Kinetic ,Thermodynamic and isotherm studies on the removal of Methyl Orange dye using Algae, *Chara*

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Abstract

Adsorption process has been found to be an efficient and economic process to remove toxic dyes from contaminated water. Algal biomass shows quite fascinating results in adsorption of toxic dyes from aquatic environment. Present investigation has been based on adsorption of methyl orange by *Chara* (water plant).The application of the adsorbent for methyl orange removal was observed to be influenced by the variation in these parameters like adsorbent dose, contact time and pH .The equilibrium data were analysed based on the Langmuir and Freundlich isotherms. Kinetic data were analysed using the pseudo –first order and pseudo –second order models. The maximum adsorption capacity is 69.93mg/g. The Kinetics of methyl orange adsorption using algae *Chara* is described by the pseudo-second order model. In addition, the thermodynamic parameters such as $\Delta H°$, $\Delta S°$ and $\Delta G°$ were determined, and the dye adsorption process is endothermic.

Keywords: Methyl orange, Adsorption isotherms, Adsorbent, Kinetic, Thermodynamic

Introduction

Dye pollution is a global issue owing to the hazardous nature of dyes. It is considerably visible in the environment, as dyes are commonly highly water- soluble and not readily degradable under natural condition, resulting in a relatively long time residence in the environment. Therefore, the removal of dyes from various toxic effluents has become of special concern to environmental specialists. Azo dyes such as methyl red and methyl orange are well known to be human carcinogens (Hildenbrand et al 1999)that pervade aqua systems from various sources, including textile, pharmaceutical and printing industries, as well as medical and chemical labs. Although most dyes are not highly toxic, they should be recognised as visual pollutants that can reduce light penetration into water, consequently decreasing the efficiency of photosynthesis and affecting the growth of aquatic organism(Huang et al 2008).Moreover, dye pollution presents aesthetic changes that are harmful in the natural environment.

Methyl orange an anionic dye belongs to the azo group of dyes.The azo group of dyes has nitrogen in their molecule. The presence of azo group (N=N) in methyl orange and low biodegradability makes it an issue of concern for environmental science(Mittal et al 2007).

Algae are ubiquitous naturally and serve as one of the biomaterials with high capacity for removing dye from contaminated waters (Panasamriut et al 2007).Compare to

physicochemical processes, biological processes have potential to convert or degrade the pollutant into water, carbon dioxide and various salts of inorganic nature. The isolation of potent species and there by degradation is one of the interest in biological aspect of effluents treatment(Mohan et al,2002).

Algal biomass is one of the potential options for dye adsorption because of its ability to grow faster due to the existing multilayer cell wall and various functional groups(Akmil-Basar et al;2005, Chandra et al ;2015).Majority of algal species has investigated for the dye removal from waste water , which includes Chlorella Vulgaris(Aksu and Tezer,2005),*Chara aspera*(K.S .Low et al;1994), *Cystoseizaindica and Gracilari aspersica* (Kousha et al ;2012).

1. MATERIALS AND METHODS

1.1Adsorbate

Methyl Orange ($C_{14}H_{14}N_3NaO_3S$, the sorbate used in this study, is an anionic dye with molecular weight 327.34 gmol^{-1}and maximum absorption (λ_{max}) 465nm. A stock solution of 1000 ppm was prepared by dissolving dye in water. Concentrations ranged between 10 and 100 ppm were prepared from the stock solution.
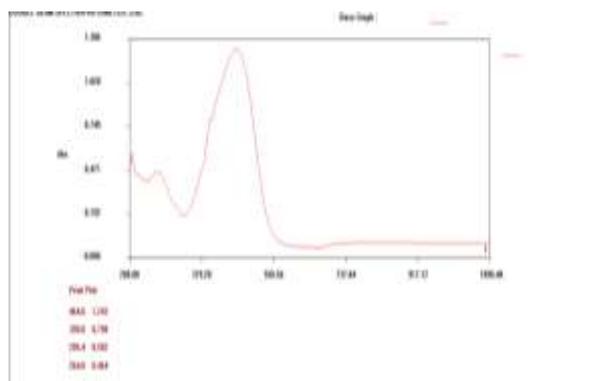

Fig1: Absorbance of MO at $\lambda_{max} = 465nm$

1.2 Adsorbent

Chara (water plant) samples were collected from the locall pond. After taking , plant algae were washed with distilled water and dried in a convection oven at 50^{0}C for 6 hours. Further it was treated with 0.1M HCl and heated it in a muffle furnace up to 650^{0}C for a period of 1hr.The resulting activated carbon materials were powdered and sieved through a 0.25mm sieve (Rumi and Pradhan 2015).

1.3 Batch adsorption experiments

The effects of pH, contact time and adsorbent dosage were investigated using 1g of each adsorbent except for adsorbent dosage experiments where various amounts were used.In all cases residual concentrations of MO after equilibration were measured at 465nm wavelength using UV/ Visible spectrophotometer.

1.4 Adsorption isotherms

In order to determine the sorption isotherm 0.1g of the *Chara* was brought into contact with 50ml of the MO dye solutions of varying concentrations (20-100 ppm).The equilibrium concentration was determined at 120 minutes. After the equilibration period ,the concentration of the filtrate was measured using UV-Visible spectrophotometer. The amount of dye adsorbed was calculated.

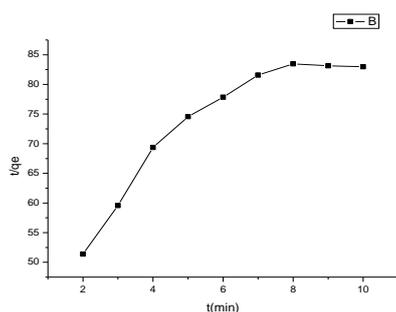## 2. Results and discussion

2.1Effect of pH on adsorption of MO dye

Fig 2 Effect of pH

The pH is the significant factor which controls the adsorption process particularly for cationic dyes. To each of nine reagent bottles 100 ml of 100 ppm methyl orange solution was taken and 1.0 gram of the carbon was added. The effect of solution on pH of MO dye adsorption has been studied by varying pH on MO dye Solution from 2 to 10 using 0.1 N NaOH and 0.1N HCl.*(Hameed,Krishni,&sata,2009)*. Each bottle was allowed to undergo shaking for 1 hour. After shaking the solutions were filtered and the absorbances of the filtrates were measured. From the initial and final absorbances the percentage of dye removal was calculated . The maximum adsorption of MO dye takes place to the extent of 81 - 83% for *chara* in the range of pH 7-9. As shown in Figure 2.1, the percentage of dye removal increases in the pH range of 2- 6, then the amount becomes constant within the range of 7-10.

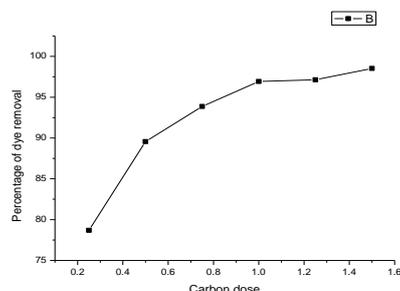### 2.2 Effect of adsorbent dose on the adsorption of MO dye

Fig 3 Effect of adsorbent dose

Effect of adsorbent, dose on removal of dye was studied by varying the dose of adsorbent (0.25 to 1.5 gram). In the test solution at the same time as keeping the initial dye concentration (100 ppm) and equilibrated using rotatary mechanical shaker for two hours. After equilibration the absorbance of the filtrate was measured using UV-Visible spectrophotometer. The maximum adsorption of *chara* was found to be 98.52 % with carbon dose of 1.5g per 100 ml of 100 ppm dye solution. As ordinary, the percentage sorption of the dye increased with increasing adsorbent dosage. The results (Figure 2.2) indicate that adsorption percentage of MO increases with the increasing of adsorbent dose, it increased from 78% for 0.25g to 98% for 2g.

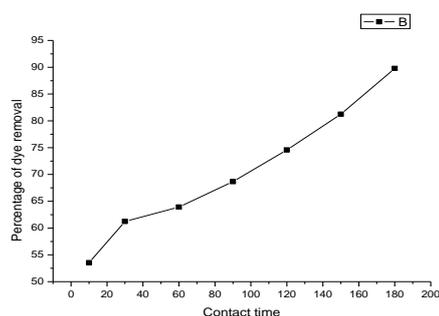*2.3Effect of contact time:*

Fig 4 Effect of contact time

The adsorption experiments were conducted by varying the contact time (10-150minutes) at fixed optimal initial concentration of dyes with a fixed dose of adsorbent and particle size. In a series of reagent bottles 100 ml of 100 ppm methyl orange dye solution was taken and carbon dose of 1gm of carbon powder was added. These bottles were agitated in a thermostatic mechanical orbit shaker and at different time intervals ,bottles were removed from the shaker and kept for settlement. Then the supernatant liquid was subjected to absorbance measurements. The adsorption increased with increase in contact time.

2.4.Sorption isotherms

The adsorption capacity and other parameters were evaluated using Langmuir and Freundlich isotherm models.

Table1 Adsorption isotherm data

Initial dye conc(ppm)	Weight of carbon(g)	Equilibrium dye conc (Ce)	Amount of dye adsorbed (qe)	Ce/qe	Log Ce	Log qe	Ln Ce
20	0.1	1.234	9.383	0.1315	0.0913	0.9723	0.210
40	0.1	2.643	18.678	0.1415	0.4220	1.2713	0.9719
60	0.1	5.982	27.009	0.2214	0.7767	1.4315	1.7887
80	0.1	9.012	35.494	0.2539	0.9548	1.5501	2.1985

| 100 | 0.1 | 12.246 | 43.877 | 0.2790 | 1.0879 | 1.6422 | 2.5051 |

2.41 *Langmuir Isotherm*

The Langmuir isotherm assumes that adsorption occurs on a homogeneous monolayer surface containing sites with uniform energy with a finite number of identical sites. It also assumes there is no interaction between the adsorbed molecules (Xing et al.,2010).
Langmuir adsorption isotherm equation can be expressed as

$$\frac{Ce}{Qe} = \frac{1}{Qm}\ Ce + \frac{1}{QmK_L}$$

Where Ce is the concentration of the adsorbate at equilibrium (mg/g), Qe the amount of MO dye adsorbed per gram of adsorbent (mg/g), Qm is maximum capacity of monolayer coverage(mg/g), K_L is the Langmuir isotherm constant (L/mg).
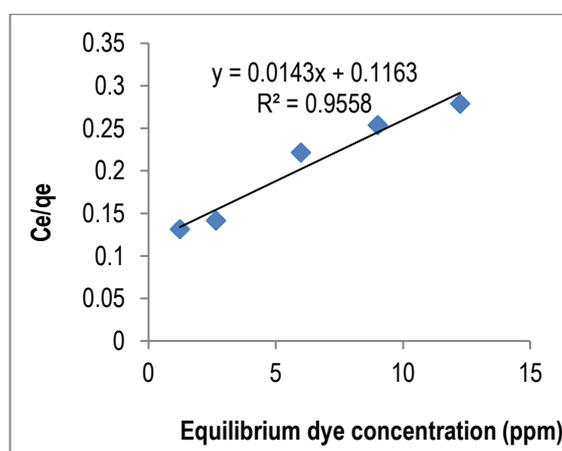

Fig 5 Langmuir isotherm for adsorption of MO

RL that is given below ,$R_L=[1/ (1+K_LC_o]$

Where , C_o is the initial dye concentration in solution (Lmg^{-1}) and K_L is the Langmuir constant(L/mg). The value of RL indicates the type of the isotherm to be either favourable(0<RL<1), unfavourable(RL>1), linear (RL=1) or irreversible(RL=0)   (Ren Jian – min et al.,2010). The RL was found to be (0.075), that's mean the adsorption process is favourable. K_L (Langmuir isotherm constant) is 0.122 Lmg^{-1}, R^2 value is 0.9558 proving that the sorption data fitted well to Langmuir Isotherm model. The maximum adsorption capacity of MO on *Chara* in the studied conditions is equal to 69.93 mg/g.

2.42 *Freundlich Isotherm*

The Freundlich expression is for a multilayer sorption to occur and it is an empirical equation for adsorption on heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface (Xing et al.,2010)
The Freundlich adsorption isotherm equation can be expressed as,

$$\log qe = log K_f \quad + \frac{1}{n}\log C_e$$

Where, q_e(mg g^{-1}) is the adsorption capacity, K_f(mg/L) is Freundlich constant related to adsorption capacity of adsorbent , n is the Freundlich exponent related to adsorption intensity, C_e(mg L^{-1}) is the equilibrium concentration of substrates in the solution.
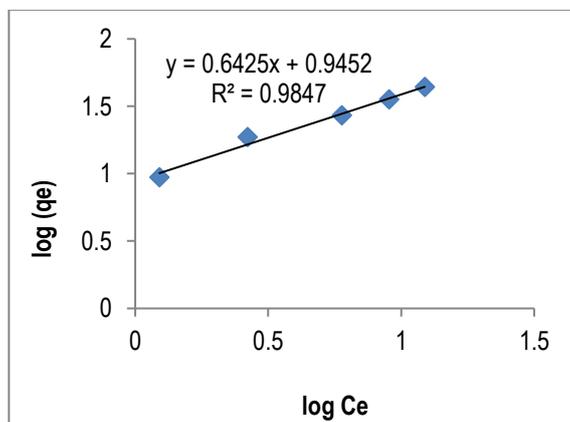

Fig 6 Freundlich isotherm for adsorption of MO

Linear plot of logq$_e$ versus log C$_e$ shows that the adsorption of MO follows the Freundlich isotherm(fig 2).The value of K$_f$ and n were calculated from the intercept and slope of the plot . The scale of the exponent (n) gives an indication of the favourability and K$_f$ the capacity of the adsorbent / adsorbate. The value of k$_f$ and n were calculated from the intercept and slope of the plot.The value of 1/n was found as 0.6425 (Table 1.2) which is less than 1, confirmed the favourability of the adsorption process (Moradi, 2011).

Table- 2Langmuir and Freundlich   parameters of adsorption isotherms

Langmuir Isotherm			Freundlich Isotherm			
R^2	R_L	K_L(L/mg)	R^2	K_F(L/mg)	1/ n	N
0.9558	0.075	0.122	0.9847	8.25	0.3992	1.556

2.5 Adsorption Thermodynamic study

The thermodynamic parameters that must be considered to determine the process are changes in Gibbs free energy (ΔG^0),standard enthalpy (ΔH^0) and standard entropy (ΔS^0) due to transfer of unit mole of solute from solution onto the solid-liquid interface. (Patil et al 2017).The adsorption characteristics of a material can be expressed in terms of thermodynamic parameters such as ΔG (Gibbs free energy),which can be calculated by the following equation (Piccin et al 2011)

$$\Delta G = -2.303RT \, logkd$$

Where kd is the thermodynamic equilibrium constant (Lg^{-1}). (R)is the universal constant($8.314\ Jmol^{-1}k-1$) and (T) is the absolute temperature(k).

The values of ($\Delta H°$) and ($\Delta S°$) was calculated using following equation.

$$\Delta G° = T\Delta S° - \Delta H$$

$$logkd = \frac{\Delta S°}{2.303R} - \frac{\Delta H°}{2.303RT}$$

The equilibrium constant (kd), standard Gibb's free energy (ΔG^0), change in enthalpy (ΔH^0) and change in entropy (ΔS^0) are evaluated for predicting the nature of adsorption.

Table -3 Calculation of Gibbs Free energy

B	ln b	T	1/T
23.694	3.1652	293	0.0034
18.917	2.9400	303	0.0033
16.519	2.8045	313	0.0031
11.9528	2.4809	323	0.003

Fig 3.ln b vs. 1/T

y = 1504.1x - 1.9655
R² = 0.9206
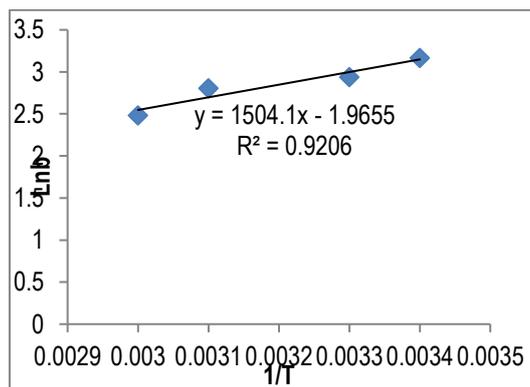
The values of Gibbs free energy ($\Delta G°$) of adsorption of MO adsorption on *Chara* were found to be negative corresponding to a spontaneous process [Jain et al 2010]. The positive value of $\Delta H°$ (12.505) confirmed that the adsorption phenomenon of MO on *Chara* is endothermic. The negative $\Delta S°$ (-16.25) value suggests a decrease in the randomness at the solid–liquid interface during the adsorption of the MO dye on *Chara* . Generally, the value of $\Delta G°$ for physical adsorption (from −20 to 0 kJ/mol) is smaller than that for chemisorption (from −80 to −400 kJ/mol) (Yang,Pyle 1999).Similarly, a $\Delta H°$ value of less than 40 kJ/mol indicates the physical process . (Xu 2018)

Table - 4 The values of the thermodynamic of MO dye adsorption at various temperatures

$\Delta H°$ KJ/mol	$\Delta S°$ J/mol.K	$\Delta G°$(KJmol^{-1})			
		293K	303K	313K	323K
12.505	-16.25	-17.268	-17.431	-17.593	-17.756

2.6 Adsorption kinetic study

The pseudo – first order kinetic model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites. The pseudo-first order equation was expressed in equation.(Ho and Mckay 2004).

$$\log(qe - qt) = \log qe - \frac{K1}{2.303} t$$

Where qe is the adsorption capacity of the adsorbent at equilibrium (mg/g), qt is the amount of dye adsorbed at time t(mg/g) and k_1 is the pseudo first order rate constant(min^{-1})

Table -5 Determination of qt values

T	Qe	Qt	qe-qt	log(qe-qt)
10	9.383	7.3172	2.0658	0.3150
30	9.383	7.5073	1.8757	0.2731
60	9.383	7.9502	1.4328	0.1561
90	9.383	8.2953	1.0877	0.0365
120	9.383	8.6008	0.7822	-0.0365
150	9.383	8.9262	0.4568	-0.3402

Figure 5 Pseudo-first order model of MO adsorption onto Chara
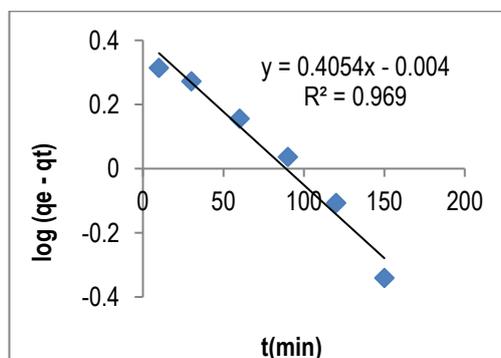
The pseudo second order kinetics can be expressed in a linear form as integrated second order rate law(Kamal 2014).
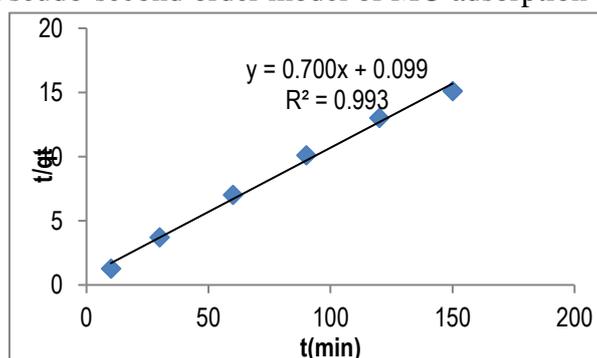
$$\frac{t}{qt} = \frac{1}{qe}t + \frac{1}{K2qe^2}$$

Where k_2 is the pseudo second order rate constant (g mg^{-1} min^{-1}).

Table -6 Determination of t/qt values

T	qt	t/qt
10	7.3172	1.3664
30	7.5073	3.9961
60	7.9502	7.5469
90	8.2953	10.8495
120	8.6008	13.9521
150	8.9262	16.8044

Figure 6 Pseudo-second order model of MO adsorption onto *Chara*

A pseudo second order suggests that this adsorption depends on the adsorbate and the adsorbent and involves chemisorptions process in addition to physisorption. The chemisorption might be the rate limiting step where valence forces are involved via electrons sharing or exchange between the adsorbent and the adsorbate.(Patil 2011).The two adsorption kinetics models mentioned above have been used to understand the adsorption kinematics and correlation coefficient, R^2 , where calculated from plots. The linearity of those plots indicates the capacity of the two kinetic models. The correlation coefficient adsorption kinetics is 0.969 and 0.993 for pseudo-first-order and second-order, respectively. The correlation coefficient shows that the pseudo-second-order models fitted the experimental data well with a compared with the pseudo-first-order models. The obtained constants for the pseudo-first- and pseudo-second-order kinetics model are tabulated in Table 1.7. Also this suggests the assumption behind the pseudo second order model that the dye uptake process is due to chemisorptions(Y.S. Ho 2003).

Table – 7 Pseudo first order and pseudo second order parameters for MO dye adsorption onto *chara* plant

Pseudo Ist order			Pseudo 2nd order		
qe(mg/g)	K$_1$ (min^{-1})	R^2	qe(mg/g)	K$_2$(mg^{-1}g.min^{-1})	R^2
1.499	0.0092	0.969	10.10	0.007	0.993

3 .Conclusion

   The main object of the present work was to explore the possibility of using algae *Chara* as adsorbents for the removal of MO dye from aqueous solution . The removal efficiency increased with increasing of adsorbent dosage, contact time and pH removal efficiency. Langmuir and Freundlich adsorption isotherm models were used for the report of the adsorption equilibrium of MO dye onto activated carbon of *Chara*. The adsorption process follows Freundlich isotherm with high value of R^2 (0.9847) as compared to Langmuir (0.9558) isotherm**.** The adsorption data was well described by the Langmuir isotherm equation with a maximum adsorption capacity of 69.93   mg/g. The   thermodynamic parameters negative ΔG values and positive ΔH values proved that the adsorption process was an endothermic and spontaneous process. The kinetics followed the pseudo-second order model. .

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