

Research Article

Brilliant Green and Acid Orange 74 Dyes Removal from Water by *Pinus roxburghii* Leaves in Naturally Benign Way: An Application of Green Chemistry

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The purpose of this study was to use low cost and easily accessible biosorbent for batch-scale elimination of brilliant green and acid orange 74 dyes from aqueous solution. *Pinus roxburghii* leaves were utilized to study their dye-eliminating capacities. The adsorbent was characterized by FTIR, TGA, DTA, and SEM. The optimized conditions for brilliant green and acid orange 74 dye elimination were adsorbent dose, 1.2 and 1.8 g; contact time, 30 and 45 min; pH, 2 and 1; temperature, 50°C and 60°C; and agitation speed, 125 rpm and 50 rpm for BG and AO-74, respectively. Adsorption records well fitted Langmuir isotherm. Possibility of the procedure was shown by negative values of the thermodynamic parameter ΔG° for both dyes. Kinetic studies showed that adsorption of BG and AO-74 dyes from watery solution by PR leaves followed pseudo-second-order kinetics.

1. Introduction

Through the increasing use of a diversity of dyes, pollution by dye wastewater is becoming a serious problem. Nearly 3000 dyes exist in the world market, and more than 6000 dyes are released in wastewater every year all over the world [1]. Textile and paper mills produce extremely colored industrial wastewater, which includes elevated BOD and floating solids that reduce the DO level for marine animals [2]. Synthetic dyes are extensively used in lots of industries [3]. Their occurrence in water is extremely lethal yet noticeable at very small concentration (1 ppm) [4]. Amongst the chemical group of dyes, azo dyes are more adaptable and account for more than half of the yearly dye manufacture [5]. It has been anticipated that, in 2003, yearly production of dyes was more than 7×10^5 metric tons [6]. Brilliant green is a synthetic organic dye. It is used in textile dyeing and paper printing [7]. It is very toxic if entered into the biological system. Its hazardous effects were studied in bacteria and rats [8], damaging their reproductive system and renal

tissues [9]. Acid orange 74 is a monoazo acidic dye, used for textile dyeing. [10]. Their structures are given in Figure 1, and their properties are given in Table 1.

A variety of techniques are used for handling wastewater such as coagulation, precipitation, photocatalytic degradation, ozonation, desalination, etc. [11], but adsorption has been set to be of better quality to other wastewater handling methods because of its low cost, simple design, easy handling property, and less susceptibility to poisonous substances [12]. This study includes batch-level elimination of BG and AO-74 dyes from aqueous solution, exploiting *Pinus roxburghii* leaves. They are also famous as chir pine or longleaf pine named after William Roxburgh. It is dispersed in the Himalayan districts of Bhutan, Nepal, Kashmir, Sikkim, Tibet, and India. It has numerous remedial uses. Its timber is pungent and used in tonic. It is helpful in eyeball, ear, and pharynx diseases [13]. This research work was carried out to characterize PR leaves to estimate their absorptive uniqueness for removal of BG and AO-74 dyes.

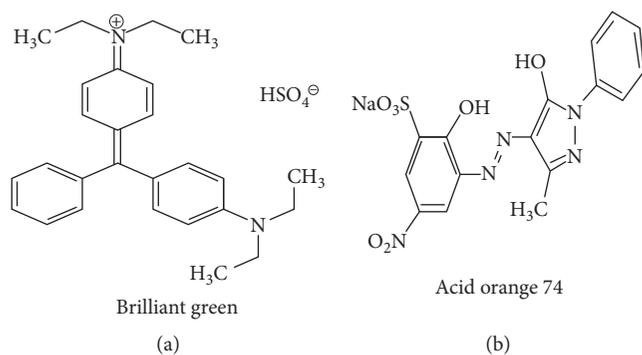


FIGURE 1: Structure of dyes. (a) Brilliant green. (b) Acid orange 74.

TABLE 1: Properties of BG and AO-74 dye.

Properties	BG values	AO-74 values
Class	Synthetic organic dye	Single azo dye
Molecular formula	$C_{27}H_{34}N_2O_4S$	$C_{16}H_{12}N_5NaO_7S$
Molecular weight	482.63 g/mol	441.35 g/mol
Maximum absorption	625 nm	455 nm
Solubility	Soluble in water and alcohol with green color	Soluble in water and ethanol

2. Experimental Work

2.1. Reagents and Instruments. Brilliant green dye (λ_{max} : 625 nm), acid orange 74 dye (λ_{max} : 455 nm), 0.1 M HCl, 0.1 M NaOH (Friends Laboratory Chemicals), UV/Vis spectrophotometer (UVD-3500), orbital shaker (model OSM-747), Agilent Cary 630 FTIR, and SEM (S2700 Hitachi, Japan).

2.2. Preparation of Biosorbent. PR leaves were taken from the botanical garden of Punjab University, Lahore. They were cleaned with water and dried in sunshine for 5-6 days. Afterwards, they were crushed into fine powder with an electric grinder and sieved through 40–60 mesh sieves.

2.3. Adsorption Experiment. Stock solution of dyes was made from 0.1 g of dye in a 100 mL measuring flask and diluting it up to the mark with distilled water. The standard solution (5–30 ppm) was made by diluting the stock solution. The batch experiments were performed with 100 ml of dye solutions of 30 ppm. A measured quantity (0.2 g) of adsorbent was added to the sample solution and agitated at 75 rpm for half an hour in an orbital shaker. The effect of contact time, sorbent dosage, pH, temperature, agitation speed, and initial dye concentration has been studied. Solutions were filtered from the flask at a prefixed time, and the absorbance of the filtrate was noted by using a UV/Vis spectrophotometer [14]. Adsorption percentage of dye can be calculated by using the following formula:

$$\text{adsorption (\%)} = C_o - \frac{C_e}{C_o} \times 100, \quad (1)$$

where C_o is the early concentration of dye and C_e is the absorption at stability.

The amount of the coloring agent adsorbed per unit of PR leaves can be calculated with the following formula:

$$q = (C_o - C_e) \frac{V}{m}, \quad (2)$$

where q is the quantity of the coloring agent adsorbed by the adsorbent (mg/g), V is the amount of dye solution in L , and m is the mass of PR leaves [15].

3. Results and Discussion

The adsorbent was characterized, and optimal state for batch-scale elimination of the colorant was established [16].

3.1. Characterization of Adsorbent. The effects of characterization of adsorbent are shown in Table 2, and FTIR spectra in Figure 2(a) had a strong peak at 3290 cm^{-1} that indicated the occurrence of O-H groups. Functional groups indicated by different vibrational frequencies were as follows: C-H stretching band was shown by peaks at 2918 cm^{-1} , C=O was shown by the band at 1612 cm^{-1} , aromatic ring was shown at 1439 cm^{-1} , C-O aliphatic acid was indicated at 1236 cm^{-1} and C-O-C functionalities were indicated at 1029 cm^{-1} . FTIR spectra of the adsorbent following color adsorption are given in Figures 2(b) and 2(c). The band of the pine leaves after dye adsorption indicated similar distinctiveness as that of the normal pine leaves apart from minute changes in the wave number of OH, C=O, and C-O-C peaks. The increase in wave number in the case of both dyes indicated that bonding of leaves might have occurred at these points [17] From Table 2, it is clear that PR leaves had 7% moisture. Bulk density and dry density were low, which showed that they are suitable material for adsorption. Porosity is the quantity for each component of the adsorbent. Porosity increases the adsorption ability of the sorbent. The iodine number confirms that it is unsaturated. The point of zero charge was three.

3.2. Effect of Adsorbent Dose. Adsorbent amount on adsorptive exclusion of BG and AO-74 dye using PR leaves as an adsorbent was calculated to be in the range of 0.2–2 g with a variation of 0.2 g. The effects are shown in Figure 3. The chart indicates relative reading of the adsorbent dosage effect of both dyes. BG and AO-74 dyes elimination increased up to a definite amount and then started decreasing to approximately stable values. Greatest % adsorption of 86.95% was obtained at 1.2 g for BG dye and 56.74% for AO-74 dye at 1.8 g. Dye exclusion effectiveness rises with rise in the adsorbent amount. But, greatest adsorption takes place when the amount is small. Active sites can be efficiently utilized when the dosage is low. When the adsorbent dose is more, less active sites are accessible, resulting in lower removal of dyes. When the process is in equilibrium, the active sites are not much inflated with the addition of more adsorbent dosage [18]. As adsorbent-adsorbent contact is more than adsorbent-adsorbate contact with increase in the sorbent amount, a minute quantity of adsorbent dosage can eradicate great quantity of dye from contaminated water [19].

TABLE 2: Analysis of leaf powder.

Characteristics	PR leaves
pH	3
Moisture	7%
Bulk density	0.44
Dry density	0.300
Porosity	0.95%
Iodine number	20.17 mg/g
pH _{pzc}	3

3.3. Effect of Contact Time. Contact time was calculated from 15 to 90 min with a difference of 15 min. Figure 4 shows the results of the relative effect of contact time on biosorptive removal of BG and AO-74 dyes using PR leaves. It is obvious from the results that BG dye showed more percentage removal than AO-74 dye. Optimal contact time for BG was 30 min with percentage exclusion of 81.44%, and for AO-74, contact time was 45 min with percentage removal of 51.54%. Biosorptive removal of dyes improved with rise in contact time till an optimal contact time was obtained [20]. The speed of biosorptive removal is better in the initial stages of process because more adsorption sites are available. But after sometime, adsorbed dye ions repel from other unadsorbed dye ions and prevent their adsorption towards inner active sites of the biosorbent [21].

3.4. Effect of pH. pH was observed within the pH range of 1–10. Results are given in Figure 5. From the graph, it is clear that the optimal pH rate for BG was 2 with a percent removal of 90.93%, and for AO-74, the pH rate was 1 with an adsorptive removal of 55.94%. It is known that, at low pH, cationic sites of functional groups are more than anionic sites, which can chelate basic dye ions during biosorption. In the alkaline range of pH, more OH⁻ ions hinder adsorption of anionic dye due to repulsion forces. While the pH of this system is reduced, more adsorptive removal of both dyes occurs because of chelation forces [22].

3.5. Temperature Effects. Temperature is an important parameter. It affects the adsorption procedure on a huge scale. The results of temperature effects were observed in the range of 20–70°C. Figure 6 indicates that greatest removal of BG dye occurred at 50°C with a percentage removal of 94.37%. AO-74 dye gave a maximum adsorption of 17.90% at 60°C. Adsorption rises by increase in temperature. This indicates that high temperature favours this process because of its exothermic nature. It results in increase in entropy of the system, which in turn speeds up the process. Dye molecules agitate more and strike more with active binding sites at higher temperature of the solution. In addition to this fact, another reason is that inflammation of biological material at higher temperature exposes more active sites of inner sides of PR leaves. This helps more in adsorptive removal of these dyes [23].

3.6. Effect of Agitation Speed. Agitation speed was observed in the range of 25–175 rpm. From Figure 7, it is observed that optimal agitation speed for exclusion of BG dye using PR

leaves was 125 rpm with adsorptive removal of 76.58%. Maximum agitation speed for AO-74 dye was 50 rpm with percent removal of 30.40%. Increase in agitation speed helps in more interaction of dye molecules with binding sites of PR leaves. Agitation is capable of reducing the external boundary sheet resistance and raises the movement of the procedure [24].

3.7. Isothermal Study. Adsorption isotherms were observed by the use of optimal state of every parameter. Mechanism of adsorption was fixed.

3.7.1. Langmuir Isotherm. Langmuir isotherm is useful for the purpose of greatest sorption ability. Linear form of representation is

$$\frac{1}{q_e} = \frac{1}{bq_{\max}} \cdot \frac{1}{C_e} + \frac{1}{q_{\max}}, \quad (3)$$

where b and q_{\max} are called the Langmuir constants, q_e is the equilibrium uptake ability (mg/g) of the adsorbent, q_{\max} is the maximum uptake ability of the adsorbent, and C_e is the equilibrium impurity absorption in solution. From the chart, standards of these effects were calculated. R_L is the separation factor, calculated from Langmuir constants via the following formula:

$$R_L = \frac{1}{1 + bC_o}. \quad (4)$$

The value of R_L shows the isotherm either to be unfavorable ($R_L > 1$), linear ($R_L = 0$), favorable ($0 < R_L < 1$), or irreversible ($R_L < 0$). The values of R_L for the adsorption of both dyes onto PR leaves were less than one, which implies that the adsorption of dyes on them was a favorable procedure [25]. Correlation coefficient values R^2 and q_{\max} were higher for BG dye, which indicates that it adsorbed better than AO-74 for adsorption. Comparative graph of Langmuir isotherm is given in Figure 8, and Langmuir parameters are given in Table 3. Maximum removing capacities were compared with reported adsorbents in Table 4, and it was found that the PR leaves are very effective like other testified agrowaste materials for elimination of these toxic dyes from wastewater streams.

3.7.2. Freundlich Isotherm. According to this, multilayer adsorption occurs on the outer uneven surfaces of PR leaves. Its mathematical form is

$$\log q_e = \log K_f + \frac{1}{n} \log C_e, \quad (5)$$

where “ K_f ” and “ n ” are the Freundlich constants, associated to adsorption ability and adsorption strength correspondingly [39]. Relative Freundlich isotherms are shown in Figure 9, and Freundlich parameters are given in Table 5.

3.8. Thermodynamic Study. Thermodynamic behavior of adsorption of BG and AO-74 dyes onto PR leaves was calculated by the following equation:

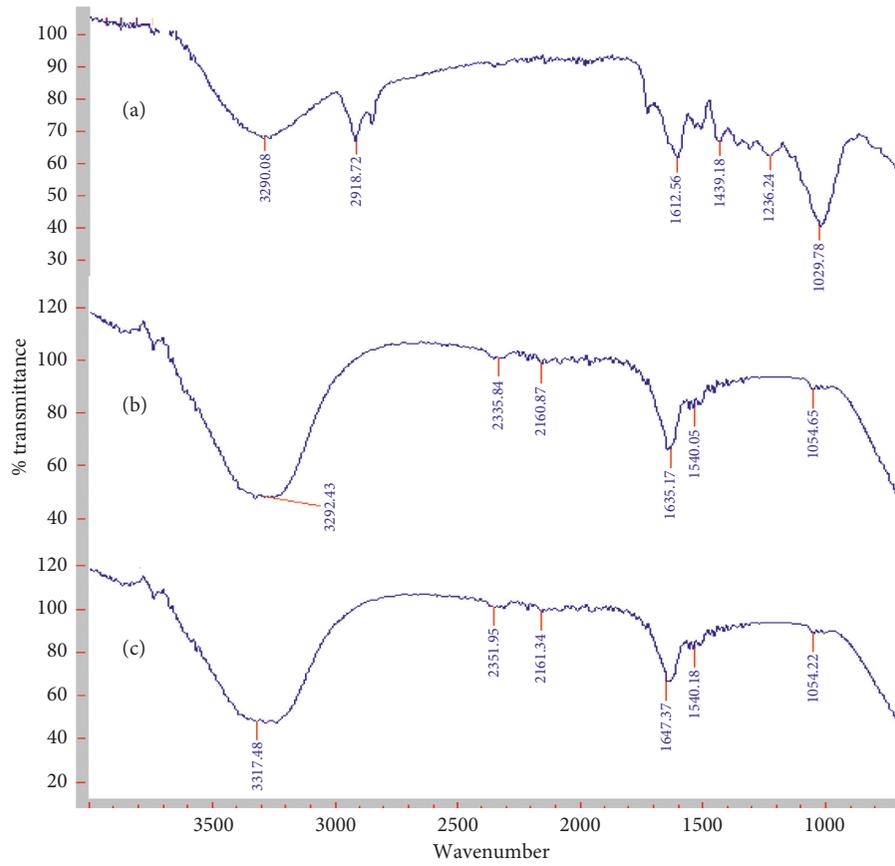


FIGURE 2: FTIR of (a) PR leaves, (b) PR leaves after adsorption of BG dye, and (c) PR leaves after adsorption of AO-74 dye.

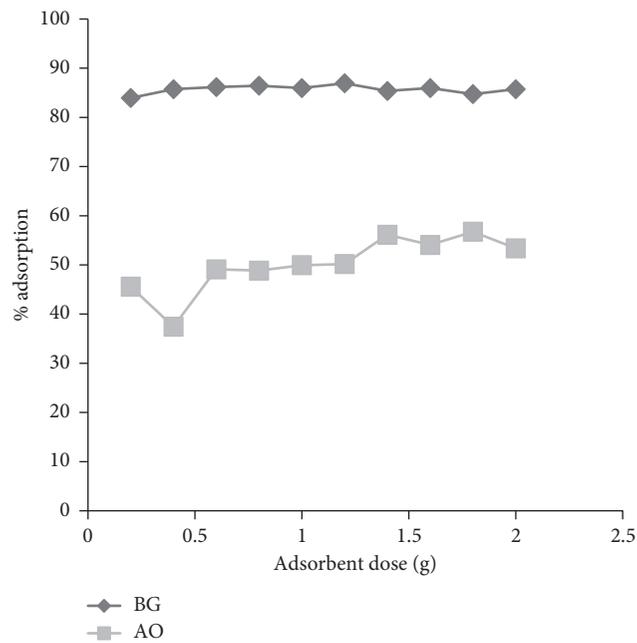


FIGURE 3: Graphical illustration of relative adsorbent dosage results for BG and AO-74 dye elimination by PR leaves.

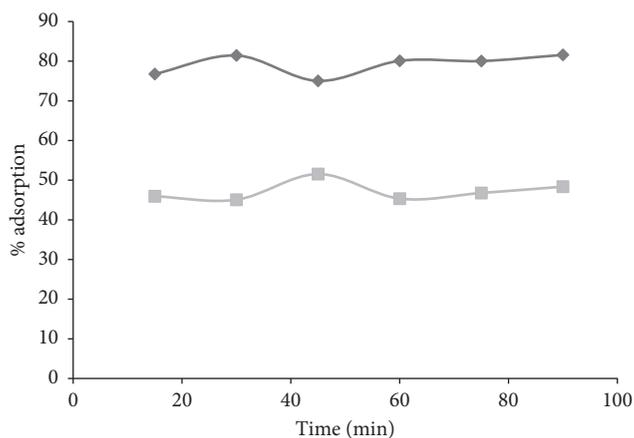


FIGURE 4: Graphical illustration of contact time effect on BG and AO-74 dyes removal by PR leaves.

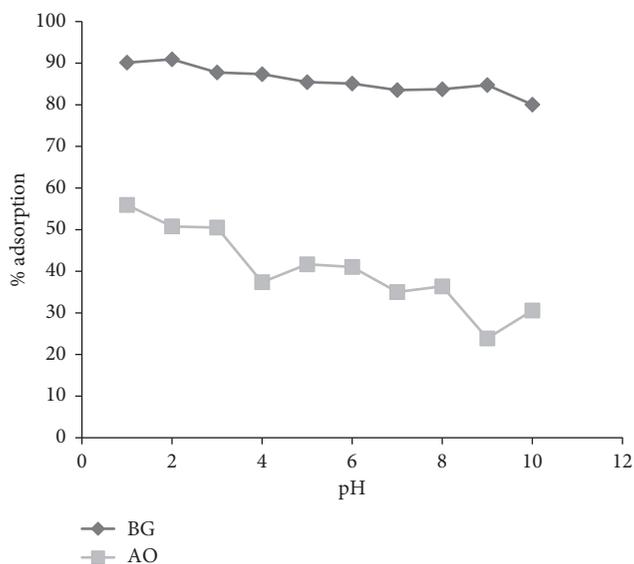


FIGURE 5: Graphical illustration of relative pH effect on BG and AO-74 dye removal by PR leaves.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ,$$

$$\log \frac{q}{C_e} = \frac{-\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R}. \quad (6)$$

A graph was plotted for $\log q/C_e$ and $1/T (K) \times 10^3$. The slope gives the value of ΔH° , and the intercept gives the value of ΔS° [40]. Thermodynamic parameters are given in Table 6. The negative values of ΔH° and positive values of ΔS° show the exothermic temperament and arbitrariness at the solid solution boundary taking place in the interior arrangement of the adsorption correspondingly [41]. The negative value of Gibbs free energy (ΔG°) indicates a favorable and spontaneous adsorption procedure at these temperatures [42, 43].

3.9. Kinetic Study. To study the procedure of adsorption, pseudo-first-order and pseudo-second-order models were

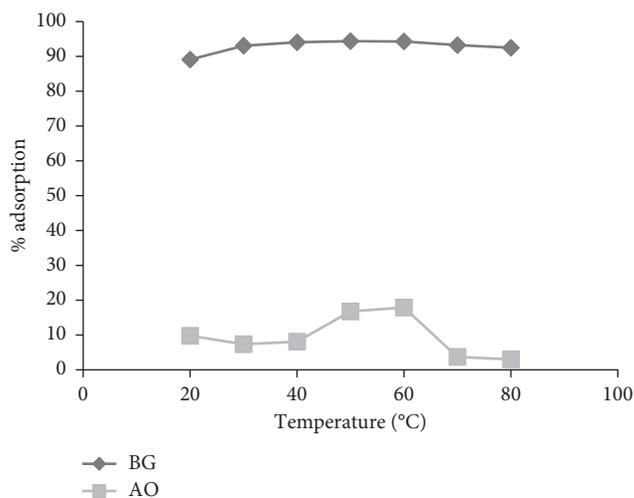


FIGURE 6: Graphical illustration of relative temperature effect on BG and AO-74 dye elimination by PR leaves.

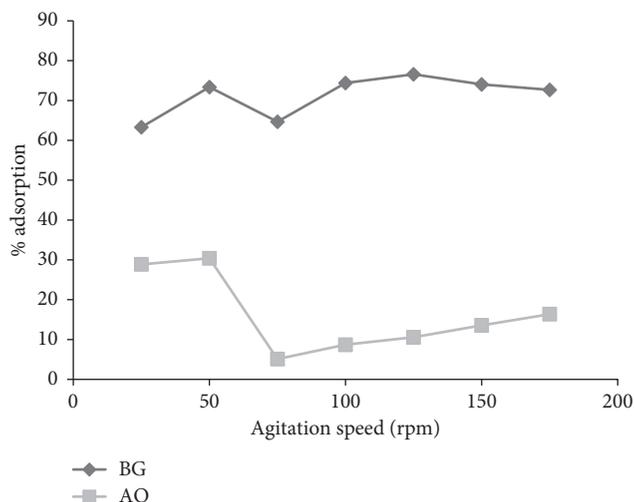


FIGURE 7: Graphical illustration of agitation speed effect on BG and AO-74 dye elimination by PR leaves.

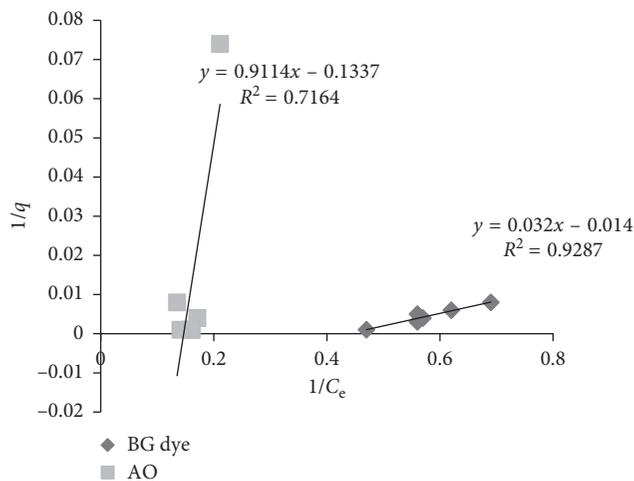


FIGURE 8: Graphical representation of comparative Langmuir isothermal parameters.

TABLE 3: Langmuir parameters for removal of dyes by PR leaves.

Dyes	R^2	q_{\max}	b	R_L
BG	0.928	71.42	0.44	0.07
AO-74	0.716	7.52	0.145	0.18

TABLE 4: Reported adsorbents and their removal capacity for BG and AO dyes.

	q_{\max} (mg/g)	Reference
<i>Adsorbents for BG dye</i>		
Kaolin	65.42	[7]
Modified rice straw	256.41	[26]
<i>Luffa cylindrica</i> sponge	18.2	[27]
<i>Cempedak durian</i>	0.203	[28]
Saklikent mud	1.18	[29]
Ashoka leaf powder	125	[30]
<i>Psidium guajava</i> leaves	1.075	
<i>Solanum tuberosum</i> peels	1.173	[31]
PR leaves	71.42	This study
<i>Adsorbents for AO dye</i>		
Clinoptilolite	44.05	[32]
Brown macro alga <i>Stoechospermum marginatum</i>	35.62	[33]
Spent brewery grains	28.54	[34]
<i>Paulownia tomentosa</i> Steud leaf powder	10.5	[35]
<i>Azolla rongpong</i>	69.93	[36]
<i>Azolla filiculoides</i>	67.1	[37]
Canola stalks	25.06	[38]
PR leaves	7.52	This study

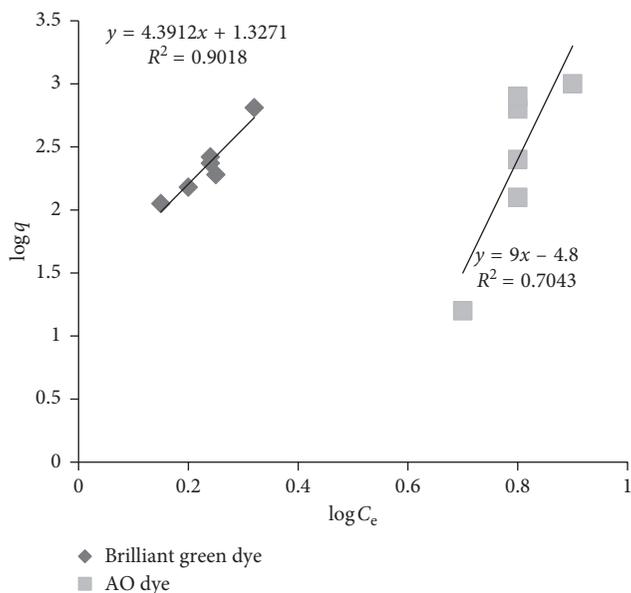


FIGURE 9: Graphical illustration of the Freundlich model.

TABLE 5: Freundlich constants for elimination of dyes by PR leaves.

Dyes	R^2	K_f	n
BG	0.901	0.123	0.23
AO-74	0.704	0.68	0.12

TABLE 6: Thermodynamic parameters.

Dyes	ΔH° (kJ/mol)	ΔS° (J/mol)	ΔG° (kJ/mol)		
			303k	313k	323k
BG	-1.592	7.97	-2.41	-2.49	-2.57
AO-74	-0.624	12.24	-3.70	-3.83	-3.95

TABLE 7: Kinetic parameters for PR leaf powder sorption of dyes.

Dye	Pseudo-first-order			Pseudo-second-order		
	$1/q$	K_2	R^2	$\text{Log}q_e$	K_1	R^2
BG	0.212	0.0005	0.992	0.9410	-0.029	0.890
AO-74	1.097	0.1594	0.995	0.3806	0.0097	0.744

employed to check the investigational facts of adsorption tests, and the results are given in Table 7. Pseudo-first-order equation of Lagergren is written as

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (7)$$

where K_1 is the rate constant [44]. Linear correlation between $\log(q_e - q_t)$ and t shows the applicability of this model on equilibrium data. The pseudo-second-order kinetic model can be calculated by using the following formula:

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where K_2 is the rate constant [45]. The plot between t/q and t shows a linear relation. This kinetic model is in accordance with chemisorption being the rate-determining step. From the results, it is concluded that the pseudo-second-order model is more applicable than the first one. Elevated correlation coefficient R^2 (0.992–0.995) was obtained when the second-order kinetic model was employed [46].

3.10. TGA. Three different temperature zones were observed in case of PR leaves before and after dye adsorption. As shown in Figure 10, maximum mass failure % was observed in the second zone. In the first and third zones, mass failure was relatively minute.

In case of DTA, three zones are able to study in case of normal PR leaves, BG treated leaves, AO-74 treated leaves, as given away in Figure 11. The first temperature zone is related to humidity and volatile component removal from the biosorbent. The second zone indicated further loss in weight due to pyrolysis and oxidation up to 16, 4, and 9%, respectively. At last, biosorbent mass left behind was 1, 22, and 18% after complete thermal decomposition. The residue left at this stage is dust and is about 70% of the original sample mass [47].

3.11. SEM Analysis. The scanning electron micrographs clearly revealed the face texture and morphology of untreated and dye-treated biosorbent (Figures 12–14). An

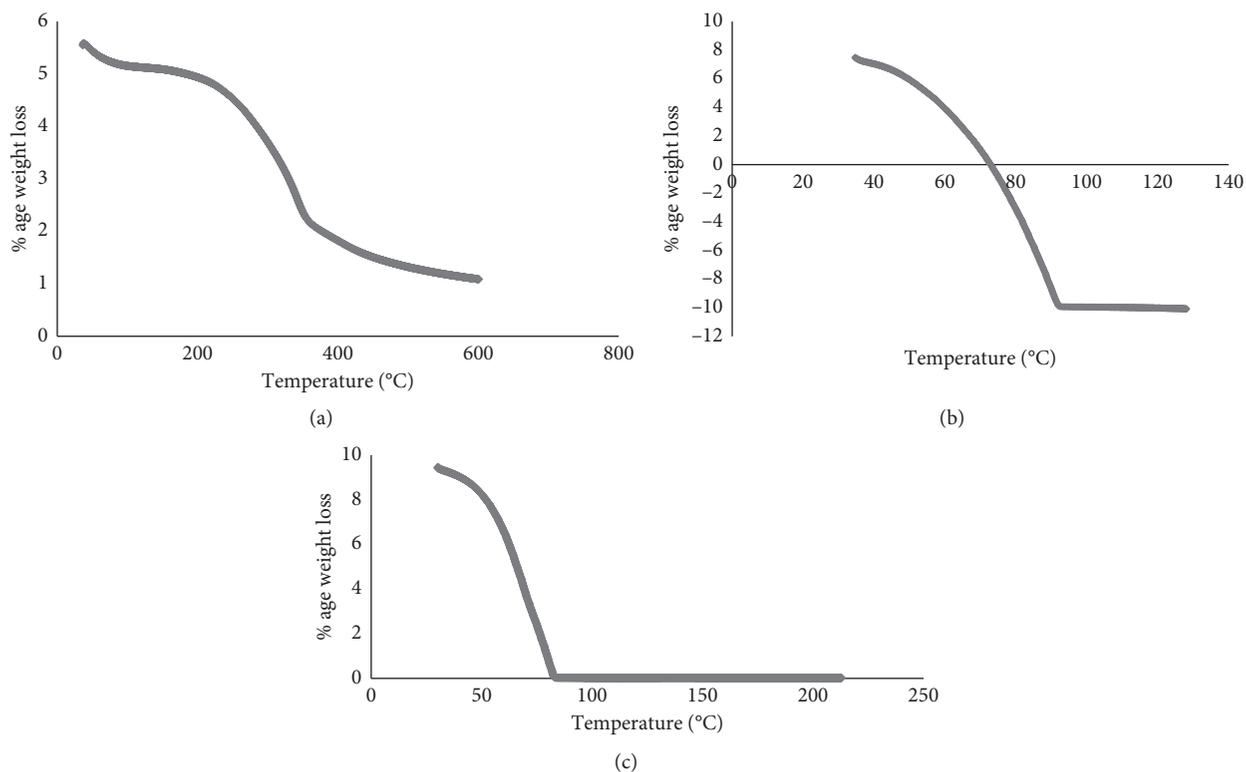


FIGURE 10: TGA curve for (a) untreated PR leaves, (b) brilliant green-treated PR leaves, and (c) acid orange-treated PR leaves.

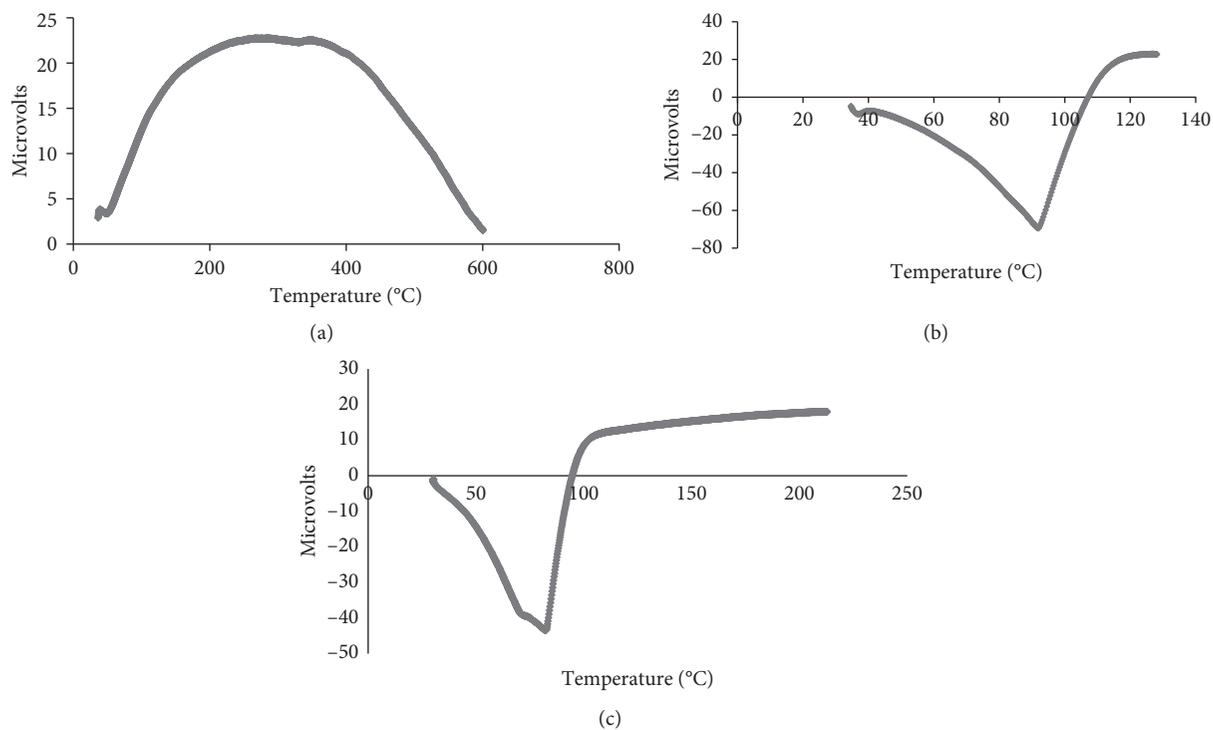
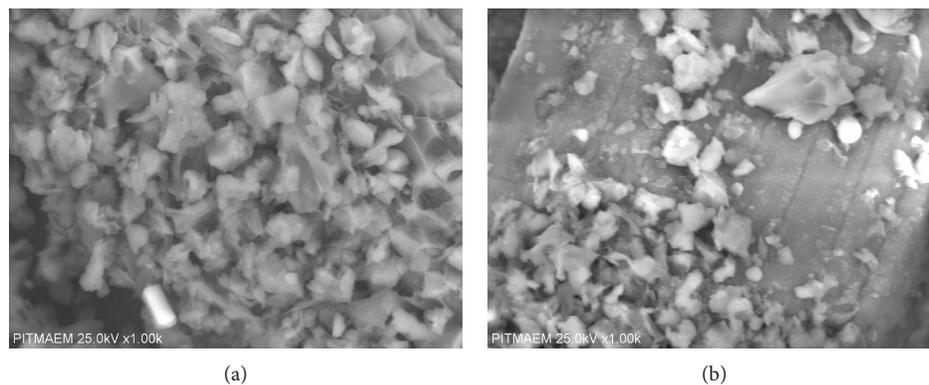


FIGURE 11: DTA curve for (a) untreated PR leaves, (b) brilliant green-treated PR leaves, and (c) acid orange-treated PR leaves.

examination of the SEM micrograph (Figure 12) indicates the presence of many pores on the surface of the biosorbent. Figure 13 shows the surface condition on BG-treated

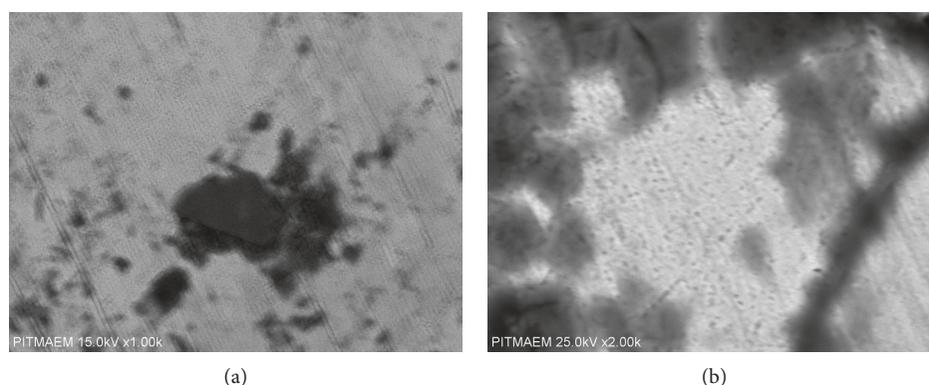
biosorbent is somewhat swollen during the contact with dye solution. Figure 14 shows AO-74-treated biosorbent is also somewhat swollen and shows cracks on the surface [48].



(a)

(b)

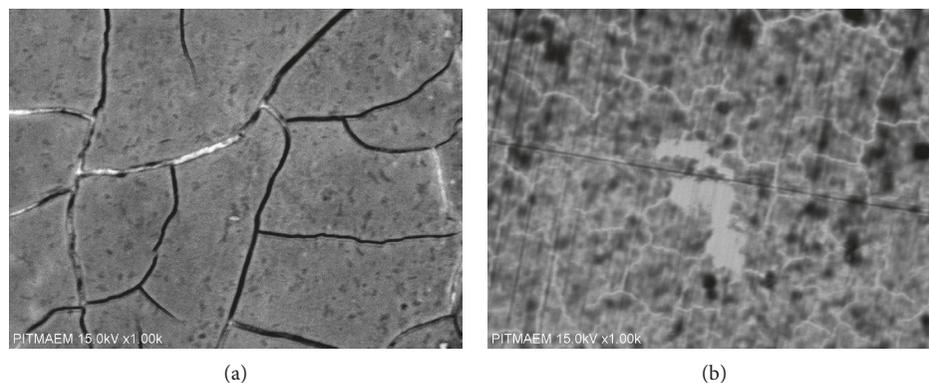
FIGURE 12: SEM image of PR leaves.



(a)

(b)

FIGURE 13: SEM images of brilliant green-treated PR leaves.



(a)

(b)

FIGURE 14: SEM images of acid orange-treated PR leaves.

3.12. *Mechanism of Adsorption.* The FTIR spectra of PR leaves indicated two major peaks after dye adsorption (Figure 2). After BG adsorption, the strength of the 3292 cm^{-1} band showing O-H stretching and the 1635 cm^{-1} band showing C=O stretching enhanced. It is mainly possible that intermolecular hydrogen bonding occurred between the O atom of C=O on PR leaves and the H atom of BG, or vice versa. FTIR of PR leaves with adsorbed BG indicated strong communication. It was supported by the environment of the negative charge of PR leaves and positive charge of BG. With AO-74, two major peaks shifted to 3317 and 1647 cm^{-1} ,

respectively. Weak interaction in case of AO is because of negative charge for both PR leaves and AO-74 dye [49].

The mechanism of dye exclusion from aqueous solution by adsorption is understood to consist of four steps. First step is the movement of dye molecule from bulkiness of solution to the outside of adsorbent. Second step is the distribution through the border sheet to the outside of sorbent. Third step is adsorption at sites. Fourth step is intraparticle distribution into the inside of sorbent. Rate-controlling step is film distribution or pore distribution [50].

4. Conclusion

In this study, it has been obviously exposed that *Pinus roxburghii* leaves could be efficiently used as a low-cost adsorbent for the exclusion of dyes from aqueous solution. Maximum monolayer adsorption capacities were found to be 71.42 and 7.52 mg/g for brilliant green and acid orange 74 dyes, respectively. Adsorption process well fitted the Langmuir isotherm. Thermodynamic data showed that the adsorption procedure was impulsive and accompanied by increase in entropy. Adsorption of both dyes followed the pseudo-second-order kinetic model.

Abbreviations

FTIR: Fourier-transform infrared spectroscopy
 BG: Brilliant green
 AO-74: Acid orange 74
 TGA: Thermogravimetric analysis
 PR: *Pinus roxburghii*
 BOD: Biological oxygen demand
 DO: Dissolved oxygen
 DTA: Differential thermal analysis
 SEM: Scanning electron microscope.

Data Availability

All data related to this work are presented in the Results section along with the references list.

Conflicts of Interest

The authors have no conflicts of interest regarding the publication of this paper.

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Supplementary Materials

Graphical representation of this work. (*Supplementary Materials*)

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