Adsorptive Removal of Methylene Blue Using Groundnut Shell Activated Carbon Coated With Fe_2O_3

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Abstract: *In this work, activated carbon prepared from groundnut shells (GSAC) by sulphuric acid treatment was coated with Fe_3O_4(GSAC- Fe_3O_4) and tested for its efficiency as an adsorbentfor the removal of methylene blue (MB) dye from aqueous solution. The structural morphology and functional groups present were investigated using scanning electron microscope (SEM) and Fourier transform infrared (FTIR) spectroscopy. Various sorption parameters such as effect of pH, contact time, initial dye concentration and adsorbent dosage were studied. The percentage removal of methylene blue increased with decrease in initial methylene blue concentration and increased with increase in contact time and dose of the adsorbent. Equilibrium data were analysed using Langmuir and Freundlich isotherm models. Kinetic data were studied using pseudo-first order and pseudo-second order kinetic models.*

Keywords: *GSAC, GSAC- Fe_3O_4, MB, Isotherm, Kinetics.*

I. Introduction

Many industries such as paper, plastics, cosmetics, detergents, leather, pharmaceutical and food industries make extensive use of dye stuffs in their production processes. These industries are continuously discharging effluents containing dyes and their breakdown products which are toxic to living organisms into the ecosystem [1-2]. These dyes are visually detected even at low concentration and can significantly affect photosynthetic activity in aquatic life due to reduced light penetration [3]. Therefore, decolourisation of dyes is an important aspect of wastewater treatment before discharge [4].

Several treatment methods such as biological, chemical and physiochemical are used for the removal of dyes from wastewater, but most of these methods have serious restrictions such as formation of hazardous by-products, intensive energy requirement or high cost [5]. Adsorption onto activated carbon is one of the most effective and efficient treatment techniques for the removal of dyes from wastewater, but commercially produced activated carbon is expensive[6].Nowadays, many novel materials, mostly agricultural waste such as rice husk, pineapple peel, sawdust, yam fibre, maize cobs, coconut shell, neem leaf, mango seed carnal, vegetable waste, banana peeletc[31-37]. are been tested as adsorbents with the sole aim of finding much cheaper alternatives to activated carbon, but the adsorption capacities of some of the mentioned adsorbents is not very high. Hence, research trend is now geared towards improving the performance of these adsorbents using several modification methods[7-12].

In this present study, groundnut shell activated carbon coated with Fe_3O_4 was tested as adsorbent for removal of methylene blue from aqueous solution.

II. Materials And Methods

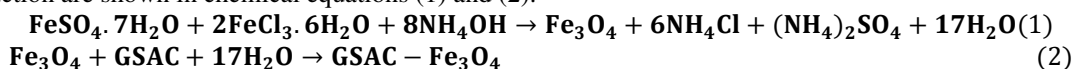### 2.1 Preparation of Stock Solution of Methylene Blue Dye

Methylene Blue dye [C.I. = 52015B; Chemical Formula = $C_6H_{18}ClN_3S$; Molecular Weight = 373.91g; Melting Point = 100 – 110°C and λ_{max} = 660nm] supplied by Avra Synthesis Pvt., Hyderabad, India was used as adsorbate without purification. A stock solution of 1000mg/L MB dye was prepared by dissolving the appropriate amount of methylene blue in double distilled water. Experimental solutions of desired concentrations were obtained by dilution of stock solution using double distilled water.

2.2 Preparation of Groundnut Shell Activated Carbon (GSAC)

Groundnut shells were obtained from shelling units. These shells were washed with deionized water and dried in hot air oven at 120°C for 3 hours and then grounded into fine particles for easy activation. The activation was carried out in a beaker by soaking thoroughly 100g of the dried sludge in 100ml of concentrated sulphuric acid and heated to 200°C with continuous agitation for 1 hour. After, agitation was then stopped and the mixture started to solidify producing a carbon like material. The resulting carbon was then allowed to cool to room temperature, washed with distilled water, soaked in dilute NaOH solution for 30 minutes and again washed with distilled water. The product was allowed to dry, sieved through 100μm sieve and stored in a closed container, ready for use.

2.3 Preparation of Groundnut Shell Activated Carbon Coated Fe$_3$O$_4$ (GSAC- Fe$_3$O$_4$)

Chemical precipitation technique was employed here [13]. In this process, 2.1g of FeSO$_4$.7H$_2$O and 3.1g of FeCl$_3$.6H$_2$O were dissolved under inert atmosphere in 80ml of double distilled water with vigorous stirring using a mechanical stirrer. While the solution was heated to 80°C, 10ml of NH$_4$OH solution (25%) was added. To ensure complete growth, 10g of the prepared groundnut shell activated carbon was added and reaction continued for 30 minutes. The resulting suspension was cooled down to room temperature and then repeatedly washed with distilled water to remove unreacted chemicals. The product was dried in an oven at 50°C for 2h, tested using a magnetic rod and then stored in a closed container ready for use. The reactions that occur in the production are shown in chemical equations (1) and (2).

$$FeSO_4.7H_2O + 2FeCl_3.6H_2O + 8NH_4OH \rightarrow Fe_3O_4 + 6NH_4Cl + (NH_4)_2SO_4 + 17H_2O \quad (1)$$
$$Fe_3O_4 + GSAC + 17H_2O \rightarrow GSAC - Fe_3O_4 \quad (2)$$

2.4 Adsorption Experiments

All adsorption experiments were carried out by batch techniques at room temperature on a mechanical shaker at 150rpm using 250ml capped conical flasks. The influence of pH (3, 5, 7, 9 and 11) was varied by adding 0.1M NaOH or 0.1M HCl for adjustment and measured using a pH meter (Systronics made), adsorbent dosage (0.1, 0.2, 0.3, 0.4 and 0.5g), initial methylene blue concentration (50, 100, 150, 200 and 300mg/L) and contact time (10, 30, 60, 90 and 120min) on the performance of GSAC-Fe$_3$O$_4$ were evaluated. After the adsorption process, the contents were filtered using a whatman filter paper no. 42 and the supernatant solution was analysed using a UV-visible spectrophotometer (Elico Model No: SL210) by recording the absorbance changes at wavelength of 660nm. The amount of MB dye adsorbed per unit weight of GSAC- Fe$_3$O$_4$ adsorbent at time 't', q$_t$(mg/L) and percentage MB dye adsorption capacity was calculated using equations (3) and (4):

$$\text{Amount of MB adsorbed } (q_t) = \frac{V(C_o - C_t)}{m} \quad (3)$$

$$\text{Percentage removal of MB} = \frac{C_o - C_t}{C_t} \times 100 \quad (4)$$

Where C$_o$, is the initial MB dye concentration (mg/L), C$_t$ is the concentration of MB dye at any time t, V is the volume of solution (ml) and m is the mass of GSAC-Fe$_3$O$_4$(gm).

III. Results And Discussion

3.1 Characterisation of Adsorbent

3.1.1 FTIR Characterisation

Fourier transform infrared spectroscopy of the adsorbent was done by using an FTIR spectrophotometer (model: FTIR Bruker IFS 66V). The FTIR spectra of GSAC, GSAC-Fe$_3$O$_4$ and GSAC-Fe$_3$O$_4$-MB were recorded in the range of 4000cm^{-1} to 400cm^{-1} using KBr disc for reference. The essence is to ascertain the possible involvement of functional groups on the surface of GSAC when coated with Fe$_3$O$_4$ and in adsorption of MB. Figure 2(a) shows the spectrum of GSAC. Several number of absorption peaks were displayed indication the complex nature of GSAC. The band at 3412cm^{-1} is due to bonded -OH groups [14]. The band observed at 2928cm^{-1} could be assigned to the aliphatic C-H group. The trough at 1621cm^{-1} represents the C=O stretching mode conjugate with the NH$_2$ [15-16]. The 1208cm^{-1} band was attributed to the vibration of C-O in lignose; and the 1031cm^{-1} band was attributed to the stretching vibrations of C-O in cellulose and hemicellulose [17-19]. When comparing the spectra in figure 2(a) and (b), various functional groups were detected on the surface of the GSAC-Fe$_3$O$_4$ as shown in figure 2(b). An obvious observation also, was the shifting, disappearance or appearance of new peaks. Most importantly, the newer peak observed at 589cm^{-1} is related to Fe-O group, and the peak around 3432cm^{-1} was assigned to the –OH group on the surface of the magnetite. Figure 2(c) shows the FTIR spectrum after the adsorption of MB onto GSAC-Fe$_3$O$_4$. When comparing figure 2(b) and (c), figure 2(c) reveals that some new peaks appeared, some remained and some were shifted after MB adsorption. The bands at 3432cm^{-1}, 2925cm^{-1}, 1631cm^{-1}, 1402cm^{-1} and 589cm^{-1} were shifted to 3417cm^{-1}, 2924cm^{-1}, 1596cm^{-1}, 1385cm^{-1} and 584cm^{-1} after MB adsorption. This is an indication that OH, C-H, C=O and Fe-O groups could be involved in the adsorption of MB onto GSAC-Fe$_3$O$_4$.
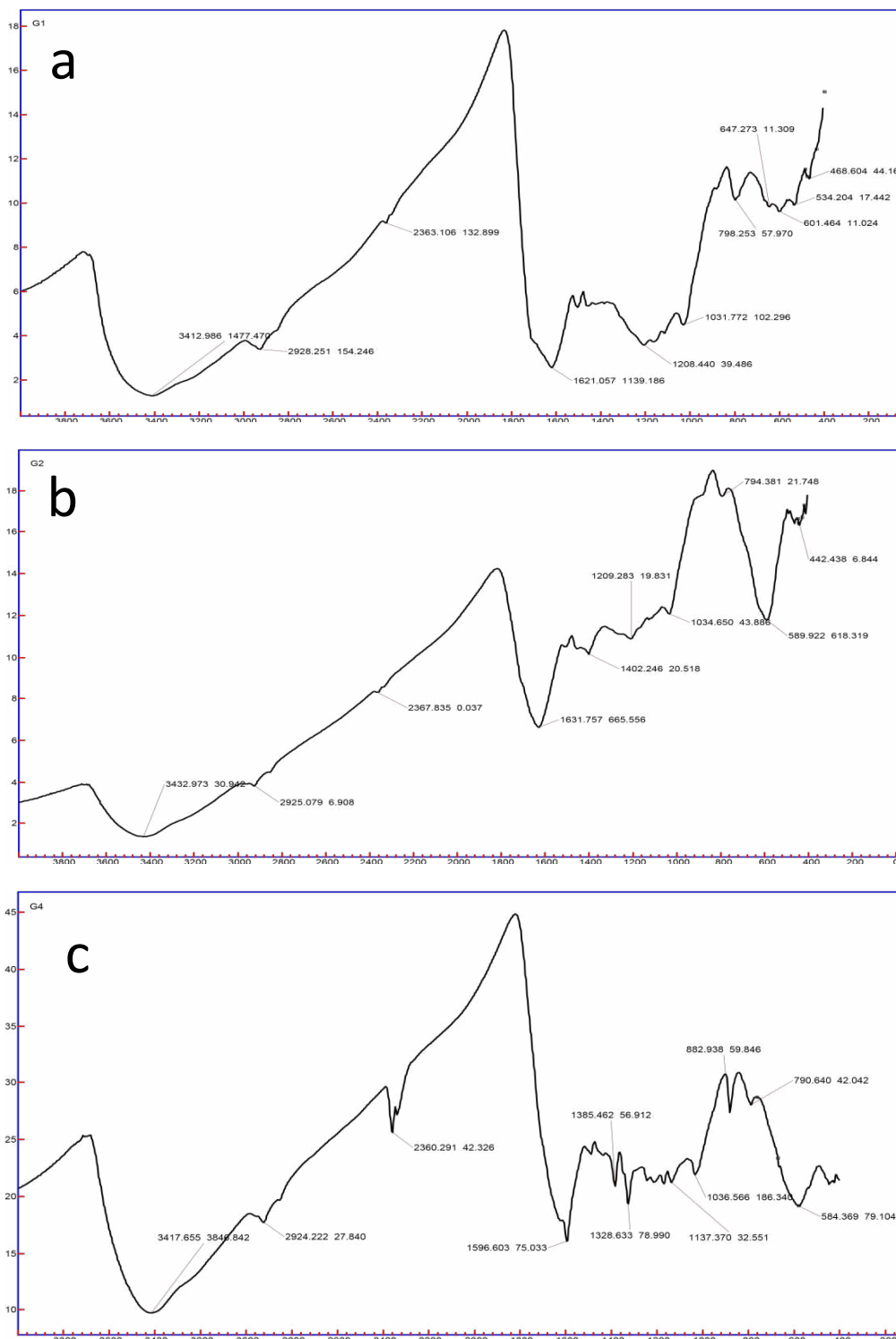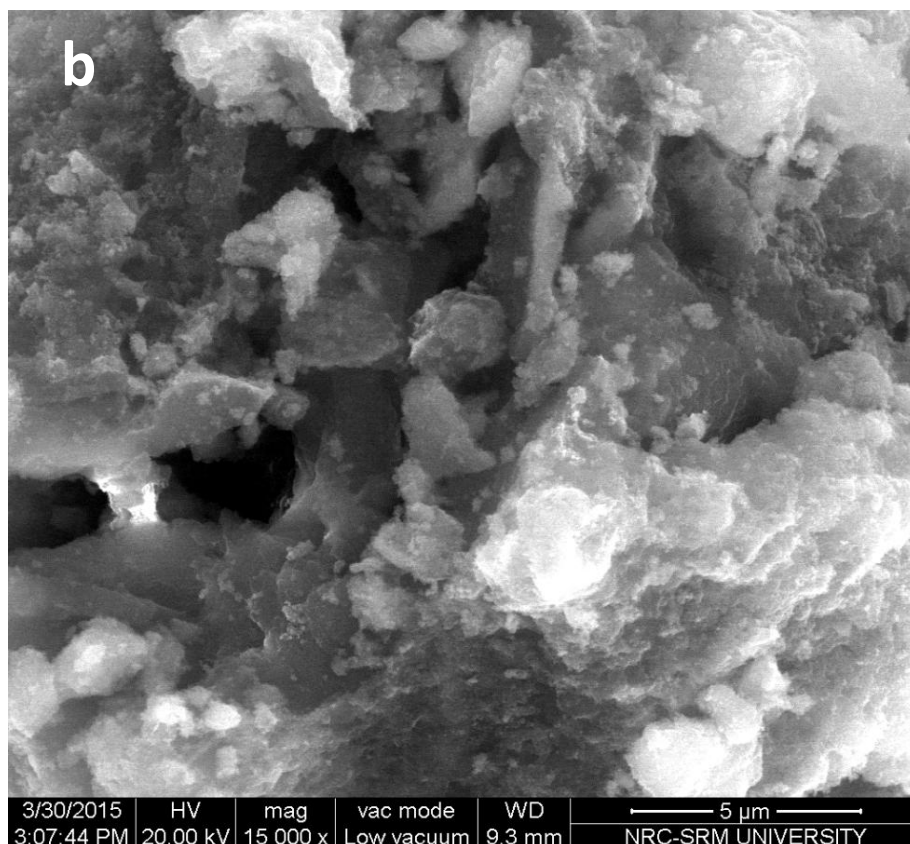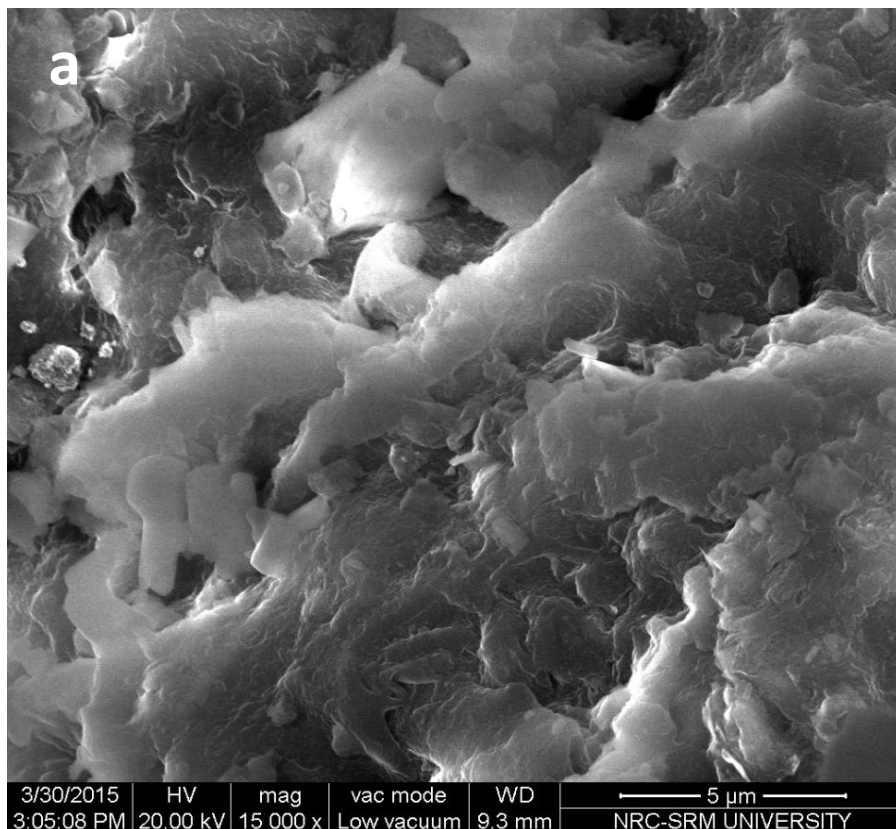
Figure 2. FTIR image of (a) GSAC, (b) GSAC- Fe_3O_4, and (c) GSAC- Fe_3O_4-MB

3.1.2 SEM Characterisation

Surface morphology of GSAC, GSAC-Fe_3O_4 and GSAC-Fe_3O_4-MB was visualised using Scanning Electron Microscopy (SEM).Measurements were taken using SEM-Quanta. The images were taken with an emission current of 100µÅ by the Tungsten filament at a magnification of 15000xand an accelerator voltage of 20kV. Figure 3(a), (b) and (c) shows the SEM micrographs of GSAC, GSAC-Fe_3O_4 and GSAC-Fe_3O_4-MB. The GSAC exhibits heterogeneous rough, dense and uneven surface morphology with a series of overlaps as shown in fig. 3(a). Fig. 3(b) shows the parent GSAC covered with Fe_3O_4. The surface of the dye loaded GSAC-Fe_3O_4 in fig. 3(c) shows the surface of GSAC-Fe_3O_4 covered with dye molecules.
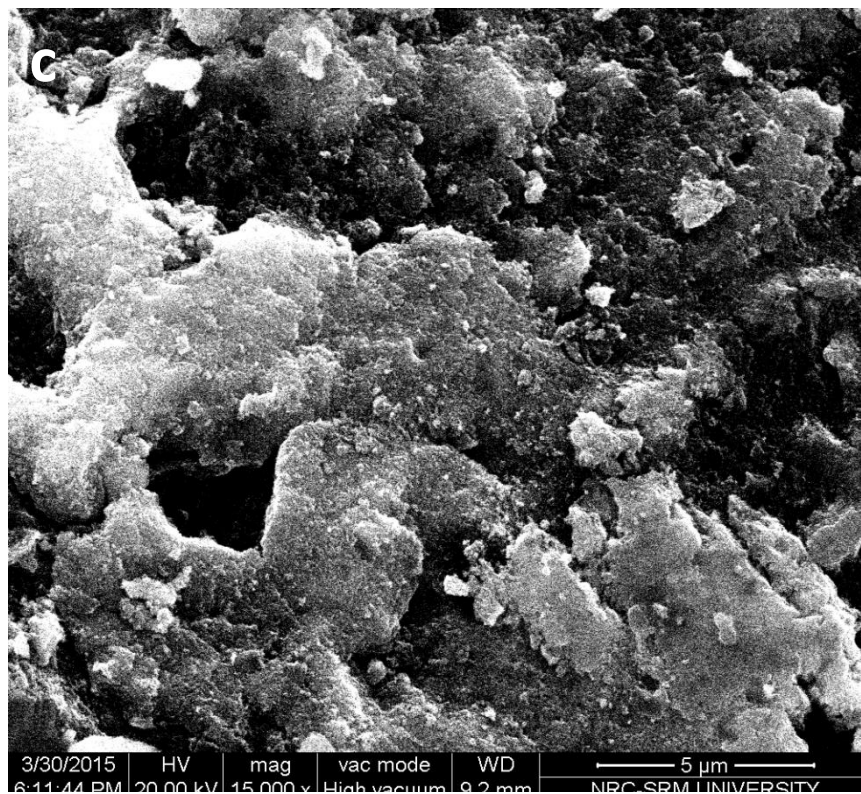
Figure 3. SEM image of (a) GSAC, (b) GSAC-Fe$_3$O$_4$, and (c) GSAC-Fe$_3$O$_4$-MB

3.2 Effect of pH

pH of the solution is a paramount controlling factor throughout the adsorption process, particularly on the adsorption capacity. The pH was determined at room temperature using a portable pH meter (systronics made) and calibrated using 4.0 buffer tablet. In this experiment,pH values were adjusted from 3-11 using dilute solutions of hydrochloric acid and sodium hydroxide.Firstly, methylene blue dye is a cationic dye andas shown in figure 3, dye uptake was found to be increasing with increase in pH. Low uptake at lower pH has been attributed to the fact that the surface charge of GSAC-Fe$_3$O$_4$ may be positive, and hence hydrogen ions (H$^+$) compete with methylene blue (cationic dye) for adsorption sites in the adsorbent. However, at higher pH, the situation was otherwise, as a significant higher uptake was recorded. This may be attributed to the fact that the surface charge of GSAC-Fe$_3$O$_4$ may be negative, and hence may be able to bind with the methylene blue (cationic dye) through electrostatic force of attraction.
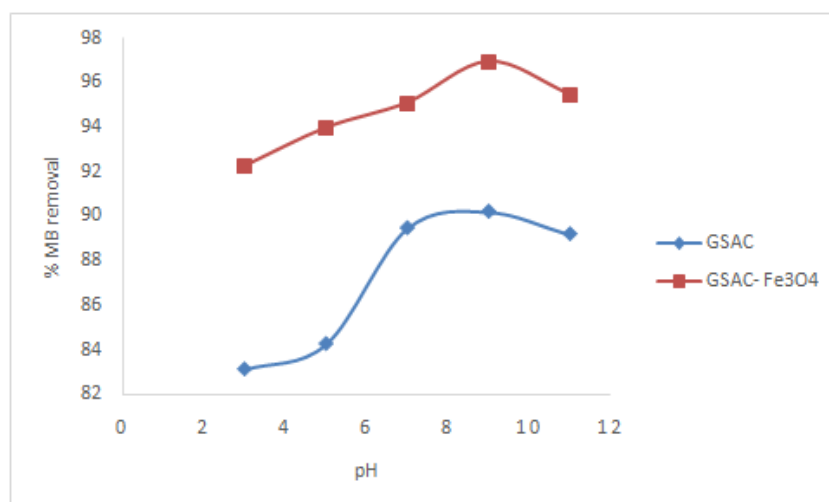

Figure 3. Effect of initial solution pH on the % removal of MB

3.3 Effect of Initial Adsorbent Dosage

Another parameter that is being used to assess the adsorption capacity of an adsorbent is the solid/solution ratio. In this experiment, the adsorption of methylene blue dye onto GSAC-Fe$_3$O$_4$ was studied by varying the GSAC-Fe$_3$O$_4$ dose (0.1 – 0.5g/50ml) for methylene blue dye concentration of 100mgL^{-1} at room temperature without changing the initial pH.It can be clearly seen in figure 4 that the % removal of methylene blue dye increases with increase in GSAC-Fe$_3$O$_4$ dose. This can be attributed to the fact that more active sites become available for adsorption with increase in GSAC-Fe$_3$O$_4$ dose. A valid reason to support this is that, adsorption sites are unsaturated during adsorption while the number of sites for adsorption increases with increase in GSAC-Fe$_3$O$_4$ dose.
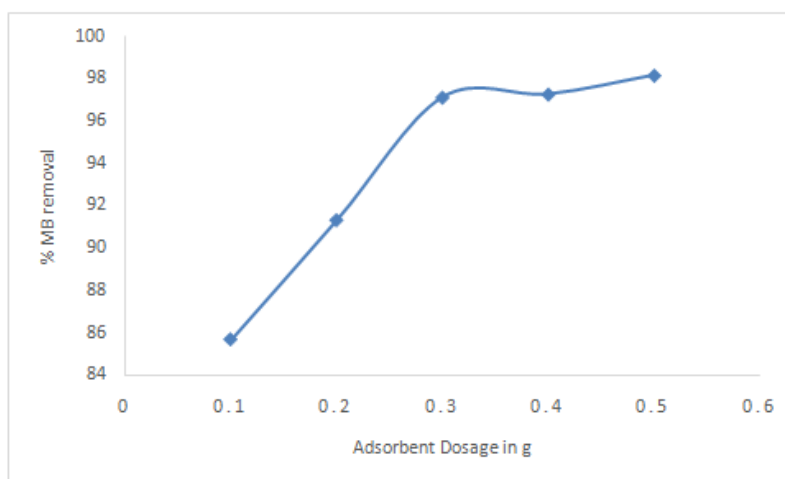

Figure 4. Effect of GSAC- Fe$_3$O$_4$ Dose on the % removal of MB

3.4 Effect of Initial Dye Concentration

This study was conducted by varying the initial dye concentration from 50 – 300 mgL^{-1} at room temperature using same amount of GSAC-Fe$_3$O$_4$ throughoutandwithout changing the initial pH. As shown in figure 5, the percentage adsorption is higher at lower concentrations, and it keeps on decreasing with increase in the initial dye concentration, while the amount of methylene blue dye adsorbed per unit mass of GSAC-Fe$_3$O$_4$ increases with increase in initial dye concentration. Thisis because, at low adsorbate/adsorbent ratio, there exists more available sites for adsorption, however, as the ratio increases, the sites becomes less/saturated, thereby decreasing the sorption efficiency. Hence, it can be concluded that the adsorption is highly dependent upon the initial concentration of the dye.
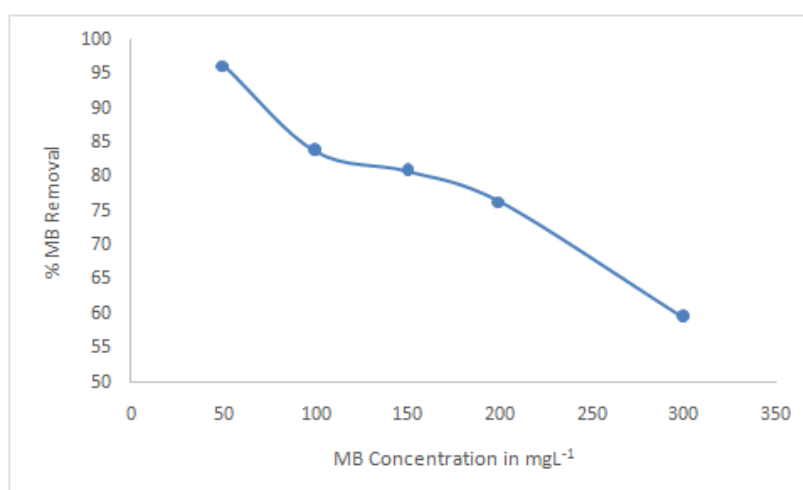

Figure 5. Effect of Initial Dye Concentration on the % removal of MB

3.5 Adsorption Isotherm

The study of isotherms in adsorption is important for understanding how the molecules of the adsorbate interact with the adsorbent surface. In this study, Langmuir andFreundlich isotherms were tested.

3.5.1 Langmuir Isotherm

The Langmuir isotherm is the most commonly used isotherm to represent data of adsorption from solution. Its basic assumption is that, adsorption takes place at specific homogeneous sites within the adsorbent [25].The linearized form of the Langmuir isotherm is represented by equation (5):

$$\frac{C_e}{q_e} = \frac{1}{K_l q_m} + \frac{C_e}{q_m} \dots \dots \dots \dots \dots \dots \dots \dots \dots (5)$$

Where, C_e is the equilibrium concentration of the adsorbate (mgL^{-1}), q_e is the amount of adsorbate adsorbed per unit mass of the adsorbent (mg/g), q_m and K_L is the Langmuir constants related to adsorption capacity and energy of adsorption. The values of q_m and K_L were determined from slope and intercepts of the plot and are presented in Table 1, respectively. The more the R^2 value approaches unity, the more fitted the adsorption is to Langmuir isotherm[26]. A plot of C_e/q_e against C_e as shown in figure 6, gave a straight line with a slope of $1/q_m$ which clearly indicate conformity to the Langmuir isotherm.
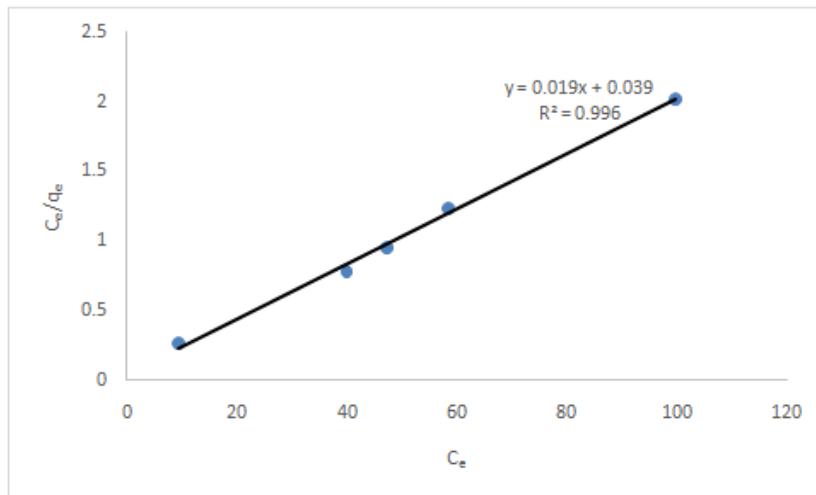

Figure 6. Langmuir Isotherm for the Adsorption of MB by GSAC-Fe₃O₄

3.5.2 Freundlich Isotherm

Another common isotherm that is been used to represent adsorption data is the Freundlich isotherm. Its basic assumption is that adsorption takes place on heterogeneous surface that has unequal adsorption sites with different energies of adsorption[1]. The linearized form of the Freundlich isotherm is represented by equation (7):

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \dots \dots \dots \dots \dots \dots \dots \dots (7)$$

Where q_e is the amount of adsorbed at equilibrium (mgg^{-1}),$C_e$is the equilibrium concentration of dye in solution (mgL^{-1}). K_f and n are Freundlich constants representing adsorption capacity and adsorption intensity or surface heterogeneity, respectively. Values of K_f, $1/n$ andR^2 are shown in Table 1.The value of Freundlich coefficient $1/n$ ranging between 0 and 1indicates favourable adsorption [27-28].
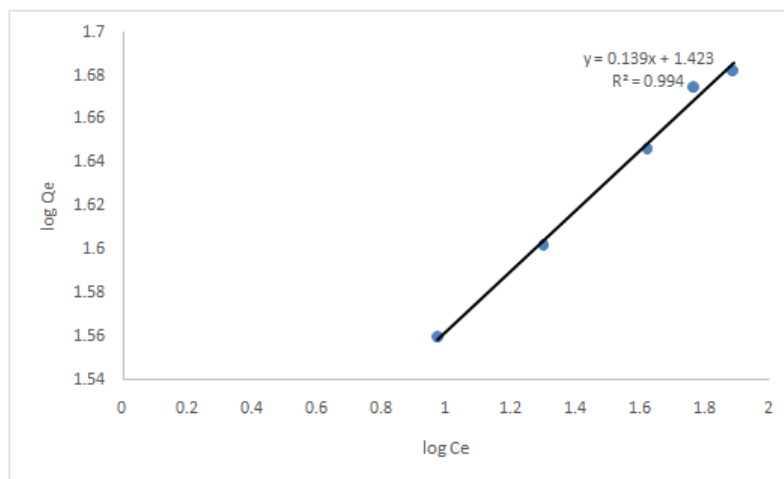

Figure 7. Freundlich Isotherm for the Adsorption of MB by GSAC-Fe₃O₄

Table 1. Isotherm Parameters for the Adsorption of MB by GSAC-Fe_3O_4

Langmuir Isotherm			Freundlich Isotherm		
qm(mgg^{-1})	K_L(mgL^{-1})	R^2	K_f(mgg^{-1})	1/n	R^2
50.51	0.5063	0.9963	26.49	0.1392	0.9945

3.6 Kinetic Studies

Kinetic studies is avery important factor that determines the efficiency of adsorption. It is used to investigate the mechanism of adsorption of MB onto GSAC- Fe_3O_4. In this process, pseudo first order and pseudo second order kinetic models were applied to the experimental data to analyse the adsorption kinetics of MB onto GSAC- Fe_3O_4.

3.6.2 Pseudo First Order Model

The linear form of pseudo first order kinetic model, proposed by Lagergren is given below[29]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \dots \dots \dots \dots \dots \dots \dots (8)$$

Where, q_e is the amount of dye adsorbed at equilibrium (mg g^{-1}), q_t is the amount of dye adsorbed at time "t" (mg g^{-1}), k_1 is the first order rate constant (min^{-1}) and t is the time (min). Definite Integration of equation (8) within the boundary of t = 0 to t = t and q_t = 0 to q_t = q_e gives equation (9);

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \dots \dots \dots \dots \dots \dots \dots (9)$$

Using the experimental results, a linear graph of log $(q_e – q_t)$ versus time (t) was plotted, which was used to find K_1 and R^2 subsequently presented in Table 2.
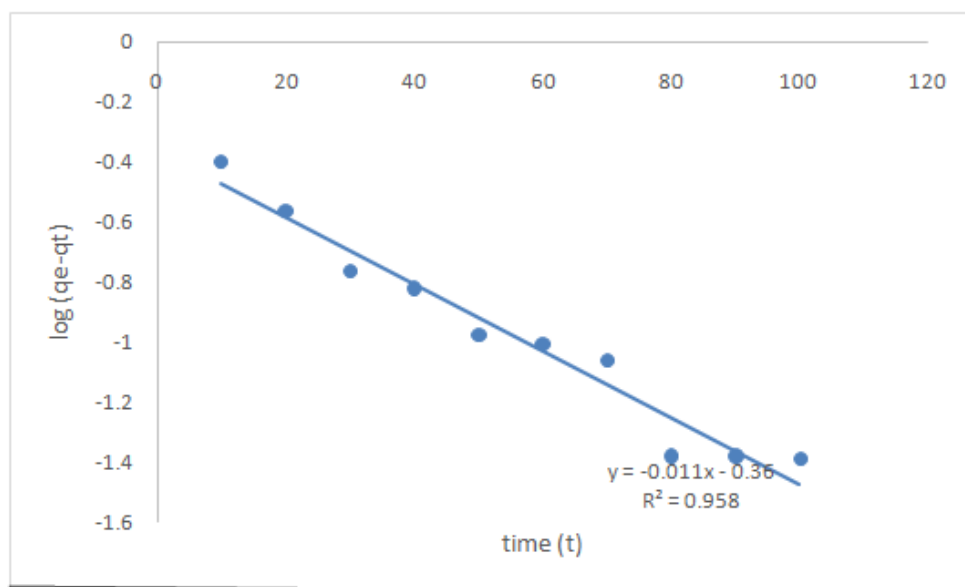

Figure 8. Pseudo First Order Kinetic Model Plot for the Adsorption of MB by GSAC-Fe_3O_4

3.6.2 Pseudo Second Order Model

Another model that may be used to describe the kinetics of adsorption is the pseudo second order kinetic model. It was develop by Ho[30] and is expressed as;

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \dots \dots \dots \dots \dots \dots \dots (10)$$

Where k_2 is the second order rate constant (g/mg min-^{1}). Definite Integration of equation (10) within the boundary of t = 0 to t = t and q_t = 0 to q_t = q_e gives equation (11), which is the expression for the integrated linearized form of the pseudo second order kinetic model.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \dots \dots \dots \dots \dots \dots \dots (11)$$

A plot of t/q_t versus t should to give a linear relationship, if at all, the adsorption process followed the pseudo second order kinetic model. The values of q_e and k_2 were determined from the slope and intercept, as presented in Table 2 respectively.
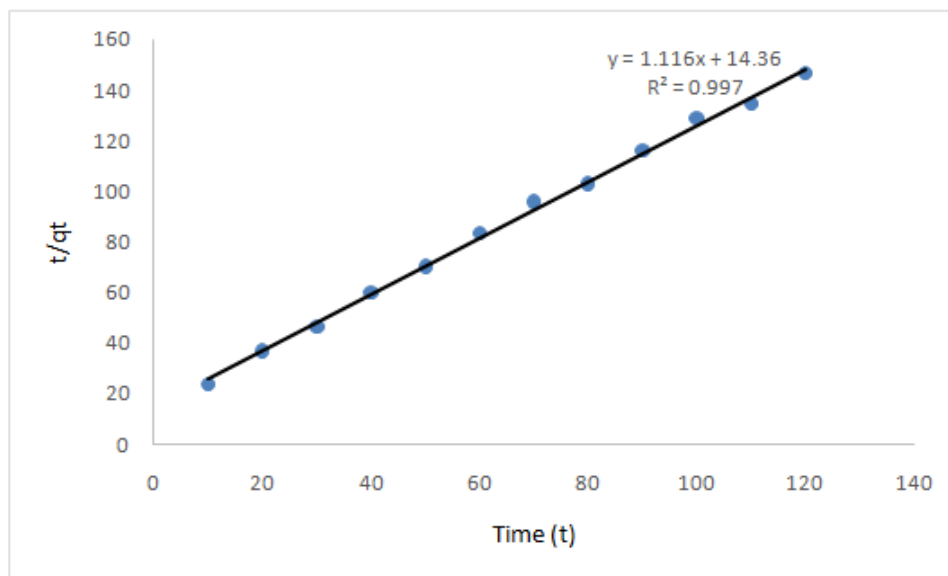
Fig. 9. Pseudo Second Order Kinetic Model Plot for the Adsorption of MB by GSAC- Fe_3O_4.

Table 1. Kinetic Parameters for the Adsorption of MB by GSAC-Fe_3O_4

Pseudo First Order			Pseudo Second Order		
qe(mgg^{-1})	K_1(min^{-1})	R^2	q_e(mgg^{-1})	K_2(g^{-1} mg min)	R^2
0.4365	0.0258	0.9584	0.8955	0.1392	0.9978

IV. Conclusion

The results of different experiments shows that groundnut shell activated carbon coated with Fe_3O_4 (GSAC-Fe_3O_4) has the ability to adsorb methylene blue (MB) dye from aqueous solutions. Kinetic data were tested using pseudo-first order and pseudo-second order kinetic models. The kinetics of the adsorption process was found to follow pseudo-second order kinetic model as the correlation coefficient for the pseudo-second order kinetic model is higher than that of pseudo-first order kinetic model, likewise, the calculated q_e agrees with the experimental q_e, indicating the applicability of pseudo-second order kinetic model. The applicability of pseudo-second order kinetic model implies that the adsorption process was controlled by chemisorption. Equilibrium data best fitted to the Langmuir adsorption isotherm, confirming the monolayer adsorption of methylene blue (MB) dye onto groundnut shell activated carbon coated with Fe_3O_4 (GSAC-Fe_3O_4). Hence, groundnut shell activated carbon coated with Fe_3O_4 (GSAC-Fe_3O_4) has a good potential as a low cost adsorbent for improving the effectiveness of waste water treatment.

Acknowledgements

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