

Removal of Methylene Blue by Adsorption onto Activated Biomass of *Prunus cerasus*. Batch Study

A. Kale Anandrao*

PG and Research Centre Department of Chemistry, Annasaheb Awate College, Manchar, Maharashtra, India

ABSTRACT

The present study deals with investigation of methylene blue by adsorption onto activated biomass of *Prunus cerasus* (ACBPC), the experimental work was carried out on methylene blue (MB) removal by ACBPC. The effect of various factors such as contact time, adsorbent dosage, initial dye concentration, temperature, and pH of dye solution was investigated. The maximum MB removal was observed at pH 8. The adsorption equilibrium was represented with Langmuir, Freundlich, and Temkin isotherm models. Langmuir and Tempkin equations were found to have the correlation coefficient value in good agreement. The high value of correlation coefficient 0.998 indicates the applicability of Langmuir isotherm which assumes a monolayer coverage and uniform activity distribution on the sorbent surface. Adsorption of MB onto ACBPC followed pseudo second order kinetics. The calculated values of ΔH° , ΔS° , and ΔG° were found to be 19.30 kJ/mol, 73.35 kJ/mol, and -1.54 kJ/mol, respectively. Adsorption process was spontaneous and endothermic in nature.

Key words: Activated biomass of *Prunus cerasus*, Adsorption isotherm, Methylene blue.

1. INTRODUCTION

Industrial effluents from dyeing and other related industries are containing highly colored species. Over 10,000 dyes with a total yearly production over 8×10^6 MT are commercially available. It is estimated that approximately 20% of the dye stuffs are lost in industrial effluents during manufacturing and processing operations. Adsorption of acid yellow dye on flakes of chitosan prepared from fishery waste [1]. Kumar and Kumaran (2005) showed removal of methylene blue (MB) by mango seed kernel powder [2]. The Langmuir has been worked on constitution and fundamental properties of solids and liquids [3]. Abd *et al.* showed the adsorption, kinetic, and equilibrium studies on removal of basic dye from aqueous solutions using hydrolyzed oak sawdust [4]. Auta and Hameed reported preparation of waste tea activated carbon using potassium acetate as an activating agent for adsorption of acid blue 25 dye [5]. Various physical, chemical, and biological methods, including adsorption, biosorption, coagulation/flocculation, advanced oxidation, ozonation, membrane filtration, and liquid-liquid extraction, have been widely used for the treatment of dye-bearing wastewater. Bhattacharya and Sharma have been reported kinetics and thermodynamics of MB sorption on neem (*Azadiracta indica*) leaf powder [6]. Barka *et al.* have been reported removal of reactive yellow 84 from aqueous solutions by adsorption onto hydroxyapatite [7]. Foo showed preparation, characterization, and evaluation of adsorptive properties of orange peel-based activated carbon through microwave-induced K_2CO_3 activation [8]. Kale has been reported biosorption of Hg^{2+} ions by sulphonated biomass of stalks of *Prunus cerasus* [9], Gilani *et al.* have been reported the ethno pharmacological studies on antispasmodic and anti-platelet activities of *Ficus carica* [10]. Gupta showed application of low-cost adsorbents for dye removal [11].

The advantages and disadvantages of every removal technique have been extensively reviewed [12,13] by Hameed *et al.* Highly colored wastes are not only esthetically unpleasant but also hinder light penetration and may disturb the ecosystem. Moreover, dyes itself

fare toxic to some organism. MB is a cationic dye having various applications in chemistry, biology, medical science, and dyeing industries. Its long-term exposure can cause vomiting, nausea, anemia, and hypertension [8] shown by Foo *et al.* have reported study of the sorption of divalent metal ions on to peat [14].

Gupta *et al.* worked on adsorption photo catalytic degradation of MB onto pectin-Cu Snanocomposite under solar light [15]. Li *et al.* has been reported novel modification pectin for heavy metal adsorption [16]. Liang *et al.* have been reported isotherms, kinetics, and thermodynamic studies of adsorption of Cu^{2+} from aqueous solutions by Mg^{2+}/K^+ type orange peel adsorbent [17]. Sud *et al.* worked on agricultural waste materials potential adsorbent for sequestering heavy metal ions from aqueous solutions [18]. The Tunc *et al.* reported that potential use of cotton plant wastes for the removal of reason black B reactive dye [19] The Wang and Qin showed equilibrium sorption isotherms for of Cu^{2+} on rice bran [20].

Kale worked on biosorption of chromium (VI) using sulfonated biomass of stalks of *P. cerasus* [21]. Malik showed that use of activated carbons prepared from sawdust and rice-husk for sorption of acid dyes: A case study of acid yellow 36 [22,23].

The removal of dyes in an economic way remains an important issue for researchers and environmentalists. Adsorption is a very effective

*Corresponding author:

A. Kale Anandrao

E-mail: anandraoakale@gmail.com

ISSN NO: 2320-0898 (p); 2320-0928 (e)

DOI: 10.22607/IJACS.2022.1002005

Received: 19th October 2021;

Revised: 21th February 2022;

Accepted: 02nd March 2022

separation technique in terms of initial cost, simplicity of design, ease of operation, and insensitive to toxic substances. Activated carbon (Activated or granular) is the most efficient adsorbent used for dye removal. Salleh *et al.* reported cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review [13]. However, it is expensive to produce and regenerate activated biomass of *P. cerasus* fiber is the main objective of this study. Activated biomass of *P. cerasus* to develop a new low cost activated carbon and study its application to remove MB dye [21] from aqueous solution. Kinetics and thermodynamic studies and adsorption isotherm models were investigated to evaluate experimental data.

2. MATERIALS AND METHODS

2.1. Adsorbent

Activated biomass of *P. cerasus* was collected from the locally available planting garden. The stalks of *P. cerasus* were washed several times with distilled water to remove adhered impurities from its surface. The biomass was dried at 100°C for 12 h. The dried biomass was milled and sieved to 100 μm particle size. The dried biomass (1.0 kg) was added in small portion to 800 mL of 98% H₂SO₄ during 6 h and the resulting reaction mixture was kept overnight followed by refluxing for 12 h in fume hood. After cooling to room temperature, the reaction mixture was poured onto cold water (3 L) and filtered. The resulting material was heated in an oven at 150°C for overnight followed by washing with 3 L distilled water and then soaked in 1% NaHCO₃ solution overnight to remove any acid. The obtained carbon was washed with distilled water until pH of activated carbon reached seven and dried in oven at 100°C for 12 h. The resulting activated carbon-activated biomass of *P. cerasus* (ACBPC) was preserved and used as an adsorbent.

2.2. Adsorbate

MB (C₁₆H₁₈N₃SCl₃H₂O) was obtained from Merck, India and was used for sorption study. The solution of required concentration was prepared by dissolving the required amount of MB dye in distilled water.

2.3. Experimental

The batch adsorption experiments were conducted in a set of 250 ml of Erlenmeyer flask containing adsorbent and 100 ml of MB solution with various initial concentrations. The flasks were agitated in an isothermal water-bath shaker at 100 rpm and 27°C until the equilibrium is reached. After decantation and filtration, the equilibrium concentrations of dye in the solution were measured at 665 nm using UV-visible spectrophotometer. The pH of solution was adjusted with 1N HCl and 1N NaOH solutions. The amount of dye adsorbed and percentage removal of MB were calculated using Equations (1) and (2), respectively:

$$q_e = (C_0 - C_e) \frac{V}{M} \quad (1)$$

$$\% \text{ Removal} = \frac{C_i - C_e}{C_i} \quad (2)$$

Where:

q_e amount of dye in mg per gram of adsorbent.

C_i and C_e are, respectively initial concentration and equilibrium time of MB (mg/l).

V volume of solution.

M mass of adsorbent.

2.4. Adsorption Isotherm

2.4.1. Langmuir isotherm

The Langmuir sorption isotherm is applied to equilibrium sorption assuming monolayer sorption onto a surface with a finite number of identical sites The Langmuir equation is written as (Langmuir, 1916):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \quad (3)$$

The shape of this isotherm can also be expressed in terms of separation factor (RL), which is given as follows [8]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

Where K_L is Langmuir constant (L/mg) related to the affinity of binding sites and the free energy of sorption. q_e is dye concentration at equilibrium onto biosorbent (mg/g). C_e is dye concentration at equilibrium in solution (mg/l). q_m is dye concentration when monolayer forms on biosorbent (mg/g).

2.4.2. Freundlich isotherm

The Freundlich equation for heterogeneous surface energy systems is given by Equation (5), [8]

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (5)$$

In $q_e = K F C_e^{1/n}$ where KF and n are Freundlich constants, determined from the plot of $\ln q_e$ versus $\ln C_e$. The parameters KF and $1/n$ are related to sorption capacity and the sorption intensity of the system. The magnitude of the term $(1/n)$ gives an indication of the favorability of the sorbent/adsorbate systems [22].

2.4.3. Tempkin isotherm

The linearized Tempkin equation is given by the following equation [8].

$$q_e = \beta \ln \alpha + \beta \ln C_e \quad (6)$$

$$\text{Where } \beta = \frac{RT}{b}$$

T is the absolute temperature in Kelvin, R is the universal gas constant (8.314 J/mol K), and b is the Tempkin constant related to heat of sorption (J/mg). The Tempkin constants a and b are calculated from the slope and intercept of q_e versus $\ln C_e$.

3. RESULTS AND DISCUSSION

3.1. Removal of MB

3.1.1. Effect of adsorbent dose and initial dye concentration

The adsorbent doses varied from 0.1 to 0.9 g/50 ml. It is evident from Figure 1 that the MB removal increased sharply with an increase in the adsorbent concentration from 0.1/100 to 0.5 g/100 ml. This may be due to the availability of more adsorbent sites as well as greater availability of specific surfaces of the adsorbents [Figure 2].

Further increase in dye concentration showed no significant changes in removal efficiency [Figure 3]. This is due to the fact that with increased dye concentration, the driving force for mass transfer also increases. At low concentrations, there will be unoccupied active sites on the adsorbent surface. Above optimal MB concentration, the active sites required for the adsorption of dye will lack [7]. This retards the overall MB adsorption by activated carbon.

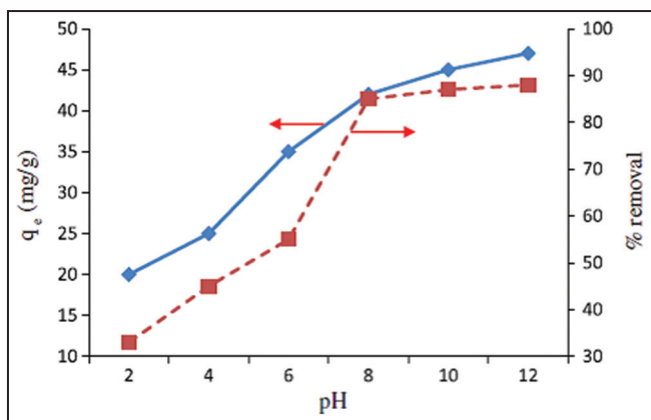


Figure 1: Effect of pH.

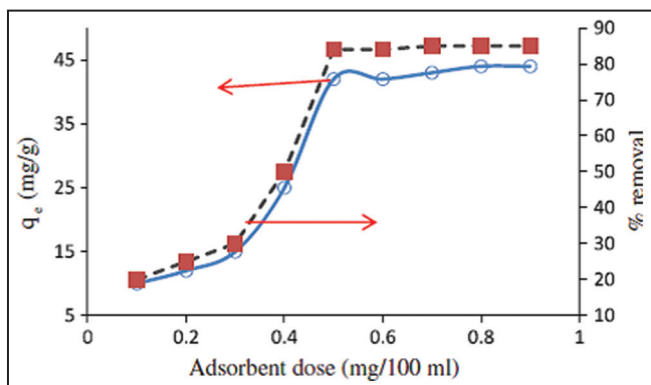


Figure 2: Effect of adsorbent dose and initial dye concentration.

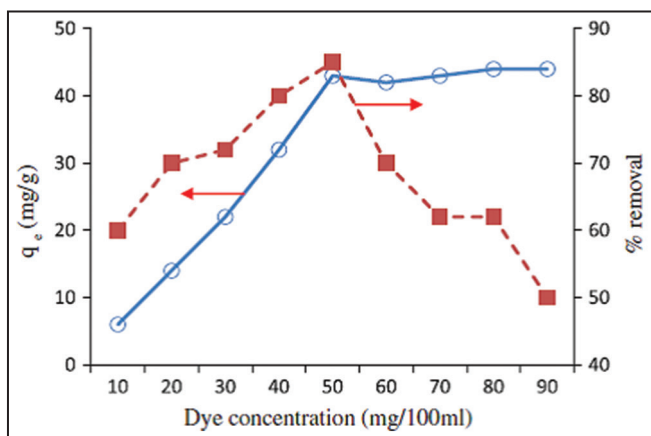


Figure 3: Effect of dye concentration.

3.1.2. Effect of contact time

The effect of contact time on the removal of MB is shown in Figure 4. About 85% dye removal takes place in 60 min for ACBPC, the equilibrium was reached after 90 min [Figure 5]. The changes in the rate of adsorption might be due to fact that initially, all the adsorbent sites are vacant and solute concentration gradient is very high. Later, the lower adsorption rate is due to a decrease in number of vacant sites of adsorbent and dye concentrations. The decreased adsorption rate, particularly, toward the end of experiments, indicates the possible monolayer formation of MB on the adsorbent surface (Abd *et al.*, 2009 and Nemer *et al.*, 2010). This may be attributed to the lack of available active sites required for further uptake after attaining the equilibrium (Liang *et al.*, 2010).

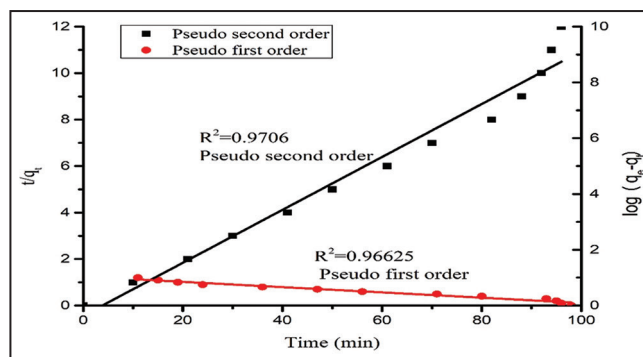


Figure 4: Kinetic modeling.

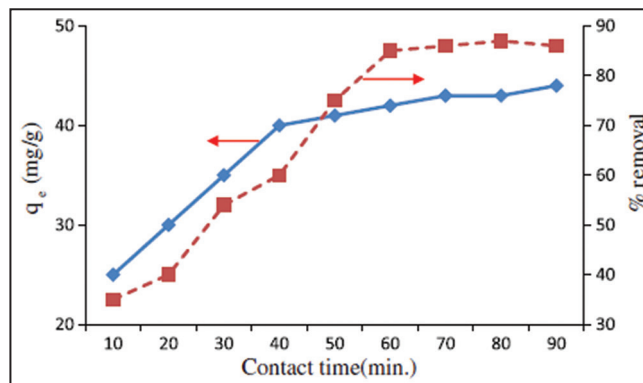


Figure 5: Effect of contact time.

3.1.3. Effect of pH

The pH of a dye solution is an important influencing factor for the adsorption of MB onto ACBPC. Figure 1 shows the effect of pH on adsorption onto ACBPC. The maximum MB removal was observed at pH 8. The ions when dissolved in water. Thus, in acidic medium, the positively charged surface of sorbent tends to oppose the adsorption of the cationic adsorb ate. When pH of dye solution is increased, the surface acquires a negative charge, there by resulting in an increased adsorption of MB due to an increase in the electrostatic attraction between positively charged dye and negatively charged adsorbent (Abd *et al.*, 2009 and Malik, 2003).

3.1.4. Effect of dye concentration

The effect of dye concentration on the sorption of MB onto ACBPC was carried out in the concentration range of 10–70 mg/100 ml. Equilibrium adsorption capacity increased with an increase in MB concentration from 50 mg to 50 ml. Further increase in dye concentration showed no significant changes in removal efficiency [Figure 3]. This is due to the fact that with increased dye concentration, the driving force for mass transfer also increases. At low concentrations, there will be unoccupied active sites on the adsorbent surface. Above optimal MB concentration, the active sites required for the adsorption of dye will lack this retards the overall MB adsorption by activated carbon.

3.1.5. Effect of temperature

The effect of temperature is an important influencing factor for the adsorption of MB onto ACBPC. Figure 6 shows that the effect of temperature on adsorption onto ACBPC the maximum MB removal was observed at about 45°C.

3.2. Adsorption Kinetics

The pseudo first order rate expression is given as:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{7}$$

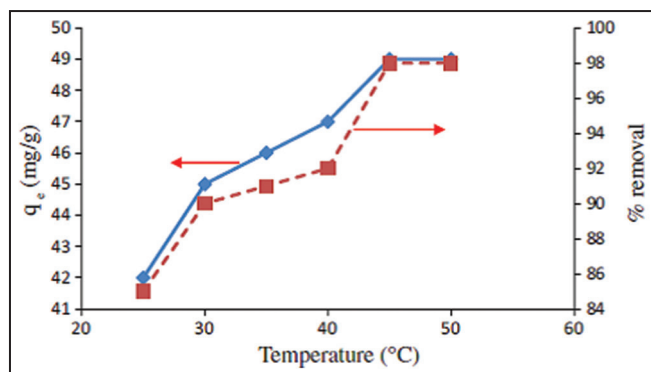


Figure 6: Effect of temperature.

Where, q_e and q_t are the amount of dye adsorbed on sorbent at equilibrium and time t (mg/g) and k_1 is the first order rate constant (min^{-1}). A plot of $\log(q_e - q_t)$ versus t gives a linear relationship, from which the value of k_1 and q_e can be determined from the slope and intercept. The linearized form of pseudo second order rate expression is given as [20]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (8)$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where q_e is the amount of adsorbate adsorbed per unit mass of sorbent at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed at contact time t (mg/g), and k_2 is the pseudo second order rate constant (g/mg min). A plot of t/q_t versus t gives a linear relationship, from which q_e and k_2 can be determined from the slope and intercept [6]. The data for the adsorption of MB on ACBPC were applied to pseudo first and pseudo second order kinetic models and the results are presented in Table 1. The correlation coefficient of second order kinetic model (0.9706) is greater than for first order kinetic model (0.9662) [Table 1 and Figure 4]. This confirmed that the rate limiting step is chemisorptions, involving valence forces through sharing or exchange of electrons [6]. The intraparticle diffusion equation is expressed as follows:

$$q_t = K_d t^{1/2} + C \quad (10)$$

Where, k_d is the intraparticle diffusion rate constant (mg/g min^{1/2}). The data for intraparticle diffusion are given in Table 1. The linear portion of the plot does not pass through origin. This deviation from the origin may be due to the variation of mass transfer in the initial and final stages of the adsorption process. This confirms that the adsorption of MB on ACBPC was a multi-step process involving adsorption on the external surface and diffusion into the interior [2].

3.3. Adsorption isotherm

The adsorption capacity and other parameters were evaluated using Langmuir, Freundlich, and Tempkin isotherm models. It has been observed that the sorption capacity (q_m) was found to be 47.20 mg/g [Table 2].

The high value of correlation coefficient (0.998) indicates the applicability of Langmuir isotherm which assumes a monolayer coverage and uniform activity distribution on the sorbent surface. In the present study, RL values ($0 < RL < 1$) favor the adsorption of MB onto ACBPC [Table 2]. Equation (5) was used to evaluate Tempkin isotherm. The value of correlation coefficient R^2 obtained from Temkin

Table 1: Kinetic and thermodynamic parameters for the sorption of MB onto ACBPC Pseudo first order model.

Pseudo first order model k_1 (min^{-1})	q_e (mg/g)	R^2
0.0195	64.76	0.9662
Pseudo second order model k_2 (g/(mg min))		
0.000189	54.55	0.9706
Intraparticle diffusion model k_d (mg/g min)	C (mg/g)	
2.98	3.32	0.998
Thermodynamic parameters ΔH° (kJ/mol)	ΔS° (J/mol K)	DG° (kJ/mol)
19.30	73.35	-1.54

Table 2: Results of various isotherm plots for the adsorption of MB onto ACBPC.

Models	Isotherm constants			
Langmuir	q_m (mg/g)	KL (L/mg)	RL	R^2
	47.20	0.039	0.06-0.34	0.998
Freundlich	N	(mg/g)	---	R^2
	45	5.50		0.946
Tempkin	(L/g)	(mg/L)	(J/mg)	R^2
	0.528	9.05	272.50	0.978

isotherm was found to be 0.978, constant b (272.50 J/mg) is related to heat of sorption indicating physiochemical nature of the sorption process. The equilibrium data were also fitted to the Freundlich equation. The parameters KF and n indicated the sorption capacity and the sorption intensity of the system. The magnitude of the term $(1/n)$ gives an indication of the favorability of the sorbent/adsorbate systems [22]. The correlation coefficient value (0.946) is lower than Langmuir and Tempkin values. Therefore, adsorption onto ACBPC does not follow Freundlich isotherm closely.

3.4. Adsorption Thermodynamics

Thermodynamic parameters evaluated for MB adsorption onto ACBPC are the free energy change (DG°), enthalpy change (ΔH°), and entropy change (ΔS°). These parameters were calculated using the following equation.

$$\Delta G^\circ = -2.303RT \log K_D \quad (11)$$

$$K_D = \frac{q_e}{C_e}$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

Where q_e is MB concentration at equilibrium onto ACBPC (mg/L), R is universal gas constant (8.314 J/mol K), and C_e is MB concentration at equilibrium in solution (mg/L). The values of ΔH° and ΔS° were determined from the slope and intercept of the plot of $\ln K_D$ versus $1/T$. Gibbs free energy change of sorption (DG°) was calculated using Equation (11). The adsorption of dye increases rapidly with an increase in temperature from 303 to 343 K [Figure 7]. The increase in adsorption capacity of ACBPC was attributed to the enlargement of pore size and activation of the sorbent surface with temperature. Further rise in temperature increases the mobility of the large dye ions and reduces the swelling effect thus enabling the large dye molecule

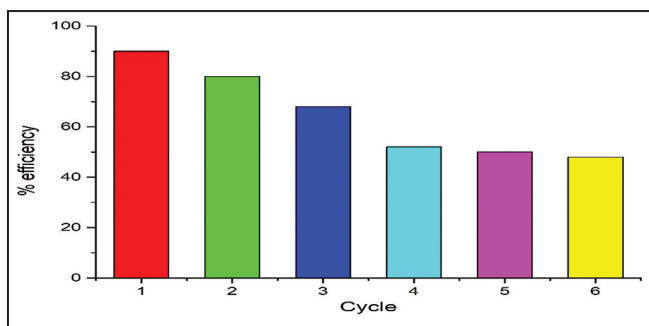


Figure 7: Recycling efficiency of ACBPC for MB removal.

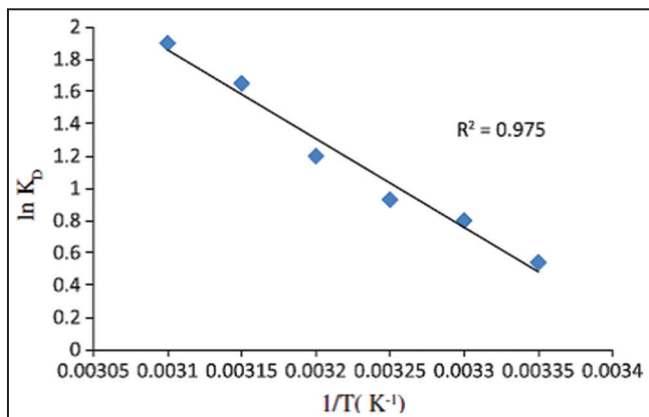


Figure 8: Plot of $\ln K_D$ Vs $1/T$.

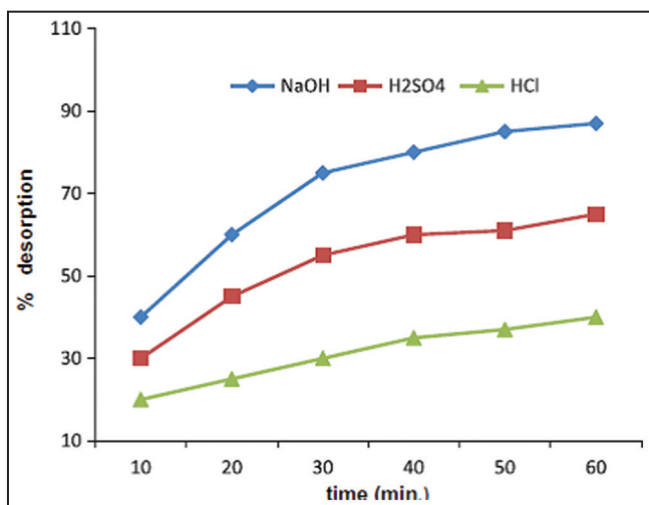


Figure 9: Desorption and recycling efficiency.

to penetrate further [16] The results also indicated that the adsorption of MB is an endothermic process. Thermodynamic parameters (ΔH° , ΔS° , and ΔG°) for MB adsorption were evaluated using Equations (10–12). The values of ΔH° and ΔS° were determined from the slope and intercept of the plot of $\ln K_D$ versus $1/T$ [Figure 8]. Table 2 shows the thermodynamic parameters for MB adsorption onto ACBPC. The positive value of ΔH° (21.55 kJ/mol) indicates that the adsorption of MB onto ACBPC is an endothermic reaction. Adsorption of MB onto ACBPC followed pseudo second order kinetics. The calculated values of DH° , DS° , and DG° were found to be 19.30 kJ/mol, 73.35 J/mol K, and -1.54 kJ/mol, respectively reflect the affinity of ACBPC for MB dye. Adsorption process was spontaneous and endothermic in nature.

3.5. Desorption and Recycling Efficiency

Desorption studies were performed with 1% HCl, H₂SO₄, and NaOH. ACBPC (100 mg/50 mL) saturated with 5 mg/L of MB was placed in different desorption media and was constantly stirred on a rotator shaker at 100 rpm for 1 h. The adsorbent was separated and washed with distilled water. NaOH was found to be an efficient desorption medium with the efficiency for the removal of chromium ion [Figure 9]. About 84% of MB was desorbed in 60 min using HCl as a desorption medium. Recycling efficiency of ACBPC was investigated for the removal of MB. After six cycles, the adsorption efficiency of ACBPC was reduced to 45% from 90% [Figure 7]. After every cycle, NaOH was used as a desorption medium to remove adsorbed MB ions from the ACBPC surface.

4. CONCLUSION

In this study, ACBPC shows promising adsorption capacity for MB removal. The operating parameters for the maximum sorption were dye solution concentration (0.05 g/100 ml), sorbent dosage (0.5 g/100 ml), contact time (80 min), and temperature (303 K). Removal of MB dye is pH dependent and the maximum removal was attained at pH 7.8. Equilibrium data were fitted well in the Langmuir, Freundlich, and Tempkin isotherm models which confirmed that the sorption is heterogeneous and occurred through physicochemical interactions. The rate of sorption was found to obey pseudo-second order kinetics and intraparticle diffusion model with correlation coefficient value 0.998 which is good. The negative DG° values indicated that the sorption of dye onto biosorbent was feasible and spontaneous. The positive ΔH° value depicted endothermic nature of the sorption.

5. ACKNOWLEDGMENTS

Kale, Head, PG, and Research Centre Department of Chemistry, Annasaheb Awate College, Manchar, thankful to Principal Dr.K.G.Kanade for providing financial help in the form of seed money for to complete research work.

6. REFERENCES

- J. Iqbal, F. H. Watto, R. Malik, S. A. Tirmizi, M. Imran, A. B. Ghangro, (2011) Adsorption of acid yellow dye on flakes of chitosan prepared from fishery waste, *Arabian Journal of Chemistry*, **4**: 389-395.
- K. V. Kumar, A. Kumaran, (2005) Removal of Methylene blue by mango seed kernel powder, *Biochemical Engineering Journal*, **27**: 83-93.
- I. Langmuir, (1916) The constitution and fundamental properties of solids and liquids, *Journal of the American Chemical Society*, **38**: 2221-2295.
- E. L. Abd, M. M. Latif, A. M. Ibrahim, (2009) Adsorption, kinetic and equilibrium studies on removal of basic dye from aqueous solutions using hydrolyzed oak sawdust, *Desalination and Water Treatment*, **6**: 252-268.
- M. Auta, B. H. Hameed, (2011) Preparation of waste tea activated carbon using potassium acetate as an activating agent for adsorption of Acid Blue 25 dye, *The Chemical Engineering Journal*, **171**: 502-509.
- K. G. Bhattacharya, A. Sharma, (2005) Kinetics and thermodynamics of methylene blue sorption on neem (*Azadirachta indica*) leaf powder, *Dyes and Pigments*, **65**: 51-59.
- N. Barka, S. Qouzal, A. Assabbane, A. Nounhan, Y. A. Icho, (2011) Removal of reactive yellow 84 from aqueous solutions by adsorption onto hydroxyapatite, *Journal of Saudi Chemical Society*, **15**: 263-267.

8. K. Y. Foo, (2012) Preparation, characterization and evaluation of adsorptive properties of orange peel based activated carbon via microwave induced K_2CO_3 activation, *Bioresource Technology*, **104**: 679-686.
9. A. A. Kale, (2020) Biosorption of Hg^{2+} ions by sulphonated biomass of stalks of *Prunus cerasus*, *International Journal of Scientific and Engineering Research*, **11**: 1319-1331.
10. A. H. Gilani, M. H. Mehmood, K. H. Janbaz, A. U. Khan, S. A. Saeed, (2008) Ethnopharmacological studies on antispasmodic and antiplatelet activities of *Ficus carica*, *Journal of Ethnopharmacology*, **119**: 1-5.
11. V. K. Gupta, (2009) Application of low-cost adsorbents for dyes removal a review, *The Journal of Environmental Management*, **90**: 2313-2342.
12. B. H. Hameed, (2009) Spent tea leaves: A new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions, *The Journal of Hazardous Materials*, **161**: 753-759.
13. S. Liang, X. Guo, N. Feng, Q. Tian, (2010) Isotherms, kinetics and thermodynamic studies of adsorption of Cu^{2+} from aqueous solutions by Mg^{2+}/K^+ type orange peel adsorbent, *The Journal of Hazardous Materials*, **174**: 756-762.
14. Y. S. Ho, G. McKay, D. A. J. Wase, C. F. Foster, (2000) Study of the sorption of divalent metal ions on to peat, *Adsorption Science and Technology*, **18**: 639-650.
15. V. K. Gupta, D. Pathania, S. Agarwal, P. Singh, (2012) Adsorption and photocatalytic degradation of methylene blue onto pectin-CuSnanocomposite under solar light, *The Journal of Hazardous Materials*, **243**: 179-186.
16. F. T. Li, H. Yang, Y. Zhao, R. Xu, (2007) Novel modification pectin for heavy metal adsorption, *Chinese Chemical Letters*, **18**: 325-328.
17. Y. Liu, Y. J. Liu, (2008) Biosorption isotherms, kinetics and the thermodynamics, *Separation and Purification Technology*, **61**: 229-242.
18. M. A. M. Salleh, D. K. Mahmoud, W. A. W. Karim, A. Idris, (2011) Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review, *Desalination*, **280**: 1-13.
19. D. Sud, G. Mahajan, M. P. Kaur, (2008) Agricultural waste materials potential adsorbent for sequestering heavy metal ions from aqueous solutions a review, *Bioresource Technology*, **99**: 6017-6027.
20. O. Tunc, H. Tanaci, Z. Aksu, (2009) Potential use of cotton plant wastes for the removal of remazol black B reactive dye, *The Journal of Hazardous Materials*, **163**: 187-198.
21. X. S. Wang, Y. Qin, (2005) Equilibrium sorption isotherms for Cu^{2+} on rice bran, *Process Biochemistry*, **40**: 677-680.
22. A. A. Kale, (2020) Biosorption of chromium (VI) by using sulphonated biomass of stalks of *Prunus cerasus*. *International Journal Of Modern Pharmaceutical Research*, **4(3)**: 90-96.
23. P. K. Malik, (2003) Use of activated carbons prepared from sawdust and rice-husk for sorption of acid dyes: A case study of acid yellow 36, *Dyes and Pigments*, **56**: 239-249.