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Use of Almond Tree (*Terminialia cattapa*) Bark Powder for Adsorption of Methylene Blue, a Basic Dye from Aqueous Solutions

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Abstract - Adsorption studies of methylene blue (MB) on Almond tree bark powder (ATBP) were carried out by batch experiments. The parameter studied includes initial dye concentration, adsorbent dose, pH, agitation time, agitation speed, particle size of adsorbent and temperature. The best fitting isotherm models was found to be Langmuir and Freundlich ($R^2 \approx 0.99$). As the particle size of adsorbent increased from > 120 mesh, 120≤ 85mesh, 85≤ 60 mesh, the monolayer (maximum) adsorption capacities (q_m) were found to decreased from 333.333, 200, 166.667 mg/g of ATBP respectively. Lagergren pseudo -second order model best fits the kinetics of adsorption. Intra particle diffusion plot showed boundary layer effect and larger intercepts indicates greater contribution of surface sorption in rate determining step. Adsorption was found to increase on increasing pH, increasing temperature and increasing particle size. Thermodynamic analysis showed that adsorption was favourable, spontaneous, endothermic physical adsorption and increased disorder and randomness at the solid- solution interface of MB with the adsorbents. ATBP was found to have excellent adsorption capacity.
Key words- Adsorption isotherm, methylene blue (MB), Almond tree bark powder (ATBP), kinetic and thermodynamic parameters.

I. INTRODUCTION

Industrial effluents largely affect ground water and pollute the environment. Every industry uses colouring matter to colour their matter. Colour is the first contaminant to be recognized, since it is visible to human eye. So, effluent treatment for removal of colour is necessary to protect the environment and the aquatic life. The colour Dyes are generally used as a colouring matter. Dyes are problematic if they are broken down anaerobically in the sediment, as toxic amines are often produced due to incomplete degradation by bacteria [1]. Some of the dyes or their metabolic products are toxic, mutagenic or carcinogenic [2, 3]. Synthetic dyes have complex aromatic structures which provide them optical, thermal, biological and physiological stability [4,5]. Recently, all governments have been under severe pressure by their people to stop dye contaminated effluents to the public watercourses, unless it is treated properly. The USEPA (environmental protection agency) has classified textile wastes into four groups- dispersible, hard to treat, high volume and hazardous and toxic wastes [6]. Basic dyes are the brightest class of soluble dyes used by textile industry [7]. Many methods such as ultra-filtration, coagulation, photo oxidation, adsorption, etc. were used for the removal of dyes from waste water. Among these methods, adsorption is widely used and versatile method because of its simplicity of design and operation, low cost and insensitivity to toxic substances. A number of agricultural wastes of cellulosic origin have been studied in literature, such as sugarcane baggage, corncobs, wheat straw and wood chips for their capacity to remove dyes from aqueous solution [8-11].
In this paper, almond tree bark powder (ATBP) is used as a low biosorbent for the removal of MB from the aqueous solutions.

II. EXPERIMENTAL

A. Adsorbent

Adsorbent used in the present study is Almond tree bark powder (ATBP). Bark of the dried stem of almond stem was taken off from one of the garden of Konkan region of Maharashtra state in India and washed thoroughly with distilled water and dried. Dried bark was cut into small pieces and grounded in a domestic mixer- grinder. After grinding, the powder was again washed and dried. Different sized ATBP's were stored in plastic bottle containers for further use.

B. Dye solution

MB (M.W. $C_{16}H_{18}ClN_3S$) is a monovalent cationic dye used as a sorbate in the present study. In dye classification it is classified as C. I. Basic blue 9 and C.I.52015. It has a molecular weight of 373.9 and was supplied by S. D. Fine Chemicals, Mumbai,

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India. A stock solution of 1000 mg/l was prepared in double- distilled water and the experimental solutions of the desired concentration were obtained by successive dilutions.

C. Methods

Efficiency of adsorbents is evaluated by conducting laboratory batch mode studies. Specific amounts (25mg) of adsorbents were shaken in 25 ml aqueous solution of dye of varying concentration for different time periods at natural pH (≈ 7) and temperature (≈ 303K). At the end of pre-determined time intervals, adsorbent was removed by centrifugation at 10000 rpm and supernant was analyzed for the residual concentration of MB, spectrophotometrically at 665 nm wavelength.

1) Effect of initial dye concentration and contact time: 25 mg of adsorbent of ≥ 120 mesh size with 25 ml of dye solution was kept constant for batch experiments. Initial MB concentration of 100, 150, 200, 250, 300, 350 and 400 mg/l were performed at nearly 303K on a oscillator at 230 rpm for 5,10, 15, 20, 30, 40, 50 and 60 minutes at pH = 7. Then optimum agitation time was identified for further batch experimental study.

2) Effect of adsorbent dosage and initial dye concentration: Initial MB concentrations of 400, 500, 600 and 700 mg/l were used in conjunction with adsorbent dose of 1, 2, 3, 4, 5, and 6 g/l. Agitation time, pH, agitation speed, temperature and particle size of 30 minutes, 7, 230 rpm, 303K and ≥ 120 mesh respectively were kept constant.

3) Effect of pH: Initial pHs of MB solutions were adjusted to 3, 4, 5, 6, 7, 8, 9, 10 and 11 for 200 mg/l concentration. Agitation time, adsorbent dose, agitation speed, temperature and particle size of 30 minutes, 1 g/l, 230 rpm, 303K and ≥ 120 mesh respectively were kept constant.

4) Effect of particle size and initial dye concentration: Three different sized particles of ≥ 120, 120 ≤ 85 and 85 ≤ 60 meshes were used in conjunction with 100, 150, 200, 250, 300 and 350 mg/l MB concentration. Agitation time, adsorbent dose, agitation speed, temperature and pH of 30 minutes, 1 g/l, 230 rpm, 303K and 7 respectively were kept constant.

5) Effect of temperature and initial dye concentration: 303K, 313K and 323K temperatures were used in conjunction with 100, 150, 200, 250, 300 and 350 mg/l MB concentration. Agitation time, adsorbent dose, agitation speed, particle size and pH of 30 minutes, 1 g/l, 230 rpm, ≥ 120 mesh and 7 respectively were kept constant.

6) Effect of agitation speed: 100, 170 and 230 rpm agitation speeds were used in conjunction with initial MB concentration of 250 mg/l for 5,10, 15, 20, 30, 40, 50 and 60 minutes. Adsorbent dose, pH, temperature and particle size of 1g/l, 7, 303K and ≥ 120 mesh respectively were kept constant.

III. RESULTS AND DISCUSSION

A. Effect of initial dye concentration and contact time

Effect of initial dye concentration with contact time on adsorption of MB is presented in Fig. 1 and Fig. 2. Uptake of MB was rapid in first 5 minutes and after 30 minutes amount of dye adsorbed was almost constant. Therefore, further batch experiments were carried out at 30 minutes optimum contact time. Percentage of adsorption decreased from 99.1 to 68.5% but amount of MB adsorbed per unit mass of adsorbent increased from 99.4 to 274mg/g with increase in MB concentration from 100 to 400 mg/l.

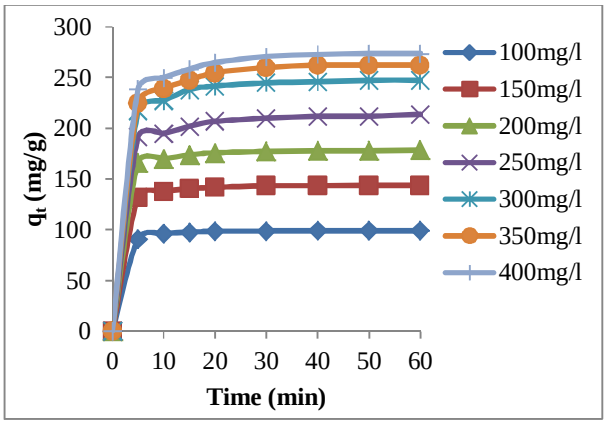

Fig. 1 Effect of initial dye concentration and contact time on adsorption of MB on ATBP.

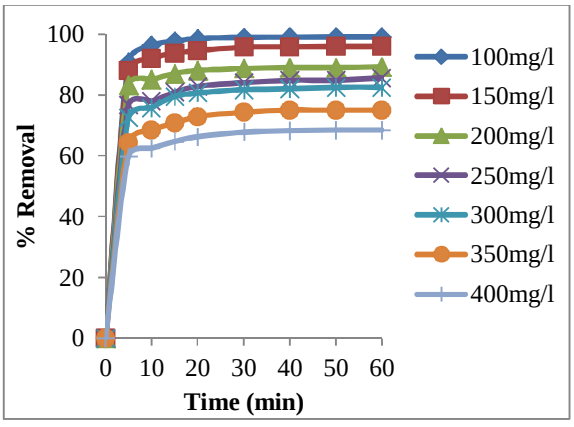

Fig. 2 Effect of initial dye concentration and contact time on % removal of MB on ATBP.

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To investigate the mechanism of adsorption, pseudo - first order, pseudo- second order, Natarajan and Khalaf first order, Bhattacharya and Venkobachar first order models were used.

The Lagergren (Singh, 1998) pseudo- first order rate expression is given as

$$\log (q_e - q_t) = \log q_e - (k_1 / 2.303)\, t \qquad (1)$$

Where q_e and q_t are amounts of dye adsorbed (mg/g) on adsorbent at equilibrium and at time t, respectively and k_1 is rate constant of pseudo first order adsorption (min^{-1}). The slope and intercept values of plots $\log(q_e - q_t)$ against t (Fig. 3) were used to determine pseudo first order rate constant (k_1) and theoretical amount of dye adsorbed per unit mass of adsorbent $q_{e(the)}$, respectively. $q_{e(the)}$ were compared with the $q_{e(exp)}$ values in Table 1. $q_{e(exp)}$ values differ from the corresponding $q_{e(the)}$ values showed that pseudo first order equation of Lagergren does not fit well with whole range of contact time and is generally applicable for initial stage of adsorption (Ho and Mckay, 1999).

The Lagergren pseudo- second order kinetic model (Ho and McKay, 1999) is given as

$$t/q_t = 1/ (k_2 q_e^2) + t/q_e \qquad (2)$$

Where k_2 is rate constant of second order adsorption ($gmg^{-1}\ min^{-1}$). The slopes and intercepts of plot of t/q_t against t (Fig. 4) were used to determine $q_{e(the)}$ and k_2 respectively. From highly linear plots it is cleared that there may be a possibility of chemisorption playing a significant role in the rate determining step. The pseudo second order parameters, $q_{e(the)}$, h and k_2 obtained from the plot are represented in Table 1. Where h is initial adsorption rate (mg/g.min), $h = k_2 q_e^2$.

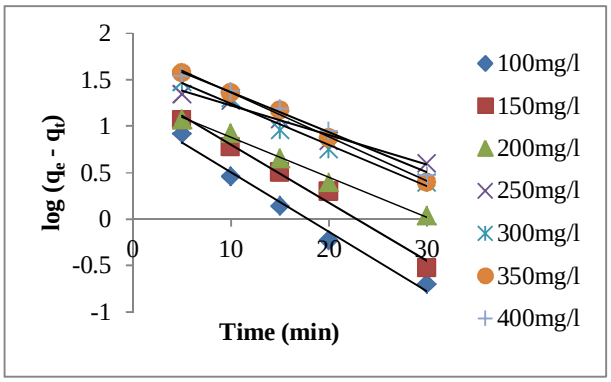

Fig. 3 Pseudo first order plot of effect of initial dye concentration and contact time on adsorption of MB on ATBP.

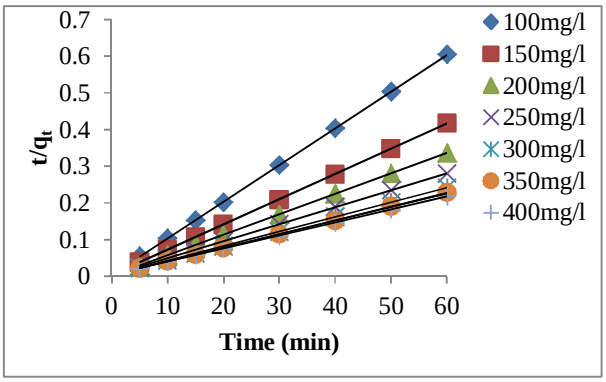

Fig. 4 Pseudo second order plot of effect of initial dye concentration and contact time on adsorption of MB on ATBP.

Table 1 Effect of initial dye concentration and contact time on adsorption of MB on ATBP

Initial MB Conc. (mg/l)	Pseudo -first order model				Pseudo -second order model				
	$q_{e(exp)}$ (mg/g)	K_1 (min^{-1})	$q_{e(the)}$ (mg/g)	R^2	$q_{e(exp)}$ (mg/g)	K_2 (g mg^{-1} min^{-1})	$q_{e(the)}$ (mg/g)	h (mg/g .min)	R^2
100	99.1	0.1474	13.996	0.983	99.1	0.0333	100	333	1
150	143.8	0.1428	26.546	0.983	143.8	0.012	166.667	333.333	1
200	178.5	0.099	20.37	0.991	178.5	0.00833	200	333.2	1
250	214	0.0713	34.514	0.978	214	0.004	250	250	0.999
300	247.5	0.1013	48.753	0.985	247.5	0.00533	250	333.125	1
350	262.5	0.1082	68.865	0.995	262.5	0.003	333.333	333.333	0.999
400	274	0.099	62.951	0.993	274	0.003	333.333	333.333	1

The correlation coefficient R^2 for second order adsorption model has very high values for both the adsorbents ($R^2 \geq 0.999$) and $q_{e(the)}$ values are consistent with $q_{e(exp)}$ showed that pseudo second order adsorption equation of Lagergren fit well with whole range of contact time and dye adsorption process appears to be controlled by chemisorption.

The linearized form of Natarajan and Khalaf first order kinetic equation is presented as

$$\log (C_o/C_t) = (K/2.303)\, t \qquad (3)$$

Where C_o and C_t are concentrations of MB (mg/l) at time zero and time t respectively. K is first order adsorption rate constant (min^{-1}) which was calculated from slope of the plot $\log (C_o/C_t)$ against t (Fig. 5, Table 2).

The linearized form of Bhattacharya and Venkobachar first order kinetic equation is presented as

$$\log [1 - U(T)] = -(k/2.303)\, t \qquad (4)$$

Where $U(T) = [(C_o-C_t) / (C_o-C_e)]$
C_e is equilibrium MB concentration (mg/l)
K is first order adsorption rate constant (min-1) which was calculated from slope of the plot log [1 – U(T)] against t (Fig. 6, Table 2).

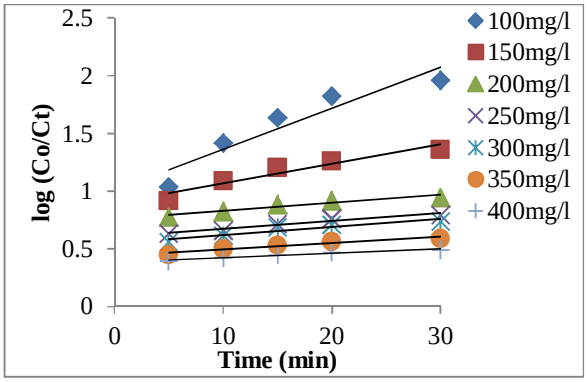

Fig. 5 Natarajan and Khalaf first order plot of effect of initial dye concentration and contact time on adsorption of MB on ATBP.

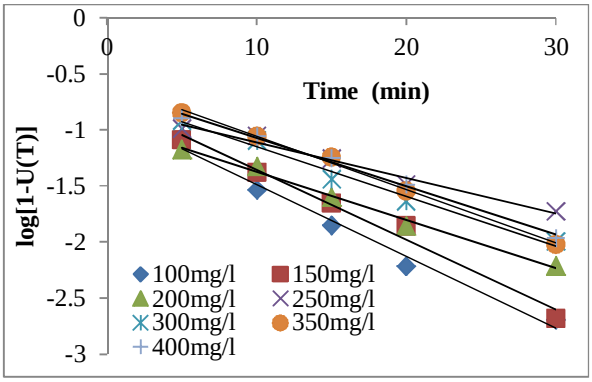

Fig. 6 Bhattacharya and Venkobachar first order plot of effect of initial dye concentration and contact time on adsorption of MB on ATBP.

Correlation coefficient values (R^2) values were not high for all concentrations showed that Natarajan and Khalaf as well as Bhattacharya and Venkobachar first order equations does not fit well with whole range of concentration for adsorption of MB on ATBP. Steps involved in sorption of the dye by adsorbent includes transport of solute from aqueous to surface of solid and diffusion of solute into the interior of pores, which is generally a slow process.

According to Weber and Morris, the intra particle diffusion rate constant (K_i) is given by the following equation

$$q_t = K_i\, t^{1/2} \qquad (5)$$

K_i ($mg/g\ min^{-1/2}$) values can be determined from the slope of the plots q_t against $t^{1/2}$ (Fig. 7) showed a linear relationship after certain time but they do not pass through origin. This is due boundary layer effect. The larger intercept showed the greater the contribution of surface sorption in rate determining step. The intercepts and Ki values of plot q_t against $t^{1/2}$ increased with increase in the initial concentration of dye (Table 2). Initial portion is attributed to the liquid film mass transfer and linear portion to the intra particle diffusion.

The linearized form of Elovich kinetic equation is presented as

$$q_t = 1/\beta\, [\ln (\alpha\beta)] + \ln t/\beta \qquad (6)$$

Where α and β are the constants calculated from the intercepts and slopes of plots q_t against ln t (Fig. 8, Table 2).
This Elovich kinetic model gave quiet satisfactory results for ATBP.

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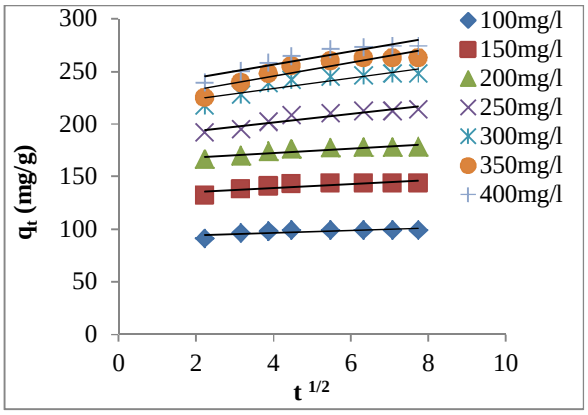

Fig. 7 Intra particle diffusion plot of effect of initial dye concentration and contact time on adsorption of MB on ATBP.

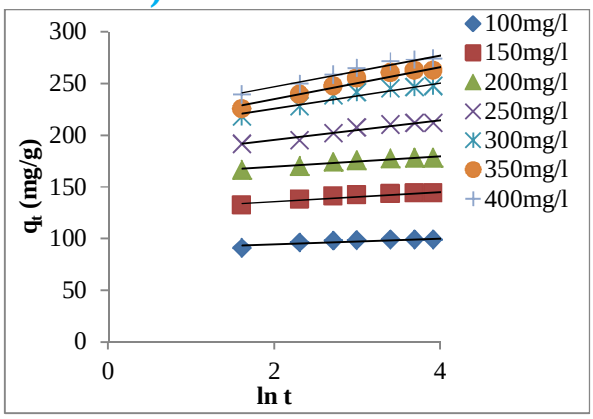

Fig. 8 Elovich plot of effect of initial dye concentration and contact time on adsorption of MB on ATBP.

Table 2 Effect of initial dye concentration and contact time on adsorption of MB on ATBP

Initial MB Conc. (mg/l)	Intra particle diffusion model			Elovich Model			Natarajan and Khalaf model		Bhattacharya and Venkobachar model	
	K_i ($mg/g/min^{1/2}$)	A (mg/g)	R^2	α ($mg/gmin^{-1}$)	β ($g.mg^{-1}$)	R^2	K (min-1)	R^2	K (min^{-1})	R^2
100	1.152	91.63	0.607	3.0417	0.3399	0.777	0.081	0.887	0.147	0.983
150	1.836	131.7	0.713	4.7572	0.218	0.887	0.037	0.918	0.143	0.983
200	2.051	164.5	0.815	5.1168	0.2016	0.931	0.016	0.908	0.099	0.991
250	4.07	185	0.885	10.115	0.1044	0.957	0.016	0.943	0.071	0.978
300	5.04	213.4	0.804	12.986	0.0818	0.917	0.016	0.872	0.101	0.985
350	6.435	219.3	0.832	16.748	0.0644	0.938	0.012	0.916	0.108	0.995
400	6.264	231	0.878	15.902	0.0673	0.959	0.007	0.941	0.099	0.993

B. Effect of adsorbent dosage and initial dye concentration

Adsorption of MB on ATBP was studied by varying the adsorbent dosage. The percentage of adsorption increased with increase in dosage of adsorbent (Fig. 9). For above 95% removal of MB, adsorbent dosage of 3, 4, 5, 5 g/l for ATBP were needed for initial MB concentrations 400, 500, 600 and 700 mg/l respectively.

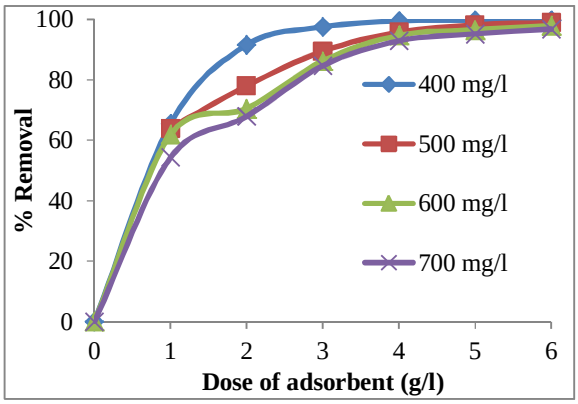

Fig. 9 Effect of adsorbent dosage and initial dye concentration on adsorption of MB on ATBP.

C. Effect of pH

pH is an important factor in controlling the adsorption of dye onto adsorbent. The adsorption of MB from 200mg/l concentration on ATBP was studied by varying the pH from 3 to 11. The amount of dye adsorbed per unit mass of adsorbent at equilibrium (q_e) increased from 77.5 to 197.2mg/g by variation in pH from 3 to 11 (Fig.10).

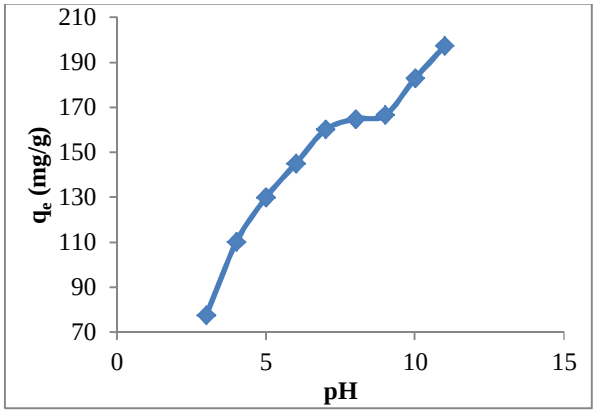

Fig. 10 Effect of pH on adsorption of MB From initial concentration 200 mg/l MB solution on ATBP.

D. Effect of particle size and initial dye concentration

Adsorption of MB on three sized particles ≥ 120, 120 ≤ 85 and 85 ≤ 60 mesh of ATBP was studied for 100 to 350 mg/l concentrations of MB. The results of variation of these particle sizes on dye adsorption are shown in Fig. 11. It was observed that as the particle size increased the adsorption of dye decreased and hence the percentage removal of dye also decreased. This is due to larger surface area that is associated with smaller particles. For larger particles, the diffusion resistance to mass transfer is higher and most of the internal surface of the particle may not be utilized for adsorption and consequently amount of dye adsorbed is small.

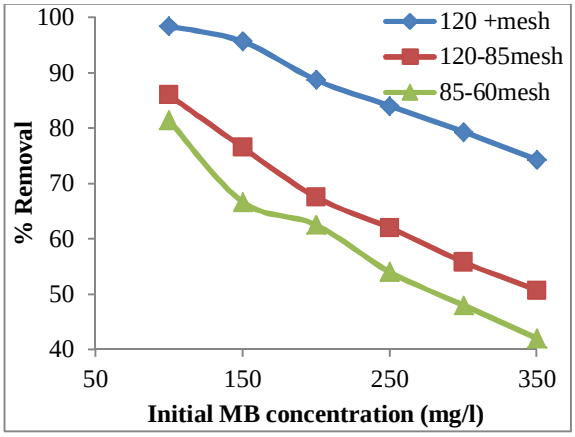

Fig. 11 Effect of particle size and initial dye concentration on % removal of MB on ATBP.

The Freundlich equation was employed for the adsorption of MB onto the adsorbent. The isotherm was represented by

$$\log q_e = \log K_f + 1/n \log C_e \quad (7)$$

Where q_e is amount of MB adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of MB in solution (mg/l), K_f and n are constant incorporating factors affecting the adsorption capacity and intensity of adsorption respectively. The plots of log q_e against log C_e showed good linearity (R^2 = 0.994 to 0.997) indicating the adsorption of MB obeys the Freundlich adsorption isotherm (Fig. 12).

The values of K_f and n are given in the Table 3. Values of n lie in between 1 to 10 indicates an effective adsorption (Potgeiter, 2005) while higher values of K_f represents an easy uptake of adsorbate from the solution (Mahvi, 2004).

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The Langmuir isotherm was represented by the following equation

$$C_e / q_e = 1/ (q_m b) + C_e /q_m \quad (8)$$

Where q_m is monolayer (maximum) adsorption capacity (mg/g) and b is Langmuir constant related to energy of adsorption (1/mg). A linear plot of C_e / q_e against C_e suggest the applicability of the Langmuir isotherm (R^2= 0.987 to 0.994). The values of q_m and b were determined slopes and intercepts of the plot (Fig. 13, Table 3). Monolayer adsorption capacity of ATBP was found to be more as compared to some previous studies (Table 4).

The essential features of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor, R_L, which is defined by the following relation given by Hall [20]

$$R_L = 1/ (1+bC_o) \quad (9)$$

Where C_o is initial MB concentration in mg/l. R_L values lies in between 0.0187 to 0.1988 for ATBP indicates favourable adsorption (Table 6).

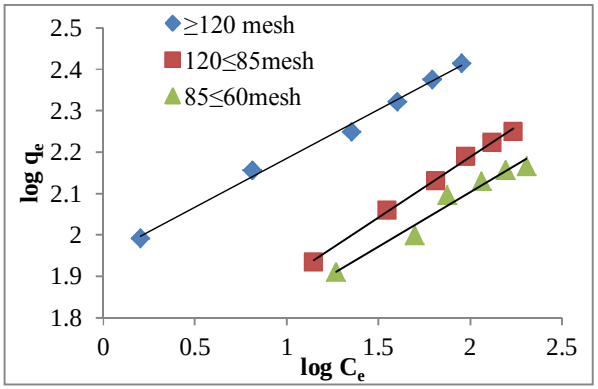

Fig. 12 Freundlich isotherm plots of effect of particle size and initial dye concentration on adsorption of MB on ATBP.

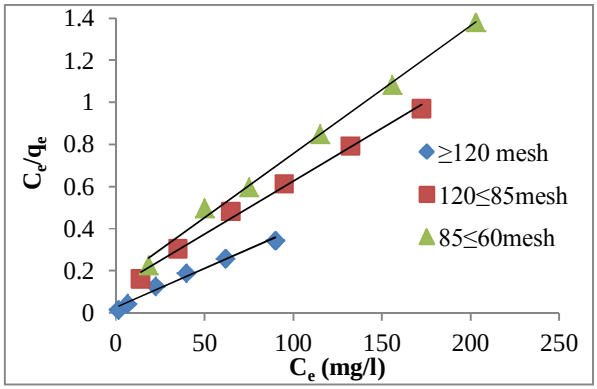

Fig. 13 Langmuir isotherm plot of effect of particle size and initial dye concentration on adsorption of MB on ATBP.

The Temkin isotherm is given as

$$q_e = B \ln A + B \ln C_e \quad (10)$$

Where constant A (1/g) is the equilibrium binding constant, corresponding to the maximum binding energy and constant B is related to heat of adsorption. A linear plots of q_e against ln C_e enables the determination of the constants B and A from the slope and intercept (Fig. 14). The results of the plot are given in Table 3.

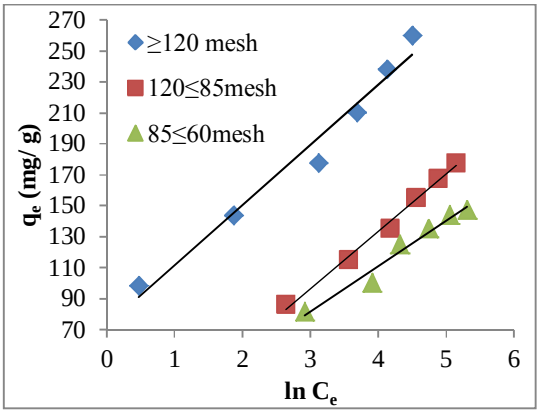

Fig. 14 Temkin isotherm plots of effect of particle size and initial dye concentration on adsorption of MB on ATBP.

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Table 3 Effect of particle size and initial dye concentration on adsorption of MB on ATBP

Mesh	Freundlich isotherm parameters			Langmuir isotherm parameters			Temkin isotherm parameters		
	K_f	n	R^2	q_m	b	R^2	A	B	R^2
≥ 120	88.716	4.255	0.994	333.333	0.1111	0.987	6.404	38.98	0.97
120 ≤ 85	40.179	3.436	0.997	200	0.0403	0.994	0.678	36.92	0.992
85 ≤ 60	37.757	3.802	0.996	166.167	0.0403	0.995	0.799	29.4	0.966

Table 4 Comparison of Langmuir sorption capacity (q_m) in mg/g of different sorbents for MB.

Sorbent	q_m (mg/g)	References
ATBP	333.333	Present study
Banana peel	15.9	*Annadurai et al.*[22]
Orange peel	13.9	*Annadurai et al.*[22]
Sewage sludge	114.94	*Otero et al.*[23]
Rice husk carbon	182 -274	*Singh et al.*[24]
Pearl millet husk carbon	82.37	*Inbaraj et al.*[25]
Sagaun sawdust	2 – 3.3	*Khatri et al.*[26]
Wheat straw	129.87	*Gong et al.*[27]

E. Effect of temperature and initial dye concentration

Temperature has important effects on adsorption process. Adsorption of MB at three different temperatures (303K, 313K and 323K) onto ATBP was studied for 100 to 350 mg/l initial MB concentrations. The results variations in temperatures on dye adsorption are shown in Fig. 15. It is observed that with increased in experimental temperature from 303K to 323K, the dye adsorption also increased. Because with increase in temperature, rate of diffusion of adsorbate molecules across external boundary layer and internal pores of adsorbent particle increases. Changing the temperature will change the equilibrium capacity of the adsorbent for particular adsorbate.

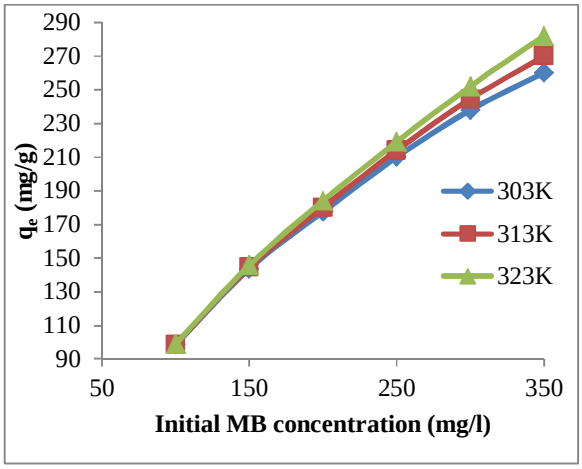

Fig 15 Effect of temperature and initial dye concentration on adsorption of MB on ATBP.

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Freundlich and Langmuir adsorption isotherms were employed for 303K, 313K and 323K temperatures. Plot of log q_e against log C_e (Fig. 16) and plot of C_e / q_e against C_e (Fig. 17) showed good linearity with regression coefficients ($R^2 \approx 0.99$). Freundlich constants K_f and n as well as Langmuir constants q_m and b are given in Table 5. Dimensionless constant separation factor (R_L) values lies in between 0 to 1 for both the adsorbents (Table 6). Monolayer (maximum) adsorption capacity (q_m) obtained from Langmuir plots were 333.333 mg/g remains same for all temperatures. Both Langmuir as well as Freundlich adsorption isotherms fits well for 313 to 323K temperature range.

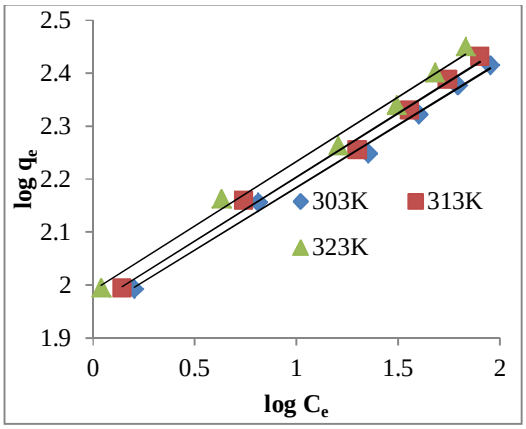

Fig. 16 Freundlich isotherm plot of effect of temperature and initial dye concentration on adsorption of MB on ATBP.

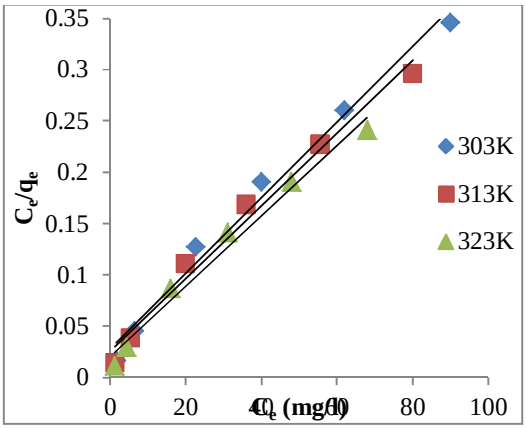

Fig. 17 Langmuir isotherm plot of effect of temperature and initial dye concentration on adsorption of MB on ATBP.

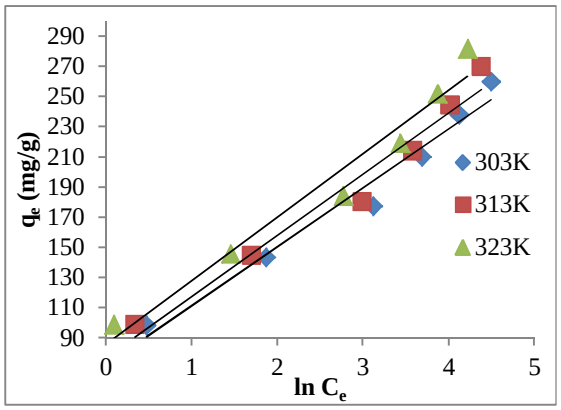

Fig 18 Temkin isotherm plot of effect of temperature and initial dye concentration on adsorption of MB on ATBP.

Temkin plot q_e against ln C_e (Fig. 18) also showed linearity (R^2 = 0.96 to 0.97). Temkin constants A and B are given in Table 5.

Table 5 Effect of temperature and initial dye concentration on adsorption of MB on ATBP

Temp. in Kelvin	Freundlich isotherm parameters			Langmuir isotherm parameters			Temkin isotherm parameters		
	K_f	n	R^2	q_m	b	R^2	A	B	R^2
303	88.716	4.255	0.994	333.333	0.1111	0.987	6.404	38.98	0.97
313	91.622	4.149	0.992	333.333	0.125	0.984	6.54	40.71	0.964
323	97.499	4.115	0.992	333.333	0.15	0.981	7.63	42.13	0.96

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Table 6 Dimensionless separation factor (R_L) calculated from Langmuir constant (b) for ATBP

Initial MB Conc. (mg/l)	Mesh			Temperature		
	≥ 120	120 ≤ 85	85 ≤ 60	303K	313K	323K
100	0.0826	0.1988	0.1988	0.0826	0.0674	0.0625
150	0.0566	0.1419	0.1419	0/0566	0.0506	0.0426
200	0.0431	0.1104	0.1104	0.0431	0.0385	0.0323
250	0.0348	0.0903	0.0903	0.0348	0.031	0.026
300	0.0291	0.0764	0.0764	0.0291	0.026	0.0217
350	0.0251	0.0662	0.0662	0.0251	0.0223	0.0187

F. Thermodynamic analysis

Thermodynamic parameters such as change in free energy (ΔG) (J/mole), enthalpy (ΔH) (J/mole) and entropy (ΔS) (J/K/mole) were determined using following equations

$$K_o = C_{solid} / C_{liquid} \quad (11)$$

$$\Delta G = - RT \ln K_o \quad (12)$$

$$\Delta G = \Delta H - T\Delta S$$

$$\ln K_o = - \Delta G/RT$$

$$\ln K_o = \Delta S/R - \Delta H/RT \quad (13)$$

Where K_o is equilibrium constant, C_{solid} is solid phase concentration at equilibrium (mg/l), C_{liquid} is liquid phase concentration at equilibrium (mg/l), T is absolute temperature in Kelvin and R is gas constant.ΔG values obtained from equation (12), ΔH and ΔS values obtained from the slope and intercept of plot ln K_o against 1/T (Fig. 19, Table 7). The negative value of ΔG indicates the adsorption is favourable and spontaneous. ΔG values increases with increase in temperature and decreases with increase in initial concentration of MB. The low positive values of ΔH indicates endothermic nature of adsorption ΔH values were lie between 12.047 to 17.385 KJ/mole indicates physical adsorption [12-14]. The positive values of ΔS indicate the increased disorder and randomness at the solid solution interface of MB with the adsorbent. The adsorbed water molecules, which were displaced by adsorbate molecules, gain more translational energy than is lost by the adsorbate molecules, thus allowing prevalence of randomness in the system. The increase of adsorption capacity of the adsorbent at higher temperatures was due to enlargement of pore size and activation of adsorbent surface [12-16].

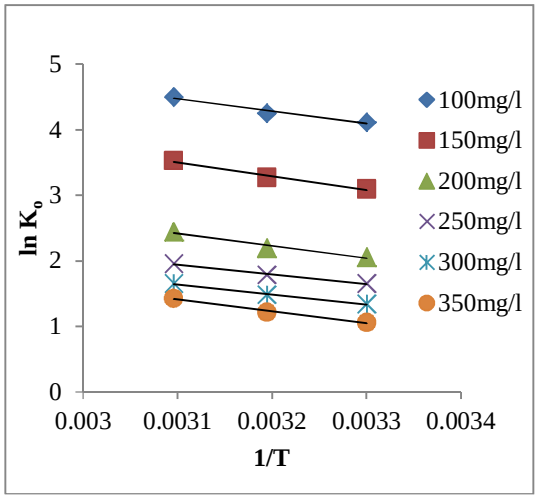

Fig. 19 Von't Hoff plot of effect of temperature and initial dye concentration on adsorption of MB on ATBP.

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Table 7 Equilibrium constants and thermodynamic parameters for the adsorption of MB on ATBP

Initial MB Conc. (mg/l)	Ko			ΔG (J/mole)			ΔH (J/mole)	ΔS (J/K/mole)
	303K	313K	323K	303K	313K	323K		
100	61.5	70.429	89.909	-10376.4	-11071.7	-12081.17	15397.53	84.88594
150	22.077	26.273	33.884	-7795.57	-8505.64	-9460.566	17384.57	82.98203
200	7.85	9	11.5	-5190.58	-5717.8	-6558.732	15480.67	68.06672
250	5.25	5.944	7.065	-4177.31	-4638.46	-5250.227	12046.99	53.48396
300	3.838	4.405	5.25	-3388.59	-3858.75	-4453.042	12712.11	53.08489
350	2.889	3.375	4.147	-2672.49	-3165.4	-3819.743	14674.21	57.18369

G. Effect of agitation speed

Sorption is influenced by mass transfer parameters. Fig. 20 illustrates the sorption kinetics of MB by ATBP for different agitation speeds ranging from 100 to 230 rpm. The amount adsorbed at equilibrium was found to increase from 192, 205 and 214 mg/g of ATBP with increased in agitation speed from 100, 170 and 230 rpm of an oscillator from 250 mg/l initial MB solution. This is because with low agitation speed the greater contact time is required to attend the equilibrium. With increasing the agitation speed , the rate of diffusion of dye molecules from bulk liquid to the liquid boundary layer surrounding the particle become higher because of an enhancement of turbulence and a decrease of thickness of the liquid boundary layer.

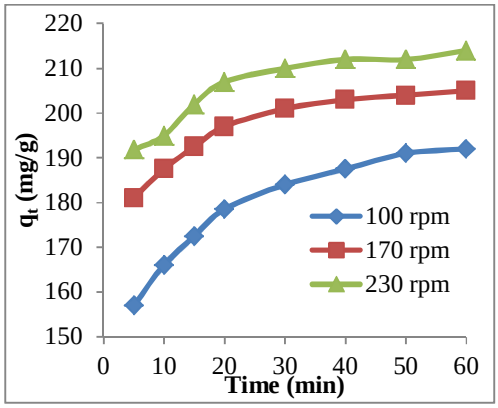

Fig. 20 Effect of agitation speed on adsorption of MB on ATBP.

IV. CONCLUSION

The objective of this paper was utilization of Almond tree bark powder (ATBP) as an adsorbent for the removal of methylene blue. ATBP has excellent adsorption capacity compared to many other conventional and non-conventional adsorbents. The monolayer (maximum) adsorption capacity (q_m) was found to be 333.333 mg/g for ATBP. Langmuir and Freundlich isotherm parameters ($R^2 \approx 0.99$, $n > 3.4$, $R_L = 0.0187$ to 0.1988) confirmed that the adsorption of MB on ATBP was favourable. As the particle size increased from > 120 mesh, 120≤ 85mesh, 85≤ 60 mesh, the monolayer (maximum) adsorption capacity (q_m) was found to decreased from 3333.333, 200, 166.667 mg/g of ATBP respectively. Langmuir and Freundlich isotherm models and Lagergren pseudo -second order model were found to be best fitting isotherm and kinetic models. Thermodynamic analysis showed that adsorption of MB on ATBP was favourable and spontaneous (negative values of ΔG, -2.672 to -12.081 KJ/mole), Endothermic (positive values of ΔH, 12.047 to 15.398 KJ/mole), Physical adsorption (small ΔH < 30 KJ/mole), Increased disorder and randomness at the solid- solution interface (positive values of ΔS, 0.0534 to 0.0848 KJ/mole).

Such non- conventional adsorbents not only the alternative to costly activated carbons but also provides additional employments and income to the marginal farmers.

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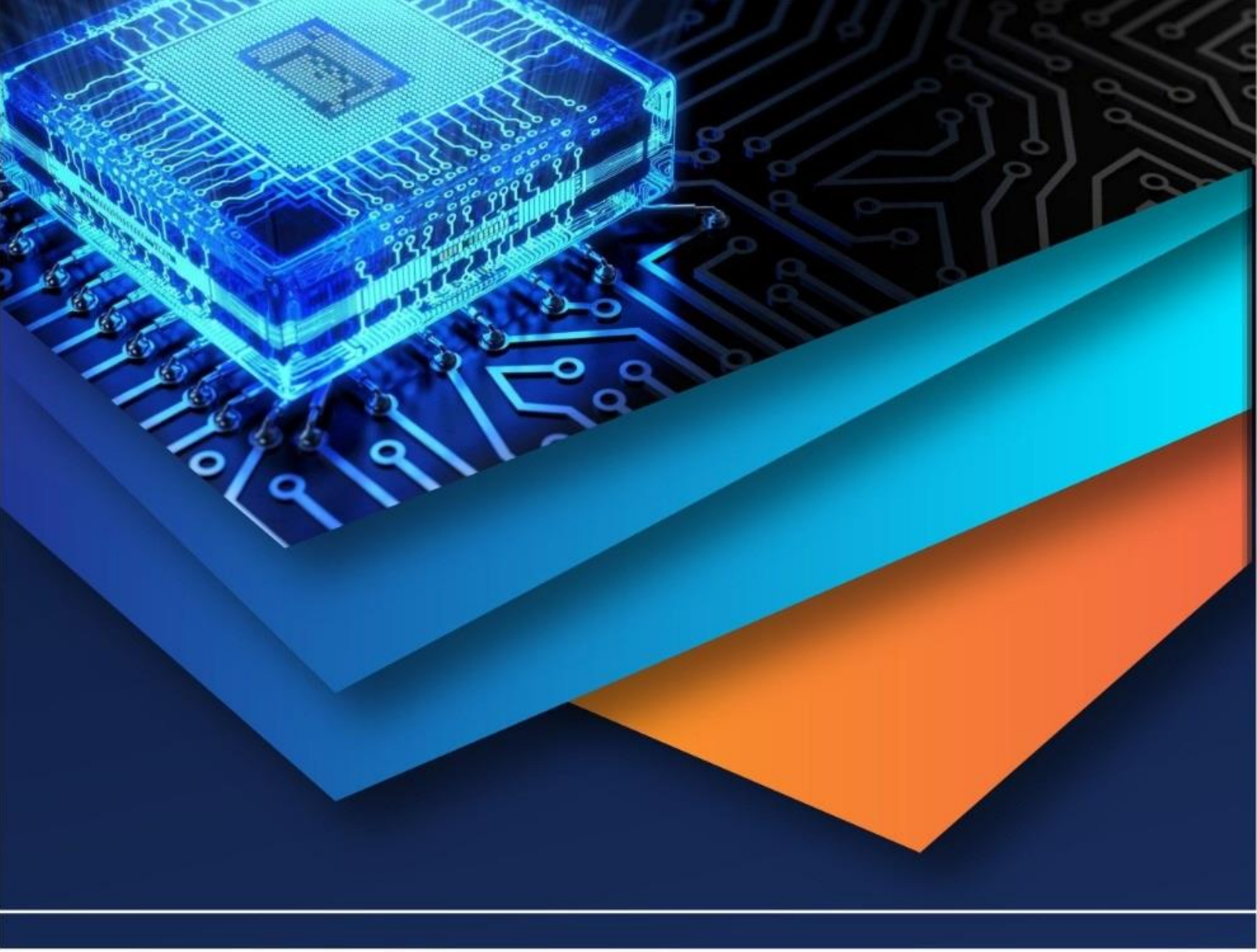

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