Use of *Polyalthia longifolia* based alumina composites for the removal of reactive dyes from aqueous medium

Khudajah Ikram[a,*], Nadia Jamil[a], Muhammad Salman[b], Maliha Shehrbano[a], Ayesha Siddique[a]

[a]*College of Earth and Environmental Science, University of the Punjab, Lahore, Pakistan, emails: khudajah.ikram@gmail.com (K. Ikram), nadia.cees@pu.edu.pk (N. Jamil), malihasb05@gmail.com (M. Sheharbano), ayeshaabubakar0@gmail.com (A. Siddique)*
[b]*Institute of Chemistry, University of the Punjab, Lahore, Pakistan, email: salman.chem@pu.edu.pk (M. Salman)*

ABSTRACT

Present study is aimed at the synthesis and use of *Polyalthia longifolia* based alumina composites for the adsorption of Methylene blue (MB, cationic dye) and Alizarin Red S (ARS, anionic dye) from wastewater generated at laboratory scale. The characterization of modified adsorbent through Fourier transformation infrared spectroscopy revealed the presence of hydroxyl, amino, and carbonyl groups. Scanning electron microscopy analysis showed the roughness on the surface of the modified biosorbent that favors the adsorption process. The point of zero charge was also determined. Adsorption of dyes was studied over several experimental factors such as dose of adsorbent, time of contact, initial solution concentration, solution pH, and temperature. The equilibrium data was evaluated by non-linear form of adsorption isotherms models (Langmuir and Freundlich) using different initial solutions concentrations (10–90 ppm). Langmuir model was followed for the adsorption of MB while for the adsorption of ARS, Freundlich model was followed. Maximum monolayer adsorption capacity (q_m) of adsorbent for MB and ARS was 74.63 and 25.06 mg/g, respectively. Equilibrium data was also evaluated by adsorption kinetic models (Pseudo-first-order and Pseudo-second-order). The studied process followed Pseudo-second-order model with ($R^2 = 0.9929$) and ($R^2 = 0.9993$) for MB and ARS, respectively. Thermodynamic parameters ($\Delta G°$, $\Delta S°$, and $\Delta H°$) were also estimated. The negative values of $\Delta G°$ for MB specified the spontaneous while positive values of $\Delta G°$ for ARS indicated non-spontaneous nature of the reaction. Positive values of $\Delta S°$ and $\Delta H°$ for both dyes indicated that the adsorption process is feasible and endothermic in nature. Thus, the modified biomass of *P. longifolia* branches can be used effectively for the treatment of dyes in wastewater.

Keywords: P. longifolia; Methylene Blue; Alizarin Red S; Alumina composites; Adsorption isotherm models; Adsorption kinetics; Thermodynamics

1. Introduction

Water pollution is considered to have major contributions in environmental pollution and is the most dangerous form of pollution [1]. Among many other sources of water pollution, wastewater that is generated by industrial processes is considered to be the major source. Organic content, heavy metals, and harmful dyes are major constituents of the wastewater [2]. Textile industry is considered as major contributor of wastewater pollution [3]. The processes that are carried out in textile industries are responsible for the production of liquid effluents in huge amounts. These liquid effluents have both organic and inorganic constituents in it. When the fabric is subjected to dyeing, every dye is not retained on it. Such dyes, not retained firmly on the fabric are present in liquid effluents in large quantities [4]. Most commonly this is the case with reactive dyes that retain

* Corresponding author.

less on the fabric and are more soluble in water. In this way, enormous amounts of colored liquid effluents are generated from textile industries. These colored liquid effluents make their way to the water bodies and pollutes them [5]. Azo dyes are mostly utilized in textile industries. If make their way to the soil, these dyes affect attributes of soil by interfering with its physico-chemical properties [4,6–8]. Wastewater generated by textile industries consists of a wide variety of different dyes. It also has a high chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solids (TDS), and total suspended solids (TSS). Thus, it is highly toxic and injurious to health and wellbeing of human beings as well as environment [9].

Methylene Blue (MB), a cationic dye, is used for the purpose of dyeing fabric [10]. Exposure to MB can cause cyanosis, sweating, headache, chest, and abdominal pain in human beings [11]. Alizarin Red S (ARS, Sodium Alizainsulfonate), an anionic dye, preferably used by the textile industry for the development of deep red color in the fabric. It has a ring structure due to which it is not degraded naturally and resistant to biological and thermal treatments. Some of the harmful toxicological effects like headaches, lungs malfunctioning, gastritis, methemoglobinemia, etc., are encountered if exposure to the wastewater containing ARS occurs in human beings [12]. Due to such side effects it is important to treat waste water prior to its release into the waterways.

Various techniques had been used for the treatment of wastewater and liquid effluents generated by textile industries, for the removal of dyes, including oxidation [13], treatment with hydrogen peroxide [14], use of fenton's reagent [15], solvent extraction process [16], and electro-coagulation method [17]. But some problems are associated with the application of such methods such as non-feasibility from economic point of view, problem of waste disposal after treatment, use of chemicals and electricity consumption. Also, these methods are not environmentally sound [18]. So, there is a need of technology that is economically feasible and at the same time ecofriendly too. In this way, adsorption can be taken into consideration [19]. Biosorption is a physicochemical technique that involves the use of biomass for the removal of dyes from liquid effluents generated by textile industries [20,21]. In this process, biological substances generate active sites on their surfaces that readily react with dyes and other contaminants [20]. Many such materials include banana peels [22], mango leaf powder [23], *Ficus religiosa* branches [24], cauliflower leaves [25], *Gardenia Jasminoides* branches [26], and *Polyalthia longifolia* leaves [27] as well as seeds [28], etc.

To date no literature is available on the use of chemically modified *P. longifolia* branches as an adsorbent for the adsorption of dyes. So the present study is focused on the utilization of chemically modified *P. longifolia* branches for the adsorption of dyes. *P. longifolia* (Ulta Shokh), shown in Fig. 1, is an ornamental plant having long and columnar shaped branches [29].

The main objective of this study was to investigate the potential of chemically modified biomass of *P. longifolia* branches for the adsorption of cationic dye (MB) and anionic dye (ARS) from wastewater generated at lab scale. The modified and unmodified material was characterized by Fourier transformation infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The dependence of dye uptake from aqueous solution was also investigated over various experimental factors such as adsorbent dosage, time of contact, initial solution concentration, pH, and temperature. Adsorption of dyes onto the adsorbent surface was also studied using mathematical models (adsorption isotherm, adsorption kinetics, and adsorption thermodynamics).

2. Materials and methods

2.1. Collection, preparation, and modification of adsorbent

P. longifolia branches were collected from gardens of University of the Punjab, Quaid-e-Azam Campus, Lahore, Pakistan. These branches were washed with distilled water and dried in sunlight. The biomass was crushed to pass 80 mesh screen (American Society for Testing and Materials). The crushed biomass was immersed in distilled water to remove any soluble material present and dried in oven (Memmert, Schwabach, Germany) at 70°C until constant mass.

Chemical modification of the adsorbent was done by following the method of Waghmare et al. [27] with slight modifications. In order to modify one batch of *P. longifolia* branches, 18.53 g of aluminum sulfate was dissolved in 84 ml of distilled water. Few drops of concentrated HCl were used to dissolve aluminum sulfate in distilled water. Ten grams of adsorbent was added in the aluminum sulfate solution. This mixture was put on the orbital shaker (Vortex model-OSM-747) for 6 h and transferred to the crucibles. The crucibles were kept into muffle furnace (SX-2.5-12 box type resistance furnace dfw-7000) for 3 h at 110°C and for 6 h at 450°C for calcination. The calcinated material was crushed in mortar and pestle. The crushed material was washed with distilled water in 1:20 ratio (material: distilled water). The mixture was put on orbital shaker for 24 h followed by one more washing. After shaking for 1 h, it was filtered and residue on the filter paper was dried in an oven for 4 h. The dried material was crushed in mortar and pestle. Similarly, many batches were prepared.

2.2. Adsorbent characterization

The chemically modified biomass of *P. longifolia* branches was characterized through different analytical techniques.

Fig. 1. *Polyalthia longifolia* plant.

The FTIR (Agilent Technologies CARY 630 FTIR, Santa Clara, California) was used to determine active functional groups on the surface of adsorbent responsible for adsorption. The SEM (JEOL-JSM 6480) was used to determine the surface morphology of the biosorbent. Point of zero charge (pH$_{PZC}$) was determined by following the procedure given by Boumediene et al. [30] with slight modifications:

Briefly, 0.1 M (5.85 g/L) solution of NaCl was prepared and nine conical flasks were filled with 100 ml of 0.1 M NaCl. Solution pH in each flask was set at 2–9, respectively. 0.5 g of adsorbent was added to each flask. Then the flasks were put on the orbital shaker at 130 rpm for 2 h. The solutions were put again on the orbital shaker for 30 min after allowing them to stand for 24 h and then filtered. pH of each solution was noted down. In order to estimate pH$_{PZC}$ of adsorbent, a graph was drawn between pH$_i$ and ΔpH. Value of ΔpH was determined using the following Eq. (1):

$$\Delta pH = pH_f - pH_i \tag{1}$$

where pH$_i$ is the initial pH of the solution, pH$_f$ is the final pH of the solution and ΔpH is the difference between pH$_f$ and pH$_i$.

2.3. Preparation of dyes solutions

The dyes used in the study were MB-cationic dye and ARS-anionic dye. These dyes were of analytical grade. Stock solutions of 1,000 ppm were made in distilled water (0.1 g/100 ml). Working solution of 50 ppm was made by diluting stock solutions of MB and ARS to study experimental factors for both dyes.

2.4. Optimum experimental factors for adsorption

Adsorption of dyes was studied by manipulating various factors such as adsorbent dosage, contact time, initial solution concentration, solution pH, and temperature to find out suitable experimental conditions for adsorption. The batch experiments were carried out in conical flasks of 250 ml. The effect of a certain factor was analyzed by manipulating that factor while keeping others constant. In order to check the effect of adsorbent dosage, it was varied from 0.1–0.9 g. Optimum pH for adsorption was determined by adjusting the pH values from two to nine using digital pH meter (pH/mV/TEMP Meter P25). Adsorption Isotherm models were used to evaluate equilibrium data for the adsorption of dyes at solution concentration in the range of 10–90 ppm. Different kinetic models were also used to evaluate the rate and mechanism for adsorption of dyes at contact time of 5–45 min. Temperature was varied from 10°C to 60°C to study adsorption thermodynamics. After batch experiments under certain conditions, the absorbance of dye solution filtrates were taken with UV-Vis Spectrophotometer (721 Visible Spectrophotometer). Adsorption Capacity of biosorbent for dye uptake was determined using the following Eq. (2):

$$q_e = \frac{C_0 - C_e}{m} \times V \tag{2}$$

where C_0 (mg/L) is the initial concentration, C_e (mg/L) is the concentration at equilibrium, m (g), and V (L) are the adsorbent dosage and volume of the solution under study, respectively.

3. Results and discussion

3.1. Characterization of adsorbent

Solid phase FTIR analysis was done for both unmodified and modified biomass of *P. longifolia* branches to identify functional groups present on the adsorbent surface. The spectrum of unmodified biomass illustrated in Fig. 2a shows the presence of numerous functional groups which may be thought of as active sites for adsorption of dyes. A broad stretching peak can be seen at the range of 3,400–3,000 cm^{-1} reveals the presence of H-bonded hydroxyl group (–OH) and amino group (–NH) as well. The peak appeared around 1,600 cm^{-1} indicates the occurrence of carbonyl group (C=O). A peak at 1,065.8 cm^{-1} indicates the presence of C–O group.

An evident change in the spectrum of chemically modified adsorbent was observed as various peaks appeared and shown in Fig. 2b. The peak observed at 2,918.5 cm^{-1} shows the occurrence of C–H group. The appearance of various peaks such as 1,420.1, 1,154.5, 1,319.5, and 1,231.9 cm^{-1} indicates asymmetric stretching frequency of carboxylate ion (O=C–O$^-$). In addition, a peak shift in carbonyl peak from 1,600 to 1,735.1 cm^{-1} is also observed.

The comparison of spectra of both unmodified and modified *Polyalthia* biomass affirms the incorporation of modifying material onto the surface of biomass which serves more active sites for the adsorption of dyes.

SEM was carried out to examine surface morphology of both modified and unmodified adsorbent. SEM images of unmodified and modified adsorbents are shown in Figs. 3a and b and compared. The surface of biosorbent scanned after chemical modification shows a visible change in morphology. The roughness on the surface of modified biosorbent indicates the incorporation of modifying material that, in turn, is responsible for efficient adsorption.

pH$_{PZC}$ is an analysis used to predict adsorbent's surface characteristics. The pH$_{PZC}$ of modified biomass of *P. longifolia* branches, as shown in Fig. 4, is 4.65. At this pH, the number of negatively and positively charged groups onto the surface of modified adsorbent are equal.

3.2. Optimum experimental factors for adsorption

3.2.1. Effect of adsorbent dosage

Various modified adsorbent dosages were used to determine the optimum dose for the adsorption of dyes from wastewater solution. The adsorbent doses were varied from 0.1 to 0.9 g/50 ml while the initial solution concentration was kept constant, that is, 50 ppm. Removal percentage and adsorption capacity of modified adsorbent for each dye is illustrated in Fig. 5 which shows that the removal percentage of each dye increased while adsorption capacity (q_e) decreased with the increase in adsorbent dose. As the adsorbent quantity is increased, the number of active sites present on the adsorbent surface also increases due to which removal
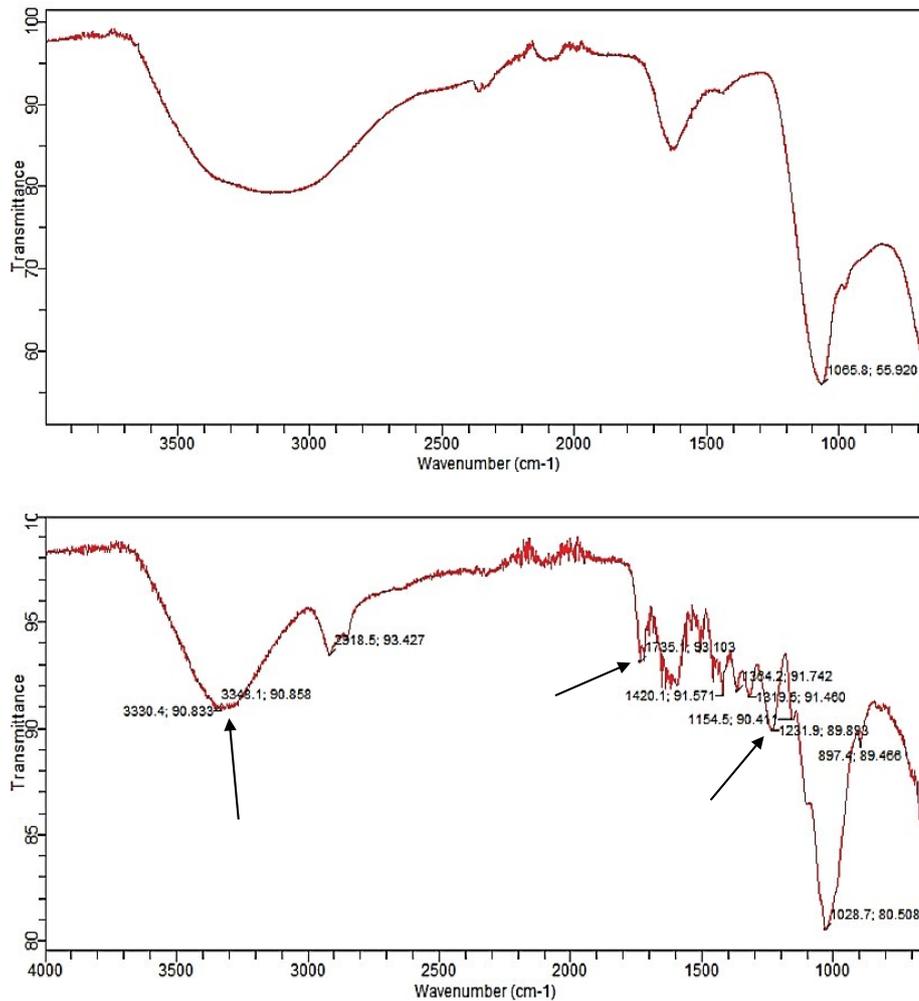
Fig. 2. FTIR spectrum of *Polyalthia longifolia* biomass (a) Unmodified and (b) Modified.

percentage of adsorbate enhances [31]. But equilibrium was attained at a certain point when further increase in the quantity of adsorbent did not enhance the removal of dyes from the aqueous solution because no more active sites were available for further adsorption.

The minimum removal percentage for MB was 83.04% at 0.1 g adsorbent dose which increased to 97.83% at 0.4 g adsorbent dose becoming constant afterwards with increasing adsorbent quantities. Similar trend was observed for ARS adsorption with maximum removal percentage as 78.68% at 0.7 g after which equilibrium achieved and removal percentage became almost constant at higher doses. The adsorption capacity (q_e) decreased with increase in the dose of adsorbent. The reason for this q_e decrease could be that the increase in the quantity of adsorbent results in the aggregation of adsorbent particles due to which surface area decreases which leads to the decrease in q_e [32].

3.2.2. Effect of pH

pH of the aqueous solution greatly influence the adsorption of dyes on the biosorbent. Experiments were conducted to study the effect of solution pH on the adsorption of dyes on the modified biosorbent by varying pH from two to nine while keeping other factors constant. At low pH values, the chromophore of MB dye was destroyed, and the chromophore of the ARS was destroyed at high pH values. The results are illustrated in Fig. 6 according to which the maximum adsorption capacity of modified adsorbent for MB is 15.44 mg/g at pH = 6 and that for the adsorption of ARS is 20.87 mg/g at pH = 4.

The reason for the maximum adsorption capacity of adsorbent for two dyes at different pH values is that MB is a cationic, while ARS is an anionic dye and pH_{PZC} of the modified adsorbent is 4.65. According to literature, the adsorption of positively charged constituents is favored at pH values greater than pH_{PZC} due to the fact that adsorbent surface is charged negatively at pH values higher than pH_{PZC} while adsorption of negatively charged constituents is favored at pH values less than pH_{PZC} because adsorbent surface is charged positively at pH values less than pH_{PZC} [33]. Therefore, pH values six and four were considered optimum for the adsorption of MB and ARS, respectively.
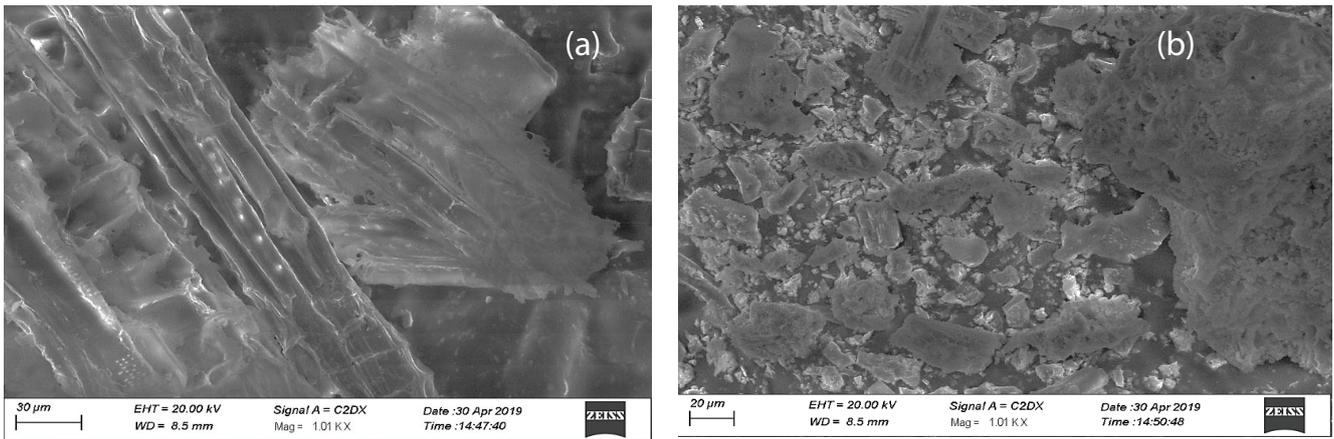
Fig. 3. SEM image of *Polyalthia longifolia* biomass (a) Unmodified and (b) Modified.
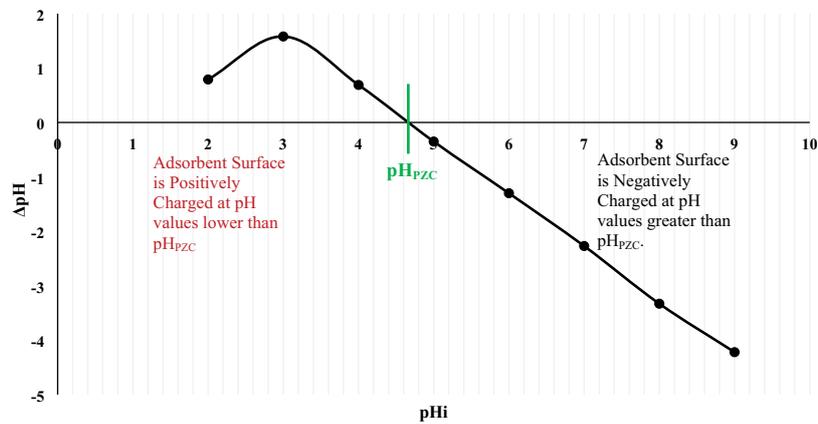
Fig. 4. Point of zero charge of modified adsorbent.
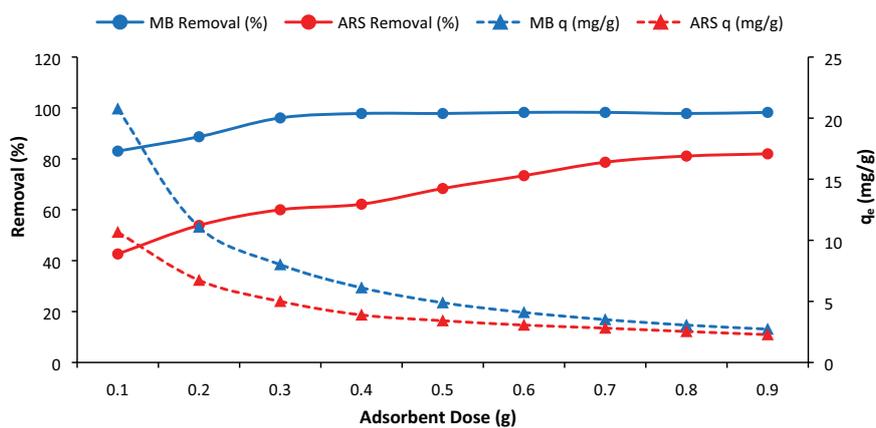
Fig. 5. Effect of modified biosorbent dosage on Methylene Blue and Alizarin Red S (50 ppm) adsorption.

3.2.3. *Effect of contact time-adsorption kinetics*

Capability of adsorption is largely influenced by time the constituents of dye are in contact with adsorbent. Time factor helps to study the rate of adsorption by providing information about minimum time required to attain equilibrium for adsorption of dyes. Keeping other factors constant, the time of contact between modified biomass of *P. longifolia* and dye molecules was increased from 5 to 45 min and illustrated in Fig. 7.
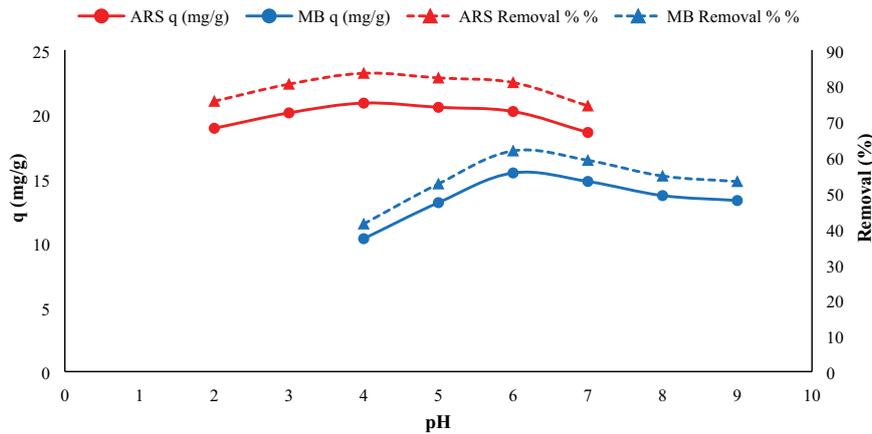
Fig. 6. Effect of pH on Methylene Blue and Alizarin Red S adsorption at pH = 2–9.
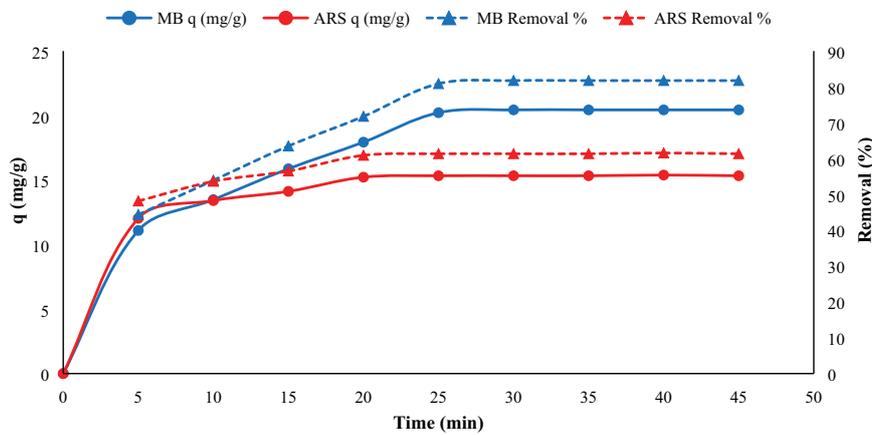
Fig. 7. Effect of contact time on Methylene Blue and Alizarin Red S adsorption at 0–45 min.

The adsorption capacity was increased with increase in time but upto a certain point at which equilibrium was established between liquid and solid phase. After this point, the adsorption capacity became constant and no further increase was observed in it. Such trend can be attributed to the fact that a great deal of active sites are occupied by dye molecules at this stage [34]. The minimum time of contact required for the adsorption of MB to achieve equilibrium was 30 min and that for the adsorption of ARS was 25 min.

In order to study the adsorption rate and mechanism for the adsorption of MB and ARS, the adsorption data was analyzed by applying two famous kinetic models, that is, pseudo-first- and second-order.

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where q_e (mg/g) and q_t (mg/g) are quantity of dye adsorbed per unit weight of adsorbent at equilibrium and at given time "t", respectively. K_1 (min^{-1}) and K_2 (mg/g*min) are pseudo-first- and second-order rate constants.

Pseudo-first-order model is based on the assumption that the adsorption rate is directly proportional to the number of available binding sites [35]. Linear equation of pseudo-first-order model [Eq. (3)] was applied to equilibrium data drawn from the time factor and parameters were also calculated and mentioned in Table 1. The correlation coefficient (R^2) for MB was 0.8057 and that for ARS was 0.8423 which suggest that pseudo-first-order kinetic model do not fit to the equilibrium data. Furthermore, the q_e calculated from the pseudo-first-order reaction was not in accordance with the q_e value determined from the experiment. It can be concluded that the adsorption of MB and ARS onto the modified biomass of *P. longifolia* did not follow the pseudo-first-order kinetic model.

Pseudo-second-order model is based on the assumption that the adsorption rate is directly proportional to the square of number of binding sites present on the surface of adsorbent [35]. Equilibrium data drawn from the time factor was plotted in Figs. 8a and b according to the linear equation of pseudo-second-order model [Eq. (4)].

Parameters of pseudo-second-order kinetic model were also calculated and mentioned in Table 1. The correlation coefficient (R^2) for MB was 0.9929 and that for ARS was 0.9993 suggesting that the pseudo-second-order kinetic model fits to

(a)

(b)
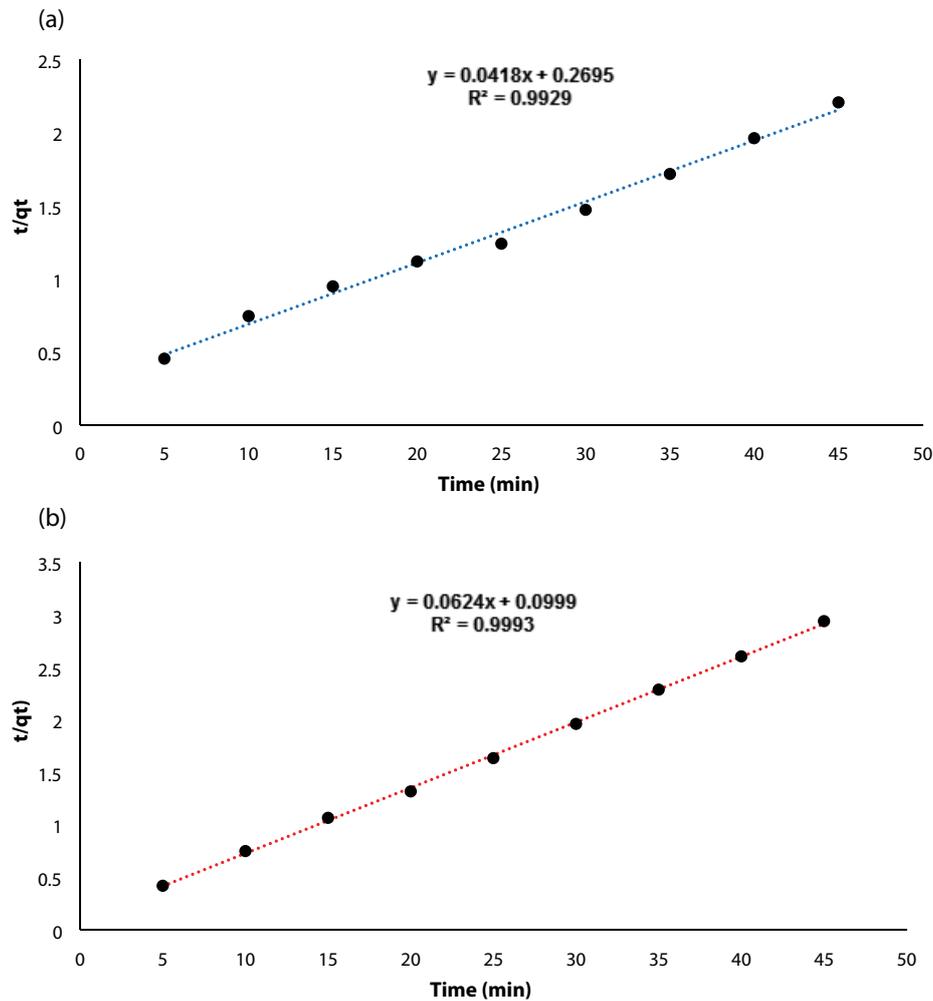
Fig. 8. Pseudo-second-order plot for adsorption of (a) Methylene Blue and (b) Alizarin Red S.

Table 1
Kinetic parameters for methylene blue and alizarin red S adsorption

Dyes	Pseudo-first-order kinetics			q_e (mg/g) experimental	Pseudo-second-order kinetics		
	K_1 (min^{-1})	R^2	q_e (mg/g) calculated		q_e (mg/g) calculated	R^2	K_2 (min^{-1})
Methylene Blue	0.1709	0.8057	35.89	20.43	23.92	0.9929	0.006
Alizarin Red S	0.2134	0.8423	13.79	15.33	16.03	0.9993	0.04

the equilibrium data. The q_e value obtained from the pseudo-second-order model was in accordance with that obtained from the experiment. So, it can be concluded that adsorption of MB and ARS onto the modified biomass of *P. longifolia* followed pseudo-second-order kinetic model.

3.2.4. Initial solution concentration-adsorption isotherms

Adsorption isotherms describe the adsorption process prior to executing in industrial operations [36]. In order to study adsorption equilibrium, two most frequently used isotherm models were applied to the adsorption data i.e., Langmuir model [Eq. (5)] and Freundlich model [Eq. (6)].

These equilibrium models were elucidated by non-linear approach for the adsorption of MB and ARS onto the modified biomass of *P. longifolia*. In recent years, non-linear modeling gained importance in comparison with linear modeling due to (i) evaluation of results and data in single figure and (ii) to reduce the ambiguity in calculations of q_{max} through linear modeling [37,38]. Root mean square error (RMSE) [Eq. (7)] was used to compare the non-linear isotherm models.

$$q_e = \frac{b \cdot q_m \cdot C_e}{1 + b \cdot C_e} \tag{5}$$

$$q_e = K_F \cdot C_e^{1/n} \qquad (6)$$

$$\text{RMSE} = \sqrt{\frac{\sum\left(q_{e(\text{cal})} - q_{e(\text{exp})}\right)^2}{N}} \qquad (7)$$

Langmuir model helps predict the adsorption of adsorbate (dye) in aqueous medium on outer surface of adsorbent in single layer [39]. Langmuir model also gives an account of maximum adsorption capacity of biosorbent to adsorb dyes. The values of RMSE, maximum adsorption capacity-q_m (mg/g) and constant associated with binding sites affinity-b (L/mg) are mentioned in Table 2.

Comparison of maximum adsorption capacity of *P. longifolia* based alumina composites with other adsorbent materials is given in Table 3.

RMSE value calculated through non-linear approach is lower for Langmuir model in case of MB adsorption that affirms the best fit of Langmuir model to the equilibrium

data as compared to Freundlich model indicating the homogenous adsorption of MB onto the surface of adsorbent in single layer (Fig. 9a).

Freundlich model states that the process of adsorption is carried out on multifold surface. This model is used to evaluate the heterogeneous surfaces for adsorption of dyes [39]. The values of RMSE, relative adsorption capacity indicator (K_F) and adsorption intensity indicator are mentioned in Table 2.

The value of "n" for MB and ARS is 1.48 and 1.78, respectively indicating the feasibility of adsorption process. As there are three cases on the basis of which value of n describes the feasibility of adsorption process [40]: (i) if the value lies in the range of 2–10, the adsorption is good, (ii) if the value lies in range of 1–2, the adsorption is moderate, and (iii) if the value is <1, it indicates poor adsorption. RMSE value calculated through non-linear approach is lower for Freundlich model in case of ARS adsorption suggesting that Freundlich model fits best to equilibrium data for the adsorption of ARS (Fig. 9b).

3.2.5. Effect of temperature-adsorption thermodynamics

Temperature is an important parameter influencing the process of adsorption. It also provides an understanding of thermodynamics of the adsorption process. The effect of temperature on the adsorption of dyes onto the modified absorbent was observed by varying temperature of dye solution from 10°C to 60°C while keeping other factors constant and shown in Fig. 10.

The adsorption capacity (q_e) of modified biosorbent for the adsorption of both dyes increases with increase in the temperature. It could be due to the fact that increasing temperature can create new active sites onto the adsorbent surface [35]. Increase in temperature can also provide more energy to the larger dye molecules so that their mobility increases and these molecules bind to the surface of adsorbent more

Table 2
Isotherm parameters for Methylene Blue and Alizarin Red S adsorption

Dyes	Langmuir parameters		
	RMSE	q_m (mg/g)	b (L/mg)
Methylene Blue	0.540	74.63	0.034
Alizarin Red S	1.440	25.06	0.084

Dyes	Freundlich parameters		
	RMSE	n	K_F
Methylene Blue	1.632	1.48	3.63
Alizarin Red S	1.320	1.78	2.78

Table 3
Comparison of maximum adsorption capacity (q_{max}) of *Polyalthia longifolia*

Adsorbent	Dyes	q_{max} (mg/g)	References
Defatted algal biomass	Methylene Blue	7.73	[42]
Carrot flowers	Methylene Blue	21	[43]
Ficus carica bast	Methylene Blue	47.62	[44]
Wheat straw biochar enhanced by magnetic field	Methylene Blue	62.5	[45]
Polyalthia logifolia based alumina composites	Methylene Blue	74.63	Present study
Aleurites Moluccana seeds	Methylene Blue	178	[46]
Prickly bark of cactus fruit	Methylene Blue	222.22	[47]
Citrus limetta peel	Methylene Blue	227.3	[48]
Musturd husk	Alizarin Red S	0.507	[49]
Cynodon dactylon	Alizarin Red S	16.32	[50]
Polyalthia logifolia based alumina composites	Alizarin Red S	25.06	Present study
Magnetic chitosan	Alizarin Red S	40.12	[51]
Mikania micrantha	Alizarin Red S	46.51	[52]
Pinus kesiya	Alizarin Red S	118.06	[53]
Pentaerythritol modified carbon nanotube	Alizarin Red S	257.73	[54]
Cationic surfactant modified clay	Alizarin Red S	666.6	[55]

Fig. 9. Non-linear isotherm plot for the adsorption of (a) Methylene Blue and (b) Alizarin Red S at initial solution concentration ranging from 10 to 90 ppm.
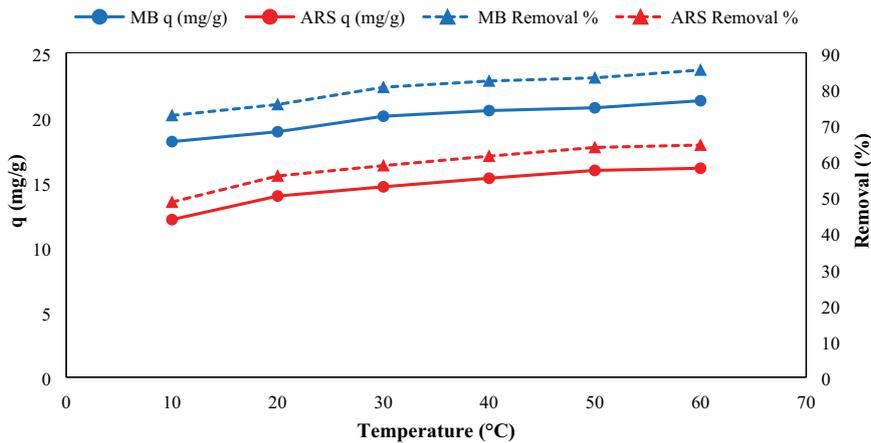
Fig. 10. Effect of temperature on Methylene Blue and Alizarin Red S adsorption at 10°C–60°C.

efficiently [41]. Thermodynamic parameters such as Gibbs free energy ($\Delta G°$), process enthalpy ($\Delta H°$), and entropy change ($\Delta S°$) are calculated using Eqs. (8), (9), and (10) and mentioned in Table 4.

$$\Delta G° = -RT \ln K_D \tag{8}$$

$$\ln K_D = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{9}$$

where R and T are the universal gas constant (8.3134 J mol⁻¹ K⁻¹) and absolute temperature (K), respectively while K_D is the coefficient of distribution that is determined using Eq. (10):

Table 4
Thermodynamic parameter of Methylene Blue and Alizarin Red S

Dyes	Temperature (°C)	$\Delta G°$	$\Delta H°$	$\Delta S°$
	10	–0.6632		
	20	–1.07378		
Methylene	30	–1.81612		
Blue	40	–2.17409	11.979	0.0449
	50	–2.40616		
	60	–2.93223		
	10	1.77		
	20	1.12		
Alizarin	30	0.86		
Red S	40	0.61	9.6452	0.0286
	50	0.35		
	60	0.28		

$$K_D = \frac{q_e}{C_e} \tag{10}$$

The values of $\Delta G°$ are negative for the adsorption of MB indicating the spontaneity of the biosorption process while that for the adsorption of ARS are positive indicating that adsorption was non-spontaneous. However, the value of $\Delta G°$ declines with increase in temperature for the adsorption of both dyes which suggests that the reaction is endothermic in nature. It was also verified by the positive value of process enthalpy ($\Delta H°$). Positive values of entropy change ($\Delta S°$) for the adsorption of both dyes onto the modified biomass of *P. longifolia* suggested an increase in disorder on the liquid-solid interface during adsorption process.

4. Conclusion

Biomass of *P. longifolia* branches was chemically modified to synthesize alumina composites which were used for the adsorption of MB and ARS dyes. The adsorption process was studied over various experimental factors including biosorbent dose, contact time, pH, temperature, and initial solution concentration. Equilibrium for MB and ARS was achieved at 30 and 25 min, respectively. Optimum pH values for the adsorption of MB and ARS are six and four, respectively. The equilibrium data was also evaluated by non-linear form of adsorption isotherms models (Langmuir and Freundlich) and adsorption kinetics (Pseudo-first-order and Pseudo-second-order). The equilibrium data fits best to the Langmuir model for the adsorption of MB while for the adsorption of ARS , the Freundlich model was followed. Pseudo-second-order kinetics was followed for the adsorption of both dyes. Thermodynamic parameters (Gibbs free energy, process enthalpy, and entropy change) were also estimated indicating the feasibility and endothermic nature of the reaction. The negative values of $\Delta G°$ for the adsorption of MB suggested that the adsorption process is spontaneous while the positive values of $\Delta G°$ in case of ARS adsorption suggested that the adsorption process is non-spontaneous. Positive values of $\Delta S°$ and $\Delta H°$ for

both dyes indicated that the adsorption process is feasible and endothermic in nature. These outcomes suggested that *P. longifolia* based alumina composite is environmental-friendly and cost effective biosorbent for the removal of dyes from aqueous medium.

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