

## STUDIES ON REMOVAL OF SAFRANINE-T AND METHYL ORANGE DYES FROM AQUEOUS SOLUTION USING NaX ZEOLITE SYNTHESIZED FROM FLY ASH

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**Abstract:** Investigations were carried out to determine whether low cost zeolite, synthesized from fly ash hold promise in removal of dyes in the textile industries. The initial findings indicated that NaX zeolite synthesized from fly ash has high adsorptive capacity for dyes and it is relatively cheap. The adsorption characteristics of one basic dye Safranin T and an acidic dye Methyl Orange onto fly ash and its two zeolitized products has been studied at different hydrothermal conditions. The coal based fly ash was used to synthesis the zeolite by alkali fusion, followed by hydrothermal treatment. The synthesized zeolite was then characterized using various techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM). Removal of dyes increased from 53% to 72% as the solution pH increased from 2 to 10. The high temperature regeneration was conducted at 540°C for 5 h which shows removal of dyes over the regenerated zeolites is only 68% whereas % removal of methyl orange over the fresh zeolite is 78%. The values of changes in enthalpy ( $\Delta H^{\circ}$ ) and entropy ( $\Delta S^{\circ}$ ) during the adsorption process were found to be -20.18 kJ/mol and -90.32 J/mol K<sup>-1</sup>. The equilibrium results were well-described by the Freundlich isotherm model. Adsorption of Methyl Orange over Zeolite NaX is much higher than NaA zeolite. For adsorption of methyl orange, experimental data was fitted to the Freundlich isotherm better than Langmuir isotherm. Correlation coefficient was found to be 0.998.

**Keywords:** Adsorption, Zeolite, fly ash, Methyl Orange, SafraninT, Kinetics.

### 1. Introduction

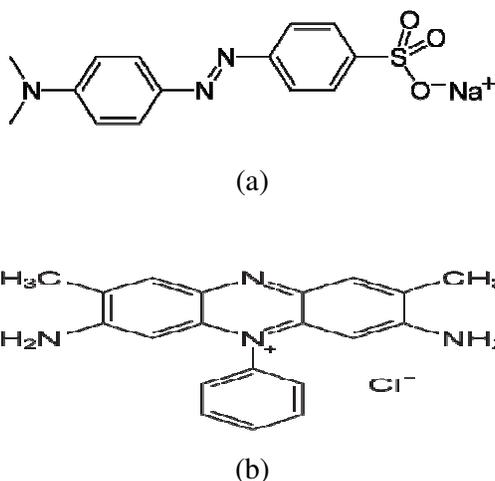
Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances. Activated carbon is the most popular adsorbent and has been used with great success, but is expensive (Chakrabarty et al. 2003). A full description of low cost adsorbents for waste and wastewater treatment: a review has been presented by S.J.T. (Yunus et al., 2006). A number of studies have been reported with regard to the adsorption equilibrium of dye removal processes using various adsorbents.

Fly ash derived from coal residues has a tremendous potential for conversion to zeolites. The present environmental concerns over fly ash disposal have sparked a resurgent interest in its

conversion to value added products such as zeolites. Still more remarkable is the subsequent utilization of these zeolites as potential adsorbent. Different varieties of fly ash have different sorption properties for inorganic and organic pollutants such as cesium, strontium, organic basic, organic acidic and organic reactive dyes. Because the adsorption capabilities of fly ash for cationic species are relatively low, they can be enhanced by surface modification, heat and acid treatment and zeolitization under alkaline hydrothermal conditions (Jing 2006)

Adsorption is one of the most efficient methods for removal of colours, odour, oils and organic pollutants from process or waste effluents. Activated carbon is most widely used adsorbent due to its excellent adsorption capacity (Jing et al. 2006; Querol et al. 2002; Mimura et al. 2001; Apak et al. 1996; Jacos et al. 2003). However its use is often limited due to high cost, making this method unfavorable. Dyes or pigments are widely used in textile industries to color some products creating environmentally hazardous waste. Waste-water from dyeing and finishing operation in the textile industries are generally high in both color and organic content. The discharge of dyes into natural streams and rivers from the industries poses severe problems as dyes give toxicity to the aquatic life and damaging to the aesthetic nature of the environment (Srivastava et al. 2006). Color removal from textile effluent has been the target of great attention in the last few years, not only because of its potential toxicity, but mainly due to its visibility problems. Recent estimate indicates that 20% of dyes enter the environment through effluent that result from the treatment of industrial wastewater. The present investigation describes the adsorption of Safranin T, a cationic organic dyestuff and Methyl Orange, an anionic organic dye stuff commonly used for adsorption over zeolite synthesized from fly ash. The existing technologies (Chang et al. 1995; Runstuck 2006) have certain efficiency in the removal of dyes but their initial and operational costs are very high (Atun et al. 2011). On the other hand, low cost technologies do not allow the desired degree of color removal (Qui et al. 2009) or have certain disadvantage. Adsorption of dyes by zeolites has evolved into one of the most effective physical processes for the decolorization of textile wastewater. Although the adsorption of dyes over zeolite has been extensively investigated (Alpat et al. 2008; Yener et al. 2006; Amagan et al. 2004; Meshko et al. 2001; Caljapheri et al. 1992) only a few studies have been reported on adsorption of dye onto fly ash based zeolite (Venkat et al. 2006; Peng et al. 2007). Based on the above mentioned fact, the present study was undertaken: (1) to synthesize the effective zeolite for adsorption (2) to investigate the adsorption capacity of zeolite (3) to determine the effect of adsorbent dosage, contact time, initial concentration of dye, kinetic equations, adsorption mechanism and

characteristic parameters. (4) to study the applicability of various equilibrium models, (5) and thermodynamic study.



**Figure 1.** Structure of (a) Methyl Orange and (b) Safranin T

## 2. Experimental

### 2.1 Materials

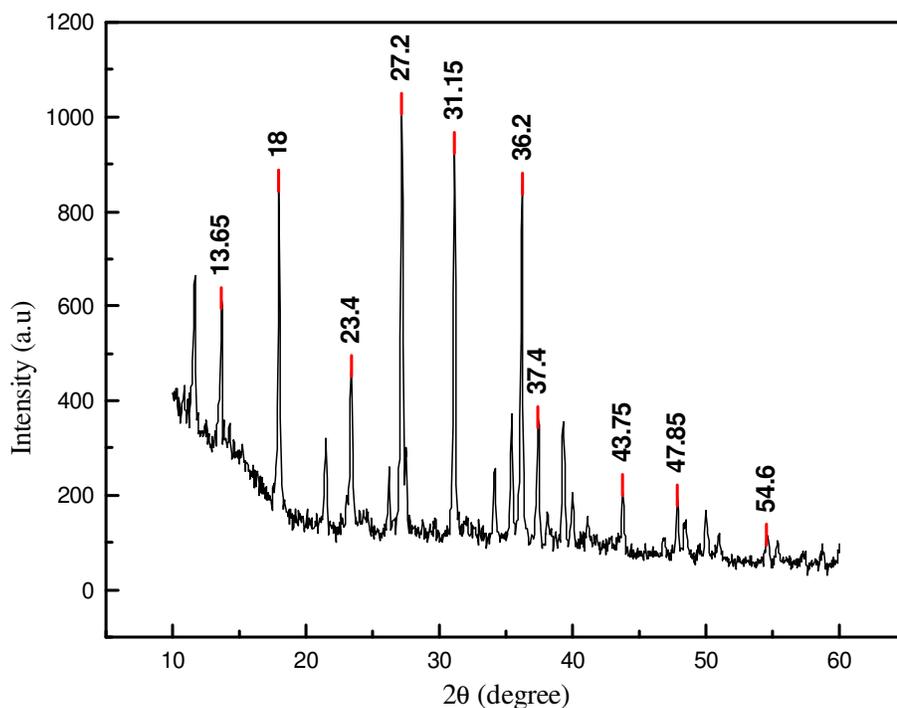
The zeolite was synthesized from fly ash (collected from NTPC, Dadri and Bathinda thermal power station) using hydrothermal treatment. Sodium Hydroxide and Hydrochloric acid and different dyes such as Methyl orange, Safranin T, were procured from Puja Chemical, Patiala. All reagents were analytically pure (99%) and used without purification.

### 2.2 Zeolite preparation

Before any treatment, the raw fly ash samples were first screened through a BSS Tyler sieve of 80-mesh size to eliminate the larger particles. The unburnt carbon (4–6%) along with other volatile materials present in fly ash were removed by calcinations at 800 (+10 or -10) °C for 2 h. Mixture of sodium hydroxide and fly ash (calcined and HCl treated) in a pre-determined ratio, was milled and fused in a stainless steel tray at different temperatures ranging from 500–650°C for 1 h. The sodium hydroxide to fly ash ratio (by weight) was varied from 1.0–1.5. The resultant fused mixture was then cooled to room temperature, ground further and added to water (10 g fly ash/100 ml water). The slurry thus obtained was agitated mechanically in a glass beaker for several hours. It was then kept at around 90°C for 6 h without any disturbance. The resultant precipitate was then repeatedly washed with distilled water to remove excess sodium hydroxide, filtered and dried and Zeolite was ready for use. The synthesis procedure of ZA<sub>1</sub> is almost same as ZX<sub>1</sub>, but the difference is in introducing Aluminium hydroxide hydrate at the curing stage.

### 2.3 Characterization

The determination of structure of zeolite ZX<sub>1</sub> was done by X-ray diffractometer (Bruker AXS, Diffractometer D8, Germany) using Cu-K $\alpha$  as a source and Ni as a filter. The formation of compounds was compared with the XRD patterns of the present work shown in Figure 3.1 with that found by other researchers as well as using JCPDS (Joint Committee of Powder Diffraction Standard) files.



**Fig 3.1 XRD of zeolite ZX<sub>1</sub>**

The determination of images and composition of zeolites were done by SEM/EDAX QUANTA 200 FEG (specifications: accelerating voltage from 200 V to 30 KV, resolution of 2 mm and magnification up to 1000KX). Scanning for zeolite samples was taken at various magnifications and voltages to account for the crystal formation and size. From EDAX, the silica alumina ratio was reported to be 1.6. The surface area of zeolite was found to be 425 m<sup>2</sup> / g. The porosity of ZX<sub>1</sub> particle size are 0.28 and 1.15 mm respectively.

### 2.4 Experimental procedure and product analysis

Adsorption kinetics and isotherm experiments for all samples were undertaken using a batch equilibrium technique. The adsorption of dye was performed by shaking 0.001 g of adsorbent

in 250 ml of dye solution with an initial concentration of 5mg/L at 100 rpm at different temperatures. The determination of dye concentration was done spectrophotometrically on a Spectronic 20 Genesis Spectrophotometer (USA) by measuring absorbance at  $\lambda_{\max}$  of 464 nm for methyl orange and 530 nm for Safranin T respectively. The data obtained from the adsorption tests were then used to calculate the adsorption capacity,  $q_t$  ( $\text{mol g}^{-1}$ ), of the adsorbent by a mass–balance relationship, which represents the amount of adsorbed dye per amount of dry adsorbent. All experimental run were conducted at 25  $^{\circ}\text{C}$ .

### 3. Results and Discussion

The time-dependent amount of dye adsorbed ( $q_t$ ) was calculated from the concentration changes during the adsorption process using the following equation:

$$q_t = (C_0 - C_t) V/W$$

Where  $C_0$  and  $C_t$  are the molar concentrations of dyes at times zero and  $t$ , respectively.  $V/W$  is the ratio of the solution to the mass of adsorbent (in L/g). The concentration of Methyl Orange and Safranin T dyes were measured with spectrophotometer at a wavelength corresponding to the maximum absorbance for each dye, 464 nm, 530 nm respectively. In accordance with the Lambert- Beer law the adsorbance was found to vary linearly with concentration and dilutions were undertaken when absorbance exceeded 0.6.

#### **Kinetic experiments over zeolite ZX<sub>1</sub>, ZA<sub>1</sub> with different dyes**

In the sorption isotherm experiments, dye solutions were added to different quantities of sorbents into glass-stoppered bottles and subsequently placed on a shaker for 15-25 h at 25 $^{\circ}\text{C}$ . From the initial concentrations of sorbents ( $\text{g l}^{-1}$ ) and dyes ( $\text{mg l}^{-1}$ ) the amount adsorbed in the sorbent were measured. Percent removal of dyes over zeolite ZX<sub>1</sub>, ZA<sub>1</sub> and Fly ash as a function of contact time, are shown in Figur 3.3, Figure 3.4 respectively. The amounts sorbed were determined by difference between initial and final concentrations and expressed as mg of dye/g of sorbent. Under the conditions of the experiments all systems approached equilibrium within 15 h of contact time. The adsorption capacity of zeolite ZX<sub>1</sub> was higher due to larger pore size and surface area compared to ZA<sub>1</sub> and Fly ash. Molecular size of Methyl Orange facilitates the adsorption, resulting in higher adsorption capacity than Safranin T. Reduced adsorption in ZA<sub>1</sub> is due to the inability of the molecule to penetrate all the internal pore structure and less available surface.

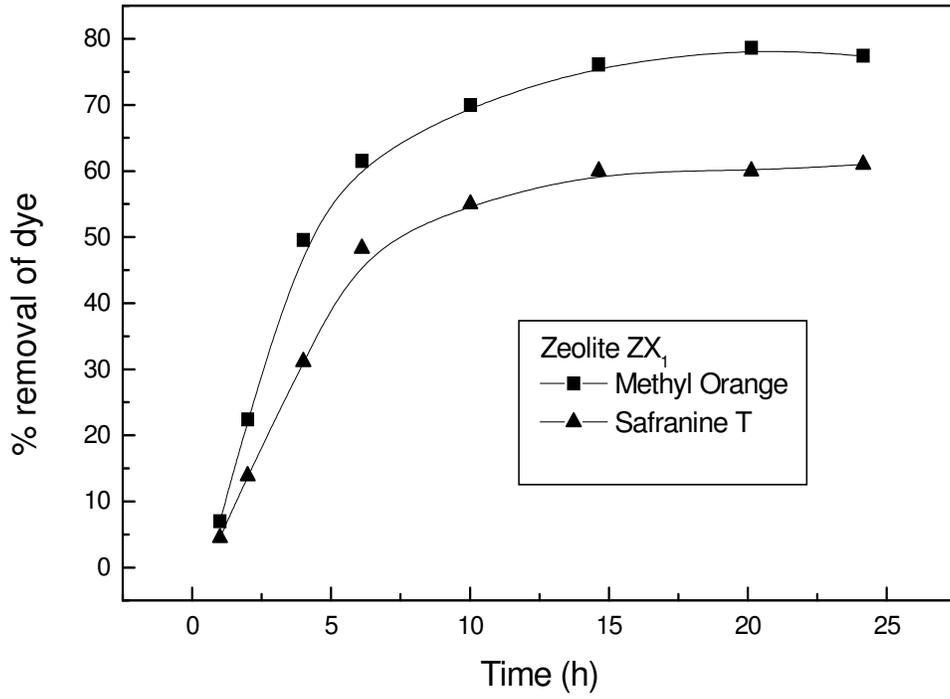


Figure 3.3: % Removal of dyes over Zeolite ZX<sub>1</sub>

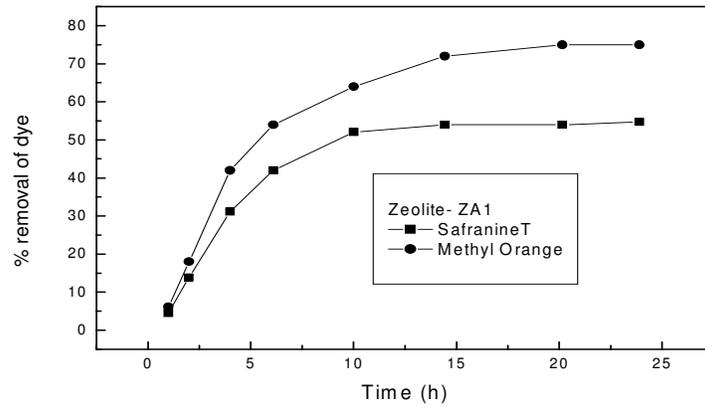
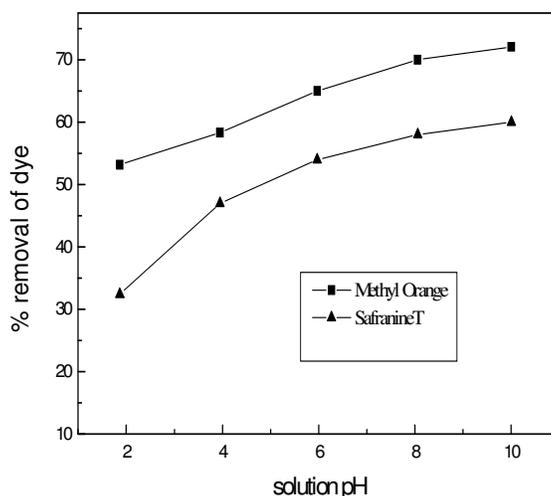


Figure 3.4: % Removal of dyes over Zeolite ZA<sub>1</sub>

**Effect of pH on dye removal:**

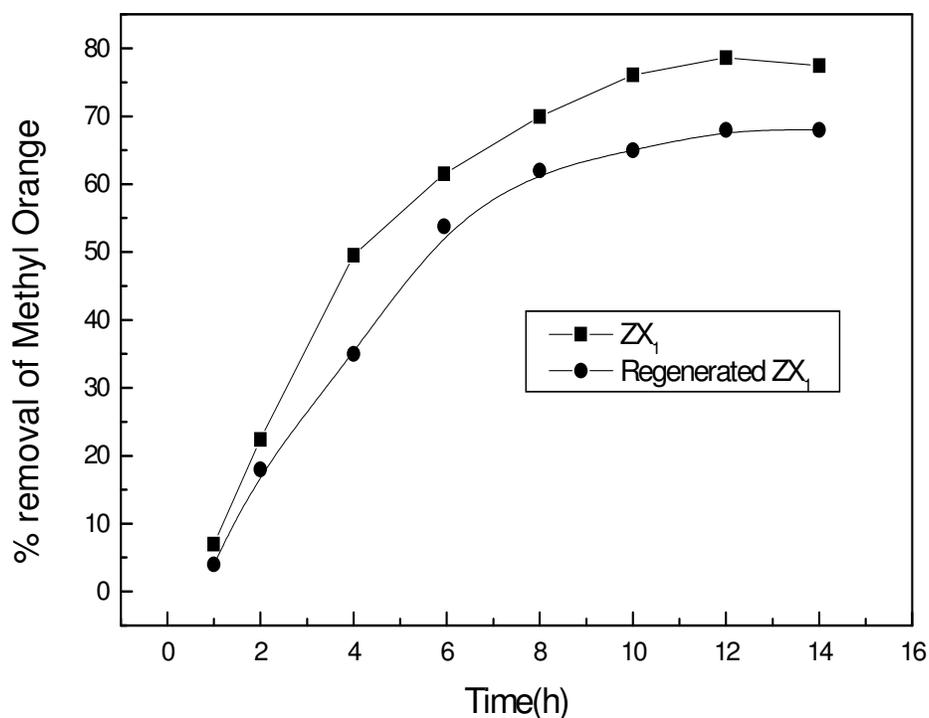
The pH values of Methyl orange and Safranin T solutions were measured as 8.92, 5.85 respectively. The effect of solution pH on dye removal at 298K was investigated by changing the initial pH (2–10) adjusting by HCl or NaOH. Figure 3.6 shows the dynamic adsorption of Methyl Orange, Safranin T on zeolite ZX<sub>1</sub> at different initial pH values at initial dye concentration of 5 mg/l, 25mg/l and 10mg/l respectively. It is seen that adsorption increases as the pH is increasing when the pH is changed from 2 to 10. Several investigations also have shown that Methyl Orange adsorption will have higher adsorption at higher pH values (Nandi et al. 2008; Gupta et al. 2004). For cationic dyes like Safranin T, lower adsorption of Safranin T at acidic pH is probably due to the presence of excess H<sup>+</sup> ions competing with the cation groups on the dye for adsorption sites. As surface charge density decreases with an increase in the solution pH, the electrostatic repulsion between the positively charged dye (Safranin T) and the surface of the adsorbent is lowered, which may result in an increase in the extent of adsorption. But in the case of Methyl Orange, adsorption is higher because even at lower pH, an excess H<sup>+</sup> ion balances the anionic charge of the dye. The excess anionic part of the Methyl Orange gets attracted to the cationic adsorption surface and thereby enhances adsorption. With increase in solution pH due to the reduction of H<sup>+</sup> ion more anionic dyes can be adsorbed on the cationic surface of the adsorbent.



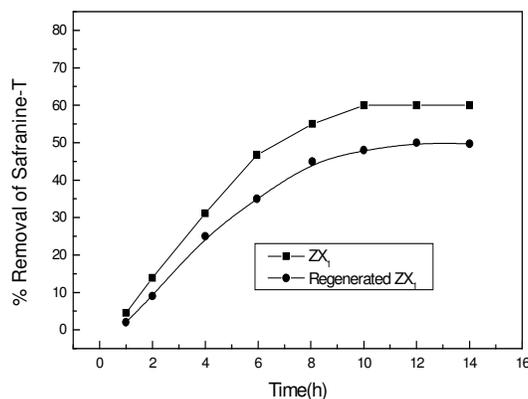
**Figure 3.6:** Effect of solution pH on removal of dye

### Adsorption behavior of regenerated adsorbents

The high temperature regeneration was conducted at 540°C for 5 h. The regenerated zeolite ZX<sub>1</sub> was tested again for Methyl Orange and Safranin T adsorption. Figure 3.7 and Figure 3.8 represent the comparison of the performance of fresh and regenerated ZX<sub>1</sub> for the adsorption of Methyl Orange and Safranin T respectively. It shows lower adsorption compared with the fresh sample. Adsorption of dyes on adsorbent will usually be deposited on the surface and pores of solids. High temperature calcination in air results in the decomposition of adsorbed dyes to gases, thus releasing the surface and pores for re-adsorption. It is seen that temperature and time will affect the regeneration efficiency. Higher temperature and longer time can recover most of the adsorption capacity but will reduce somewhat the adsorption capacity, probably due to pore collapse.



**Figure 3.7:** % Removal of Methyl Orange dye over regenerated zeolite ZX<sub>1</sub>



**Figure 3. 8:** % Removal of Safranin T dye over regenerated zeolite X

Fitting of the experimental data of methyl Orange over ZX<sub>1</sub> was attempted as removal of Methyl Orange is more than Safranin T over zeolite ZX<sub>1</sub> than ZA<sub>1</sub> and fly ash,

Langmuir and Freundlich isotherms were used for fitting the experimental data in adsorption studies to understand the extent and degree of favorability of adsorption. In the present case, adsorption of methyl orange was found to fit the Freundlich isotherms better than the Langmuir isotherm for the specific type of adsorbent used. The two isotherms depend on temperature and they have two constants each in their general form given respectively by equations (1) and (2), indicating

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{1}$$

Where C<sub>e</sub> (mg/L) and q<sub>e</sub> (mg/g) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium, and Q<sub>m</sub> (mg/g) corresponds to the maximum adsorption capacity of the adsorbent where as K<sub>L</sub> (L/mg) corresponds to the equilibrium adsorption constant of the Langmuir isotherm.

$$q_e = K_F C_e^{1/n} \tag{2}$$

Where, ‘K<sub>F</sub>’ is the Freundlich constant [(mg/g).(mg/L)<sup>-n</sup>] related to the bonding energy, and n is the heterogeneity factor (exponent). Here, ‘n’ is a measure of the deviation from linearity of the adsorption and indicates the degree of non-linearity between the solution concentration and the adsorption rate. A power-law model curve fit to the data of q<sub>e</sub> versus C<sub>e</sub> could yield the values of K<sub>F</sub> and n.

Both the isotherms depend upon temperature (T). The Freundlich constant, n should have values lying in the range of 1 to 10 for classification as favorable adsorption. The constants are used to estimate the enthalpy of adsorption (vasnath et al. 2005). From the enthalpy of adsorption, the spontaneity (Rafatullah et al. 2010) and nature of adsorption as to whether it is exothermic or endothermic is predicted (Muquing et al. 2009). A smaller value of (1/n) indicates a stronger bond between adsorbate and adsorbent while a higher value for K indicates rate of adsorbate removal is high (Gupta et al 2004). Hence it should be noted that the Isotherm constants are important in understanding the adsorption mechanism and their subsequent application for prediction of some important design parameters. They are dependent on temperature since temperature is an important parameter in estimating the thermodynamic parameters. The trend observed in the experimental data is very close to the Freundlich isotherm but it is deviating considerably from the Langmuir isotherm. This indicates that the adsorption process is of multi-layer type with some interaction among the adsorbed molecules. The evaluated model parameters for both Langmuir and Freundlich adsorption isotherms are presented in Table 3.

**Table: 3**

Langmuir isotherm		Freundlich isotherm	
Parameter	Value	Parameter	Value
$Q_m$	1.2678	$K_F$	0.01266
$K_L$	0.5222	1/n	0.714
$R^2$	0.9221	$R^2$	0.998

### Thermodynamics of adsorption

The thermodynamic parameters, such as the changes in the Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) of adsorption process are estimated from the following correlations Eq. (4.1) and (4.2). The change in standard free energy ( $\Delta G^\circ$ ) at various temperatures can be estimated as follows.

$$\Delta G^\circ = -RT \ln K_d = -RT \ln \left( \frac{q_e}{C_e} \right) \quad (4.1)$$

The relation among the thermodynamic parameters mentioned above is given by

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4.2)$$

In this study thermodynamic parameters for the adsorption are calculated by plotting Gibb's free energy versus temperature. Then the slope and intercept are used to determine the values of entropy change  $\Delta S^\circ$  and enthalpy change of  $\Delta H^\circ$ . The values of  $\Delta G^\circ$  obtained using Eq. (4.1) at the temperatures 293, 313 and 333 K are -3.8, -5.3 and -7.5 kJ/mol respectively. The values of changes in enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) during the adsorption process determined from the slope and intercept are  $-18.85$  kJ/mol and  $-91.32$  J/mol  $K^{-1}$ . The negative values indicate that the adsorption process considered here is exothermic in nature and hence lower temperatures are favored.

### Conclusion

Zeolites of X-type and A-type were synthesized from fly ash by alkali fusion, followed by hydrothermal treatment. The main crystalline phase of fly ash could be converted to zeolite at suitable treatment conditions. The surface area of zeolite was found to be  $425$   $m^2/g$  and porosity 0.28 and particle size 1.15 mm. The cost of synthesized zeolites was very low as compared to commercial zeolite available in the market as it has been prepared from waste fly ash. The synthesized zeolites used successfully for removal of dyes from aqueous solution. ZX<sub>1</sub> showed better adsorptive property than ZA<sub>1</sub> and fly ash. It is seen that removal of dyes increases from 53% to 72% as the solution pH increases from 2 to 10. The high temperature regeneration was conducted at 540°C for 5 h. which shows removal of dyes over the regenerated zeolites is only 68% where as % removal of methyl orange over the fresh zeolite is 78%. The values of changes in enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) during the adsorption process determined are  $-20.85$  kJ/mol and  $-90.61$  J/mol  $K^{-1}$ . The negative value of  $\Delta G^\circ$  indicates spontaneous nature of adsorption takes place over the adsorbent. For Methyl Orange dye the experimental data exactly fitted the freundlich isotherm than Langmuir isotherm. Value of n was found to be 1.4. The correlation coefficient was found to be 0.998.

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