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A COMPARISION OF SYNTHESIZED ZEOLITE FROM FLY ASH USING FUSION AND HYDROTHERMAL METHOD FOR REMOVAL OF COD AND COLOUR REMOVAL FROM TEXTILE MILL WASTEWATER – COLUMN STUDY

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Abstract

The industries which give raise to dye – bearing effluents in their production processes. In the present study fly ash was converted to zeolite form by using fusion and hydrothermal method. In fusion method, fly ash and NaOH was mixed with the ratio of 1:1 and in hydrothermal method, fly ash and 3M NaOH solution with ratio of 1:8. The finally product from the both methods obtained was zeolite Z_1 and Z_2. Using SEM the synthesized zeolite Z_1 and Z_2 were characterized. Column study was conducted for different bed depth from 10 cm to 20 cm and flow rates from 7.5 mL/min to 15 mL/min for the removal of Colour and COD from the textile wastewater. From the column study, the critical depth was fixed for the synthesized zeolite Z_1 and Z_2 are 9 cm and 6 cm, respectively for flow maximum removal of Colour and COD from the textile wastewater. Form these bed depths the BDST model was applied and N_0 was calculated for synthesized zeolite Z_1 and Z_2 are 9.429 mg/L and 12.672 mg/L, respectively. For column studies, Thomas model and Yoon and Nelson model were applied and Thomas model was well fitted. From the Yoon and Nelson model the time required for 50% adsorbate breakthrough for synthesized zeolite Z_1 and Z_2 are 516 and 466 min, respectively.

Key words: *Synthesized zeolite$_1$, Hydrothermal method$_2$, Fusion method$_3$, Thomas model$_4$, Yoon and Nelson model$_5$ and BDST model$_6$.*

1 Introduction

Approximately 10–15% of synthetic textile dyes are lost in waste streams during manufacturing or processing operations. The colored effluents not only create environmental and aesthetic problems, but also pose a great potential toxic threat to ecological and human health, as most of these dyes are toxic and carcinogenic in nature. Various treatment technologies, such as chemical coagulation=flocculation, photocatalytic degradation biological processes, membrane-based separation processes and adsorption among others, are in use for the removal of colored dye from wastewater. Each of the above processes has its own benefits and limitations. Adsorption, being the simplest method, has gained much importance in the treatment of wastewater containing colored impurities. In addition, adsorption is superior to other techniques for water reuse in terms of initial cost, simplicity of design, ease of operation, and insensitivity to toxic substances (14). Fly ash is mainly generated from the thermal power generation, incinerators, boilers, etc. Nearly 73% of India's total installed power generation capacity is thermal, in which 90% is coal based generation, with diesel, wind gas and steam. From the thermal power plant minute particles of ash generates and that causes serious environmental problems. Fly ash mainly consist of silica, alumina, oxides of iron, calcium and magnesium and toxic heavy metals like lead, arsenic, cobalt and copper. Now a day's 30% of fly ash generated is used as admixture in cement industry. The main objective of this study is to compare synthesized zeolite from fly ash using fusion and hydrothermal method for removal of COD and Colour from the textile wastewater.

2. Materials and Methodology

The textile mill wastewater (adsorbate), synthesized zeolite using fusion and hydrothermal method (adsorbent) and fly ash (adsorbent) are used in this adsorption process. The details of materials procured, processed and used in the batch and column adsorption studies have been discussed in the following sub sections.

2.1 Adsorbate

Adsorbate is any substance that has undergone adsorption on the surface. The wastewater collected from the Silk Weaving Factory (Karnataka Silks Industries Corporation Ltd), Mysuru.

2.2 Adsorbent

The fly ash was collected from the Silk Weaving Factory (KSIC Ltd.,), Mysuru, which is used as adsorbent in the study. The fly ash is collected from the boiler section of the industry and then sieved for size of 150μm and used for the adsorption process.

2.2.1 Synthesis of Zeolite Using Fusion Method and Hydrothermal method

In the fusion method, fly ash was preheated at 1050C. Fly ash was sieved to less than 150μm. During synthesis, of zeolite 10g of fly ash is mixed with 10g of NaOH and burn at 600^0C in the muffle furnace for about 90 minutes and the cooled to room temperature. The product was cursed and transferred into 250mL conical flask and added 85mL of distilled water to it and keep in the water bath shaker for 22 hours at 150rpm. Crystallization was the performed under static condition of 20^0C for 2 hours. The product was washed with distilled water to reduce the pH upto 11 and dried for 24 hours at 105^0C. The final product obtained was zeolite (Z_1).

In the hydrothermal method, the fly ash was preheated at 105^0C before sieve. Fly ash was sieved at less than 150μm. During synthesis, 20g of fly ash was mixed will 160mL of 3M NaOH solution, and dried in hot air oven for 24 hours at 90^0C. After dried, it was repeatedly washed with distilled water to reduce the pH to 11. Again dried in hot air oven for 24 hours at 100^0C. The final product obtained was zeolite (Z_2).

2.3 Characterization of adsorbent

The SEM analysis was conducted for fly ash and synthesized zeolites (Z_1 and Z_2) before and after adsorption to study the morphology, texture and heterogeneity of the adsorbent.

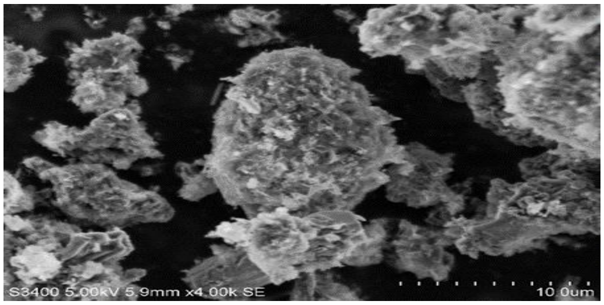
2.4 Column Study

Column adsorption studies were conducted using Perplex glass column having 3.5 cm diameter, 0.3 cm thickness and 50 cm height. The column was provided with four sampling ports along the height of the reactor (10 cm apart). The wastewater was fed into the column in the upward direction using peristaltic pump. The flow rate and bed depth was varied from 7.5 mL/min to 15 mL/min and 10 cm to 20 cm, respectively. Samples were collected at regular time intervals.

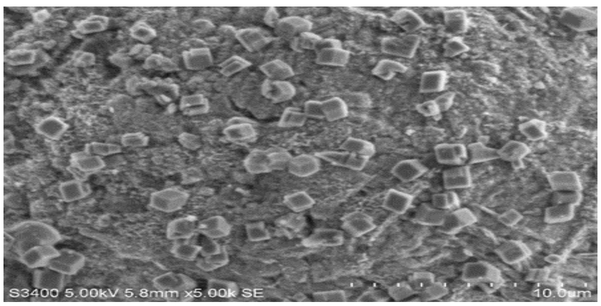
3 Result and discussion

3.1 Characterization of adsorbent

Scanning electron microscopy is a method for high resolution imaging for surface. The advantages of SEM over light microscopy include much higher magnification and greater depth of field up to 100 times that of light microscopy. The SEM images is used to study the surface morphology of the adsorbent. The SEM images provide the morphology of the voids on the surface of the adsorbents to study the adsorption capacity of the adsorbent. The analysis done for the adsorbents before the adsorption to study the morphology of void of the adsorbents. Plate 1 shows the SEM images of (a) synthesized zeolite using fusion method (Z_1) and (b) hydrothermal method (Z_2). Synthesized zeolite (Z_1) has observed cluster of iron (Fe-oxide) and irregular surface of glass matrix which may be responsible for the increase in adsorbent pore volume. Synthesized zeolite (Z_2) has observed crystal structure to be an octahedral shape.



(a)



(b)

Plate 1 SEM images of (a) Synthesized zeolite (Z_1) and (b) Synthesized zeolite (Z_2).

3.2 Column Studies

Column study was conducted in lab scale to design for the practical application that is for the treatment of industrial wastewater or water treatment. From the column experiments the breakthrough curves generated from the fixed bed column studies has the significant value in the column studies. In the present study the column made by perplex glass with an internal diameter of 3 cm and height of 50 cm was used for the column study. The flow rate was maintained at 15 mL/min for varying depth of 10 cm, 15 cm and 20 cm and the flow rates of 7.5 mL/min, 10 mL/min, 12 mL/min and 15 mL/min. In the present study Bed Depth Service Time (BDST) model, Thomas model and Yoon and Nelson model are used.

3.2.1 Effect of Bed Depth

Bed depth is the height of the filter media in a column after it has been properly conditioned for effective operation, usually expressed in inches or cm. By maintaining the flow rate of 15 mL/min the bed depths was varied for 10 cm, 15 cm and 20 cm to generated breakthrough curve for the column studies. The plots C/C_0 verses time in min represents the breakthrough curves for the column adsorption study. In the present study the breakthrough curve obtained for the different bed depth are represented in Chart 1 and 2 for the adsorbent of synthesized zeolite Z_1 and Z_2, respectively for the flow rate of 15 mL/min. From the curves obtained observed that the increase in the bed depth increase in the removal efficiency by providing the large sites for adsorption of colour and COD from the textile mill wastewater.

3.2.2 Effect of Flow Rate

To study the effect of flow rate on the removal of colour and COD the flow rate was varied from 7.5 mL/min to 15 mL/min for the bed depth of 9 cm and 6 cm for synthesized zeolite Z_1 and Z_2 respectively. The plots C/C_0 versus time gives the breakthrough curve for various flow rates. In the present study it was observed that increase the flow rate reduce the removal efficiency. This may be due to the adsorption of the COD on the adsorbents at lower flow rate and the maximum adsorption was higher at the lower flow rate and also increase in the contact time at the flow rate provides more binding sites for COD concentration. The plots C/C_0 versus time representing the breakthrough curves for synthesized zeolite Z_1 and Z_2 represented in Chart 3 and 4, respectively. In the present study the ideal S shape curves was observed at the flow rate of 12 mL/min for synthesized zeolite Z_1 and for synthesized zeolite Z_2 at the ideal S shape curve was obtained at the flow rate of 15 mL/min.

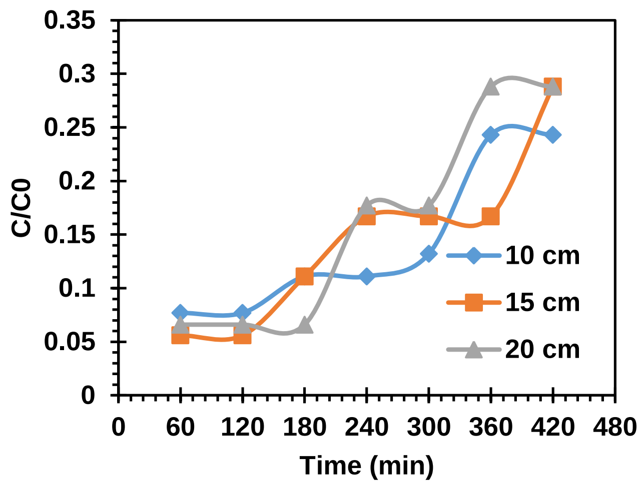


Chart 1 Breakthrough Curves at Different Bed Depths for Synthesized Zeolite Z_1 at a Flow Rate of 15 mL/min.

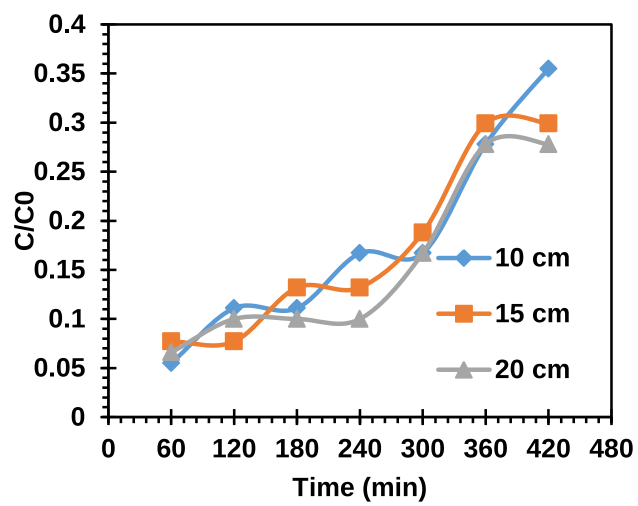


Chart 2 Breakthrough Curve at Different Bed Depths for Synthesized Zeolite Z_2 at a Flow Rate of 15 mL/min.

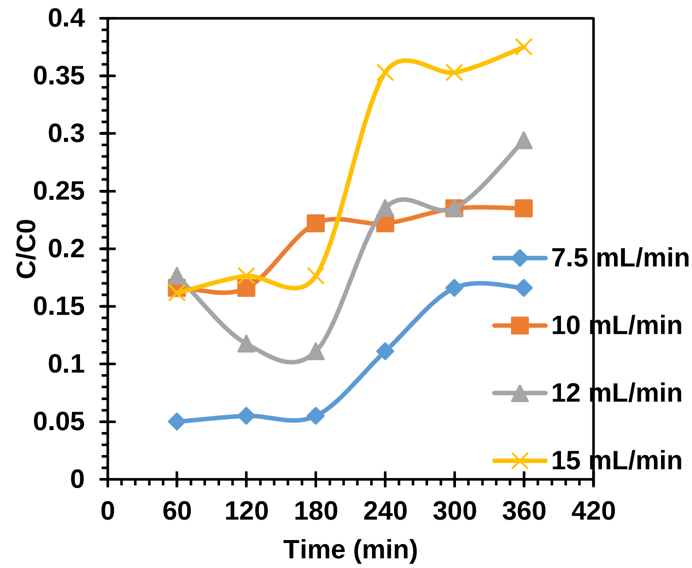


Chart 3 Breakthrough Curves for Effect of Flow Rate at Critical Depth for Synthesized Zeolite Z_1.

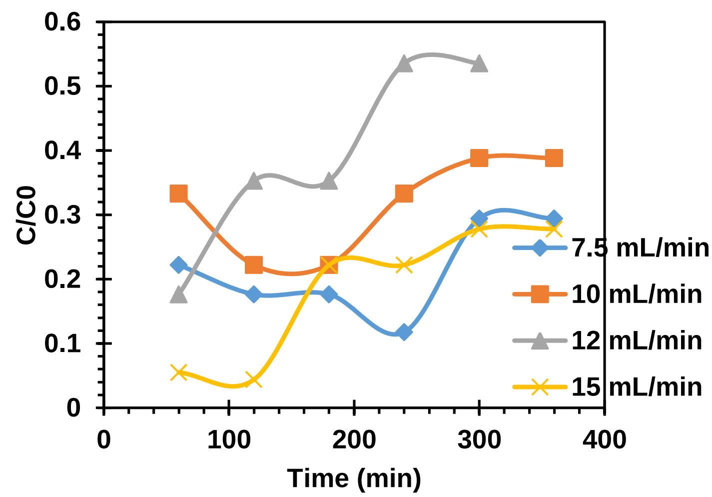


Chart 4 Breakthrough Curves for the Effect of Flow Rate at Critical Depth for Synthesized Zeolite Z_2.

3.3 Bed Depth Service Time Model (BDST)

The BDST is a model for predicting the relationship between bed depth X and service time t. This BDST model focused on the estimation of characteristics parameter such as the maximum adsorption capacity (N_0) and kinetic constant K. This model assumes that the adsorption rate is proportional to residual capacity of the sorbent and the concentration of the sorbing species. The linear relation between bed depth and service time is given by equation (24).

$$t = \frac{N_0}{C_0 v} X - \frac{1}{K C_0} \ln\left(\frac{C_0}{C} - 1\right)$$

Where, C_0 and C are the initial and desired concentration of solute at breakthrough (μg/L), K is the adsorption rate constant (L/μg/h), N_0 is the adsorption capacity (mg/L), X bed depth of column (cm), v is the linear flow velocity of feed to bed (cm/h), t is the service time. The adsorption capacity and adsorption rate constants was computed for the removal of COD by synthesized zeolite Z_1 and Z_2. In the present the adsorption rate constant (K) was found to be 0.0108 L/μg/h and 0.0157 L/μg/h for synthesized zeolite Z_1 and Z_2 respectively. The maximum adsorption capacity (N_0) was found to be 9.429 mg/L and 12.672 mg/L for synthesized zeolite Z_1 and Z_2, respectively.

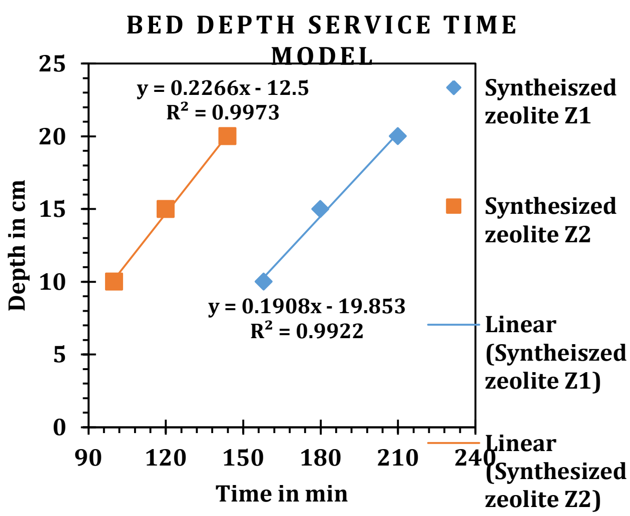


Chart 5 Bed depth service time model for synthesized zeolite Z_1 and Z_2.

Table 2 Bed Depth Service Time Model Constant for Synthesized Zeolite Z_1 and Z_2.

Bed Depth Service Time Model			
Adsorbents	**K**	**N_0 mg/L**	**X cm**
Synthesized zeolite Z_1	0.0108	9.429	9
Synthesized zeolite Z_2	0.0157	12.672	6

3.4 Thomas Model

Thomas model used to calculate the performance of a column and predict its breakthrough curves. It is based on the assumption of negligible axial dispersion. Its main limitation is that the model is based on second order kinetics and hence doesn't restrict the sorption by a chemical reaction and is controlled by mass transfer at the surface. The model is represented by the following equation (23).

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_{TH} q_0 m}{v} - k_{TH} C_o t$$

Where, k_{TH} is the Thomas rate constant (mL/min/mg), q_0 is the maximum dye adsorption capacity of adsorbent (mg/g), C and C_0 are effluent dye concentration and initial concentration (mg/L) respectively, v is flow rate (mL/min), X is the amount of adsorbent in the column (g). The k_{TH} and q_0 for synthesized zeolite Z_1 and Z_2 are represented in Table 8 In the present study Thomas rate constant k_{TH} and equilibrium concentration of the adsorbate q_0 were found to be 2.647 X 10^{-6} mL/min/mg and 181.65 mg/g for synthesized zeolite Z_1 and 2.638 X 10^{-6} mL/min/mg and 293.517 mg/g for synthesized zeolite Z_2, respectively.

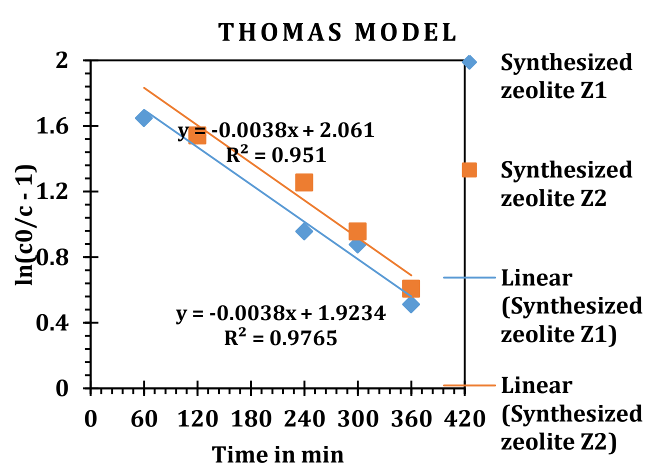


Chart 6 Thomas model for synthesized zeolite Z_1 and Z_2.

Table 3 Thomas Model Constant for Synthesized Zeolite Z_1 and Z_2.

Thomas Model			
Adsorbents	**k_{TH} (mL/min/mg)**	**q_0 (mg/g)**	**R^2**
Synthesized zeolite Z_1	2.647 X 10^{-6}	181.65	0.9765
Synthesized zeolite Z_2	2.637 X 10^{-6}	293.517	0.9707

3.5 Yoon and Nelson Model

The Yoon and Nelson model is applied in the present work to predict the breakthrough curves. It is described in following equation (20).

$$\ln(\frac{C}{C_0 - C}) = k_{YN}t - \tau k_{YN}$$

Where, k_{YN} and τ are the Yoon and Nelson rate constant (/min) and time required for 50% of adsorbate breakthrough (min) respectively. By plots the graph $\ln(C/C_0 - C)$ versus time, the slope and the intercept gives the value of Yoon and Nelson constant and time required for 50% of adsorbate breakthrough for the removal of COD from textile mill wastewater by synthesized zeolite Z_1 and Z_2. The values of k_{YN} and τ were obtained from the linearized equation are represented in Table 4.

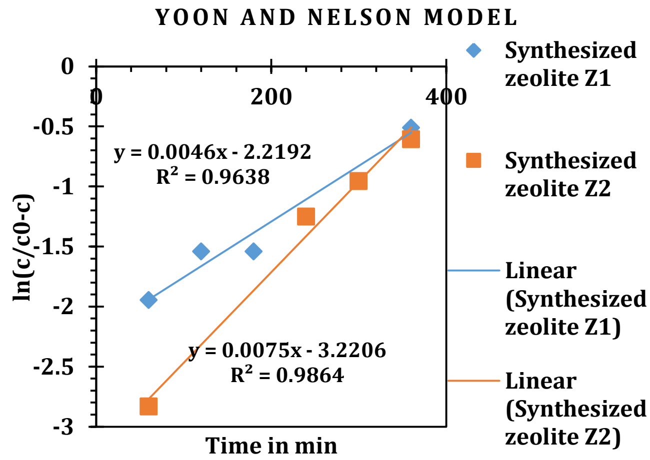


Chart 7 Yoon and Nelson model for synthesized zeolite Z_1 and Z_2.

Table 4 Yoon and Nelson Model Constant for Synthesized Zeolite Z_1 and Z_2.

Yoon and Nelson Model			
Adsorbents	**k_{YN} /min**	**τ min**	**R^2**
Synthesized zeolite Z_1	0.0046	482	0.9638
Synthesized zeolite Z_2	0.0075	429	0.9864

The Yoon and Nelson model well fits for the adsorption and in the present study with the increase in the flow rate the value of k_{YN} found to be decreased and also the τ also decreased.

4 Conclusion

In the present study the batch and column studies are conducted for the removal of colour and COD from textile mill wastewater by synthesized zeolite Z_1 and Z_2. From the results of EDS the elements present in synthesized zeolite Z_1 are Si – 3.21%, Al – 1.66%, C – 10.38%, O – 42.19% and Fe – 35.25% and synthesized zeolite Z_2 are Si – 8.66%, Al – 3.59%, C – 23.46%, O – 46.15% and Fe – 1.68%. From the SEM images the synthesized zeolite Z_1 have the glass clustered surface and synthesized zeolite Z_2 have crystal structure to be an octahedral shape. The column studies were conducted for the various flow rates of 7.5 mL/min, 10 mL/min, 12 mL/min and 15 mL/min where S shape of the curve was observed at the 15 mL/min for synthesized zeolite Z_1 and Z_2. From the bed depth service time (BDST) the critical depth was found to be 9 cm and 6 cm for synthesized zeolite Z_1 and Z_2 respectively. The adsorption capacity q_0 calculated from the Thomas model was 181.65mg/g and 293.517 mg/g for synthesized zeolite Z_1 and Z_2 respectively and k_{TH} value obtained was 2.647 X 10^{-6} mL/min/mg and 2.638 X 10^{-6} for synthesized zeolite Z_1 and Z_2 respectively. From the Yoon and Nelson model calculated the time required for 50% adsorbate breakthrough for synthesized zeolite Z_1 and Z_2 are 482 min and 429 min respectively.

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