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ISOTHERMAL KINETIC STUDY ON REMOVAL OF METHYL RED DYE FROM AQUEOUS SOLUTIONS USING GUAVA BARK

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In this work, bark of the Guava tree, *Psidium guajava* L. was used as adsorbent for removal of synthetic dye, *i.e.* Methyl Red which has given promising results in industrial application. The present investigation involves an isothermal kinetic study of the use of Guava bark as an efficient, low cost adsorbent to remove methyl red dye from aqueous solutions. Guava bark powder is used as a biosorbent. Methyl red dye concentration is determined in prepared aqueous absorbance - concentration curve. The solutions through structural characterization of Guava bark (GB) powder was done by electron microscopy. The adsorption behaviour of the biosorbent was investigated by performing both kinetic and equilibrium isothermal studies. During study the adsorption conditions were calculated by changing different experimental parameters *i.e.* agitation time, adsorbate concentration, adsorbent concentration, and pH of the solution. Langmuir and Freundlich adsorption isotherms are plotted for analyzing the percentage of methyl red removal. The adsorption studies fit with Langmuir isotherm. The correlation coefficient value indicates a moderate fit for monolayer Langmuir model. Pseudo second order kinetics found to provide a better fit to the data than pseudo first order kinetics.

Key words: Adsorption, Guava bark, Isothermal studies, Langmuir Isotherm and Methyl Red.

Introduction

Textile industry is a booming industry in Rajasthan. Several dyes are used in textile industry for dyeing different types of fabrics^{1,2}. The practice of dyeing has been used from ancient times. Sea snails from the Mediterranean Sea were crushed in their thousands to obtain very small quantities of the dye which was used to dye the robes of Emperors of Rome³. Dyes have been traditionally obtained from many natural sources such as roots, berries, bark, and leaves². However, dyes which are obtained naturally, encounter various problems such as reproducibility of colour, sustainaibility and cost of production⁴. These problems have largely been resolved by the creation of synthetic dyes as evidenced by the modern omnipresence of cheap, colorful clothing⁵. But the advent of synthetic dyeing has however created its own problems. Among them, the major problem is issue of waste.

Synthetic dyes from many industrial effluents exhibit a certain degree of toxicity when ejected into the water supply and are showing adverse effects on aquatic flora and fauna⁶. Therefore, there is an utmost need of their safe and effective isolation or any possible neutralization of their toxic effects, without creation of further toxicity. There are so many methods used currently for dye removal such as Ion Exchange⁷. Coagulation⁸ and membrane processes⁹ but each one of the methods has some distinct disadvantages

that are impedimental to their deployment on an industrial scale. For this reason, an alternative process is being investigated as a method of removing dyes from solution *i.e.* Adsorption. Adsorption is the process of an adsorbate molecule adhering to the surface of adsorbent molecule¹⁰. Adsorption has gained prime importance in industry and environment protection over the last few years¹¹. Adsorbents from natural sources like mango peel¹², banana peel¹³, coconut bunch waste¹⁴, Wheat husk¹⁵, tree bark¹⁶, orange peel¹⁷ have been used for this purpose.

In the present work, efforts have been made to determine adsorption efficacy of one of the low costs biosorbent as Guava bark (GB) powder for removal of Methyl Red (MR) from aqueous solutions. Guava tree *(Psidium guajava)* is a source of Guava bark.

Material and Methods

The following instruments are employed in this work: Digital Electronic weighing balance (Citizen, Model no.100 C); Digital pH meter (Electronic India, El Model 112) ,a Spectrophotometer (Digital UV Spectrophotometer, Model GE Ultrospec 7000 UV Spectrometer); Orbital Shaker (Remi Instrument Ltd., IHB, 597) ; Oven (220/230 AC supply, Tanco, QS 9001; 2008, WHO, GMP); 40 BSS sieve (Bhushan Engineering and Scientific Traders)¹⁸.

Preparation of Adsorbate (Methyl Red Dye solution) –

Solid Methyl Red (MR) of analytical grade (1 g) was placed in a 1 L volumetric flask, which was then filled up to the mark with distilled water. The flask was shaken until all the MR had dissolved. This resulted in the creation of a 1000 ppm solution (stock solution). Solutions of different concentrations (100, 200, 300, 400 and 500 ppm) were then prepared from the stock solution by dilution. The physical characteristics of MR dye is given in Table 1.

Property	Value
Name	Methyl Red /
	2-(N,N-dimethyl-4-aminophenyl)azobenzenecarboxylic acid
Molecular Formula	C15H15N3O2
Molecular Weight / g mol ⁻¹	269.30
State	Crystalline Solid
Melting Point / ^o C	179 – 182

Table 1: Physical characteristics of dye



Figure 1: Chemical structure of Methyl Red Dye

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Wavelength(nm)	Absorbance
220	1.434
240	1.258
260	1.127
280	1.022
300	0.850
320	0.612
340	0.513
360	0.528
380	0.576
400	0.604
420	0.591
440	0.553
460	0.463
480	0.318
500	0.179
520	0.105
540	0.081
560	0.074
580	0.073
600	0.073
620	0.070
640	0.065
660	0.056
680	0.089
700	0.081

Table 2: Variation in absorbance withwavelength for MR dye

Preparation of Adsorbent (Guava Bark Powder)¹⁹ and its characterization.

- 1. The bark was scraped off using a sharp knife from a Guava *(Psidium guajava)* tree found in Malviya Nagar, Jaipur, Rajasthan (India).
- 2. The bark was manually cleaned to separate unwanted substances from it.
- 3. The bark was then washed four times with tap water.
- 4. This was followed by washing three times with distilled water to remove dust and water soluble particles.
- 5. The wetted bark was wiped four times with filter paper to remove extra adhered water drops on outer surface.
- 6. After that the pieces of bark were ground into a fine powder with a mortar and pestle.

Finally, the powder was sieved through sieve 40 BSS. The powder so obtained was named as Guava Bark Powder (GBP) and stored in vacuum desiccators until required for adsorption experiments till then no other physical and chemical treatments were done.



Figure 2: Absorbance and wavelength curve

Determination of λ_{max}

 λ_{max} for MR dye was obtained by GE Ultrospec 7000 UV Visible spectrophotometer. A graph was plotted of absorbance versus wavelength from the data in Table 2 and shown in Figure 2. λ_{max} was found to be 400nm.

Calibration curve

Absorbance readings were taken from Table 3 for each of the 100, 200, 300, 400 and 500 ppm solutions at λ_{max} in order to construct a calibration curve of Absorbance vs Concentration (Figure 3).

From this curve, the concentration of MR was extrapolated from absorbance readings.

Table 3: Absorbance for different concentration of MR dye solution

Concentration / ppm	Absorbance
100	0.609
200	1.142
300	1.735
400	2.454
500	2.821



Figure 3: Calibration Curve

Adsorption studies

250 ml Erlenmeyer flask was utilized to carry out batch sorption experiments in which 0.20 g of the adsorbent, guava bark powder (GBP) and 50 ml of MR dye solution (100 – 500 ppm) at a pH of 4.2 were added at 30° C. 1 M NaOH and 1 M HCl solutions were introduced to maintain the pH of solution.

The Erlenmeyer flasks were capped and agitated in an isothermal shaker at 100 rpm at 30° C for 3 hours to achieve equilibrium. UV-Visible spectrophotometer for MR dye is used to determine concentrations of dye in the solution after equilibrium adsorption at 400 nm¹⁸.

The amount of adsorption at

equilibrium, qe (mg/g), was calculated by eqn.1:

Where C_0 and C_e (mg/L) are the liquid – phase concentration of dye at initial and equilibrium state respectively, V is the volume of the solution (L) and W is the mass of adsorbent used in grams (g).

Kinetic studies of adsorption were also carried out at various concentrations of MR and the extent of adsorption was investigated as a function of time. The amount of adsorption at time t, q_t (mg/g), was calculated by eqn. 2:

Langmuir and Freundlich isotherms were used for studying mode of adsorption.

Kinetic study was done by using pseudo first order and second order plots.

Results And Discussion

Effect of initial dye concentration-

Figure 4 shows the effect of initial MR concentration (100 - 500 ppm) on the intake rate of MR by GBP with an adsorbent dosage of 0.20 g and mixing speed of 100 rpm by plotting a graph between Concentration of Adsorbate V/s Time. A gradual decrease in the rate of adsorption at all concentrations with agitation time until equilibrium was attainted within three hours was noticed. The amount of MR dye increased from

17.4 to 50.9 mg/g adsorbed at equilibrium (qe) as the concentration of dye was increased from 100 to 500 ppm. The reason being the generation of a driving force by the initial dye concentration to overcome all mass transfer resistances of the dye between the aqueous and solid phases. So, the adsorption process accelerates due to a higher initial concentration of dye.

The % MR removal decreased from 69.6% to 41.8% as concentration was increased from 100 to 500 ppm (Figure 5). Equilibrium conditions were reached within 3 hours^{20,21}.



Figure 4: Effect of initial dye concentration on removal of MR by GBP (conditions: sorbent dosage, 0.20 g; initial pH, 4.2; temperature, 30°C; particle size, 40 BSS; stirring rate, 100 rpm; V, 50 ml, dye concentration, 100-500 ppm: agitation time, 3 h)



Figure 5: Percentage removal of MR by GBP (conditions: sorbent dosage, 0.20 g; initial pH, 4.2; temperature, 30°C; particle size, 40 BSS; stirring rate, 100 rpm; V, 50 ml; dye concentration, 100 – 500 ppm; agitation time, 3 h)

Effect of biosorbent dose -

Another important criterion is biosorbent dose as it regulates the capacity of a biosorbent for a given initial concentration of adsorbate. Experiments were performed with constant dye concentration (300 ppm) and samples with biosorbent dosages ranging from 0.10 to 0.50 g under a constant temperature of 30 °C and at a pH of 4.2 for 3h to explore the effect of biosorbent dosage on adsorption. It was noted that the percentage of dye adsorption increased with adsorbent dose¹⁸. Dye removal increased from 42.9% to 78.3% with the increase of sorbent dose from 0.10 to 0.50 g (Figure.6). The reason being an increase in the adsorbent surface area and the availability of more active and available sites.



Figure 6: Effect of Biosorbent Dosage (g) on percentage removal of MR by GBP (conditions: initial pH, 4.2; temperature, 30°C; particle size, 40 BSS; stirring rate, 100 rpm; V, 50 ml; time, 3 h; Dye concentration, 300 ppm)

The above plot indicates that adsorption increases with adsorbent dose. A certain amount of dye is adsorbed by a fixed mass of adsorbent. The higher the adsorbent dose, the greater the purifiable volume of aqueous solution of dye. Removal of methyl red from aqueous solution by activated carbon prepared from the *Annona* squamosa seed²², banana pseudostem fibers^{22,23} was also observed. Effect of Agitation Time-

The efficiency of adsorption can well be explained with the help of Variation in agitation time. Batch equilibrium studies were carried out by adding a fixed amount of sorbent (0.20 g) to 100 ppm dye solution at 4.2 pH at 30° C (Figure 7).



Figure 7: Effect of Agitation time on percentage removal of MR by GBP (conditions: sorbent dosage, 0.20 g; initial pH, 4.2; temperature, 30°C; particle size, 40 BSS; stirring rate,100 rpm; V, 50 ml; time, 3h; dye concentration, 100 ppm)

Agitation of the flasks in a shaker at 100 rpm for 3 hours is carried out. Aliquots were taken at different times (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 h) and their concentrations were analyzed. Percentage removal of dye increases with increased contact time, percentage removal of dye increased from 26.2% to 69.6% and correspondingly equilibrium concentration Ce decreased from 73.8 ppm to 30.4 ppm on increasing agitation time from 0.5 to 3h. It is because of greater number of collisions between adsorbate and adsorbent taking place in an increased time span^{21,23}.

Effect of pH –

Study of the effect of pH on adsorption was done using a dye solution of concentration 100 ppm over a pH range of 2 -12 at 30 °C as given in Figure 8 Dye removal increased from 52.24% to 69.6% as pH increased from 2 to 4 and then decreased and became constant up to pH 12. qe was found to increase with increasing pH from 13.06 to 13.93 mg/g. In the acidic medium, a positive charge accumulates on the adsorbent surface, causing an increase in the electrostatic attraction between anionic dye molecules and the surface of the adsorbent. As a result, there is an increase in rate of dye adsorption. On the other hand, the presence of a high concentration of hydroxyl ions (OH⁻) on the adsorbent in the basic medium at pH range of 8 - 12 competes effectively with the dye molecules, leading to decreased percentage adsorption for both dyes onto the surface of the adsorbent.

 Table 4: pH and percentage removal

pН	C _e (ppm)	% removal	<u>e</u> (mg/g)
2	47.76	52.24	13.06
4	30.37	69.63	17.41
6	39.06	60.94	15.24
8	40.8	59.2	14.8
10	44.28	55.72	13.93
12	44.28	55.72	13.93

The result show similarity as findings of removal of methyl red from

aqueous solution by activated carbon prepared from the *Annona squamosa* seed²² and by Neem (*Azadirachta indica*) leaves for removal of organic pollutants²⁴.

The results of all parameters are summarized in table 5.

Adsorption isotherms

The adsorbate concentration in the bulk and the adsorbed amount at the interface can be related by means of adsorption isotherms. The isotherm results were analyzed using the Langmuir and Freundlich isotherms. The Langmuir adsorption model²⁵. It assumes that maximum adsorption corresponds to a saturated mono layer of solute molecules on the adsorbent surface, with no later interaction between the adsorbed The expression of the molecules. Langmuir model is given by Eq. (3)

$$q_e = \frac{Q_o b C_e}{(1 + b C_e)} \tag{3}$$

Where qe (mg/g) and Ce (mg/L or ppm) are the amount of adsorbed dye per unit mass of sorbent and unadsorbed dye concentration in solution at equilibrium, respectively. Qo is the maximum amount of dye per unit mass of sorbent that forms a complete monolayer on the surface bound at high C_e, and b is a constant related to the affinity of the binding sites (L/mg). The Langmuir equation can be described by the linearized form:

$$\frac{C_e}{q_e} = \frac{1 + C_e}{Q_o}$$

А

graph between specific Ce/qe against equilibrium Ce gives linear plot (Figure

adsorption Ce/qe against equilibrium concentration Ce gives linear plot (Figure 9) which shows that adsorption of MR obeys the Langmuir model. The value of correlation constant (\mathbb{R}^2) is 0.990, which further indicates that adsorption linearly fits according to the Langmuir model. The Langmuir constants Q₀ and b were determined from the slope and intercept of the plot. The maximum adsorption capacity (Q₀) was found to be 66.66 mg/g.

Table 5: Result of parameters for adsorption of MR onto GBP (conditions: sorbent dosage, 0.20 g; initial pH, 4.2; temperature, 30 °C; particle size, 40 BSS; stirring rate, 100 rpm; V, 50 ml; agitation time, 3h; dye concentration, 100 – 500 ppm)

sunning rai	e, 100 Ipili, v, 30 Ill	i, agitation	time, Jii,	uye concer	illation, i	<u>00 – 300 p</u>	pin)
Agitation time / Dye concentration		0.5 h	1.0 h	1.5 h	2.0 h	2.5 h	3.0 h
	absorbance	0.45	0.38	0.32	0.28	0.25	0.20
	C _e (ppm)	73.8	61.7	51.2	44.3	39.1	30.4
	% removal	26.2	38.3	48.8	55.7	60.9	69.6
100 ppm	$q_e(mg/g)$	6.54	9.58	12.2	13.9	15.2	17.4
	C_e / q_e	11.3	6.44	4.20	3.18	2.56	1.74
	ln q _e	1.88	2.26	2.50	2.63	2.72	2.85
	ln C _e	4.3	4.12	3.94	3.79	3.67	3.41
	$q_e - q_t$	10.87	7.83	5.2	3.5	2.2	-
	$\log (q_e - q_t)$	2.40	2.06	1.65	1.25	0.78	-
	t/q_t	0.08	0.10	0.12	0.14	0.16	0.17
	absorbance	0.99	0.84	0.70	0.60	0.46	0.40
	C _e (ppm)	167.76	141.67	117.32	99.93	75.6	65.1
	% removal	16.1	29.2	41.3	50.0	62.2	67.4
E	$q_e(mg/g)$	8.06	14.58	20.67	25.02	31.10	33.7
udo	C_{e}/q_{e}	20.8	9.71	5.68	3.99	2.43	1.93
0 p	ln a.	5.12	2.68	3.03	4.60	4.33	4.18
200	In C.	2.08	4.95	4.76	3.22	3.43	3.52
	0 0.	25.65	19.13	13.04	8 70	2.61	-
	$\log (q_s - q_t)$	3 24	2.95	2 57	2.16	0.96	_
	t/a	0.062	0.069	0.073	0.080	0.080	0.089
	absorbance	1.35	1.16	1.03	0.000	0.85	0.005
	C. (ppm)	230.4	196.6	175.1	166.0	143.4	126.0
	% removal	23 2	34.5	41.6	44 7	52.2	58
-	a (mg/g)	17.4	25.8	31.2	33.5	39.1	43.5
ud	$q_e(ing/g)$	13.26	7.60	5.60	1.96	3.66	2 00
d (C_e / q_e	2.86	3.25	3.00	4.90	3.67	2.90
300	$\ln q_e$	5.44	5.25	5.17	5.11	1.07	1.87
		26.1	17.7	12.3	10.0	4.27	7.07
	$q_e - q_t$	20.1	2.87	2.51	2 20	4.5	-
	t/q	0.03	2.07	2.51	2.50	0.06	-
	t / q _t	1.60	1.58	1.40	1.22	1.15	1.15
	$C_{\rm c}$ (nnm)	273.8	270.2	220.1	225.1	1.15	1.15
	C_{e} (ppin)	215.0	270.5	40.0	42 7	50.0	50.0
_		21.54	22.4	40.0	45.7	50.9	50.9
ud	$q_e(mg/g)$	31.34	32.41	40.23	45./1	30.93	2.95
ld	C_e / q_e	8.68	8.34	5.94	2.79	3.85	3.85
00	$\ln q_e$	3.45	3.48	3.68	5.78	5.93	5.93
4	In C _e	5.61	5.60	5.48	5.42	5.28	5.28
	$q_e - q_t$	19.39	18.52	10.69	1.00	-	-
	$\log (q_e - q_t)$	2.96	2.92	2.37	1.98	-	-
	t/q_t	0.016	0.031	0.037	0.046	0,049	0.05
	absorbance	2.15	2.10	1.96	1.82	1.70	1./0
	C_e (ppm)	369.5	336.8	337.3	312.1	291.8	291.8
udd	% removal	26.1	37.8	32.5	37.6	41.8	41.8
	$q_e(mg/g)$	32.6	34.8	40.7	46.9	52.2	52.2
	C_e / q_e	11.3	10.4	8.29	6.64	5.58	5.58
00	ln q _e	3.49	3.55	3.71	3.85	3.96	3.96
2i	ln C _e	5.91	5.89	5.82	5.74	5.67	5.67
	q _e - q _t	19.57	17.39	11.52	5.22	-	-
	$\log (q_e - q_t)$	2.97	2.86	2.44	1.65	-	-
	t / q _t	0.015	0.029	0.037	0.043	0.048	0.057

The essential characteristic of the Langmuir isotherm can be expressed in term of a dimensionless constant separation factor R_L which is given by the following eq. (5):

where C₀ is the highest initial concentration of adsorbate (mg/L or ppm) and b (L/mg) the Langmuir constant. The value of R_L indicates the shape of the isotherms to be either unfavorable (R_L > 1), linear (R_L = 1), favorable ($0 < R_L < 1$), or irreversible (R_L = 0).



Figure 8: Effect of solution pH on removal of MR by GBP (conditions: sorbent dosage, 0.20 g; initial pH, 4.2; temperature, 30 °C; particle size, 40 BSS; stirring rate, 100 rpm; V, 50 ml; agitation time, 3 h; dye concentration, 100 ppm)



Figure 9: Langmuir isotherm for MR sorption onto GBP at 30°C

RL was found to be 0.126, indicating favorable linear adsorption of MR onto GBP. The

Freundlich Isotherm²⁵ describes a heterogeneous system by eq. 6. The Freundlich equation is expressed as:

To determine the constants K_F and n, the linear form of the equation was used to produce a graph of ln (qe) against ln (Ce) as in Figure 10. Values of K_F and n are calculated from the intercept and slope of the plot given by eq. (7).

$$\ln qe = \ln KF + (1/n) \ln Ce$$
(7)

The value of R^2 according to the Freundlich isotherm comes out to be 0.914. Given that this value is less than that of the Langmuir isotherm, it can be deduced that the Langmuir isotherm provides a better fit to the data, which in turn indicates that the system is best described by a monolayer adsorption model. The values of all constants are given in Table 6.

Table 6: Langmuir and Freundlich modelconstants and correlation coefficients forbiosorption of MR by GBP

Isotherm	Parameters
Langmuir isotherm	
Qo (mg/g)	66.66
b (L/mg)	0.0139
R ²	0.990
R _L	0.126
Freundlich Isotherm	
$K_{ m F}$	3.87
n	2.074
R ²	0.914



Figure 10: Freundlich isotherm for MR sorption onto GBP at 30°C

As seen in Table 6, the Langmuir isotherm provides a better fit to the experimental data as its correlation coefficient R^2 is 0.990, whereas in the case of Freundlich, the correlation coefficient R^2 is less than 0.99, indicating relatively poor agreement with the experimental data. The monolayer adsorption capacity according to the Langmuir model was 66.66 mg/g. The Langmuir isotherm fits well because of homogeneous distribution of active sites on the GBP surface.

Adsorption Kinetics

A linear form of pseudo-first-order kinetics²⁷ is given by Lagergren:

$$\log (qe - qt) = \log qe - k_1 t/2.303$$
.....(8)

A linear plot of log (qe - qt) against time allows one to obtain the rate constant (Figure 11). If the plot was linear with a good correlation coefficient, then it would indicate that Lagergren's equation is appropriate. Therefore, the adsorption process would be a pseudo-first-order process²⁸. Lagergren's first order rate constant (k_1) and qe as determined from the model 10 along with the corresponding correlation coefficients. It was found that the calculated qe values do not agree with the experimental qe values, which suggests that the adsorption of MR does not follow first order kinetics.

Pseudo second order kinetics²⁸may be expressed in a linear form as eq. (9)

$$t/qt = 1/k_2 q_e^2 + 1/q_e t$$
(9)

where the equilibrium adsorption capacity (qe), and the second order constants k_2 can be determined experimentally from the slope and intercept of a plot of t/qt versus t (Figure 12).



Figure 11: Pseudo first order sorption kinetics of MR onto GBP



Figure 12: Pseudo second order sorption kinetics of MR onto GBP

The values of k_2 and q_e determined from the model are presented in table 7 with their corresponding correlation coefficients. There is better agreement in terms of correlation coefficient values (R₂) for the pseudo second order model than for the pseudo first order model (table 7).

The equilibrium adsorption capacity according to the pseudo first

order model was found to be 58.55 mg/g while according to the pseudo second order it was 63.7 mg/g. The value obtained by the pseudo second order model better correlated with the maximum adsorption capacity obtained by the Langmuir adsorption isotherm (66.66 mg/g). Hence, the pseudo second order model better represents the adsorption kinetics.

P	Pseudo first order kinetic model			Pseudo s model	econd order kir	netic	
C initial,	q _e exp	K ₁	q _e cal	R ²	K ₂	q _e cal	R ²
(mg/L)	(mg/g)	(1/h)	(mg/g)		(g/mg h)	(mg/g)	
100	17.4	2.13	19.49	0.977	0.024	25.7	0.982
200	33.7	2.97	69.40	0.925	0.002	99.0	0.972
300	43.5	2.72	62.80	0.880	0.012	60.6	0.974
400	50.9	3.15	60.46	0.874	0.021	62.9	0.970
500	52.2	3.18	58.55	0.903	0.023	63.7	0.980

Table 7: Comparison of the pseudo first order and pseudo second order adsorption rate constants and calculated and experimental qe values obtained at different initial MR concentrations

Conclusion

Guava bark powder was investigated as an environmentally friendly adsorbent for use in adsorbing MR dye. It was found that on increasing concentration of MR, the percentage removal of dve decreased. The maximum absorption capacity according to Langmuir model was found to be 66.66 mg/g. On increasing adsorbent dose (0.10) g to 0.50 g), the percentage removal of dye increased (42.93% to 78.35%). The effects of pH on dye adsorption were also studied. The Langmuir isotherm $(R^2=0.99)$ provided a better fit for the data than the Freundlich isotherm, indicating GBP underwent that monolaver adsorption. Pseudo second order kinetics was found to provide a better fit to the data than pseudo first order kinetics.

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