Rhodamine-B dye removal using aliquat-336 modified amberlite XAD-4 resin in fixed-bed columns in series

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ABSTRACT

The present work reports studies on the effective removal of Rhodamine-B (RhB) using Aliquat-336 modified Amberlite XAD-4 resin in the fixed-bed columns in series. The effect of flow rate ($Q = 2$ to $6$ mL·min$^{-1}$), bed height ($h = 3.5$ to $7$ cm) and initial RhB dye concentration ($C_{in} = 10$ to $20$ mg·L$^{-1}$) was studied. When a single column was used, $93\%$ RhB dye was removed in $3$ h at $Q = 2$ mL·min$^{-1}$, $C_{in} = 10$ mg·L$^{-1}$, and $h = 7$ cm. When three columns in series were used, almost $100\%$ dye was removed until $80$ h. The maximum breakthrough time ($244$ h) were found by keeping $Q = 2$ mL·min$^{-1}$, $h = 7$ cm of each column and $C_{in} = 10$ mg·L$^{-1}$. Mathematical modeling of the breakthrough curves was done by using Yoon-Nelson, Clark, Wolborska, and pore diffusion models. The Clark model best fitted the experimental data. The possible interaction mechanism between Aliquat-336 and RhB dye was proposed. The column was regenerated in continuous mode using $1$ M HCl solution and maintaining a flow rate of $2$ mL·min$^{-1}$.

Key words: Aliquat 336, Amberlite XAD-4, columns in series, mathematical modeling, Rhodamine-B

HIGHLIGHTS

- Amberlite XAD-4 resin was modified using Aliquat-336.
- Rhodamine-B was removed in fixed-bed columns in series.
- Influence of flow rate, bed height and initial dye concentration was studied.
- Breakthrough curves were modeled.
- Columns were successfully regenerated in continuous mode.

ABBREVIATIONS

- $R_e$ Reynolds number ($-$)
- $\nu$ interstitial velocity of the packed bed (cm·min$^{-1}$)
- $C_{RAB}^0$ initial concentration of solute in solution (kg·m$^{-3}$)
- $\rho$ bed density (kg·m$^{-3}$)
- $\mu$ constant velocity (m·s$^{-1}$)
- $b$ Langmuir isotherm constant (mL·mg$^{-1}$)
- $D_p$ pore diffusion coefficient (m$^2$·s$^{-1}$)
- $D_m$ molecular diffusivity (m$^2$·s$^{-1}$)
- $D_{ax}$ axial dispersion coefficient (m$^2$·s$^{-1}$)
- $k_f'$ film resistance coefficient (m·s$^{-1}$)
- $h$ bed length (cm)
- $\phi$ association factor of water ($-$)
- $S_c$ Schmidt number ($-$)
- $\mu$ viscosity of dye solution (cp)
- $t$ time (min)
- $t_b$ breakthrough time (min)
- $V_s$ volume of saturated solution (mL·g$^{-1}$)
- $V_A$ molar volume of RhB dye (cc·g$^{-1}$·mol$^{-1}$)

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These resins are used for the removal of several pollutants like heavy metals (Belkhouche & Didi 2010; Turanov, et al. 2017; Sharma et al. 2018). The regenerability and reusability of the adsorbent are always a big concern for the economical use of these adsorbents. The choking and pressure drop problem of the powder adsorbents in the fixed bed column restricts its use at an industrial scale. Therefore, an adsorbent in a granular form can solve the choking problems in the columns, and regeneration of these adsorbents becomes easy.

Recently, polymeric resin modified with some reagent has gained attention to remove specific pollutants from wastewater. These resins are used for the removal of several heavy metals (Belkhouche & Didi 2010; Turanov et al. 2017), butyric acid (Blahušiak et al. 2015), amino acids (Oshima et al. 2009), bisphenol-A (Batra & Datta 2020), phenol and its derivatives (Lin & Juang 2009), etc. Modifying these resins with chemical binding is a tedious method, while resin modification by impregnation is simple, easy, and cost-effective method (Tetgure et al. 2017). In the impregnation process, a suitable solvent is dissolved in an appropriate diluent and is impregnated into the pores of macro-porous resin by the wet/dry impregnation method. The resin after modification is known as solvent impregnated resin (SIR). The use of SIR for the treatment of different dye-containing wastewaters has some advantages over other types of adsorbent used. Generally, the solvent is impregnated inside the resin pores. Therefore, it is required in a lesser amount compared to the extraction process. There is a tendency of third phase/emulsion formation in the extraction process, which creates difficulty in phase separation. This problem can be minimized by using SIR. The impregnation of solvent can be done based on the type of pollutant that is to be treated. It facilitates selective separation of adsorbate by the SIR. SIR can be synthesized so that it can handle any aqueous medium, whether acidic or alkaline. Further, powdered activated carbon or nano-particles increases the pressure drop and choking the fixed-bed column, whereas the granular form of SIR can be effectively used in continuous column experiments (Batra et al. 2020). SIR so formed should be hydrophobic in nature, interact with pollutant molecules effectively, should have good physical and chemical stability, and the impregnating solvent should not be leached out from the SIR. For this purpose, Amberlite XAD resins are widely used because of their excellent physical and chemical properties like hydrophobicity, and being highly porous, non-ionic, and chemically and thermally stable. Amberlite XAD-4 (AX4) is a styrene

1. INTRODUCTION

Refractory chemicals present in industrial effluents are creating significant problems in developing countries. These effluents contain several carcinogenic and pathogenic pollutants, which are difficult to be removed by conventional treatment plants. The color of the wastewater creates a feeling of displeasure. About 90% to 75% of the total dyes used in textiles are bonded with the fabric and the remaining 10% to 25% is discharged in the environment as colored effluent (Saini 2017). Around 2,80,000 tons of dyes are wasted during the application because of the ineffective practices adopted all over the world (Berdawi et al. 2019). The unchecked release of wastewater containing dyes creates serious hazards to living beings and the environment. Dyes restrict the penetration of light in the water bodies and cause several ailments in human beings like tissue necrosis, vomiting, neurotoxicity, reproductive and developmental toxicity, etc. Even 1 ppm of dye concentration may impart significant color in drinking water (Srinivasan & Viraraghavan 2010). Organic ionic dyes have delocalized electrons in their aromatic rings. Rhodamine-B (RhB) is an organic cationic dye extensively used in the textile industry for coloring cotton, wool, and silk (Chemwatch 2010; Safiri et al. 2015). Therefore, wastewater containing RhB dye should be treated before discharging into water bodies.

Several methods like oxidation (Jonstrup et al. 2011), hydrodynamic cavitation (Rajoriya et al. 2018), membrane separation (Baghel et al. 2018), photocatalytic degradation (Inamuddin 2019), adsorption (Awasthi & Datta 2019), adsorption accelerated by ultrasonication (Iqbal & Datta 2019), biochemical degradation (Lucas et al. 2007), coagulation and flocculation (Dotto et al. 2019) have been used for the removal of dyes. Among all these methods, adsorption is widely and effectively used for the removal of toxic textile dyes. Many synthetic and natural adsorbents were used for the removal of textile dyes, but the majority of the adsorbents were prepared by some tedious procedure (Datta et al. 2017; Sharma et al. 2018). Also, specific inexpensive adsorbents were prepared from waste biomass to remove textile dyes, but their disposal is a significant concern for the environment (Srivatsav et al. 2020). The regenerability and reusability of the adsorbent are always a big concern for the economical use of these adsorbents. The choking and pressure drop problem of the powder adsorbents in the fixed bed column restricts its use at an industrial scale. Therefore, an adsorbent in a granular form can solve the choking problems in the columns, and regeneration of these adsorbents becomes easy.
divinyl-benzene based cross-linked macro-porous polymer (average pore diameter = 5 nm, surface area = 725 m²·g⁻¹, pore volume = 0.98 mL·g⁻¹) (Dave et al. 2010). It is hydrophobic, non-polar, non-ionic, and remains stable up to a temperature of 522 K, and applicable in a wide range of pH (as published by Sigma Aldrich 1991). The cross-linking provides mechanical and thermal stability, which helps the resin to withstand physical forces during the impregnation and adsorption process (Li et al. 2013; Du et al. 2014). Aliquat-336 (A-336) is an amine-based ionic liquid and a mixture of octa and deca chains with the three branched-chain of the alkyl group, which makes it hydrophobic and easily soluble in organic solvents (like hexane). A-336 makes the physical bond with the resin matrix, which stabilizes the SIR during the adsorption process and interacts with many pollutants, making a chemical bond with them.

To date, no literature is available for the removal of rhodamine-B or any other cationic dye using solvent-impregnated resin in fixed-bed columns in series and to find the effect of different parameters on the separation capacity of the impregnated resin. Further, the interaction of dye molecules with the impregnated resin could also be explored in the fixed bed column. Fixed-bed columns used in series have their advantages. The effluent flow rate can be controlled by adding or removing a particular column from the process using a control valve. When any column gets saturated, the inlet of the solution could be bypassed to another column using a controlled bypass valve, and the same column may be separated from the main-streams. Then, some suitable regenerating solution can be passed through that column to regenerate it. Therefore, the process can be continued without any hindrance or interruption in the separation process. There is no study in which a column is regenerated in continuous mode for the treatment of rhodamine-B using SIR. Therefore, the aim of the present work is to investigate the performance of three fixed-bed columns in series using A-336 wet impregnated AX4 resin. The column bed height, influent flow rate, and dye concentration were varied to see their effect on the breakthrough curve and saturation time. The kinetic model equations were fitted to the experimental breakthrough curves, and the best-described kinetic model was proposed. Again, the breakthrough curves were also predicted by the pore diffusion model, which was programmed in Matlab software (Matlab R 2015b). Finally, the columns were regenerated using 1 M HCl solution in continuous mode and reused to see the efficiency and reusability of the column. A-336 impregnated AX4 resin was compared with other available adsorbents used for the separation of rhodamine-Bt, and the possible mechanism of dye interaction with the resin was proposed.

2. EXPERIMENTAL

2.1. Materials

Amberlite XAD-4 (20–60 mesh) and Aliquat-336 (97 vol.%) were purchased from Sigma-Aldrich (Germany). Rhodamine-B (molecular weight = 479.02 g·mol⁻¹, molecular formula = C₂₈H₃₁ClN₂NaO₃, 85 wt.% pure) received from Loba Chem (India). Ethanol (99 vol.%), hydrogen chloride (37 vol.%), and n-hexane (99 vol.%), and n-hexane (99 vol.%), were purchased from Merck (Germany). For the preparation of aqueous dye solutions, double-distilled water was used.

2.2. Method

Analytical balance (MAB 220 Wensar, India) was used for weighing dye, resin, and other chemicals. For the drying of washed and impregnated resin, a hot air oven (Pro-Lab Scientific Instruments, India) was used. A-336 was diluted in n-hexane using a magnetic stirrer (5 MLH Plus, REMI, India). The method of preparation of SIR was published in detail in our previous study (Iqbal & Datta 2020). A336 was impregnated in the macro-porous AX4 resin by the wet impregnation method (Kabay et al. 2003). At first, the original resin was washed with ethanol, followed by double-distilled water, and then dried. After that, A-336 was impregnated into the pores of the resin by maintaining an impregnation ratio of 1 g A-336 per g of resin. The prepared resin was filtered with a Nylon cloth of 100 mesh size and dried. SIR so formed was ready for use. The characterization of prepared SIR before and after adsorption is already published in our previous study, which was performed in batch mode (Iqbal & Datta 2020). In FTIR, sharp and long peaks at 2,854 cm⁻¹ and 2,923 cm⁻¹ showed CH₂-N and CH₃-N groups, respectively, present in A336. The EDS analysis of the washed, impregnated, and used adsorbent showed a change in the elemental composition of the resin. The increase in chlorine weight percent indicated impregnation of A336 and adsorption of RhB dye as no chlorine atom was present in the washed resin. The dye solution's initial and final absorbance was noted using a double beam UV-Vis spectrophotometer (Evolution 220, Thermo Fisher Scientific, USA). To maintain a constant flow rate of dye solution, a peristaltic pump (RH-P110S-50, Ravel, India) was used. A constant temperature of the columns was maintained by circulating water in the column jacket using a centrifugal pump. The stock solution of rhodamine-B (RhB) dye with a concentration of 200 mg·L⁻¹ was prepared using double-distilled water in an amber colour volumetric flask of
250 mL. This stock solution was used for making the dye solution of requisite concentrations whenever required. In the present work, fixed-bed column continuous experimental studies were performed using three borosilicate glass columns in series with an internal diameter of 7 mm, and the total length of column 32 cm (shown in Figure 1). The length of the bed of the fixed bed column was varied according to the amount of SIR used (3.5 cm = 0.50 g, 5.25 cm = 0.75 g, and 7 cm = 1.0 g). The initial concentrations of RhB dye in the aqueous solution were 10, 15, and 20 mg·L$^{-1}$. RhB dye solution was pumped in the down-flow direction through the column at a controlled flow rate (2, 4, or 6 mL·min$^{-1}$) using a peristaltic pump. A two-level full factorial design was used to plan the fixed-bed column experiments by varying the input variables like bed height (3.5 to 7 cm in each column), initial dye concentration (10 to 20 mg·L$^{-1}$), and volumetric flow rate (2 to 6 mL·min$^{-1}$). The above input variables were decided by performing some preliminary studies using a single column. The two-level full factorial design was applied using MINITAB software (v.17.1.0.). Breakthrough and saturation time was considered as the response of the input variables. All the experiments were performed in duplicate, and their average value was used for the calculation.

2.3. Theoretical

The mathematical modeling is very much crucial for scaling up the experimental laboratory results. It helps to analyze the experimental data by varying different parameters and operating conditions of the process and to optimize the overall process economically. Different mathematical breakthrough curve models have been used to analyze the performance of the fixed bed column by calculating the following model parameters (Maheshwari & Gupta 2016):

- The volume of dye solution treated at saturation (mL·g$^{-1}$): $V_s = \frac{t_s \times Q}{m}$ (1)

- Column adsorption capacity (mg·g$^{-1}$): $q_{\text{total}} = \frac{Q}{m \times 1,000} \int_{t=0}^{t} C_{\text{ad}} \, dt$ (2)

- The empty bed residence time: $\text{EBRT} = \frac{\text{Resin bed volume}}{\text{Volumetric flow rate of dye solution}}$ (3)

where, $Q =$ flow rate (mL·min$^{-1}$), $m =$ mass of SIR (g), $t =$ time (min), $C_{\text{ad}}$ (mg·L$^{-1}$) = $C_{\text{in}}$ - $C_t$, the amount of adsorbed dye.

Figure 1 | Schematic diagram for experimental set-up for fixed bed columns in series.
2.3.1. Kinetic models
Since the initial concentration changes with time in the second and third columns, column models were applied by considering the three columns as one. The Yoon-Nelson model is a simple model to predict the shape of the breakthrough curve for the adsorption of adsorbate in a fixed bed column. It is based on the assumption that the probability of the rate of decrease of adsorbate amount is proportional to the probability of adsorption and the breakthrough probability on the adsorbent surface (Equation (3), (Yoon & Nelson 1984)). It does not depend on the characteristics of the adsorbate, properties of the adsorbent, and physical properties of the adsorbent bed. The model can estimate the breakthrough curve for the adsorbent with a large micro-pore and large average diameter (Mastral et al. 2002). The parameter \( \tau \) (min) is half the time to saturate the bed completely. The model proposed by Clark (Equation (4), (Clark 1987)) depends on the utilization of a mass-transfer blend with the Freundlich model. The heterogeneity factor \( 'n' \) of the model obtained from the Freundlich model estimated the value from the batch study. In the fixed-bed column, the breakthrough curve with a low solute concentration solution can be described by the Wolborska model (Equation (5) (Wolborska 1989)). The initial section of the breakthrough curve is controlled by film diffusion with a constant kinetic coefficient, and the concentration profile of the initial stage moves axially in the column at a constant velocity.

\[
\ln\left(\frac{c_t}{c_{in} - c_t}\right) = k_{YN}(t - \tau) \tag{4}
\]

\[
\left(\frac{c_{in}}{c_t}\right)^{(n-1)} - 1 = Ae^{-rt} \tag{5}
\]

\[
\ln\left(\frac{c_t}{c_{in}}\right) = \beta \frac{C_{in} t}{N_o} - \beta \frac{h}{Q} \tag{6}
\]

where, \( K_{YN} \) (min\(^{-1}\)) = rate constant of the Yoon-Nelson model for the adsorption of RhB dye by SIR. \( \tau \) (min) = time required to achieve 50% adsorbate breakthrough from Yoon-Nelson model. \( 'n' \) is the heterogeneity factor of the Freundlich model, \( A \) and \( r \) (h\(^{-1}\)) are the Clark model. \( \beta \) is the kinetic coefficient of external mass transfer (min\(^{-1}\)), and \( N_o \) is the saturation concentration of the effluent (mg·L\(^{-1}\)).

2.3.2. Pore diffusion model
In the pore diffusion model, the film diffusion is considered to be zero, and the experimental breakthrough curve for inlet concentration can be taken from the experimental data. Fick’s law of diffusion is followed by the liquid inside the pore. For the adsorption of dye using a spherical particle with pore diffusion, the standard model equations are used (Ma et al. 1996; Kavand et al. 2018). Film mass transfer coefficient \( (k_f) \) and axial dispersion coefficient \( (D_{ax}) \), the molecular diffusivity \( (D_m) \) of RhB dye in the aqueous solution was calculated using Equations (6)–(8), respectively (Che-Galicia et al. 2014).

\[
Sh = \frac{k_f}{D_m} \times \left(\frac{1.09}{e_b}\right) \times S_c^{1/3} \times R_e^{1/3} \tag{7}
\]

\[
D_m = 7.4 \times 10^{-8} \left(\frac{\phi \times M_B}{\eta_B \times V^{0.6}}\right)^{1/2} \times T \tag{8}
\]

\[
D_p = \frac{\varepsilon_p}{(2-\varepsilon_p)^2} \times D_m \tag{9}
\]

3. RESULTS AND DISCUSSION
3.1. Influence of operation conditions on RhB dye removal
3.1.1. Effect of dye concentration
The breakthrough point was taken when the effluent concentration was more than 90% of the initial dye concentration. Since rhodamine-B dye has very excellent color imparting properties, even 2 mg·L\(^{-1}\) concentration imparts significant color in the aqueous solution. Therefore, a saturation of the bed was considered when the effluent of the dye solution of the column
exceeded 4 mg·L\(^{-1}\). The change of the initial dye concentration has a significant effect on the saturation and breakthrough curve of the fixed-bed column. The effect of dye concentration on the removal of rhodamine-B dye was investigated and compared in Figure 2(a) and 2(b) for 10 and 20 mg·L\(^{-1}\), respectively, at a fixed flow rate of 2 mL·min\(^{-1}\) and a bed height of 7 cm in all three columns. In column 1, the breakthrough and the saturation point were achieved after 4 and 45 h, respectively, at \(C_{in} = 10\) mg·L\(^{-1}\). As the dye concentration increased to 20 mg·L\(^{-1}\), the breakthrough \(t_t\) and the saturation point \(t_s\) were achieved in 25 min and 9 h, respectively. On increasing the dye concentration from 10 mg·L\(^{-1}\) to 20 mg·L\(^{-1}\), the dye molecules are doubled, whereas the availability of active sites for the adsorption of dye was constant. Therefore, a significant decrease in \(t_t\) and \(t_s\) was observed in increasing the dye concentration. In column 2, the breakthrough and saturation point was observed after 70 and 130 h with 10 mg·L\(^{-1}\) of dye solution, whereas with 20 mg·L\(^{-1}\), the breakthrough and saturation point was observed after 34 and 60 h, respectively. In column 3, the breakthrough and saturation point was observed after 142 and 244 h, respectively, for 10 mg·L\(^{-1}\) and 96 and 120 h, respectively, for 20 mg·L\(^{-1}\). The saturation time was almost double with 10 mg·L\(^{-1}\) of dye solution than 20 mg·L\(^{-1}\) of dye solution in column 3. The breakthrough and saturation were reached earlier in all columns when the initial concentration of dye was increased.

3.1.2. Effect of bed height

The effect of bed height for the removal of rhodamine-B dye is shown in Figure 2(a) and 2(c) by keeping the flow rate at 2 mL·min\(^{-1}\) and dye concentration at 10 mg·L\(^{-1}\). A clear \(t_t\) was not observed in column 1 for 3.5 cm of bed height, and comparatively low dye removal was observed (71%) in the initial time of 5 min. The bed saturation achieved within 3 h in a 3.5 cm column, whereas bed saturation was achieved in 45 h in a 7 cm column. With the increase in the bed depth of the resin in the column, a greater number of active sites are available for the adsorption of dye molecules. Therefore, more time will be required for the column to be saturated. In column 2 with \(h = 5.5\) cm, the \(t_t\) and \(t_s\) occurred in 1 and 12 h, respectively. With \(h = 7\) cm, it takes 70 and 130 h to reach the \(t_t\) and \(t_s\), respectively. In the third column at \(h = 5.5\) cm, the \(t_t\) and the \(t_s\) were observed at 18 and 95 h, respectively. With the same condition of dye concentration and flow rate (\(C_{in} = 10\) mg·L\(^{-1}\) and \(Q = 2\) mL·min\(^{-1}\)) at a bed height of 7 cm, the breakthrough point and the saturation point increased to 142 and 244 h, respectively (Figure 2(a)). For 3.5 cm bed height (\(C_{in} = 20\) mg·L\(^{-1}\) and \(Q = 2\) mL·min\(^{-1}\)), the breakthrough point was not observed and the saturation was achieved immediately for columns 1 and 2. In column 3, the breakthrough and saturation point were observed after 10 and 16 h, respectively (Figure 2(b) – 2(d)).

3.1.3. Effect of flow rate

The feed flow rate on the adsorption of rhodamine-B dye on the surface of the resin has a significant effect, and the removal of dye was compared by varying the feed flow rate from 2 to 6 mL·min\(^{-1}\) as shown in Figure 2(a) and 2(e) for \(C_{in} = 10\) mg·L\(^{-1}\) and \(h = 7\) cm. The results showed that the dye uptake on the resin surface decreased with an increase in the flow rate of the influent solution through the resin bed because of the insufficient time between the dye molecule and the resin. The volume of effluent treated also decreased. At \(Q = 2\) mL·min\(^{-1}\) (\(C_{in} = 10\) mg·L\(^{-1}\) and \(h = 7\) cm), high breakthrough (142 h) and saturation time (244 h) was achieved in the effluent of the third column. On increasing the flow rate from 2 to 6 mL·min\(^{-1}\), the initial removal decreased to 26% and observed no breakthrough point in columns 1, 2, and 3 (Figure 2(e)). The saturation point was achieved in 3 and 6 h in columns 2 and 3, respectively. On increasing the concentration to 20 mg·L\(^{-1}\) (at \(Q = 6\) mL·min\(^{-1}\) and \(h = 7\) cm), the removal of rhodamine-B dye increases significantly (Figure 2(f)). Due to the high flow rate and high initial concentration of the dye solution, the breakthrough point was not observed in columns 1, 2, and 3 (Figure 2(f)). However, in the third column, the saturation point was observed after 7 h. Whereas, when the flow rate was increased to 6 mL·min\(^{-1}\) (\(C_{in} = 20\) mg·L\(^{-1}\) and \(h = 3.5\) cm), the breakthrough and the saturation were observed immediately in all three columns (within 5 min), which indicates high flow rate and high concentration significantly diminishes the removal efficiency of resin for rhodamine-B dye removal (Figure 2(g)). With 10 mg·L\(^{-1}\) of dye solution (\(Q = 6\) mL·min\(^{-1}\) and \(h = 3.5\) cm), the breakthrough point was not observed in all three columns and the saturation was achieved earlier in columns 1 and 2 (Figure 2(h)). In column 3, the saturation was achieved after 1 h. The effect of the three parameters was also analyzed by keeping the three parameters at their middle values (\(Q = 4\) mL·min\(^{-1}\), \(C_{in} = 15\) mg·L\(^{-1}\), and \(h = 5.25\) cm) shown in Figure 2(i). The clear breakthrough point was not observed in any of the three columns, whereas it took 1, 16, 42 h to reach the saturation point for columns 1, 2, and 3 respectively. The equilibrium time for the complete removal of rhodamine-B dye was 3 h in the batch study. Due to the slow rate of adsorption, with an increase in the feed flow
rate, the removal of rhodamine-B dye was significantly decreased as the resin particles did not get sufficient time to interact with the dye molecules.
3.2. Estimation of column parameters and mathematical modeling

Column parameters were calculated by considering three columns as a single one; that is, inlet concentration of the first column and outlet concentration of the third column was considered. The adsorption capacity of the resin was calculated at saturation. Column data with different calculated parameters are listed in Table 1. The increase in the mass of the resin in the fixed bed column has a significant positive effect on the $t_b$, $t_s$, and $Q_t$ of the resin. When the bed height increased from 0.105 m to 0.210 m ($Q = 2 \text{ mL} \cdot \text{min}^{-1}$, and $C_{in} = 10 \text{ mg} \cdot \text{L}^{-1}$), $t_b$ increased from 33 h to 111.5 h, $t_s$ increased from 128 to 281 h, and $Q_t$ increased from 16.43 mg g$^{-1}$ to 28.09 mg g$^{-1}$. The increase in the $C_{in}$ had a negative effect on all the parameters, as shown in Table 1. With an increase in $C_{in}$ from 10 mg L$^{-1}$ to 20 mg L$^{-1}$ ($Q = 2 \text{ mL} \cdot \text{min}^{-1}$, and $m = 1.5$ g), $t_b$ decreased from 33 to 9 h, $t_s$ decreased from 128 to 34 h, and $Q_t$ decreased from 16.43 mg g$^{-1}$ to 3.13 mg g$^{-1}$. An increase in $Q$ also had a negative effect on $t_b$, $t_s$, and $Q_t$. When the $Q$ increased from 2 mL min$^{-1}$ to 6 mL min$^{-1}$ ($C_{in} = 10 \text{ mg} \cdot \text{L}^{-1}$, and $h = 0.105$ m), $t_b$ decreased from 33 to 5 h, $t_s$ decreased from 128 to 21 h, and $Q_t$ decreased from 16.43 mg g$^{-1}$ to 0.40 mg g$^{-1}$. Empty bed residence time (EBRT) is a function of the volume of the resin bed and the volumetric flow rate. It is also known as the empty bed contact time and is defined as the time required for filling the resin bed. It is used to determine the optimum resin amount for a fixed-bed column. EBRT also increased from 1.51 to 3.01 min with increase in the mass of resin from 1.5 to 3 g ($Q = 2 \text{ mL} \cdot \text{min}^{-1}$, and $C_{in} = 10 \text{ mg} \cdot \text{L}^{-1}$). The higher EBRT values are responsible for the lower exhaustion of the resin. The EBRT decreased as the $Q$ and $C_{in}$ increased.

$K_{YN}$ (rate constant, h$^{-1}$) values do not have much effect by changing the bed height of the fixed bed column ($K_{YN} = 5.09 \times 10^{-4}$ at $h = 0.105$ m and $K_{YN} = 4.78 \times 10^{-4}$ h$^{-1}$ at $h = 0.210$ m). The values of '$r'$ decreased from 108 h to 26.84 h when the $C_{in}$ increased from 10 mg L$^{-1}$ to 20 mg L$^{-1}$ and the value of '$r'$ increased from 108 h to 242.29 h when the bed height
Table 1 | Different model parameter values for the removal of rhodamine-B dye using Aliquat-336 impregnated Amberlite XAD-4 resin

| S. No. | Column condition | Column parameters | Yoon-Nelson model | Clark model | Wolborska model |
|--------|------------------|-------------------|-------------------|-------------|-----------------|
|        | Q (mL·min⁻¹)    | h (m)             | C₀ (mg·L⁻¹) | t₀ (h) | tₛ (h) | Vₛ (L·g⁻¹) | EBRT (min) | Qₛ (mg·g⁻¹) | Kᵥn (h⁻¹) | τ (h) | R² | r (h⁻¹) | lnA (-) | R² | ϕ (min⁻¹) | Nᵥ (mg·L⁻¹) | R² |
| 1      | 2                | 0.105             | 10               | 33  | 128   | 10.24     | 1.51      | 16.43 | 5.09 x 10⁻⁴ | 108.06 | 0.904 | 0.03 | 3.20 | 0.907 | 0.64 | 263.96 | 0.850 |
| 2      | 2                | 0.210             | 10               | 118.5 | 281 | 11.24     | 3.01      | 28.09 | 4.78 x 10⁻⁴ | 242.29 | 0.959 | 0.03 | 6.68 | 0.960 | 0.65 | 246.25 | 0.943 |
| 3      | 6                | 0.105             | 10               | 5   | 21    | 5.04     | 0.50      | 0.40  | 1.62 x 10⁻³ | 11.46 | 0.931 | 0.10 | 1.04 | 0.933 | 0.77 | 283.67 | 0.861 |
| 4      | 6                | 0.210             | 10               | 5   | 21    | 2.52     | 1.00      | 0.83  | 1.56 x 10⁻³ | 11.88 | 0.932 | 0.10 | 1.04 | 0.933 | 0.39 | 72.77  | 0.863 |
| 5      | 2                | 0.105             | 20               | 9   | 34    | 2.72     | 1.51      | 3.13  | 2.23 x 10⁻³ | 26.84 | 0.971 | 0.13 | 3.45 | 0.971 | 0.67 | 130.93 | 0.954 |
| 6      | 2                | 0.210             | 20               | 72  | 132   | 5.28     | 3.01      | 15.89 | 8.93 x 10⁻⁴ | 140.08 | 0.952 | 0.05 | 7.21 | 0.953 | 0.71 | 275.78 | 0.948 |
| 7      | 6                | 0.105             | 20               | 3   | 19    | 4.56     | 0.50      | 0.10  | 1.43 x 10⁻³ | 8.15 | 0.841 | 0.08 | 0.63 | 0.842 | 0.63 | 272.26 | 0.779 |
| 8      | 6                | 0.210             | 20               | 6   | 31    | 3.72     | 1.00      | 0.10  | 9.09 x 10⁻⁴ | 25.91 | 0.909 | 0.02 | 1.33 | 0.909 | 0.47 | 703.26 | 0.902 |
| 9      | 4                | 0.158             | 15               | 8   | 27    | 2.88     | 1.13      | 0.17  | 3.56 x 10⁻⁴ | 38.65 | 0.824 | 0.02 | 0.13 | 0.829 | 0.19 | 303.84 | 0.746 |
increased from 0.105 m to 0.210 m with $R^2 = 0.959$ shown in Table 1. The above results indicate the half-saturation time of the fixed-bed increase with an increase in bed height and decreased with the increase in the flow rate and initial concentration of dye solution. In our previous batch mode equilibrium study, the Freundlich isotherm was best fitted for the equilibrium data of rhodamine-B dye removal by Aliquat-336 impregnated Amberlite XAD-4 resin, which is the basic requirement for applying the Clark model in fixed bed column data. Therefore, the heterogeneity factor \(n_F\) of the Freundlich model was used to calculate the Clark model constant in the column. The Clark model parameters with the correlation coefficient for all the experimental runs are listed in Table 1. As the flow rate (from 2 to 6 mL·min$^{-1}$) and initial concentration of rhodamine-B dye solution (from 10 to 20 mg·L$^{-1}$) increased, the value of \(r'\) also increased from 0.0278 to 0.0921 and 0.0278 to 0.0517, respectively. The low value of \(r'\) is favorable for the higher breakthrough and saturation time, and as the value of \(r'\) increased, the time required for breakthrough and saturation of the column bed decreased (Table 1) (Hu et al. 2020). The Clark model best fitted the column data (Figure 3(a) – 3(c)). In the Wolborska model, as the flow rate increased from 2 mL·min$^{-1}$ to 6 mL·min$^{-1}$ (keeping other column parameters constant), the value of the kinetic coefficient of external mass transfer ($\beta$) increased from 0.64 to 0.77 min$^{-1}$ and as the concentration increases from 10 to 20 mg·L$^{-1}$, the values of $\beta$ increased from 0.65 to 0.71 min$^{-1}$ which result in the decrease of the breakthrough curve. The saturation concentration ($N_o$) in the effluent stream increases from 263.96 to 283.67 mg·L$^{-1}$ with an increase in the flow rate from 2 mL·min$^{-1}$ to 6 mL·min$^{-1}$ and as the initial concentration of dye increases from 10 mg·L$^{-1}$ to 20 mg·L$^{-1}$, in the flow $N_o$ increases from $263.96$ to $283.67$ mg·L$^{-1}$.

**Figure 3** | Experimental and predicted breakthrough curves (a) $Q = 2$ mL·min$^{-1}$, $C_{in} = 10$ mg·L$^{-1}$, $\sigma = 0.033$ for $h = 0.105$ m, $\sigma = 0.025$ for $h = 0.21$ m, (b) $C_{in} = 10$ mg·L$^{-1}$, $h = 0.21$, $\sigma = 0.018$ for $Q = 6$ mL·min$^{-1}$, $\sigma = 0.025$ for $Q = 2$ mL·min$^{-1}$, (c) $h = 0.21$, $Q = 2$ mL·min$^{-1}$, $\sigma = 0.025$ for $C_{in} = 10$ mg·L$^{-1}$, $\sigma = 0.004$ for $C_{in} = 20$ mg·L$^{-1}$. 

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246.25 to 275.78 mg·L$^{-1}$. It indicates that the efficiency of the resin decreases with the increase in flow rate and initial dye concentration. In contrast, resin efficiency increases with an increase in the bed height of the column.

In the pore diffusion model, the film diffusion is considered to be zero, and the experimental breakthrough curve and predicted by the pore diffusion model is shown in Figure 4(a) – 4(b). The packed bed column parameters like inner diameter ($d$), the porosity of adsorbent ($\varepsilon_p$), and their radius ($R_p$) are constant values. Other parameters like bed length ($L$) and bed porosity or bed void fraction ($\varepsilon_b$) depend upon the amount of adsorbent taken and packing status (Table 2). The simulated curve for the pore diffusion model was obtained in a purely predicted way using independently determined isotherm and their calculated parameters. The parameters calculated from the batch and column mode of operation and mass transport parameters were used for simulating the breakthrough curve. The experimental and predicted (by pore diffusion model) breakthrough point was almost the same ($t_b = 144$ h).

3.3. Regeneration and reuse of packed bed-column, comparison with other adsorbents, and possible mechanism for RhB dye with Aliquat-336

The regeneration of adsorbent is an essential aspect of designing and evaluating the sorption system. The used resin was regenerated in three columns in series using 1 M HCl solution at a flow rate of 2 mL·min$^{-1}$. Three columns in series were successfully regenerated, and their RhB dye desorption behavior is shown in Figure 5(a) and 5(b). The regenerated

![Figure 4](http://iwaponline.com/wst/article-pdf/85/1/1/985724/wst085010001.pdf)

Figure 4 | Experimental and predicted by pore diffusion model breakthrough curve of RhB dye at optimum condition (a) $h = 21$ cm, $Q = 2$ mL·min$^{-1}$, and $C_{in} = 10$ mg·L$^{-1}$ (b) $h = 21$ cm, $Q = 2$ mL·min$^{-1}$, and $C_{in} = 20$ mg·L$^{-1}$. 
**Table 2** | Experimental and calculated values used in the pore diffusion model

| Parameters                                      | Values            |
|-------------------------------------------------|-------------------|
| Feed flow rate ($m^3\cdot s^{-1}$)              | $3 \times 10^{-8}$|
| Film mass transfer coefficient ($m\cdot s^{-1}$) | $2.5 \times 10^{-3}$|
| Initial concentration of solute in solution ($kg\cdot m^{-3}$) | $3 \times 10^{-8}$|
| Langmuir isotherm constant ($mL\cdot mg^{-1}$) | 0.79              |
| Porosity of adsorbent particle (–)              | 0.1957            |
| Pore diffusion coefficient ($m^2\cdot s^{-1}$)   | $8.62 \times 10^{-5}$|
| Axial dispersion coefficient ($m^2\cdot s^{-1}$) | $4.31 \times 10^{-5}$|
| Bed height (m)                                  | 0.21              |

**Figure 5** | (a) Regeneration of used Aliquat-336 impregnated Amberlite XAD-4 resin using 1 M HCl solution at $Q = 2$ mL·min$^{-1}$, (b) adsorption of rhodamine-B dye using the regenerated resin at $Q = 2$ mL·min$^{-1}$ and $C_m = 10$ mg·L$^{-1}$ in three columns in series; (c) possible mechanism of RhB dye adsorption.
column was used again, and \( t_b \) and \( t_s \) were achieved in 42 and 130 h, respectively. The breakthrough curve obtained at optimized condition \( (h = 7 \text{ cm}, \ Q = 2 \text{ mL} \cdot \text{min}^{-1}, \text{and} \ C_{\text{in}} = 10 \text{ mg} \cdot \text{L}^{-1}) \) using the prepared adsorbent was compared with the other adsorbents (Table 3). The result indicates that the prepared adsorbent (A336 impregnated AX4 resin) was more effective than other adsorbents for the removal of RhB dye in a fixed-bed column process. Aliquat-336 is a tertiary amine-based solvent, having a positively charged ion. The hydrogen in the carboxylic group (-COOH) of the RhB dye molecule interacts with the amine group of Aliquat-336. There is a possible interaction between these groups facilitating the adsorption of the RhB dye molecule (Figure 5(c)).

Here in this study, a small amount of prepared resin (1 g in each column) could remove almost 100% of dye from the aqueous solution. A very high breakthrough (142 h) and saturation (244 h) time revealed the effective and practical usage of the resin. The studies on the removal of RhB dye showed that a comparatively shorter breakthrough time was obtained when activated carbon \( (t_b = 40 \text{ h}) \) (Gopal et al. 2016) and fine clay \( (t_b = 40 \text{ h}) \) (Ghribi & Bagane 2016) were used as adsorbents. Also, the problems of regenerability and choking in the fixed bed column were observed using these adsorbents. Therefore, the prepared adsorbent could be one alternative to the adsorbents available for the treatment of wastewater containing RhB dye.

4. CONCLUSION

In this study, extensive laboratory experiments were performed to evaluate the fixed bed column performance containing Aliquat-336 impregnated Amberlite XAD-4 resin for the adsorption of Rhodamine-B dye from the aqueous solution. The adsorbent was found to be very effective for the removal of Rhodamine-B dye from an aqueous solution. The three-column in series removes the dyes almost 100% continuously up to 80 h, and no contamination of dye was observed in the treated solution by keeping three parameters fixed at \( Q = 2 \text{ mL} \cdot \text{min}^{-1}, \ C_{\text{in}} = 10 \text{ mg} \cdot \text{L}^{-1} \text{ and} \ h = 7 \text{ cm} \). At the same condition, breakthrough and saturation time was found to be 142 and 244 h, respectively. Also, adsorption capacity at saturation and empty bed residence time was found to be 28.09 mg·g\(^{-1}\) and 3.01 min, respectively. Clark's model adequately described the breakthrough curve in the fixed bed column kinetic data. Successful regeneration of the column was done using 1 M HCl solution in continuous mode and was used again, and breakthrough and saturation point was achieved in 42 and 130 h, respectively.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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**Table 3** A comparison for different adsorbents used for rhodamine-B dye removal in column studies

| Adsorbent                     | \( C_{\text{in}} \) (mg·L\(^{-1}\)) | \( Q \) (mL·min\(^{-1}\)) | \( h \) (cm) | I.D. (cm) | \( t_b \) (h) | Ref.                |
|-------------------------------|-------------------------------------|-----------------------------|--------------|----------|--------------|-------------------|
| Activated carbon from oil palm empty fruit | 50                                 | 10                          | 10           | 1.2      | 2            | Auta (2012)       |
| Modified *Volvariella volvacea* | 50                                 | 2                           | 4            | 1.5      | 2            | Li et al. (2015)  |
| Polyaniline coated activated carbon | 50                                 | 5                           | 50           | 1.5      | 12.33        | Gopal et al. (2016) |
| Raw clay                     | 20                                 | 4                           | 10           | 1.5      | 40           | Ghribi & Bagane (2016) |
| Modified waste sugarcane bagasse | 10.65                              | 4.5                         | 1            | 1.0      | 5.83         | Yu et al. (2019)  |
| AX4 + A-336                  | 10                                 | 2                           | 21 (3 g)     | 0.7      | 142          | Present study     |
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