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Methylene blue removal using Eucalyptus Leaves: A Low Cost Protocol towards Environmental Sustainability

Soumen Dey, Priyanka Bhagat, Jhilirani Mohanta, and Banashree Dey

ABSTRACT

Indiscriminate use of dyes pollutes water bodies and poses a serious threat to mankind. Hence there is a need to address the problem. Eucalyptus leaves, being abundantly available were tested for the removal of methylene blue dye from water by both batch and column experiments. The material was characterized by Scanning electron microscopy, proximate analysis, and FT-IR spectroscopy. SEM Images show a fractured surface with heterogeneous morphology. Batch experiments were conducted with respect to various physico-chemical parameters such as pH, agitation speed, concentration, etc. The maximum adsorption capacity was found to be 66 mg/g. Over a pH range of 4-8, high adsorption was seen. Adsorption follows a pseudo-second-order kinetic model (R^2=0.999). Regeneration was achieved with dilute hydrochloric acid and the material can be reused. Column studies show the possibility of field application. In a nutshell, a low-cost methodology was established with eucalyptus leaves for a safer environment.

Keywords: Methylene blue, Eucalyptus leaves, adsorption, regeneration.

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I. Introduction

In past few decades, a rapid increase in the number of textile and other dyes based industries have grown up. To add up, use of various dyes are increasing day by day. Dyes are used to color diverse products and large quantities of wastewater are discharge into streams and rivers which is a major source of water pollution. Azo dyes are non-biodegradable, highly toxic and proven carcinogens [1]. Dyes are mainly used in textile, paint, plastic industries; effluent from this industries are toxic in nature [2]-[4]. Dyes imposeserious threat to biological processes inside water bodies as the color of dyes prevent penetration of sunlight [5]-[6]. The presence of dyes in water bodies inhibits the growth of aquatic biota and decreases the oxygen solubility [7]. Wastewater containing dyes represents a threat to aquatic life so it's necessary to remove from wastewater [8].

But if methylene blue dose is higher than 0.09 mL per pound of body weight it cause dangerous side effects like chest pain, vomiting and confusion. Kidney and diabetics patient never takes it because it permanently destroyed the eyes. [9] Many methods are developed for removal of dyes in wastewater such as: coagulation and flocculation, sonochemical degradation, micellar enhanced ultrafiltration, cation exchange membranes, electrochemical degradation, membrane separation, oxidation and adsorption/precipitation [10]. Among all these, adsorption is easier and economically inexpensive process. In adsorption process adsorbents are used which are readily available and have very low cost. Activated carbon was used for the removal of color effluents in polluted wastewater [11]-[12]. Also different types of bio-adsorbents are reported from many years, such as *carpobrotus edulis* plant, sugarcane bagasse, agro-biomass, coconut husk, peat, straw, orange and uvaia seed. Recently neem leaf and orange peel powder has been reported. The adsorption of cationic dye on CTAB modified multi-component biosorbent is reported to be feasible [13]-[20].

Among all the purification process adsorption is easy, low cost, high efficiency, and recyclable process. An extensive variety of adsorbents like biomass, Zeolitic imidazolate frameworks-67 (ZIF-67), chitosan and its nanoparticles, carboxymethyl cellulose, acrylamide and graphene oxide, corn stalk polyethyleneimine-modified graphene oxide hydrogel, saw dust, clay based materials, rice husk, graphene,

silica-sand/starch composite, magnetic porous organic Polymers, activated carbon, bio-char, graphitic magnetic nanocomposite, polyoxometalate@UiO-66, Fe@graphitecore–shell magnetic nanocomposite, porous diatomite microsphere, CMC-g-P(SPMA) superadsorbent hydrogel, bioconjugated graphene oxide hydrogel, reduced grapheme oxide, graphene oxide intercalated montmorillonite nanocomposite, cement kiln dust, aminated calcium lignosulfonate, palygorskite, manganese oxide, zinc oxide, ZnO/NiO hollow microspheres, ZnO-Al_2O_3microspheres, MeSrCuO (Me = Mg and Ce) metal Oxides, CeO_2-Fe_2O_3-Al_2O_3, Ag/ZnO/3D, CuMgAl layered double hydroxide, binary oxides, polyaniline-alumina composite material, amberlite Ira-938 etc were tested [21]-[70]. With this line, we have demonstrated previously the application of various phytosorbents and chemisorbents for dye removal from contaminated water [71]-[82].

II. Materials and Methods

A. Biosorbent Preparation and Characterization

Eucalyptus leaves are collected from the university campus and washed thoroughly to remove all the dirt. It was then refluxed with distilled water to completely remove any natural color present within, and dried it to 70 ºC overnight. Dried leaves were crushed, sieved in different mesh sizes and used as such.
Methylene blue is cationic dye. Molecular weight (MW) is 319.65 $gmol^{-1}$. Structure is given in Fig 1.

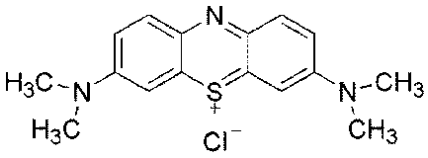

Fig 1. Structure of methylene blue.

100 mg/L stock solution was prepared by dissolving 0.05gm of MB in 500 mL distilled water. LR grade hydrochloric acid and sodium hydroxide was used to adjust solution pH.

Analytical balance (Denver instrument corp.) was used for weighing of samples. Systronic digital pH meter 802 was used for pH measurements. Sohag orbital shaker incubator was used for shaking in the shaking range 100-150 rpm. Muffle furnace (Thermo-Scientific) was used for drying of samples. ZIESS SEM Analyzer was used for SEM study. Hitachi double beam spectrophotometer (model U-2900) equipped with UV solutions program NSJ was used for all UV measurements. Perkin Elmer (spectrum-II) and Remi-bench top centrifuge (R-8 M) were used for centrifugation.

The different concentration was measured using an UV-Visible spectrophotometer at a wavelength of 664nm. Calibration curve was obtained by using standard MB solution at pH 7 and was fitted by a straight line with high coefficient value (R^2=0.987) as shown in Fig. 2.

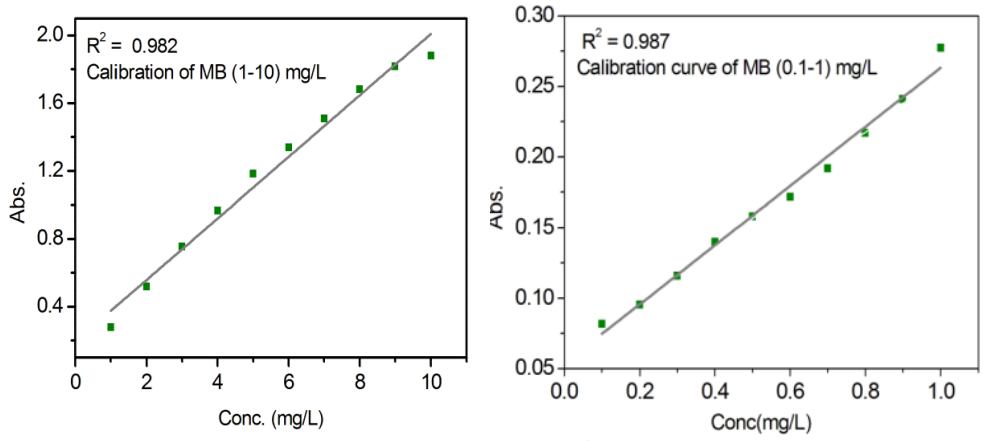

Fig. 2. Calibration curve of MB.

Batch studies were carried out by varying the initial dye concentration, contact time, agitation speed, adsorbent dose, particle size, pH and time. In this experiment 100mL bottle was used in which appropriate amount of adsorbent is used in 50mL dye solution with a known concentration. After equilibriation is reached, bottles were withdrawn from the shaker, centrifuged and absorbance was measured using UV-visible spectrophotometer. Concentration of dye was calculated using above calibration curves. The amount of dye adsorbed and the percentage removal was calculated using equation (1) and (2).

$$q_{t=}\frac{c_e-c_i}{m}\times\frac{V}{1000} \quad (1)$$

$$R\% = \frac{c_e - c_i}{c_e}\times 100 \quad (2)$$

where q_t (mg/gm) is the amount of dye adsorbed at equilibrium, C_e (mg/L) is the initial and C_i is concentration of dye after shaking at any time (min). V is the volume (mL) of dye, m (g) is the mass of adsorbent. R% is the percentage of dye removal.

III. Results and Discussion

Proximate Analysis was done for determination of ash, moisture, fixed carbon and volatile matter contents. It was carried out on eucalyptus leaves with 0.05µm mesh size.

TABLE I. Proximate Analyses of the Samples

Sl. No	Parameter	Content (%)
1.	Moisture content	9.8
2.	Ash content	73.10
3.	Volatile content	2.21
4.	Fixed carbon content	14.89

A. FT-IR Analysis

This technique is used for the prediction of functional groups present in the sample. In this experiment FT-IR shows the difference before adsorption and when adsorption takes place. The FTIR analysis indicated broad band at 3467 cm^{-1}, representing bonded O–H groups which gets shifted to 3363 cm^{-1} after adsorption (Fig. 3). The shift is attributed by interaction of dye with eucalyptus leaves.

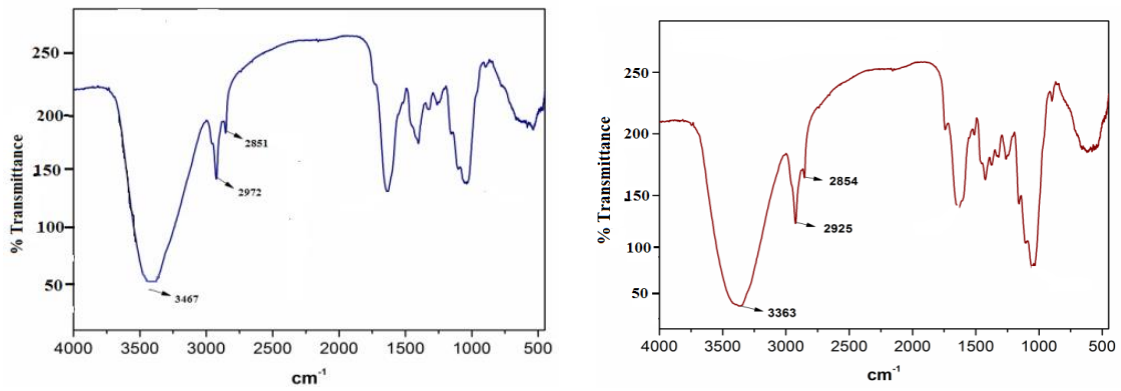

Fig. 3. FT-IR image of Eucalyptus leaves before and after adsorption of MB.

B. SEM Analysis

Scanning electron microscopy helps in determining the nature of the surface. Fig.4 (a) and (b) show the SEM images of prepared eucalyptus leaves and adsorption with MB solution. It was observed that pore size reduces after adsorption. This indicates that EU is effective in adsorbing methylene blue. Fig 4 represents SEM images of EU before and after adsorption.

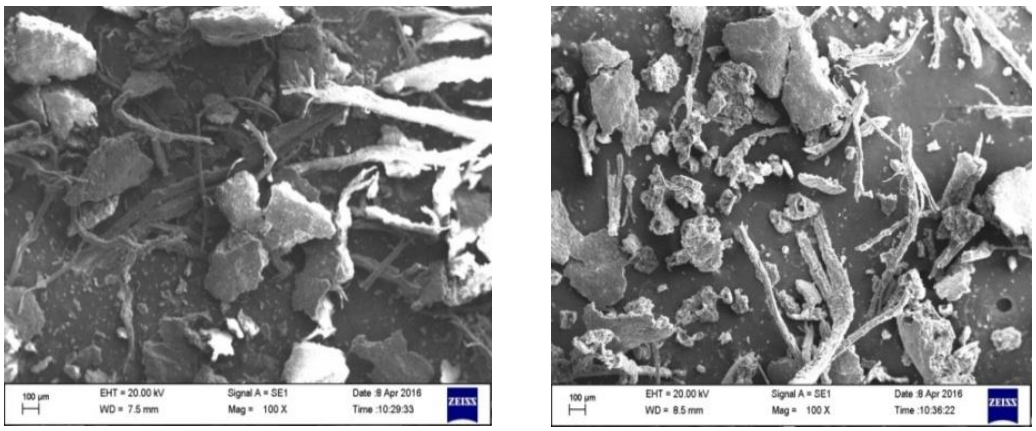

Fig. 4. SEM image of EU before (left) and after (right) adsorption of MB

C. Effect of Contact Time

The effect of contact time on the adsorption of MB onto EU ranges from 10 to 60 min. 5 mg/L MB solution was prepared by diluting 100 mg/L stock solution. 0.1g EU was taken and kept in shaker at room temperature in different time interval. Fig. 5 shows percentage removal of MB dye versus time. It was seen that the 88% adsorption occur in 10 min, after that there is no sharp increase in adsorption (Fig. 5). This suggests that equilibrium sets at 10 min.

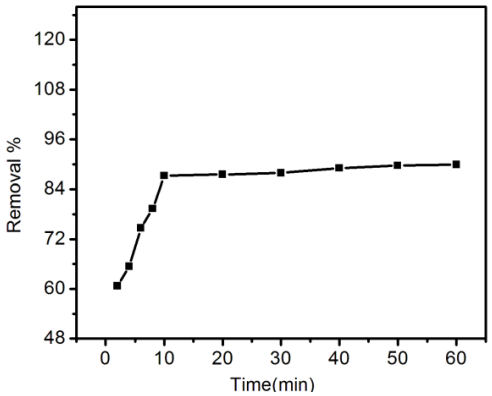

Fig. 5. Effect of contact time on MB adsorption.

D. Effect of Initial Dye Concentration

To demonstrate the effect of initial concentration, 5-30 mg/L concentration was taken. 0.1gm EU was added in different MB solution and shakes for 10min. Fig 6 shows the percentage removal vs concentration. There is a decrease in adsorption efficiency with increases of dye concentration. It was observed that at `lower concentration there are sufficiently available active sites, due to this adsorption is fast. This is might be due to increase the competition for active site and adsorption process will decreases slowly.

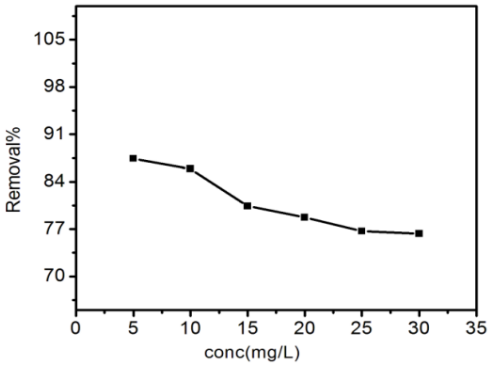

Fig. 6. Effect of initial dye concentration.

E. Effect of Agitation Speed

To evaluate the effect of agitation speed, 5 mg/L dye solution was taken in four bottles. The speed was ranges from 80 to 140 rpm and shaken it for equilibrium time one by one. Fig. 7 shows the effect of agitation speed. It was observed that increase in agitation speed decreases the adsorption insignificantly. This may be due to slight occurrence of desorption.

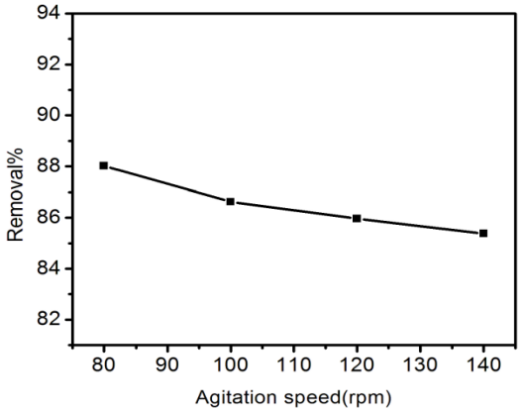

Fig. 7. Effect of agitation speed on adsorption of MB.

F. Effect of Adsorbent Dose

Fig. 8 shows the effect of adsorbent dose which was carried out by using different amount of EU (0.05 to 0.25 g), added to fixed initial dye concentration of MB. Initially concentration increases rapidly with increase in dose. This is due to availability of greater surface area. But after certain dosage efficiency becomes constant. This is due to fast superficial adsorption onto the adsorbent surface. Thus when adsorbent doses increases, amount of dye adsorbed per unit mass decreases.

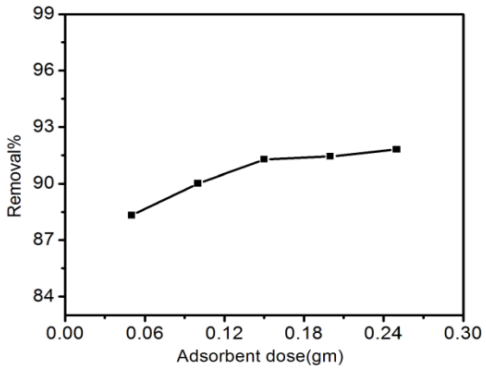

Fig. 8. Effect of adsorbent dose on adsorption of MB onto EU.

G. Effect of Particle Size

Fig. 9 shows the adsorption of MB of different particle sizes. Here initial dye concentration was taken and agitated for equilibrium time. It was observed that there is slow decrease in adsorption removal with increase in mesh size. Size is inversely proportional to surface area. Larger the size, lower was the adsorption. Hence small size was used which leads to greater adsorption.

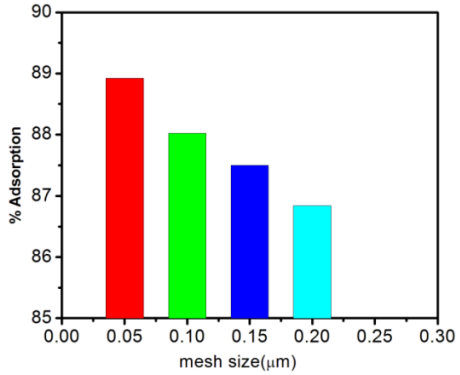

Fig. 9. Effect of particle size on adsorption of MB onto EU.

H. Effect of pH

The effect of pH was shown in Fig. 10. pH of initial dye solution is adjusted by adding small amount of 0.1M NaOH or HCl. Adsorption capacity increases with increasing pH. EU has larger number of active sites. In pH 2 there is large number of H^+ ions present which compete with active sites of EU for MB adsorption. When pH is gradually increased, number of H^+ ion deceases and electrostatic interaction between MB and EU gets better and efficiency increases. Fig. 10 represents the effect of pH on adsorption of dye.

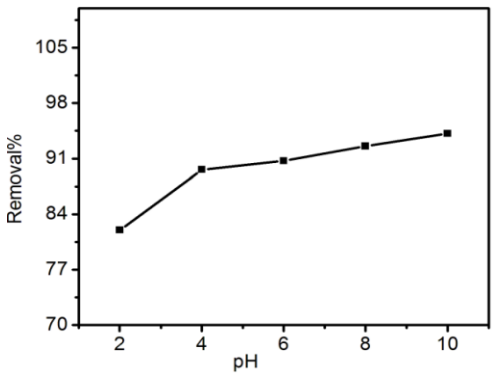

Fig. 10. Effect of pH on adsorption of MB onto EU.

I. Adsorption Kinetics

For knowing the mechanism of dye adsorption and designing the adsorption system, kinetics is one of the important parameter. For this pseudo-first-order, pseudo-second-order and intra-particle diffusion models were evaluated to fit the kinetics experiments data.

1) Pseudo first order kinetics model

In 1898 Lagergren developed the pseudo-first-order kinetic model is shown in (3).

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

where q_e and $q_t$are the amounts of dyes adsorbed at equilibrium and at time t (mg/g), respectively, and k_1 is the pseudo-first-order rate constant (min^{-1}) The integrated form of (3) with the initial condition, q_t=0 at t = 0 is shown in (4). The rate constant can be determined from linear plot of log ($q_e - q_t$) versus time.

$$log(q_e - q_t) = logq_e - \frac{k_{1t}}{2.303} \tag{4}$$

2) Pseudo second order kinetics model

Linearized form of the Pseudo second-order kinetic model is shown in below (5):

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)2} + \frac{t}{q_e} \tag{5}$$

where K_2 is the equilibrium rate constant of pseudo-second-order adsorption [g/(mg.min)]. A plot between t/q_t vs. t gives the value of rate constant K_2 (g/mg.min).

3) Intra particle diffusion model

Weber-Morris developed the intra-particle diffusion model which is shown in (6):

$$q_t = k_3 t^{1/2} + c \tag{6}$$

where k_3 is the inter particle diffusion rate constant ($mg.g^{-1}\ min^{0.5}$) and C is intercept ($mg.g^{-1}$), which is the thickness of boundary layer.

The kinetics of MB adsorption was analyzed with respect to pseudo-first order, pseudo-second order and intra-particle diffusion model. By using relevant equations all the graphs was plotted and shown below. The 1st and 2nd order rate constants were determined. The kinetic data of Pseudo2nd order model are fitted with highest correlation coefficient (R^2=0.999) which is better than pseudo-first (R^2=0.982) intra particle model (R^2=0.933). These result shows that adsorption of MB onto EU might be best described by pseudo2nd order kinetic model. Fig. 11 shows all the kinetic models. From the observations, it seems that there is a combining effect of physi-sorption and chemi-sorption.

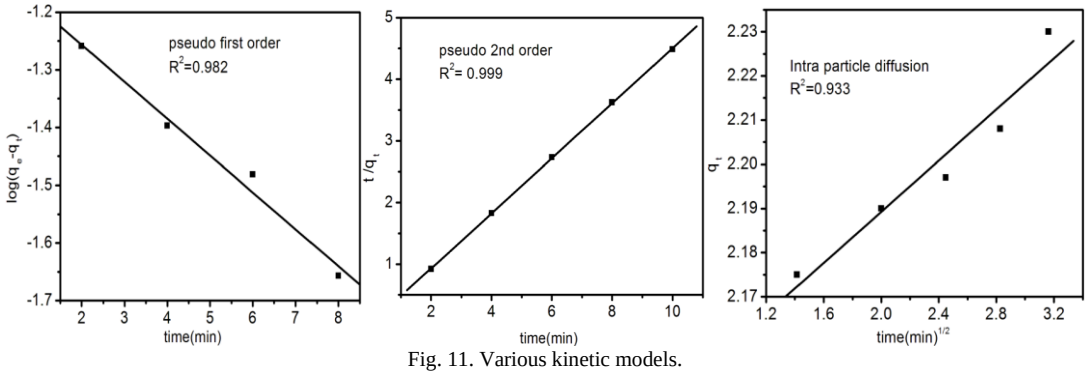

Fig. 11. Various kinetic models.

IV. COLUMN STUDY

Only batch experiment may not be conducive whether a material will work on pilot scale. Column study was carried out to check whether EU can be used in industrial wastewater treatment. In this experiment adsorbent bed of knowing amount was prepared and 5mg/L methylene blue solution was passed through dropwise. A constant flow rate is maintained. Fixed bed glass column was used and experiments were performed at pH 7. Results are summarized in Table 2.

TABLE II. SELECTED COLUMN PARAMETERS

Particle size of adsorbent (μm)	Amount of adsorbent (g)	Diameter of column (cm)	Height of adsorbent bed (cm)	Total amount of contaminant passed (mL)	Bed volume (mL)
1.5	1	1.2	7.3	600	72.72
1	1	1.2	7.3	1400	169.69
0.5	1	1.2	7.3	2300	282.9

V. REGENERATION AND REUSE

Regeneration study helps to understand the mechanism of adsorption. The scope of recovery of adsorbate as well as adsorbent also called regeneration. If the adsorbent can be successfully regenerated, then it will make the treatment process more economically advantageous. To achieve that, 0.5 g MB treated EU was taken in three 50 mL of conical flask. In these flasks, one acidic (25 mL, 1N HCl), one basic (25 mL, 1N NaOH) and one neutral (25 mL, 1N NaCl) solution was taken and shaken for overnight. The final readings of concentration were noted down. A graph between percentage desorption and 0.1 N solution was plotted. In case of hydrochloric acid, the percentage desorption was very high. EU was then thoroughly washed with distilled water and adjusted to pH 7. A continuous cycle experiments were conducted for three cycles. It was found that after each cycle efficiency is retained by almost 95%. Fig. 12 shows desorption with HCl and NaOH solution. This is in accordance to our previous works where we have demonstrated highly efficient regeneration and reuse of various materials for diverse dye removal from contaminated water [71]-[82].

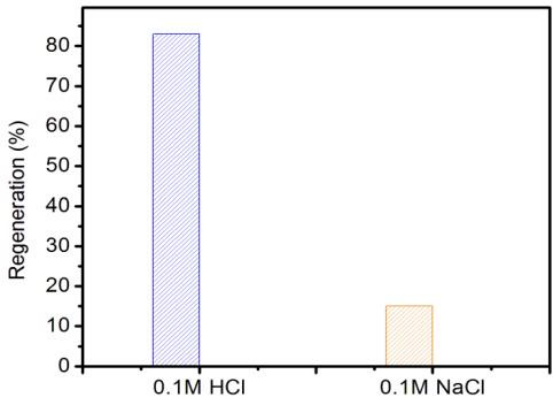

Fig. 12. desorption of dye loaded material in 0.1N HCl and 0.1N NaCl.

VI. CONCLUSION

Present study shows that Eucalyptus leaves, a cheap and easily available material, that can be effectively used to remove methylene blue from solution. Proximate analysis showed good carbon content which favors adsorption. Percentage carbon was found to be. The moisture content (9.8%), volatile content (2.21%) and ash content (76.10%) were also found to be quite reasonable. FTIR spectra show little change in the surface properties of adsorbent after adsorption as compared to that of before adsorption. Scanning Electron micrographs exhibited that EU had a considerable number of pores where there is a good possibility of methylene blue dye to be trapped and adsorbed into these pores and also there is no significantly change in the surface topography of EU before and after adsorption of dye due to lack of dye and adsorbent ratio. Adsorption tends to increase with contact time. At first the increase in adsorption is very rapid as there are lots of free sites for the adsorption to take place. Rate of adsorption decreases at later stages till saturation is reached due to saturation of active sites. The optimum contact time for equilibrium was found to be ten minutes. The removal efficiency of adsorbent is maximum at higher pH range. As adsorbent dose increases, adsorption increases due to the availability of free sites. Concentration of adsorbent is taken as the optimum adsorbate dose. As we increase adsorbate dose more than the optimum, the subsequent increase in adsorption is very less and it becomes cost ineffective. There is decrease in adsorption with the increase in initial dye concentrations due to the high driving force for mass transfer at a high initial dye concentration. The adsorption process follows pseudo second order kinetics.

CONFLICT OF INTEREST STATEMENT

All the authors declare that there is no conflict of interest.

ACKNOWLEDGEMENT

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Some representative publications are as follows:

1. Mohanta, J.; Dey, B.; Dey S*. (2020) Magnetic Cobalt Oxide Nanoparticles: Sucrose-Assisted Self-Sustained Combustion Synthesis, Characterization, and Efficient Removal of Malachite Green from Water. *J. Chem. Eng. Data*, 65: 2819−2829.

2. Kumari,R.; Khan,Md. A.; Mahto,M.; Qaiyum,Md. A. Mohanta, J.;Dey,B.; Dey. S*. (2020) Dewaxed Honeycomb as a Promising Scavenger for Malachite Green from Water, ACS Omega, 5: 19548−19556.

3. Kumari, R., & Dey, S*. (2019). A breakthrough column study for removal of malachite green using coco-peat. *International Journal of Phytoremediation*, 21(12), 1263–1271.

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