International Journal of Engineering Research and Technology. ISSN 0974-3154 Volume 10, Number 1 (2017)

Adsorption of Methylene Blue in waste water by low cost adsorbent Rice husk.

M.A.Patil
Asst. Professor, Chemical dept. D.Y.P.C.E.T, Kolhapur.

Prof.J.K.Shinde
Professor, Chemical dept. T.K.I.E.T.Warananagar.

A.L.Jadhav
Asst. Professor, Chemical dept. D.Y.P.C.E.T, Kolhapur.

S.R.Deshpande
ICT Mumbai.

Abstract:
The aim of the present work was to investigate both the adsorption mechanism and adsorption kinetics of a cationic dye, methylene blue, onto rice husk from aqueous solution with respect to the initial dye concentration, temperature, pH, mixing rate and sorbent dosage. Equilibrium parameter has analyzed and it was found that Langmuir and Freundlich isotherm fit for all material but Freundlich fit better than other isotherm. The adsorption kinetics study shows adsorption mechanism follows pseudo second order kinetics mechanism. Thermodynamics standard Gibbs free energy (ΔG˚) is negative which indicates parameter shows negative for all material it indicates adsorption is spontaneous while standard enthalpy (ΔH˚) is negative shows that adsorption of methylene blue onto these material is exothermic. While positive value standard entropy (ΔS˚) reflects the affinity of adsorbents for methylene blue. The main objective of the study was to remove methylene blue by using low cost adsorbent like rice husk and it was found this material can used as adsorbent for removal of methylene blue dye.

Keywords: *Methylene Blue dye, Adsorption Isotherms, Standard Gibbs free energy (ΔG˚), Standard enthalpy (ΔH˚), Standard entropy (ΔS˚), Sorption kinetics, Adsorbents.*

I INTRODUCTION

The presence or introduction of unwanted materials in the environment which have harmful or poisonous effects is called Pollution. It is the introduction of contaminants in the surroundings which have adverse effects. There are various ways of polluting water, most important being the discharge of industrial waste water through spillage from into water bodies. The sewage discharge from homes is not treated before being discharged to environment which is also a main cause of pollution. Thus it can be concluded that any kind of change in properties of water which may be physical, chemical or biological and which have harmful consequences is water pollution. Chemical, textiles, tannery industries etc. cause high rate of pollution. The waste water containing heavy metals, chemicals, dyes, oils and many other harmful materials are discharged by the industries into the water bodies without proper treatment, thus leading to contamination of water bodies. Many industries, such as textiles, pulp mills, leather, printing, food, and plastics, use dyes in order to colour their products and consume substantial volumes of water. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable. Dyes are widely used in the textile industry. Effluents from the textile industry, which are dye-containing wastewater, often cause serious environmental problems due to the deep color present in the wastewater that requires pre-treatment or color removal prior to disposal into a river. Although it is low toxicity, it can cause various harmful effects. It has various ill effects on eco system. Excessive amount of MB causes cardiovascular disorder, dizziness, fever, headache skin problem and anaemia. MB is carcinogenic and very difficult to decompose. Hence removal of this dye from industrial waste is very important. The methods of color removal from industrial effluents include biological treatment, coagulation, flotation, adsorption, oxidation and hyper filtration. Among the treatment options, adsorption has become one of the most effective and comparable low cost method for the de-colorization of dye wash water. Physical methods: Physical treatment includes membrane – filtration process, reverse osmosis, electrolysis and adsorption techniques. Chemical treatment: The major agents of chemical treatment of dye wastewater are coagulants/ flocculants. It involves the addition of substances such as calcium, aluminium, or ferric ions in to the effluent, as such flocculation is induced. Biological methods: Biological treatment of wastewater is an alternative and most economical method as compare to physical and chemical methods. Biodegradation methods such as adsorption by (living or dead) microbial biomass, fungal decolourization, bioremediation systems and microbial degradation are commonly used in the treatment of industrial effluents.

II MATERIALS AND METHODS

2.1 Selection of Process

Activated carbon is widely chosen as adsorbent in the industries but due to its high cost and limited regeneration capacity it is better to use low cost bio-adsorbent. We have chosen Rice husk, wheat shell in the experiment as these materials are widely available and generally discarded from farm field. Bentonite powder as innovative material (Type of soil) is chosen as it has very high adsorption capacity[8] mention in some literature review papers.

Methylene Blue is basic dye .It doesn't change its property indifferent temperature and ph condition. The MB was chosen in this study because of its known strong adsorption onto solids. The dye is to be used in this study (Methylene Blue) has many uses in different fields, such as biology, chemistry, and textile industry.

2.2 Experimental Methods

The batch adsorption was carried in 250 ml Borosil conical flasks by mixing a pre-weighed amount of the adsorbent with 100 ml of aqueous dye solution of a particular concentration. The conical flasks were kept on a magnetic shaker and were agitated for a pre-determined time interval at a constant speed. The system parameter such as adsorbent amount, agitation time and temperature were controlled during the experiments.

Adsorbate:

The fluid which is accumulated on the surface of a liquid or solid is called as adsorbate.

Methylene blue ([7-(dimethylamino) phenothiazin-3-ylidene] dimethylazanium chloride, molecular formula: C16H18N3SCl), a heterocyclic aromatic chemical compound, has a molecular weight of 319.85. It is a cationic thiazine dye and a dark green powder that turn to deep blue colour when dissolved in water or alcohol.

Adsorbent:

The solid or liquid on whose surface, the molecules of other substance are adsorbed.

Rice husk : Fresh rice husk to be used in this work will be obtained from a local farm nearer by Kolhapur city. The impurities in rice husk and wheat shell will be first picked out. Then the rice husk and wheat shell will be washed thoroughly with distilled water before oven drying at 60 ^{0} C until the constant weight will be obtained.

III RESULTS AND DISCUSSIONS

1. Effect of Adsorbent Dosage

Different amount of bentonite soil is added to 60 ppm MB dye solution .It is treated foer 80 min on rotary shaker at 100 rpm. Then known volume of solution was removal and centrifuged for analysis of the supernatant.

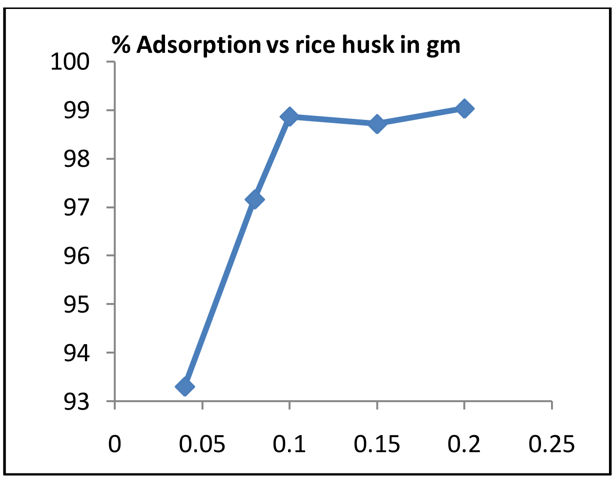

Figure 1: % adsorption vs. rice husk in gm

It was observed that equilibrium was reached for 0.2 gm within the first 60 minutes of the experiment. Thus 60 minutes would be taken as optimum time for further adsorption studies.

The reason is that the number of available adsorption sites increased by increasing adsorbent dosage. While the decrease in adsorption density with increasing adsorbent dosage is mainly due to unsaturated adsorption sites through the adsorption reaction. Another reason may be owing to the particle interactions, such as aggregation, caused by high adsorbent concentration. Such aggregation would lead to a decrease in the total surface area of the adsorbent.

2. Effect of Initial Dye Concentration and Contact Time

Different initial dye concentration solution (20 ppm to 100ppm) is treated with known quantity of adsorbent. Samples were collected after each 10 minutes from rotary shaker and centrifuged for analysis of supernatant.

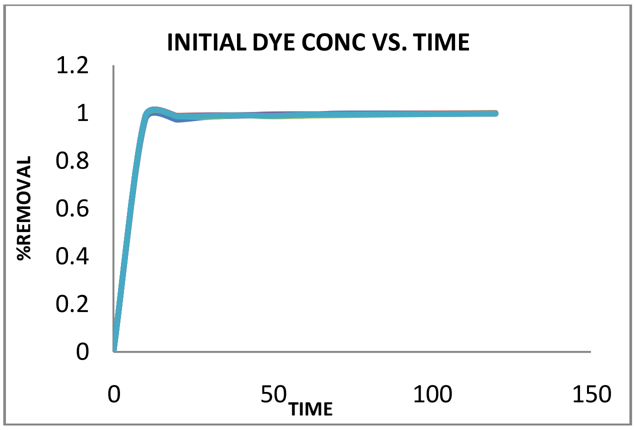

Figure 2: Effect of Initial Dye Concentration and Contact Time

Figure 3: qe vs. time

It is clear that the extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation is allowed. The final dye concentration did not vary significantly after 0.5 hours from the start of adsorption process. This shows that equilibrium can be assumed to be achieved after 0.5 hours (30 min). It is basically due to saturation of the active site which do not allow further adsorption to take place as a large number of surface sites are available for adsorption at the initial stages and after a lapse of time, the remaining surface sites are difficult to be occupied because of repulsion between the solute molecules of the solid and bulk phases

3. Effect of pH

A fixed concentrated MB dye and adsorbent were used. The pH is changed and maintain by 0.1 N NaOH and 0.1N HCL solution.

The reason for choosing these pH values were that from the literature it was evident that the adsorption of methylene blue was highest in the neutral range. At low pH, the surface of the adsorbent was surrounded by H+ ions, which prevented the metal ions from approaching the adsorptive sites of the adsorbent. However, with increasing pH value, the competitive adsorption of H+ ions decreased and the rice husk surface became more negatively charged. Thus, the positively charged metal ions can be readily adsorbed onto the negatively charged sites of the adsorbent.

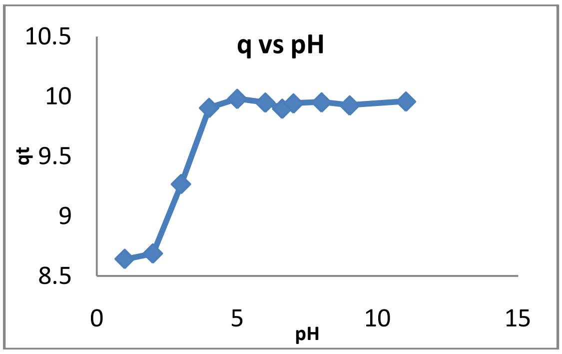

Figure 4: q_t vs. pH

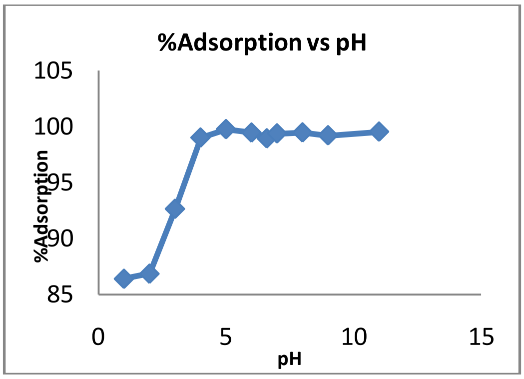

Figure 5: %adsorption vs. pH

As the concentration of ion increases, more and more surface sites are covered and hence at higher concentrations of ions the capacity of the adsorbent get exhausted due to non-availability of the surface sites. It is therefore evident that at low concentration ranges the percentage of adsorption is high because of the availability of more active sites on the surface of the adsorbent.

4. Effect of Temperature

Different concentrated MB dye solution (20 to 100 ppm) is treated with fixed amount of bentonite soil at initially at 30^{0}c, 40^{0}c and 50^{0}c.using orbital shaker incubator for fixed amount of time.

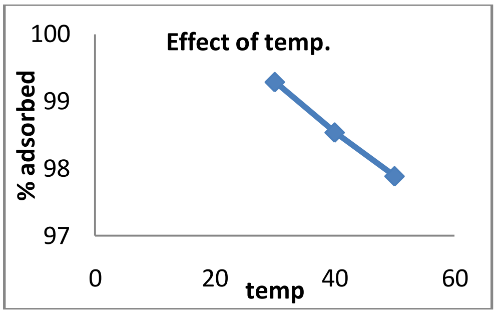

Figure 6: % adsorbed vs. temperature for 20 ppm

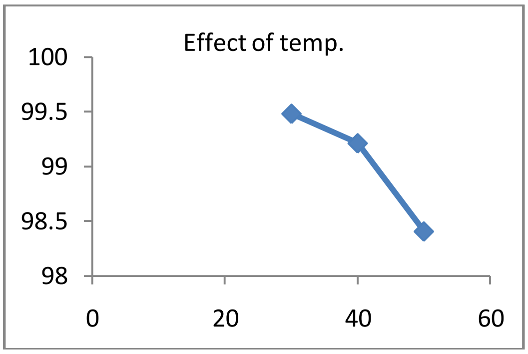

Figure 7: %adsorbed vs. temperature for 40 ppm

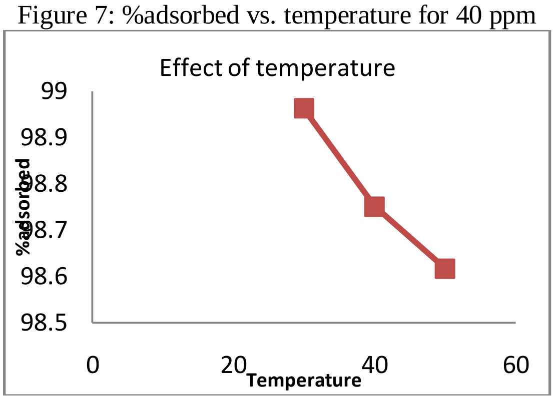

Figure 8: % adsorbed vs. temperature for 60 ppm

It was observed that the amount of substance adsorbed per unit mass of adsorbent is highest at a temperature of 30 °C. Temperature has important effects on the adsorption process. As the temperature increase, rate of diffusion of adsorbate molecules across the external boundary layer and interval pores of the adsorbent particle increase. Changing to temperature will change the equilibrium capacity of the adsorbent for particular adsorbate.

5. Adsorption Equilibrium Study

Adsorption isotherms help in describing how molecules of adsorbate interact with adsorbent surface. Equilibrium adsorption equations are required in the design of an adsorption system and their subsequent optimization.In order to optimize the design of an adsorption system, it is important to establish the most appropriate correlation for the equilibrium curves. Adsorption isotherms are often employed to characterize adsorption of dyes onto adsorbents from aqueous solutions. Adsorption isotherms can provide information about the nature of the physico-chemical interaction involved in the adsorption process.

Various Isotherms models:

The adsorption equilibrium data obtained for the MB onto natural bentonite, wheat shell and rice husk will be fitted into four different isotherm models to determine the most suitable model to represent the adsorption process. The isotherms used are the Langmuir isotherm, the Freundlich, the Temkin isotherm, and the Redlich-Peterson isotherm.

A) Langmuir isotherm:

Langmuir equation is based on several assumptions they are:

(i) The sorption takes place at specific homogeneous sites within the adsorbent.

(ii) There is no interaction between adsorbates in the plane of the surface and

(iii) Monolayer type of adsorption.

The Langmuir equation can be represented in the form of following equations.

The Langmuir isotherm is valid for monolayer adsorption on a homogenous adsorbent surface containing a finite number of identical site and no interaction between adsorbate molecules.

The Langmuir expression is represented by the following equation:

$$q_e = \frac{q_0\, k_l\, C_e}{1 + k_l C_e}$$

The linear form of Langmuir equation can be represented in following form.

$$\frac{c_e}{q_e} = \frac{1}{k_l * q_0} + \frac{c_e}{q_0}$$

If we plot a graph $\frac{c_e}{q_e}$ vs. C_e we can get slope as $1/q_o$ and intercept of $\frac{1}{k_l * q_0}$. From that we can get values of q_0 adsorption capacity and k_l Langmuir adsorption constant.

Where, Ce= Dye concentration at equilibrium is in mg/l.

q_e=Dye adsorption capacity at equilibrium is in mg/g.

K_l =Langmuir constant related to the adsorption energy is in L/mg.

q_0=Maximum Adsorption capacity is in mg/g.

B) Freundlich isotherm:

The Freundlich isotherm is derived by assuming a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface. The experimental equilibrium data for the adsorption of MB onto RH, WS, clay at different temperatures, particle size ranges and solution pH values have been analyzed using the Freundlich isotherm as given by equation.

$$q_e = K_F * Ce^{1/n}$$

The linear form of Freundlich equation can be represented in following form.

$$\log q_e = \log K_F + \frac{1}{n}\log c_e$$

If we plot a graph Log q_e vs. log c_e we can get slope as 1/n and intercept of log K_F . From that we can get values of K_F adsorption capacity and n Freundlich adsorption constant.

Where, Ce = Dye concentration at equilibrium is in mg/l. q_e =Dye adsorption capacity at equilibrium is in mg/g.

K_F= Freundlich r constant related to the adsorption energy is in L/mg.

n=Adsorption capacity is in mg/g.

Table 2: Freundlich (Qe) and Langmuir (Qe)

Freundlich (qe)	Langmuir (qe)
6.0277124	5.06349
7.68337	7.67002
15.74401	16.85229
19.98302	20.61777
24.5508	23.88954

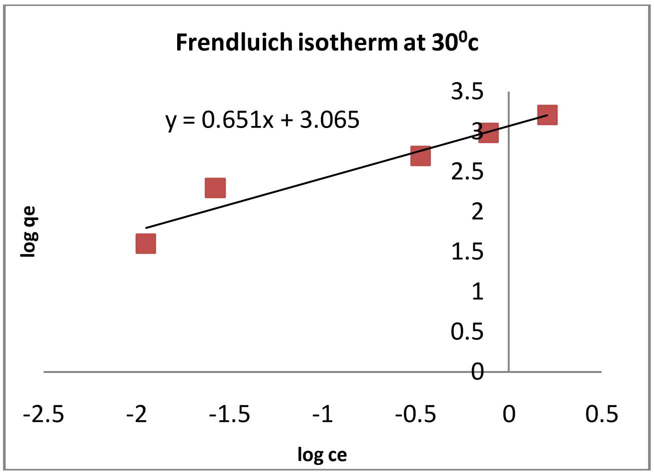

Figure 9: log qe vs. log ce for 30 deg C

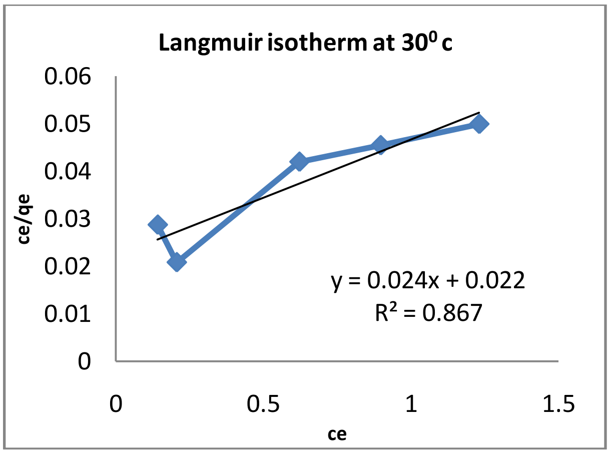

Figure 10: ce/qe vs. ce for 30 deg C

Table 10: Isotherm data for 30 degree Celsius.

Initial conc.	Conc.	qe	log(qe)	log(Ce)	Ce/qe
20	0.142431	4.9643	1.6022	-1.94889	0.0286
40	0.20681	9.9482	2.29741	-1.57595	0.0207
60	0.622539	14.844	2.69762	-0.47395	0.0419
80	0.897891	19.775	2.98445	-0.10771	0.0450
100	1.23185	24.692	3.20648	0.208517	0.0498

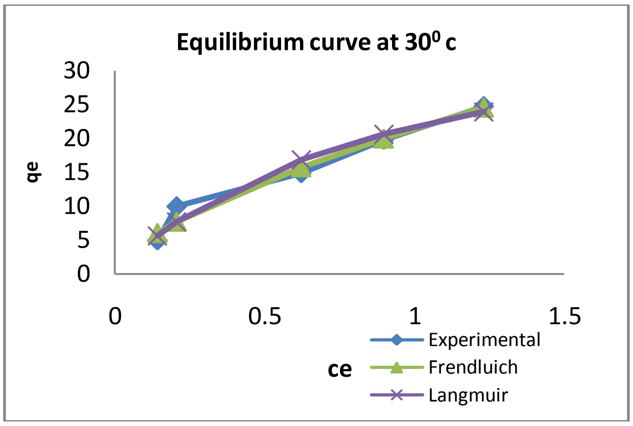

Figure 11: Equilibrium curve for 30 deg C

From R^2 value Freundlich isotherm describes system well. Temperature has important effects on the adsorption process. As the temperature increase, rate of diffusion of adsorbate molecules across the external boundary layer and interval pores of the adsorbent particle increase. Changing to temperature will change the equilibrium capacity of the adsorbent for particular adsorbate. where log kf is roughly a measure of the adsorption capacity and 1/n is an indicator of adsorption effectiveness; qe is the amount of dye adsorbed per unit mass of adsorbent (in mg g-1) and Ce is the equilibrium concentration of dye (in mg l-1). The values of Freundlich parameters were obtained from the linear correlations between values of log qe versus log Ce.

6. Adsorption Kinetic Study

Adsorption is a physicochemical process that involves mass transfer of a solute from liquid phase to the adsorbent surface. In order to investigate the controlling mechanisms of the adsorption processes like mass transfer and chemical reactions, pseudo first-order, pseudo second-order kinetic studies and Intraparticle diffusion equation are used to test the experimental data. Three of the most widely used kinetic models, i.e. Lagergren-first-order equation, pseudo-second-order equation and Intraparticle diffusion equation were used to research the adsorption kinetic behaviour of MB. The best fit model was selected based on the linear regression correlation coefficient values (R^2). It is important to be able to predict the rate at which contamination is removed from aqueous solutions in order to design an adsorption treatment plant. In order to investigate the mechanism of adsorption, characteristic constants of adsorption rate were determined using a pseudo first-order equation of Lagergren based on solid capacity, and pseudo second-order equation based on solid phase adsorption and an Intraparticle diffusion model.

1) **Pseudo first-order**

$$\frac{dq}{dt} = k_1(q_e - q)$$

Linear form: $\log(q_e - q) = \log q_e + \frac{k1\,t}{2.303}$

2) **Pseudo second-order**

$$\frac{dq}{dt} = k_2(q_e - q)^2$$

Linear form: $\frac{t}{q} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e}t$

Where, q_e= amount of dye adsorbed (mg/g) at equilibrium.
q =amount of dye adsorbed onto the adsorbent at any time t.
k_1=Rate constant for frist order reaction(min^{-1}).
k_2=Rate constant for second order reaction(g.mg^{-1}.min^{-1})

3) **Intraparticle diffusion**

$$q_t = k_d t^{-0.5}$$

Where, k_d =Intra partical diffusion rate constant (g.mg^{-1}.min^{-1})

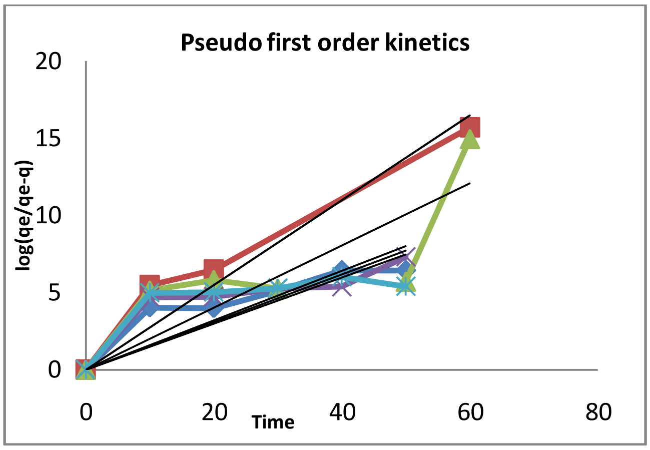

Figure 12: For pseudo first order

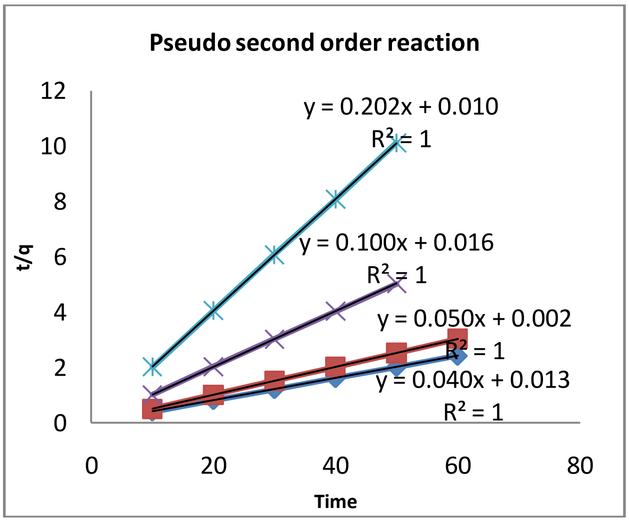

Figure 13: For pseudo second order

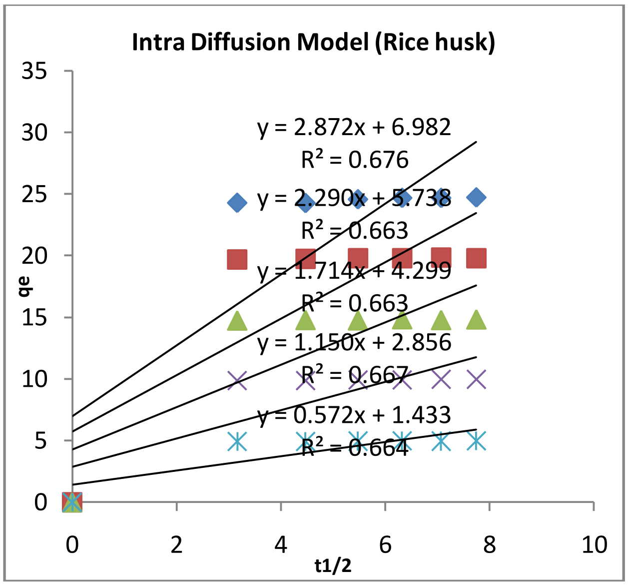

Figure 14: Intra Diffusion Model for Rice Husk

The validity of kinetic model is tested by the magnitude of regression coefficient R^2. It is important to note that for a pseudo first order model, the correlation coefficient is less than 0.98, which is indicative of bad correlation. The first order model did not provide a good fit. For pseudo second order the magnitude of regression coefficient R^2 is nearly one and intra partial diffusion modal gives r2 value nearly 06 to 0.7.Thus the pseudo 2nd order describes the adsorption phenomenon more accurately. Also this suggests the assumption behind the pseudo second order model that the dye uptake process is due to chemisorption[16].The result also indicates that adsorption of methylene blue on Rice husk is not diffusion controlled.

7. Adsorption Thermodynamic Study

The thermodynamic parameters that must be considered to determine the process are changes in Gibbs free energy (ΔGº), standard enthalpy (ΔHº), and standard entropy (ΔSº) due to transfer of unit mole of solute from solution onto the solid–liquid interface. The Gibbs free energy change of adsorption is defined using Van't Hoff equation.

$$\Delta G^o = -2.303\ RT.\log K_l$$

Where K_l is Langmuir equilibrium constant (g/lit), (R) is the universal gas constant (8.314 J.mol-1.K-1) and (T) is the absolute temperature (K).

The values of (ΔHº) and (ΔSº) was computed using following equation.

$\Delta G^o = T\Delta S^\circ - \Delta H$

$$\text{Log}\, K_l = \frac{\Delta S^\circ}{2.303\, R} - \frac{\Delta H^\circ}{2.303RT}$$

The equilibrium constant (Kl), standard Gibb's free energy (ΔGº), change in enthalpy (ΔHº) and change in entropy (ΔSº) are evaluated for predicting the nature of adsorption.

The value of (ΔGº) in all cases are indicates of the spontaneous nature of the interaction without requiring large activation energies of adsorption and no energy input from outside of the system is required .If standard Gibb's free energy (ΔGº) is negative, then adsorption will be spontaneous and feasible. If the change in enthalpy (ΔHº) is positive, then the adsorption will be endothermic in nature. If the change in entropy (ΔSº) is positive, then adsorption will be irreversible and reflects the increased randomness at solid –solution interface.

From equilibrium data it was observed that Freundlich isotherm fits to our system.

Table 3: Calculation of Gibbs Energy

Sr no	b	ln b	(ΔG)	T	1/T
1	21.4345	3.065	-7721.17	303	0.0033
2	23.7362	3.167	-8241.43	313	0.003195
3	14.2963	2.66	-7143.22	323	0.003096

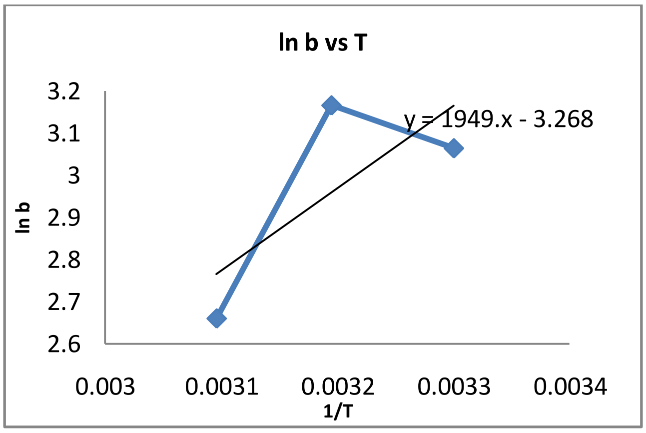

Figure 15: ln b vs. 1/T

Table 4: Enthalpy and Entropy values

No	T	ΔG	ΔH	ΔS
1	303	-7721.17	ΔH=-1949*8.314	ΔS=3.268*8.314
2	313	-8241.43	ΔH=-16203.98	ΔS=27.170
3	323	-7143.22		

The values of ΔG◦ were negative at all temperatures studied, which confirms the feasibility of the process and the spontaneous nature of MB adsorption. The negative value of ΔH indicates that the adsorption of MB onto rice husk was an exothermic process. The positive value ΔS reflects the affinity of the adsorbent for the dye and increased randomness at the solid-solution interface during adsorption.

IV CONCLUSIONS

1) The present study shows that rice husk can be used as low cost adsorbent .

2) Adsorption capacity is rice husk is upto 25mg/g.

3)Contact time study shows that maximum adsorption happen within first 30 for rice husk. Adsorption capacity increases with increase in Initial dye concentration of methylene blue dye.
4) Adsorption dosage varies with material .it is observed that for rice husk it require 0.2 gm.
5) Effect of pH shows that maximum adsorption happens in neutral to basic range. Temperature study shows with increase in temperature adsorption decrease rice husk Hence it is endothermic for wheat shell.
6) Equilibrium isotherm study shows that all material follows Langmuir and Freundlich isotherm while Freundlich follows more accurately comparing r^2 values of linear equations.
7) Kinetics study shows rate of adsorption follows pseudo second order kinetics model.
8) Thermodynamic study shows that Gibbs free is negative for rice husk it indicates adsorption is spontaneous while enthalpy is negative shows that adsorption of methylene blue onto these material is exothermic . While positive value entropy reflects the affinity of adsorbents for methylene blue.

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