of 4.64, 6, 6.33, 8.00, 10 and 11.80 by adding 0.1M hydrogen chloride or 0.1M sodium hydroxide solutions. Then 0.15g of each sample was added to 50ml at each pH and the final pH taken after 48hrs under agitation at room temperature. (150rpm)

2.5 EFFECTS OF ADSORBENT DOSE ON METHYLENE BLUE UPTAKE FROM SOLUTION

A concentration of 100mg/dm^3 was prepared from the stock solution. Masses of 0.5, 1, 1.5, and 2g of the carbon were added to 25ml of the solution. The solutions were agitated for 6hrs at 150rpm with the absorbancies taken thereafter.

2.6 EFFECT OF PH ON METHYLENE BLUE UPTAKE FROM SOLUTION

A concentration of 100mg/dm^3 was prepared from the stock solution. A constant mass of 2g was added to 25ml of the solution at pH of 3, 4, 5, 7 and 9. The samples were agitated for 6hrs at 150rpm with the absorbencies taken thereafter, pH corrections was done using dilute HCl and NaOH

2.7 EFFECT OF INITIAL CONCENTRATION ON ADSORPTION KINETICS

2g of each sample was added to 100ml concentration of 100mg/dm^3, at pH 7 and stirred with a magnetic stirrer, 5ml was withdrawn with syringe at intervals of 0, 30, 60, 90, 120mins respectively. Their various absorbencies were then taken.

2.8 ADSORPTION ISOTHERM

Adsorption isotherm was carried out at concentrations of 100mg/dm^3. 2g of each sample was put into 25ml of each concentration. It was then shaken briefly and allowed to stand for two days after which the solution is filtered and absorbance taken.

3.0 RESULT AND DISCUSSION

3.1 DETERMINATION OF SURFACE ACIDIC GROUPS BY INFRARED SPECTROSCOPY

Untreated Carbon

The spectrograph of the untreated sample shows that it contains OH group at 3444.7cm^{-1}, carbony group at 1680.1cm^{-1} aldehyde groups at 2745.3cm^{-1} and 2876.6cm^{-1}, alkyl group at 1427.2cm^{-1}.

Modified carbon; alkaline modification

The spectrograph fig. 1 shows a peak 3460cm^{-1} is a hydrogen bonded OH stretch and the peak at 3638.7cm^{-1} which is sharp indicates a high concentration of -OH functional group. The medium band at 2513.3cm^{-1} represents an aldehyde group and the peak at 1804.8cm^{-1} represents C = O of aldehydes. The peak at 1644.1cm^{-1} is the C = C stretch of alkenes.

3.2 HNO_3 MODIFICATION OF ACTIVATED CARBON

There was less increase sensitivity of the -OH group as compared to that of alkaline activation. The band at 1694.6cm^{-1} is a C = O stretch which corresponds to the wavelength of absorbance of amide group $RCONH_2$

3.3 POINT ZERO CHARGE

Experimental results of the pH_{pzc} (pH of the point zero charge) determination are illustrated in table 1 below. They are given as the pH values of filtered solutions after equilibrium (pH_f) of solution. Taking values from where they cut the x-axis which is their point of electro-neutrality it is shown that the pH_{pzc} of the unmodified carbon, alkaline modified carbon and HNO_3 modified carbon, 8.88, 8.91 and 8.83 respectively.

POINT ZERO CHARGE AT 100mg/dm^3

Table 1 Unmodified activated carbon

Initial pH	Final pH	Change in pH
4.64	8.62	4.00
6.00	8.71	2.75
6.33	8.83	2.44
8.00	8.87	0.85
10.00	8.96	-1.05
11.80	9.44	-2.4

Table 2 Modified alkaline activated carbon

Initial pH	Final pH	Change in pH
4.64	8.64	3.98
6.00	8.74	2.71
6.33	8.77	2.50
8.00	8.85	0.87
10.00	8.95	-1.04
11.80	9.40	-2.36

Table 3 HNO_3 modified activated carbon

Initial pH	Final pH	Change in pH
4.64	8.42	3.78
6.00	8.56	2.56
6.33	8.65	2.32
8.00	8.74	0.74
10.00	8.95	-1.05
11.80	9.59	-2.21

3.4 EFFECT OF SORBENT DOSE ON THE SORPTION OF METHYLENE BLUE UNTO ACTIVATED CARBON WITH 100mg/dm^3 AQUEOUS SOLUTION OF METHYLENE BLUE

The effect of absorbent mass on the rate of uptake was studied with other conditions remaining constant with concentration of 100mg/dm3 of the aqueous solution of methylene blue shows a decrease in absorbance, from 0.5g – 2g in table 4 – 6 for each carbon sample indicating an increase in the removal of methylene blue from aqueous solutions with increase in adsorbent mass due to presence of more site for adsorption as the mass increase.

Comparison between the three samples viz, the modified alkaline and acid modification shows a better adsorption with the alkaline as compared to that of the unmodified and acidic adsorbent. This could be due to increase of negative charges on the surface of the adsorbent, for the alkaline modified activated carbon 2g of activated carbon showed a better performance as compared to others. It was shown in the determination of the effect of pH on the adsorption efficiency of the adsorbent.

Table 4 Effect of Aqueous NaOH modified carbon with percentage dye removed

Mass(g)	Absorbance	Equilibrium conc (mg/dm3)	Amount adsorbed (mg/g)	% Dye removed
0.50	6.96	55.20	2.24	44.8
1.00	6.40	50.80	1.23	49.2
1.50	5.72	45.40	0.91	54.6
2.00	5.44	43.20	0.71	56.8

Table 5 Effect of HNO3 activated adsorbent dosage on percentage dye removed

Mass(g)	Absorbance	Equilibrium conc (mg/dm3)	Amount adsorbed (mg/g)	% Dye removed
0.50	0.24	61.40	1.93	38.60
1.00	0.12	60.80	0.98	39.20
1.50	0.10	55.20	0.78	46.80
2,00	0.08	52.00	0.60	48.00

Table 6 Effect of unmodified adsorbent dosage on percentage dye removed

Mass(g)	Absorbance	Equilibrium conc (mg/dm3)	Amount adsorbed (mg/g)	% Dye removed
0.50	0.21	67.20	1.64	32.80
1.00	0.11	66.40	0.84	33.60
1.50	0.07	66.40	0.56	33.60
2.00	0.05	65.60	0.43	34.40

3.5 EFFECT OF pH ON SORPTION OF METHYLENE BLUE UNTO ACTIVATED CARBON AT 100mg/dm3

The pH value of the solution was an important controlling parameter in the adsorption process, and the initial pH value of the solution has more influence than the final pH. The amount of methylene blue absorbed at 100mg/dm3 initial concentration was minimum at initial pH 3, then increased and remained nearly constant over the initial pH range from 7 – 9. The amount of methylene blue adsorbed was not seriously altered from pH 7 – 9. Hence pH 7 was chosen for study of contact time. The amount of dye adsorbed on the carbon samples as a function of 100mg/dm^3 of dye addition is shown in tables 7 – 9. there was a sharp increase in amount adsorbed for the alkaline treated carbon as compared with the others from pH 3 – 6. The other samples did not show such sharp increase although adsorption increased. This result thus shows that pH is essential in providing favourable adsorbent surface change for adsorption to occur. As the pH of a dye solution increase, the association of dye cations with more negatively charged carbon could more easily take place.

EFFECT OF pH ON SORPTION OF METHYLENE BLUE

Table 7 Effect of pH on methylene blue adsorption by using (2g) of alkaline modified carbon

pH	Absorbance	Equilibrium conc. (mg/dm3)	Amount adsorbed (mg/g)	% Dye removed
3	10.99	87.20	0.16	12.80
4	6.40	56.80	0.54	43.20
6	2.11	16.84	1.04	83.20
7	1.31	10.40	1.12	89.60
9	1.31	10.40	1.12	89.60

Table 8 Effect of pH on methylene blue adsorption by using (2g) of HNO_3 modified carbon

pH	Absorbance	Equivalent conc. (mg/dm3)	Amount adsorbed (mg/g)	% Dye removed
3	12.50	99.20	0.01	0.80
4	11.49	91.20	0.11	8.80
6	9.48	75.20	0.31	24.80
7	8.47	67.20	0.41	32.80
9	7.96	63.20	0.46	36.80

Table 9 Effect of pH on methylene blue adsorption by using (2g) of HNO_3 modified carbon

pH	Absorbance	Equivalent conc. (mg/dm3)	Amount adsorbed (mg/g)	% Dye removed
3	12.30	97.60	0.03	2.40
4	10.53	85.60	0.18	14.40
6	7.36	58.40	0.52	41.60
7	6.45	51.20	0.61	48.20
9	6.05	48.00	0.65	52.00

3.6 EFFECT OF CONTACT TIME

It can be observed from table 10 – 12 that uptake increased with time and at some point in time reached an almost constant value where no more dye is removed from the solution. At this point, the amount of dye being adsorbed onto the adsorbent is in a state of dynamic equilibrium with the amount of dye desorbed from the adsorbent. The time required to attain this state of equilibrium was termed the equilibrium time and the amount of dye adsorbed at the equilibrium time reflected the equilibrium dye adsorption capacity of adsorbent under these particular conditions. The result showed that the equilibrium states were attained at 210mins. for the alkaline treated carbon, 210mins, for the acid treated and 210mins for the untreated samples respectively. The maximum amount of dyes adsorbed at the different times were 1.20, 0.79, 1.09mg/g respectively. The study showed that treatment of the activated carbon had no effect on the time to reach equilibrium.

Table 10 Effect of contact time on methylene blue adsorption at 100mg/dm^3 for alkaline modified carbon

Time (mins)	Absorbance	Equilibrium conc. (mg/dm3)	Amount adsorbed (mg/g)	% Dye removed
0	0	0	0	0
30	5.54	44.00	0.70	56.00
60	3.23	25.60	0.93	74.40
90	2.12	16.80	1.04	83.20
120	1.51	12.00	1.10	88.00
150	0.91	7.20	1.16	92.80
180	0.61	4.80	1.19	95.20
210	0.50	4.00	1.20	96.00
240	0.30	2.40	1.22	97.60
270	0.20	1.60	1.23	98.40
300	0.20	1.60	1.23	98.40

Table 11 Effect of contact time on methylene blue adsorption at 100mg/dm^3 for HNO_3 modified carbon

Time (mins)	Absorbance	Equilibrium conc. (mg/dm3)	Amount adsorbed (mg/g)	% Dye removed
0	0	0	0	0
30	10.28	81.60	0.23	18.40

60	7.76	1.60	0.48	38.40
90	6.45	51.20	0.01	48.80
120	5.65	44.80	0.69	55.20
150	5.04	40.00	0.75	60.00
180	4.84	30.40	0.77	1.60
210	6.64	36.80	0.79	63.20
240	4.54	36.00	0.80	64.00
270	4.44	35.20	0.81	64.80
300	4.33	34.40	0.82	65.60

Table 12 Effect of contact time on methylene blue adsorption at 100mg/dm^3 for unmodified carbon

Time (mins)	Absorbance	Equilibrium conc. (mg/dm3)	Amount adsorbed (mg/g)	% Dye removed
0	0	0	0	0
30	7.36	58.4	0.52	41.60
60	4.13	32.80	0.84	67.20
90	2.62	20.80	0.99	79.20
120	1.36	16.80	1.04	83.20
150	1.81	14.40	1.07	85.60
180	1.71	13.60	1.08	86.40
210	1.61	12.8	1.09	87.20
240	1.51	12.0	1.10	88.00
270	1.41	11.2	1.11	88.80
300	1.31	10.4	1.12	89.60

Table 13 Equilibrium study of NaOH modified carbon at 100mg/dm^3 concentration of methylene blue

Time (mins)	Equivalent conc. (mg/dm3) (x)	Log (a - x)
0	0	0
30	19.05	1.9082
60	16.52	1.9216

90	12.88	1.9401
120	9.95	1.9545
150	7.20	1.9675
180	4.80	1.9786
210	2.43	1.9893
240	2.40	1.9985

Table 14 Equilibrium study of unmodified carbon at 100mg/dm^3 concentration of methylene blue

Time (mins)	Equivalent conc. (mg/dm3) (x)	Log (a - x)
0	0	0
30	20.37	1.8991
60	19.20	1.9074
90	17.24	1.9169
120	16.23	1.9231
150	14.79	1.9305
180	13.60	1.9365
210	12.60	1.9415
240	11.61	1.9464

Table 15 Kinetics of acid modified carbon at 100mg/dm^3 concentration of methylene blue

Time (mins)	Equivalent conc. (mg/dm3) (x)	Log (a - x)
0	0	0
30	60.66	1.5948
60	56.92	1.6343
90	51.20	1.6884
120	44.80	1.7419

150	40.00	1.7782
180	36.96	1.7996
210	32.28	1.8307
240	26.51	1.8662

3.7 EQUILIBRIUM STUDY

The analysis of the isotherm data is important to develop an equation, which accurately represents the results and could be used for the design purpose. In order to investigate the sorption isotherm, two models were analyzed: the Langmuir and the Freundlich [31], the Langmuir is perhaps the best known of all the isotherms describing sorption. The theoretical Langmuir isotherm is often used to describe sorption of a solute from a liquid solution as:

$$q_c=\frac{qm\ ka\ ca}{1+kaCc} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2.8$$

The constants q_m and k_a are the characteristics of the Langmuir equation and can be determined from a linearized form of equation 2.8 represented by.

$$\frac{Cc}{qc}=\frac{1}{qmka}+\frac{Cc}{qm}$$

Where C_c is the equilibrium concentration (mg/dm3); q_c the amount of methylene blue sorbed (mg/g), k_a is sorption equilibrium constant (dm^3/mg)

CONCLUSION

The activated carbon from periwinkle shell showed appreciable sensitivity towards modification especially for the alkaline modification. There was a slight increase in the amount of surface charge as a result of chemical treatment. Despite this fact, the unmodified sample performed better due to low positive charges on the surface as compared to that of acid activated sample.

The peaks in the spectrograph showed the presence of alkyl. Aldehyde, hydroxyl groups. There was increase in percentage removal with increase in sorbent dose due to more reactive sites but a decrease in amount absorbed per unit mass. The adsorption was pH dependent with adsorption increasing with increase in pH for the three samples. The kinetics and isotherm fitted well into both first-order kinetics and their Langmuir isotherm respectively.

From the observation, it is seen that carbonized periwinkle shell, modified or unmodified produce a significant removal of methylene blue from aqueous solution, Hence it can serve as a good, cheap and readily available alternative for adsorbing dyes from textile effluents.

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