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Fixed-bed column analysis for adsorption of Acid scarlet 3R dye from aqueous solution onto chemically modified betel nut husk fibre

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ABSTRACT

In this study Na_2CO_3 modified betel nut husk fibre was used as an adsorbent for the removal of Acid scarlet 3R (AS 3R) dye by analysing fixed-bed column. Experiments were carried out to obtain the effect of initial concentration of dyes or influent concentration, the depth of bed and the effect of the rate of flow of influent solution with influent concentration of 55, 150, and 250 mg/L, the depth of bed of 12, 22, and 32 cm and rate of flow of 15 and 25 mL/min respectively. The time of exhaustion corresponding to $C/C_0 = 0.85$ and the time of breakthrough corresponding to $C/C_0 = 0.15$ is given by the breakthrough curve. The studies were conducted at the room temperature of 27°C ± 2°C and the influent of pH were adjusted at 7.0 ± 0.2. Cost analysis for removal reveal that modified betel nut husk fibre has effectively employed for the removal of AS 3R dyes using fixed-bed column analysis.

Keywords: Modified betel nut husk fibre; Acid scarlet 3R; Breakthrough curve; Fixed-bed column analysis; Bed depth

1. Introduction

Dyes are complex chemical compounds that, when exposed to the majority of a substance, can easily adhere to it and provide colour, as they do for cloth and fabrics. According to the most recent data, there are around 100,000 distinct dyes with an annual production of over 7×10^5 ton/y [1]. Furthermore, the textile sector consumes 10,000 tonnes of dye per year globally, with 100 tonnes of dyes being released into water bodies each year [2]. They are difficult to break due to their complex bonding structure, posing major environmental and health hazards. Aside from other impacts, certain dyes have been discovered to have carcinogenic properties [3]. Dyes are divided into two categories: natural dyes and synthetic dyes. The majority of natural colours come from vegetable dyes obtained from plant sources such as roots, berries, berk, leaves, wood, and so on, which are easily biodegradable and do little or no environmental harm [4]. Synthetic dyes, on the other hand, are used in practically every colour we see today, from food to wood, clothing to paper [5]. The fundamental advantage of synthetic dyes is that they are inexpensive to create and apply to fabrics and other materials. Synthetic azo dyes (which contain an amino group) are used in a variety of industries, although they are most commonly linked with the textile industry [6]. Textile industry effluents can contain a significant quantity of dye content. The environmental and health hazards associated with dye generated by textile manufacturers are becoming a focus of scientific research [6]. As a result, environmental legislation has been enacted to regulate the release of dyes, particularly azo-based dyes, directly into free-flowing water bodies. Researchers have used a variety of techniques to remove colour from wastewater

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solutions, depending on the technique. Biological treatments [7], oxidation [8], ultrasonic irradiation [9], coagulation–flocculation [10], photocatalysis [11], ozonation [12], and membrane separation [13] are some of the approaches. Among them, activated carbon adsorption has been found to be one of the most effective methods for removing practically all colours from aqueous solutions. However, activated carbon has its own set of limitations, including a high initial cost of manufacture, complexity in regeneration after depletion, and a reduction in removal effectiveness upon regeneration [14,15]. As a result, researchers are currently focusing their efforts on the use of low-cost bio-sorbents that are inexpensive, biodegradable, and readily available for adsorption [16–19].

Acid scarlet 3R is one such azo dye which finds its use in textile industries and betel nut husk fibre is an agricultural waste which was used to check its applicability as an effective bio-sorbent for the removal of the dye using adsorption technique. Now, adsorption using batch study [1–19] and column study [20] both finds its use in removal of wastewater pollutants but literature reviews clearly suggests that use of batch analysis is more compared to the later one. Hence attempt was made to analyse the adsorption capacity of the adsorbent using column analysis. From the practical utility point of view also, the column studies are significant than batch studies. As the adsorption rate depend upon the adsorbate concentration in the solution, therefore the continuous flow operation has a significant advantage over batch study. During batch operation, the main component, that is, concentration gradient in the adsorbate–adsorbent system decreases slowly, but in case of a continuous flow system, that is, in column analysis, a solution of a constant initial concentration will come close to the adsorbent layer [21]. Hence the column studies are more practical and reasonable for engineering point of view. To obtain the contact time for the adsorbate, columns studies need to be conducted to get equilibrium as the obtained results from the batch studies for the dyes adsorption studies may not be suitable for direct application in the field of waste water treatment [22,23].

The work also justifies its novelty as the work reported in this article is not done before specially if we look at the selection of the adsorbent and adsorbate. For the current work we have selected modified betel nut husk fibre (MBNHF) as the adsorbent and a mono azo dye Acid scarlet 3R. Selection and reasoning of the materials are discussed in section 2 as below.

Betel nut husk fibre is a multi-component, multicellular fibrous material with a high cellulose content. In contains considerable quantity of cellulose (70%), other chemical components in betel nut husk fibre include lignin (14%) and traces of fat, wax, and ash. Researchers suggests that the hydroxyl groups of lignin and those of carboxyl groups of cellulose and hemicellulose form an ester linkage between parts of cellulose, hemicellulose, and lignin, which are chemically linked by the hydroxyl groups of lignin and those of carboxyl groups of cellulose and hemicellulose [24]. The presence of functional groups such as hydroxyl and carboxyl groups on the surfaces of the adsorbent is one of the causes for dye adsorption from aqueous solution. In this study, the adsorbent is pre-treated with an alkali (Na_2CO_3), which is one of the most commonly used chemical treatments (alkali treatment) for surface modification of cellulose-based materials with the goal of increasing their adsorption capabilities [24]. According to studies [25], treating a cellulose-based component like betel nut husk fibre with alkali disrupts the covalent bond between lignocellulose components, hydrolyzing hemicellulose, and depolymerizing lignin. Alkali treatment of adsorbents has a significant impact on the molecular, supra molecular and morphological characteristics of cellulose, resulting in changes in accessibility, unit cell structure, crystallinity, stiffness, pore structure and fibril orientation in cellulosic fibres [25]. The chemical and mechanical features of cellulose, including as natural ion-exchange capacity, reactivity and structural durability are all improved by alkali treatment. Natural lipids and waxes are removed from the cellulose fibre surfaces by alkali treatment, revealing chemically reactive functional groups like – OH [26]. Previous research suggested that alkali-modified adsorbents, such as NaOH-treated rice husk (high in cellulose component), might be used to effectively remove azo dyes from aqueous solutions [27]. Because cellulose components are abundant in betel nut husk fibre and Acid scarlet 3R is fundamentally an azo dye, the feasibility of employing Na_2CO_3 MBNHF to remove Acid scarlet 3R dye from aqueous solution was investigated.

A mono azo dye Acid scarlet 3R (AS 3R) (having amino group, –N=N–) was obtained from having molecular formula $C_{20}H_{11}N_2Na_3O_{10}S_3$ with molecular weight 604.473 g/mol. It is used in dying and printing of nylon, silk, leather, wool, paper, and wood stain. As understood from the uses, the dye has a strong affinity towards cellulose based materials like paper, silk etc. hence an adsorbent is selected looking at the affinity of the dye as betel nut husk fibre is also very rich in cellulose. Natural dried betel nut husk fibre was chopped into 1 mm pieces and washed with distilled water at 60°C. The sample was then treated for 4 h with 0.01 M Na_2CO_3 at 27°C. The resulting sample was then distilled rinsed to eliminate any remaining chemicals in the fibre, pH was corrected to 7.0 using 0.1 M NaOH or 0.1 M HCL, and the sample was maintained in a container for 24 h after drying at 100°C. The resultant product was dubbed Na_2CO_3 MBNHF and was used as the adsorbent. Fig. 1 shows the molecular structure of Acid scarlet 3R dye.

2. Materials and methods

By the use of a column having 2.5 cm diameter and 50 cm length, the fixed-bed column study in order to remove Acid scarlet 3R (AS 3R) dye from wastewater by Na_2CO_3 MBNHF was conducted. Between layers of glass wool those were already equilibrated, the column was filled with MBNHF. Fig. 2 shows a general schematic diagram of column study. The experiments on column were carried out to understand the influence of initial concentration of the influent, the depth of the bed and the rate of flow rate. The experiments were done at a temperature of 27°C ± 2°C and the influent of pH was adjusted at 7.0 ± 0.2. When the value of C/C_0 became 15, the breakthrough point was taken into consideration. The samples of the effluent were obtained at certain fixed time interval and the concentration of the AS 3R dye in the effluent were found out by using the atomic absorption spectrophotometer. The effects of various parameters have been discussed in the subsequent sections.

3. Surface morphology and characterization

The surface morphology of Na_2CO_3 MBNHF, as well as AS 3R adsorbed MBNHF, was studied using a scanning electron microscope with the following operating parameters: resolution: 2 nm in the secondary electron mode at a working distance of 8 mm and an accelerating voltage of 30 kV, accelerating voltage: 1–30 kV in 1 kV step. Scanning electron microscopy (SEM) images are displayed as in Fig. 3, where Fig. 3a shows morphology of unused MBNHF and Fig. 3b shows the SEM image where large number of AS 3R dye particles that have attached to the surface of the MBNHF (i.e., dye adsorbed MBNHF). Both figures have a resolution of 20 μm.

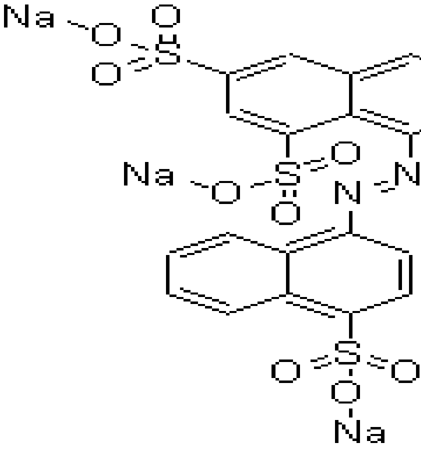

Fig. 1. Molecular structure of Acid scarlet 3R dye.

Characterization of the virgin and used adsorbent is an essential component to technically justify the adsorption of any dye onto the surface of adsorbent. This is to understand that not all the functional groups present in an adsorbent surface, do actively take part on adsorption process and rather only a few functional groups are responsible for adsorption and hence the need of characterization, as this particular analysis reveals the specific functional groups which are responsible for the intake of dyes from solution. The influence of functional groups for the adsorption of AS 3R dye onto adsorbent surfaces is confirmed by the Fourier-transform infrared (FTIR) spectra. FTIR analysis was done at IIT Bombay SAIF Research Facility. The study's instrument has the following specifications (Make: Bruker, Germany). Model: Hyperion Microscope 3000 with Vertex 80 FTIR System). Figs. 4a and b show the FTIR spectra of virgin MBNHF and Acid scarlet 3R (AS 3R) loaded MBNHF, respectively. Due to the constrained hydroxyl or amine groups the broad and strong band was seen at 3,433.89 cm^{-1}. Due to the –CH asymmetric stretching, the next high value of 2,902.79 cm^{-1} was observed. The carboxyl group stretching vibration has a wavelength of 1,742.88 cm^{-1}. The bands at 1,642.96, 1,504.94 and 1,463.00 cm^{-1} were used to assign asymmetric and symmetric stretching vibrations of C=O groups. At 1,374.97 cm^{-1}, the C–N stretching band was discovered. C–O stretching of alcohols and carboxylic acids was assigned by the band to 1,030.92 cm^{-1}. After AS 3R dye adsorption, the symmetrical stretching vibration bands of hydroxyl or amine groups in AS 3R loaded MBNHF were modified from 3,433.89 to 3,435.52 cm^{-1}, as shown in Fig. 4b. The stretching band of carboxyl groups was changed from 1,742.88 to 1,741.37 cm^{-1}. 1,642.96, 1,504.94, and 1,463.00 cm^{-1} stretching bands were likewise changed to 1,639.31, 1,508.24.18, and 1,461.03 cm^{-1}

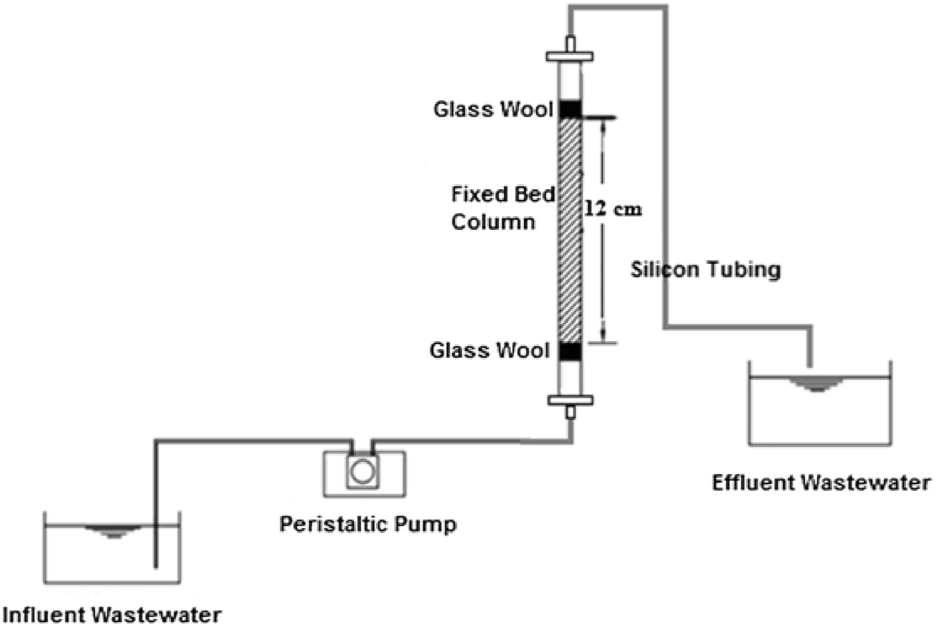

Fig. 2. General schematic diagram for fixed-bed column design.

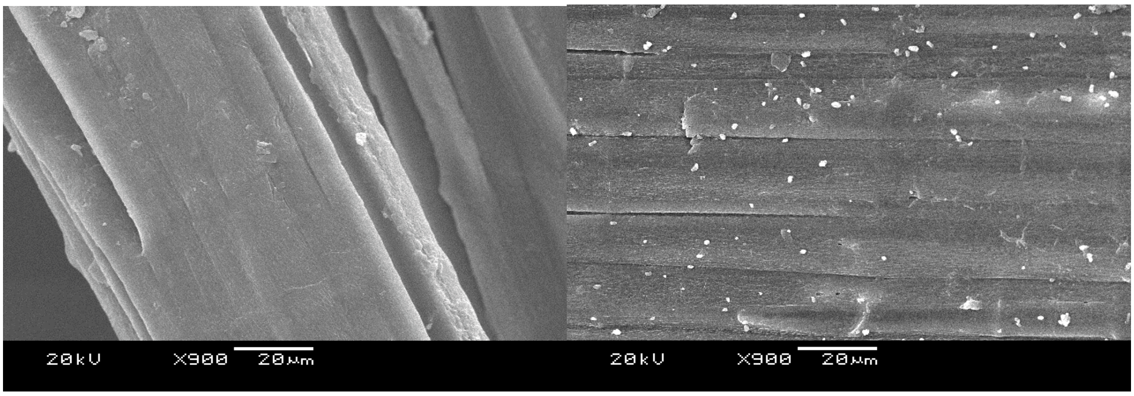

Fig. 3. (a) Unused MBNHF and 3 and (b) AS 3R dye adsorbed MBNHF.

correspondingly. The C–O peak was moved from 1,030.92 to 1,025.67 cm^{-1}, respectively. Similarly, following adsorption, other values moved their positions. Thus, from the FTIR studies, it may be inferred that functional groups are the key operators responsible for the binding of AS 3R onto the surface of the MBNHF, which is justified according to the examination of FTIR spectra which shows frequency shifts.

4. Fixed bed operation system

The conventional method of using adsorption of fixed-bed column is mainly used for the water and wastewater treatments in spite of many advanced techniques like reactors consisting of pulse bed and fluidized bed reactors etc. Generally, the batch adsorption isotherms are used for the primary investigation before running fixed-bed columns that are more costly tests. The sorption isotherms from batch studies are of limited use, as it is not possible to provide proper information to enhance the process for practical applications in the column operation systems because of the following distinct phenomena encountered in column operations:

- Sorption in the column is not in equilibrium.
- Incomplete exhaustion of the adsorbent in a column operation.
- Incomplete exhaustion of the bed due to uneven flow patterns.

When a clean fixed-bed column is introduced by wastewater, solute removal mainly occurs at the top most part of the column also known as adsorption zone. Due to the continuation of the process, the adsorption zone goes downward as the top layer of the fixed bed becomes saturated. When the adsorption zone is reached to the bottom most part of the fixed bed, it results in the increase of the solute concentration. An S-shaped breakthrough curve is obtained by plotting influent concentrations [C/C_0] vs. time. The point breakthrough in the S-shaped curve is reached when the value of effluent solute concentration becomes its maximum permissible value. Also a point of exhaustion of the column is obtained when the effluent solute concentration becomes 85% equal to the influent solute concentration [28]. The type of waste water that is being treated greatly influences the shape and pattern of the breakthrough curve. The adsorption zone will be short and the pattern of breakthrough curve will be steep, if the absorbable component in the waste water is only one. For the system of adsorption, one of the major parameters is the residence time. The required amount of adsorbent and the depth of adsorbing column are determined by the optimum residence time. The other design and operating parameters are included as: linear flow rate, influent concentration, composition of the influent and effluent of pH, temperature and viscosity. The additional factors, which affect the removal process, are the particle size of the adsorbent, pore size distribution and chemical characteristics of the surface of adsorbent [29]. The following observations may be made about breakpoint.

- When the bed depth got reduced, breakpoint also decreased.
- With increase in the size of adsorbent, breakpoint got reduced.
- When the rate of flow got increased, breakpoint reduced, and
- With increase in influent adsorbate concentration breakpoint decreased [30].

In the fixed bed operations, the flow velocity, pressure drop and bed diameter plays vital role. The design manual of USEPA for the carbon absorber has suggest a maximum flow rate of 3.5 m^3/m^2/h, so that the head loss developed is only nominal. In the present study, the flow rate adopted was in the range of 2.5 m^3/m^2/h, where the head loss was nominal (≤1.5 mm), but it increases with increase in hydraulic loading rate in the column packed with betel nut husk fibre. The extent of mass transfer of the sorbate is a significant function of the inlet and outlet disturbances, which is termed as the channelling effect. In the present study, to minimize the channelling effect, the betel nut husk fibre adsorbent was sandwiched between layers of glass wool those were pre-equilibrated of 8 mm thickness each. The wall effect is dependent on the column diameter to the ratio of particle size, which should be greater than 25:1 to prevent wall effect [31]. In the present study, this ratio was maintained at 40:1; hence no wall is expected to be encountered. The fixed bed absorbers

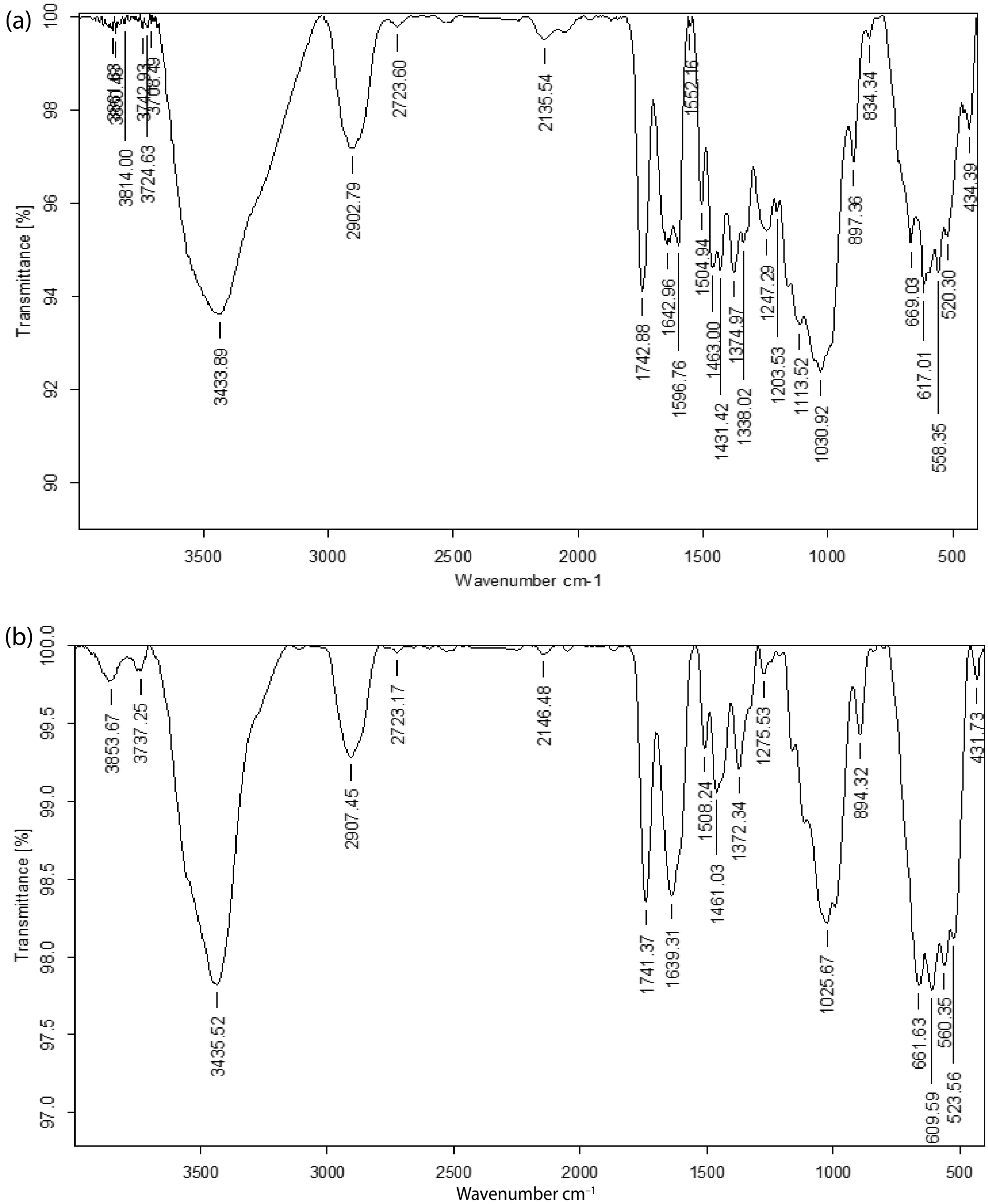

Fig. 4. FTIR image of (a) unused MBNHF and (b) dye adsorbed MBNHF.

can be designed to operate in either up flow or down flow directions. A down flow mode must be used where the adsorbent is relied upon to perform the dual roles of adsorption and filtration. Although the lower capital costs can be realized by eliminating the pre-treatment filters, more efficient and frequent backwashing of the absorber is required. If the absorber is not required to the function as a filter, in order to decrease the drop in pressure, adsorbent fouling and channelling, it can be made operational in the mode of up-flow. To enhance the rate of adsorption, the up-flow design is necessary [32]. In this study, the up-flow mode was adopted mainly to decrease the pressure drop, and avoid channelling, and fouling of the adsorbent.

5. Results and discussions

5.1. Impact of concentration of initial influent dye

The breakthrough graph between the concentration of effluent to influent in the column vs. time at bed depths 12 cm, flow rate 15 mL/min for the concentration of initial solution of 15, 25, and 35 mg/L for AS 3R sorption onto MBNHF is shown in Fig. 5. It can be observed from the figure that the time to reach the breakthrough became less with increase in the initial concentration of influent.

5.2. Impact of depth of bed of the column on breakthrough time

The experiments were done with three bed depth of 12, 22 and 32 cm keeping other parameters, that is, concentration of influent solution 55 mg/L, flow rate 15 mL/min unchanged. The plot between C/C_0 in the column vs. time also known as breakthrough plot for AS 3R sorption onto MBNHF is shown in Fig. 6. Observation from the figure shows that the time to reach the breakthrough became more with increase in the depth of the column.

5.3. Effect of rate of flow of influent on breakthrough time

All the upcoming experiments were done with initial influent concentration, depth of bed, 55 mm/L and 12 cm respectively with a set of flow rate of 15 and 25 mL/min.

The graph between effluent to influent concentration also known as breakthrough in the column vs. time are for AS 3R+MBNHF is shown in Fig. 7. It can be depicted from

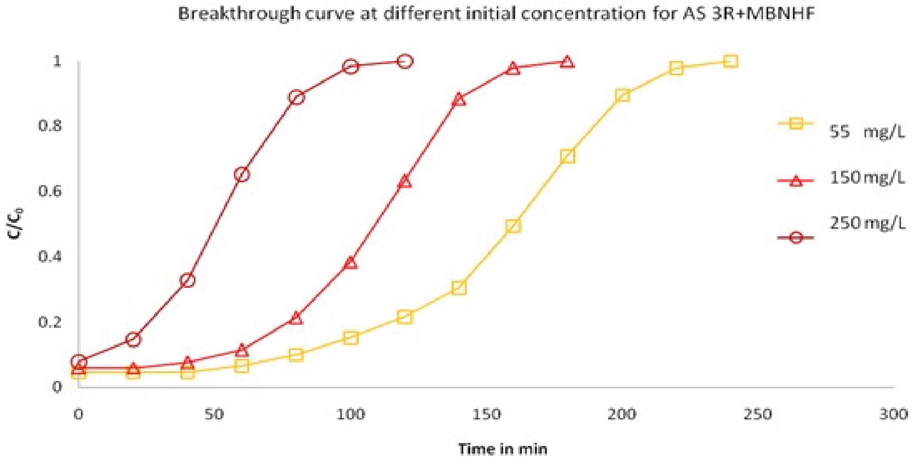

Fig. 5. Impact of concentration of initial solution on breakthrough curve for AS 3R+MBNHF with bed depth of 12 cm, flow rate 15 mL/min.

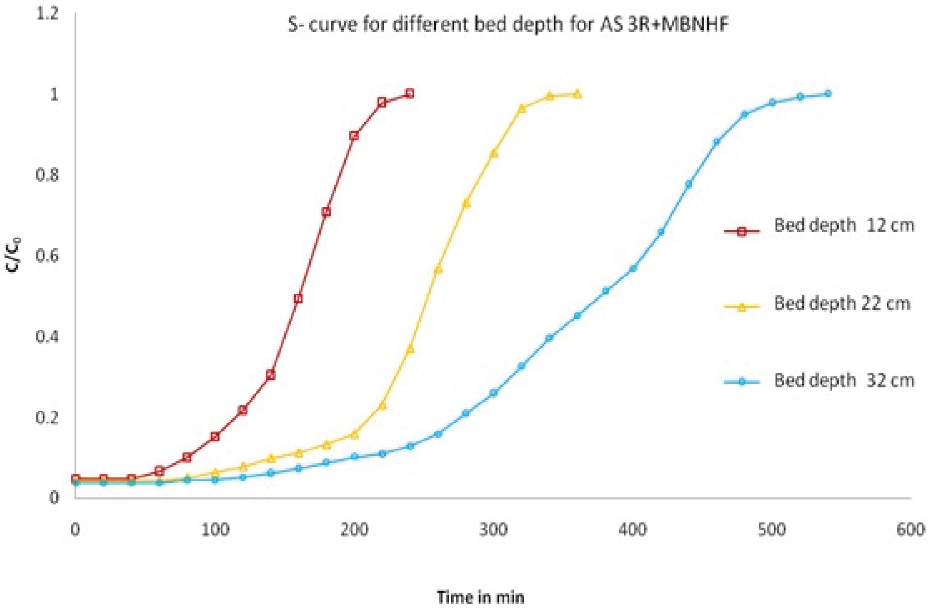

Fig. 6. Impact of depth of bed on breakthrough curve for AS 3R+MBNHF with concentration of influent solution 55 mg/L, flow rate 15 mL/min.

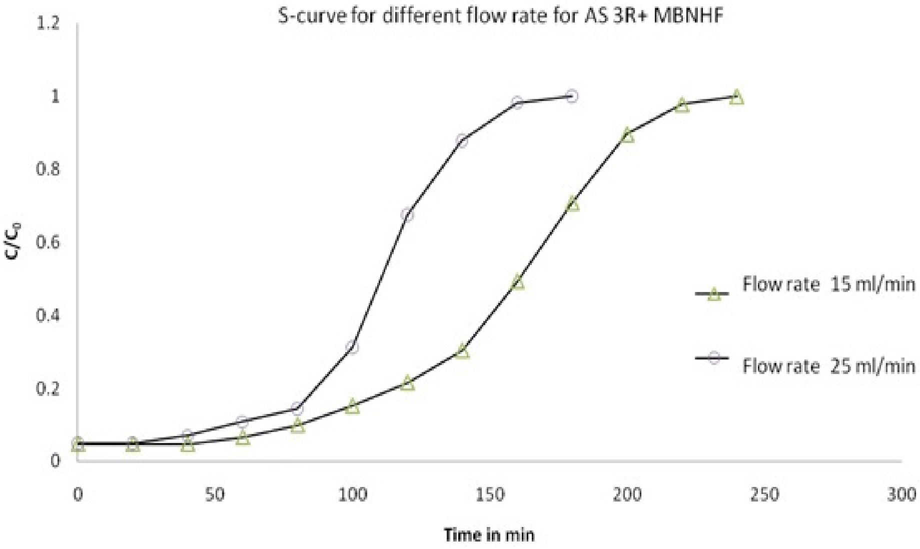

Fig. 7. Effect of rate of flow of influent on breakthrough curve for AS 3R+MBNHF with initial influent concentration of 55 mm/L, depth of bed 12 cm, for flow rate of 15 and 25 mL/min.

the figure that the time to get the breakthrough was became less with increase in the flow rate of the influent.

6. Design parameters for the adsorption of column: mathematical modelling

The generation and the shifting of the zone of adsorption has been described as mathematically [28,33] and applied by many researcher, [34] in their research. After its setting, the time needed by the zone of exchange in order to move its length equal to its height upward or downward is given by:

$$t_z = \frac{V_E - V_B}{Q_W} \tag{1}$$

where V_E = wastewater volume that was treated to the exhaustion point (L); V_B = wastewater volume that was treated to the breakthrough point (L); Q_w = flow rate of wastewater (L/h)

The time needed by the zone of exchange to get established and to completely shift out of the bed is:

$$t_E = \frac{V_E}{Q_w} \tag{2}$$

The rate of shifting of exchange zone upward or downward through the bed is:

$$U_z = \frac{h_z}{t_z} = \frac{h}{t_E - t_f} \tag{3}$$

where h_E = height of exchange zone (cm); h = total depth of bed (cm); t_f = time needed by the zone of exchange for its initial formation (h).

After reshuffling Eq. (4), gives the formula to determine the height of the zone of exchange as described below:

$$h_z = \frac{h \times t_z}{t_E - t_f} \tag{4}$$

The value of t_f can be determined as under.

$$t_f = (1 - F)t_z \tag{5}$$

where F, it is the adsorbate fraction in the zone of adsorption, having capacity to eliminate the solute at breakthrough is given as:

$$F = \frac{S_z}{S_{\max}} = \frac{\int_{V_B}^{V_E} (C_0 - C)\,dV}{C_0 (V_E - V_B)} \tag{6}$$

where C_0 = initial concentration (mg/L); S_z = solute eliminated by the zone of adsorption from the point of breakthrough to the point of exhaustion; $S_{\max}$ = amount of solute eliminated by the zone of adsorption when it is fully exhausted.

The percentage of the total column saturated at breakthrough is given as:

$$\%\,\text{Saturation} = \frac{h + (f - 1)h_z}{h} \times 100 \tag{7}$$

The breakthrough curve for the adsorption of AS 3R onto MBNHF, for the initial concentration of influent of 55 mg/L, depth of bed of 12 cm and flow rate of influent of 15 mL/min were used to calculate the important parameters which are shown in Table 1. The value of F was calculated by graphical method from the respective breakthrough curve.

7. Fixed-bed column design parameters: depth of bed/time of service modelling (BDST)

The complete design of the adsorption columns was based on the data collected from the laboratory tests. A lot of mathematical models were used in the design. In this research work, the fixed-bed column was designed by Logit method [35–37]. The equation of Logit can be given as:

$$\ln\left[\frac{C/C_0}{1-C/C_0}\right] = -\frac{K\times N_0\times X}{V} + K\times C_0\times t \tag{8}$$

where C = concentration of solution at time t; C_0 = concentration of initial or influent dye (55 mg/L); V = velocity of approach (215 cm/h); X = depth of bed (12 cm); K = rate constant of adsorption (L/mg-h); N_0 = constant for adsorption capacity (mg/L).

Rearranging Eq. (9) as:

$$\ln\left(\frac{C}{C_0-C}\right) = -\frac{K\times N_0\times X}{V} + K\times C_0\times t \tag{9}$$

A straight line is obtained by plotting graph of $\ln C/(C_0-C)$ vs. t with the slope of $K\times C_0$ and intercept $(-KN_0X)/V$ from which K and N_0 could be determined. The plot of $\ln C/(C_0-C)$ vs. t for AS 3R sorption onto MBNHF is shown in Fig. 8.

Setting $t = 0$ and $C = C_B$ and solving Eq. (9) we get,

$$X_0 = \frac{V}{K\times N_0}\times\ln\left(\frac{C_0-C_B}{C_B}\right) \tag{10}$$

where X_0 refers to the minimum height of column required to generate of effluent C_B. It is also called as critical bed depth. The values of design parameter K, N_0 and X_0 for our studied adsorption fixed-bed column system are shown in Table 2. The values thus obtained can be used to design the adsorption columns. The adsorption ability was also found to be satisfactory. Therefore, conclusion can be made that modified betel nut husk fibre using sodium carbonate is effective for removal of Acid scarlet 3R dye.

8. Cost analysis

The cost analysis for the metal effluent volume treated up to breakthrough per kg of MBNHF has been calculated and also has been presented in Tables 3 and 4.

Table 1
Design parameter for fixed-bed column adsorption system

S. No.	Design parameter	Fixed-bed column adsorption system
		AS 3R+MBNHF
1	*F*	0.49
2	Height of adsorption zone (h_z) in cm	8.96
3	Rate at which the zone of adsorption shifts through the bed in cm/h	5.13
4	Percentage of the complete saturation of column at the point of breakthrough (% saturation)	55.67

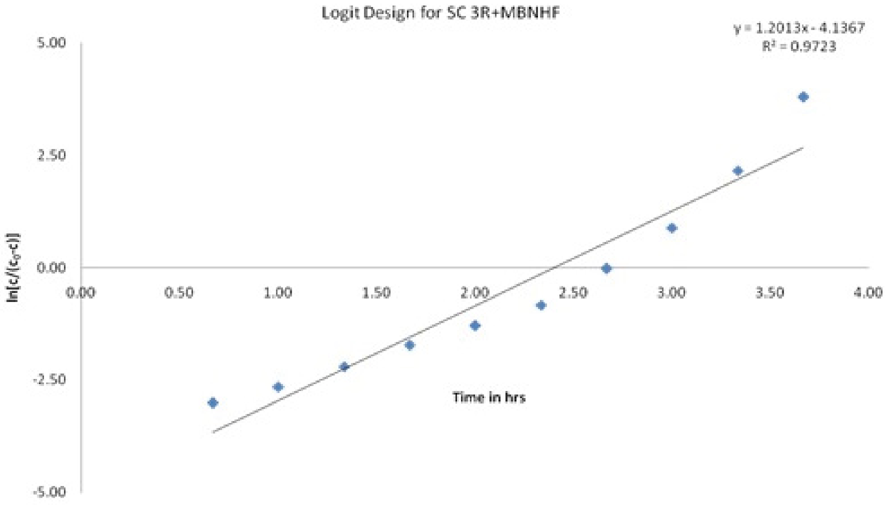

Fig. 8. Showing straight line between $\ln[C/(C_0-C)]$ vs. time for fixed-bed column AS 3R+MBNHF system.

Table 4
Cost analysis for removal of dyes of initial concentration of 50 mg/L up to breakthrough per kg of adsorbent

Adsorbate	Dye	Initial concentration mg/L	Dye treated per 1 kg of adsorbent (L)	Cost required per 1 kg of adsorbent	
				@ Rs. 5	@ US$0.08
MBNHF	AS 3R	55	95.28	21.23 L/Rs.	1,145 L/$

Table 2
Showing the Logit design parameters of fixed-bed column adsorption system

Adsorbent	Dye	Logit design parameters		
		K (L/mg h)	N_0 (mg/L)	X_0 (cm)
MBNHF	AS 3R	0.0387	2,634	3.94

Table 3
Mass and volume of effluent treated MBNHF needed up to breakthrough

Adsorbate	MBNHF
Dye	AS 3R
Initial concentration (mg/L)	55
Depth of bed (cm)	12
10% time of breakthrough (h)	1.42
Volume treated (L)	0.873
Total adsorbent mass (g)	9.12
Mass treated (g/L)	11.34

9. Conclusion

The usage of Na_2CO_3 MBNHF for the removal of a synthetic azo dye AS 3R from its aqueous solution was described in the current study. Because betel nut fibre husk was readily available in the area, it was easily obtained and modified accordingly. SEM and FTIR were used to characterize the virgin and dye-adsorbed betel nut fibres. S-shaped breakthrough curves were obtained validates the suitability of the column study. With two separate flow rate, the effects of the quantity of materials in the column (bed heights) and the inlet dye concentration were investigated. The BDST model was built using the experimental data. The model parameters and coefficient of determination revealed that the BDST model was a good fit. As can be seen from the R^2 value of 0.9723, which is extremely close to 0.98, the breakthrough parameters suggested that Na_2CO_3 modified betel nut husk fibre was a suitable adsorbent for AS 3R dye.

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