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Adsorption Potentialities of Bio-Sorbents Derived from Pomegranate in the Removal of Methyl Red Dye from Polluted Waters

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Abstract:

Synthetically prepared simulated waste waters was used for exploring sorption abilities of the sorbent substance obtained from barks and leaves of *Pomegranate* towards Methyl Red. Factors that affect adsorption like temperature, adsorbent dosage, starting dye concentration and time of contact were evaluated. Four adsorption isotherms namely Freundlich, Langmuir, Temkin and Dubinin-Radushkevich were analyzed for studying equilibrium of adsorption. Rate and adsorption process kinetics were identified by applying Weber and Morrish intraparticle diffusion, Bangham's pore diffusion, pseudo-first-order, pseudo-second-order and Elovich equations.Fivefold excess of common ions interference in natural aquifers, have been analyzed. Cations such as Ca^{2+}, Mg^{2+} and Cu^{2+}have shown little interference but Fe^{2+} and Zn^{2+}ions combinedly maintained maximum withdrawal of the dye. Procedures that were developed could be successfully applied to few industrial effluents.Data collected out of experimentation was suitable to the pseudo-First order kinetic standard. Correlation coefficient (R^2) and dimensionless separation factor (R_L) valuesconformed that adsorption process follows Langmuir adsorption indicating single layer formation.The adsorption process had good correlation coefficient equivalence with pseudo-second-order model. Temperature effect was also studied.

Keywords: Methyl Red(MeR); Equilibrium model; Bio-sorbent; Kinetics; Adsorption isotherms; Pomegranate.

Introduction:

Water infected by contaminates that degrade the water quality is known as polluted water. It includes the discharge of noxious materials, heavy metals, dyes,infectious germs, aerobic bacteria, solvable substances, etc. The main causes for dye pollution are the materials discharged from fibre, cloth, fur, food stuffs, cosmetics, dye, pulp and papermanufacturing industries [1]. Artificial dyes aren't consistently susceptibletowardbiodegradation, non-conventional biological waste water treatment, and protest towards microbial azo-dyes that are widely used in several industries, are the biggest class with diverse range of colours and structures. The need for the treatment of waste water contaminated with dye, arose because of environmental impact [2].The usual waste water treatment is generally not effective and various chemical, physical and biological treatments or their combinations are being studied at present [3, 4]. Silica[5],alumina, with activated carbon [6] act as common adsorbents to treat waste water asevidenced by numerous researchers [7, 8].

To remove dyes from waste water, various techniques have been developed. Electro-kinetic coagulation, ion-exchange, membrane filtration, electrochemical oxidation and photo-catalytic degradation process [9-15] are the widely used techniques, but these methods are costly and may not be favourable in large scale treatments.

The current research is a thorough study on optimizing extraction requisites like sorption quiddity of active bio-sorbent concerningMR - methyl red by varying contact time, pH, dose level of adsorbent, MR dye (methyl red) initial concentration, temperature, and ions that areinterfering. The Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (D-R) isotherms and kinetics of adsorption processes were used to analyze pseudo first-order, pseudo second-order, Weber and Morrish intraparticle diffusion, Bangham's pore diffusion and Elovich equations. Temperature effect on adsorption was also studied.For removal of MR from polluted waste water samples with biomaterials extracted from Pomegranate's barks & leaves, the developed methodologies have been applied**.** Pomegranate is a commonly available plant, which is used in fencing property perimeter in Kerala.

Bark of Pomegranate Leaves of Pomegranate

Figure 1: Bark and leaves of Pomegranate

3. Materials and Methods:

Chemicals-Chemicals of analytical reagent grade were utilized.

MR's Stock solution-Required amount of analytical reagent grade MR dye was dissolved in double distilled water to prepare 100 mg/L of MR solution. It was diluted as of required.

Preparation of Adsorbent-Pomegranate leaves and bark were gathered, chopped into tiny pieces, cleaned by double water, and left to dry for 2 days in the sun. We investigated the sorption capacities of plant materials against Methyl Red & found favourable findings.

Adsorption Experiment-For extraction process the batch system has been adopted [16-18]. The adsorbents were weighed carefully and taken into well cleaned 1 L/500 mL stopper bottles that contain 500 mL/250 mL of MR Dye solution of pre-decided concentrations. pH meter was used to adjust several starting pH values of the suspensions with dilute HCl or dilute NaOH solutions. Samples were shacked strenuously using mechanical shakers for allowing them to be in equilibrium up to required time. An aliquot of the sample was used to determine MR dye using Spectrophotometric method [19-20]. λmax of the dye was found as 464.9 nm alsoat low concentrations law of Beers-Lambert obeyed. Optical density measurements were taken at λmax 464.9 nm by making use of UV-Visible Spectrophotometer of Systronics make. The optical density attained for un-known solution was compared with reference graphs of known concentrations of MR Dye using Least Squares method.

By using various physicochemical parameters, adsorbents - sorption characteristics were studied. MR dye percentage removal from simulated water samples at different pH values was studied in relation to time of equilibration at a permanent sorbent concentration. The results attained were shown in **Figure 2-5** and **6.**Extraction studies were made to determine the least dosage required for the maximum removal of the MRDye.Extraction percentage in relation to sorbent dosage was studied to determine optimum pH and equilibration times. The results attained were shown in the **Figure 7.**

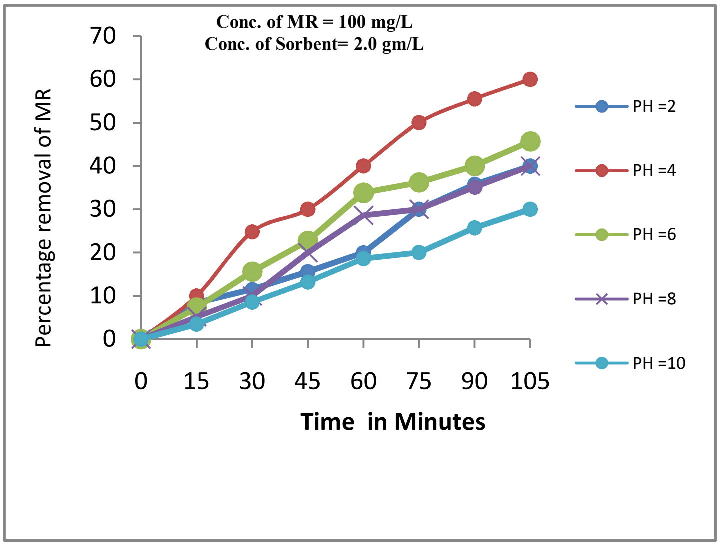


Figure 2:% Removal of MRin relation to equilibration time at a fixed sorbent concentration from powder form of Pomegranate leaves

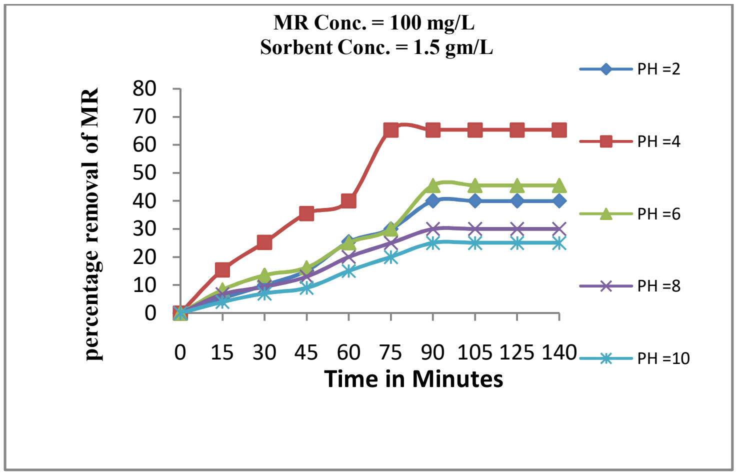


Figure 3:% Removal of MR in relation to equilibration time at fixed sorbent concentration from ash of Pomegranate leaves

Analysis of MR dye

Following equations were used to determine the percentage removal and the amount of MR adsorbed (mg/g) -

Percentage of Removal (% R) $= \frac{Ci - Ce}{Ci} \times 100$

Amount of MR adsorbed (qe) = $\frac{\mathrm{Ci}-}{\mathrm{m}} \times \mathrm{V}$

Where,Ci = Starting MR concentration in mg/L; Ce = Equilibrium concentration of MR solution in mg/L;

m = Adsorbent mass in gm; V = Volume of MR solution in liters

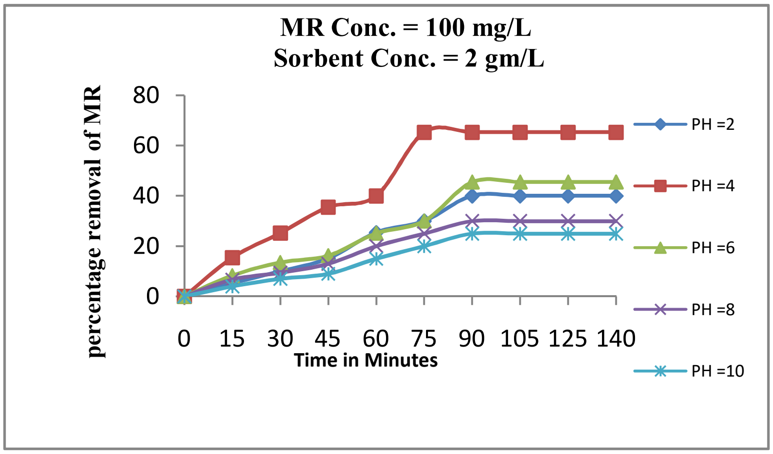


Figure 4:% Removal of MR in relation to equilibration time at a fixed sorbent concentration from bark powder of Pomegranate

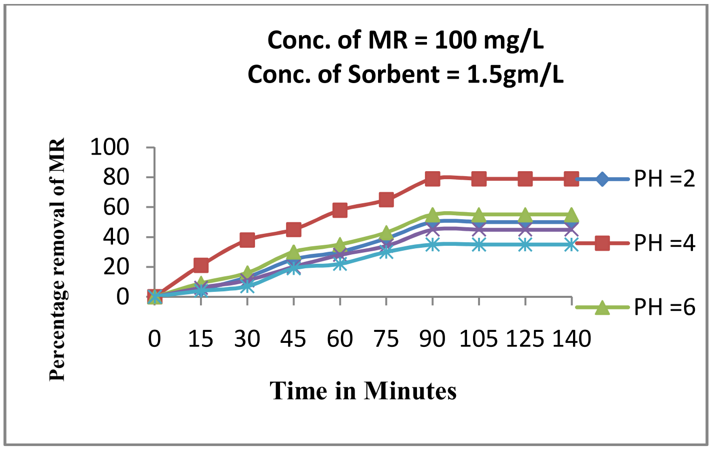


Figure 5:% Removal of MRin relation to equilibration time at a fixed sorbent concentration from bark ash of Pomegranate

The above equations were used in the experiments done for determining several physical and chemical characteristics like weight of adsorbent, pH of the MR solution, MR solution strength, and equilibration time, particle size of the adsorbent, temperature and presence of foreign ions.

Effect of Co-Ions (Interfering Ions/Common ions)

NO_3^-, $CO_3^{2-,}SO_4^{2}$-, Cl^-, PO_4^{3-}, Ca^{2+}, $Mg^{2+,}Fe^{2+}$, Cu^{2+} and Zn^{2+} are the interfering ions chosen for study were the common ions present in natural water.

MR dye and synthetic mixtures common ions were prepared and the strength of the foreign ion was kept at fivefold excess than the dye strength. 500 mL of this solution was transferred into Stoppard bottles and ideal amount of accurately weighed adsorbents were added.Ideal pH was adjusted with dilute HCl or dilutes NaOH using pH meter. Mechanical shakers were used to shake the samples at regular intervals and small amount of the samples were estimated for MR dye after filtration and extraction percentage was determined.

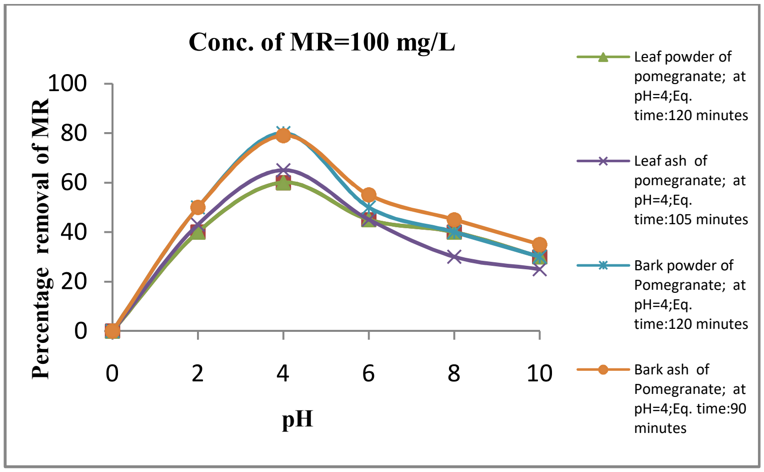


Figure 6:% Removal of Methyl Red at different Ph

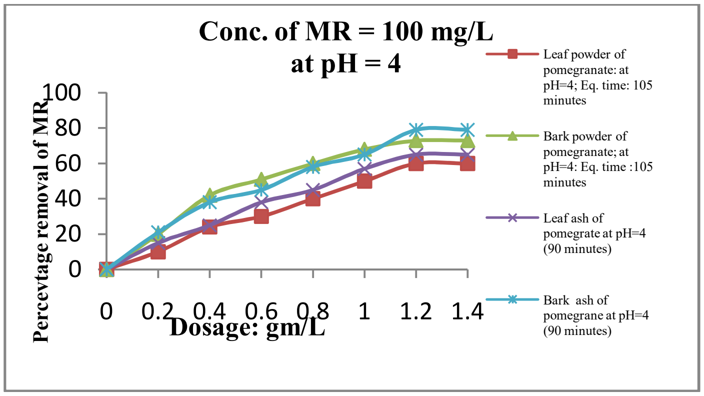


Figure 7:% Removal of Methyl Redin relation to sorbent dosage

Results and Discussion:

The sorbent materials derived from Pomegranate plant were determined in relation to several physicochemical characters like pH, equilibration time and sorption abilities for extractability of MR **Figure 2-5, Figure 6 and Figure 7.** The results of adsorption isotherm curves, kinetic parameter graphs and adsorption temperature graphs are given in the **Tables 1-10**.

Table 1: Freundlich Isotherm

S.No.	Name of Sorbent	Intercept	Slope	R^2
1a	**Leaves Powder of Pomegranate (LPOP)**	1.0107	0.3616	0.9384
1b	**Leaves ash of Pomegranate (LAOP)**	1.148	0.3363	0.9945
1c	**Bark Powder of Pomegranate (BPOP)**	1.0282	0.4077	0.9965
1d	**Bark ash of Pomegranate (BAOP)**	1.19	0.3821	0.9962

Table 2: Langmuir Isotherm

Sl. No	Name of Sorbent	R_L	Slope	Intercept	R^2
2a	**LPOP**	0.0200	0.0031	0.0634	0.9964
2b	**LAOP**	0.0267	0.0220	0.0605	0.9872
2c	**BPOP**	0.0320	0.0245	0.0811	0.9813
2d	**BAOP**	0.0219	0.0206	0.0463	0.9832

Table 3: Temkin Isotherm Results of Temkin Isotherm

Sl. No.	Name of Sorbent	b	Slope(B)	Intercept	R^2
3a	**LPOP**	43.9127	5.6799	11.915	0.9769
3b	**LAOP**	36.1421	6.9011	16.668	0.9574
3c	**BPOP**	36.8637	6.766	12.775	0.9418
3d	**BAOP**	32.9489	7.5699	19.329	0.9406

Table 4: Dubinin-Radushkevich

Sl. No.	Name of Sorbent	E	Slope	Intercept	R^2
4a	**LPOP**	4.0825	$3x10^{-8}$	0.855	0.816
4b	**LAOP**	1.000	$2x10^{-7}$	0.8131	0.501
4c	**BPOP**	5.0203	$2x10^{-8}$	0.859	0.697
4d	**BAOP**	7.0711	$1x10^{-8}$	0.907	0.728

Table 5: Pseudo first Order

Sl. No.	Name of Sorbent	K_1	Slope	InterceptResult	R^2
5a	**LPOP**	0.0309	0.0134	1.6829	0.9363
5b	**LAOP**	0.0189	0.0082	1.6646	0.9673
5c	**BPOP**	0.0253	0.011	1.7867	0.8616
5d	**BAOP**	0.0235	0.0102	1.6897	0.982

Table 6: Pseudo Second Order

Sl. No.	Name of Sorbent	K_2	Slope	Intercept	R^2
6a	**LPOP**	9.8098×10^{-5}	0.014	1.998	0.925
6b	**LAOP**	3.6232×10^{-4}	0.020	1.104	0.951
6c	**BPOP**	2.0181×10^{-5}	0.007	2.428	0.375
6d	**BAOP**	1.6866×10^{-4}	0.013	1.002	0.921

Table7: Weber and Morris

Sl. No	Name of Sorbent	K_0	Slope	Intercept	R^2
7a	**LPOP**	0.1678	1.112	-2.619	0.986
7b	**LAOP**	0.2651	0.861	-2.162	0.992
7c	**BPOP**	0.1932	1.048	-2.478	0.953
7d	**BAOP**	0.2938	0.914	-2.059	0.991

Table 8: Bangham's pore diffusion

Sl. No	Name of Sorbent	Slope	Intercept	R^2
8a	**LPOP**	4.031	-10.66	0.989
8b	**LAOP**	4.700	-8.373	0.988
8c	**BPOP**	4.437	-12.73	0.961
8d	**BAOP**	5.212	-7.903	0.991

Table 9: Elovich

Sl. No..	Name of Sorbent	A	Slope	Intercept	R^2
9a	**LPOP**	1.1294	12.50	-30.05	0.964
9b	**LAOP**	1.1577	13.76	-28.30	0.963
9c	**BPOP**	1.1785	14.10	-35.01	0.887
9d	**BAOP**	2.1257	15.36	-30.38	0.979

Table 10: Effect of temperature

Sl. No	Temperature (K)	ΔH(kJ/mol)	ΔS(J/mol/K)	ΔG(kJ/mol)	R^2
10a	**LPOP**	18.5402	0.0536	-0.9594	0.975
10b	**LAOP**	18.4321	0.0573	-0.3623	0.975
10c	**BPOP**	21.0178	0.0667	-0.8606	0.985
10d	**BAOP**	25.9563	0.0845	-1.7597	0.978

The following observations have been reported

Equilibration time

Adsorbent's extractability rises at certain pH with time but at equilibration time, it remains constant indicating the approach of equilibrium state i.e., no further adsorption takes place after certain equilibration time (**Figure 2-5**).

In LPOP, the percentage removal of MR was found to be 10 % at 15 min, 24.8 % at 30 min 30.0 % at 45 min and 40.0 % at 60 min, 50.0 % at 75 min, 55.5 % at 90 min 60.0% at 105 min or above at pH: 4. Similarly the percentage removal of MR using the bark and ashes of Pomegranate was determined.

pHeffect

Removal of MR was found with respect to pH of the agitating equilibration time for certain adsorbent. Figure 6 shows maximum removal of 35.8 % at pH: 2; 55.5 % at pH: 4; 40.0 % at pH: 6; 35.1 % at pH: 8 and 25.7 % at pH: 10, after an equilibration span of 90 min for LPOP. With the bark powder of pomegranate (BPOP) the percentage of extraction was found to be 50.0 % at pH: 2; 75.2 % at pH: 4; 55.9 % at pH: 6; 45.4% at pH: 8 and 30.0 % at pH: 10 after an equilibration span of 125 min.Similarly the percentage extraction of MR, by using the pomegranate ashes has been studied. The optimum time of equilibration needed for maximum removal of MRwas found to be 90 min at pH: 4, while with the BPOP, the equilibration spanwas found to be 125 min.

Sorbent Concentration

For the maximum extractability of the MR, the optimum sorbent concentration requiredfor leaves and bark powders of Pomegranate was1.0 gm/500 mL.

Interfering Ions

The consequences of MR extractability in proximity of fivefold overabundance of principalsubstances found in characteristic waters likeSO_4^{2}-, Cl^-, CO_3^{2-}, PO_4^{3-}, MR, Ca^{2+}, $Mg^{2+,}$ Fe^{2+}, $Cu^{2+}$and Zn^{2+}, was contemplated and displayed in Table 11. Negatively charged ionsshowedless impact on extractability rate of MR with the sorbents of current work at the absolute states of equilibration time, pH and sorbent focus.

Table 11: Interfering ions effect on MR extractability with various bio-sorbents: 63 - 99 in the middle of values

S.No	Adsorbent and its concentration	Maximum Extractability at optimum conditions	**% of MR** At **optimal conditions, fivefold excess of interfering ions extraction. : Conc. of MR: 100 ppm at pH:4**									
			SO_4^{2-} %	PO_4^{3-} %	Cl^- %	CO_3^{2-} %	F^- %	Fe^{2+}%	Ca^{2+} %	Mg^{2+} %	Cu^{2+} %	Zn^{2+} %
11	**LPOP:** 2.0 g/L	60.0%; pH:4, 105 min	83.0	99.2	92.0	88.9	91.2	86.6	83.4	66.5	89.4	93.0
22	**BPOP:** 2.0 g/L	75.0%; pH:4, 125 min	92.0	77.5	84.2	87.0	86.0	82.5	67.5	74.0	68.0	63.0
33	**LAOP**: 1.5 g/L	65.3%; pH:4, 90 min	79.2	81.4	83.7	86.5	85.2	81.3	67.1	73.8	67.6	62.0
44	**BAOP:** 1.75 g/L	79.0% pH:4, 90 min	92.5	76.2	86.1	78.5	92.1	98.5	68.3	74.0	68.0	63.0

Adsorption Isotherms

Freundlich [21], Langmuir [22], Temkin [23], and Dubinin-Radushkevich [24] are well- acquainted adsorption isotherm models that assessed the relationship combining the MR fixations leavings in the mass answer to estimate MR adsorbed there at situating interface so at given temperature.

Freundlich condition's straight type: $\log(q_e) = \log k_f + \frac{1}{n}\log C_e$

Langmuir equation in linear form; $C_e/q_e) = (a_L/k_L)C_e + 1/k_L$

As laid out by Hall et al. [25], adsorption phenomena character was annoyingin$R_L > 1$, straight in $R_L=1$, great in $1>R_L>0$ and unalterable in $R_L=0$ alsoLangmuir isotherm model's critical component was identified thru measureless schismfigure, $R_L = 1/(1+aLCi)$.Adsorption isotherms outputs were shown in **Tables 1** and **2**. The closeness of R^2 values to oneindicates the materialness of 2 adsorption isotherms affirmingadsorbent's diversified surface and MR's single layer possibilityover bio-sorbent.The isotherm state's appropriateness is thought about from the connection coefficient (R^2). Regarding Freundlich isotherm with R2 = 0.9965 esteem, Langmuir isotherm with R2 = 0.9964 as well as dimensionless separation figure with RL = 0.0200, the link coefficient estimation of leaves, bark dust, and fiery remnants of Pomegranate was determined to be about 0-1. This indicates that Langmuir isotherm is more agreeable than Freundlich isotherm.

Linear form of Temkin equation:$q_e = B\ln Ce + B\ln A$, where $RT/b = B$

Linear form of Dubinin-Radushkevich equation:$\ln q_e = -\beta\varepsilon^2 + \ln qm$

in which, $\varepsilon = RT\ln(1+1/C_e)$

Tables 3 and **4** exhibit the linear graphs of all these two adsorption isotherms with isothermal constants, as well as the correlation coefficient estimates.

The R^2- relationship coefficients are close to one. Temkin amiability of sorption, B=7.5699 J/mol was computed from liability of direct plot of Temkin [26, 27], and mean free vitality of Dubinin-Radushkevich $E = \sqrt{(1/2\beta)}$, [28] was found as E=7.0711 KJ/mol. In current extraction investigation E< 8 kJ/mol, relates to physical adsorption [29] profuse adsorptions also particle trade. Physical adsorption was called indefiniteadsorption that takes place after long range powerless van der Waals force in the middle of MR and adsorbent. According to Atkins [30], Physical adsorption is nothing but mean free vitality (E) plus sorption warms (B) of lesser than 20 kJ/mol.

Adsorption Kinetics

The rate & energy of MR adsorption here to bio-sorbent acquired in Pomegranate were contrasted to pseudo first-order exhibit [31-32], pseudo second-order exhibit [32-33], Weber and Morris intra-particle dissemination show [34], Bangham's pore dispersion display [35], as well as Elovich state [36-37].

The pseudo 1st-orderequation:$\log(qe - qt) = \log q_e - \frac{k1}{2.303} \times t$

The pseudo 2nd-order equation:$t/qt = \frac{1}{k2qe2} + (1/qe)\,t$

Weber & Morris diffusion equation for intraparticle:$q_t = k_{ip}t^{1/2} + c$

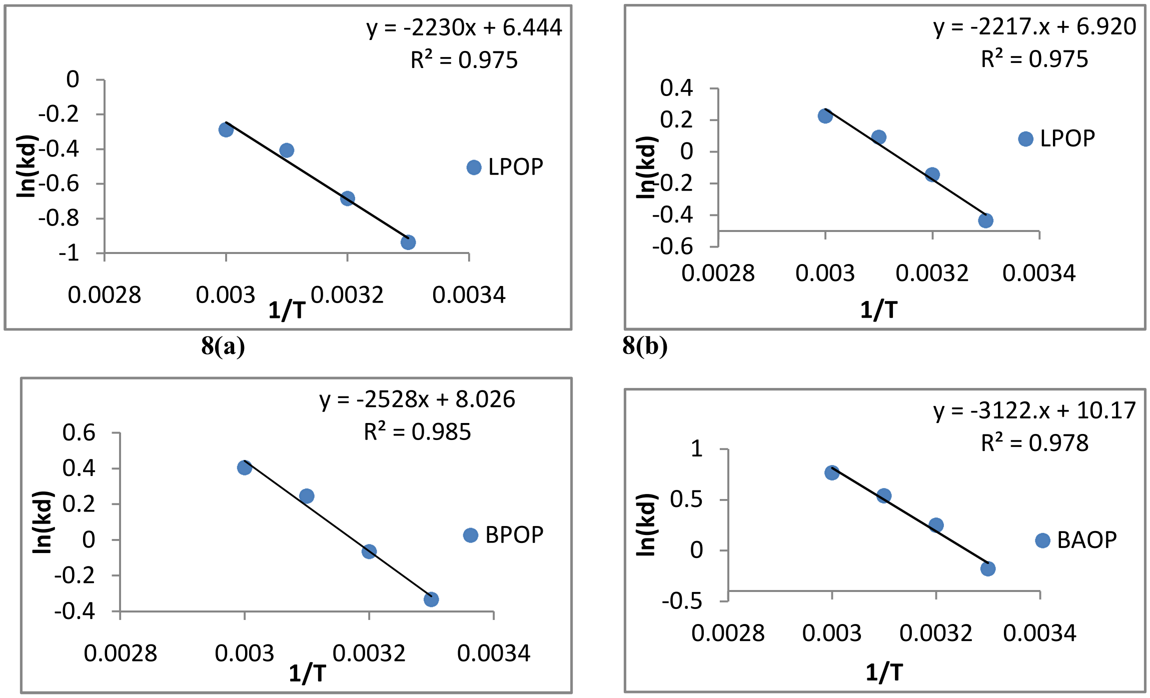
Bangham's pore diffusion equation:$\log[\log(C_i/C_i - q_t m)] = \log(ko/2.303V) + \alpha\log(t)$

Elovich equation:$q_t = 1/\beta\ln(\alpha\beta) + 1/\beta\ln(t)$

Graphs of the above said dynamic models, rate constants and correlation coefficients were displayed in **Tables 5-9.**Among the five dynamic models, leaves, bark powder ash of Pomegranate's R^2 determination for Weber and Morris is $R^2 = 0.991$, Bangham's pore dispersion is $R^2 = 0.991$ pseudo first-arrange is $R^2 = 0.982$, pseudo second-arrange is $R^2=0.951$ and Elovich demonstrate is $R^2=0.979$.

Effect of Temperature

By administering the extraction experiments at various temperatures of 298, 308, 318, and 328 K at absolute extraction states, the influence of temperature upon that MR's percent evaluation MR was studied: pH - 4.0; sorbent measurement - 3.0 mg/L; contact time - 90 min; particle determiner - 45 work; MR colour arrangement mixing - 100 mg/L; results plotted as ln(Kd) Vs 1/T as shown in **Figure 8**.



8(a) **8(b)**

8(c) **8(d)**

Figure 8 Effect of temperature

Thermodyanamic characters of the adsorption method, like variation in free vitality (ΔG) kJ/mole, enthalpy variation - ΔH kJ/mole also entropy variation - ΔS KJ/mole too were found in varyingbyusing the conditions [38-40].

$$\Delta G = -RT\ln K_d$$

$$\ln K_d = \Delta S/R - \Delta H/RT$$

$$K_d = q_e/C_e$$

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

Here, Kd - dissemination adsorption coefficient, q_e- amount of MR adsorbed on adsorbent per lit. of deposition at harmony, C_e- the MR colour deposition's steadiness centralization, T - outright temperature in Kelvin and R - the gas steady.

ΔG, ΔH and ΔS are the adaptations in free vitality, enthalpy and entropy.

The approximations of ΔH and ΔS were obtained from slope and apprehend of a plot in the middle of ln(Kd) and 1/T and ΔG characters were acquired from the relation ΔG = ΔH-TΔS and classified [41-42]. It has been observed that with rise in temperature from 298-328K, 25-55°C, maximum extraction of MR takes place at 328K.

The results shown in Table 10, indicates that the determinations of ΔH are possible, thereby illustrates the physical sorption and endothermic nature of adsorption [43]. Endothermic nature of adsorption process is shown by the 2 values close to one. The constructive determinations of ΔS illustrate enlarge matter and deformity at the powerful ordering interface of MR colour with adsorbent [44,45].The obstruction findings of ΔG show that the adsorption method's spontaneous process indicates that the adsorptive strength is sufficiently solid to overcome the potential impediment [46,47].

Applications of the developed Bio-Sorbents

The acceptability of the strategies generated with the latest bio-sorbents obtained from Pomegranate for expelling MR dye in waste waters, was tried with few authentic sewage/emanating tests of a small number of businesses. At that moment the samples were exposed to withdrawal of the colour using the bio-sorbents generated as a segment of present study at absolute states of extraction. The end results acquired were exhibited in **Table 12**.

Table 12 % Removal of MR from effluviumusing bio-sorbents proceeded in current work 80 - 90 middlevalues

Bio-Sorbents	**% Removal of MeR in varied samples**					
	Sample -1 Delivered with 10.0 ppm MR dye	**Sample -2** Delivered with 15.0 ppm MR dye	**Sample -3** Delivered with 20.0 ppm MR dye	**Sample -4** Delivered with 25.0 ppm MR dye	**Sample -5** Delivered with 30.0 ppm MR dye	**Sample -6** Delivered with 35.0 ppm MR dye
Powder of Pomegranate leaves: 2.0 g/L	83.5%	89.1%	86.5%	88.3%	87.4%	82.1%
Powder of Pomegranate bark: 2.0 g/L	89.1%	88.2%	85.2%	86.4%	88.2%	85.5%
Ashes of Pomegranateleaves: 1.75g/L	88.5 %	82.3%	86.4%	81.5%	85.3%	84.6%
Ashes of Pomegranate bark: 1.5 g/L	86.3%	86.5%	84.4%	88.3%	89.5%	83.5%

Conclusion:

The circumstances for the majority uttermost removal of MR at lowest measurement and time of equilibration were upgraded. At pH: 4 the leaves and bark of Pomegranatehave shown reasonable bias MR. Sorbent quantity and time needed for greatest expulsion of MR is low for the blazing leftovers than with the raw powder of the plant substances. Fivefold abundance of normal negative ions found in common waters, haven't interfere the withdrawal of MR at absolute conditions of pH, equilibration time and sorbent focus. Cations like $Ca^{2+,}$ Mg^{2+} and Cu^{2+} have illustrated little obstruction, whereas Fe^{2+} and Zn^{2+} have collectively shown the most extreme removal of the colour.

The four Isotherms, the interconnection coefficient determination of leaves, bark powders and fiery debris of Pomegranate for the large interconnection coefficient for Freundlich isotherm esteem, Langmuir isotherm and indefinite splitting calculateisperceivedas a part in0-1 span, illustrate the favourabilityof Langmuir isotherm upon Freundlich isotherm. The five dynamic models, Weber and Morris' interconnectivity coefficient determination for leaves, bark powders, with fiery remnants of Pomegranate, and Bangham's pore dispersion exhibit pseudo first-order, pseudo second-order, and Elovich displays, respectively. It illustrates that pseudo second-order model is pre-eminently suited to the examined data of the current contemplate adsorption substructure.The determinations ofΔH are definite; this displaysendothermic character and physical sorption of adsorption. The R^2readings close to, demonstrate the endothermic character of adsorption process. The productive determinations of ΔSmake evidenttheenlarged matter & irregularity inMR colour's tough ordering interface with adsorbent.

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