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Acid Blue 74 Dye Removal from Industrial Wastewater Using Tigris River Reed Biomass: Packed Bed Column and Batch System Study

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Keywords:
Acid blue 74 dye; Biomass; Chemisorption; Tigris river reed; Industrial wastewater treatment.

Highlights:

- *The removal of AB74 dye from wastewater using TRR was successfully investigated.*
- *The η_{dye} and α_{dye} were remarkably enhanced by increasing the operating pressure.*
- *High AB74 dye sorption performance was observed in an acidic medium.*
- *Higher η_{dye} and α_{dye} values were achieved of 99.5 % and 10.4 $mg\ g^{-1}$, respectively.*
- *Chemisorption was found to be the mechanism of the biosorption of AB74 on TRR.*

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Abstract: A low-cost and environmentally friendly biosorption material, i.e., Tigris River reed, was used to remove the Acid Blue 74 dye from synthetic industrial wastewater in a continuous flow-backed bed column. The impact of operating conditions, such as operating pressure, initial dye concentration, pH of solution, wastewater volumetric flow rate, and biomass particle size, on the dye removal efficiency and biosorption capacity of biomass was investigated. The results revealed that the dye removal efficiency in an acidic medium was higher than in an alkaline medium. The optimum pH value was 3. Moreover, the results exhibited that the dye removal efficiency and biosorption capacity were significantly improved with increased operating pressure. In addition, the increase in the initial dye concentration and wastewater flow rate led to an increase in the biosorption capacity of biomass and a decrease in dye removal efficiency. The maximum achieved values of dye removal efficiency and biosorption capacity of biomass were 99.5% and 10.4 $mg\ g^{-1}$, respectively, at pressure, initial dye concentration, wastewater flow rate, and particle size of 6 bar, 150 ppm, 25 $mL\ min^{-1}$, and 500-850 µm, respectively. The encouraging dye removal efficiency (99.5%) achieved by using low-cost and environmentally friendly reed in a continuous flow process could be considered an attractive method for industrial wastewater treatment. Furthermore, batch biosorption experiments were performed to establish the sorption mechanism of AB74 dye on the Tigris River reed. Chemisorption was found to be the mechanism of biosorption.

أزالة صبغة ٧٤ الحامضية الزرقاء من مياه الصرف الصناعي باستخدام قصب نهر دجلة كمادة حيوية: دراسة باستخدام عمود ذو حشوة ونظام الدفعات

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الخلاصة

من مياه (AB74) في هذه الدراسة تم استخدام قصب نهر دجلة كمادة ذات كلفة منخفضة وصديقة للبيئة لإزالة صبغة 74 الحامضية الزرقاء وسعة صناعية تم تحضيرها في المختبر باستخدام عمود ذات حشوة مع جريان مستمر .تم دراسة تأثير الظروف التشغيلية على نسبة ازالة الصبغة للمحلول، معدل الجريان الحجمي لمياه الصرف، وحجم جسيمات المادة pH مثل الضغط التشغيلي، تركيز الصبغة، قيمة الامتزاز للمادة الحيوية .تساوي pH 3 الحيوية .اظهرت النتائج ان نسبة ازالة الصبغة في الوسط الحامضي أفضل من الوسط القاعدي وان أفضل اداء كان عند قيمة تركيز الصبغة يؤدي الى زيادة تزداد بشكل كبير بزيادة الضغط التشغيلي .اضافة الى ذلك زيادة علاوة على ذلك اظهرت النتائج ان نسبة ازالة الصبغة وسعة الامتزاز للمادة الحيوية تم الحصول ازالة الصبغة اعلى قيمة لنسبة .نسبة ازالة الصبغة سعة الامتزاز للمادة الحيوية ونقصان في قيمة في قيمة على التوالي، عند ظروف تشغيلية لـتركيز الصبغة، معدل الجريان الحجمي لمياه الصرف، وحجم جسيمات $mg\ g^{-1}$ 10.4% و عليها كانت 99.5 باستخدام (99.5 %) على التوالي .ان القيمة المشجعة التي تم الحصول عليها لنسبة ازالة الصبغة $mL\ min^{-1}$ 25، 150 ppm، 6 bar عند القصب كمادة رخيصة وصديقة للبيئة في عملية ذات جريان مستمر يمكن اعتبارها طريقة جذابة في عملية معالجة مياه الصرف الصناعي .اضافة لذلك تم على سطح القصب .وقد لوحظ ان الية الامتزاز هي الامتزاز الكيمياوي AB74 اجراء تجارب في نظام الدفعات لغرض الكشف عن الية امتزاز صبغة.

الكلمات الدالة: صبغة ٧٤ الحامضية الزرقاء، الكتلة الحيوية، امتصاص كيميائي، قصب نهر دجلة، معالجة مياه الصرف الصناعي.

1.INTRODUCTION

Recently, a significant increase in various pollutants in the aquatic environment has been observed due to increasing industrial activity. Pollutant removal from wastewater is a crucial issue in eliminating the environmental damage caused by these pollutants to humans and other living organisms. Typically, the pollutants existing in industrial wastewater are hydrocarbon compounds like phenols and dyes [1] or non-hydrocarbon compounds like heavy metals [2]. Dyes are the first contaminant to be demarcated in wastewater due to their visibility, even at low concentrations in the wastewater (<1 ppm). Dyes are highly conspicuous due to their colors and undesired effects [3]. Physical methods involving membranes, ion exchange, and adsorption are widely used for dye removal from wastewater. The adsorption method is an attractive technology due to the high dye removal efficiency, particularly at low concentration, simple design, and low cost [4, 5]. Several studies have been performed to reduce the treatment cost of wastewater by developing a new sorbent characterized by a low-cost and effective adsorbent. Biomass is used as an alternative sorbent for dyes, such as waste of tea [6], pine tree leaf [7], lupine and pumpkin seeds [8], and fruit shells [9]. Giant reed is an attractive biomass for wastewater treatment due to low-cost, eco-friendly, and widely available agricultural wastes [10-13]. Alwared et al. [11] suggested the giant reed (Arundo donax L) as a biosorbent for removing reactive black and blue dyes from the wastewater using a batch sorption system. Results exhibited that the biosorption capacities of giant reed for the uptake of the reactive blue and black dyes are 3.94 and 2.816 $mg\ g^{-1}$, respectively. In addition, they reported that the loaded giant reed with dye can be used in the concrete mixes, which makes the dye biosorption a sustainable process. A comprehensive study was conducted by Aghdasinia et al. [13] to remove basic yellow 2 dye from aqueous solutions using reed stem and poplar leaf. They pointed out that the dye removal efficiency was more than 90%. Acid Blue 74 dye, i.e., (AB74) dye, is a water-soluble blue dye (indigo derivative), widely used in the textile industry due to its ability to dye wool fibers and cotton clothes (blue jeans). Indigo carmine is a highly toxic indigoid dye, and it causes injury to the cornea and conjunctiva when it contacts the eyes and skin [14, 15]. Therefore, this study aims to evaluate the performance of Tigris River reed (TRR) biomass for AB74 dye from wastewater. The dye sorption was conducted in a continuous flow packed bed column. The impact of operating conditions, such as operating pressure, initial dye concentration (IDC), pH, wastewater flow rate (Q_w), and biomass particle size, on the dye removal efficiency (η_{dye}) and biosorption capacity of biomass (α_{dye}) was investigated. Using TRR as a biosorbent for AB74 could be considered a sustainable process because the loaded reed with dye can be used in the concrete mixes [11]. In addition, batch adsorption experiments were conducted for a kinetics study, establishing the sorption mechanism of AB74 dye on the TRR.

2.EXPERIMENTAL WORK

2.1.Materials

The target contaminator used in this study is AB74 dye (MERCK, 99.9%, Germany), which has a chemical formula of $C_{16}H_8N_2Na_2O_8S_2$ and a molecular weight of 466.36 g/mol. Fig. 1 shows the chemical structure of the used dye. The main functional groups present in AB74 are the Azo group ($-N=N-$): This group is responsible for the blue color of the dye, and it is formed by the coupling of two aromatic amines. Carboxyl

group($-COOH$): This group is a type of organic acid group composed of a carbon atom bonded to a hydroxyl group ($-OH$) and an oxygen atom. The carboxyl group imparts acidic properties to the molecule and contributes to its solubility in water. Sulfonate group ($-SO_3H$), which contributes to the molecule's solubility in water, is an organic sulfonic acid group consisting of a sulfur atom bonded to one hydrogen atom and three oxygen atoms. The sulfonate group also. Naphthalene group: This group is a type of aromatic hydrocarbon composed of two fused aromatic rings. It is a stable, non-polar group that contributes to the chemical stability of the molecule. AB74 is an azo dye that contains several functional groups, which are groups of atoms within a molecule that contribute specific chemical properties. These functional groups can influence the chemical reactivity of the molecule and determine its solubility, stability, and other physical properties. NaOH (MERCK, 99.5%, Germany) and HCl (Riedel-de Haen, 37%, Germany) were used to regulate the pH of the treated solution.

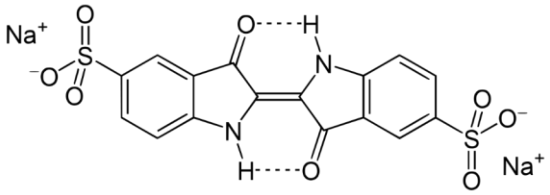


Fig. 1 Chemical Structure of AB74 Dye [16].

2.2.Preparation of Dye Biosorbent

Reed was collected from the banks of the Tigris River located in Tikrit city, north of Baghdad, the capital of Iraq. The collected reed was washed using tap water and then dried and crushed. The obtained powder was separated into three categories based on size: fin particles (FP, 500-850 µm), medium particles (MP, 850-1180 µm), and large particles (LP, 1180-1700 µm), using a sieve shaker (Wykehan Farrance Slough, England), as shown in Fig. 2. The obtained biosorbent investigated in the present study was used as such in its natural form without chemical treatments.

Fig. 2 Physical Pictures of Different Sizes of the Prepared TRR.

2.3.Characterization of Biosorbent

The chemical composition and chemical bonds on the perpetrated biosorbent surface were identified by using Fourier-Transform Infrared (FTIR) Spectroscopy (Shimadzu FT-IR 8400 S (KBr), Japan). The biosorbent surface after the adsorption process was analyzed by FTIR Spectroscopy to identify the changes in chemical composition and chemical bonds on its surface. The biosorbent surface was scanned from a wavenumber of 400 to 4000 cm^{-1}.

2.4.Preparation of Dye Aqueous Solution

A weighted amount of AB74 dye was dissolved into deionized water to prepare a concentrated dye aqueous solution (1500 $mg\,L^{-1}$). To prepare the required concentration of dye solution, a certain volume of concentrated dye aqueous solution was diluted with deionized water. The pH of the aqueous solution was regulated via 1M NaOH solution and drops of HCl. The pH value of the solution was measured by a calibrated pH meter (Bioevopeak Co. Ltd., PH-B500T, China) with buffer solutions.

2.5.Experimental Setup

2.5.1.Continuous System

The experiments were conducted using a continuous system in a packed bed column, as shown in Fig. 3. A stainless steel pipe was used as an adsorption column with a 1.9 cm inner diameter and a height of 25 cm. The packed bed was isolated from the inlet section and the outlet section via a screen made from stainless steel of mesh size (400 µm) to enhance liquid distribution in the inlet section and prevent sorbent leakage from the outlet section. The liquid solution was introduced to the sorption column using a diaphragm pump (maximum pressure of 7.6 bar, Upright, Taiwan). A floating ball flow meter (0-250 mL min^{-1}, ZYIA Instrument Company, China) was installed before the sorption column to measure and control the volumetric flow rate of the liquid solution. The flowmeter was calibrated before performing the experiments. The column pressure has been controlled via the outlet needle valve and measured by two-gauge pressure installed at the inlet and outlet streams of the sorption column. Figure 4 illustrates the photo of the continuous system used

in the present study. The effects of the considered operating conditions on the dye removal process are listed in Table 1. The operating time for the continuous process was 40 *min*, and samples were collected at 5-*min* intervals to assess the biosorbent stability.

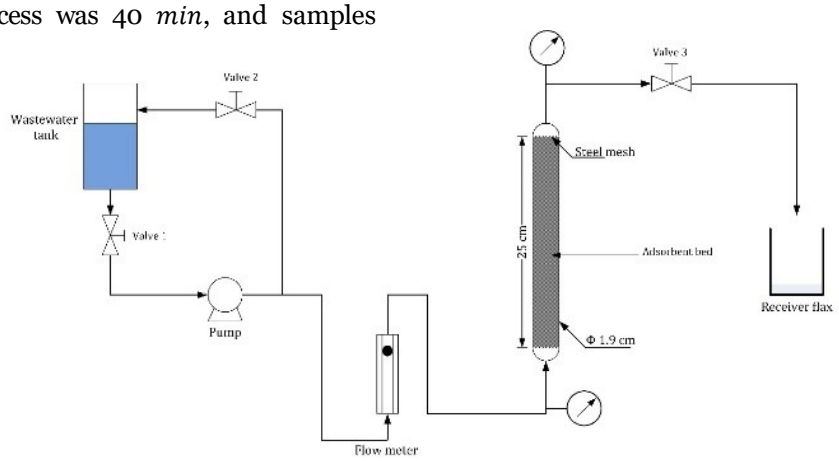


Fig. 3 Schematic Diagram of the Continuous Biosorption Process.

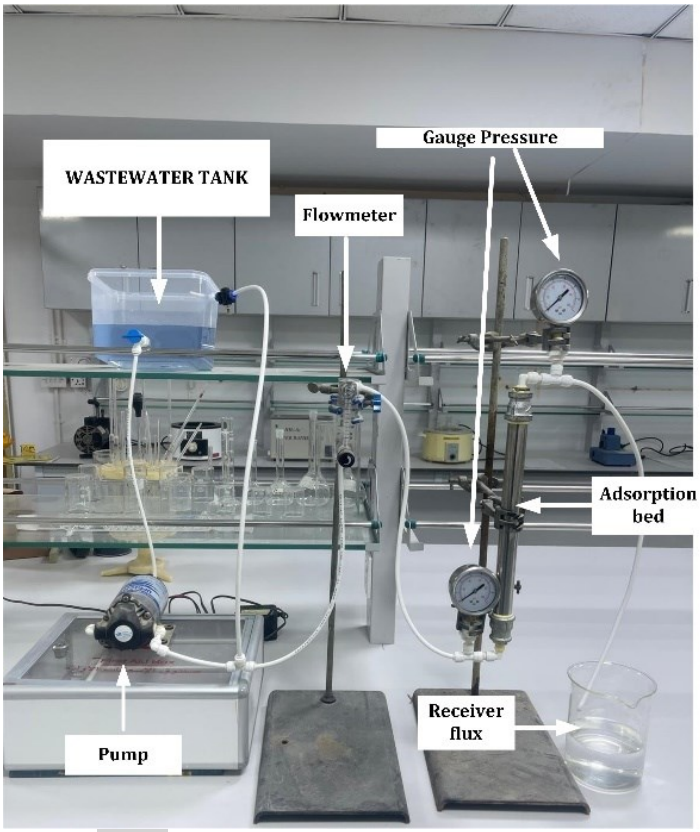


Fig. 4 Photo Image for the Continuous System.

Table 1 The Considered Operating Conditions in the Continuous System.

Operating condition	Unit	Value
pressure	bars	2,4, and 6
pH	-	2, 3, 4, 6, 8, and 10
Wastewater flow rate	$mL\ min^{-1}$	25, 50, and 75
Initial dye concentration	ppm	70, 150, 230, and 300
particle size range of reed	µm	((500-850), (850-1180), and (1180-1700)

2.5.2.Batch System

A batch mode has also been used to conduct the isothermal model calculations. The experiments were performed by mixing the wastewater with reed in a small beaker using a magnetic stirrer. The mixing ratio of sorbent to the liquid solution was 0.0143 $g\ mL^{-1}$ and the speed of the mixer was 250 rpm. Figure 5 illustrates the batch system used in the present study. The optimum pH value estimated in the continuous process was used in the batch system. The dye concentrations in the collected samples from the outlet stream of the sorption column and batch experiments were predicted using a spectrophotometer (JASCO V-

530 UV/VIS, Japan). The η_{dye} and biosorption capacity of α_{dye} for continuous and batch experiments were calculated using the following equations.

$$\eta_{dye} = \frac{C_i - C_o}{C_i} \times 100\% \quad (1)$$

$$\alpha_{dye} = V \times \frac{C_i - C_o}{m} \quad (2)$$

where C_i and C_o $(mg\,L^{-1})$ are the dye concentration before the biosorption treatment (initial concentration) and dye concentration after the biosorption process, respectively. V (L) is the total volume of a treated solution, and m (g) is the weight of the biomass used in the biosorption column.

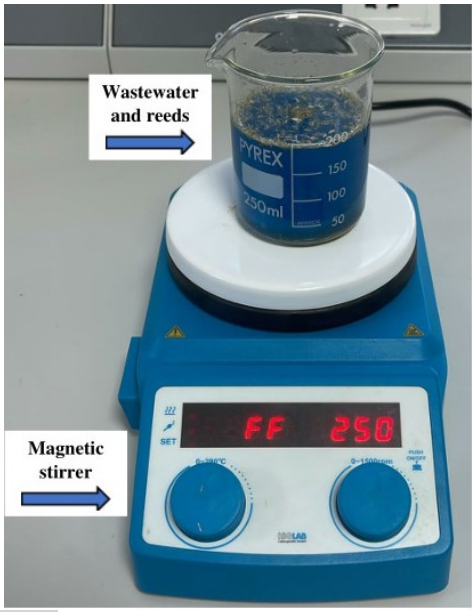


Fig. 5 Photo Image for the Batch System that Used.

3.KINETIC MODELS AND THEORY

To demarcate the isothermal kinetics parameters, the obtained experimental data from the batch system were fitted according to the Langmuir model, Eq. (3), and the Freundlich model, Eq. (4), which are expressed as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{(q_m \times b)} \times \frac{1}{C_e} \quad (3)$$

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e \quad (4)$$

where C_e $(mg\,L^{-1})$ and q_e $(mg\,g^{-1})$ are the equilibrium concentration of the solution and equilibrium adsorption capacity, respectively. The q_m $(mg\,g^{-1})$ is the maximum capacity of the adsorbent dye. b $(L\,mg^{-1})$, k $(mg/g)(L/mg)^{1/n}$, and n are parameters that refer to binding sits alliance, adsorbent sorption capacity, and adsorption intensity, respectively. For a better understanding of the mechanism of sorption and evaluation of the performance of the adsorbent process, two sorption kinetics models have been suggested, i.e., the pseudo-first-order (PFO) and pseudo-second-order (PSO), as given in Eq. (5) and Eq. (6), respectively. The experimental data were fitted to estimate the kinetic model parameters using nonlinear regression analysis.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (5)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (6)$$

where $k_1(\text{min}^{-1})$ and $k_2(g\,mg^{-1}min^{-1})$ are the rate constants.

4.RESULTS AND DISCUSSION

4.1.FTIR Spectroscopy Results

Changing in the function groups on TRR surface before and after the sorption of AB74 dye was assessed by using FTIR Spectroscopy analysis, as shown in Fig. 6. Wavelength between 3200 to 3600 cm^{-1} and 1750 to 1500 cm^{-1} indicate the existence of hydroxyl groups of macromolecular and carboxylic groups [17-19], respectively, on the surface of the reed. As presented in Fig. 6, the wavelength of 3254 cm^{-1} for pristine reed was increased to about 3291 cm^{-1} after dye sorption. However, the wavelength of 1631.8 cm^{-1} for pristine reed has an insignificant change, 1633.7 cm^{-1}, after dye sorption. Accordingly, hydroxyl groups are responsible for the adsorption of AB74 dye on the reed surface.

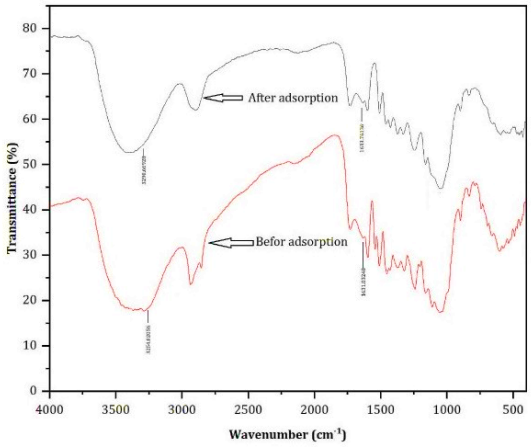


Fig. 6 FTIR Spectroscopy for TRR before and after the Sorption Process.

4.2.Continuous Process

4.2.1.Effect of pH

Dye adsorption on the reed surface strongly depends on the electrostatic attraction between them when they have opposite charges [20, 21]. The pH of the treated solution plays an important role in the performance of the adsorption process. Wherein, pH is responsible for creating the required charge on the reed surface, depending on the dye charge. In addition, pH significantly impacted the dye solubility in the solution. In the present study, the pH solution was changed from 2 to 10 to investigate the impact of pH on η_{dye} and α_{dye} in the continuous biosorption column. The experiments were conducted at atmospheric pressure, and the IDC and Q_w were fixed at 150 ppm and 25 $mL\,min^{-1}$, respectively. Fine particle size was adopted, i.e., 500-850 µm. The concentration of dye in the outlet stream was measured after 40 min of the experiment starting, as shown in Fig. 7.

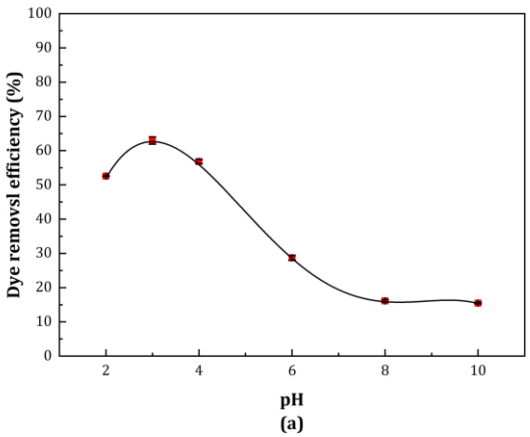


Fig. 7 Effect of pH on (a) η_{dye} (b) α_{dye} at Atmospheric Pressure, IDC = 150 ppm, Q_w = 25 mL min^{-1}, and 850–1180 µm Particle Size.

As presented, it can be observed that the highest values of η_{dye} and α_{dye} were at acidic medium and the maximum η_{dye} and α_{dye} were 62% and 6.5 $mg\ g^{-1}$, respectively, at pH = 3 and this result is agreed with the results that obtained by Alwared et al. [11], attributed to the protonation of the reed surface at acidic medium and subsequently inducing the interaction between the positive charge (cation) of the reed surface and the negative charge (anion) of AB74 dye. Furthermore, the solubility of AB74 dye increased with the pH solution, contributing to the improvement of dye adsorption. However, η_{dye} and α_{dye} declined when pH was lower than 3, η_{dye} = 52.7 % and α_{dye} = 5.5 $mg\ g^{-1}$, which can be explained by the creation of cation sites on AB74, and thus electrostatic repulsion occurred between the reed surface and dye. In addition, η_{dye} and α_{dye} were deteriorated to 15.5 % and 1.6 $mg\ g^{-1}$, respectively, when pH increased to 10. Electrostatic repulsion between the anion nature of reed and AB74 dye could have occurred at high pH, which is responsible for declining η_{dye} and α_{dye}.

4.2.2.Effect of Operating Pressure

The impact of the operating pressure on η_{dye} and α_{dye} in a continuous biosorption process has been investigated. The pressure was varied from atmospheric (zero-gauge pressure) to 6 bar, and the IDC, pH, and Q_w were maintained at 150 ppm, 3, and 25 $mL\ min^{-1}$, respectively. The particle size of reed was 500-850 µm. Figures 8 (a) and (b) represent the effect of operating pressure on η_{dye} and α_{dye}, respectively, with a period of 40 min. The results revealed that η_{dye} and α_{dye} were remarkably enhanced when the pressure increased from 0 to 6 bar, wherein η_{dye} was increased from 62 % to 98 %, and α_{dye} increased from 6.5 to 10.3 $mg\ g^{-1}$. AB74 dye could be introduced into the reed pores at elevated pressure, and thereby the free cations of dyes meet the vacant anions inside the reed pores. The archived α_{dye}, 10.3 $mg\ g^{-1}$, is higher than the maximum biosorption capacity of reactive blue dye, 3.94 $mg\ g^{-1}$, obtained by Alwared et al. [11]. The results provided evidence that operating pressure significantly affected the performance of biosorption in a continuous process.

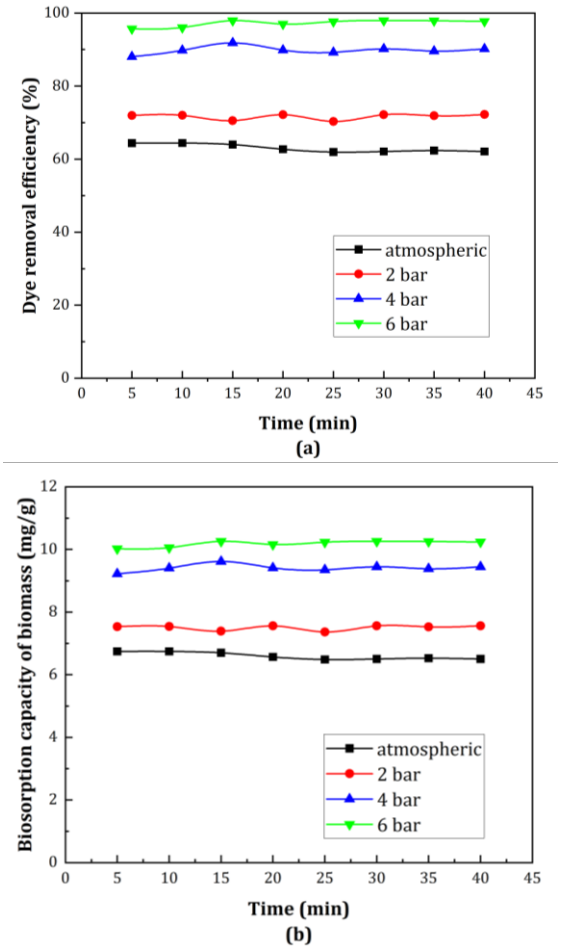


Fig. 8 Effect of the Operating Pressure on (a) η_{dye} (b) α_{dye} at pH = 3, IDC = 150 ppm, Q_w = 25 mL min–1, and Particle Size = 850–1180 µm.

4.2.3.Effect of IDC

The IDC is one of the key operational parameters that impact the performance of the biosorption process. To investigate the impact of IDC on the biosorption process, four concentrations of dye (70, 150, 230, and 300 ppm) were examined at constant operating pressure, pH, and Q_w of 6 bar, 3, and 25 $mL\ min^{-1}$, respectively. The particle size of reed

was 500-850 µm. Figure 9 (a) shows the influence of IDC on the dye removal efficiency during the 40-*min* period. As presented, η_{dye} has a negligible reduction when IDC increased from 70 to 150 ppm. However, a remarkable reduction in η_{dye} was observed when the IDC exceeded 150 ppm. On the contrary, α_{dye} was increased with an increase in IDC, as shown in Fig. 9 (b). The presence of a high number of free cations due to an increase in IDC could increase the driving force; therefore, the free cations occupy the vacant anions on the reed surface. Subsequently, low vacant active sites on the reed surface are responsible for the η_{dye} reduction and α_{dye} rising in the continuous biosorption process. Alwared et al. [11] pointed out that reactive blue dye removal efficiency decreased with an increase in the initial dye concentration, even at a dye concentration less than 150 ppm.

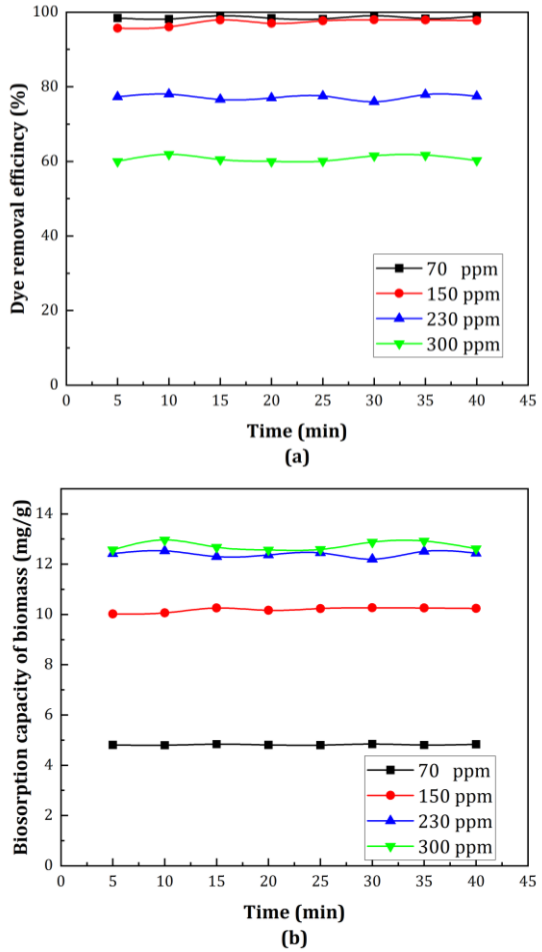


Fig. 9 Effect of the IDC on (a) η_{dye} and (b) α_{dye} at Pressure = 6 bar, pH = 3, Q_w = 25 mL min^{-1}, and Particle Size is 850-1180 µm.

4.2.4.Effect of Wastewater Flow Rate

Typically, the wastewater flow rate is a considerable parameter in the continuous biosorption process. Therefore, three liquid flow rates (25, 50, and 75 mL min^{-1}) were adopted to evaluate the effect of Q_w on the dye sorption in a continuous biosorption process. The IDC and operating pressure were fixed at 150 mg L^{-1} and 6 *bar*, respectively. The fine particle size of reed (500-850 µm) was considered. Figure 10 (a) shows that η_{dye} was decreased with the increase in Q_w, attributed to the low residence time of dye molecules through the biosorption column at high flow rate conditions, reducing the required time to create electrostatic attraction between cations of the dye and anions on the reed surface. In contrast, α_{dye} was dramatically increased with Q_w, as shown in Fig. 10 (b). The dye concentration inside the biosorption column could rise inside the column at high Q_w, increasing mass driving force and thereby increasing α_{dye}.

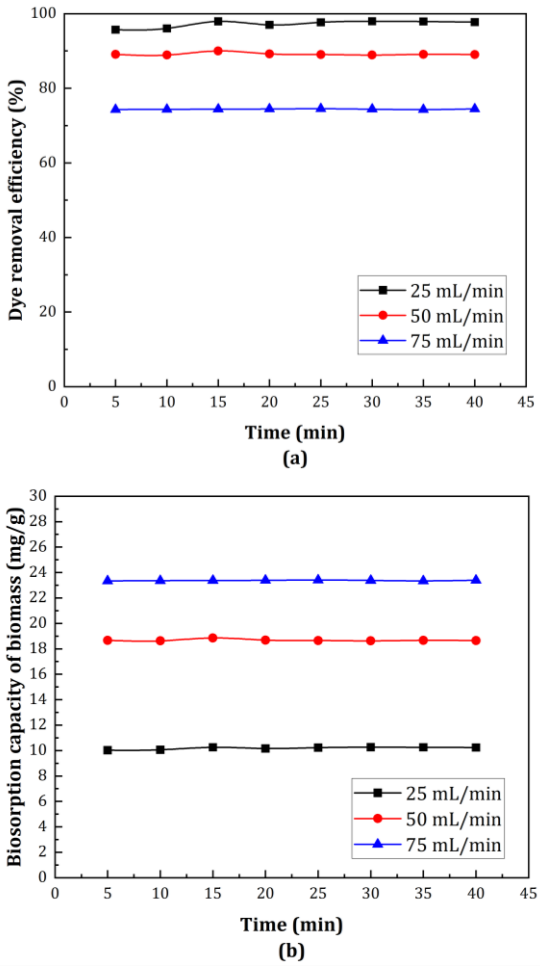


Fig. 10 Effect of Wastewater Flow Rate on the (a) η_{dye} and (b) α_{dye} at Pressure = 6 bar, pH = 3, IDC = 150 ppm, and Particle Size= 850–1180 µm.

4.2.5.Effect of Biomass Particle Size

Three particle sizes of the reed have been adopted, classified as fine particle (FP, 500-850 µm), medium particle (MP, 850-1180 µm), and large particle (LP, 1180-1700 µm). The operating pressure, IDC, and Q_w were maintained at 6 bar, 150 $mg\ L^{-1}$, and 25 $mL\ min^{-1}$, respectively. Figures 11 (a) and (b) illustrate η_{dye} and α_{dye} as a function of the particle size, respectively. As presented, FP and MP had high η_{dye} of 99.5 and 98.5 %, respectively, compared to LP of 64.2 %.

Meanwhile, α_{dye} for FP, MP, and LP were 10.5, 10.3, and 6.7 $mg\ g^{-1}$, respectively, because FP and MP can provide a large surface area compared to LP. As a result, FP and MP provided active sites on the reed surface more than LP, consequently improving the biosorption process. Alwared et al. [11] and Prasath et al. [22] reported that the small particle size of biomass had high-capacity adsorption compared to the larger particle size.

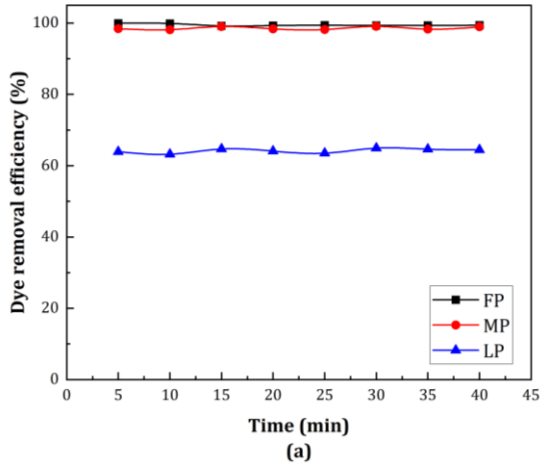
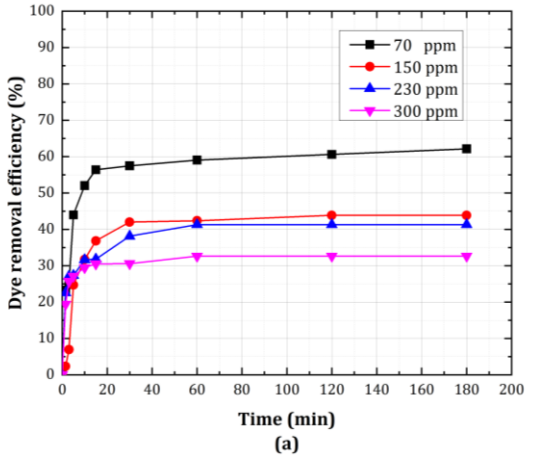


Fig. 11 Effect of the Biomass Particle Size on the (a) η_{dye} and (b) α_{dye} at Pressure = 6 bar, pH = 3, IDC = 150 ppm, and Q_w = 25 mL min^{-1}.

4.3.Batch Experiments

4.3.1.Effect of the Contact Time and the IDC

The influence of contact time on dye adsorption of TRR was assessed in a batch biosorption system over the range of IDC from 70 to 300 ppm, as illustrated in Figs. 12 (a) and (b). The maximum dye removal was observed within 30 *min* and 60 *min* at IDC 70-150 ppm and 230-300 ppm, respectively, attributed that the experiment conducted with initial dye concentrations of (230-300) ppm needing more time to occupy all available active sites due to it having large numbers of dye particles. The time distribution exhibited that the adsorption equilibrium was reached by a treatment time of 180 *min*. At the initial time of adsorption, the free active sites were available at a maximum level, and hence, the adsorption capacity and removal efficiency increased rapidly. Later, the number of occupied active sites increased; therefore, the adsorption capacity and the efficiency of removal became stable with the treatment time. Jain and Gogate [20] revealed a similar result for Acid Blue 25 dye adsorption using activated Ficus racemosa. They reported that beyond 180 *min* of the processing time, the rate of dye removal was mostly stable, attributed to the equilibrium of the adsorption process [23]. Furthermore, Fig. 12 (b) exhibits that increasing the IDC from 70 to 300 ppm increased the α_{dye} from 3.05 to 7.14 $mg\ g^{-1}$, respectively. That increase could be attributed to the increase in the dye particles, as a result of increasing the initial concentration, which led to an increase in the concentration driving force, thereby inhibiting the mass transfer resistance between the bulk and biosorbent surface, promoting the adsorption capacity of dye. A similar result was obtained by Jain and Gogate [24] for removing Acid green 25 using activated Prunus Dulcis. Figure 12 (a) shows that increasing the initial concentration from 70 to 300 ppm, in turn, decreased the removal efficiency from 62.1 to 32.6 %, respectively. The decrease in the IDC in the treated solution reduced the number of dye particles in the solution, thus increasing the possibility of the particle adsorbing into the active sites. At high initial concentrations, this possibility was decreased due to the fixed number of active sites [24-25]. The data obtained from the continuous system in terms of η_{dye} and α_{dye} were higher than those obtained from the batch system. For example, at an IDC of 70 ppm, η_{dye} of the batch and continuous systems were 62.1% and 99.7%, respectively, while α_{dye} for batch and continuous systems were 3.05 $mg\ g^{-1}$ and 4.83 $mg\ g^{-1}$, respectively. This result proves the dye sorption performance is significantly improved using a continuous process at elevated pressure.



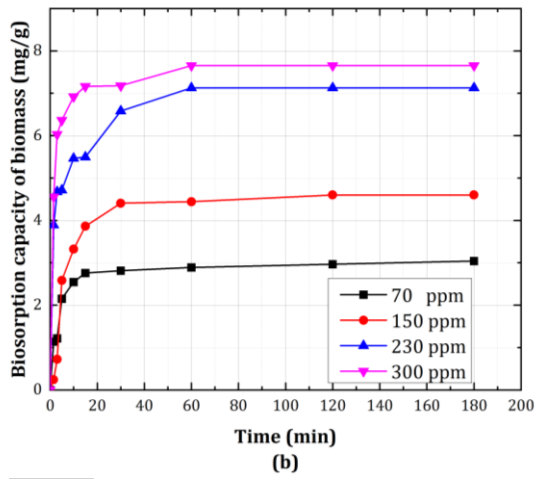


Fig. 12 Effect of the Contact Time and IDC on (a) η_{dye} and (b) α_{dye} in the Batch System at Different IDC at pH = 3 and the Particle Size = 850–1180 µm.

4.3.2.Isothermal Kinetic Models

The parameters for the adopted models in the kinetic study were determined. The obtained kinetic model parameters from the slope and intercept of Eqs. (3) and (4) for experiments of different sets are listed in Table 2. Langmuir isotherm model is based on the mechanism of the adsorption layer, in which the adsorption sites on the sorbent surface have an occupation rate proportional to the number of vacant sites available for the adsorption, while the Freundlich adsorption equation is based on the heterogeneous level of energy states. Table 2 shows that the values of the determination coefficient (R^2) obtained data properly fit with the Freundlich model (R^2=0.9636) compared with the Langmuir model (R^2=0.9409), thereby suggesting that the process was dominated by the chemisorption process.

Table 2 Langmuir and Freundlich Isothermal Parameters.

Isothermal model	Parameters	Values
Langmuir model	$q_m\ (mg\ g^{-1})$	8.62
	$b\ (L\ mg^{-1})$	0.02
	R^2	0.94
Freundlich model	$k\ (mg/g)(L/mg)^{1/n}$	0.67
	n	2.20
	R^2	0.96

4.3.3.Kinetic Study

In this study, the kinetic parameters for PFO and PSO were determined. The obtained kinetic parameters of different sets of experiments, i.e., q_e, k_1, and k_1, are listed in Table 3. It can be observed from Table 2 that the average values of the coefficient of determination for the PFO and PSO models were R^2 = 0.721 and R^2 = 0.9995, respectively. The PSO model is close to unity, whereas the PFO model significantly deviates from unity. Furthermore, Fig. 13 shows a comparison between the calculated adsorption capacity (q_{cal}) and the experimental adsorption capacity (q_{exp}). Figure 13 exhibits that the calculated adsorption capacity (q_{cal}) using the PFO model deviated from the experimental adsorption capacity (q_{exp}). Meanwhile, the calculated data of the PSO model, for all times of the process, are closer to the experimental data. Accordingly, the data confirmed that the PSO model properly fitted with the results. However, the data obtained were aligned to Liu et al. [6] and Chowdhury et al. [25].

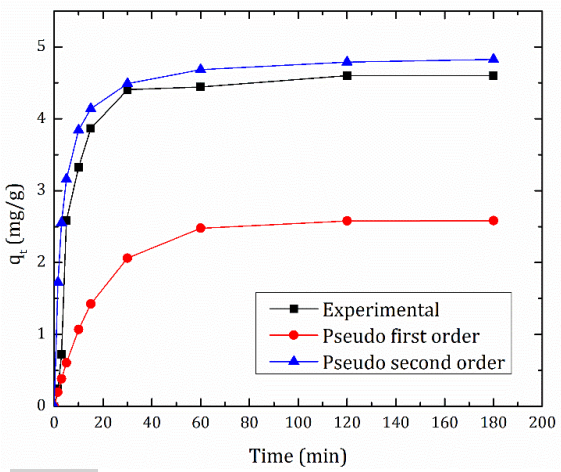


Fig. 13 Comparison of Calculated Adsorption Capacity $(q_t)_{cal}$ with the Experimental Adsorption Capacity $(q_t)_{exp}$ at IDC = 100 ppm and pH=3.

Table 3 Kinetic Parameters for the Removal of Acid Blue 74 Dye Using TRR.

Kinetic model	Parameters	Initial dye concentration (ppm)			
		70	150	230	300
Pseudo first-order	$k_1(min^{-1})$	0.027	0.054	0.046	0.047
	Equilibrium $q_{exp}(mg\ g^{-1})$	3.05	4.60	7.14	7.66
	Equilibrium $q_{cal}(mg\ g^{-1})$	1.12	2.58	5.28	3.34
	R^2	0.85	0.92	0.56	0.53
Pseudo second-order	$k_2(g\ mg^{-1}\ min^{-1})$	0.137	0.074	0.064	0.137
	Equilibrium $q_{exp}(mg\ g^{-1})$	3.05	4.60	7.14	7.66
	Equilibrium $q_{cal}(mg\ g^{-1})$	3.06	4.89	7.23	7.69
	R^2	0.99	0.98	0.99	0.99

5.CONCLUSIONS

The performance of the continuous biosorption process for AB74 dye removal from wastewater using TRR biomass was successfully investigated. The following conclusions are reported:

- The operating pressure significantly affected η_{dye} and α_{dye}. They increased with operating pressure.
- The optimum pH value was 3.
- η_{dye} was decreased when IDC and Q_w increased, and in the meantime, α_{dye} was increased.
- High biosorption performance was observed at FP (500-850 µm) and MP (850-1180 µm).
- The encouraging dye removal efficiency of 99.5% achieved using low-cost biosobents could reduce the overall process cost, making it an attractive method for treating industrial wastewater.
- Batch biosorption of the dye was performed to investigate the mechanism of AB74 dye sorption. The equilibrium time was 30 minutes and 60 minutes for dye concentrations of 70-150 ppm and 230-300 ppm, respectively. The batch experimental data were analyzed using kinetic and isotherm models. The pseudo-second-order kinetic model exhibited a better fit with the experimental data (R^2 = 0.9995) compared to the Langmuir model (R^2=0.9409), suggesting that the process was controlled by chemical adsorption. The Freundlich isotherm model was found to provide the best fit with the experimental data (R^2=0.9636), further supporting the conclusion that the process was dominated by chemisorption.
- In conclusion, this study's results establish that TRR can be used as an effective, low-cost, and environmentally friendly biosorbent for removing AB74 dye from industrial wastewater. The results could be used as a valuable source of experimental data for scaling up and simulation purposes for further validation and pilot-plant studies.

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