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BIOSORPTION OF METHYLENE BLUE DYE FROM WASTEWATER USING MODIFIED CHICKPEA HUSK AS AN ADSORBENT

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ABSTRACT

The purpose of this study was to extract activated carbons by chemical activation from chickpea husks (H_2SO_4) and to investigate the adsorbent potential for removing dye from aqueous solutions. SEM and FTIR techniques were initially defined as adsorbent. The experimental data were evaluated to optimize the initial ion concentration, pH, contact time and adsorbent dose of the different parameters. Various kinetic models and isotherm adsorption were used to illustrate the adsorbent's proper mechanism and performance. Langmuir adsorption isotherm found to have the maximum adsorption potential of 200 mg/g.

KEY WORDS: Adsorption isotherms, Kinetics, Optimization, Chickpea husk.

INTRODUCTION

Dyes have for quite some time been utilized in the dyeing, paper ventures; printing, materials, plastics, cowhide, beautifiers, pharmaceuticals and agri-nourishment businesses, yet the effluents released by these enterprises represent certain dangers and ecological issues (Hassaan *et al.,* 2017). These businesses have demonstrated a noteworthy increment in the utilization of engineered colors as a shading material. Since dyes have a manufactured inception and complex sweet-smelling atomic structures, they are dormant and hard to biodegrade when released into waste streams (Kumar *et al.,* 2011). The expulsion of engineered dyes is of extraordinary worry, since certain dye and their debasement items might be cancer-causing agents and poisonous and, therefore, their treatment can't rely upon biodegradation alone. The precious methylene blue dye has been considered due to its known solid 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).

Numerous physico-chemical strategies have been tried, yet just that of adsorption was viewed as better 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 contaminations, 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 include 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 chickpea husk *(Cicer arientum)* to eliminate methylene blue dye from aqueous medium. Chickpea husk is an agricultural waste produced from husking mill.

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. The synthetic structure of MB is appeared in Fig. 1. Multiple distillation of water was used for making preparationof all the experimental solutions to be examined.

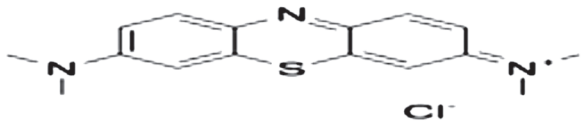

Fig. 1. Chemical Structure of methylene blue dye

Preparation of adsorbent: Chickpea husk *(Cicer arientum)* was collected initially from the local market. 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 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 withdouble distilled water many times until neutral pH was obtained. Then after drying, activated chickpea huskwas stored in sealed container for further experimental study (Rani and Chaudhary, 2022a).

Batch adsorption study

With the aid of double distilled water, a stock solution of MB 1000ppm was prepared. 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:

$$removal\ efficiency = \frac{(Co-Ce)x100}{Co} \quad (1)$$

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 2). Before adsorption image clearly specifies the lots 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 and Chaudhary, 2022b).

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 3). Peaks at 3400, 2900, 1600, 1100 cm^{-1} represents carboxylic group, C-N, C-H vibrations and N-H stretching. After

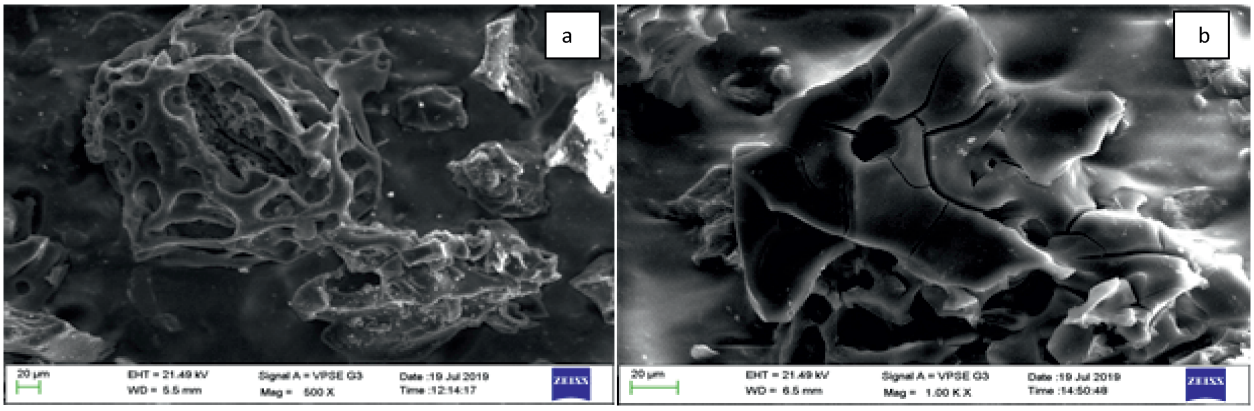

Fig. 2. SEM morphological images of adsorbent a) before adsorption and b) after adsorption.

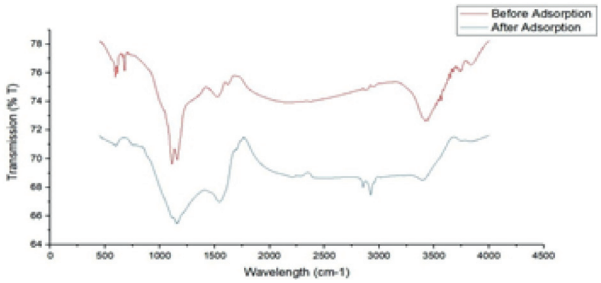

Fig. 3. FTIR spectrum of the adsorbent before and after adsorption

adsorption some new peaks has introduced due to bonding concept and some peaks shifted to new position because of bond length increased or decreased concept. The physical or chemical adsorptiontake place due to functional groups present between the adsorbent and molecules of dye (Garg *et al.*, 2004).

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 is vary 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 Figure 4 (a).

Effect of initial ion concentration

Effect of initial ion concentration is checked by different level of concentration from 20-100 ppm the word keeping remaining parameters pH, adsorbent dose fixed {fig 4 (b)}. Volume of the sample 20ppm was taken for all the samples. 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 5 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

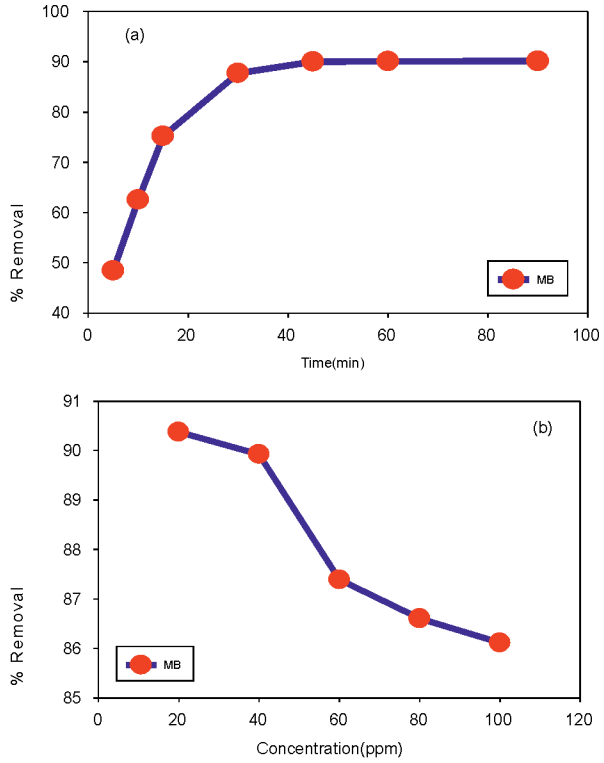

Fig. 4. Influence of parameters (a) contact timeand (b) initial ion concentration

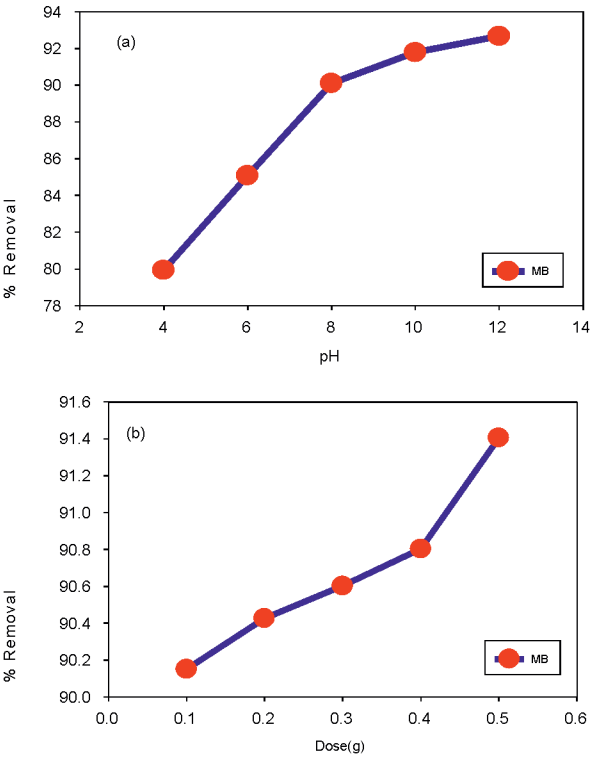

Fig. 5. Influence of parameters (a) pHand (b) adsorbent dose

upon increasing dose from 0.1-0.5 g (Fig 5 b). Removal percentage increased due to more number of vacant sites available more will be adsorption (Rahman *et al.*, 2012).

Kinetics adsorption

Kinetics adsorption was done to know the mechanism of the adsorption, different models were employed to know the mechanism and order of the reaction. Pseudo-first-order, pseudo-second-order and intra particle diffusion models were employed (Ghanbarnezhad *et al.*, 2014 and 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: $\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_t}$ (3)

Intraparticle diffusion equation: $q_t = K_{id} t^{0.5} + C$ (4)

When pseudo first order and second order models were used to find out the mechanism and order of the reaction, then from graph analysis (Fig. 6), it was revealed that pseudo first order failed to explain order of reaction because of negative value of slopeand Intra particle diffusion model failed to explain order of reaction due to low correlation coefficient value (Table 2). 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.

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 chickpea husk derived activated carbon, Langmuir, Freundlich and Temkin isotherm models were tested in the presented study (Langmuir, 1916 and Weber *et al.*, 1974 and Foo, 2012).

Langmuir equation: $\frac{C_e}{q_e} = \frac{1}{K_0 q_m} + \frac{1}{q_m} C_e$ (5)

Freundlich equation: $\log q_e = \log K_F + (1/n) * \log C_e$ (6)

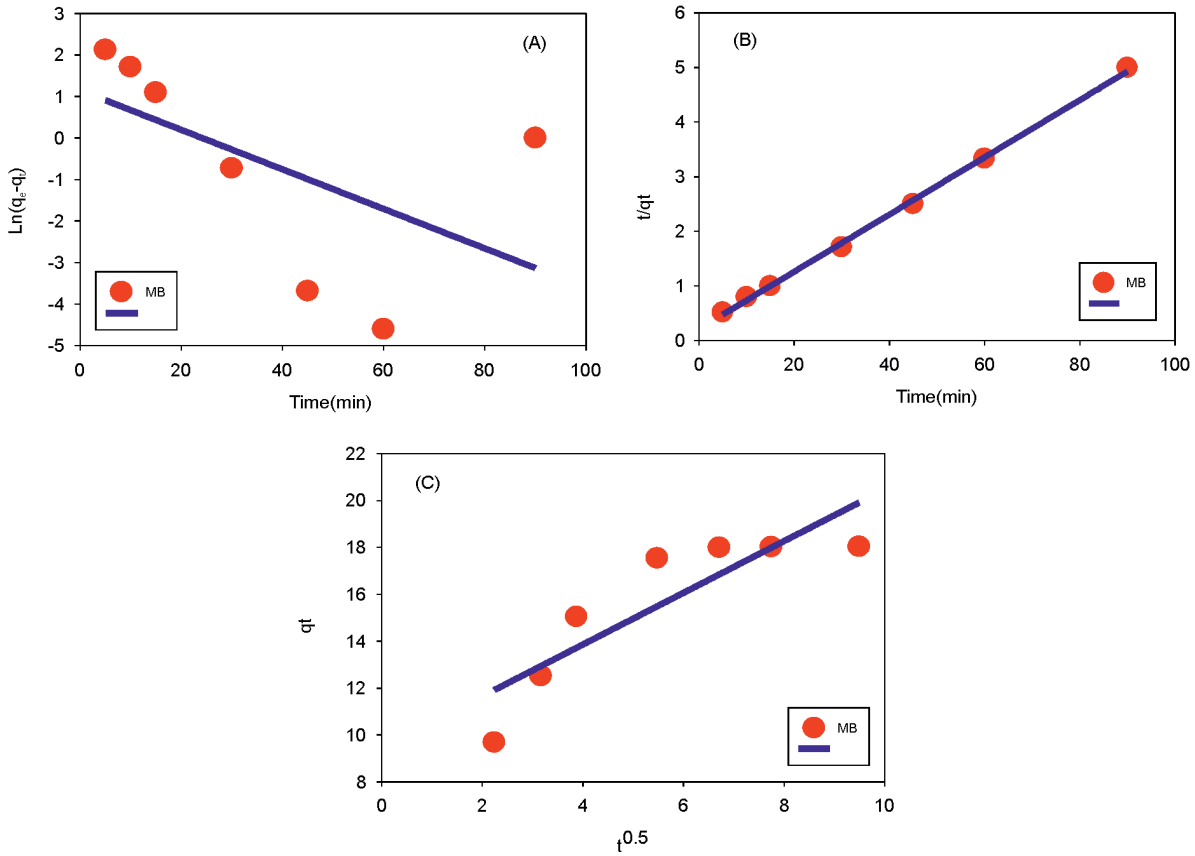

Fig. 6. Kinetic adsorption models (A) pseudo-first-order, (B) pseudo-second-order and (C) Intra particle Diffusion

Table 2. Kinetic parameters calculated from the models.

Pseudo-first-order		Pseudo-second-order		Intraparticle Diffusion	
q_e (mg/g)	3.15	q_e (mg/g)	19.23	K_{id}	1.10
K_1	0.047	K_2	0.012	C	9.44
R^2	0.606	R^2	0.998	R^2	0.757

Temkin equation: $q_e = B \ln A_T + B \ln Ce$ (7)

Langmuir adsorption isotherm as tells about the monolayer adsorption phenomenon and Freundlich about the multilayer adsorption process and Temkin model tells about heat of adsorption. So from the figure analysis (Fig 7), all the isotherm models are quite suitable but Freundlich isotherm was most superior due to fact that exact value of slope and intercept able to calculate all parameters. Calculated parameters from these isotherms are listed in the table 3.

CONCLUSION

This study presented an eco-friendly process for the removal of MB dye from aqueous medium.

Table 3. Calculated equilibrium modeling parameters

Langmuir		Freundlich		Temkin	
q_e (mg/g)	200	N	1.3	A_T	1.40
K_L	0.05	K_2	2.87	B	16.58
R^2	0.937	R^2	0.994	R^2	0.956

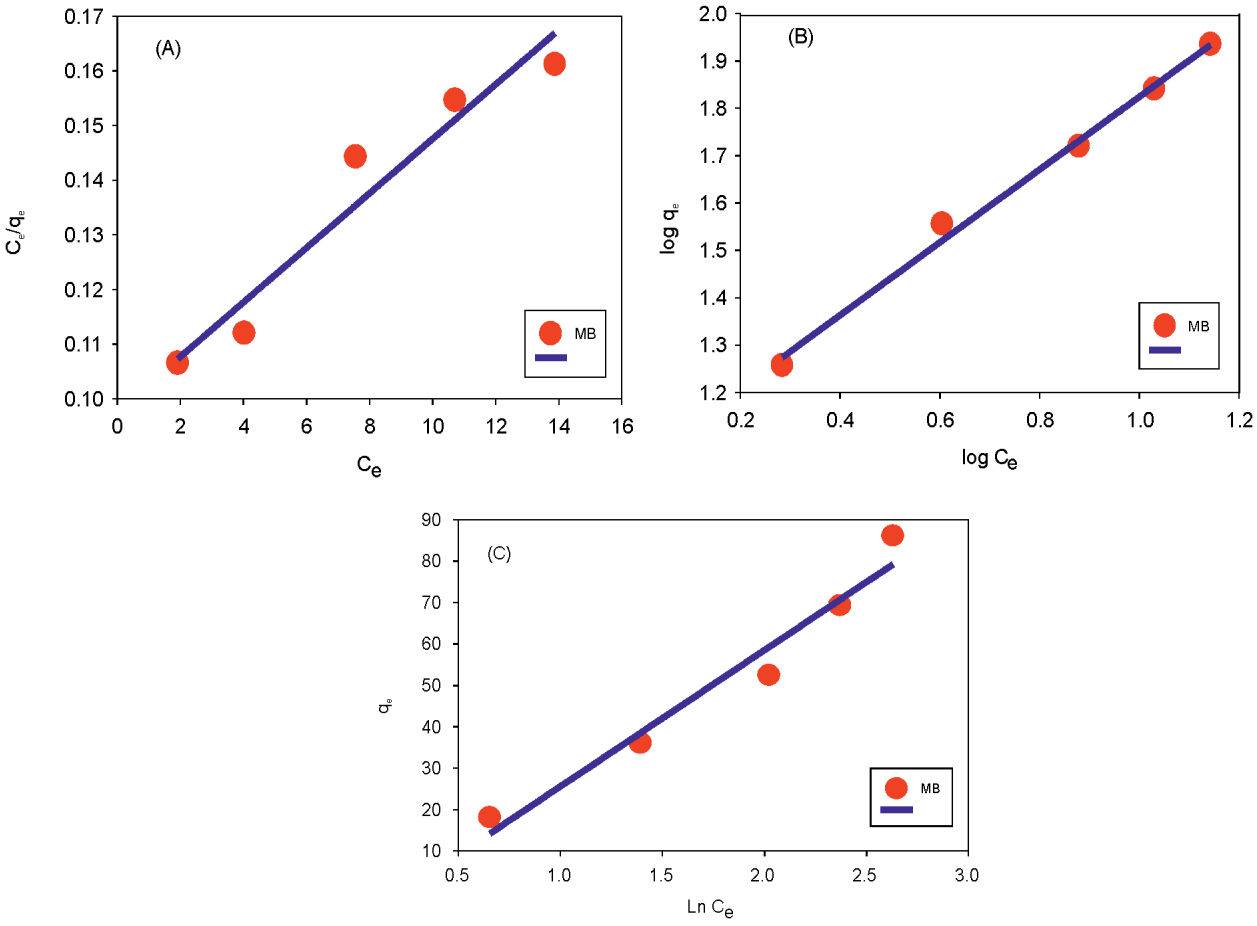

Fig. 7. Adsorptione quilibrium modeling (A) Langmuir, (B) Freundlich, (C) Temkin

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.

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