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Methylene Blue Dye Removal from Waste Water Using Activated lemon Peel

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ABSTRACT

In this study we prepared activated carbons by chemical activation from lemon peel with (H_2SO_4) method and to explore the adsorbent capacity for removing MB dye from waste water. SEM and FTIR techniques were used to study the adsorbent characteristics. The experimental data was used to study the effect of various parameters the initial ion concentration, pH, contact time and adsorbent dose of lemon peel based activated carbon. Various kinetic models and isotherm adsorption were used to demonstrate the adsorption proper mechanism. Langmuir adsorption isotherm was found to have the maximum adsorption potential of 300 mg/g.

Key words : *Adsorption isotherms, Kinetics, Langmuir isotherm, Lemon peel.*

Introduction

Dyes have been utilized in the dying, paper printing, materials, plastics, cowhide, beautifiers, pharmaceuticals and agri-nourishment businesses; the effluents released by these industries are hazardous to mankind and creates ecological issues (Hassaan *et al.,* 2017). These businesses have established a significant increment in the utilization of engineered colors as a shading material (Kumar *et al.,* 2011). Dyes are dormant and hard to biodegrade when released into waste streams. Their degradation items might be cancer-causing agents and poisonous and, therefore, their treatment is necessary. The precious methylene blue dye has been considered due to its known adsorption onto solids, and it regularly fills as a model compound for evacuating natural contaminants and colored substances from fluid arrangements (Hameed *et al.,* 2007).

Various physicochemical methods have been used, adsorption is best method than different procedures (Subramaniam *et al.,* 2015). Adsorption procedure is an appropriate method for inorganic and natural contaminations expulsion from wastewater, as a result of the noteworthy preferences like ease, accessibility, gainfulness, simplicity of activity, proficiency, and adequacy than different strategies. This procedure is anything but difficult to work and similarly compelling in the evacuation of dangerous contaminants, even at low fixations (Uddin, 2017). Adsorption is ordinarily a surface marvel, its exhibition being emphatically identified with the interesting properties of explicitly structured sorbent material. Adsorption procedure can be a physical adsorption which includes just moderately powerless intermolecular powers, and chemisorptions which include the development of a synthetic security between the adsorbate particle and the outside of the adsorbent

(Sintayehu *et al.,* 2016). In the present study, we are investigating adsorption capacity of activated lemon peel *(Citrus limon)* to eliminate methylene blue dye from aqueous medium. Lemon peel is an agricultural waste produced from juice shop and food industries.

Materials and Methods

Adsorbate : The cationic dye, methylene blue (MB) was utilized as an adsorbate in this investigation of extremely high virtue. It has the sub-atomic recipe $C_{16}H_{18}CLPN_3S$ and the sub-atomic load of 319.85 g/mol. Multiple distillation of water was used for making preparationof all the experimental solutions to be examined.

Preparation of adsorbent: Lemon peel *(Citrus limon)* was collected initially from juice vendors. Followed by the washing with double distilled water then dried in oven at 70° C temperature for 24 hrs. After drying, grinding was done to reduce the size and continuously sieved to mesh size between 0.150-0.300 mm. Chemical treatment was done with the help of concentrated sulfuric acid ($H_2SO_{4)}$ in 1:1 ratio. This mixture was activated in muffle furnace for 2hrs at 500° C followed by washing with double distilled water many times until neutral pH was obtained. Then after drying, activated lemon peel was stored in sealed container for further experimental study (Rani *et al.,* 2022).

Batch adsorption study

The stock solution of MB 1000ppm was prepared using double distilled water. Subsequently, the stock solution was diluted to allow fresh concentration solutions. Samples of different concentration 20, 40, 60, 80 and 100 ppm and pH 4, 6, 8, 10 and 12 range used for batch operation study. The remaining MB concentration was measured using a UV / visible spectrophotometer available in the university department to measure the absorbance at 570 nm (Bhatnagar *et al.,* 2013). The removal efficiency was enumerated using the equation:

$$\text{Removal efficiency} = \frac{(Co–Ce)}{Co} \times 100 \quad .. (1)$$

Where, C_0 = Concentration of MB in the sample solution before treatment and

C_e= Concentration of MB in the sample solution after treatment.

Results and Discussion

Characterization

SEM (Scanning Electron Microscope) and FTIR (Fourier Transform infra red) techniques have used for the characterisation of adsorbent sample, number of observations comes from the pictures of FTIR and SEM before and after adsorption of the sample. SEM gives the morphological images of adsorbent sample before and after adsorption (Fig. 1). Before adsorption image clearly specifies the of cavities and pores on the surface of adsorbent. On other side after adsorption image also gives clear picture of how adsorbate get settled onto the pores present on the surface of adsorbent (Rani *et al.,* 2022).

FTIR analysis describes various functional groups information with respect to the wavelength which is responsible for favorable adsorption.

Various peaks of different intensity have been observed pre and post the adsorption of dye (Fig. 2). Peaks at 3400, 2900, 1600, 1100 cm^{-1} represents car-

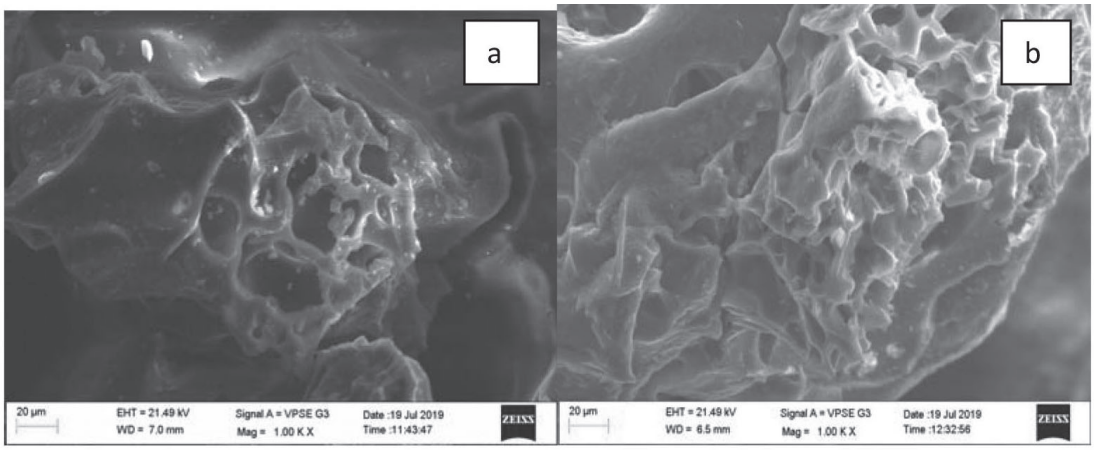

Fig. 1. SEM morphological images of adsorbent a) before adsorption and b) after adsorption.

boxylic group, C-N, C-H vibrations and N-H stretching. After adsorption some new peaks have been introduced due to bonding concept and some peaks shifted to new position because of bond length increased or decreased concept. The physical or chemical adsorption takes place due to functional groups present between the adsorbent and molecules of dye (Garg *et al.,* 2004).

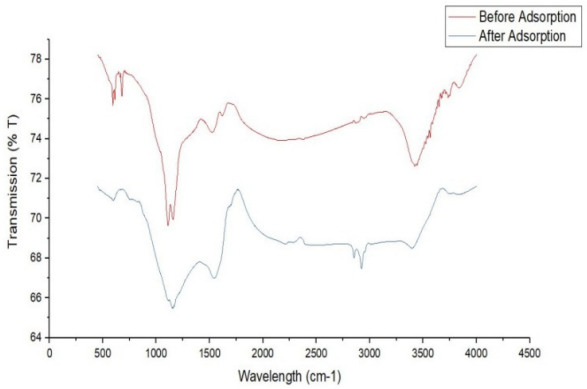

Fig. 2. FTIR spectrum of the adsorbent before and after adsorption

Effect of Contact time

Contact time basically represents the kinetics in such a manner how well an adsorbate is distributed on the surface of given adsorbent. It represents time rate diffusion with respect to % removal. When time varies such as 5, 10, 15, 20, 30, 60 min, %removal was increased from 48 to 90, beyond that no % removal is obtained as shown in Fig. 3 (a).

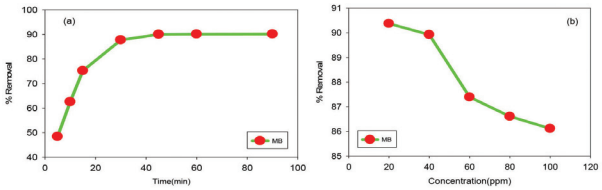

Fig. 3. Influence of parameters (a) contact time and (b) initial ion concentration

Effect of initial ion concentration

Effect of initial ion concentration is checked by different level of concentration from 20-100 ppm remaining parameters pH, adsorbent dose fixed {fig 3 (b)}. From the analysis it was clear that as increasing initial ion concentration % removal was decreased from 90 to 86 but adsorption capacity was increased. This is because of the reason that at initial points all the vacant sites had been occupied (Mohan *et al.,* 2014).

Effect of pH

Effect of pH performs an important role to decide the optimization of parameters for ideal experiment. As increased pH range from 4, 6, 8, 10 and 12 while keeping all other factors fixed, % removal also increased which indicates the basic nature of dyes (Fig. 4 a). All this happened totally due to nature of the adsorbent (Zhang *et al.,* 2014).

Effect of Adsorbent dose

Adsorbent dose also declares the same behavior upon increasing dose from 0.1-0.5 g (Fig. 4b). Removal percentage increased due to more number of vacant sites available more will be adsorption (Rahman *et al.,* 2012).

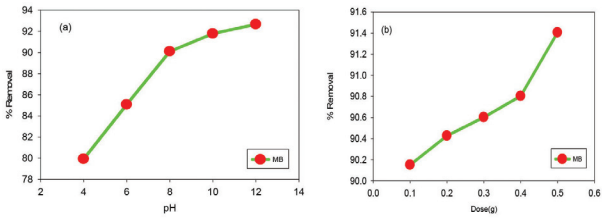

Fig. 4. Influence of parameters (a) pH and (b) adsorbent dose

Kinetics adsorption

Kinetics adsorption was done to know the mechanism of the adsorption; differentmodels were employed to know the mechanism and order of the reaction. Pseudo-first-order and pseudo-second-order models were employed (Zaker *et al.,* 2013).

Pseudo-first-order equation: $\log (q_e - q_t) =$

$$\log q_e - \frac{k1}{2.303} t \quad .. (2)$$

Pseudo-second-order equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_t} \quad .. (3)$$

From the analysis of the graph (Fig. 5), it was revealed that pseudo first order failed to explain order of reaction because of negative value of slope. On other side, pseudo second order model was more appropriate to define order of the reaction with respect to high value of correlation coefficient andfollowed chemical adsorption nature. All the calculated parameters from these models are listed in the Table 2.

Table 2. Kinetic and thermodynamic parameters calculated from the models.

Pseudo-first-order		Pseudo-second-order		Langmuir		Freundlich	
q_e (mg/g)	3.2	q_e (mg/g)	21.23	q_e (mg/g)	300	N	1.4
K_1	0.037	K_2	0.016	K_L	0.03	K_2	2.77
R^2	0.616	R^2	0.997	R^2	0.935	R^2	0.993

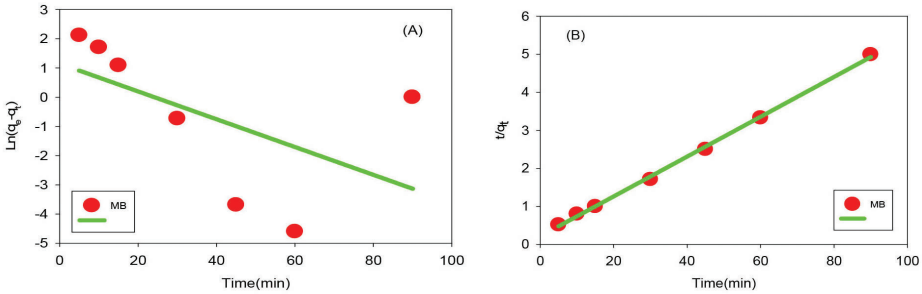

Fig. 5. Kinetic adsorption models (A) pseudo-first-order, (B) pseudo-second-order

Adsorption isotherms

Adsorption isotherms clarify the idea of the solute–surface cooperation just as the particular connection between the convergence of adsorbate and its level of aggregation onto the surface at a predefined temperature. For equilibrium modeling of dye on to lemon peel derived activated carbon, Langmuir and Freundlich isotherm models were tested in the presented study (Langmuir, 1916 and Weber *et al.*, 1974).

Langmuir equation: $\frac{C_e}{q_e} = \frac{1}{K_0 q_m} + \frac{1}{q_m} C_e$ .. (4)

Freundlich equation: $\log q_e = \log K_F + (1/n) * \log C_e$ (5)

Langmuir adsorption isotherm as tells about the monolayer adsorption phenomenon and Freundlich about the multilayer adsorption process.

So from the figure analysis (Fig. 6), all the isotherm models are quite suitable but Freundlich isotherm was most superior due to fact that exact value of slope andintercept able to calculate all parameters. Calculated parameters from these isotherms are listed in the Table 2.

Conclusion

This study presented an eco-friendly process for the removal of MB dye from aqueous medium. Characterization of the adsorbent sample defines the relevant bonding between adsorbate-adsorbent and describe the morphological surface of the prepared adsorbent with full of cavities. The MB dye adsorption is found to be effective optimized by parameters initial ion concentration, contact time, pH and adsorbent dose. Comparison of equilibrium modeling confirms multilayer adsorption phenomenon over to monolayer adsorption. Adsorption process found to be followed by second order kinetics and revealed chemical adsorption process.

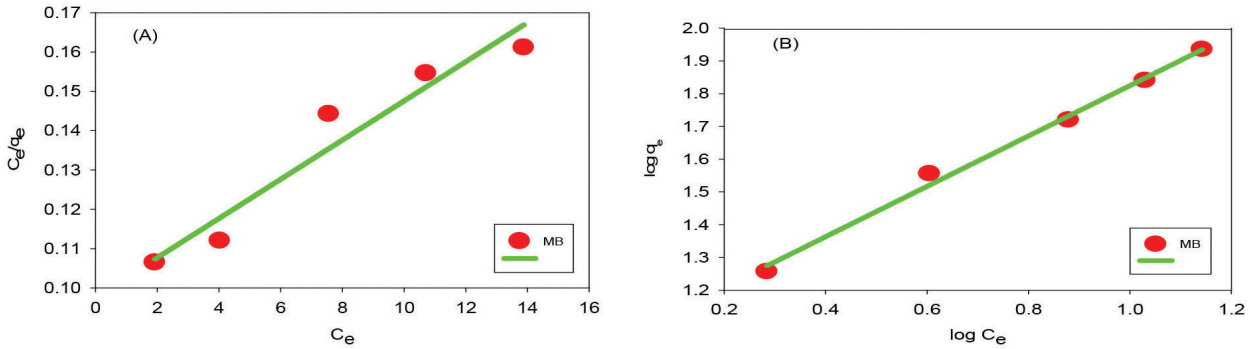

Fig. 6. Adsorptionequilibrium modeling (A) Langmuir, (B) Freundlich

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