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

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Abstract

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. In batch study optimum dosage was fixed for synthesized zeolite Z_1 and Z_2 are 4g/L. Synthesized zeolite Z_1 the removal of Colour and COD from wastewater are 44.32% and 92.42%, respectively. Synthesized zeolite Z2 the removal of Colour and COD from wastewater are 43.06% and 84.84%, respectively. For the results of the batch studies, Langmuir, Freundlich and Temkin isotherm was applied. Langmuir isotherm was most well fitted for the experimental data. The adsorbents are in exothermic in reaction. The adsorbents of synthesized zeolite Z_1 and Z_2 follows Pseudo first order kinetics.

Key words: *Synthesized zeolite$_1$, Hydrothermal method$_2$, Fusion method$_3$, Isotherm$_4$, Kinetics$_5$.*

1.1 Introduction

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. Textile industry is traditional after agriculture and also generate the largest employment for both skilled and unskilled employees. India is the second largest producer of fiber in the world and the major produced is cotton. The wastewater with obtain from the industry is high in strength because of the colour concentration in the wastewater. The most difficult in treatment is removal of colour. The methods for the treatment of coloured wastewater are physical, chemical and biological treatments. Adsorption is a physic-chemical method. Adsorption of contaminants present in wastewater or water onto activated carbon is frequently used for purification of the water. However, activated carbon is an expensive adsorbent due to its high costs of manufacturing and regeneration. For the purpose of removing unwanted hazardous compounds from contaminated water at a low cost, much attention has been focused on various naturally occurring adsorbents such as chitosan, zeolites, fly ash, coal, paper mill sludge, and various clay minerals. An attempt to develop cheaper and effective adsorbent of zeolite using fly ash. Zeolites are micro porous, aluminosilicate minerals commonly used as commercial adsorbents and catalysts. Zeolites have a porous structure that can accommodate a wide variety of cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. 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 – batch study.

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. In the study 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 Batch study

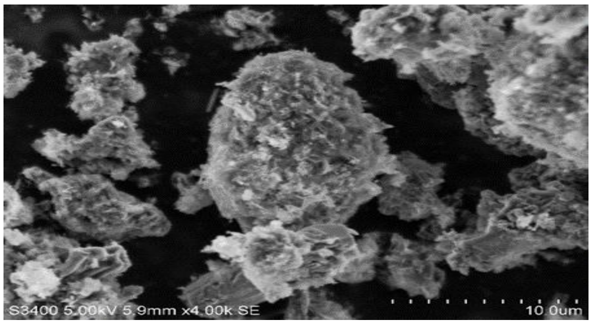
The batch adsorption study were carried out in 250 mL conical flask over a period of 120 minutes to optimize the dosage and contact time. The adsorbents dosage was varied from 0.2 to 1.0 g/L for a period of 120 minutes, to know the effective dosage to remove colour and COD which was determined using measuring the absorbance and concentration respectively. The contact time varied from 10 – 120 minutes for all three adsorbents with the optimum dosage. The sample was determined, the percentage removal of COD and colour was studied by the absorbance taken from UV-visible Spectrophotometer at the wavelength of 655 nm. From the batch studies the optimum dosage and contact time was obtained. The percentage of colour removal efficiency was calculated using following equation:

$$\%\text{ Colour removal} = \frac{\text{Initia colour absorbance} - \text{Final colour absorbance}}{\text{Initial colour absorbance}} \times 100$$

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.



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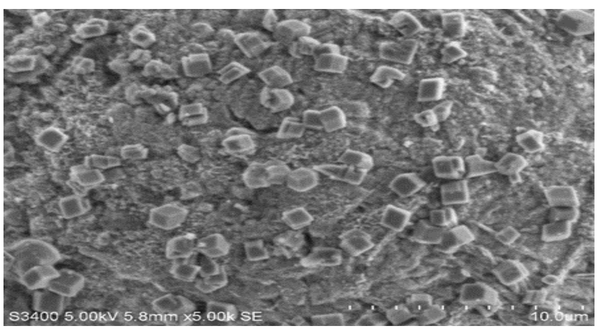

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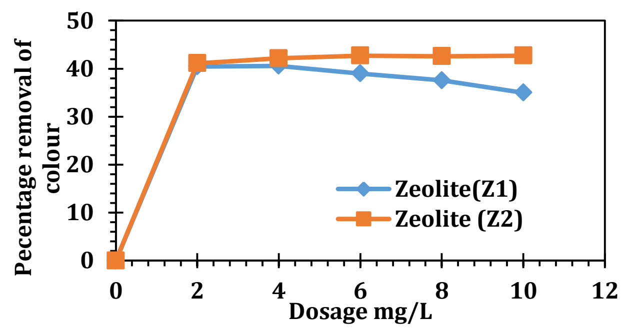
Plate 1 SEM images of (a) Synthesized zeolite (Z_1) and (b) Synthesized zeolite (Z_2).

3.2 Batch study

Batch studies were conducted for all three adsorbents for various operating parameter such as contact time and adsorbent dosage.

3.2.1 Effect of Adsorbent Dosage

The adsorbents are synthesized zeolite Z_1 and Z_2 dosages are added to the wastewater to obtain the maximum adsorption capacity with an optimum dosage of adsorbent. The adsorbent dosage was varied from 2- 10 g/L of wastewater. 100 mL of sample was taken in a conical flask and the adsorbent dosage was added and allowed in water shaker bath shaker for 120 min. The sample were collected at regular time intervals to read absorbance of wastewater and to check the percentage removal of COD. Chart 1 shows the effect of adsorbent dosage on removal of colour and COD from textile wastewater. The optimum dosage obtained was 2 g/L for an adsorbent of Synthesized Zeolite Z_1 and Z_2. The percentage removal of colour for the adsorbent dosage of 2 g/L synthesized zeolite (Z_1 and Z_2) are 40.46% and 43.05%, respectively. The percentage removal of COD for synthesized zeolites (Z_1 and Z_2) are increased 77.77% to 84.84%. The removal efficiency further decreases with the increased in the adsorbent dosage.



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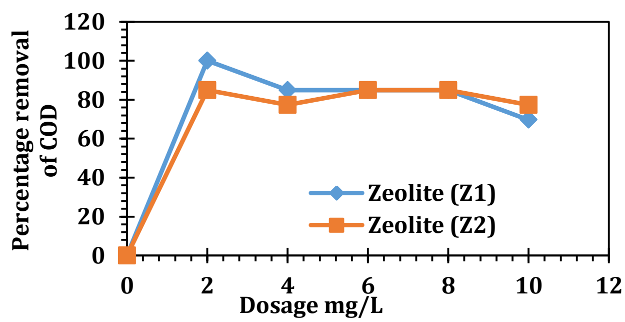

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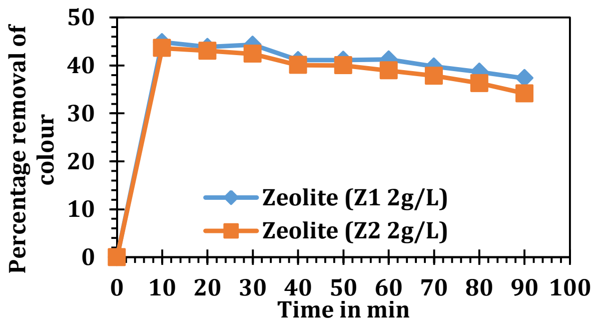
Chart 1 The effect of dosage on removal of (a) colour and (b) COD from textile wastewater.

3.2.2 Effect of Contact Time

The effect of contact time was studied as a function of removal of colour and COD for both the adsorbents. To study effect of contact time, the optimum dosage of 2 g/L for synthesized zeolite Z_1 and Z_2 was added to 100 mL of textile mill wastewater. The effect of contact time for removal of colour and COD shown in Fig 2. From Chart 2, it is observed that there was gradual increased in the removal of colour and COD in till 10 min and gradually it reached the equilibrium. This is due to the availability of the surface on the adsorbents for adsorption at the initial time and the after the equilibrium is achieved the voids of the adsorbents for which the removal of colour and COD efficiency become constant.



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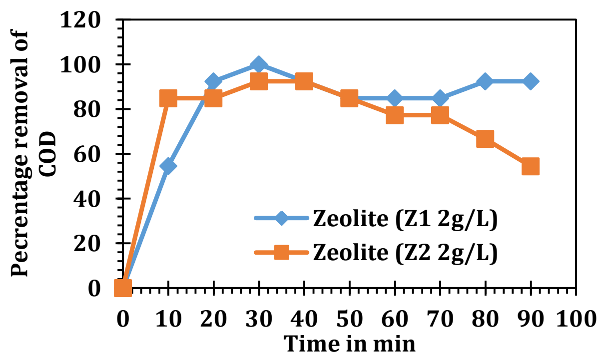

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Chart 2 The effect of contact time for removal of (a) colour and (b) COD from textile wastewater.

3.3 Adsorption Isotherm

The adsorption isotherm indicates how the adsorption molecules distributes between liquid phase and the solid phase when the adsorption process attains its equilibrium state. . In the present study, equilibrium data of adsorption of Colour and COD from the wastewater on to fly ash and synthesized zeolite Z_1 and Z_2 were analyzed using Langmuir, Freundlich and Temkin isotherm equations.

3.3.1 Langmuir Adsorption Isotherm

Langmuir isotherm described quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. . The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based upon these assumption. Langmuir represents the following linear equation (18).

$$\frac{1}{q} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C}$$

Where, C = the equilibrium concentration of the adsorbate (mg/L), q = the amount of adsorbate adsorbed per gram of the adsorbent at equilibrium (mg/g), Q_0 = maximum monolayer coverage capacity (mg/g) and K_L = Langmuir isotherm constant (L/mg).

The values of Langmuir isotherm constant K_L and Q_0 was determined and represented in Table 1. The Langmuir constant and maximum monolayer coverage capacity was found to be 0.3993 and 0.447 for synthesized zeolite Z_1 and Z_2, respectively. Langmuir isotherm may be expressed in term of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter, which define in equation

$$R_L = \frac{1}{1 + (1 + K_L C_0)}$$

Where, K_L = Langmuir constant and C_0 = initial concentration mg/L. The value of R_L indicates the adsorption nature to be either: **$R_L > 1$**: Unfavorable, **$R_L = 1$**: Linear, **$R_L < 1$**: Favourable, **$R_L = 0$**: Irreversible. The R_L value for synthesized zeolite Z_1 and Z_2 are 0.0008 and 0.0009, respectively. From these value indicates that the adsorption is favourable.

3.3.2 Freundlich Adsorption Isotherm

Freundlich isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface. The well-known linear form of Freundlich model is given by following equation

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

Where, q_e = the amount of adsorbed per gram of the adsorbent at equilibrium (mg/g), C_e = the equilibrium concentration of adsorbate (mg/g), K_f = Freundlich isotherm constant (mg/g) and n = adsorption intensity. The constant K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process. If value of 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption (9). The obtained value of K_f and 1/n values are shown in Table 2. The value of 1/n shows that the adsorption process is normal adsorption where 1/n value is greater than 1.

3.3.3 Temkin Adsorption Isotherm

This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. The model is given by the following equation.

$$q = \frac{R\,T}{b}\ln A_T + \frac{R\,T}{b}\ln C$$

Where, A_T = Temkin isotherm equilibrium binding constant (L/g), b = Temkin isotherm constant, R = universal gas constant (8.134J/mol/K) and T = Temperature at 298K. Temkin constant A_T and B were calculated for the removal of COD using synthesized zeolite Z_1 and Z_2 presented in Table 3. The value of B shows the positive the adsorption reaction is in endothermic in reaction.

3.4 Adsorption Kinetics

For the equilibrium data obtained from the present study the adsorption kinetics pseudo first order and pseudo second order kinetics were studied.

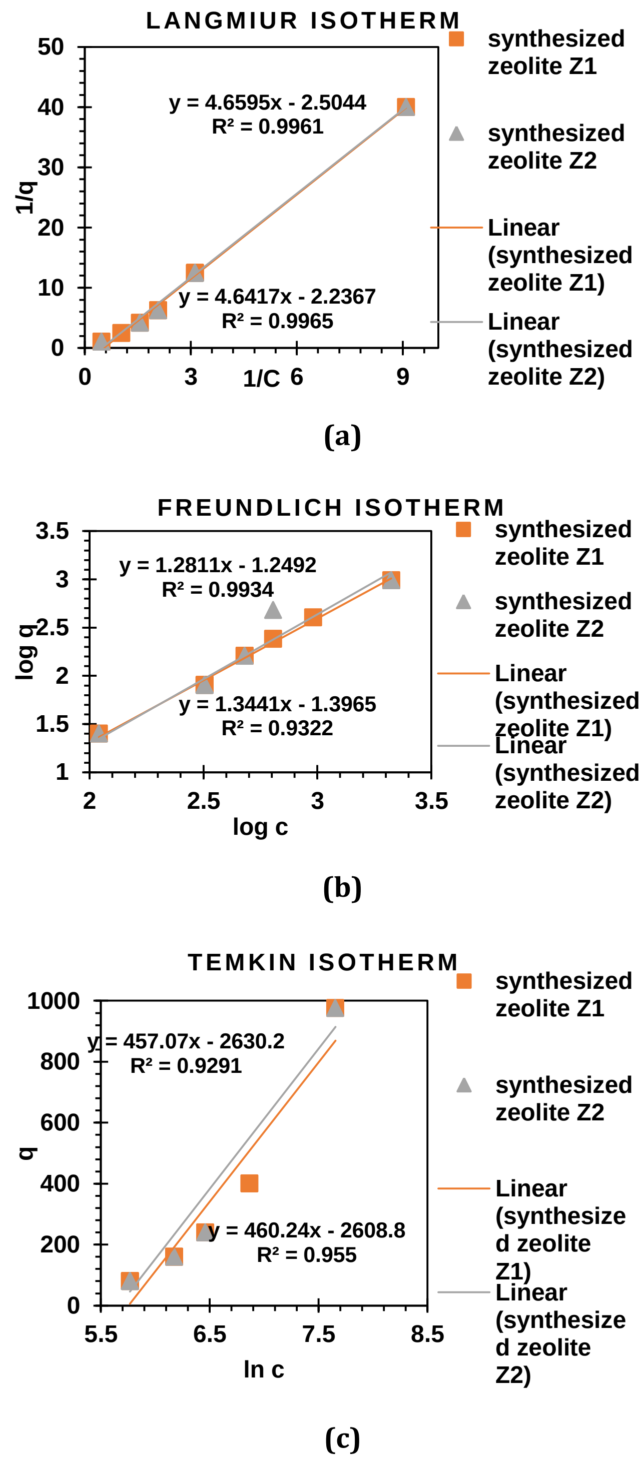


Chart 3 Adsorption isotherm (a) Langmuir, (b) Freundlich and (c) Temkin isotherm.

Table 1 Adsorption isotherms constant values of Langmuir isotherm for synthesized zeolite Z_1 and Z_2.

Adsorption isotherm	Langmuir isotherm			
	Q_0 (mg/g)	K_L (L/mg)	R_L	R^2
Synthesized zeolite Z_1	0.3993	0.5374	0.0008	0.9961
Synthesized zeolite Z_2	0.447	0.4819	0.0009	0.9965

Table 2 Adsorption isotherms constant values of Freundlich isotherm for synthesized zeolite Z_1 and Z_2.

Adsorption isotherm	Freundlich isotherm		
	K $((\frac{mg}{L})(\frac{L}{mg})^{\frac{1}{n}})$	$\frac{1}{n}$	R^2
Synthesized zeolite Z_1	319.44	4.6959	0.9931
Synthesized zeolite Z_2	24.19	1.3441	0.9322

Table 3 Adsorption isotherms constant values of Temkin isotherm for synthesized zeolite Z_1 and Z_2.

Adsorption isotherm	Temkin isotherm		
	B	A_T (L/mg)	R^2
Synthesized zeolite Z_1	5.420	0.0032	0.9291
Synthesized zeolite Z_2	5.583	0.0035	0.955

3.4.1 Pseudo First Order Kinetics

The rate constant of adsorption is determine from the pseudo first order equation given by Langergren and Svenska 1898 equation. (18)

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

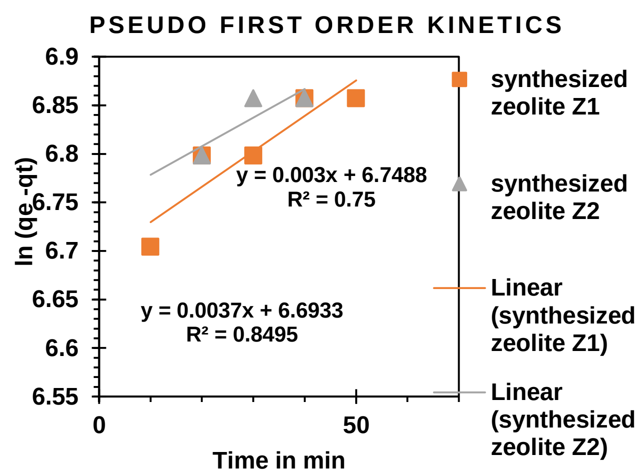
Where, q_e and q_t are the sorbed concentration at equilibrium (mg/g) and at time t in min. k_1 is the first order rate constant. The values of k_1 was found to be 0.0037 and 0.0068 for synthesized zeolite Z_1 and Z_2, respectively. The value of q_e was found to be 778.057 mg/g and 705.42 mg/g synthesized zeolite Z_1 and Z_2, respectively. Table 4 shows pseudo first order kinetics constant vale for synthesized zeolite Z_1 and Z_2.

3.4.2 Pseudo Second Order Kinetics

A pseudo second order equation is based on equilibrium adsorption is expressed in equation. (18)

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

Where, k_2 is the rate constant of second order adsorption g/mg/min. The value of k_2 was found to be 0.00179 and 0.0034 for synthesized zeolite Z_1 and Z_2. The value of q_e was found to be 68.49 and 20.408 mg/g for synthesized zeolite Z_1 and Z_2 respectively. Because of the intercept of the straight line plots of ln (q_e – q_t) against t should be equal to ln q_t. Then it follows the pseudo first order kinetics. (3). Synthesized zeolite Z_1 and Z_2 were follows the pseudo first order equation.



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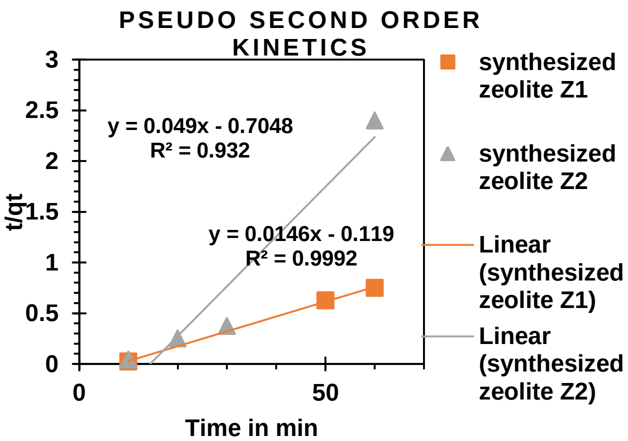

(b)

Chart 4 Adsorption kinetics (a) Pseudo first order and (b) Pseudo second order kinetics.

Table 4 Adsorption Pseudo first order kinetics constants.

Adsorption kinetics	Pseudo first order kinetics		
	k_1	q_e mg/g	R^2
Synthesized zeolite Z_1	0.0037	778.057	0.8495
Synthesized zeolite Z_2	0.0068	705.42	0.9021

Table 5 Adsorption Pseudo second order kinetics constants.

Adsorption kinetics	Pseudo second order kinetics		
	k_2	q_e mg/g	R^2
Synthesized zeolite Z_1	0.00179	68.49	0.9992
Synthesized zeolite Z_2	0.00340	20.408	0.932

4 Conclusion

In the present study the batch studies are conducted for the removal of colour and COD from textile mill wastewater by synthesized zeolite Z_1 and Z_2. 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. From the batch study, it was observed that the optimum dosage for synthesized zeolite Z_1 and Z_2 the optimum dosage was obtained for both 2 g/L and the removal efficiency achieved for colour and COD for zeolite Z_1 are 44.32% and 92.42%, respectively. For the zeolite Z_2 the removal of colour and COD achieved 43.06% and 84.84%, respectively. Synthesized zeolite Z_1 and Z_2 achieved equilibrium at the initial 30 min and become constant with a removal 42% and 92% of colour and COD from the textile mill wastewater respectively. Langmuir isotherm was applied to study the monolayer adsorption of the system. The maximum adsorption capacity of 0.3993 mg/g and 0.447 mg/g for synthesized zeolite Z_1 and Z_2, respectively. By comparing the correlation value of Langmuir isotherm was high value compared with Freundlich and Temkin isotherm for all three adsorbents. Freundlich isotherm was obeyed for all three adsorbents with cooperative adsorption and the adsorption process was favourable (n value lies between 0 and 10). The positive value of B from the Temkin isotherm indicates the exothermic reaction. The adsorption followed pseudo first order synthesized zeolite Z_1 and Z_2.

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