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STUDIES ON THE REMOVAL OF METHYLENE BLUE DYE FROM WATER USING CHITOSAN

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ABSTRACT

The use of cheap and eco-friendly adsorbents studied as an alternative substitution of activated carbon for removal of dyes from waste water. Chitosan was utilized as adsorbent to remove methylene blue (MB) by adsorption. Batch experiments were conducted to study the effect of pH, initial dye concentration, various adsorbent dosage and these were analyzed using both pseudo first order and pseudo second order equations. The equilibrium adsorption data were analyzed by using the Freundlich and Langmuir isotherms. The equilibrium adsorption capacity (qe) increases with increasing the initial concentration of dye and with decreasing the pH. The maximum colour removal efficiencies of chitosan at dosage of 0.1 g for time duration of 30 min found to be 99% of the dye from a solution of 10 ppm. The pseudo second order kinetic model agrees very well with the dynamic behavior of the adsorption of dye MB on chitosan under different pH, initial dye concentrations and adsorbent dosages. The Freundlich equation is the best fit equilibrium isotherm for the sorption of dye MB onto chitosan based on a linearlized correlation coefficient.

INTRODUCTION

With economic and technological development, water pollution is a common problem worldwide. Water pollution has become more and more serious, especially regarding dye ions. Dye ions mainly from dyeing industries have become a serious threat to human beings and the aquatic eco-system, due to their toxicity and persistence after being released in natural water. Therefore, discharge regulations are progressively becoming more stringent. Many recent studies have been focused on the development of efficient processes for the recovery of these organic contaminants from the effluents of textile industries. Usually conventional techniques such as precipitation, coagulation and flocculation have been used in wastewater treatment. Photo-oxidation has also been proposed for the treatment of dye containing effluents. However, this process is relatively expensive and not appropriate for treatment of large flows. More recently, biological degradation has been cited as an alternative process for decolourization of the reactive dye. On the other hand, adsorption process remains the most common and useful technique for the decontamination of the effluents of textile and dyeing industries. Many studies have been made on the possibility of adsorbents using mineral sorbents, activated carbon, peat, chitin, rice husk, soy meal hull and agro wastes. However, the adsorption capacity of the adsorbents is not very effective to improve adsorption performance and new adsorbents are still under development. It is well known that the chitosan has widely been used in preparation of various bio medical products. Chitosan is easily prepared from chitin by deacetylating its acetoamide groups with a strong alkaline solution. This is the most abundant biopolymer in nature after cellulose. The high proportions of amino functions in chitosan have been found to provide novel adsorption properties for many metal ions and organic dyes. The deacetylated amino groups in chitosan can be protonated and the polycationic properties of the polymer are expected to contribute to the charged interactions with a model dye, methylene blue, which is a basic dye. In this study, chitosan (90% deacetylated) was used as adsorbent to remove dye MB from aqueous solution. The investigation for dye removal was carried out through a series of batch adsorption experiments. The attention has been placed in understanding kinetics, mechanisms and equilibrium processes involved in the adsorption of MB onto chitosan. The effects of pH, initial dye concentration and adsorbent dosages on the adsorption phenomena have been studied.

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MATERIALS AND METHODS

Chemicals and Preliminary Characteristics of Adsorbent

Chitosan (90% deacetylated, Indian marine sea foods limited) was used without further purification. The dye methylene blue was used without further purification. The chemical structure of methylene blue is shown in above figure. The other reagents

used in this study were of pure analytical grade. De-ionized water prepared by passing distilled water through a de-ionizing column.

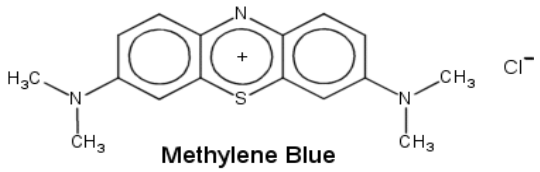
Dye Solution Preparations

The characteristics of methylene blue used for the present work are given in Table 1. An accurately weighed quantity of dye dissolved in distilled water to prepare a stock solution (1000 ppm). Solution used in the experiment for the desired concentration obtained by successive dilution. Dye concentration was determined by using absorbance values measured before and after the treatment at 660nm with Elico India Limited (SL159) UV visible spectrophotometer.

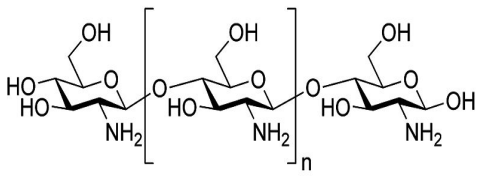
Table 1: Properties of Methylene Blue

Chemical formula	$C_{14}H_{18}N_3SCl$
Molecular weight	319.95 g/mol
Melting point	100-110ºc
Type of dye	Basic blue
Boiling point	Decomposes
Λmax	660 nm

The structures of (a) Methylene blue; (b) Chitosan



Methylene Blue



Chitosan

Calibration of Methylene Blue

The synthetic dye sample calibrated in order to find out various optical densities at various concentrations. The calibrated results are very effective to identify respective colour removal capacities of various adsorbents Figure 1 showing the graphical representation of calibration of Methylene blue.

The amount of methylene blue adsorbed (q_e) was determined by using the following equation:

$$q_e = V(C_0 - C_e)/m$$

Where C_0 and C_e represent initial and equilibrium methylene blue concentrations (μmol/L), V is the volume of methylene blue solution (L) and m is the amount (g) of chitosan.

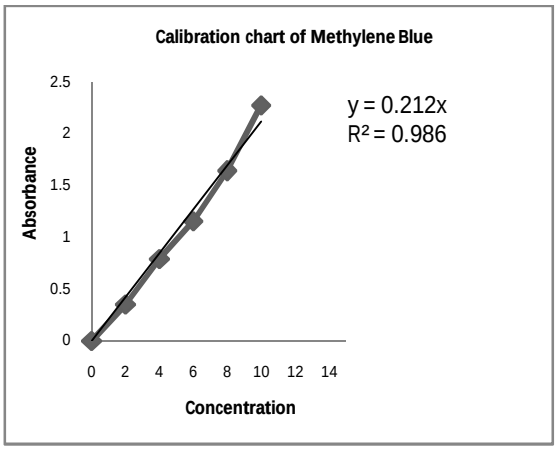


Figure 1. Calibration of Methylene Blue

RESULTS AND DISCUSSIONS

Kinetics of Adsorption

Effect of adsorbent dosage

100ml of the stock solution of 100ppm taken and with various amounts (0.1-1g) of adsorbent fed into 250ml conical flask and kept for agitation at 120rpm using an orbitex shaker for the regular interval of 10min. At the end the agitated sample taken from the shaker and filtered and tested for its optical density using UV spectrophotometer. From the comparative results it is clearly understood that the effect of adsorbent dosage is also plays a very vital role in adsorption process for colour removal. The maximum colour removal at dosage of 1g for time duration of 30 min.

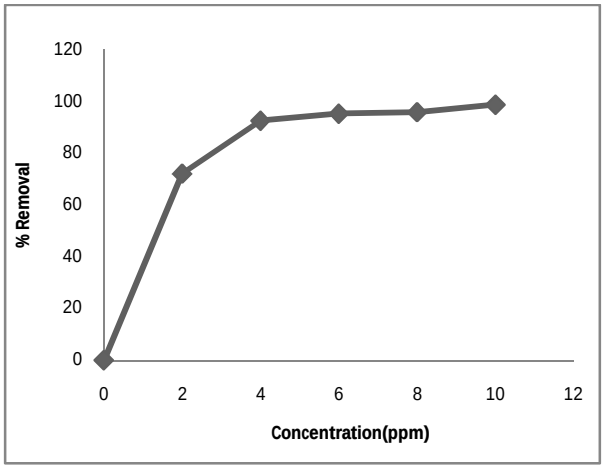


Figure 2. Effect of initial concentration on removal of Methylene Blue

Effect of Initial Concentration

Removal efficiency is greatly depended on the initial concentration of solution of adsorbate for the evaluation of the effect of initial concentration 100ml solution of different initial concentration was treated onto the adsorbent. Initial concentration was varied from 0.1 mg/l to 1 mg/l. The results were illustrated in Figure 2.

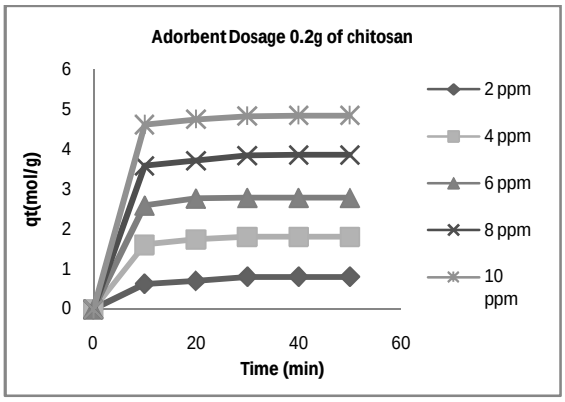


Figure 3. Effect of Adsorbent dosage of 0.2g of chitosan at different ppm

Effect of pH

In order to find the effect of pH, series of experiments conducted at various pH values from 4 to 9 in acidic and alkaline conditions respectively. The value of pH is controlled by addition of NaOH and HCl. For the work we have taken 10 ppm of methylene blue dye and 0.1 g of chitosan as our optimum the sample withdrawn from the shaker at predetermine time interval for 10min each. At the end of 10 min each the agitated sample is taken from the shaker and tested for its optical densities using the UV visible spectrophotometer.

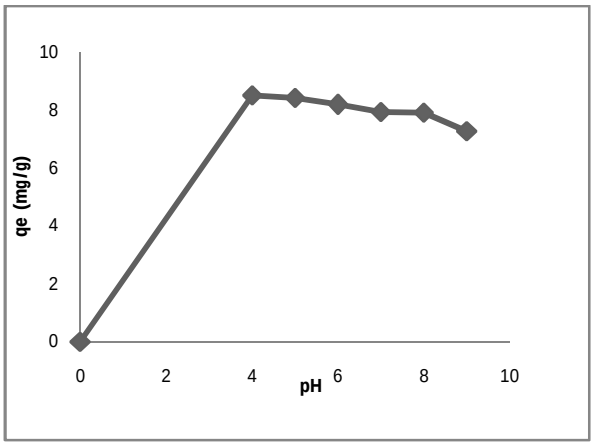


Figure 4. Effect of pH on adsorption of 10ppm Methylene Blue and 0.1g of chitosan

EQULIBRIUM ADSORPTION

Adsorption isotherm describe how adsorbate interact with adsorbents and so are critical and optimizing the use of adsorbents. Thus, the correlation of equilibrium data by either theoretical or empirical equations is essential to the practical design and operation of adsorptions system. The isotherm constants obtained from the linearized plots of Freundlich and Langmuir equation and values of correlation (R^2) are discussed in the following sections. Where x is the amount adsorbed per mass of adsorbent (m), Co is the initial concentration of the solution (ppm), C is the equilibrium concentration (ppm),K and n are Freundlich constants. The constant K partition coefficient in equilibrium is positively related to extent of degree of adsorption while constant 'n' provides a rough estimation of intensity of adsorption. A linear form of Freundlich expression will yield the constant K and n.

Hence,

Log x/m=logK+1/n log C

The analysis and design of adsorption separation process are required the relevant adsorption equilibrium, which is the most important piece of information in understanding the adsorption process. The adsorption isotherms and equilibrium equations and applied to condition resulting after the adsorbate-containing phase has seen in contact with the adsorbent of sufficient time to reach equilibrium. The adsorbent capacity of any adsorbent may be determine by the use of an adsorption isotherm. Knowledge of adsorption capacity of an adsorbent material such as chitosan enables the designer to develop the treatment system of particular adsorbate/adsorbent systems.

Table 1. Frendlich Isotherm Constants

Parameter	Freundlich		
Adsorbent dosage (g)	K_F (µmol/g)	n (g/L)	R^2
0.1	2.12	1.66	0.997
0.2	2.48	1.42	0.986
0.3	1.76	1.68	0.995
0.5	2.048	1.85	0.992
0.6	2.408	1.45	0.992
0.8	2.442	1.43	0.976
0.9	2.180	1.63	0.994
1.0	2.310	1.30	0.974

Langmuir Isotherm

The Langmuir model was developed based on the assumption of the formation of a mono layer of adsorbate species onto the surface of the adsorbent. It has also been assumed that the surface sites are completely energetically homogeneous. But in the true sense, the adsorbent surface is energetically homogeneous. The study of Langmuir isotherm is essential in assessing the adsorption efficiency of the adsorbent. isotherm is important, though the restrictions and the limitations of this model have been well recognized.

$Ce/qe = 1/K_L + (\alpha L/KL)\ Ce$

Where qe is the amount of dye adsorbed per unit weight of adsorbent. Ce is the concentration of dye remaining in solution at equilibrium. K_L and α_L are the Langmuir constant

Table 2. Langmiur Isotherm Constants

Parameter	Langmuir		
Adsorbentdosage (g)	α_L (L/µmol)	q_m µmol/g)	R^2
0.1	0.0145	6.041	0.928
0.2	0.0116	8.483	0.955
0.3	0.0132	6.825	0.874
0.5	0.011	8.172	0.976
0.6	0.015	6.060	0.823
0.8	0.010	9.43	0.910
0.9	0.010	7.64	0.927
1.0	0.009	8.686	0.986

Rate Constant Studies

In order to investigate the mechanism of adsorption kinetics, the pseudo first order and pseudo second order equations were used to test the experimental data of pH, initial concentration

of the dye and adsorption dosage respectively. The pseudo first order rate expression of Langergren and Annadurai and Krishnan is given as:

$\log(q_e - q_t) = \log qe - (k1/2.303)t$

where q_e and q_t are the amounts of dye adsorbed on chitosan (µmol/g) at equilibrium and at time t and k_1 is a rate constant of pseudo first order onstant (per min). A straight line of (q_e - q_t) versus t suggest the applicability of this kinetic model to fit the experimental data. But in many cases the pseudo first order equation of Langergren does not fit very well and is generally applicable over the initial stage of the adsorption process.

Table 3. Pseudo First Order Rate Kinetics

Parameters (Initial dye conc.(µmol/L)	Experimental qe(exp) (µmol/g)	First order kinetic model		
		K1 (per min)	qe(cal) (µmol/g)	R^2
2	8.031	0.041	1.0418	0.772
4	8.893	0.0115	1.1618	0.824
6	7.762	0.016	1.220	0.825
8	7.391	0.0506	1.171	0.931
10	9.876	0.05089	1.274	0.948

The study is also useful in optimizing the operating conditions for effective adsorption. In the respect, the Langmuir isotherm is important, though the restrictions and the limitations of this model have been well recognized.

The pseudo second order rate expression is given as follows

$t/qt = 1/k2qe2 + (1/qe)t$

where k_2 (g/µmol per min) is a rate constant of the pseudo second order adsorption.

If second order kinetics is applicable, the plot of t/q_t versus t should show a linear relationship. The slopes and y intercepts of plots of log ($q_e - q_t$) versus t were used to determine the pseudo first order rate constant (k_1) and equilibrium adsorption capacity. A comparison of results with the correlation coefficients (R^2) is shown in table 2. The values of R^2 for the pseudo first order kinetic model were low. The values of q_e calculated were not reasonable values when compared to experimental values. These results suggest that the adsorption of methylene blue dye onto chitosan is not a pseudo first order reaction. The slopes and y intercepts of plots of t/q_t versus t were used to calculate the pseudo second order rate constant (k_2) and q_e. The computed results obtained from pseudo second order kinetic model are shown in table 2. The values of correlation coefficients (R^2) for the pseudo second order kinetic model are $\geq$ 0.999 for almost all cases. The q_e calculated values agree very well with the experimental data.

Table 4. Pseudo Second order Rate Kinetics

Parameters (Initial dye conc.(µmol/L)	Experimental qe(exp) (µmol/g)	Second order kinetic model		
		K2 (g/µmol/min)	qe(cal) (µmol/g)	R^2
2	8.031	0.028	9.09	0.949
4	8.893	0.0055	10	0.982
6	7.762	0.0316	8.01	0.989
8	7.391	0.0994	7.09	0.991
10	9.876	0.0078	9.81	0.974

Conclusion

The kinetic and adsorption mechanism of methylene blue onto chitosan were studied in the present work. Batch experiments showed that both the initial dye concentration and the pH of aqueous solutions significantly affect the adsorption capacity of methylene blue onto chitosan. The pseudo second order kinetic model agrees very well with the dynamical behavior for the adsorption of methylene blue onto chitosan under several different pHs, initial dye concentrations and different adsorbent dosages were studied. The q_e values calculated from this kinetic model are very similar to the experimental q_e values obtained from several experiments. Moreover the experimental adsorption kinetic profiles are perfectly reproduced in the simulated data obtained from numerically on the basis of the pseudo second order kinetic model and using the isotherm constant. On the contrary, the pseudo first order kinetic model fits the experimental data poorly for the entire range under study. The Langmuir equation is a best fit equilibrium isotherm for the sorption of methylene blue onto chitosan based on a linearized correlation coefficient. The experimental adsorption isotherm are also perfectly reproduced in the simulated data obtained from numerical analysis on the basis of Langmuir mode land using the Langmuir isotherm constant. It is concluded that chitosan can be used as a natural and abundant source for the removal of dyes from water as an alternative materials such as activated carbon.

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