Removal of Methyleneblue From Dye Industrial Effluents Using Adsorption- Comparative Study

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Abstract- *In this study, the removal of methylene blue from dye industrial effluents using various simple, highly efficient, eco-friendly, locally and abundantly available, low cost adsorbents were investigated. Experiments were conducted to study the efficiency of activated carbon prepared from various adsorbents for removal of Methylene blue. However, there is need to investigate more on the effect of other pollutants on adsorption of methylene blue dye so as reduce its environmental and health effects. The effect of various process parameters such as temperature, initial pH, contact time, adsorbent dosage and initial dye concentration of the solution were studied by running batch experiments. The adsorption facts were analysed by using Langmuir, Freundlich, Temkin and Dubinin-Radushkveich isotherm models. The kinetic data were fitted to pseudo – second order kinetic model which shows that intraparticle diffusion has a significant role in the adsorption process. This study demonstrates that the suitability of highly efficient of various low-cost adsorbents for removal of Methylene blue from dye industrial effluents.*

Keywords- Methylene blue, pollution control, adsorption, activated carbon, dye industry.

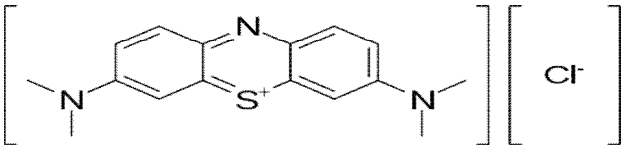
I. INTRODUCTION

Lack of water is the major concern of today's Biosphere. The Lack of water is due to rapid population growth, increased industrialization, deforestation; carbon dioxide increased and decreased amounts of rainfall in the previous decades. Water pollution by untreated synthetic dye effluents released from industries has been identified as one of the consequences of falling situation of water lack in the society[1]. Water pollution due to colour dyestuff industrial waste becomes a major problem worldwide. Many industries including leather and textile industries use dyes extensively in different unit operations. The major pollution in textile industries came from dyeing and finishing industries. These processes require a wide range of input chemicals and dyestuff, which was generally an organic compound of complex structures[2]. Discharge of colored wastewater without proper treatment can results in numerous problems such as chemical oxygen demand (COD) by the water body, and an increase in toxicity. Currently, there are about 10,000 different commercial dyes and pigments exist and over $7x10^5$ tones of synthetic dyes are produced annually world-wide[3]. It is estimated that from these dyes 10-15% is lost in effluent during dyeing processes. Most problems associated with dye effluent are lowering of photosynthesis, light penetration and damage of the aesthetic nature of water surface.[4-6] these dyes causes degradation of products which may be mutagenic and carcinogenic[7-9] Methylene blue has wider applications, which include coloring paper, temporary hair colorant, dyeing cottons, wools, coating for paper stock, etc. In addition, dyes are toxic to some organisms and hence harmful to aquatic animals. Acute exposure to methylene blue will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in humans. Furthermore, the expanded uses of azo dyes have shown that some of them and their reaction products such as aromatic amines are highly carcigenic [10-11]. However, a recent study conducted under the National Biodiversity strategy and Action Plan (BSAP) has revealed that chemical colors have all been wiped out India's wonderful vegetable dyes. Hence, removal of dyes from effluent water is of great concern. The complete removal of dyes from wastewater effluents is highly difficult since most of the dyes are stable to light, oxidation, heat and biologically non-degradable.[12] The conventional methods such as coagulation, flocculation, and membrane separation processes are not suitable for dye removal because of their complex nature and ability to survive in different process conditions. Moreover, these methods are expensive and produce large amounts of sludge[13-16]. Among various methods of dye removal, adsorption found to be very effective. Activated carbon is extensively used as adsorbent in most of the adsorption processes, however its high cost and difficulty in regeneration makes its usage restricted in most of the developing countries[17-18] Adsorption is the phenomenon of accumulation of large number of molecular species at the surface of liquid or solid phase in comparison to the bulk. Necessity of adsorption (1) To gain maximum efficiency in pollutants removal. (2) It is used in water treatment, waste water treatment and in many industries. (3) Applied in both physical and chemical process in pollutant removal. (4) To reduce the load of waste water treatment plants. (5) To remove

the colour from the water. (6) To reduce solid waste disposal due to dumping of solid waste material available locally. The main objectives of adsorption were (a) Removal of dyes by sludge free method. (b) The feasibility of using different adsorbents for treatment of wastewater containing Methylene blue dye. (c) To investigate the effect of pH, variation of dose and agitation time of adsorbents on the sorption of Methylene blue dye. (d) To study the sorption isotherm and kinetic modelling of Methylene blue dye removal process. Among the treatment technologies biosorption is getting prominence because it is economically favourable, effective and technically feasible[19]. Recent research has been concentrated on the low cost adsorbents such as grape peel[20], Rice husk[21], groundnut shells[22], Raphanus Raphanistrum [23], Eichhornia crassipes[24] Anthacephalous Cadambaleaf[25], Corn husk[26], Urea formaldehyde resin[27], Delonix Regia Seed Powder[28], Banana peel powder[29], lignocellulosic precursors[30] , Acacia Arabica[31].Hence in this present study various adsorbents for removal of methylene blue dye from industrial effluents were compared.

II. MATERIALS AND METHODS

Preparation of Dye Solution: - The dye used in this study is Methylene blue Solution with concentration of 1000mg/L was prepared by dissolving 1 gm of dye powder in 1000mL of distilled water. Physical properties of the methylene blue are Molecular Weight 319.859, Molecular formula $C_{16}H_{18}ClN_3S$,Absorption maxima 665nm.



Batch adsorption experiment is conducted in order to determine the optimum adsorbent mass and equilibrium time, to generate adsorption kinetics data, adsorption isotherm data and the data used to derive response surface model equations. Blank solutions (solution without the adsorbent) are also included to check if there was any adsorption on the surface of the conical flask. Before the beginning of an adsorption experiment, the initial concentrations of all the adsorbates are determined. After equilibrium, the supernatant is separated by filtration. Final concentrations of the adsorbates are determined and the adsorption capacity, qe, was calculated as: qe = V (Co-Ce) /M Where Co and Ce are the initial and equilibrium adsorbate concentrations in solution (mg/l), respectively, V is a known volume of synthetic wastewater (l), and m is a known mass of dry adsorbent (g). Percentage Removal = (Co-Ce)/Co X100.

Preparation of biosorbent:

The adsorbents used in this study were collected from the nearby places. The collected biomass was thoroughly washed with tap water until all the dirt was removed and then it was dried in sunlight for one week. At the end of one week, biomass was cut into small pieces and grounded in a commercial grinder. The finely grounded material was washed with de-ionized water until the entire colour of the material was removed. The resulted wet biomass was dried again in sunlight for three more weeks; and dried product was then screened into different sized particles and stored in air-tight containers kept in desiccators for further use.

Prior to 1914 only a few theoretical interpretations of biosorption isotherms were in use. But thereafter, a number of isotherm equations were proposed by different investigators. Some of those in frequent use are:

- Langmuir isotherm
- Freundlich isotherm
- Temkin isotherm

1. Langmuir isotherm

The Langmuir biosorption isotherm[32] was based on the following assumptions:

- Fixed number of biosorption sites: at equilibrium, at any temperature, a fraction of the biosorbent surface sites (θ) is occupied by adsorbed molecules and the rest (1-θ) is free.
- All sorption processes are homogeneous.
- There is only one sorbate
- One sorbate molecule reacts with only one active site.
- No interaction between the sorbate species.
- A monolayer surface phase is formed.

The equation proposed by Langmuir was universally applicable to chemisorption with some restrictions involving physical biosorption. This equation is applicable to the physical or chemical biosorption on solid surface with one type of biosorption active center. As long as its restrictions and limitations are clearly recognized, the Langmuir equation can be used for describing equilibrium conditions for sorption behavior in different sorbate-sorbent systems or for varied conditions within any given system. The Langmuir equation is given by:

$$q = \frac{q_{\max} K_{a\,eq}}{1 + K_{a\,eq}} \quad (3)$$

Where Q_{max} indicates the monolayer biosorption capacity of biosorbent (mg/g) and the Langmuir constant b (L/mg) is related to the energy of biosorption. For fitting the experimental data, the Langmuir model was linearized as

$$\frac{1}{q} = \frac{1}{q_{\max}} + \frac{1}{K_a q_{\max} C_{eq}} \quad (4)$$

2. Freundlich isotherm

Freundlich biosorption isotherm was proposed by Boedecker in 1895 as an empirical equation. Later Freundlich[33] made some useful modifications as a result of which, it assumed great importance. The Freundlich biosorption equation can be written as:

$$q = K C_{eq}^{\frac{1}{n}} \quad (5)$$

Taking the ln of both sides,

$$\ln q = \ln K + \frac{1}{n} \ln C_{eq} \quad (6)$$

Where 'q' is equilibrium biosorption capacity (mg/g), 'C_e' is the equilibrium concentration of the adsorbate in solution, 'K', and 'n' are constants related to the biosorption process such as biosorption capacity and intensity respectively.

3. Temkin isotherm

Temkin and Pyzhev suggested that due to the indirect adsorbate/biosorbent interaction, the heat of biosorption of all the molecules in the layer would decrease linearly with coverage[34]. The linear form of Temkin isotherm can be written as:

$$q = \frac{RT}{b} \ln\left(A_T C_{eq}\right) \quad (7)$$

Where A_T (L/mg) and b_T are Temkin isotherm constants, 'T' is absolute temperature in Kelvin and 'R' is the universal gas constant (J/mol.K). C_{eq} is the equilibrium concentration of the adsorbate.

4. Biosorption kinetic models

The study of biosorption kinetics in wastewater is significant as it provides valuable insight into the reaction pathways and into the mechanism of the reaction. Further, it is important to predict the time at which the adsorbate is removed from aqueous solution in order to design an appropriate sorption treatment plant. Any biosorption process is normally controlled by three diffusive transport processes for the adsorbate:

- From bulk solution to the film surrounding the biosorbent.
- From the film to the biosorbent surface.
- From the surface to the internal sites followed by binding of the dyes onto

the active sites.

But in kinetic modeling, all these three steps are grouped together and it is assumed that the difference between the average solid phase concentration and equilibrium concentration is the driving force for biosorption. Further, it is established from the experimental observations that at optimum agitation speed, the external boundaries have hardly any effect. So application of the kinetic model depends only on the initial and final concentrations of the solution at different time intervals. It is incorrect to apply simple kinetic model such as first and second order rate equations to a sorption process with solid surface, which is rarely homogenous. Secondly, the effects of transport and chemical reaction are often experimentally inseparable.

Several kinetic models have been proposed to clarify the mechanism of a solute sorption from aqueous solution onto a biosorbent:

- Lagergren first order kinetic model
- Pseudo second order kinetic model

4.1. Lagergen first order kinetic model

The Pseudo first order or Lagergen kinetic rate equation for the sorption of liquid solid system was derived based on solid biosorption capacity. It is one of the most widely used sorption rate equations for sorption of a solute from a liquid solution[35]. According to the authors, the overall

biosorption rate is directly proportional to the driving force, i.e., the difference between initial and equilibrium concentrations of the adsorbate (q_e-q). Therefore, the pseudo first order kinetic equation can be expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (8)$$

Where q_e and q_t are the sorption capacities at equilibrium and at time *t*, respectively (mg/g) and k_1 is the rate constant of pseudo first-order sorption (min^{-1}). After integration and applying boundary conditions, q_t =0 at t = 0 to $q_t = q_t$ at *t* = t; the integrated form of Eq. (8) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (9)$$

'k_1'can be calculated from the slope of the linear plot between log (q_e-q_t) vs't' for different adsorbate concentrations.

4.2. The pseudo-second-order equation

If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed as[36]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (10)$$

Where q_e and q_t are the sorption capacity at equilibrium and at time *t*, respectively (mg/g) and *k* is the rate constant of pseudo-second-order sorption (g/(mg min)). For the boundary conditions q_t =0 at t = 0 to $q_t = q_t$ at *t* = *t*; the integrated form of Eq. (10) becomes:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (11)$$

where *t* is the contact time (min), q_e (mg/g) and q_1 (mg/g) are the amount of the solute adsorbed at equilibrium and at any time, *t*. Eq. (1) does not have the problem of assigning as effective q_e. If pseudo-second-order kinetics is applicable, the plot of t/q_t against *t* of Eq. (11) should give a linear relationship, from which q_e and *k can* be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand.

5. Thermodynamic parameters

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. Gibb's free energy change, Δ*G*°, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if Δ*G*° is a negative value. The thermodynamic parameters, Gibbs free energy change (Δ*G*°), enthalpy change (Δ*H*°), and entropy change (Δ*S*°), for the biosorption processes are calculated using the following equations[37,38]:

$$\Delta G° = - RT1nK_d \quad (12)$$

And

$$\ln K_d = \Delta S^0/R - \Delta H^0/RT \quad (13)$$

Substitution of Eqn. 13 in Eqn 12. gives the Van't Hoff equation as follows:

$$\ln K_d = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (14)$$

where *R* is universal gas constant (8.314 J/mol K) and *T* is the absolute temperature in K. A plot ln K_d versus temperature 1/*T*, was found to be linear. The values of Δ*H*° and Δ*S*° were determined from the slope and intercept of the vant Hoff's plot.

Response Surface Methodology*:*

Optimization of different process parameters depending on the Methylene blue dye removal is highly required for the effective design and accurate control of bio sorption technique. So, response surface methodology is time saving and precise alternative to conventional optimization methods. The main objective is to optimize the response surface that is shaped under the influence of process parameters.

The effect of different process parameters such as solution pH (X_1), initial dye concentration (X_2), bio sorbent dosage (X_3) and temperature (X_4) on congored dye removal

from aqueous solutions was studied by using full factorial rotatable central composite design (CCD)[39] . Total thirty experiments, which include 16 cube point runs, 8 axial point runs and 2 centre point were required and all of them were done in duplicate. All the experiments were conducted at contact time (t) and a constant speed of agitation 180 rpm.

All independent variables were coded to five levels as X_i according to Eqn.15 [40]

$$X_i = \frac{(X_i - X_{oi})}{\Delta X_i}, \quad i= 1,2,3,\ldots\ldots\ldots k \qquad (15)$$

Where X_i is the dimensionless value of an independent variable, x_i is the real value of an independent variable, x_{0i} is the real value of the independent variable at the centre point, and Δx_i is the step change. A second degree polynomial equation (Eqn. 16) was developed to estimate the percentage of bio sorption of dyes at different operating conditions of the bio sorption process by using STATISTICA 6.0 (Stat Soft Inc.).

$$Y=b_0+b_1X_1+b_2X_2+b_3X_3+b_4X_4+b_{11}X_1^2+b_{22}X_2^2+b_{33}X_3^2+b_{44}X_4^2+ b_{12}X_1X_2+b_{13}X_1X_3+b_{14}X_1X_4+b_{23}X2X_3+b_{24}X_2X_4+ b_{34}X_3X_4 \qquad (16)$$

Where , Y is the predicted response, X_1, X_2, X_3 and X_4 are independent variables: b_0 is an offset term; b_1,b_2,b_3 and b_4 are linear effects; b_{11}, b_{22}, b_{33} and b_{44} are squared effects and b_{12}, b_{13}, b_{14}, b_{23}, b_{24} and b_{34} are interaction terms.

III. RESULT AND DISCUSSION

Table 1 percentage removal of Methylene blue dye using various low cost adsorbents.

Adsorbent	% Bio sorption	Time(min)	particle size(µm)	pH	initial concentration of dye(mg/l)	bio sorbent dosage (gm)	Temperature(k)
grape peel	98.5	180	**60**	11	500	0.5	298
Rice husk	99	150	-	12	100	0.25	303
groundnut shells	99.63	120	100	11	300	0.5	298
Raphanus Raphanistrum	98.8	135	63	10	100	0.2	303
Eichhomia crassipes	98.77	120	75	8	200	0.8	298
AnthacephalousCadambaleaf	92.54	120	-	10	30	0.1	298
Corn husk	90	120	-	6.2	30	0.25	298
Urea formaldehyde resin	98.5	60	-	6.4	5	0.5	298
Delonix Regia Seed Powder	64	45	-	9	10	4.0	298
Banana peel powder	90	120	350	12	8	0.1	298
lignocellulosic precursors	80	120	100	10	200	1.6	303
Acacia Arabica	96.9	120	-	11	150	0.25	293

Table 2: removal of Methylene blue dye using various RPM

Adsorbent	RPM	researcher	Year	references
grape peel	240	Lin Ma et al	2018	20
Rice husk	100	M.A.Patil et al	2017	21
groundnut shells	150	S.S. Imam and M.Abdullahi	2017	22
Raphanus Raphanistrum	180	Pallavi et al	2017	23
Eichhornia crassipes	125	Mupa Mathew et al	2016	24
AnthacephalousCadambaleaf	180	Kalpana P et al	2016	25
Corn husk	700	D.S. Malik et al	2016	26
Urea formaldehyde resin	-	Alyaa kareem et al	2016	27
Delonix Regia Seed Powder	-	Mithun Moniram et al	2016	28
Banana peel powder	180	Shalini Gautam and Saima H. Khan	2016	29
lignocellulosic precursors	250	Silvia et al	2015	30
Acacia Arabica	150	Narayana Saibaba KV and Pulipati King	2015	31

IV. CONCLUSION

In this review the removal of methylene blue from dye industrial effluents using various simple, highly efficient, eco-friendly, locally and abundantly available, low cost adsorbents were investigated. Adsorption was more efficient method for removal of methylene blue from dye industry. Groundnut shells and Rice husk adsorbents were removed more percentage of dye from industrial effluents such as 99.63% and 99% respectively.

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