



A Comparative Study on Adsorption Kinetics of Azo Dye (Reactive orange 16, Methylene blue and Methyl violet) Using Groundnut Shell

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ABSTRACT

Dye containing waste water is a major environmental problem. The treatment method for the removal of dye is costly. For this the use of low cost easily available adsorbent was studied. sorption of Azo dye on to groundnut shell was studied by varying the parameters like initial dye concentration, pH and sorbent dosage. Dye biosorption was rapid up to 60 minutes and equilibrium was attained at 240 minutes after 60 minutes the removal rate was slow due to the decrease in the number of vacant sites. Also the uptake capacity decreases as the amount of sorbent dosage was increased this is due to the increase in the number of solute particles and as the pH varies there is a considerable change in the uptake capacity of the sorbent and all the dyes follow pseudo second order kinetics and also the data fit to Langmuir isotherm very well.

1. INTRODUCTION

In recent years the treatment of highly colored aqueous effluent streams in textile dye house industries has attracted the attention of environmentalists and entrepreneurs due to its socio economic and political dimensions in particular the effluent from reactive dye baths are of greater priority due to the highly colored streams which

contain unutilized hydrolyzed dyes as well as salts and auxiliary chemicals etc. thus potential technology which is able to treat these high concentrated reactive dye bath effluent in an environmentally clean low cost manner is on the horizon.(1). Among the various kinds of dyes water-soluble and brightly colored acid and reactive dyes are the most problematic as they tend to pass through conventional decolorization systems unaffected (5). Reactive dyes are extensively used for coloring fabrics, because they present medium to high fastness to cellulose fibers. High volumes of aqueous effluents contaminated with dyes are generated by textile industries(2). The removal of synthetic dyes from aquatic systems, is extremely important from the healthiness viewpoint because most of these dyes are toxic, causing allergy, skin irritation, besides most of them are mutagenic and/or carcinogenic. Therefore, industrial effluents containing dyes need to be treated before being delivered to environment (2).

1.1 Treatment Methods:

1.2.1 Physical methods:

Physical methods used in the colour removal includes the following,

- 1) Membrane – filtration processes (nanofiltration, reverse osmosis, Electro dialysis)



2) Adsorption Techniques.

Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants.

1.1.2 Chemical methods:

Chemical methods include

1. Coagulation or flocculation combined with flotation and filtration
2. Precipitation
3. Flocculation with Fe (II)/Ca (OH)₂,
4. Electro flotation,
5. Electro kinetic coagulation,
6. Conventional oxidation methods by oxidizing agents (ozone),
7. Irradiation or electrochemical processes.

These chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use. Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems.

1.1.3 Biological treatments:

Biological treatment is often the most economical alternative when compared with other physical and chemical processes. Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents

because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants however, their application is often restricted because of technical constraints. Biological treatment

Requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation. Biological treatment is incapable of obtaining satisfactory color elimination with current conventional biodegradation processes. Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin. In particular, due to their xenobiotic nature, azo dyes are not totally degraded.

Therefore, there is a growing interest in using low-cost, easily available materials for the adsorption of dye colours. In the present study groundnut shell is used as biosorbent for the removal of azo dyes since it is easily available and cheap.

2. LITERATURE REVIEW

B.H. Hameed(2007) The results obtained show that sunflower seed hull (SSH) waste is an efficient sorbent in the removal of MV from aqueous solutions. Equilibrium adsorption data for MV is in good agreement with Freundlich isotherm. The monolayer adsorption capacity of SSH was evaluated as 92.59 mg/g. Kinetics of MV sorption on SSH waste follows pseudo-second-order rate expression. Since sunflower seed hull, waste material from the food industry, used in this work is freely, abundantly available and the sorbent does not require an additional pretreatment step such as activation before its application, the sorbent is expected to be economically viable for removal of basic dye from aqueous solution.

Mehmet Doğan et al (2007) present investigation show that hazelnut shell, low cost material, has suitable adsorption capacity with regard to the removal of MB from its aqueous solution. The cost and adsorption characteristics favor hazelnut shell to be used as an effective adsorbent for the removal of



MB from wastewater. The adsorption of MB on hazelnut shell was endothermic indicating that a temperature above the ambient temperature would be favourable for carrying out the removal of the dye. The results indicate that MB adsorption onto hazelnut shell is physical in nature. The experimental equilibrium data obtained were applied to the Langmuir and Freundlich isotherm equations to test the fitness of these equations

I.A.W. Tan et al(2007) The present investigation showed that activated carbon prepared from coconut husk was a promising adsorbent for the removal of methylene blue dye from aqueous solutions over a wide range of concentrations. The surface area of the prepared activated carbon was relatively high with large pore volume and was found to be mesoporous. Methylene blue was found to adsorb strongly on the surface of the activated carbon. Equilibrium data were fitted to Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms and the equilibrium data were best described by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 434.78 mg/g at 30 °C. The maximum monolayer adsorption capacity decreased with increasing temperature. The adsorption kinetics was found to follow closely the pseudo-second-order kinetic model. The negative $-H^\circ$ value confirmed the exothermic nature of the adsorption interaction whereas the positive S° value showed the increased randomness at the solid–solution interface during the adsorption process.

3. MATERIALS AND METHODS

3.1 CHEMICALS:

The dye used in this study was obtained from the Department Of Textile Technology, A.C.College of Technology.

3.2 PREPARATION OF SORBENT:

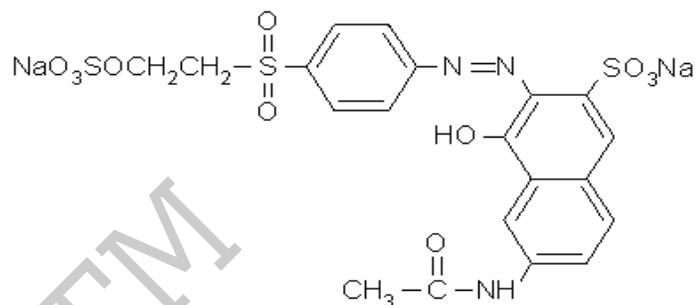
The groundnut shell used in this work was collected from farm in virudhunagar. The groundnut shell was washed with distilled water to remove dirt and soil that are adhered on the surface of the sorbent. Then it was spread on tray and oven dried at 60 °C for 48 hours. The dried sorbent was ground and sieved in a 60 mesh size sieve and the underflow was

stored in plastic bottle for further use. No other chemical or physical treatments were used prior to adsorption experiments.

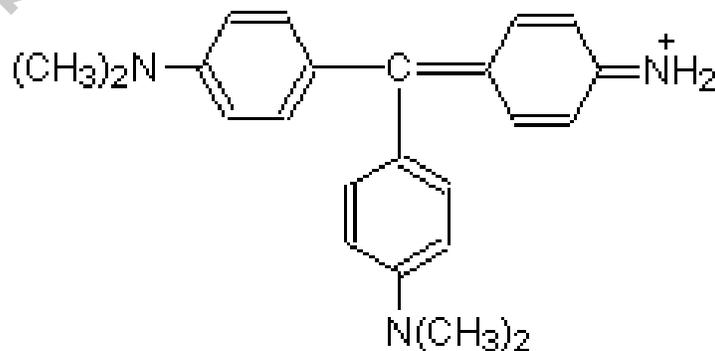
3.3 CHARACTERIZATION OF SORBENT:

The Fourier Transform Infrared Spectroscopy (FTIR) spectrum was obtained for groundnut shell

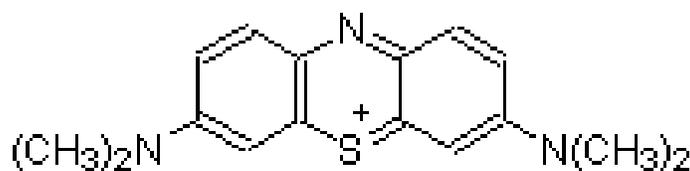
3.4 STRUCTURE OF DYE:



(a)



(b)



(c)



Fig 3.1. Structure of (a) Reactive orange 16, (b) Methyl violet, (c) Methylene blue

3.5 PREPARATION OF DYE SOLUTION:

A 1000 ppm stock solution of dye was prepared by dissolving 1g of Reactive orange 16 dyes in 1 L of distilled water. Similarly Methylene blue and Methyl violet stock solution were prepared. This stock solution was used for further studies.

3.6 EFFECT OF INITIAL CONCENTRATION OF DYE:

Batch adsorption experiments were carried out by adding a fixed amount of sorbent (0.3 g) into 100 ml of different initial concentrations such as 50, 100, 150, 200 ppm of dye solution. The initial and equilibrium dye concentrations were determined by absorbance measurement using colorimeter at 47 filter range for reactive orange 16, 67 filter range for methylene blue and 54 filter range for methyl violet. It was then computed to dye concentration using calibration curve.

3.7 EFFECT OF SORBENT DOSAGE:

A 50ppm dye solution was prepared from the stock solution and the different amount of sorbent was added (0.1, 0.2, 0.3, 0.4, 0.5 g) to the 100ml of dye solution and the system is kept in a shaker for the equilibrium time of 4 hours for reactive orange 16 and methylene blue and 3hours for methyl violet. Then the dye concentrations were measured with time interval of 60,120,180 and 240 minutes.

3.8 EFFECT OF pH:

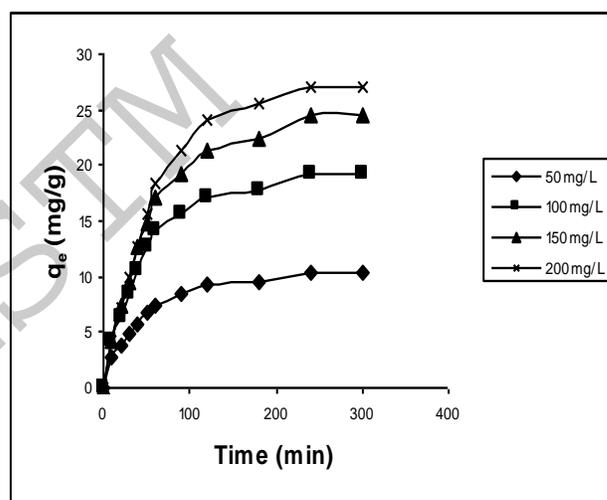
The effect of pH on equilibrium uptake capacity of Groundnut shell was measured by adding a fixed amount of sorbent (0.3g) into 100 ml of 50 ppm dye solutions of reactive orange 16, Methylene blue and methyl violet dye having different pH such as 2, 4, 6, 8, 10 and 12. The pH of the dye solution was varied by using 0.1N H₂SO₄ and 0.1N NaOH. The initial and equilibrium dye concentrations were determined by absorbance measurement using

colorimeter in the filter range of 47, 67 and 54 respectively. It was then computed to dye concentration using a calibration curve

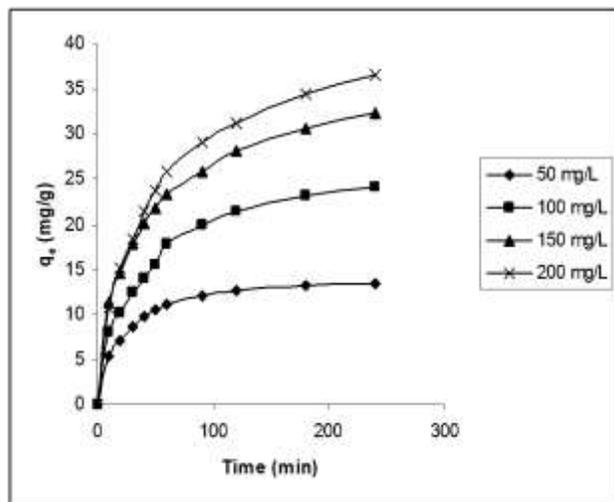
4. RESULTS AND DISCUSSION

4.1 Effect of initial concentration

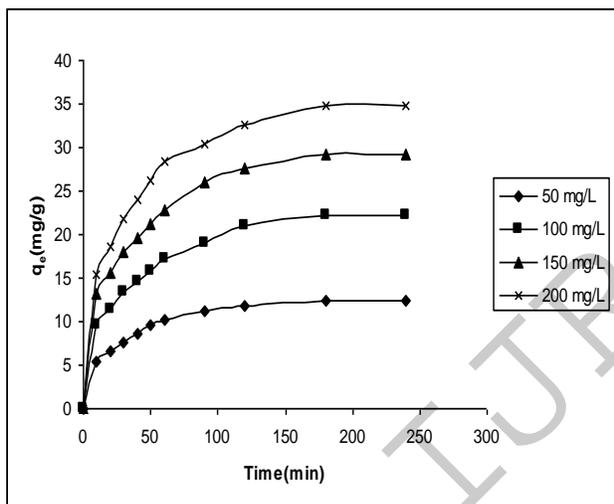
Various concentrations of 50,100,150,200 ppm dye solution was prepared and then 0.3g of sorbent was added and the system was kept in a shaker for four hours for Reactive orange 16 and Methylene blue and three hours for Methyl violet, and the dye concentration was measured with time interval of 10,20,30,40,50,60,120,180 and 240 min and the result is shown below,



(a)



(b)



(c)

Fig 4.1 Effect of initial concentration on adsorption of (a) Reactive orange 16 (b) Methylene blue and (c) Methyl violet

The dye removal occurs in the first rapid phase (60 min) and thereafter the sorption rate was found to decrease. The higher sorption rate at the initial period (60min) may be due to an increased number of functional sites available at the initial stage. The increased in concentration gradients tends to increase in dye sorption at the initial stages. As time precedes this concentration is reduced due to the accumulation of dye particles in the functional sites

leading to a decrease in the sorption rate at the later stages from 60 to 240 min.

4. 2. Effect of dosage:

A 50ppm dye solution was prepared and different amount of adsorbent added (0.1, 0.2, 0.3, 0.4, 0.5 g) and the system is kept in a shaker for four hours. The dye concentration was measured with time interval of 60, 120, 180, 240, min and the result is shown below,

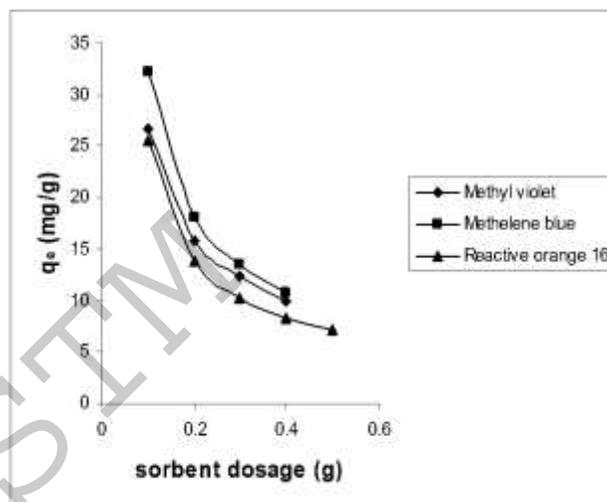


Fig 4.2. The effect of sorbent dosage on adsorption of Reactive orange 16, Methylene blue and Methyl violet solutions

The percentage removal of dye increased with the increase in sorbent dosage. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase dosage of the sorbent

4.3 EFFECT OF pH:

The effect of pH on equilibrium uptake capacity of Groundnut shell was measured by adding a fixed amount of sorbent (0.3 g) into 100 ml of 50 ppm dye solution having different pH such as 2, 4, 6, 8, 10 and 12 of dye solution. The pH of the dye solution was varied by using 0.1N H₂SO₄ and 0.1 NaOH. The initial and equilibrium dye concentrations were determined by absorbance measurement using colorimeter in the filter range of



47, 67 and 54 respectively. It was then computed to dye concentration using a calibration curve.

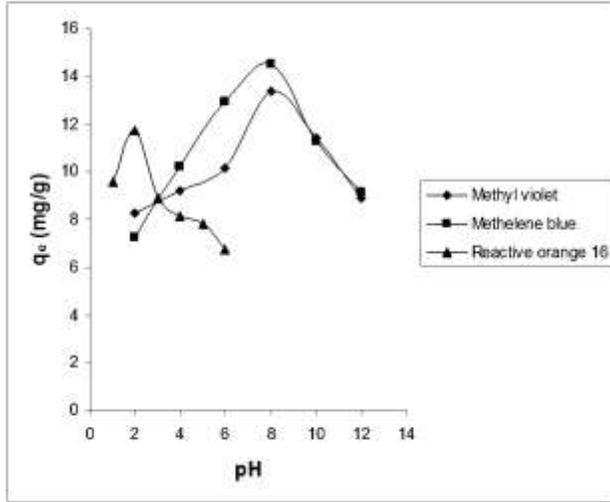


Fig.4.3 Effect of pH on adsorption of dye on to groundnut shell

From the graph it can be seen that as the pH of the solution decreases the adsorption of reactive orange 16 is high and at a pH of 2 it is at the maximum while in case of methylene blue and methyl violet the maximum uptake was reached at a pH of 8.

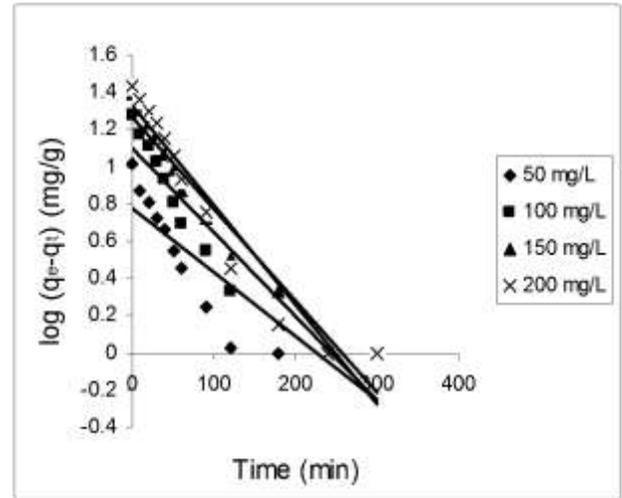
4.4 Adsorption kinetics:

The biosorption mechanism and potential rate controlling steps have been investigated by using the pseudo first and pseudo second order kinetic models.

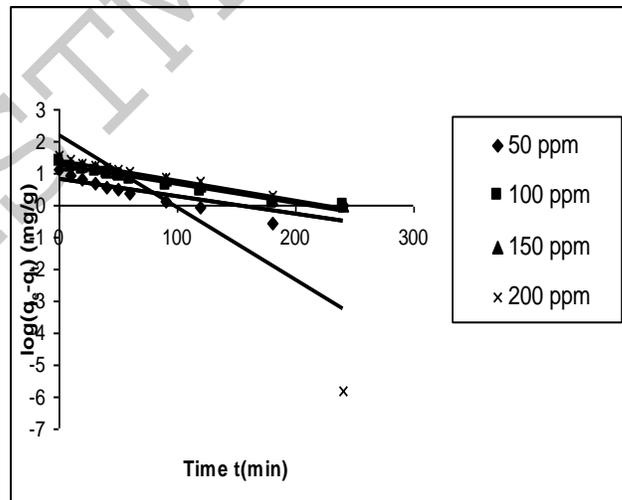
4.4.1 The pseudo first order kinetic model:

The pseudo first order rate expression of lagergen is of the form:

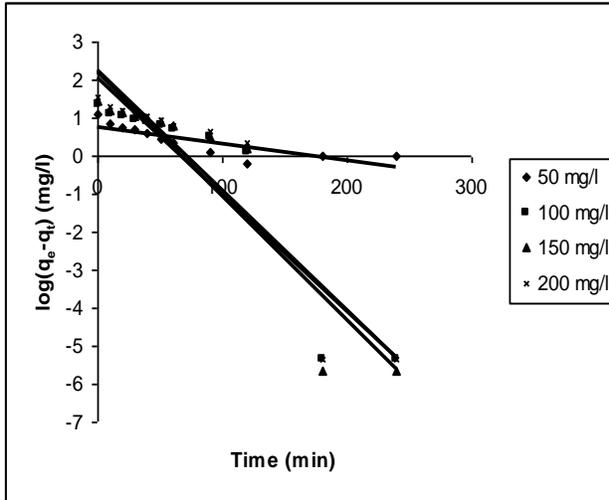
$$dq_t / dt = k_1(q_e - q_t) \quad -1$$



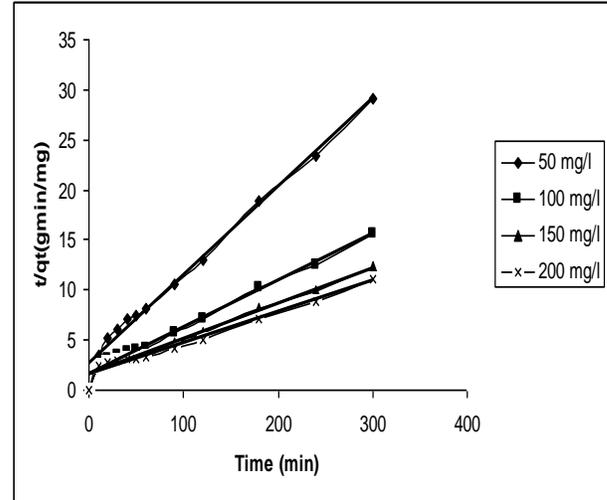
(a)



(b)



(c)



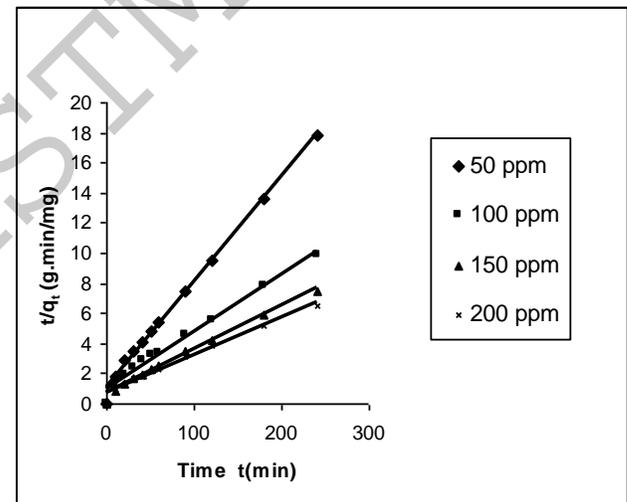
(a)

Fig 4.4 The pseudo first order kinetic model of adsorption of (a) Reactive orange 16 (b) Methylene blue and (c) Methyl violet solution

Integrating this for the boundary conditions $t=0$ to $t = t$ and $q_t=0$ to $q_t = q_t$, gives

$$\log(q_e - q_t) = \log q_e - k_1 / 2.303 (t) \quad -2$$

where k_1 is the rate constant (1/h), q_e the amount of solute adsorbed on the surface at equilibrium (mg/g), q_t the amount of solute adsorbed at any time (mg/g). The value of the adsorption rate constant (k_1) for dyes sorption by groundnut shell was determined from the plot of $\log(q_e - q_t)$ against t . The parameters of pseudo-first-order model are summarized in Table 1 to 4. In many cases the first-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes. Although the correlation coefficients, R_2 , for the application of the pseudo-first-order model are reasonably high in some cases, the calculated q_e is not equal to experimental q_e , suggesting that the Adsorption of dyes on groundnut shell is not likely to be a pseudo-first-order for the initial concentrations examined.



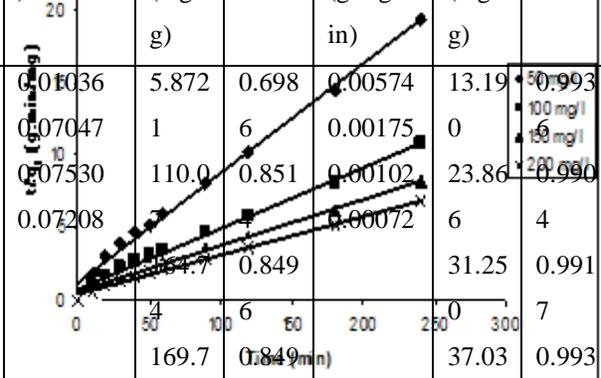
(b)

4.4.2 The pseudo-second-order kinetic model:



Initial concentration	Q _{e,exp} (mg/g)	Pseudo first order kinetic model			Pseudo second order kinetic model		
		K ₁ (L/min)	q _{e,cal} (mg/g)	R ²	K ₂ (g/mg.m)	q _{e,cal} (mg/g)	R ²
50	12.380	0.01036	5.872	0.698	0.00574	13.19	0.993
100	9	0.07047	16	0.851	0.00175	10	0.990
150	22.222	0.07530	110.0	0.849	0.00102	23.86	0.990
200	29.242	0.07208	164.7	0.849	0.00072	6	4
2	34.777		169.7	0.849		37.03	0.993
2			4	3		7	3

Table 4.3: The pseudo first and second order kinetic model for adsorption of Methyl violet solution



4.5 Isotherm studies:

The adsorption data were analyzed with three adsorption isotherm models, namely Langmuir, and Freundlich.

4.5.1 Langmuir isotherm model:

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface.

Initial concentration	Q _{e,exp} (mg/g)	Pseudo first order kinetic model			Pseudo second order kinetic model		
		K ₁ (L/min)	q _{e,cal} (mg/g)	R ²	K ₂ (g/mg.m)	q _{e,cal} (mg/g)	R ²
50	13.40	0.0138	1	0.7	0.00457	14.20	0.9947
100	8	0.0138	1	0.7	0.00146	4	0.9833
150	24.193	0.0140	17.5	0.95	0.00125	26.24	0.9866
200	5	0.0522	15	0.95	0.00091	6	0.9822

Fig 4.5 The pseudo second order kinetic model for adsorption of (a) Reactive orange 16, (b) Methylene blue and (c) Methyl violet solution

The pseudo-second-order equation based on the equilibrium adsorption is expressed as $t/q_t = 1/k_2 q_e^2 + 1/q_e t$ Where k_2 (g/mg.h) is the pseudo-second-order rate constant determined from the plot of t/q_t versus t as shown in Fig. 5. If the experiment data fits the plot of t/q_t versus t as a linear relationship the pseudo-second order kinetic model is valid

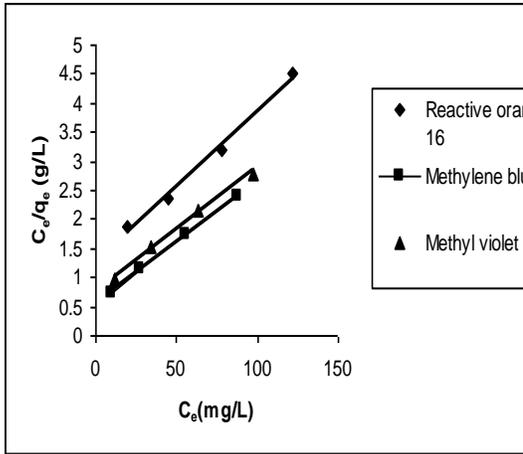


Fig.4.6 Langmuir isotherm for adsorption of dyes using groundnut shell

The expression of the Langmuir model is given by the following equation:

$$q_e = Q_0 b C_e / (1 + b C_e) \quad -4$$

where q_e (mg/g) and C_e (mg/L) are the amount of adsorbed dye per unit mass of sorbent and unadsorbed dye concentration in solution at equilibrium, respectively. Q_0 is the maximum amount of the adsorbed dye per unit mass of sorbent to form a complete monolayer on the surface bound at high C_e (mg/g), and b (L/mg) is a constant related to the affinity of the binding sites. The linear form of Langmuir model is

$$C_e/q_e = 1/Q_0 b + C_e/Q_0 \quad -5$$

The linear plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) (Fig. 7) shows that the adsorption obeys the Langmuir model. The Langmuir constants Q_0 and b were determined from the slope and intercept of the plot and are presented in table 4.

4.5.2 The Freundlich isotherm model:

The Freundlich model is an empirical equation that assumes heterogeneous adsorption due to the diversity of adsorption sites.

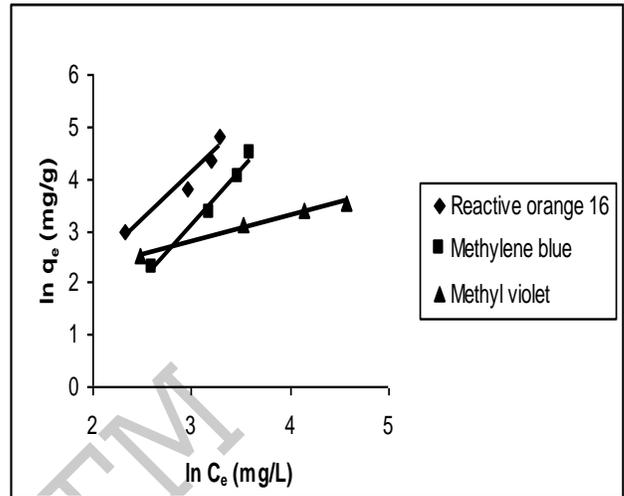


Fig.4.7. Freundlich isotherm for adsorption of dyes using groundnut shell

The Freundlich equation is expressed as

$$q_e = K_F C_e^{1/n} \quad -6$$

where K_F (mg/g (L/mg)^{1/n}) is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. The magnitude of the exponent, $1/n$, gives an indication of the favorability of adsorption. Values of $n > 1$ represent favorable adsorption conditions. Eq. may also be written in the logarithmic form as

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad -7$$

Values of K_F and n are calculated from the intercept and slope of the plot and are listed in Table 4

Table 4.4: Langmuir and Freundlich isotherm for adsorption of dyes using groundnut shell

Isotherm	Reactive orange 16	Methylene blue	Methyl violet
Langmuir			
Q ₀ (mg/g)	38.46	47.16981	47.61905
b(L/mg)	0.02052	0.038913	0.027704
R ²	0.9901	0.9997	0.9953
Freundlich			
K _f (mg/g(L/g) ^{1/n})	0.2811	0.039633	3.725869
n	0.5607	0.475602	2.021836
R ²	0.954	0.9827	0.9943

4.6 FOURIER TRANSFORM INFRARED ANALYSIS (FTIR) AND SCANNING ELECTRON MICROSCOPY:

The FTIR analysis was carried out to confirm the existence of amine, carboxyl and phosphonate group in groundnut shell biomass. the FTIR spectroscopy analysis had showed a strong band in the range of 1730-1750cm⁻¹ indicative of c=O of the carbonyl in carboxylic group .the spectrum showed the peaks 1644,1370,1264 cm⁻¹, representing carboxyl groups. some absorption bands(P=O) stretching at 1103 cm⁻¹ and the P-OH stretching at 1055cm⁻¹where the phosphonate group is present .the spectrum showed some characteristic absorption of amine group : N-H bonding band at 1512 cm⁻¹ and also C-N stretching band at 1264 cm⁻¹.

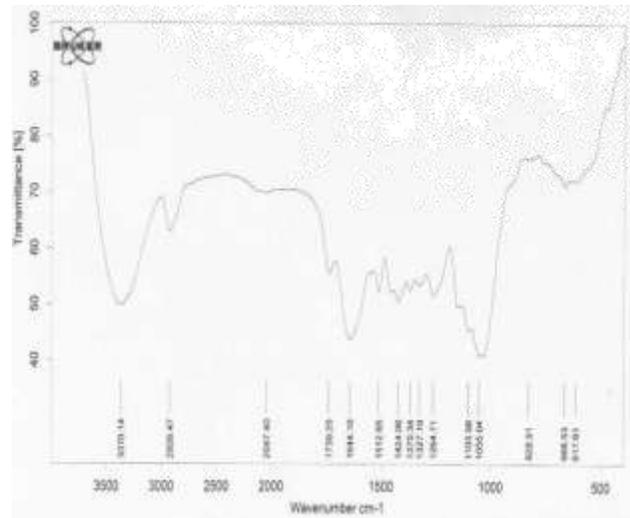


Fig 4.8.FTIR spectrum of Groundnut shell

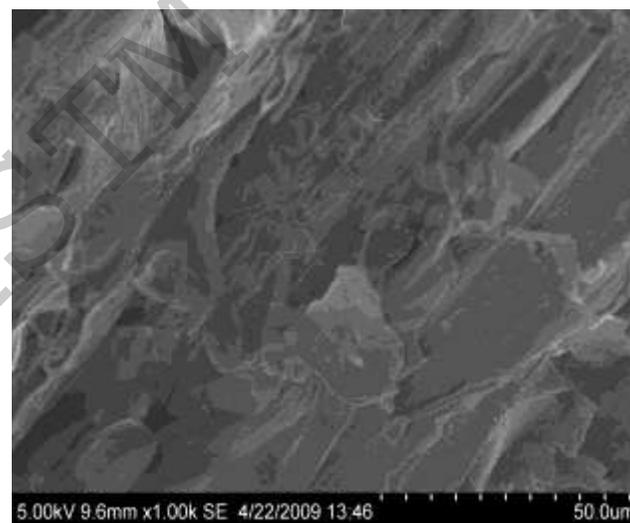


Fig 4.9. Scanning electron microscope image of Groundnut shell (before adsorption)

5. CONCLUSION

Batch experiment was conducted to study the effect of sorbent dosage, initial dye concentration and contact time for the removal of reactive orange 16, Methylene blue and Methyl violet from solution by using groundnut shell. Based on the above experiment it was observed that as the initial dye concentration increases from 50mg/L to 200mg/L the



dye uptake capacity increased from 10.28 mg/g to 26.95 mg/g, 13.44 mg/g to 36.55 mg/g and 12.38 mg/g to 34.77 mg/g respectively. As the sorbent dosage 0.1 g to 0.5g increases the amount of dye uptake decreased from 25.53 mg/g to 7.23 mg/g, 32.25 mg/g to 10.68 mg/g and 26.66 mg/g to 10mg/g respectively. In the case of pH the maximum uptake was observed at 2 for reactive orange 16 and at 8 for methylene blue and methyl violet. The adsorption kinetics for reactive orange 16, methylene blue and methyl violet on to groundnut shell is well described by pseudo second order kinetics and the equilibrium data are analyzed against Langmuir and Freundlich isotherms. The Langmuire isotherm was demonstrated to provide the best correlation for the sorption of the dyes on to groundnut shell

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