Sorption Equilibrium and Kinetics for Adsorption of Methelene Blue 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 methylene blue 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 the 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

Synthetic dyes have been increasingly used in the textile, paper, rubber, cosmetics, pharmaceuticals and food industries because of their easy to use, inexpensive cost for production, stability and variety of colour compared to natural dyes. Colored dye wastewater arises as a direct result of the production of the dye and also as a consequence of its use in the textile and other industries. Greater part of this dyes are synthetic in nature and are usually composed of aromatic rings in their structure, which makes them carcinogenic and mutagenic, inert and non-biodegradable when discharged into waste streams. These results in the creating anoxic condition which cause death of aquatic life Therefore, the removal of such colored agents from aqueous effluents is of significant environmental, technical, and commercial importance. Adsorption

of various dyes from aqueous solution has proven to be an excellent way to treat effluent also a cost effective technique. Of which adsorption by biomass is very easy to use and also cheap this method is called as Biosorption.

Activated carbon is the most popular and widely used adsorbent, but there are certain problems with its use. It is expensive and the higher the quality the greater the cost. Furthermore, regeneration using solutions produces a small additional effluent, while regeneration by refractory technique results in loss of adsorbent and its uptake capacity.

1.1 Treatment Methods:
1.1.1 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 coagulation or flocculation combined with flotation and filtration, precipitation, flocculation with Fe (II)/Ca (OH) 2, electro flotation, electro kinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), 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.

1.2 Scope and Objective of the Present study:

Methelene Blue synthetic Dye solution treatment using groundnut shell as a sorbent

The Objectives of the Present Investigation are to study,

- ➢ Effect of initial dye concentration
- ➢ Effect of Adsorbent Dosage
- ➢ Effect of pH
- ➢ Adsorption Kinetics
- ➢ Adsorption Equilibrium

2. LITERATURE REVIEW

Juan Mao et al (2008) studied the Surface modification of Corynebacterium glutamicum for enhanced reactive Red 4 biosorption. Cross-linking the biomass via the

reaction with polyethylenimine introduced primary and secondary amine groups, which in turn enhanced the RR 4 biosorption capacity. Also the FT-IR spectra confirmed the presence of amine, hydroxyl and carboxyl groups. According to the Langmuir model, the maximum uptake capacity of PEI-modified biomass was 2.8 times higher than that of raw biomass. The PEI modified biomass was regenerated and reused over four successive sorption–desorption cycles. Thus, cross-linking the bacterial biomass via polyethylenimine is an attractive option for enhancing the biosorption potential towards reactive dyes.

Gre´gorio Crini(2006) Non-conventional low-cost adsorbents for dye removal: A review

S. Saiful Azhar et al (2005) studied dye removal from aqueous solution by using adsorption on treated sugarcane bagasse and concluded From this study, it was found that the pretreated sugar cane bagasse with formaldehyde (PCSB) and sulphuric acid (PCSBC) has a lower adsorption efficiency compared to powdered activated carbon (PAC) at the any given initial dye concentration. The adsorption efficiency can be arranged in the following order GAC>PCSBC>PCSB

A.Abdul and F. Aberuagba et al (2005) the comparative study of the adsorption of phosphate by activated charcoal from corncobs, groundnut shells and rice-husks. Of all the three activated charcoals studied, charcoal from corncobs was found to be the most effective for the adsorption of phosphate from water

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 ground nutshell

3.4 PREPARATION OF DYE SOLUTION:

A 1000 ppm stock solution of dye was prepared by dissolving 1g of Methelene Blue dye in 1 L of distilled water. This stock solution was used for further studies.

3.5 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 UV spectrometer at 668 nm. It was then computed to dye concentration using standard 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. Then the dye concentrations were measured with time interval of 60,120,180 and 240 min.

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 (0.3 g) into 100 ml of 50 ppm Methelene blue 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 H_2SO_4 and 0.1 NaOH. The initial and equilibrium dye concentrations were determined by absorbance measurement using UV spectrometer at 668 nm. 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 and the dye concentration was measured with time interval of 10,20,to 240 min and the result is shown below,
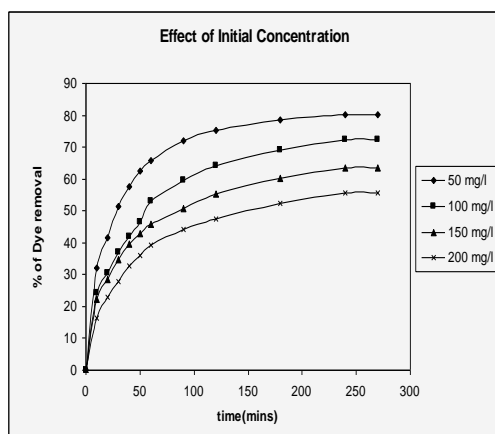

Fig.2 Effect of initial concentration on adsorption of Methelene Blue solution

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 larger 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 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,
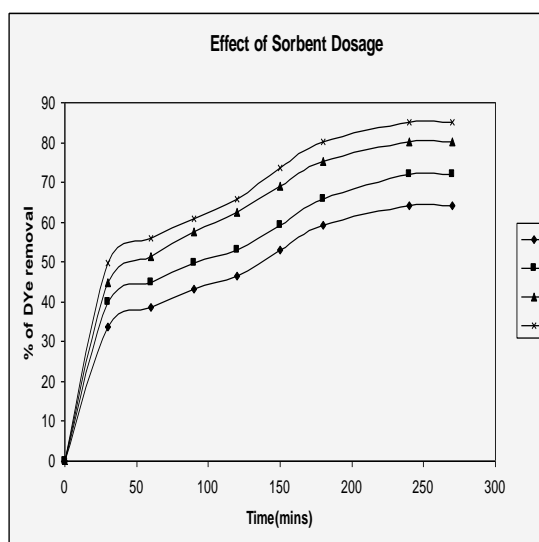
Fig.3 The effect of adsorbent dosage on adsorption of Methelene Blue solution

The percentage removal of Methelene Blue 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 Methelene blue 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 H_2SO_4 and 0.1 NaOH. The initial and equilibrium dye concentrations were determined by absorbance measurement using UV spectrometer at 668 nm. It was then computed to dye concentration using a calibration curve.
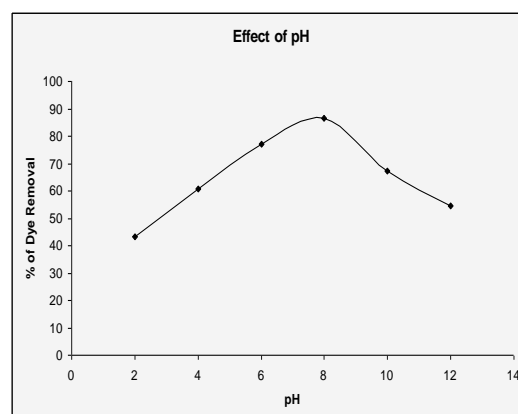

Fig.4 The effect of pH on adsorption of Methelene Blue solution.

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:
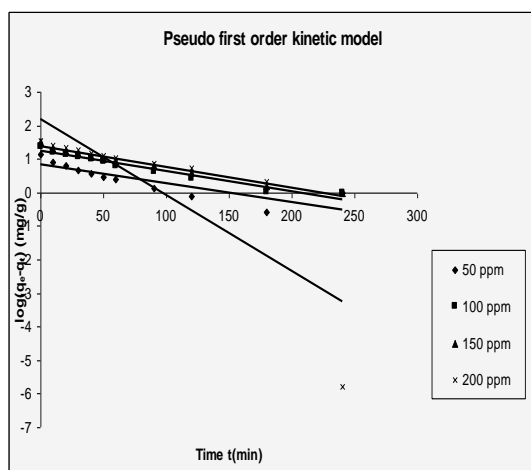
$$dq_t / d_t = k_1(q_e - q_t) \qquad -1$$

Fig.5 The pseudo first order kinetic model of adsorption of Methelene Blue solution

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

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

where k_1 is the rate constant (1/h), q_e the amount of solute adsorbed on the surface at gequilibrium (mg/g), q_t the amount of solute adsorbed at any time (mg/g). The value of the adsorption rate constant (k_1) for *Methelene Blue* 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. 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 Methelene Blue on groundnut shell is not likely to be a pseudo-first-order for the initial concentrations examined.

Table 1. Pseudo - first order kinetic model

Concentration C_0 (mg/l)	q_e (mg/g)	K_1 (L/min)	R^2
50	14.20455	0.004576	0.9947
100	26.24672	0.001462	0.9833
150	34.36426	0.001252	0.9866
200	39.52569	0.000914	0.9822

4.4.2 The pseudo-second-order kinetic model:

C_0 (mg/l)	g)	min)	
50	6.821	0.0115	0.737
100	17.55	0.0138	0.955
150	23.25	0.0140	0.981
200	155.8	0.0522	0.671

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.
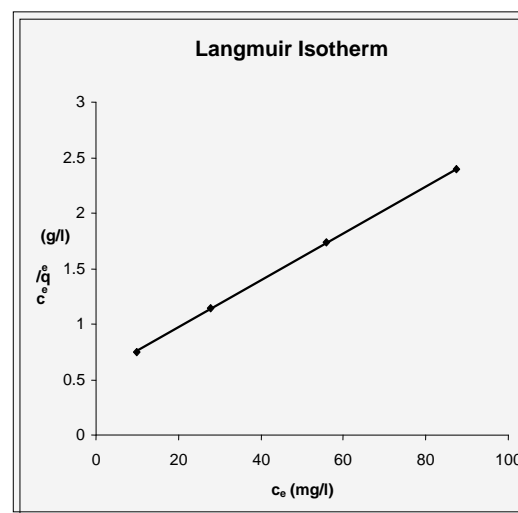

Fig.6 The pseudo second order kinetic model fo adsorption of Methelene Blue solution

The pseudo-second-order equation based on equilibrium adsorption is expressed as

$$t/q_t = 1/k_2 q^2 e + 1/q_e t \qquad -3$$

Where $k2$ (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 vrsus t as a linear relationship the pseudo second order kinetic model is valid

Fig.7. Langmuir isotherm for adsorption of Methelene Blue using groundnut shell

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

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

Table 2. Pseudo - second order kinetic model

Concentration	q_e (mg/	K_2 (g/mg.	R^2

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

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

Table 3. Langmuir isotherm

Langmuir constant	Values
Q_0	47.16981
b(L/mg)	0.038913
R^2	0.9997

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 3.

4.5.2 The Freundlich isotherm model:

. The Freundlich model is an empirical equation that assumes

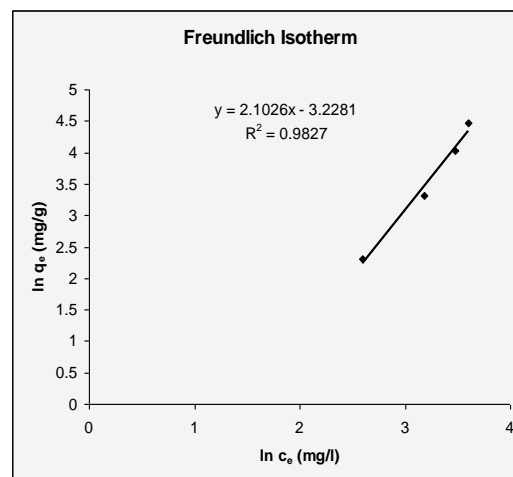heterogeneous adsorption due to the diversity of adsorption sites.

Fig.8. Freundlich isotherm for adsorption of Methelene Blue using groundnut shell

The Freundlich equation is expressed as

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

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

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

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

Table 4. Freundlich isotherm:

Freundlich constant	Values
K_f (mg/g(L/g)$^{1/n}$)	0.039633
n	0.475602
R^2	0.9827

4.6 FOURIER TRANSFORM INFRARED ANALYSIS (FTIR):

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^{-1} where 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}
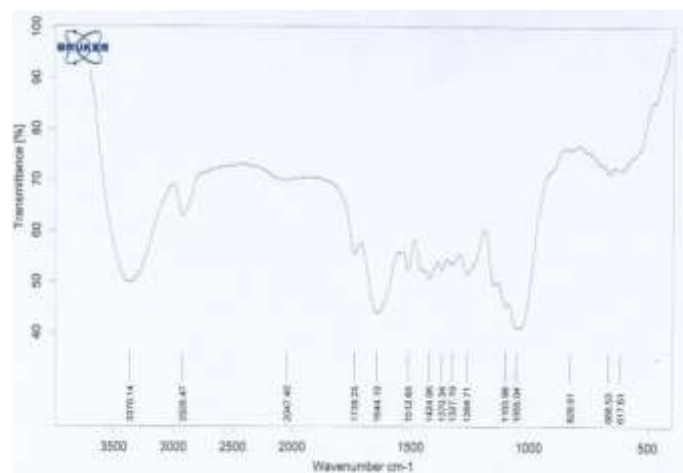
5. CONCLUSION:

Batch experiment was conducted to study the effect of sorbent dosage, initial dye concentration, contact time and pH for the removal of Methelene Blue from solution by using groundnut shell. Based on the above experiment it was observed that as the initial dye concentration increases from 50ppm to 200ppm the removal percentage of dye was decreased from 80.12% to 55.64% and as the sorbent dosage 0.1 g to 0.4g increases the amount of dye adsorbed increased from 64.10% to 84.93%.For the effect of pH, at a pH of 8 the adsorption of Methelene blue was maximum. The adsorption kinetics for Methelene

Blue on to groundnut shell is well described by pseudo second order kinetics and the equilibrium data are analyzed against Langmuir and Freundlich isotherms. The Langmuir isotherm was demonstrated to provide the best correlation for the sorption of Methelene Blue on to groundnut shell.

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