ADSORPTION OF ACID BLUE 29 DYE USING FLUIDIZED GRANULAR ACTIVATED CARBON

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ABSTRACT

The study focus on the application of four sorption kinetic models for predicting the uptake of Acid Blue 29 dye inside Tapered Fluidized Bed Reactor. Experiments were conducted at three different flow rates (150, 350 and 450 l h⁻¹), dye concentration of 0.1 g l⁻¹ and GAC dose of 80 g. The data was analysed using Pseudo-first-order, Pseudo-second-order, Intraparticle diffusion model and Elovich model. The data fitted well to pseudo-first-order model which indicates physioadsorption. Elovich and intra-particle diffusion model also fitted well to the data.

Keywords: Acid Blue 29, adsorption, fluidized bed reactor, kinetics, tapered.

INTRODUCTION

Effluent generated from textile effluent is highly coloured because of the residual dye in it which does not attaches to the fabric. 10 - 15 % of dye utilized for the process remains in effluent because of the non attachment to the fabric [1]. Different techniques have been used to remove dye from wastewater like physical methods (adsorption by various adsorbents, membrane filtration, ion exchange, irradiation and electro-kinetic coagulation), chemical methods (oxidative process like advance oxidation process, sodium hypochloride and electrochemical) and biological methods (anaerobic bacteria culture, white rot fungi). Adsorption method has been proved as one of the best treatment technology for dye removal [2 - 6]. Many researchers have integrated two or more techniques to obtain better result [1, 6].

Acid Blue 29 (AB 29) dye is widely used in textile industries, it is a double azo class dye. The structure of the dye is given in Fig. 1. Azo dyes are characterised by the existence of nitrogen nitrogen double bond (-N=N-) and brightness of dye is due to these azo bonds and associated chromophores [6].

Batch studies on the removal of AB 29 has been investigated using waste tea activated carbon [7], peat [8], biosorption on Aspergillus niger fungal biomass [9]. Very few work related to continuous flow conditions are reported, which are more useful in large scale textile wastewater treatment [10].

Tapered Fluidized Bed Reactor (TFBR) has been used for the present study to investigate the AB 29 dye removal. In TFBR the dye water to be treated flows upwards through an expanded bed of GAC, which provides a better fluid-solid contact to enable better mass transfer. Furthermore, the problem of fouling often associated with packed bed reactors is not encountered in
fluid-bed reactors [11]. Advantage of tapered column is that it allows better saturation of adsorption column by lowering the effluent velocity at the outlet of bed [12].

EXPERIMENTAL

Adsorbant

Granular activated carbon (GAC), grade BW 250, was used as an adsorbent inside TFBR. The morphology of the GAC was studied using Scanning electron microscope (SEM) and Fourier Transformation Infra Red (FTIR) Spectroscopy. Granular form of activated carbon was used inside TFBR instead of powdered form to avoid large pressure drops [13].

Adsorbate

For the present study, Acid Blue 29 dye (C.I. 20460, Sigma Aldrich) was selected. The synthetic wastewater was prepared by dissolving the dye into distilled water. The concentration of the dye solution was 1 g l⁻¹. The wavelength at maximum absorbance (λ_max) determined by the spectrophotometer was 593 nm. Calibration curves were made for dye at its maximum absorbance.

Fluidized bed adsorption column

A Tapered Fluidized Bed Reactor (TFBR) has been fabricated using Borocil glass tube with diameter 5.8 cm, height 1.25 m including the taper height, taper angle of 5° and working volume of 2.5 l was used for the present study. Two outlets for the effluent collection from the top have been provided for collection and recirculation. The feed solution has been supplied from the bottom with the help of pump (0.125 HP, Crompton).
Flow rate was regulated with the help of rotameter (capacity 0 - 600 l h\(^{-1}\)). At the bottom of the reactor a fine stainless steel mesh is provided to prevent the back flow of the adsorbent i.e. GAC, a mesh is also used at top with the help of inverted funnel type arrangement to cover the two outlets, to prevent the loss of light fluidized particles from the reactor. Fig. 2 shows the schematic diagram of the experimental set up.

**Methodology**

The wastewater containing dye was fed through a bed of GAC in an up-flow mode. A peristaltic pump was used to pump the dye wastewater from the reservoir into the tank. Flow rate was regulated with the help of rotameter having a non return valve. Samples were collected at a regular period and analysed with UV-VIS Spectrophotometer -1800 (Shimadzu).

**RESULTS AND DISCUSSION**

**Characterization of the adsorbant**

A Scanning Electron Microscope (JEOL- JSM-6490 Japan) has been used for characterizing the surface morphology. It is clear from Fig. 3 that, activated carbon used appears to have number of pores having good possibility for dye to be trapped and adsorbed into these pores.

Fourier Transformation Infra Red Spectroscopy analysis helps to determine the specific functional groups that exist in a material. A PerkinElmer Spectrum 400 FT-IR/FT-FIR infra spectrometer was used for the investigation of the surface functional groups of activated carbon. The activated carbon samples were mixed with KBr of spectroscopic grade and made into pellets at a pressure of about 8*10^4 N. The samples were scanned in the range of 4000 – 400 cm\(^{-1}\). The resulting spectrum was the average of 4 scans.

If specific interactions of the AB 29 dye takes place with virgin GAC Fig. 4 (A), the most obvious and significant difference would be the appearance of new peaks or shifting of existing peaks. Fig. 4(B) shows the GAC sample after the dye adsorption it is clearly visible that an additional peak at 1971 cm\(^{-1}\) is observed which indicates the interaction of the dye with the GAC.

**Effect of contact time, adsorbent dose and flow rate inside TFBR**

The effect of contact time for removal of Acid blue 29 by adsorption inside TFBR is shown in Fig. 5. The dye was rapidly adsorbed during the first 40 - 60 min, and then the adsorption rate gradually decreased and reached equilibrium in 420 min. In the beginning the adsorption rate was fast as the dye ions were adsorbed on the exterior surface of the GAC. After saturation of the exterior surface, the dye ions entered into the interior surface of the adsorbent pores, which is a slow process as compared to the adsorption on the exterior surface [15]. The effect of contact time was observed at three different flow rates which followed the same trend of rapid adsorption during the first 45 - 60 min and slow adsorption in the later stages in all the three flow rates i.e. 150, 350 and 450 l h\(^{-1}\).

In the present study, three adsorbent dose and three flow rates were investigated for the removal of the AB 29 dye. Different bed height of GAC at three flow rates 150, 350 and 450 l h\(^{-1}\) without fluidization was 12 cm and with fluidization of GAC were 15, 20 and 30 cm, respectively.

Fig. 5 shows that from flow rate of 150 to 350 l h\(^{-1}\), the dye removal (R %) increases. However it decreases at a higher flow rate of 450 l h\(^{-1}\). This may be due to the fact that at higher flow rate adsorption may be less due to less time of contact and less interaction of adsorbent particles with dye.

**Kinetic modeling**

In order to design industrial scale reactor knowledge of kinetics is important. Therefore, the data obtained was used to study the kinetics of adsorption process. The pseudo first order and pseudo second order kinetics models were tested to obtain the rate constants and elucidate the adsorption mechanism. To understand the diffusion mechanism, the intra-particle diffusion model was studied to determine the rate controlling step for the reaction. Elovich model was also used to analyse the data.
Pseudo first and pseudo second order model

The pseudo-first order model was described by Lagergren [15]. The linear form of the equation is represented in equation 1. The plot of log \((q_e - q_t)\) versus time is shown in Fig. 6 from which values of constant \(K_1\) is evaluated from slope and \(q_e\) is given by intercept. The value of \(k_1\) is given in Table 1.

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t
\]

(1)

where \(q_t\) is dye adsorption capacity at time \(t\) (mg g\(^{-1}\)), \(q_e\) is dye adsorption capacity at equilibrium (mg g\(^{-1}\)) and \(k_1\) is pseudo-first-order rate constant for adsorption (min\(^{-1}\)).

Pseudo second – order indicates chemisorptions during the process involving valence forces through the sharing or exchange of electrons between the adsorbent and dye molecules.
and the adsorbate [16 - 19]. The linear form of Pseudo second order equation is given in eq. 2. This model has an advantage of calculating equilibrium capacity directly via model unlike in the case of pseudo first order [19]. The plot of \( \frac{t}{q_t} \) versus time is shown in Fig. 7 from which values of constant \( q_e \) and \( K_2 \) are evaluated from slope and intercept, respectively. The values are given in Table 1.

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]  

(2)

where \( k_2 \) is second-order- rate constant of adsorption (g mg\(^{-1}\) min\(^{-1}\)).

From the comparison of above both models, it is clear that system obeys pseudo first order model as the values of correlation coefficient (\( R^2 \)) are higher. This also shows that adsorption is not chemisorption.

**Intra particle diffusion model**

The dye adsorption process takes place in three stages: film diffusion, pore diffusion and intra particle transport. Slowest of the three steps controls the overall rate of the process [15]. The linear equation of Intra particle diffusion [11, 20] model is given by eq. 3. The plot of \( q_t \) versus \( t^{0.5} \) is shown in figure 8 from which values of constants \( K_{id(I)} \) and \( K_{id(II)} \) and Constant

![Graph](image-url)

**Fig. 6.** Pseudo-first-order kinetics for Acid Blue 29 dye adsorption onto GAC at three different flow rates 150, 350 and 450 l h\(^{-1}\), dye concentration 0.1 g l\(^{-1}\) and adsorbent dose 80 g.

![Graph](image-url)

**Fig. 7.** Pseudo-second-order kinetics for Acid Blue 29 dye adsorption onto GAC at three different flow rates 150, 350 and 450 l h\(^{-1}\), dye concentration 0.1 g l\(^{-1}\) and adsorbent dose 80 g.
The values are given in Table 1.

\[ q_t = K_{id} t^\frac{1}{2} + c \]  

where \( K_{id} \) is intraparticle diffusion rate constant (mg g\(^{-1}\) min\(^{-1/2}\)) and \( C \) is intercept (mg g\(^{-1}\)).

The results indicate two separate regions, i.e. phase I and phase II. The first part at all flow rates can be due to immediate utilization of the readily available sites on the adsorbent surface (bulk diffusion). Phase II is attributed to very slow diffusion from the surface sites into the inner pores. Thus, the initial portion is controlled by surface diffusion and second by pore diffusion. The results indicate that Intra - particle diffusion controls the adsorption rate.

Also the value of intercept (\( C \)) gives the idea of thickness of boundary layer i.e. the larger the thickness, greater is the boundary layer effect [19, 21].

![Fig. 8. Intra- particle diffusion model for Acid Blue 29 dye adsorption onto GAC at dye concentration 0.1 g l\(^{-1}\), adsorbent dose 80 g and three different flow rates (A) 150 l h\(^{-1}\), (B) 350 l h\(^{-1}\) and (C) 450 l h\(^{-1}\).](image)

![Fig. 9. Elovich model for Acid Blue 29 dye adsorption onto GAC at three different flow rates 150, 350 and 450 l h\(^{-1}\), dye concentration 0.1 g l\(^{-1}\) and adsorbent dose 80 g.](image)

<table>
<thead>
<tr>
<th>Flow Rate (l/h)</th>
<th>Intra-particle diffusion</th>
<th>Elovich model</th>
<th>Pseudo first order constants</th>
<th>Pseudo second order constants</th>
<th>Exp q_e</th>
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<td></td>
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<td>R'(I)</td>
<td>C(I)</td>
<td>k_{id}(II)</td>
<td>R'(II)</td>
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<td>0.781</td>
<td>0.454</td>
<td>-4.21</td>
</tr>
</tbody>
</table>

Table 1. Kinetic constants for Intra particle diffusion, Elovich model, Pseudo first and Pseudo second order models (for dye concentration 0.1 g l\(^{-1}\) and 80 g of GAC).
Elovich model

Elovich model is generally expressed by the equation 4. The slope and intercept of plot of \( q \) vs. \( \ln(t) \) were used to calculate the values of constants \( a \) and \( b \) respectively as shown in Fig. 9. The values are given in Table 1.

\[
q = a + b \ln t
\]  

(4)

The adsorption data for the AB 29 dye fits well for the Elovich model.

CONCLUSIONS

The present investigation showed that activated carbon in the fluidized form inside TFBR is effective for the removal of Acid Blue 29 dye from aqueous solution. The kinetic study of AB 29 data inside TFBR was performed based on pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich model. The data indicated that adsorption kinetics follows pseudo-first order kinetics at all the three flow rates with intra-particle diffusion as rate determining step, Elovich model also fitted well to the data.

The results show, that adsorption is fast in the beginning and then slows down with time. This is because of the fact that in the beginning sorbate molecules are sorbing onto the surface. It can be seen that sorption efficiency is higher at lower flow rates.

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