Chem. Chem. Technol., 2022,
Vol. 16, No. 2, pp. 274–283

Chemical Technology

BIO-SORBENT DERIVED FROM *ANNONA SQUAMOSA* FOR THE REMOVAL OF METHYL RED DYE IN POLLUTED WATERS: A STUDY ON ADSORPTION POTENTIAL

Kokkiligadda Venkata Ramana[1], Kurmarayuni Chandra Mohan[1], Kunta Ravindhranath[2], Bollikolla Hari Babu[1,*]

https://doi.org/10.23939/chcht16.02.274

Abstract. Sorbent got from leaves and barks of *Annona squamosa* has been investigated for its sorption capacity towards Methyl Red (MR) utilizing artificially arranged recreated squander waters. Different components influencing adsorption, *viz.*, initial color concentration, contact time, adsorbent dosage, along with the impact of temperature were assessed. The equilibrium of adsorption was demonstrated by Freundlich; Langmuir, Temkin, and Dubinin-Radushkevich isotherms. Pseudo-first order, pseudo-second order, Weber and Morrish intraparticle diffusion, Bangham's pore dispersion and Elovich equations were applied in order to distinguish the rate and kinetics of adsorption progression. Interference of a five-fold abundance of regular anions and cations present in common waters, have been examined. Cation like Ca^{2+}, Mg^{2+} and Cu^{2+} have showed some impedance, however, Fe^{2+} and Zn^{2+} have synergistically maintained the greatest extraction of the MR. The methods developed were effectively applied to some effluent. The results of experimental data were found appropriate to the pseudo-first order kinetic model. Correlation coefficient (R^2) and dimensionless division or separation factor (R_L) values have affirmed that adsorption obeys Langmuir adsorption showing monolayer development.

Keywords: Methyl Red (MR), pollution control, bio-adsorbent, adsorption isotherm, kinetics, equilibrium models.

1. Introduction

Water contamination is the pollution of water by outside matter that disintegrates the nature of water. It includes arrival of harmful substances, overwhelming metals, colors, pathogenic germs, substances that require much oxygen to decay, simple dissolvable substances, radioactivity, and so on. The effluents from textile material industry, cowhide/leather processing, nourishment handling, beauty care products, coloring, paper, and color assembling enterprises are critical wellsprings of color contamination.[1] Synthetic dyes are not uniformly susceptible to biodegradation. In conventional biological waste water treatment, microbial azo dyes, which are used extensively in many industries, are the largest class with a wide variety of colors and structures.[2]

The regular wastewater treatment is along these lines normally not compelling and diverse physical, compound and natural medications or their mixes are right now being considered.[3,4] The most well-known adsorbents for wastewater treatment are alumina, silica[5], and activated carbon[6] as demonstrated by numerous scientists.[7,8]

Annona Squamosa is a commonly available plant, which is used in fencing property perimeter in Kerala state of India. Different strategies have been developed to remove dyes from wastewater. The widely used techniques include ion-exchange, electro-kinetic coagulation, electrochemical oxidation, membrane filtration, and photo-catalytic degradation process[9-15] but these methods are expensive and are not useful for application in inexpensive scale treatments.

In the present work, the authors made an attempt to optimize the extraction conditions, like sorption potential of the active biosorbent for MR by fluctuating pH, contact

[1] Department of Chemistry, Acharya Nagarjuna University, Guntur-522510, AP-India
[2] Department of Chemistry, KL University, Vaddeswaram, Guntur Dist., AP-India
[*] *dr.b.haribabu@gmail.com*

period, adsorbent dosage, initial concentration of the dye, temperature, and co-particles or ions. The adsorption forms were examined using Freundlich, Langmuir, Temkin, and Dubinin-Radushkevich (D-R) isotherms and kinetics of adsorption was contemplated utilizing pseudo-first order, pseudo-second order Weber and Morrish intraparticle diffusion, Bangham's pore diffusion and Elovich equation. The role of temperature on the adsorption is additionally examined. The strategies created were connected to the extraction of MR from dirtied squander water samples utilizing biomaterials derived from the leaves and barks of *Annona squamosa*.

2. Experimental

2.1. Materials and Methods

Chemicals: The chemicals utilized were of Analytical Reagent grade.

Methods of evaluation: All the experiments were repeated 6 times and the average values are shown in the respective Graphs.

2.2. Stock Arrangement of Methyl Red

Hundred ppm concentration of MR arrangement was set up by dissolving an essential measure of A.R. grade MR color in double distilled water. It was appropriately diluted according to the need.

2.3. Preparation of Adsorbent

The leaves and barks of *Annona squamosa* plant were gathered, sliced into little pieces, washed well with double distilled water and dried under daylight for 48 h. The authors used this for investigating the plant materials for their sorption abilities towards the MR, to acquire positive outcomes.

a) b)

Fig. 1. Leaves (a) and bark (b) of *Annona squamosa*

2.4. Adsorption Experiment

A batch arrangement of extraction methodology was made as per literature models.[16-18] Deliberately weighted amounts of adsorbent materials were taken in already washed 1 L or 500 mL plug bottles containing 500 or 250 mL of MR dye arrangement of predetermined concentrations. Using pH meter different starting pH estimations of the suspensions were balanced with dil. HCl or dil. NaOH arrangements. The samples were thoroughly shaken enthusiastically in perfunctory shakers and were allowed for equilibrium to attain for the desired time period. After the attainment of equilibration time frame, an aliquot of the specimen was taken for the assurance of MR dye utilizing Spectrophotometric strategy.[19] The taken dye for this study has λ_{max} at 464.9 nm and obeys Beer-Lambert law at low concentrations. The optical density (OD) estimations were made at the said λ_{max} utilizing UV-Visible instrument (Systronics). The acquired OD value for unknown solution was referred to standard diagrams drawn between OD *vs.* concentration prepared with known concentrations of selected dye by adopting method of least squares.

The sorption attributes of the adsorbents were examined on the subject of different physic-chemical parameters. At constant sorbent concentration, the rate extraction of MR dye from reproduced water samples was studied concerning the time of equilibration, at different pH points. The outcomes acquired were displayed in Figs. 1–5. To settle the minimum dosage required for the most extreme evacuation of the MR, for a specific sorbent at ideal pH value and equilibration times, extraction studies were made by studying the percentage of extraction with concern to the sorbent dosage. The results were exhibited in the Fig. 6.

2.5. Methyl Red Dye Investigation

The rate of evacuation of MR dye and quantity adsorbed (in mg/g) were computed utilizing the equations reported for sorbents derived from *Hyacinth* and *Tinospora Cordifolia*[20], and *Tephrosia purpurea*, *Terminalia Arjuna* bivalves snail shell.[21] The same method was employed for the samples completed by various physical and chemical attributes, for example, adsorbent dose, pH of the MR solution, agitation time, starting centralization of MR solution, particle size, temperature, and presence of foreign ions.

2.6. Impact of other Interfering Ions (Co-Ions)

The interfering ions selected in this study are the basic particles exhibit in normal water [anions – sulfate, chloride, carbonate, nitrate, phosphate; cations – Ferrous(II), Calcium(II), Magnesium(II), Copper(II), and Zinc(II)]. The synthetic mixtures of MR dye and the co-particles mixtures were made by keeping the foreign ions concentration at five-fold abundant *versus* the dye concentrations. 500 mL of these arranged solutions were taken in plug bottles and after that the accurately weighted ideal amounts of the promising adsorbents were added according to Figs. 1–5. Optimum pH was balanced with dil. HCl or dil. NaOH utilizing pH meter. The specimen samples were shaken in shaking machines for ideal periods and then little portions of the samples were taken out, filtered, and examined for MR dye. The % of extraction was ascertained from the data obtained.

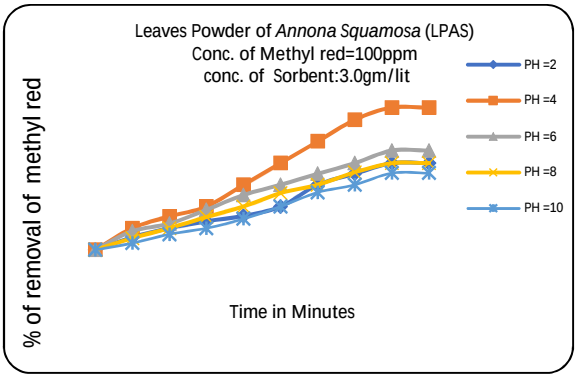

Fig. 1. Equalibration Time vs % of removal of methyl red

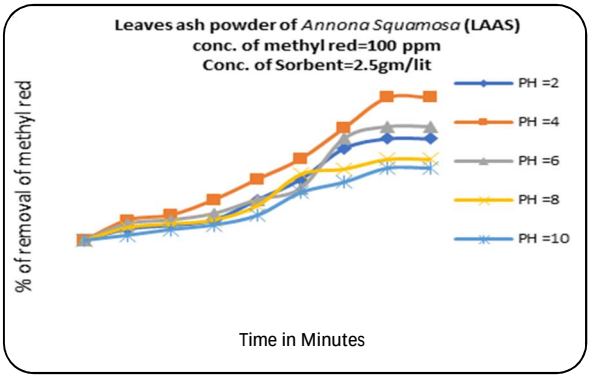

Fig. 2. Equalibration Time vs % of removal of methyl red

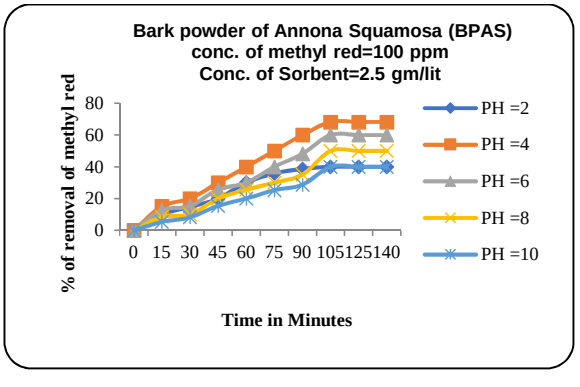

Fig. 3. Equalibration Time vs %of removal of methyl red

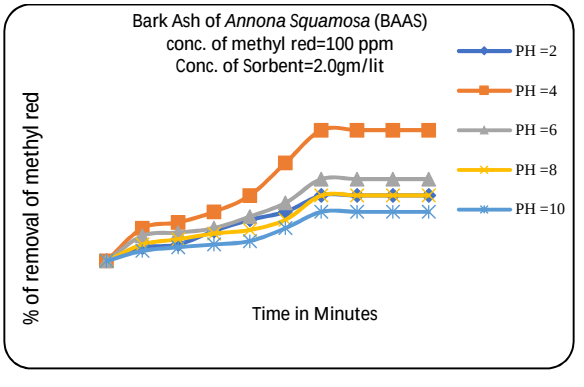

Fig. 4. Equalibration Time vs % removal of methyl red

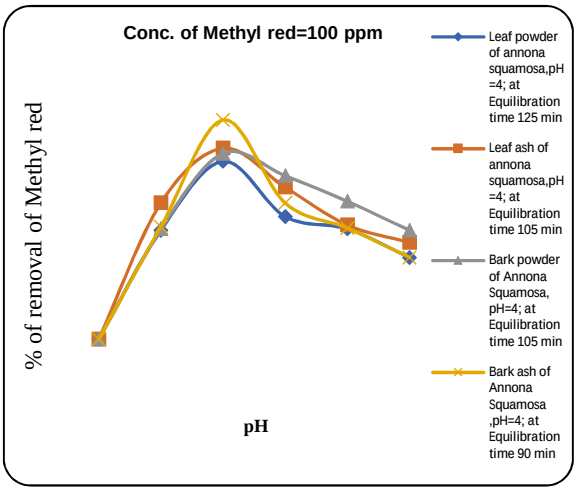

Fig. 5. pH Vs % of removal of Methyl red

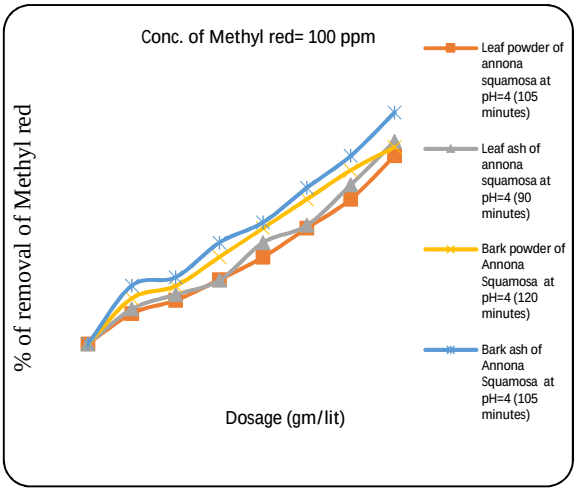

Fig. 6. Dosage Vs % of removal of Methyl red

3. Results and Discussions

In the present investigation, the extracting capability of the sorbents derived from *Annona squamosa* plant material towards MR dye was examined. Concerning this study, different physico-chemical parameters, such as pH, equilibration time and sorption concentration were considered and the results acquired were exhibited in the Fig. 1–6. After that the isotherm curves, kinetic parameters diagrams, and dependence of adsorption on temperature change, were also established. The accompanying perceptions which are significant are described below.

3.1. Time of Equilibration

Figs. 1 and 2 describe the nature of MR removal by sorbent of leaves powder (LPAS) and leaves ash powder (LAAS) of *Annona squamosa* with respect to time at constant MR and sorbent concentrations at different pH values maintained. Similarly, the Figs. 3 and represent bark powder (BPAS) and bark ash (BAAS) of *Annona squamosa*. From the graphs it was observed that the percent quantity of extractability increments with time for a constant adsorbent at constant pH and after certain span of time, the extractability stays steady, *i.e.*, an equilibrium state is reached. As such, there will not be any further adsorption after certain period of equilibration time. From Fig. 1, on account of leaves powders (LPAS) of *Annona squamosa*, the % of extraction of Methyl Red has been observed to be 10 % at 15 min, 15.4 % at 30 min, 20 % at 45 min, 30 % at 60 min, 40 % at 75 min, 50 % at 90 min, 60 % at 105 min, and 65.6 % at 125 min or above at pH 4. Similarly, the rates of extraction of Methyl Red (Fig. 2) are: LAAS 10 % at 15 min, 12.4 % at 30 min, 20 % at 45 min, 30 % at 60 min, 40 % at 75 min, 50 % at 90 min and 70 % at 105 min or above at pH 4, BPAS 15.1 % at 15 min, 20 % at 30 min, 30 % at 45 min, 40 % at 60 min, 50 % at 75 min, 60 % at 90 min, and 68.2 % at 105 min or above at pH 4, BAAS 20 % at 15 min, 23.5 % at 30 min, 30 % at 45 min, 40 % at 60 min, 60 % at 75 min, and 80 % at 90 min or above at pH 4. In Figs. 1–4 the highest % of MR removal is observed at pH 4.

3.2. Effect of pH

The extraction of MR dye was found to be highly sensitive to the change in pH (Fig. 5). Extractability of 68.2 % at pH 4; the equilibration time of 125 min for the LPAS as sorbent was observed. With the BPAS the % of extraction has been observed to be 40.5 % at pH 2, 68.2 % at pH 4, 60.0 % at pH 6; 50.6 % at pH 8 and 40 % at pH 10 after the equilibration time of 105 min. Similarly, with the leaves ash of *Annona squamosa* (LAAS) the maximum of 70.1 % at pH 4 was extracted, the equilibration time being 105 min. For BAAS 80.5 % at pH 4 are observed, the time of equilibration being 90 min. Thus, the rate of extraction of MR, by utilizing the fiery debris of *Annona squamosa* has been considered. It is intriguing to note that if there should arise an occurrence of powder of leaves of *Annona squamosa*, the ideal equilibration time requirement for most extreme extraction of MR was observed to be 125 min. At pH

equal to 4, at the same time as with the barks powder of a similar plant, the equilibration time was lessened to 20 min. Similar result was observed also for ash, and the time was lessened to 15 min compared to bark powders.

3.3. Sorbent Concentration

The optimum sorbent dosage needed for maximum extractability of MR was found to be more in the case of leaves and bark powders than with their ashes. With the bark powders of *Annona squamosa* it is 3.0 g/L but reduced to 2.5 g/L with the ashes of the same plant. Similarly, with the bark powders of *Annona squamosa*, the optimum dosage is found to be 2.5 g/L, while with its ashes 2.0 g/L (*vide* Fig. 6).

3.4. Effect of Interfering Ions

The extractability of MR in the presence of five-fold excess of common ions found in normal waters, such as sulfate, phosphate, chloride, carbonate, MR, iron, zinc, calcium, copper, and magnesium particles, was considered and reported in Table 1. Anions visualized minimal impact on the rate extractability of Methyl Red with the sorbents of the present work at the ideal states of time of equilibration, pH and sorbent concentration. Cations like Fe^{2+} and Zn^{2+} have not meddled and synergistically kept up the greatest % of extraction while cations like Ca^{2+}, Mg^{2+} and Cu^{2+} have interfered to a less degree with the % of extraction of the color.

Table 1. Effect of interfering ions on the extractability of Methyl Red with different bio-sorbents

Adsorbent and its concentration	Maximum extractability under optimum conditions	% of Extraction of Methyl Red in presence of five-fold excess of interfering ions under optimum conditions (Methyl Red conc. is 100 ppm; pH 4)									
		SO_4^{2-}	PO_4^{3-}	Cl^-	CO_3^{2-}	F^-	Fe^{2+}	Ca^{2+}	Mg^{2+}	Cu^{2+}	Zn^{2+}
Leaves powder of *Annona Squamosa* 3.0 g/L	65.6 %, pH 4, 125 min	79.0	82.1	84.2	87.0	86.0	82.5	67.5	74.0	68.	63.0
Bark powder of *Annona Squamosa* 2.5 g/L	68.2 %, pH 4, 105 min	77.0	69.2	87.5	82.1	98.3	77.5	69.1	68.3	77.5	85.5
Leaves ashes of *Annona Squamosa* 2.5 g/L	70.0%, pH 4, 105 min	83.1	84.0	85.0	88.1	92.0	89.5	83.1	80.0	78.5	83.0
Bark ashes of *Annona Squamosa* 2.0 g/L	90.0 %, pH 4, 105 min	82.6	83.2	84.6	87.2	91.8	88.0	82.4	79.2	77.6	82.1

3.5. Adsorption Isotherms

Four recognizable adsorption isotherm models, for example, Freundlich,[22] Langmuir,[23] Temkin,[24] and Dubinin-Radushkevich[25] were studied for the adsorption of MR with different adsorbents of *Annona squamosa* by using the following equations. The results of Freundlich and Langmuir adsorption isotherms were reported in Tables 2 and 3.

Freundlich isotherm equation is:

$$\log(q_e) = \log kf + \frac{1}{n}\log C_e \quad (1)$$

Linear form of Langmuir equation is:

$$\frac{C_e}{q_e} = \frac{a_L}{k_L}C_e + \frac{1}{k_L} \quad (2)$$

Table 2. Freundlich isotherm

S. No.	Name of the sorbent	Slope	Intercept	R^2	χ^2
1a	Leaves powder of *AnnonaSqumosa* (LPAS)	0.3449	0.7693	0.8905	0.1367
1b	Leaves ash of *Annona Squmosa* (LAAS)	0.3538	0.9346	0.9727	0.0153
1c	Bark powder of *Annona Squmosa*BPAS)	0.3293	0.9353	0.9934	0.0048
1d	Bark ash of *Annona Squmosa* (BAAS)	0.285	1.2073	0.9796	0.1152

Table 3. Langmuir isotherm

S. No.	Name of the sorbent	R_L	Slope	Intercept	R^2	χ^2
2a	LPAS	0.0901	0.0375	0.3718	0.9200	1.2274
2b	LAAS	0.0417	0.0317	0.138	0.9661	0.4836
2c	BPAS	0.0301	0.0364	0.113	0.9691	0.00329
2d	BAAS	0.0189	0.0242	0.0468	0.9762	0.0469

As indicated by Hall *et al.*,[26] the nature of the adsorption procedure is unfavourable (R_L> 1), linear (R_L=1), positive or favourable (0 <R_L< 1), and irreversible (R_L=0); the noteworthy element of the Langmuir isotherm model can be characterized by the dimensionless separation factor, R_L= 1/(1+$a_L C_i$). The results of linear plots of these studied adsorption isotherms and isothermal constants, along with the correlation coefficient values were exhibited in Tables 1 and 2 for Freundlich and Langmuir. As the correlation coefficients (R^2-values) is near unity, it shows the relevance of these two adsorption isotherms affirmed the heterogeneous surface of the adsorbent and the monolayer coverage of MR degradation on the bio-sorbent.[27-29] The relevance of the isotherm conditions is analyzed from the correlation coefficient (R^2). Among these four adsorption isotherm models, the high correlation coefficient for Freundlich isotherm R^2 = 0.9934, Langmuir isotherm R^2 = 0.9762 and dimensionless partition factor R_L = 0.0901, observed for leaves and bark powders of *Annona squamosa*, show the favourability of Langmuir isotherm. The Langmuir isotherm is considered to be more suitable than Freundlich isotherm for this particular biosorbent, *i.e.,* bark powder of *Annona squamosa*. Even though the R^2 value of Langmuir adsorption isotherm is less than that of Freundlich isotherm of BPAS, the concerned parameter χ^2 of Langmuir adsorption isotherm is 0.003299 (Table 2), which is less than that of Freundlich isotherm (χ^2 = 0.0048, Table 1). So, the Langmuir isotherm is considered to be more favourable than Freundlich isotherm.

The linear plots of the Temkin and Dubinin-Radushkevich adsorption isotherms and isothermal constants along with the relationship or correlation coefficient results are shown in Tables 4 and 5.

Temkin linear isotherm is:

$$q_e = B\ln C_e + B\ln A, \text{ where } B = RT/b \quad (3)$$

Dubinin-Radushkevich isotherm equation is:

$$\ln q_e = -\beta\varepsilon^2 + \ln q_m, \text{ where } \varepsilon = RT\ln(1+1/C_e) \quad (4)$$

Table 4. Results of Temkin isotherm

S. No.	Name of the sorbent	b	Slope (B)	Intercept	R^2
3a	LPAS	59.3602	4.2018	4.4067	0.8109
3b	LAAS	88.1903	2.8282	10.620	0.8562
3c	BPAS	62.3300	4.0016	10.268	0.9390
3d	BAAS	52.6291	4.7392	20.036	0.8516

Table 5. Results of Dubinin-Radushkevich isotherm

S. No.	Name of the sorbent	E	Slope (β)	Intercept	R^2
4a	LPAS	3.5339	$4x10^{-8}$	0.728	0.345
4b	LAAS	2.3570	$9x10^{-9}$	0.775	0.563
4c	BPAS	7.0711	$1x10^{-8}$	0.779	0.713
4d	BAAS	12.9099	$3x10^{-9}$	0.863	0.623

As the connection coefficients R^2 are near to unity, the Temkin heat of sorption B = 4.7392 J/mol was ascertained from the slope of the Temkin linear plot,[30,31] and the Dubinin-Radushkevich mean free energy[32] $E = \sqrt{(\frac{1}{2\beta})}$ was observed to be 2.3570 kJ/mol calculated for the leaves and bark powders and ashes of *Annona squamosa*. The E< 8 kJ/mol means that physical adsorption dominates over the chemical adsorptions and ion exchange, *etc*.[33]The physical adsorption is likewise called nonspecific adsorption, which happens as a consequence of long-range weak Vander Waal's forces between Methyl Red and the adsorbent. As per Atkins[34], characteristics for "physical adsorption" is the mean free energy (E)and heats of sorption (B) values lower than 20 kJ/mol.

3.6. Adsorption Kinetics

The rate and kinetics of MR adsorption onto the bio-sorbent got from *Annona squamosa* was studied with pseudo-first order model,[35,36] pseudo-second order model,[36,37] and Weber and Morris intra-particle diffusion model.[38] Bangham's pore diffusion model[39] and Elovich equations[40,41] were examined for good correlation.

The pseudo first-order equation is:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t \quad (5)$$

The pseudo second-order equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}} + \frac{1}{q_e} t \quad (6)$$

Weber and Morris intraparticle diffusion equation is:

$$q_t = k_{ip} t^{1/2} + c \quad (7)$$

Bangham's pore diffusion equation is:

$$\log[\log \frac{C_i}{(C_i - q_t m)}] = \log \frac{k_0}{2.303V} + \alpha \log(t) \quad (8)$$

Elovich equation is:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \quad (9)$$

The linear plots of all these five kinetic models and rate constants along with the correlation coefficients were studied and the applicability of the kinetic conditions was analyzed from the correlation coefficient R^2. Among these five kinetic models, the relationship coefficient value of leaves and bark powders and ashes of *Annona squamosa* for the Weber and Morris is found to be more (R^2 = 0.956), compared to Bangham's pore diffusion model (R^2 = 0.951), pseudo-first order model (R^2 = 0.9056), pseudo-second order model (R^2 = 0.873) and Elovich model (R^2 = 0.888).

3.7. Effect of Temperature

The impact of solution temperature on the % of MR removal was studied at the temperatures of 298, 308, 318, and 328 K under optimum conditions of extraction at pH 4.0, contact time of 90 min, sorbent dose of 3.0 mg/l; MR solution of 100 mg/L, particles size of 45 µ mesh and the outcomes got were plotted as lnK_d *vs.*1/*T*. Thermodynamic parameters of the adsorption procedure, for example, change in Gibbs free energy (Δ*G*, kJ/mol), change in enthalpy (Δ*H*, kJ/mol) and change in entropy (Δ*S*, J/mol·K) were determined at various temperatures by using the following equations:[42-44]

$$\Delta G = -RT\ln K_d \quad (10)$$

$$\ln K_d = \Delta S/R - \Delta H/RT \quad (11)$$

$$K_d = q_e/C_e \quad (12)$$

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

where K_d is the dispersion coefficient for the adsorption;q_e is the measure of MR adsorbed on the adsorbent per liter of solution at equilibrium;C_e is the equilibrium concentration of MR solution, mg/L; *T* is the temperature, K;*R* is the gas constant.

The Δ*H* and Δ*S* were calculated from the slope and intercept of graph plotted between lnK_d*vs.* 1/*T*, and Δ*G* values were calculated from Eq. (13) and arranged by kinetics and equilibrium adsorption of MR studied.[45,46]

It was observed that with the increase in temperature from 298 to 328 K the most extreme extraction of MR happened at 328 K. As the temperature affects the thickness of the adsorbent external surface in such a way that the increase in temperature decreases the thickness, the diffusion rate of Methyl Red increases across the external boundary layer and internal pores of the adsorbent. The estimations of Δ*H* values are positive (Table 6), which shows the physical sorption and endothermic nature of adsorption.[47] The R^2 value close to one also indicates that adsorption procedure is endothermic in nature. The positive values of Δ*S* demonstrate the increased disorder and randomness at the solid solution interface of MR dye with the adsorbent.[48] The negative values of Δ*G* show the spontaneous nature of adsorption process, *i.e.*, the adsorptive strengths are sufficiently strong to overcome the potential barrier.[49]

Table 6. Effect of temperature

S. No.	Parameter	Δ*H*, kJ/mol	Δ*S*, J/mol/K	Δ*G*, kJ/mol	R^2
10a	LPAS	12.7287	0.0346	1.3799	0.986
10b	LAAS	21.0261	0.0630	0.3621	0.957
10c	BPAS	19.4880	0.0575	0.628	0.981
10d	BAAS	22.2067	0.0725	-1.5733	0.998

Note**:** Temperature is 328 K

Applications of the created bio-sorbents: The acceptability of the systems developed with the new bio-sorbent derived from *Annona squamosa*, in the present work for the extraction of MR dye from wastewaters, was attempted with some genuine sewage/emanating samples of a few industries. The collected samples were subjected to extraction of the color utilizing the bio-sorbents developed as a part of this work at optimum conditions of extraction. The outcomes got were introduced in Table 7.

The outcomes demonstrated that a maximum of 90 % of MR has been separated by utilizing ash of *Annona squamosa* bark for the sample fed with 15 ppm MR dye. However, when consider the average efficiencies of all four bio-sorbents, it was found that a higher average efficiency of 87 % and 86 % were showed for ashes of bark and ashes of leaves, respectively, compared to 85 % and 84 % of bark powder and leaves powder, respectively.

Table 7. % of Extractability of Methyl Red dye from effluents with developed bio-sorbents

Adsorbent and its concentration	% of Extraction of MR in diverse samples						
	Sample -1 Fed with 10.0ppm MR	Sample -2 Fed with 15.0ppm MR	Sample -3 Fed with 20.0ppm MR	Sample -4 Fed with 25.0ppm MR	Sample -5 Fed with 30.0ppm MR	Sample -6 Fed with 35.0ppm MR	Average
Powder of *Annona Squamosa l*eaves; 3.0 g/L	81.5	88.3	82.3	81.2	85.5	86.3	84.18
Powder *of Annona Squamosa* bark;2.5g/L	88.1	82.2	85.6	88.3	81.5	83.5	84.86
Ashes *of Annona Squamosa* leaves; 2.5 g/L	86.3	81.5	85.5	88.4	89.0	85.2	85.98
Ashes *of Annona Squamosa* bark; 2.0 g/L	86.5	90.0	89.0	85.2	83.5	86.5	86.78

4. Conclusions

Leaves and barks of *Annona Squamosa* were found to have strong affinity towards Methyl Red at pH 4. The conditions for the maximum % of extraction of MR dye, at least dosage and equilibration time were optimized. Sorbent dose and time required for the most extreme evacuation of MR was less for ashes than with the crude powders of the plant materials. Five-fold abundance of regular anions present in normal waters has not interfered with the extractability of MR at optimum values of pH, equilibration time and sorbent dosage. Cation like Ca^{2+}, Mg^{+2}, and Cu^{2+} have some interference, while Fe^{2+} and Zn^{2+} have synergistically kept up the greatest extraction of the dye.

The high correlation coefficient and non-dimensional measurement (R_L), four isotherm designs, the coefficient of correlation of leaves and barks of powder *Annona Squamosa* observed in the scope of 0-1, demonstrated the favorability of the Langmuir isotherm to the Freundlich isotherm. Five kinetic models have been found for leaves, bark powders and ashes of *Annona squamosa*: Weber and Morris, Bingham's pore diffusion model, pseudo-first order, pseudo-second order mechanism, and Elovich mechanism. Among these, the pseudo-second order mechanism is the best fit for the adsorption framework. From the ΔH and R^2 values it was found that the physical sorption has an endothermic nature. The positive sign of ΔS shows the strong arrangement interface of Methyl Red dye with the adsorbent. ΔG indicates the power of adsorptive is adequately strong to overcome boundary of potentiality.

References

[1] Bhatnagar, A.; Jain, A.K. A comparative adsorption study with different industrial wastes as adsorbents for the removal of Cationic Dyes from Water. *J. Colloid Interf. Sci.* **2005**, *281*, 49-55. https://doi.org/10.1016/j.jcis.2004.08.076

[2] Bhattacharyya, K.; Sharma A. Kinetics and Thermodynamics of Methylene Blue Adsorption on Neem Leaf Powder. *Dyes Pigm.* **2005**, *65*, 51-59. https://doi.org/10.1016/j.dyepig.2004.06.016

[3] Robinson, T.; Chandran, B.; Nigam, P. Studies on the Production of Enzymes by White-Rot Fungi for the Decolorization of Textile Dyes. *Enzyme Microb. Technol.* **2001**, *29*, 575-579. https://doi.org/10.1016/S0141-0229(01)00430-6

[4] Shah, V.; Nerud, F. Lignin Degrading System of White-Rot Fungi and its Exploitation for Dye Decolorization, *Can. J. Microbiol.* **2002**, *48*, 857-870. https://doi.org/10.1139/w02-090

[5] Josefa, S.Y.M.; De Oliveria, E. Heavy Metals Removal in Industrial Effluents by Sequential Adsorption Treatment. *Adv. Environ. Research.* **2003**, *7*, 263-272. https://doi.org/10.1016/S1093-0191(01)00128-9

[6] Malik, D.J.; Strelko, V.J.; Streat, M.; Puziy, A.M. Characterization of Novel Modified Active Carbons and Marinealgal Biomass for the Selective Adsorption of Lead. *Water Research.* **2002**, *369*, 1527-1538. https://doi.org/10.1016/S0043-1354(01)00348-7

[7] Arslanoglue, F.N.; Kar, F.; Arslan, N. Adsorption of Dark Colored Compounds from Peach Pulp by Using Powdered Activated Carbon. *J. Food. Eng.* **2005**, *71*, 156-163. https://doi.org/10.1016/j.jfoodeng.2004.10.029

[8] Senthilkumaar, S.; Varadarajab, P.R.; Porkodi K.; Subbhuraam, C.V. Adsorption of Methylene Blue onto Jute Fiber

Carbon: Kinetics and Equilibrium Studies. *J. Colloid. Inter. Sci.* **2005**, *284*, 78-82. https://doi.org/10.1016/j.jcis.2004.09.027
[9] Laszlo, J.A. Preparing an Ion Exchange Resin from Sugarcane Bagasse to Remove Reactive Dye from Wastewater. *Text. Chem. Color*.**1996**, *28*, 13-17.
[10] Gemea, A.H.; Mansour, I.A.; El-Sharkawy, R.G.; Zaki, A.B. Kinetics and Mechanism of the Heterogeneous Catalyzed Oxidative Degradation of Indigo Carmine. *J. Mol. Catal. Chem.* **2003**, *193*, 109-120. https://doi.org/10.1016/S1381-1169(02)00477-6
[11] Grimau, V.L.; Gutierrez, M.C. Decolorization of Simulated Reactive Dyebath Effluents by Electrochemical Oxidation Assisted by UV Light. *Chemosphere.* **2006**, *62*, 106-112. https://doi.org/10.1016/j.chemosphere.2005.03.076
[12] Hachem, C.; Bocquillon F.; Zahraa, O.; Bouchy, M. Decolorization of Textil Industry Wastewater by the Photocatalytic Degradation Process. *Dyes. Pigm.* **2001**, *49*, 117-125. https://doi.org/10.1016/S0143-7208(01)00014-6
[13] Cisneros, R.L.; Espinoza, A.G.; Litter, M.I. Photodegradation of an Azo Dye of the Textile Industry. *Chemosphere*. **2002**, *48*, 393-399. https://doi.org/10.1016/S0045-6535(02)00117-0
[14] Gupta V. K.; Suhas. Application of Low-Cost Adsorbents for Dye Removal – A Review. *J. Environ. Manage.* **2009**, *90*, 2313-2342. https://doi.org/10.1016/j.jenvman.2008.11.017
[15] Srivastava, V.; Mall, I.D.; Mishra, I.M. Equilibrium Modelling of Single and Binary Adsorption of Cadmium and Nickel onto Bagasse Fly Ash. *Chem. Eng. J.* **2006**, *117*, 79-91. https://doi.org/10.1016/j.cej.2005.11.021
[16] Trivedy, R.K. *Pollution Management in Industries*, 2nd ed.; Karad (India): Environmental Publications, 1995.
[17] Kiely, G. *Environmental Engineering*; McGraw-hall International Editions, 1998.
[18] Tchobanoglous, G.; Burton, F.L.; Stensel, D.H. *Wastewater Engineering: Treatment and Reuse*, 4th ed; McGraw Hill, 2003.
[19] APHA, Standard methods for the Examination of Water and Waste water. American Public Health Association, Washington DC, 1985.
[20] Ramana, K.V.; Latha, K.S.; Ravindranath, K.; Babu, B.H. Methyl Red Dye Removal Using New Bio-Sorbents Derived from Hycinth and Tinosporacardifolia Plants from Waste Waters, *Rasayan J. Chem*. **2017**, *10*, 349-362.
[21] Srinivasa Reddy, B.; Venkata Ramana, K.; Ravindranath, K. Extraction of Methylene Blue Dye from Polluted Waters Using Some Bio-sorbents. *Int. J. Appl. Biol.Pharm.* **2012**, *3* (4), 215-224.
[22] Freundlich, H.M.F. Über die Adsorption in Lösungen. *Z. Phys. Chem*. **1906**, *57*, 385-470. https://doi.org/10.1515/zpch-1907-5723
[23] Langmuir, I. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum, *J. Am. Chem. Soc.*, **1918**, *40*, 1361-1403. https://doi.org/10.1021/ja02242a004
[24] Temkin, M.; Pyzhev, V. Kinetics of Ammonia Synthesis on Promoted Iron Catalysts. *Acta Physicochimica URSS.* **1940**, ***12***, 217-222.
[25] Dubinin, M.M.; Radushkevich, L.V. The Equation of the Characteristic Curve of Activated Charcoal. *Proc. Natl. Acad. Sci., Phys. Chem. Section*. **1947**, *55*, 331.
[26] Hall, K. R.; Eagleton, L. C.; Acrivos A.; Vermeulen, T. Pore and Solid Diffusion Kinetics in Fixed Bed Adsorption under Constant Pattern Conditions. *Ind. Eng. Chem. Fundam.* **1966**, *5*, 212-223. https://doi.org/10.1021/i160018a011
[27] Sari. I.P.; Simarani, K. Comparative Static and Shaking Culture of Metabolite Derived from Methyl Red Degradation by Lysinibacillusfusiformis Strain W1B6. *R. Soc. Open Sci.* **2019**, *6*, 190152. https://doi.org/10.1098/rsos.190152
[28] Ajaz, M.; Rehman, A.; Khan, Z.; Nisar M.A.; Hussain S. Degradation of Azo Dyes by Alcaligenesaquatilis 3c and its Potential Use in the Wastewater Treatment. *AMB Expr*. **2019**, *9*, 64. https://doi.org/10.1186/s13568-019-0788-3
[29] Kpilraj, N.; Keerthanan, S.; Sithambaresan, M. Natural Plant Extracts as Acid-Base Indicator and Determination of Their Pka Value. *J. Chem.* 2019, *2019*, Article ID 2031342. https://doi.org/10.1155/2019/2031342
[30] Hameed, B.H. Evaluation of Papaya Seeds as a Novel Non-Conventional Low-Cost Adsorbent for Removal of Methylene Blue. *J. Hazard. Mater.*, **2009**, *162*, 939-944. https://doi.org/10.1016/j.jhazmat.2008.05.120
[31] Nunes, A.; Franca, S.A.; Olievera, L.S. Activated Carbon from Waste Biomass: An alternative Use for Biodiesel Production Solid Residues. *Biores. Technol.* **2009**, *100*, 1786-1792. https://doi.org/10.1016/j.biortech.2008.09.032
[32] Onyango, M.S.; Kojima, Y. Aoyi, O. Bernardo, E.C.; Matsuda, H.J. Adsorption Equilibrium Modeling and Solution Chemistry Dependence of Fluoride Removal from Water by Trivalent-Cation-Exchanged Zeolite F-9. *Colloid Interface Sci.* **2004**, *279*, 341-350. https://doi.org/10.1016/j.jcis.2004.06.038
[33] Jain, M.; Garg, V.K.; Kadirvelu, K. Chromium(VI) Removal from Aqueous Solution, Using Sunflower Stem Waste. *J. Hazard. Mater.* **2008**, *162*, 365-372. https://doi.org/10.1016/j.jhazmat.2008.05.048
[34] Atkins, P.; de Paulo J. *Physical Chemistry*, 8th ed.; Oxford University Press, 2006.
[35] Yuh-Shan, H. Citation Review of Lagergren Kinetic Rate Equation on Adsorption Reactions. *Scientometrics*. **2004**, *59*, 171-177. https://doi.org/10.1023/B:SCIE.0000013305.99473.cf
[36] Ho, Y.S.; McKay, G. Pseudo-Second Order Model for Sorption Processes. *Process Biochem.* **1999**, *34*, 451-465. https://doi.org/10.1016/S0032-9592(98)00112-5
[37] Ho, Y.S.; Ng, J.C.Y.; McKay, G. Kinetics of Pollutant Sorption by Biosorbents: Review. *Sep. Purif. Methods*. **2000**, *29*,189-232. https://doi.org/10.1081/SPM-100100009
[38] Weber Jr., W.J.; Morris, J.C. Kinetics of Adsorption on Carbon from Solution, *J. Sanit. Eng. Div.* **1963**, *89*, 31-59. https://doi.org/10.1061/JSEDAI.0000430
[39] Aharoni, C.; Ungarish, M. Kinetics of Activated Chemisorption. Part 2. – Theoretical Models, *J. Chem. Soc., Faraday Trans. 1*. **1977**, *73*, 456-464. https://doi.org/10.1039/f19777300456

[40] Ozacar, M.; Sengil, V. A Kinetic Study of Metal Complex Dye Sorption onto Pine Sawdust. *Process Biochem.* **2005**, *40*, 565-572. https://doi.org/10.1016/j.procbio.2004.01.032
[41] Gerente C., Lee, V.K.C.; Le Cloirec, P.; McKay, G. Application of Chitosan for the Removal of Metals from Wastewaters by Adsorption – Mechanisms and Models Review. *Crit. Rev. Environ. Sci. Technol.* **2007**, *37*, 41-127. https://doi.org/10.1080/10643380600729089
[42] Alagumuthu, G.; Rajan, M. Monitoring of Fluoride Concentration in Ground Water of Kadayam Block of Tirunelveli District, India. *Rasayan J. Chem.* **2008**, *4*, 757-765.
[43] Karthikeyan, G.; Siva Ilango S. Fluoride Sorption Using Morringa Indica-Based Activated Carbon. *Iran J. Environ. Health. Sci. Eng.* **2007**, *4*, 21-28.
[44] Sakthi S.M.; Rengaraj, V. Kinetics and Equilibrium Adsorption Study of Lead(II) onto Activated Carbon Prepared from Coconut Shell. *J. Colloid. Interface Sci.* **2004**, *279*, 307-313. https://doi.org/10.1016/j.jcis.2004.06.042
[45] Venkata Ramana, K.; Swarna Latha, K.; Ravindranath, K.; Hari Babu, B. Methyl Red Dye Removal Using New Bio-Sorbents Derived from Hyacinth and Tinospora Cordifolia Plants from Waste Waters. *Rasayan J. Chem.* **2017**, *10*, 349-362. https://doi.org/10.7324/RJC.2017.1021537
[46] Viswanathan, N.; Meenakshi, S. Enriched Fluoride Sorption Using Alumina/Chitosan Composite. *J. Hazard. Mater.* **2010**, *178*, 226-232. https://doi.org/10.1016/j.jhazmat.2010.01.067
[47] Bouberka, Z.; Kacha, S.; Kameche M.; Elmaleh, S.; Derriche, Z. *J. Hazard. Mater.* **2005**, *119*, 117-124. https://doi.org/10.1016/j.jhazmat.2004.11.026
[48] Sairam Sundaram, C.; Viswanathan, N.; Meenakshi S. *J. Hazard. Mater.* **2009**, *163*, 618-624. https://doi.org/10.1016/j.jhazmat.2008.07.009
[49] Chaturvedi, A.K.; Pathak, K.C.; Singh, V.N. *Appl. Clay Sci.* **1988**, *3*, 337-346. https://doi.org/10.1016/0169-1317(88)90024-5

Received: May 25, 2020 / Revised: August 18, 2020 / Accepted: May 8, 2021

БІО-СОРБЕНТ, ОДЕРЖАНИЙ З *ANNONA SQUAMOSA*, ДЛЯ ВИДАЛЕННЯ БАРВНИКА МЕТИЛОВОГО ЧЕРВОНОГО З ВОДИ: ДОСЛІДЖЕННЯ АДСОРБЦІЙНОГО ПОТЕНЦІАЛУ

Анотація. *Проведені дослідження сорбційної здатності до метилового червоного (МЧ) сорбенту, отриманого з листя та кори* Annona squamosa, *з використанням штучно створених стоків. Визначено різні чинники, що впливають на адсорбцію, а саме: початкова концентрація, час контакту, дозування адсорбенту, а також встановлено вплив температури. Рівновага адсорбції проаналізована за допомогою ізотерм Фройндліха, Лангмюра, Темкіна та Дубініна-Радушкевича. Для визначення швидкості та кінетики адсорбції застосовували рівняння псевдопершого і псевдодругого порядку, дифузії Вебера та Морріша, дисперсії пор Бангема та рівняння Еловіча. Досліджено інтерференцію п'ятикратної кількості регулярних аніонів і катіонів, присутніх у звичайних водах. Встановлено, що такі катіони, як* Ca^{2+}, Mg^{2+} *та* Cu^{2+}, *демонструють певний опір, однак найбільшу екстракцію МЧ синергетично демонструють* Fe^{2+} *та* Zn^{2+}. *Показано, що розроблені методи ефективно застосовані до деяких стоків. Результати експериментальних даних визнані відповідними кінетичній моделі псевдо-першого порядку. Значення коефіцієнта кореляції* (R^2) *та коефіцієнта поділу* (R_L) *підтверджують, що адсорбція підпорядковується адсорбції Ленгмюра.*

Ключові слова: *метиловий червоний, контроль забруднення, біоадсорбент, ізотерма адсорбції, кінетика, моделі рівноваги.*