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Removal of Methylene Blue from Wastewater by using Delonix Regia Seed Powder as Adsorbent

Mithun Motiram Gangadware, Dr. M.V. Jadhav

***Abstract*— One of the most serious environmental problems is the existence of hazardous and toxic pollutants in industrial wastewaters. Adsorption is considered to be one of the most promising techniques for wastewater treatment over the few decades. The economic crisis of the 2000s led researchers to turn their interest in adsorbent materials with lower cost. a new term will be introduced, which is called "green adsorption". Under this term, it is meant the low-cost materials originated from agricultural sources and by-products (fruits, vegetables, foods); agricultural residues and wastes; low-cost sources from which most complex adsorbents will be produced. In this project, adsorbent prepare from seeds of Delonix regia (Gulmohar) & Prosopis juliflora (Vilayti Babhul) was used & functional group was found by using FTIR test, which is responsible for adsorption. Adsorption of methylene blue from aqueous solution on the surface of Delonix regia and prosopis Juliflora seed was accomplished under the optimize conditions of temperature, concentration, pH, contact time and quantity of adsorbent. Spectrophotometer was used for the measurements of concentration of dye before and after adsorption**

The optimum dose of Delonix Regia (Gulmohar) seed as bio-adsorbent at dosage of 4.0g for time duration of 45 min found to be 64 % removal of the dye from an aqueous solution of 10 mg/l concentration. From the study it is understood that pH, contact time and adsorbent dosage plays a vital role in removal of dye.

***Index Terms*—Methyelene blue, delonix regia, prosopis juliflora, bio-adsorbent**

I. INTRODUCTION

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.

A. 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 color from the water.
6) To reduce solid waste disposal due to dumping of solid waste material available locally.

B Objectives

1) Removal of dyes by sludge free method.
2) The feasibility of using delonix regia, prosopis juliflor for treatment of wastewater containing Methyelene blue dye.
3) To investigate the effect of pH, variation of dose and agitation time of adsorbents on the sorption of Methylene blue dye.
4) To study the sorption isotherm and kinetic modeling of Methylene blue dye removal process.

II. MATERIALS AND METHODS

Material: - the Delonix regia is locally available material and is of low cost so it is used to remove Methylene blue dye.

A) *Preparation of delonix regia seed powder*

1) Delonix regia seed pods obtained from neighborhood tree.
2) These seed dried on oven at 70^0c for 24 hr. and ground to fine powder and sieved through 600 micron and 300micron.
3) The 600 micron particle dipped in 1N HCL for 5.hr then washed with distilled water, dried and used for study.
4) The proportion was 70ml HCL and 930ml of distilled water to make 1n HCL solution

B) *Preparation of Dye Solution*:-

The dye used in this study is Methyelene blue purchased from Sudarshan scientific laboratory, Nandagaon. Solution with concentration of 1000mg/L was prepared by dissolving 1 gm of dye powder in 1000mL of distilled water.

Mithun.M.Gangadware, sanjivani k.b.p.poly. Kopargaon. Dist: Ahmednagar India.
Dr.M.V.Jadhav, Civil Engg. Department S.R.E.S College of Engineering Kopargaon Dist:Ahmednagar , India.

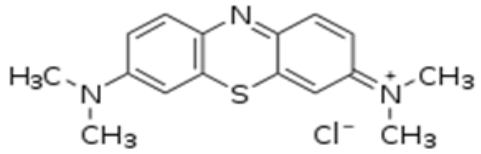

Fig 1: Structure of Methylene blue dye

TABLE I
PHYSICAL PROPERTIES OF THE METHYLENE BLUE

Parameters	Values
Molecular Weight	319.859
Molecular formula	$C_{16}H_{18}CIN_3SxH_2O$
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:

$$q_e = V (Co-Ce) /M$$

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

A. *Method Applied For Adsorption*:-

As various methods are available for carrying out the adsorption process, In this study bottle shaking methods was applied to carry out the experiments as this method provides complete and continuous mixing of materials. (Adsorbent as well as adsorbate)In the bottle for a particular time period. A stock solution of Methylene blue dye with a concentration of 1000 ppm was prepared. Batch adsorption experiments were conducted by shaking a series of eight bottles containing 50ml dye solution with different adsorbent dosage such as 1,2,3,4,5and 6 gm.) Were poured into each of the bottles, and the bottles were tightly fixed in the shaker (Shaker with 8clamps, Stuart Scientific). Then shaking proceeded for different contact times, to establish equilibrium, after which the mixture was left to settle for 10 min. then filtered.

B. Effect of contact time on color removal by delonix regia seed powder:

50 ml of dye solution was taken in each bottle with adsorbent concentration (100mg/l) and kept inside the shaker. Dye concentration to be estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, λmax, using a spectrophotometer (SHIMADZU). The samples to be withdrawn from the bottle shaker at predetermined time intervals. The absorbance of solution is then measured. The dye concentration is to be measured after 5, 10, 20, 30, 60, 100,120mins until the equilibrium is reached.

C. Effect of adsorbent delonix regia seed powder dose on methylene blue dye removal :-

50ml of dye solution was taken in different bottles with dye conc. (100 mg/L) and adsorbent concentration 1,2.3,4,5&6 gm is added in 50 ml of dye solution. The final dye concentration readings were taken after putting the bottles inside the shaker for 5,10,20,40,50,60,80,100,120 min respectively.

TABLE II
INFORMATION ABOUT PARAMETERS USED IN PROJECT

Parameters	Values
Initial concentration of MB (ppm)	100
Amount of adsorbent dose(gm/l)	1,2,3,4,5,&6
PH	4,7,9,
Agitation time(min)	5,10,20,30,40.50,60, 70.80.100,120

III RESULT AND DISCUSSION

1) Effect of adsorbent dose on Methylene blue removal.
2) Effect of contact time of adsorbent on Methylene blue removal.
3) Effect of pH on Methylene blue removal.
4) Validation of results through Modeling (Langmuir and Freundlich Models) for Methylene blue removal
5) Infra Red (FT IR) Spectra Study.

A. Calibration of Methylene blue dye.

For the calibration of Methyelne blue dye ten samples of different concentration of Methyelne blue dye (10 mg/L, 20 mg/ L, 30 mg/L, 40 mg/L, 50mg/L , 60mg/L ,70 mg/L ,80 mg/L 90 mg/L and 100 mg/L) were prepared from the dilution of the stock solution. Next, maximum wavelength of Methylene lue dye and the absorbance value for each sample were taken using UV-Visible Spectrophotometer and the calibration curve was constructed .For future reference, the concentration of a sample can be found directly from the calibration curve using its absorbance value λmax = 665nm

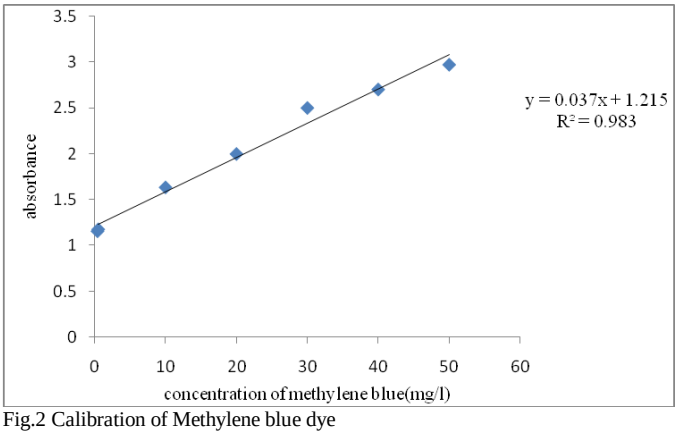

Fig.2 Calibration of Methylene blue dye

B. Effect of variation of adsorbent doses and contact time on Methylene blue dye removal

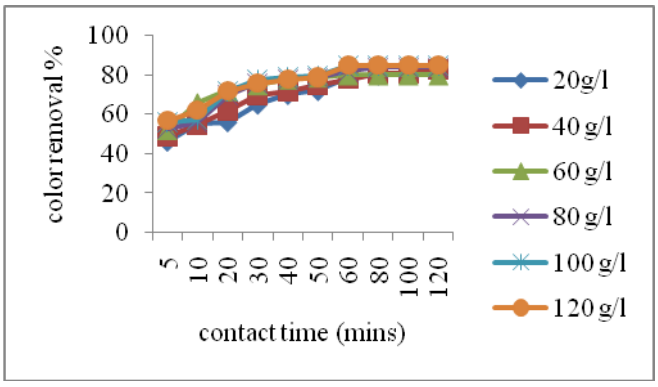

Fig 3:- Variation of dose of delonix regia seed powder & contact time for removal of Methylene blue dye

The study of adsorbent dose for the removal of the MB dye from aqueous solution was carried out using Delonix regia seed powder with their amount varying from 1to 6 gm. The maximum % age of dye removal for MB is 85 % attained for 60 min as shown in Fig.3,4 The percentages of the dye removal decreases with increase in adsorbent dose because of all available sites were covered and no active site available for further binding of dye molecules to bio-sorbent surface

C. Effect of variation of pH on Methylene blue dye removal.

Low cost adsorbent powders are used to remove the Methylene blue dye; the effect of variation of pH is studied at acidic, neutral and alkaline solution i.e. at pH 4, 7, and 9 using 0.1N HCl or NaOH solutions to change the pH. Following tables and figures show the reading for the adsorbent used respectively for various pH .

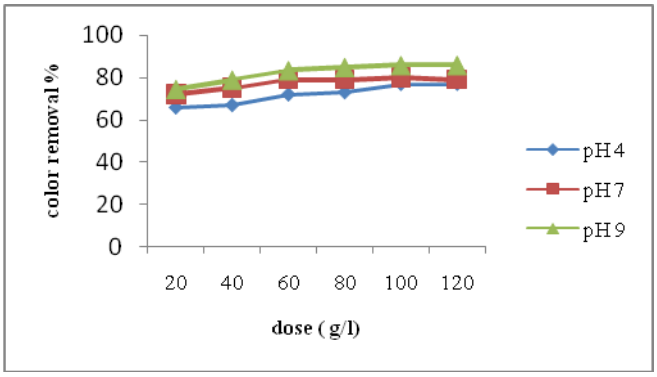

Fig 4:- Delonix regia seed powder for Methylene blue dye removal for PH 4, 7 and 9

The influence of pH on MB removal was studied by varying the initial pH of MB solutions from 4 to 9 using 0.1N HCl or NaOH solutions, with the initial MB concentration fixed at100 mg/l. The change in pH during adsorption was studied at acidic pH (4), neutral pH (7) and alkaline pH (9), with the initial MB concentration at 100 mg/l. At the end of the adsorption period of 40 min the amount of MB in the solutions before and after adsorption was analyzed at 665 nm using a spectrophotometer The maximum % age removal of Methylene blue was 76.99% at pH 4.0 ,79 % at pH 7 and 85.9 % at pH 9 by using Delonix regia seed powder In general, initial pH value may enhance or depress the uptake. This is attributed to the charge of the adsorbent surface with the change in pH value. It can be seen from the figure 4 that as the solution pH increases, the adsorption capacity increases. Increasing solution pH increases the number of hydroxyl groups thus, increases the number of negatively charge sites and enlarges the attraction between dye and adsorbent.

D. Validation of result through Modeling (Langmuir and Freundlich model) for Methyelne blue removal.

Langmuir

The Langmuir isotherm is based on the assumption that adsorption takes place only at specific homogenous sites within the adsorbent surface with uniform distribution of energy level. Once the adsorbate attaches onto a site, no further adsorption can take place at that site and therefore the adsorption process is monolayer in nature. The linear form of the Langmuir equation is:

$$Ce/qe = 1/ (Q_o b) + Ce/Q_o$$

Where Ce (mg/L) is the equilibrium concentration of phenol, qe (mg/g) is the amount of phenol adsorbed per unit mass of adsorbent, and Q_o (mg/g) and b (L/mg) are Langmuir constants related to adsorption capacity and rate of adsorption respectively. A graph of Ce/qe versus Ce would give a straight line having a slope of $1/Q_o$ and intercept of $1/Q_o b$.

Freundlich

The Freundlich model is an empirical equation based on adsorption onto a heterogeneous surface supporting sites of varied affinities. It is assumed that stronger binding sites are occupied first and that the binding strength decreases with the

increasing degree of site occupation. The linear form of the Freundlich equation is:

$$\text{Log } (x/m) = \log kf + (1/n) \log Ce$$

Where x (mg) is the amount of phenol adsorbed and m (g) is the mass of adsorbent used, Ce (mg/L) is the equilibrium concentration of phenol in the solution, kf and n are Freundlich constants. A plot of log (x/m) versus log Ce gives a straight line having a slope 1/n and an intercept of log kf. The evaluation of color removal by using Langmuir and Freundlich Adsorption Equilibrium models for Methylene blue dye the experimental data obtained while performing modeling for Methylene blue and delonix regia was used as adsorbent. Initial concentration of methylene blue was 100 mg/l. After the addition of various adsorbent dosages (20, 40, 60, 80, 100, 120mg/l), there was a considerable reduction in color concentration and it has been shown in fig.5 and fig. 6 below . .

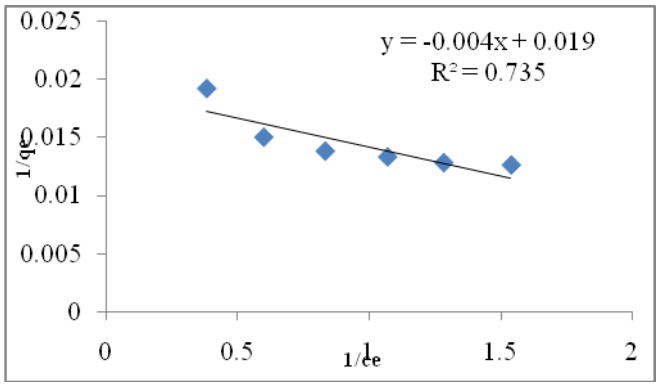

Fig.5 Langmuir models for Delonix regia as adsorbent

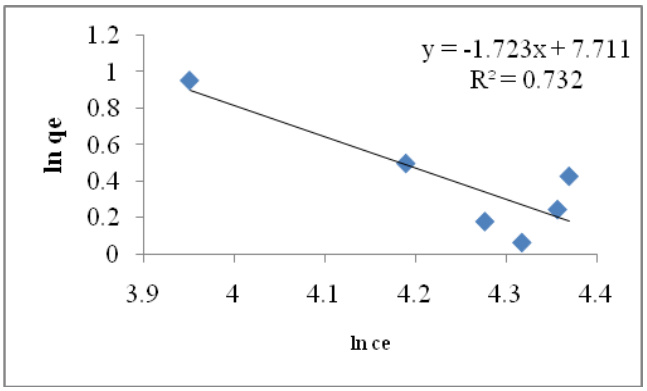

Fig. 6 Freundlich Model for Delonix regia seed as Adsorbent

The study showed that the Langmuir equilibrium model is having R^2 = 0.735 and freundlichm model having R^2 = 0.732 so that, Langmuir model is best fitted for removal of methylene blue dye removal

IR Spectra of Delonix regia seed Powder IR Spectra graphs taken between the wave numbers 4000 cm^{-1} and 1000 cm^{-1} of delonix regia seed powder are presented in fig 7.The peaks appearing in the FTIR spectrum were assigned to various functional groups according to their respective wave numbers. The FT-IR spectrum of Prosopis juliflora seed, delonix regia seed and seed shell powder, presenting the plot of percentage transmission versus wave number, is given in respective Figures IR Spectra graphs taken between the wave numbers 4000 cm^{-1} and 1000 cm^{-1} of delonix regia .The peaks appearing in the FTIR spectrum were assigned to various functional groups according to their respective wave numbers. the IR Spectra Graph of delonix regia seed powder. Group responsible for adsorption property at 2250-2300 cm^{-1} wave length shows C≡N which is a nitrite group having strong bond and at 1600 cm^{-1} shows aromatic bonding i.e. C=C again a strong bond is present at 3200-3400 cm^{-1} indicate stretch of amides (N-H) , Molecules containing a carbonyl group bonded to an amino group and an alkyl group. C=O is shown at wavelength 1150 -1200 cm^{-1} is Alcoholic group. Wavelength at 2800-2900 cm^{-1}shows C-H i.e. alkali bond it's having Molecules containing one or more hydroxyl groups bonded to alkyl groups.

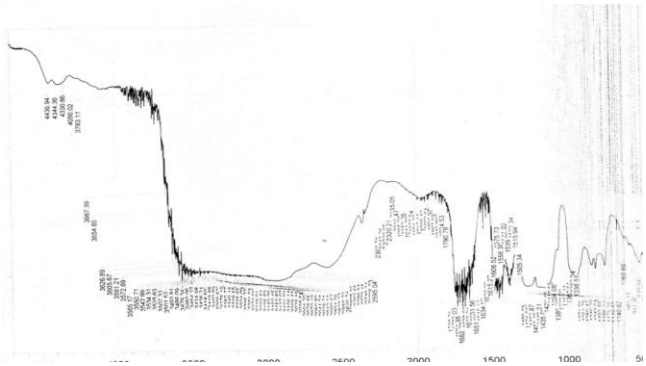

Fig 7 FTIR spectra for delonix regia seed powder

IV Conclusion

1) Adsorption is one of the technical phenomenons which can be used in water treatment, waste water treatment, industrial waste water treatment and pharmaceutical industries. It is one of the methods which can be effectively used in all fields including air pollution too.
2) The knowledge of adsorption is essential to apply it in various fields so a brief introduction is given in this work to get the through information regarding this topic.
3) Adsorption isotherm is the one which helps in understanding the rate of reaction and gives graph, showing extent of adsorption.
4) From the study of adsorption it is clear that it can be a simple and cost effective method.
5) Low cost adsorbents are locally available at cheap rate and are very effective adsorbents, used to remove dyes from various industries.
6) Use of low cost adsorbents decreases the solid waste.

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