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REMOVAL OF CONGO RED AND METHYLENE BLUE BY USING LOW COST ADSORBENT

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Key words : Congo red, Methylene blue, *Pistia stratiotes* (jalkumbhi), Adsorbtion.

ABSTRACT

Waste water generated from dyeing unit is highly coloured and exerts high BOD, COD, turbidity, etc. Low cost adsorbent for the treatment of waste water can make the treatment process more economical, variation in the pollution load make the treatment more difficult since most of the dyeing units are located in small scale sector. The object of this work is to determine adsorption behavior of a low cost adsorbent for the adsorption of Dyes – Methylene blue and Congo Red. The experiment was carried out at the temperature 25°C±2°C (Constant temperature) and hence adsorption Isotherms are helpful in determining the various parameters known as-well-as unknown. The values form Langmuir Isotherm for CR and MB are R2 - 0.9269 and0.9382, Q_{max} - 0.150 and 0.8851, KL - 50.393 and 0.263 respectively. And the Values from Frenudlich Isotherm for MB and CR are R2 – 0.9354 and 0.9952, Kf – 6394.5 and 9.1084, n – 0.1948 and 0.58018 respectively. From this result it is clear that for this experiment Freundlich isotherm is best fitted. This result shows that the experiment was successfully performed.

INTRODUCTION

Dyes are used primarily in the production of consumer products, including paints, textiles, printing inks, paper, and plastics. They add color and patterns to materials. Natural dyes extracted from vegetables, fruit and flowers have been used since 3500 BC to color fabrics and other materials. These dyes were replaced by chemical dyes that bond with the fabric, providing and retaining richer color throughout washing and exposure.Many different types of dyes consisting of varied chemical compounds are used in production, depending on the type of textile or product being dyed. There are more than 3600 different types of textiles dyes alone. Other dye types include acid dyes for coloring animal fibers, basic dyes for use on paper, direct dyes for use on cotton-wool or cotton-silk, and pigment dyes used in paint and inks. These dyes are manufactured out of a number of different chemicals, but most notably, sulfuric acid, chromium, copper and other metallic elements are used. Dyes are mixed, synthesized in a reactor, filtered for impurities, dried out and then blended. Along the way many other additives, solvents and chemical compounds are used to instigate reactions. The variation in chemical use is closely tied to the high demand for variable patterns

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and unique colors for clothing and other textiles. These constantly evolving demands result in a highly fluctuating and diverse waste stream. The textile industry is one of the largest sectors globally and produces an astonishing 60 billion kilograms of fabric annually, using up to 9 trillion gallons of water. This massive water use is a key component of pollution. Water is used as cooling water, to clean equipment, and for rinsing and processing dyes and products. Dye bath wastewater generated by textile mills is often rated as the most polluting among all industrial sectors. The pollution load is characterized by high color content, suspended solids, salts, nutrients and toxic substances such as heavy metals and chlorinated organic compounds. Many textile mills in the state currently discharge their wastewater to local wastewater treatment plants with minimum treatment such as pH neutralization. This process removes much of the residual dye colour. Larger mills can discharge more than 2 million gallons of wastewater of this kind per day Sundar (2007).

The dye industry is responsible for almost 50 sites in the Blacksmith Institute's database, potentially putting more than one million people at risk. The majority of problematic dye industry sites are in South Asia, a global center of textile production; however the dye industry is global in scale and is spread over many different countries. Dye plants can range from small and informal to large and organized, in India for example there are estimated to be about 1,000 small-scale entities and 50 large industrial plants. While the organized dye industry does dominate the market, there are many unorganized small-scale plants that disproportionately add to the problem of pollution. Wastewater is a key pathway for exposure. In legacy pollution sites wastewater from the dye industry is directly dumped into surface waters without treatment. Wastewater carries a host of different chemicals from the processing of dyes and The World Bank estimates that textile dyeing and treatment contribute up to 17-20 percent of total industrial water pollution. The majority of pollution exposure in the Blacksmith Institute's database comes from ingestion of contaminated water and ingestion of food, which has been irrigated with contaminated water (http://www.worstpolluted.org/projects_reports/display/105).

There are about 200,000 tons of dyes uses in textile industry. Designated as water soluble, it was estimated that 10 – 20 % of dye was lost during the dyeing process and released as effluent (Zhiqiao, 2007). The reagents used in textile industry are very diverse in chemical composition. Organic dyes released to surface waters during printing and dyeing of textiles and clothing may be toxic above certain threshold concentrations to aquatic organisms (Al-Degs, 2000; Ozkaya, 2006). In addition, dye containing wastewaters are commonly characterized by high salt content and slow biodegradation (Alinsafi, 2005) which makes removal by conventional wastewater treatment processes difficult (Vimonses, 2009).

MATERIALS AND METHODS

Adsorbate

Congo red, is an anionic azo dye having IUPAC name as 1-napthalenesulfonic acid, 3,3-(4,4-biphenylenebis (azo))bis(4-aminodisodium) . Its stock solution was prepared in double-distilled water. Standard solution of CR was taken from the market All the test solutions were prepared by diluting the stock with double-distilled water. Twenty mL of Congo red was dissolved in 1L of double distilled water to obtain stock solution. pH was adjusted by adding 0.1 M NaOH soln and 0.1 M HCl soln according to the conditions.

Methlylene Blue

Fig. 1.1 Structure of Congo Red

Methlylene Blue, C16H18N3SCI.3H2O, is a cationic dye. It was chosen in this study because of its known strong adsorption onto the solids. The structure of this dye is shown in Figure 1.2. The dye is not regarded as acutely toxic, but it can have various harmful effects.

Preparation of basic dye solution

Basic dye, Methlylene Blue, was used without further purification. Standard solution of Methlylene Blue was taken from the market. The stock solution of MB was prepared by dissolving 20 mL Methlylene Blue in 1000 mL distilled water. The experimental solution was prepared by diluting the stock solution with distilled water when necessary.

Basic dye, Methlylene Blue, was used without fur-

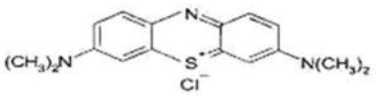

Fig. 1.2 Structure of Methlyene Blue

ther purification. Methlylene Blue was dried at 110 °C for 2h before use. All of the Methlylene Blue solution was prepared with distilled water.

Its stock solution was prepared in double-distilled water. All the test solutions were prepared by diluting the stock with double- distilled water. 2 mL of Methylene Blue was dissolved in 98 mL of double distilled water to obtain stock solution of 100mL (20ppm). pH was adjusted by adding 0.1 M NaOH solution and 0.1 M HCl solution according to the conditions.

Adsorbent

Material used in the present research work, *Pistia stratiotes*, also known as 'Jalkumbhi', is an aquatic plant, stoloniferous, floating on lakes, streams and stagnant water ponds and in lime-rich water, throughout India. It is distributed in the tropical and subtropical region of Asia, Africa, and America. Four varieties are distinguished. The Indian variety is known as var. cuneta. It is propagated by seeds or more rapidly by stolons. It forms a dense mat on the water surface and causes serious clogging on water ways. It is also responsible for harboring mosquito larvae, which carry the filarial parasites. It flowers in hot season and fruits appear after the rain. Plant used in this experiment was collected from local area, river Shipra near 'Mangal Nath' temple, Ujjain. It was collected as a whole plant, washed several times and the various stages from plant to powder are shown in the Figure 3. The adsorbent is sun dried and is untreated powder.

Fig. 1.3 Various stages of Adsorbent

Plant is easily available, abundantly found from local sources and can be converted into powder very easily and therefore comes under the category of low cost adsorbent. *Pistia stratious* (jalkumbhi) washed with tap water to remove soil and dust, sprayed with distilled water, and dried to a constant weight at 105 °C. These extracts were grounded and sieved to obtain particle sizes of 0.25-0.40 mm as adsorbent, and then stored in desiccators for use. (http://www.ncbi.nlm. nih.gov/pmc/articles/PMC3249915/)

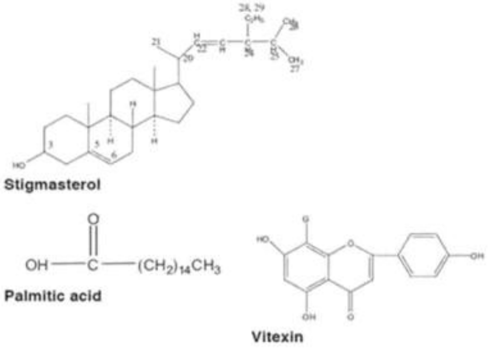

Fig. 1.4 Structure of *Pistia statiotes* [http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3249915/]

Batch Adsorption Study

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 predetermined time interval at a constant speed. The system parameter such as adsorbent amount, agitation time and temperature were controlled during the experiments. After adsorption was over, the mixture was allowed to settle for 1 hour. The dye remaining unadsorbed was determined spectrophotometrically. The adsorption experiments were carried out under the following conditions:

Table 1.1 Operating Conditions

S. No.	Parameters	Values
1.	Initial concentration of Congored solution	Vary for various Readings 5ppm, 10ppm, 15ppm, 20ppm and 25ppm
2.	Amount of adsorbent (g/L)	100g
3.	Temperature	25°C - 28°C

Adsorption Studies

Experiments were performed to study the effects of important parameters such as effect of Concentration, amount of adsorbent, time of contact and pH. For this, 10 mL of dye solutions was taken in 250 mL airtight volumetric flasks with 1g of adsorbents. The flasks were then subjected to intermittent shaking for proper adsorption. After the fixed time of contact these solutions were filtered with filter (whatman filter size 0.45µm PES filter media) and the amount of the dye adsorbed was analyzed at λ_{max} 498 nm. In order to determine the uptake of the dye, an entire set of experiments was performed at different time of contact (40min, 60min, 80min, 100min and 120 min),Different Concentrations(5ppm, 10ppm, 15ppm, 20ppm and 25ppm) and pH (2,4,7,8 and 10) etc. for both adsorbent materials. The amount of Congo red uptake by *Pistia stratious* (Jalkumbhi) after each experiment was measured was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

where q is the amount of Congo Red(CR) and Metylene Blue(MB) adsorbed by adsorbents (mg/g); C0 and Ce are the initial and final dye concentrations (mg/L), respectively, V is the volume of solution (l) and W is the adsorbent weight (g).

In batch kinetic studies, the procedures of these experiments are basically identical to those of equilibrium tests described above. The samples were taken at fixed time intervals, and the concentrations of dye were measured using UV–vis spectrophotometer. The amount of adsorption at time't' for every time interval, qt (mg/g), is calculated by using this equation:-

$$q_t = \frac{(C_0 - C_t)V}{W}$$

Where, Ct = the liquid-phase concentrations of dye at time't' when the aqueous samples were taken (mg/L); Ce = the liquidphase concentrations of dye at equilibrium (mg/L); V =volume of the solution (L);W = mass of dry adsorbent used (g) Lutpi (2011).

Langmuir Isotherm Model

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process is allowed to reach an equilibrium condition. The type of an adsorption isotherm model is very important in order to understand the adsorptive behavior for solid-liquid adsorption systems. To optimize the adsorbent's usage, the adsorption isotherm is applied successfully for describing how solutes interact with adsorbents. A Langmuir isotherm refers to adsorption of a homogeneous monolayer to a surface holding a limited number of adsorption sites with identical qualities and with no transmigration of adsorbate in the plane of the surface. On the other hand, the Freundlich isotherm model is derived by assuming a heterogeneous surface of sorption capacity and sorption intensity with dissimilar distribution of the heat of adsorption. The equation for Langmuir model is given as follows:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{MAX}} C_e + \frac{1}{Q_{MAX} K_L}$$

Eq. (2) is known as a Langmuir isotherm where Q_e, is the amount of adsorbate in the adsorbent at equilibrium (kg/kg) C_e, is the equilibrium concentration (kg/C^3) while Q_{MAX} and K_L are the Langmuir isotherm constants related to adsorption capacity and rate of adsorption, respectively. The above equation can be linearized to deduce the maximum capacity, Q_{MAX} by plotting a graph of

$\frac{C_e}{Q_e}$ versus C_e (Figure 8) and this is listed in Table 1. The value of Q_{MAX} has shown that the Langmuir isotherm is the most appropriate isotherm (R2 values closer to unity. to describe the adsorptive behavior for MB dye system. The separation factor can be written as in Eq.

$$R_L = \frac{1}{1 + K_L C_0}$$

Where the R_L dimensionless separation is factor and C_o is the initial solution concentration (kg/m^3). The parameter indicates the shape of the isotherm accordingly (Uddin, 2013).

Freundlich Isotherm Model

The Freundlich isotherm can be written in linear form as follows:

$$\ln Q_e = \ln K_f + \frac{1}{n_f} \ln C_e$$

where adsorption capacity, K_f and adsorption intensity, $\frac{1}{n_f}$ are known as Freundlich constants, respectively. The K_f represents the quantity of dye adsorbed for unit equilibrium concentration. When $\frac{1}{n_f} < 1$, the adsorption process obeys the normal Langmuir isotherm while when $\frac{1}{n_f} > 1$, the adsorption represents a cooperative process. The plot of versus should give a straight line (Uddin, 2013).

RESULTS AND DISCUSSION

Analytical determination of CR and MB

CR and MB in the aqueous solution was analyzed using UV spectrophotometer (. A standard solution of the CR and MB was scanned to determine the wavelength (λ_{max}) corresponding to maximum absorbance. The wavelength corresponding to maximum absorbance was 498 nm.

Table 2.1 Concentration (mg/L) v/s Absorbance (nm)

S.No.	Concentration (mg/L)	Absorbance (nm)
1.	5	0.151
2.	10	0.296
3.	15	0.431
4.	20	0.631
5.	25	0.68

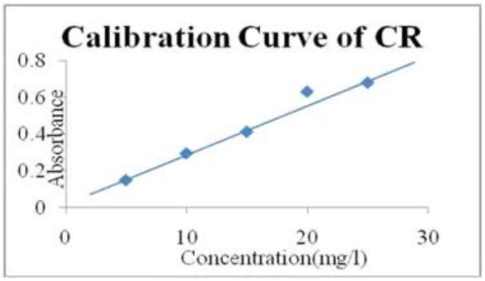

Fig. 2. 1 Calibration curve of CR

Figure 2.1 shows the calibration curve of CR, which is in between the absorbance and concentration. From the calibration it will easy to determine the different concentration at the different absorbance if required.

Now let us study the calibration curve of MB. For this we should determine the absorbance of various concentration of MB. The tables showing the required data is as follows:

Table 2.2 Concentration (mg/L) v/s Absorbance (nm)

S.No.	Concentration (mg/L)	Absorbance (nm)
1.	5	1.672
2.	10	1.786
3.	15	2.309
4.	20	2.71
5.	25	3.434

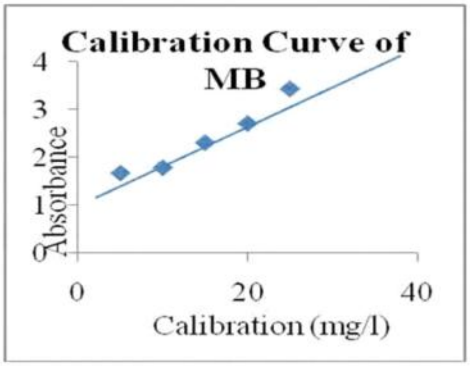

Fig. 2.2 Calibration curve of MB

Figure 3.2 shows the calibration curve of MB, which is in between the absorbance and concentration. From the calibration it will easy to determine the different concentration at the different absorbance if required. Now the work will look upon the various changes with respect to pH, time and dosing for Mb as-well-as for CR. The data will look upon is as follows:

Figure 2.3 shows the peentage removal of MB with respect to time. At zero time the removal is also zero. As the time increases the removal is also increasing and the pores on the adsorbent is gradually decreasing with the time and hence after some time we can absorbed that the equilibrium stage has reached at the room temperature (25 ±2°C). This stage can be seen from the last three points.

Figure 2. 4 shows the percentage removal of CR

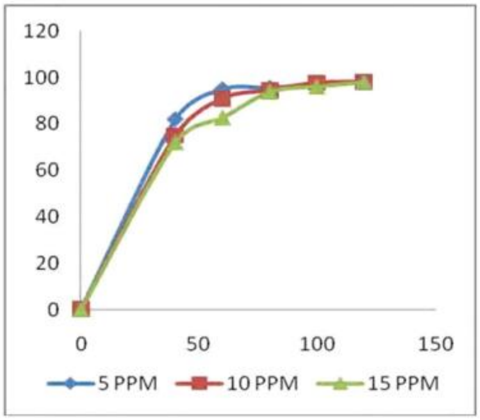

Fig. 2.3 Percentage removal of MB with respect to time.

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Table 2.3 Langmuir Isotherm (CR Dye)

Ce	Ce/Qe	Qe
0.001	0.02	0.0499
0.1	1.021	0.0979
0.21	1.42	0.1479

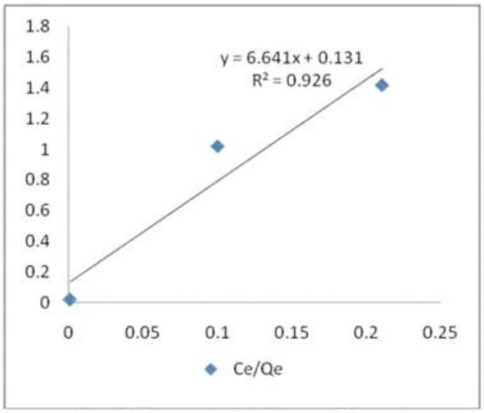

Fig. 2.5 Langmuir Isotherm (CR Dye)

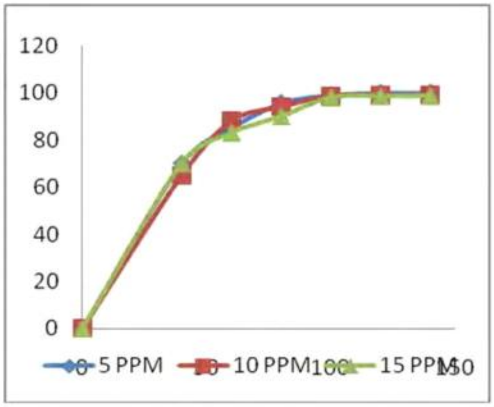

Fig. 2.4 Percentage removal with respect to time of CR

Table 2.4 Langmuir Isotherm (MB Dye)

Ce	Ce/Qe	Qe
0.05	1.01	0.0495
0.18	1.83	0.0982
0.321	2.18	0.1468

For a Langmuir type adsorption process it is necessary to investigate the type of isotherm by using separation factor values, to determine whether the MB adsorption process by adsorbent is favorable or not. The separation factor can be written as :

$$R_L = \frac{1}{1 + K_L C_0}$$

Where R_L is the dimensionless separation factor (Khalid *et al.*, 2012) and C_o is the initial solution concentration (kg/m^3). The parameter indicates the shape of the isotherm accordingly where:

$R_L > 1$	Unfavorable Isotherm
$R_L = 1$	Linear Isotherm
$0 < > 1$	Favorable Isotherm
$R_L = 0$	Irreversible

A plot of versus different initial MB and CR concentrations is shown in Figure 2.5, 2.6, 2.7 and 52.8 respectively. It can be visualized from Figures that for all initial MB and CR dye concentrations, the uptake of MB and CR are more favorable within the range of R_L valuesor not (Uddin, 2013).

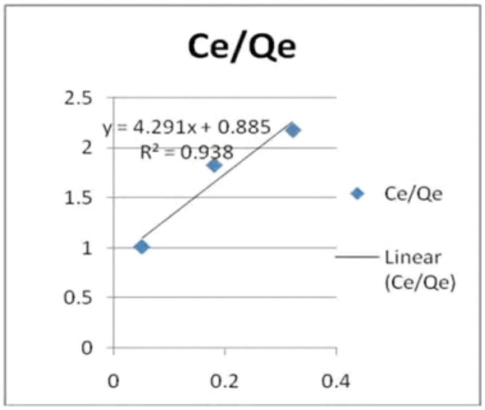

Fig. 2.6 Langmuir Isotherm (MB Dye)

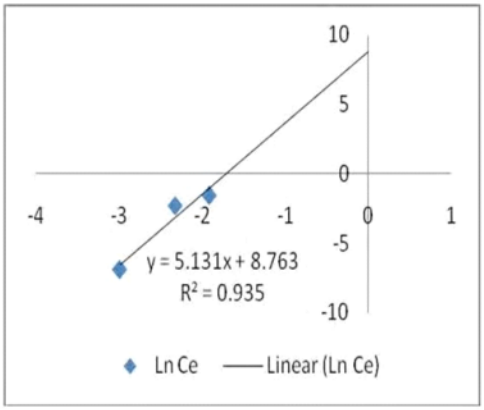

Fig. 2.7 Freundlich Isotherm (CR Dye)

Table 2.5 Freundlich Isotherm (CR Dye)

Ln Qe	Ln Ce
-2.99	-6.9
-2.32	-2.302
-1.91	-1.56

Table 2.6 Freundlich Isotherm (MB Dye)

Ln Qe	Ln Ce
-3	-2.99
-2.32	-1.714
-1.91	-1.13

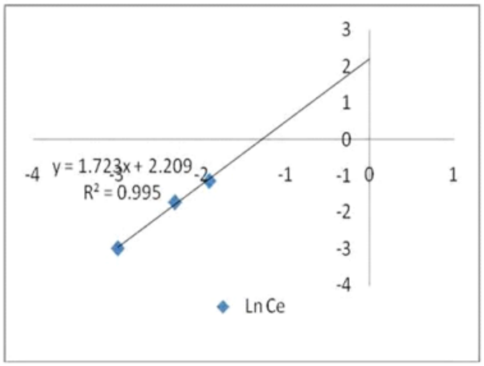

Fig. 2.8 Freundlich Isotherm (MB Dye)

Table 2.7 Isotherm Constants for the Adsorption of 'CR' and 'MB' by 'PS'

Isotherm	Parameters	CR	MB
Langmuir	Q_{MAX}	0.150	0.8851
	K_L	50.393	0.263
	R^2	0.926	0.9382
Freundlich	K_f	6394.5	9.1084
	n	0.1948	0.58018
	R^2	0.9354	0.9952

CONCLUSION

1. During the experiment we found that, after sometime the roots of PS was making the water turbid by its colour hence we have to activate the basic adsorbent.
2. Secondly with the values of we can easily predict that the Frenudlich Isotherm is best suited for this experiment both for MB and CR.
3. It was found that PS is very effective in terms of adsorbent for Dye for MB as-well-as for CR. While performing the experiment it was found that small quantity of PS was very effective for both MB and CR.
4. The adsorbent being natural and aquatic becomes low cost which is very good for and industry using dye. One more conclusion can also drawn from the present experiment that best removal is obtained at pH 8.

The experiment was successful and we can use *Pistia stratious* for the removal of MB and CR

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