# Malachite green dye removal from aqueous solution using fly ash based zeolites

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This thesis is submitted to the department of chemical engineering, university of engineering and technology Lahore for the partial fulfillment of the requirement for the master's degree in chemical engineering.

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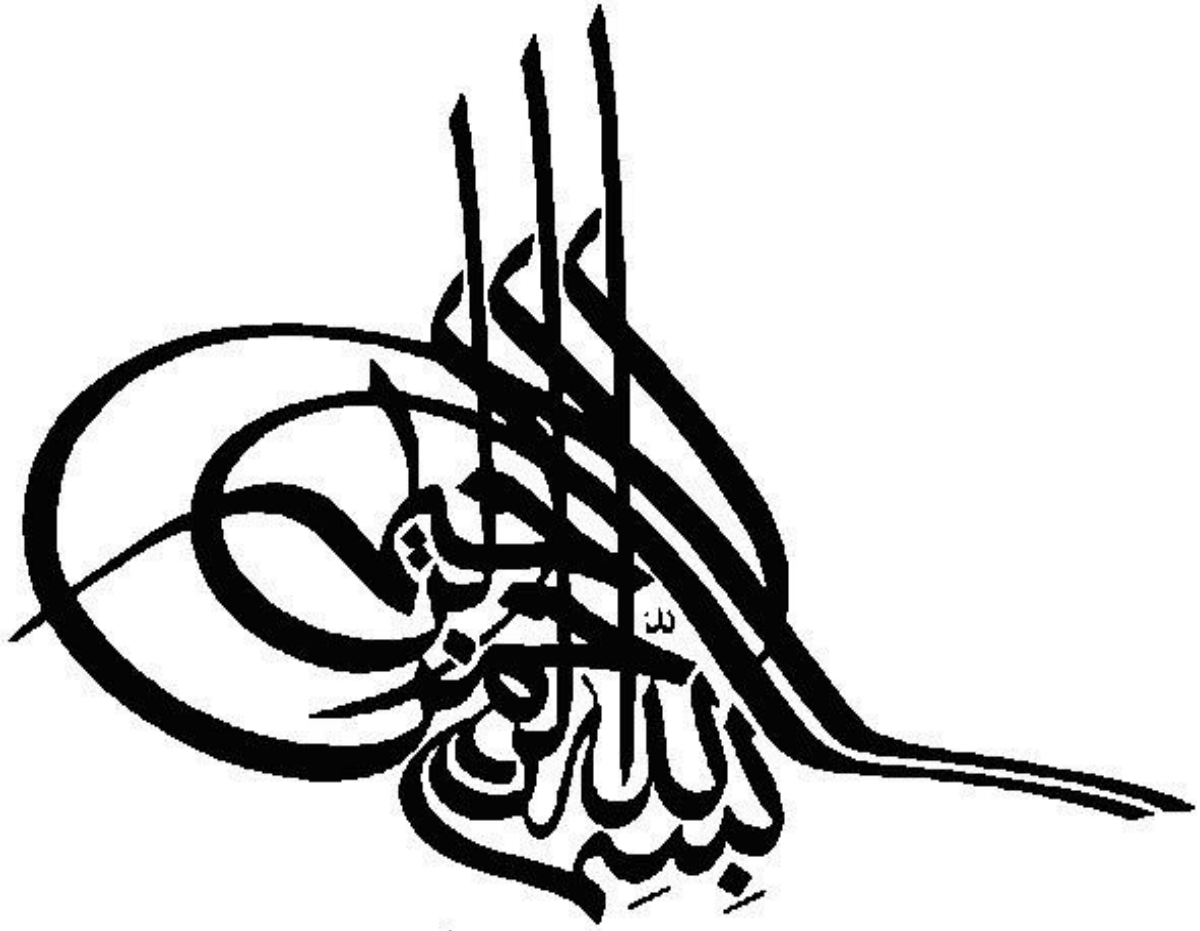
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In the name of ALLAH, the most beneficent and merciful. It is only with his almighty grace who gave me courage to accomplish this task. All my gratitude is for Allah Almighty. I am very grateful to my parents and my research fellows who motivated me and encouraged me at each step. Thanks to Mr. Zubair (Technician Environmental Lab) for supporting me for Analysis**.**

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<div align="right">Saeed ul Hassan</div>

# Abstract

Industries where colors and dyes are being widely used have a liquid colored waste that is directly sent to water streams without implementing any type of operation that can decrease its colored load. Such wastewaters have adverse effects on human being and also disturb agricultural ecosystem through blocking the photosynthesis process. Malachite green dye (MG) has several uses in industries as well as antifungal agent for aquatic system. The intended research utilized the waste of boilers and coal power plant i.e. coal fly ash (CFA) to treat such wastewater contaminated with MG dye through batch adsorption process. CFA was successfully modified to Na-zeolite and Li-zeolite through fusion treatment followed by hydrothermal treatment and characterized using thermal gravimetric analysis (TGA), X-ray diffractometer (XRD) analysis and SEM analysis. Parametric studies were performed by varying adsorbent amount, contact time, initial conc. of dye solution and temperature to estimate the effect on percent removal of MG dye. Kinetic studies were performed using pseudo-first order, pseudo-second order, intra-particle diffusion and elovich model. Elovich model was the best fitted model and the adsorption process was controlled by a diffusion layer inside the particles. Adsorption isotherm was also analyzed by applying Langmuir isotherms model and Freundlich isotherm model. Freundlich isotherms model well explained the adsorption system that was backed-up by elovich model explaining the adsorption was happening in multi-layers. Thermodynamic parameters were also taken in consideration and evaluated that covers Gibbs free energy ($\Delta G^0$), enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$).

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# CHAPTER #1

# INTRODUCTION

# 1. Introduction & literature survey

Wastewater discharge from textile, leather tanning, food technology, paper production and hair coloring industries contain some fractions of dyes [1]. These wastewater streams are discharged into open environment without any treatment [2]. It has been estimated that dyes are of 10000 types which are being used with the annual production of $7*10^5$ tons. The amount of discharged dyes-into ecosystem especially through wastewater is about 200 tons [3]. Such wastewater streams are being used as water source for agricultural products and aquatic system. If these contaminated food ingredients used by human beings then it results in carcinogenic, mutagenic, teratogenic, respiratory toxicity and many more effects. So, it's compulsory to treat such wastewaters before disposing in canals and rivers [4].

Dyes can be classified in terms of chemical structure, color and application method. There are several classes of dyes that are in-use now-a-days. These are acidic, basic, azo, anionic, cationic, nitro, direct, disperse and many more [5]. Malachite green dye is synthetic cationic dye that is used in textile, leather and ceramic industries. It is also used as antifungal, anti-parasitical, and anathematic agent for aquatic ecosystem [6]. Besides its uses, it has hostile effects on human beings and agricultural systems. By some means, when MG mixes with food trail, it ends with the effects on immune system, reproductive system and carcinogenic properties [7]. To treat such dye loaded wastewater, different techniques including chemical coagulation, sorption, electrochemical oxidation, solvent extraction, photo catalytic degradation, bioremediation and adsorption were reported [8]. Among all these techniques, adsorption is the most proficient, simple, time saving and economical technique to decrease the load of dyes from wastewaters [9]. Different types of adsorbents like activated carbon, natural zeolite, raw coal fly ash and functionalized carbon nano-tubes have been commonly used for adsorption of dyes [10]. Most of the adsorbents are modified

from other raw materials. Some adsorbents required simple modifications and some desired complex processes to result projected adsorbents. Zeolites are abundantly available as adsorbent in form of synthetic zeolite and mineral zeolite [2]. In presented study, synthetic zeolites were used for the adsorption purposes. The use of coal in industries produces coal ash that is about 5% of total coal being used. This ash is of two types i.e. fly ash and bottom ash [11]. The handling and wastage of such ash contents is an immense problem for industries to meet the environmental standards. A number of studies have reported to reuse these ash contents to make some other useful products in different aspects. Reported studies explain the different ways to treat the coal fly ash (CFA) to useful materials. Wei Ming Soh et al. [12] investigated the vertical thermal flame (VTF) process to produce the cenosphere by using CFA. Cenospheres are inert, low density, thin walled hollow spheres having large contents of silica and alumina. Yand Luo et al. [13] reported the development of sintered foam ceramic using CFA. CFA was pretreated for the purpose of coating of CFA particles with hydroxy-sodalite crystals using alkali activation. During sintering process at $1200^0C$, CFA coated particles achieved a self-foamed shape that was further processed to sintered foam ceramic. H. Agusta et al. [11] work represented the use of CFA where it was used for the manufacturing of granules at pilot plant of Surfactant and Bioenergy research Center (SBRCC) LPPM IPB . Songxiong Zhong et al. [14] reported the preparation and characterization of modified CFA by soaking raw CFA with sulfuric acid. A number of studies also reported where CFA was used as raw material for the manufacturing of zeolites that were used for adsorption purposes of dyes and heavy metals from wastewater. The synthesis techniques are different i.e. using microwave and ultrasound energies [15], zeolite based geo-polymer for the adsorption of Cd (II) [16], by microwave hydrothermal treatment with pulverization process [17] and many more.

Sodium and lithium zeolites were used to investigate the removal of MG dye from aqueous solution. These zeolites were manufactured from boilers waste i.e. Coal Fly Ash (CFA) by alkali fusion treatment at $600^0$c. It is the dual utilization of two wastes into environmental healthy results. CFA is the waste of boiler that is driven out of the boiler with the flue gases. Zeolites are rich in hydrated alumino silicates with framework structures having a network of internally connected tunnels and cages [18]. With such a micro porous structure and a large scale of substitution of other groups approaches it to several excellent properties like adsorption and ion exchange [17]. Such zeolites are in the form of powdered small size particles to enhance the surface area for capturing the dye molecules.

## 1.1 Research objective

The current research work investigated the adsorption of toxic cationic malachite green (MG) dye by using synthetic zeolites i.e. sodium zeolite and lithium zeolite from coal fly ash (CFA). Both adsorbents were separately used for adsorption purposes to create a comparison for best promising adsorption results. The final adsorbents were well characterized using analytical techniques including scanning electron microscopy imaging (SEM), x-ray diffraction analysis (XRD) and thermal gravimetric analysis (TGA). The influence of different substantial parameters that includes adsorbent dosage, initial concentration of MG dye, time for adsorption and temperature were well examined and adjusted using the batch experimentation. It further preceded by making a comparison between both adsorbents and the final results were explicated through well-known adsorption isotherms and kinetic models.
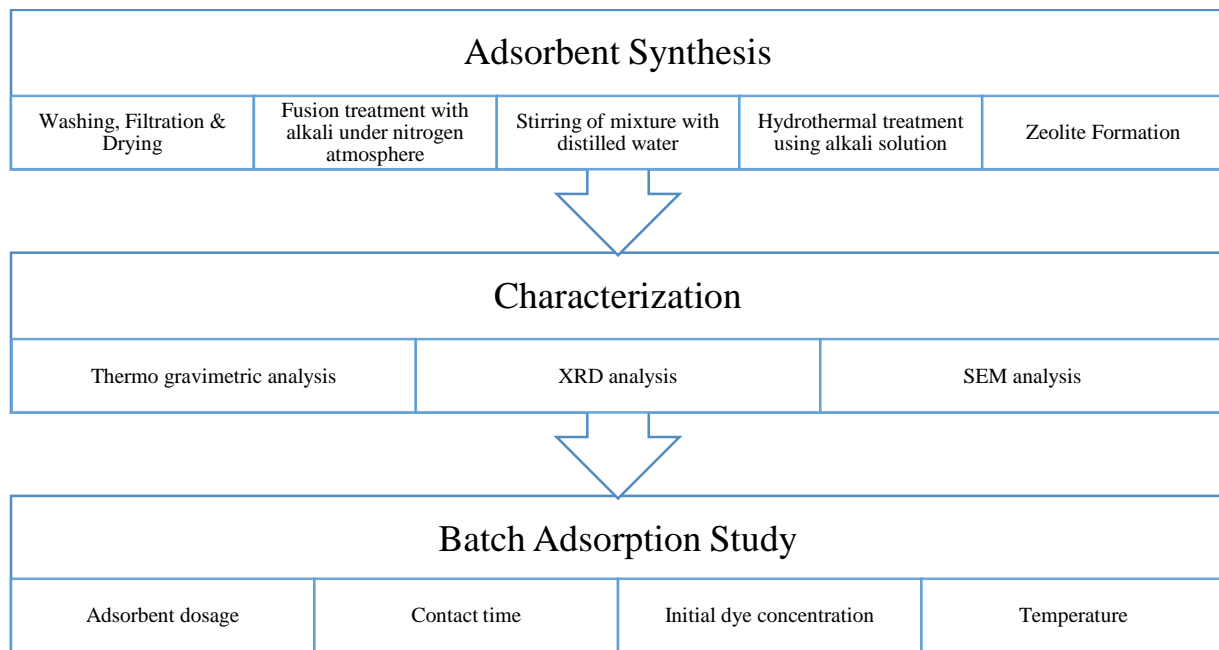
# CHAPTER # 2
# RESEARCH METHODOLOGY

## 2. Materials and methods

## 2.1 Materials

Coal Fly Ash (CFA) was attained from ICI Pakistan Limited. Lithium hydroxide (purity: 56.3%) and Sodium hydroxide (purity: 99.9%) were purchased from Xilong Chemicals China and Sigma-Aldrich Germany, respectively. Other chemicals including ammonium acetate (purity: 99.9%), sodium aluminate (purity: 99.9%), sodium acetate (purity: 99.9%) and methanol (purity: 99.9%) were procured from Sigma-Aldrich United States, Fisher Chemicals United States and Daejung Chemicals South Korea, respectively. Malachite green (MG) dye was purchased from China National Chemicals, Shijiazuang Branch. All chemicals used in this research work were of analytical reagent grade and used without further purification.

## 2.2 Research methodology

| Adsorbent Synthesis | | | | |
|---|---|---|---|---|
| Washing, Filtration & Drying | Fusion treatment with alkali under nitrogen atmosphere | Stirring of mixture with distilled water | Hydrothermal treatment using alkali solution | Zeolite Formation |

| Characterization | | |
|---|---|---|
| Thermo gravimetric analysis | XRD analysis | SEM analysis |

| Batch Adsorption Study | | | |
|---|---|---|---|
| Adsorbent dosage | Contact time | Initial dye concentration | Temperature |

## 2.3 Synthesis of adsorbent

In this study, raw CFA was successfully modified to zeolites by applying fusion method followed by hydrothermal treatment [18]. Raw CFA was sieved using (80 mesh) screen to separate from large particles and to obtain uniform distribution of fine CFA particles [20]. The CFA was washed with distilled water and dried at 105 $^0$C followed by heating at 870 $^0$C for 2h to remove combustible sulfur and un-burnt carbon impurities [21]. After cooling for 30 min at room temperature, CFA-C was mixed separately with sodium hydroxide (NaOH) and lithium hydroxide (LiOH) with 1:1.2 ratios in a grinder. Both samples were fused in an electric furnace at 550 $^0$C for 2 h. The resulting mixtures were cooled and converted into fine particles in grinder [22]. The material was mixed with water in 1:7 ratio (fussed material: water) and allowed to shake for 7 h for aging purpose. During aging process, the mixture was mixed with the sodium aluminate solution for 3h to adjust the Si/Al molar ratio in synthesized zeolites [23]. The resulting mixture was crystallized in oven at 100 $^0$C for 2 h. Synthesized zeolites obtained in the form of crystals were filtered, washed and dehydrated at 70 $^0$C for 15h and named as Na-Zeolite and Li-Zeolite. Both zeolites were saved in zipped plastic bags for adsorption studies.

## 2.4 Material Characterization

Morphological changes of raw CFA from CFA-C to Na-zeolite and Li-zeolite was analyzed using Scanning Electron Microscope (Zeiss EVO 50 Uk), that creates images using secondary electron scattered of the sample surface at very small scale. TGA analysis was performed using Mettler Toledo (TGA/SDTA851-2 Thermo Gravimetric Analyzer, Canada). Heating temperature was applied from 25-900$^0$C having heating rate of 10$^0$C/min where $N_2$ was used as purge gas with the rate of 30mL/min. XRD analysis was attained using PAN analytical Xpert (Powder

Diffractometer, Netherlands) with Cu-Xray generator. The operating speed was of $2^0$/min ranging $10^0$-$80^0$.

## 2.5 Batch adsorption studies

Batch mode adsorption studies were carried out to investigate and optimize the effect of various parameters on the removal of MG dye from aqueous solution using synthetic zeolites i.e. Na-zeolite and Li-zeolite. The conc. of stock solution prepared was 1000 mg/L. This stock solution was used for experiments by making the appropriate dilutions. The parametric; studies are shown in table 1;

Table 1

Batch adsorption study parameters

| Adsorbent Dose (mg) | | | Contact time (min) | | Initial Concentration (mg/L) | | Temperature ($^0$C) | |
|---|---|---|---|---|---|---|---|---|
| CFA-C | Na-zeolite | Li-zeolite | Na-zeolite | Li-zeolite | Na-zeolite | Li-zeolite | Na-zeolite | Li-zeolite |
| 25-300 | 25-400 | 25-400 | 180 | | 100 | | 25 | |
| NA | 50 | | 1-400 | 1-400 | 100 | | 25 | |
| NA | 50 | | 250 | | 10-400 | 10-400 | 20-40 | 20-40 |

All batch adsorption studies were conducted at a constant speed of 150 rpm in orbital shaker and filtered using Whatman Filter Paper grade 41 after experiment completion.

## 2.6 Analysis

Treatment efficiency of MG dye was evaluated using OPTIMA SP-300 UV-Vis Spectrometer at wavelength ($\lambda_{max}$) of 617 nm[24]. The pH of adsorbents and MG dye solution was measured using

Hanna precision pH meter (pH 213). The adsorbed amount of MG dye by Na-zeolite and Li-zeolite was calculated in the form of adsorbent uptake by equation[25],

$$q_e = \frac{v(c_i - c_f)}{w} \tag{1}$$

Where $q_e$ is the amount of dye at equilibrium (mg/g), $v$ is the volume of dye solution (L), $c_i$ is the initial concentration of dye solution (mg/L), $c_f$ is final concentration of dye solution at equilibrium and $w$ stands for amount of adsorbent (g). The percentage removal of MG dye was also considered as[26],

$$\% \ Removal = 100 * \left(\frac{c_i - c_f}{c_i}\right) \tag{2}$$

Furthermore, Kinetic and isotherm studies were also performed to explain the adsorption system in detail. For kinetic adsorption studies, pseudo first order, pseudo second order, intra-particle diffusion model and elovich model were considered. Isotherm studies were explained by Langmuir isotherm model and Freundlich isotherm model. Effect of temperature on thermodynamics of the adsorption system was also analyzed.

# CHAPTER # 3

# RESULTS & DISCUSSIONS

## 3. Results and discussions

## 3.1 Adsorbent characterization

### 3.1.1 Thermo gravimetric analysis

TGA was performed for CFA-C, Na-zeolite and Li-zeolite to understand the thermal properties of these adsorbents at elevated temperatures. TGA analysis was performed on Mettler Toledo TGA/SDTA851eThermo gravimetric analyzer. 10 mg of sample was taken in alumina pan and heated from 25-900 $^0$C because there was not a significant weight loss at high temperature with heating rate of 10 $^0$C/min using $N_2$ as purge gas with amount of about 30 mL/min [27]. Thermo gravimetric curves (fig.1) for CFA-C, CFA-Na and CFA-Li almost have similar temperature ranges for weight loss [28].

Fig.1 (a) shows the TGA analysis curves for CFA-C, CFA-Na and CFA-Li. For CFA-C, the change in mass is 12 percent. The first weight loss of about 2% occurs in the range of 60-110 $^0$C dehydration of physically adsorbed water contents during the washing step of CFA-C [29]. Although the CFA-C was dried and saved in zipped bags but it is possible that CFA-C had adsorb some moisture from atmosphere during handling and transportation that is of very little quantity so at this stage the weight loss is very small [30]. CFA-C has less weight loss at this stage comparing with treated samples of Na-zeolite and Li-zeolite because it contains physically adsorbed water contents. Modified CFA samples contain physically and chemically bound moisture contents results in more weight loss [27]. Next weight loss of 8% attributed at about 440-630 $^0$C that might occur degradation of un-burnt coal in raw CFA-C [31]. The final weight loss which is 3% arises in the range of 680-720 $^0$C due to the presence of some volatile metals [32]. Weight loss for Na-zeolite is 23 % as shown in fig.1 (a) that accomplish in three steps. Weight loss

at 60-180 $^0$C is due to the removal of surface moisture content and bound moisture that removes about 20% weight of initial sample. For Li-zeolite, the total weight loss is approximately 57% that shows it has more moisture contents at its surface and in capillaries (bound moisture) that were removed in temperature range of 40-180 $^0$C which is about 55%. There was negligible weight loss for both modified samples comparing with CFA-C because during fusion and hydrothermal treatment, most of the carbon and volatile metals were removed. Fig.1 (b) shows the DTGA analysis for all three samples i.e. CFA-C, Na-zeolite and Li-zeolite. For all samples the peaks are almost of same trend except for Li-zeolite where the major weight loss occurs about 36% at first peak but the remaining trend is similar with other two samples of raw CFA and Na-zeolite.
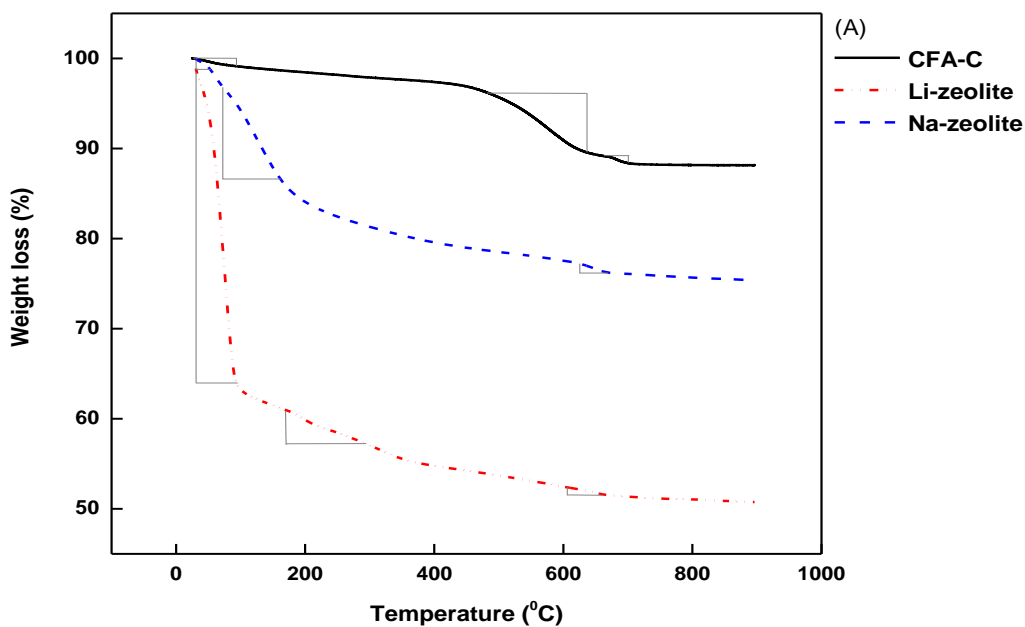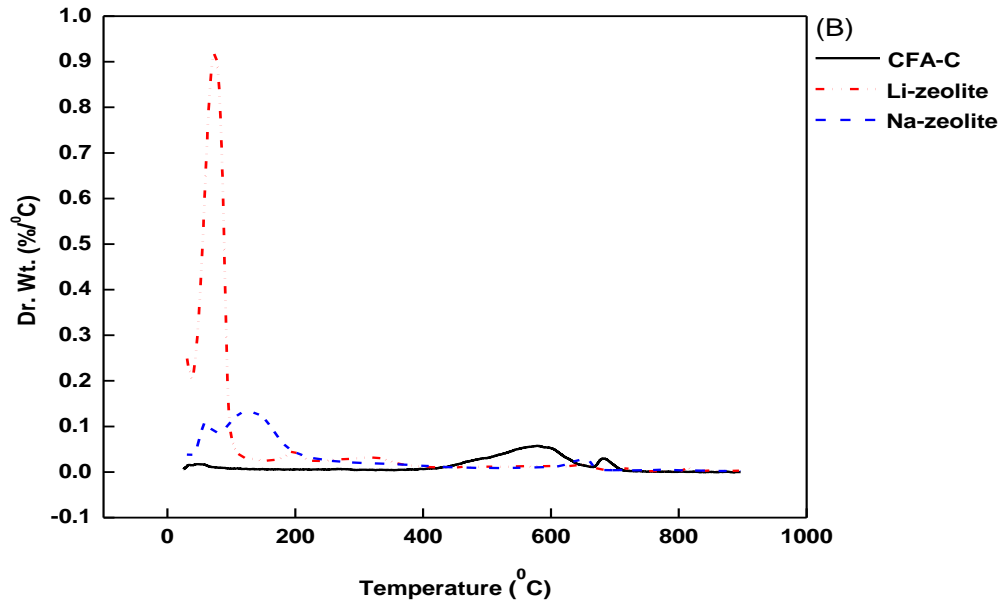
Fig.1-(A) TGA analysis (B) DTGA analysis for CFA-C, Na-zeolite and Li-zeolite

## 3.1.2 XRD analysis

XRD is the basic tool for the description of crystallinity. XRD analysis for raw CFA, Na-zeolite and Li-zeolite was performed with PAN analytical X'pert Powder Diffractometer, Netherlands with Cu X-ray generator. XRD patterns are shown in fig.2 for raw CFA, Na-zeolite and Li-zeolite. The major constituents in raw CFA are $SiO_2$, $Al_2O_3$, $SO_3$, mulite, magnetite and hematite. $SiO_2$ and $Al_2O_3$ are considered as the main components in raw CFA. As previously reported in literature, the key factor of raw CFA is the ratio of $SiO_2/Al_2O_3$ [ref], in the presented raw CFA it is about 2.1. The other constituents that are hematite, mulite and magnetite are the responsible for the presence of crystalline phases in raw CFA.
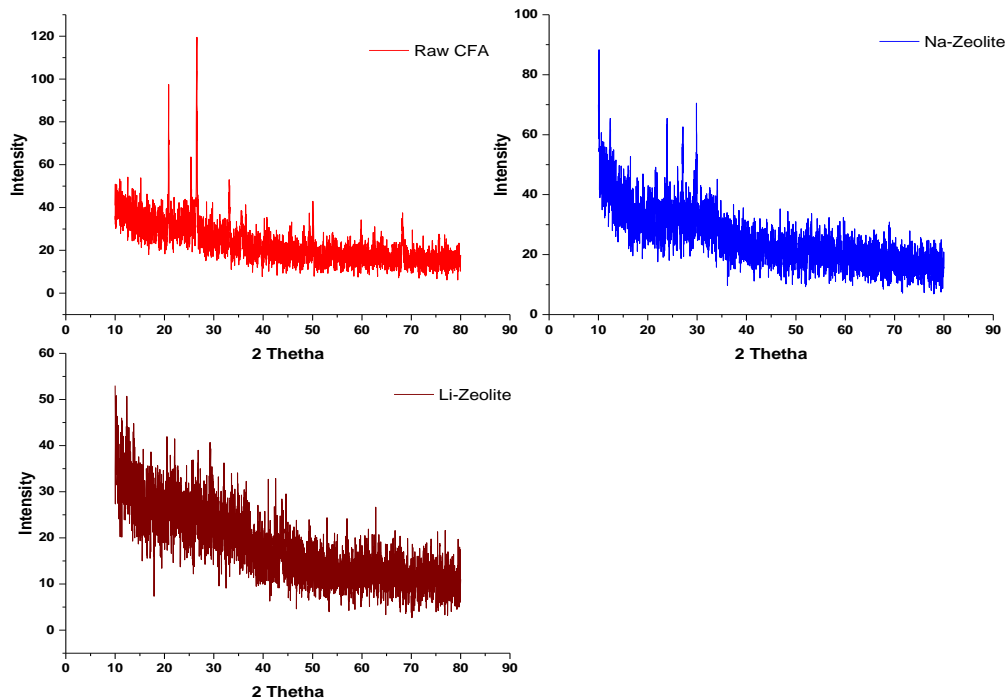
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Fig.2- XRD patterns for raw CFA, Na-zeolite and Li-zeolite

The key components like $SiO_2$ and $Al_2O_3$ in the synthesized zeolites from raw CFA have changed their ratios. During the synthesis process of zeolites the Si replaced with Al. In case of Na-zeolite, hematite, magnetite and mulite have been disappeared after the implementation of fusion followed by hydrothermal treatment of raw CFA for the formation of Na-zeolite. Quartz also accepts the effect of this treatment that results in the form of lowering its amount but not completely disappeared. In Na-zeolite XRD pattern, only quartz has the characteristic peak verifying that Na-zeolite has an amorphous arrangement. XRD pattern has ambiguous shape for Li-zeolite but has almost similar assessment for key components i.e. $SiO_2$ and $Al_2O_3$. Li-zeolite's XRD pattern shows that it has some characteristic peak of hematite and quartz that confirms its amorphous shape.

### 3.1.3 SEM analysis

Morphological changes in raw CFA during the synthesis of Na/Li-zeolites were analysed using Scanning Electron Microscope Zeiss EVO 50,UK, are shown on figure 3. Fig.3(A), shows the raw CFA particles have dense,rough and non-uniformed surface with crystallinity due to the presence of Si & Al components as predicted in XRD analysis. The final images show reasonable changes after the fusion followed by hydrothermal treatment for the synthesis of Na/Li-zeolite. In the morphology of syntesized zeolites i.e. Na/Li zeolite, the presence of crystals has been predicted which is not present in raw CFA.

The surfaces of modified CFA are entirely coated with hydroxyl compounds used during zeolite synthesis process. The images are shown in fig3,(A) for CFA-C, (B) for Na-zeolite and (C) for Li-zeolite.
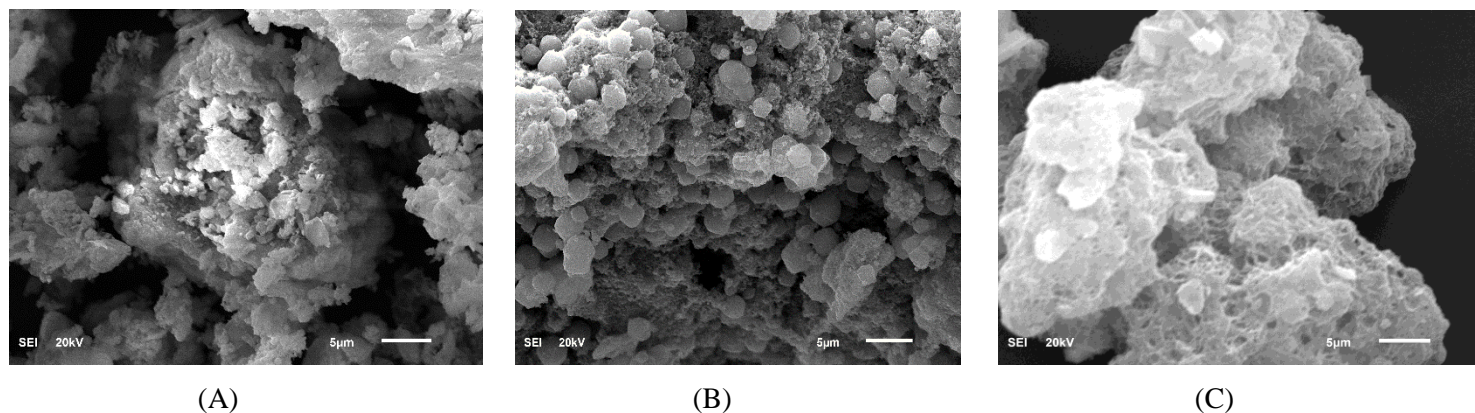


(A)  (B)  (C)

Fig.3-Morphological Analysis (A) raw CFA, (B) Na-zeolite (C) Li-zeolite

## 3.2    Adsorption studies

### 3.2.1  Effect of adsorbent dosage

Effect of adsorbent amount was studied by taking the amounts of adsorbents separately from 25 to 400 mg for the deduction of MG dye molecules from aqueous solution having the initial conc. 100 mg/L for 3 h of shaking in water bath shaker. Raw CFA, Na-Zeolite and Li-Zeolite were used to investigate the removal % of MG dye. It can be seen from Fig.4, with the increase in the amount of adsorbent, percent removal of MG dye from aqueous solution also increases.

Gradually, equilibrium stage comes where there is no removal of MG dye molecules is occurring because there is approximately no dye molecule left at later stages for the higher amounts of adsorbents. At 25 mg of dose, raw CFA removes only 51% MG from aqueous solution whereas Li-Zeolite and Na-Zeolite remove 69% and 92% at the same adsorbent dose, respectively. At initial stages for CFA and Na/Li-zeolites when adsorbents amount was less, there were not enough active spots for the adsorption of MG dye molecules [26]. On the other hand, at higher amount of adsorbents, the active sights were still there for absorbing the dye molecules but no MG dye molecule left behind to get adsorbed by adsorbents [33].
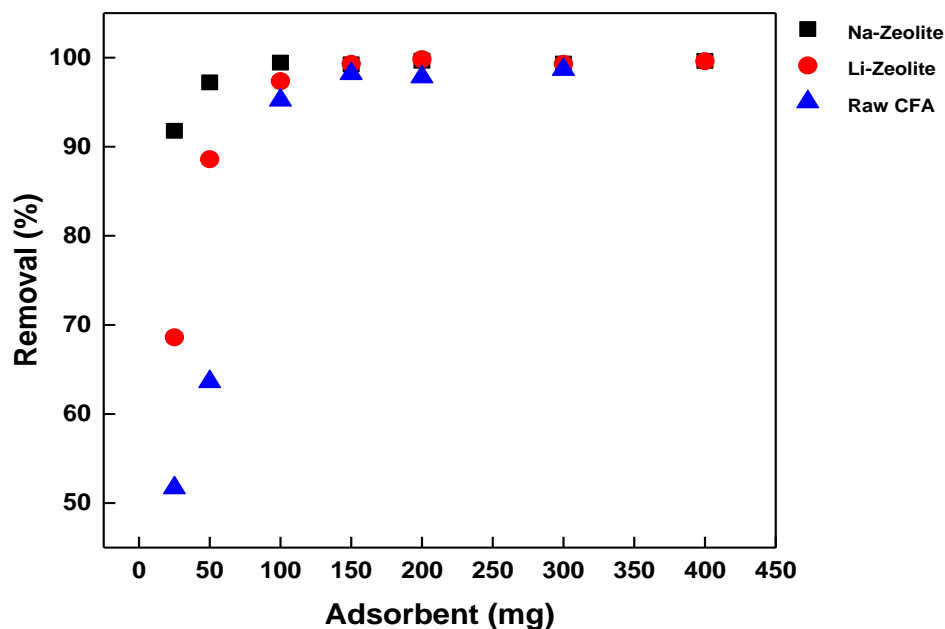
Fig.4-Effect of Adsorbent dose on the percentage removal of MG dye

Previously reported study for the deduction of malachite green dye with water soluble melamine/maleic anhydride sorbent showed that the 60 mg was significant dosage that has 97 % removal of MG dye from aqueous solution [34]. Comparing the percentage removal for Na/Li-zeolites with each other, Na-zeolite is showing the better results comparing with Li-zeolite. The reason behind this variation is the intermolecular interaction forces which are higher for the Na-zeolite for exchanging the cation MG dye than that of Li-zeolite[35]. The percentage removal for raw CFA comparing with synthetic zeolites is much lesser because raw CFA was not treated with alkali solution that increases its ability to exchange cation of MG dye that's why further study was done only by considering the Na-zeolite and Li-zeolite. The remaining study was done by fixing the amount of adsorbent of 50 mg because Na-Zeolite and Li-Zeolite is showing satisfactory results. From literature natural zeolite was investigated for the removal similar dye with a fixed dosage of 30 mg that have the capability to remove about 93% of MG dye [2].

### 3.2.2  Effect of contact time

Optimum adsorption time for the adsorption of MG dye was evaluated via different time of 1 to 400 min with optimized amount of 50 mg of Na-zeolite and Li-zeolite with initial conc. of 100 mg/L of MG dye solution. With the passage of time, the removal percent of MG dye from aqueous solution is going on increasing because there is more settling time for dye molecules to settle down on adsorbent's available active sites but at later time intervals the further removal was approximately stopped and equilibrium achieved because all the active sites have been occupied by MG dye molecules and there was no more available space for remaining dye molecules [36].Initially, the percentage removal for Na-Zeolite is much higher than Li-Zeolite. The maximum equilibrium adsorption for Na-Zeolite is also higher than that of Li-Zeolite because Na-zeolite has more attraction forces for cation of MG dye than Li-zeolite that enhanced the removal efficiency of Na-zeolite for MG dye [37]. From fig.5, the optimum adsorption time for each adsorbent is250 min for the evaluation of other parameter because this time limit is sufficient to adsorb enough amount of MG dye. Removal of MG dye with organically modified clay as adsorbent was also reported previously where optimum adsorption time was about 240 min when equilibrium was achieved [38].
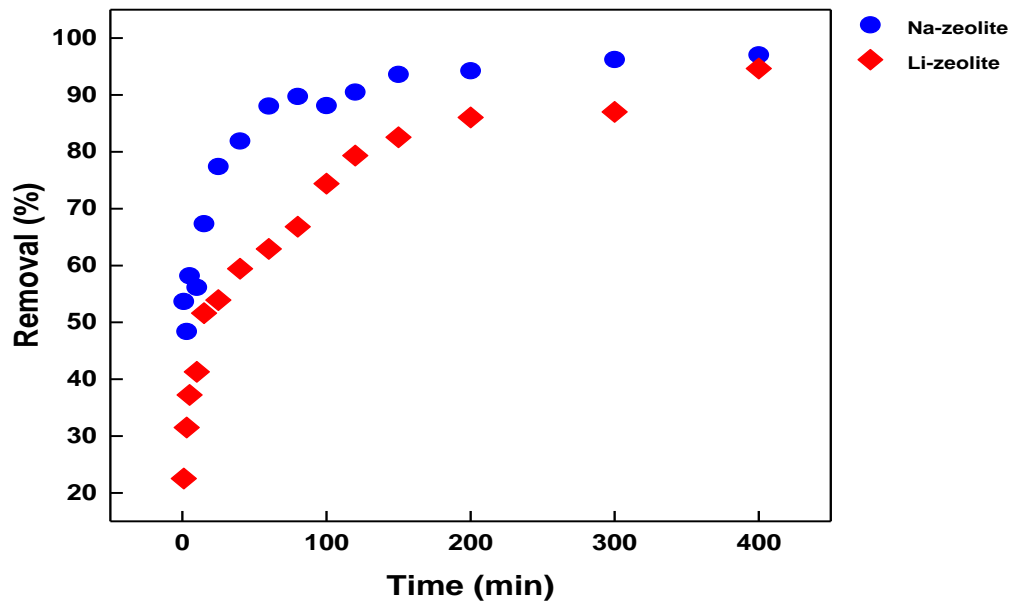
Fig.5- Effect of Contact Time on the percentage removal of MG dye

## 3.2.3 Effect of initial MG dye concentration and temperature

The fixed amount of adsorbent enables to adsorb only the suitable amount of dye molecules [39]. So it is essential to investigate the initial conc. of dye solution. The effect of initial conc. of MG dye solution was studied simultaneously with the diff. temperatures. The initial MG dye concentration varies from 10-400 mg/L with the temperature variation of 20 $^0$C, 30 $^0$C and 40 $^0$C. Fig. 6 shows the percentage removal with initial dye concentration having different operation temperatures. The graphical sketch explains that at initial stages the percentage removal of MG dye by both Na/Li-zeolite is high. This is due to the more availability of unoccupied spots of adsorbents. When those active sites were occupied by dye molecules, the percentage removal rate of MG dye became lower because there is no more active site available for more dye molecules [40]. At that stage further treatment offers no removal of dye molecules by adsorbents and equilibrium achieved [41]. The temperature is also a rate controlling aspect while adsorption is

happening of dyes by adsorbent. So temperature effect also included while investigating the initial dye concentration study. Optimum initial dye concentration should be 100 mg/L because at that stage the percentage removal of dye is quite significant comparing with higher concentration i.e. 400 mg/L where there are still remaining dye molecules that can't be adsorbed by adsorbents. Fig.6 shows that with the rise in temperature the removal % also increase that demonstrate that the process is endothermic in nature.
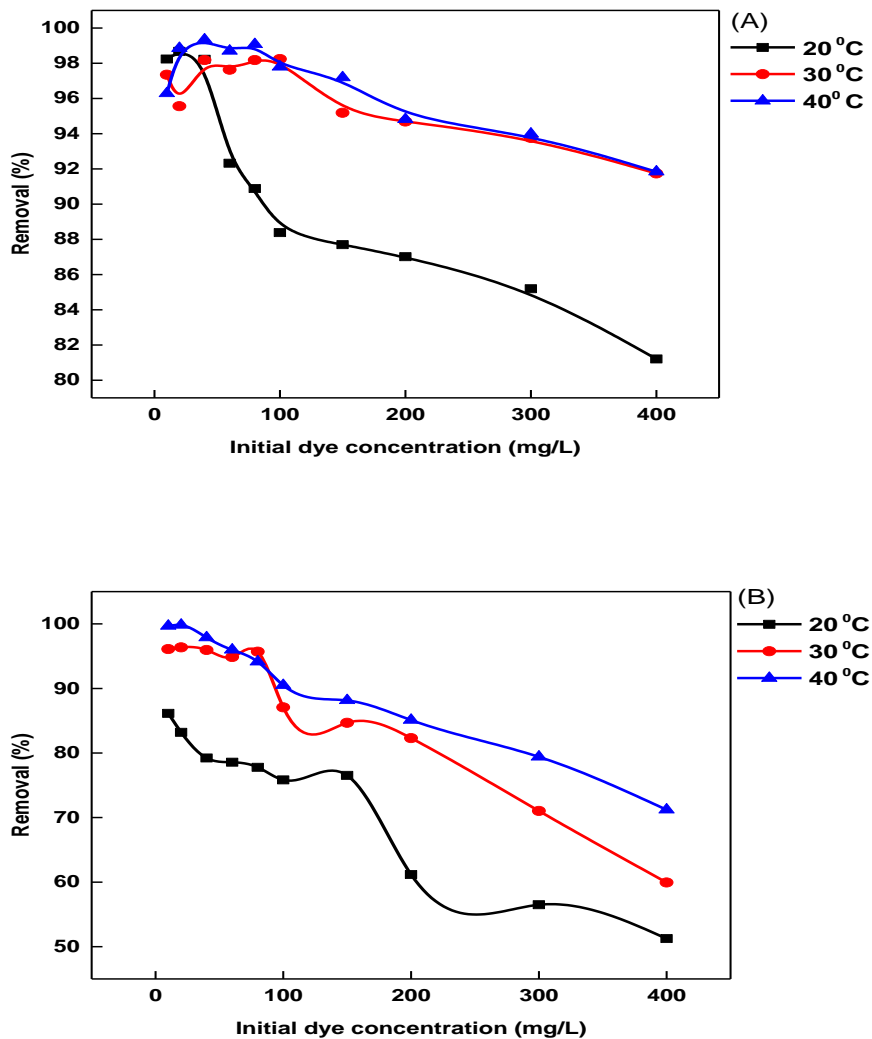
Fig.6- Initial Dye concentration with temperature effects for (A) Na-zeolite & (B) Li-zeolite

### 3.2.4 Kinetic studies

Adsorption process of MG dye on Na-zeolite and Li-zeolite was investigated by considering the two simple kinetic models, which are pseudo first order and pseud second order models. The mathematical nonlinear expression for pseudo first order model is [42]:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

where $q_e$ and $q_t$ are the amount of MG dye adsorbed (mg/g) at equilibrium and at time $t$ (min) respectively, and $k_1$ is the rate constant (min$^{-1}$) of adsorption for pseudo first order model. The nonlinear expression for pseudo second order model is[42]:

$$q_t = \frac{q_e^2 k_2 t}{1 - k_2 q_e t} \qquad (4)$$

where $k_2$ is rate constant (g/mg. min) for pseudo-second order model. The nonlinear models were analyzed using OriginPro 9.1 software.

The graphical expressions for both kinetic models are shown in fig.7, which explained that experimental data was not well explained by both models i.e. pseudo first order & pseudo second order [43].So, Intra-particle diffusion model and Elovich model for further description of adsorption were also considered.
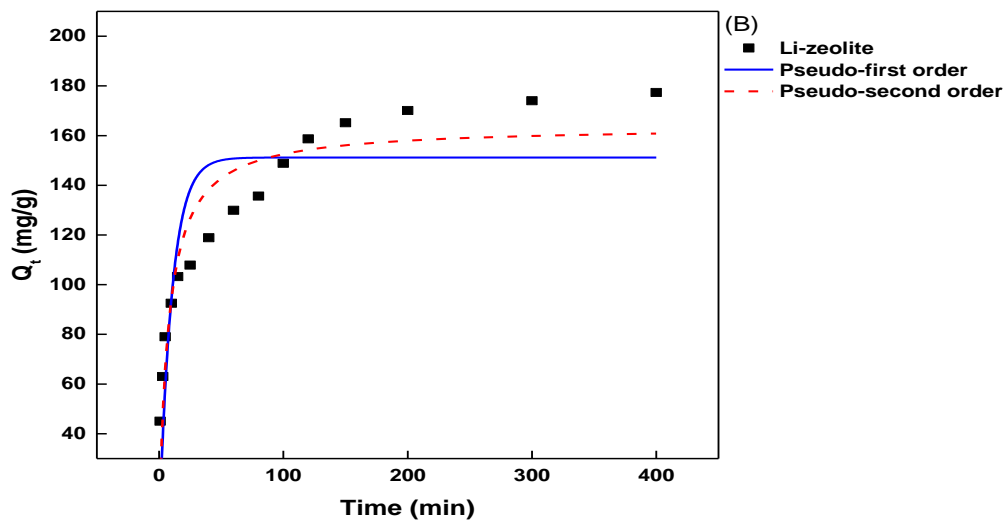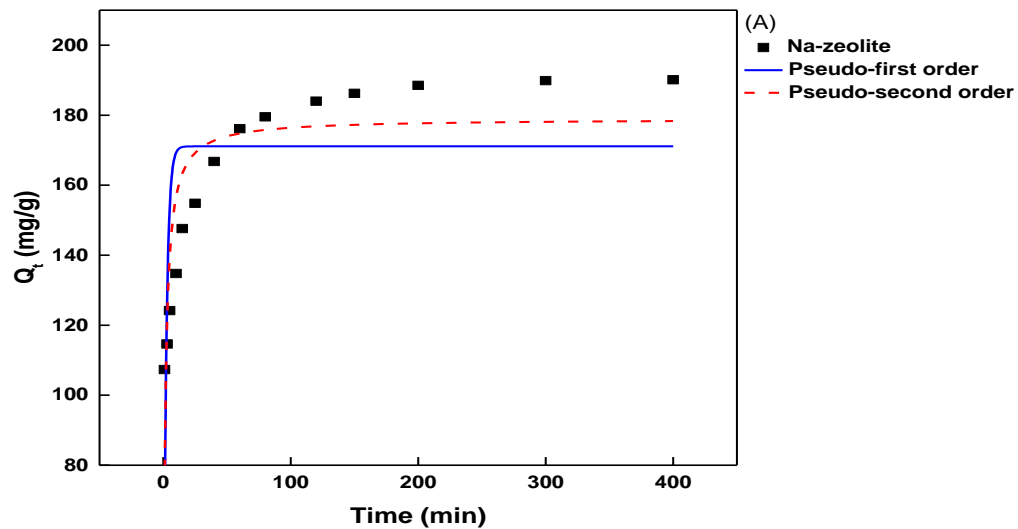
Fig.7- Comparison for Pseudo first and Pseudo second order model for (A) Na-zeolite & (B) Li-zeolite

Weber and Morris model explains rate and adsorption mechanism that is ruled by means of three successive steps: (i) the outside diffusion of the adsorbate via boundary layer on

adsorbent surface, (ii) intra-particle diffusion and (iii) the adsorption of the adsorbate at inner energetic spots[44]. This model is presented is as follows:

$$q = k_{ip}t^{1/2} + C \qquad\qquad (5)$$

where $q$ (mg/g) is the quantity of MG adsorbed on Na/Li zeolite at any time t (min), $k_{ip}$ (g.min$^{0.5}$) is the intra-particle diffusion constant and $C$ is intercept. Plots between $Q_t$ vs. $t^{0.5}$ for both adsorbents are shown in fig.8. Three different adsorption stages were shown in the plots for both zeolites. First stage with higher slope for both adsorbents explains the film diffusion or external surface diffusion that occurred within first 5 min. The second stage is the intraparticle diffusion stage with the decrease in slope that shows that most of the active sites on the surface of adsorbents were occupied initially in external diffusion process and now the dye molecules are penetrating in the interstitial spaces of zeolites.
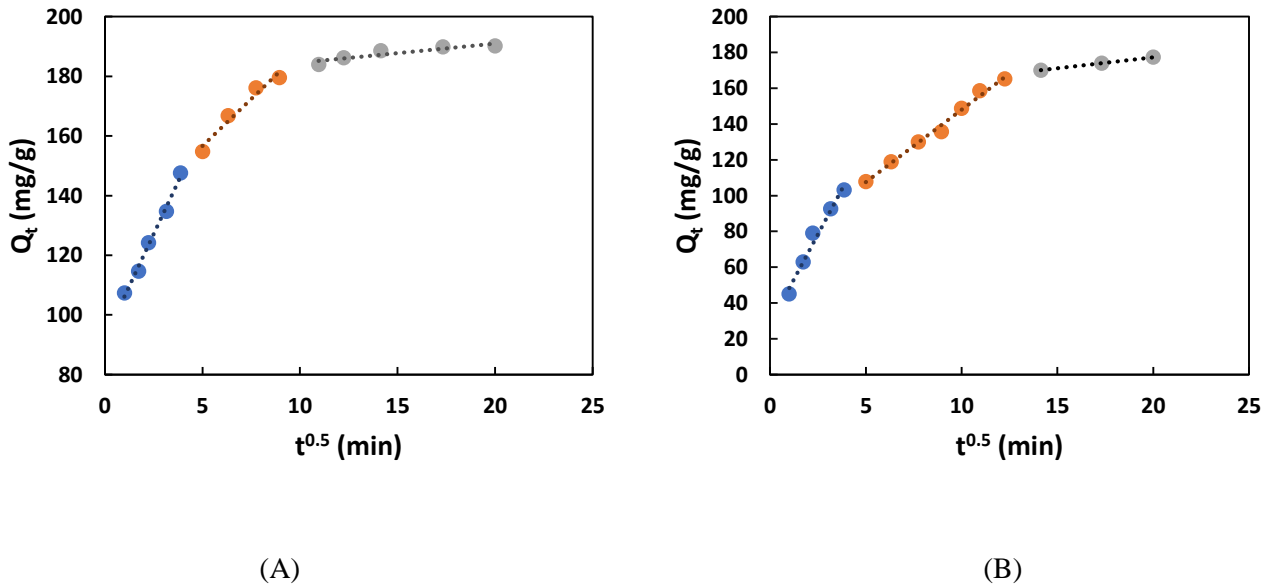


(A)  (B)

Fig.8- Intra-Particle Diffusion Model for (A) Na-zeolite & (B) Li-zeolite

The third stage shows the equilibrium of adsorption process with smallest slope. This shows that now there is not enough capacity of adsorbent to further adsorb MG dye particles. From both plots, the rate of adsorption was controlled by intra-particle diffusion (second stage) step.

Elovich model was also applied indicating that the sorption is a chemisorption process on the active heterogeneous surfaces of Na/Li-zeolites for the adsorption of MG dye. It is equated as [45]:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad\qquad (6)$$

Where $\alpha$ is the initial adsorption rate (mg/g.min) and $\beta$ is the desorption rate (mg/g). The plot between $q_t$ vs $\ln(t)$ is a straight line where $\alpha$ and $\beta$ are obtained from slope and intercept. From fig.9, it is clear that the values of $\alpha$ for both adsorbents are much higher than $\beta$, that shows that the adsorption process is on dominating side comparing with desorption side or irreversible process.

Making the comparison between pseudo first order, pseudo second order and elovich model, elovich model better describes the adsorption process that shows adsorption is occurring on heterogeneous active surfaces for both CFA based zeolites.
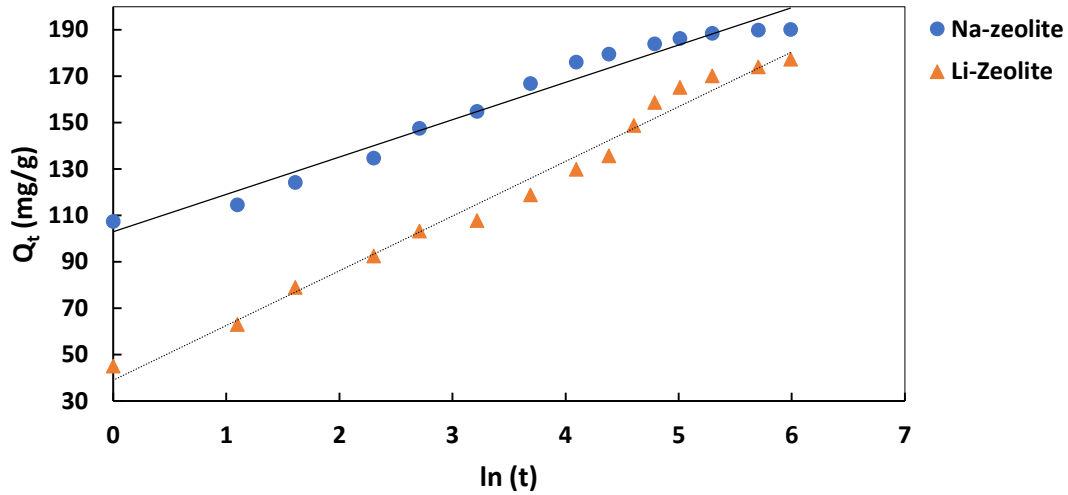
Fig.9- Elovich Model for Na-zeolite and Li-zeolite

### 3.2.5 Adsorption isotherm

The adsorption relationship between adsorbate at equilibrium concentration and the amount adsorbed by the adsorbent is resolved by a number of available adsorption isotherm models. Such isotherms optimize the adsorption process and also give the adsorbent up-take while designing an adsorption system [46]. Adsorption isotherms are characterized by corresponding constants that describe the adsorption phenomena for the respective adsorption isotherm model. Several isotherm models have been practiced to understand adsorption process. Langmuir isotherm model and Freundlich isotherm model were used for explanation of MG dye adsorption on Na-Zeolite and Li-Zeolite.

Langmuir isotherm model is effective only for monolayer adsorption on homogeneous adsorbent surface with limited and specific active places. It also considers that adsorbed molecules of dyes on adsorbent active sites have no interaction between each other [47]. Because of such properties,

further adsorption process stops after saturation point and equilibrium is achieved. The non-linear

mathematical expression of Langmuir isotherm model is:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (7)$$

Where $C_e$ is the conc. of MG dye (mg/l) at equilibrium, $q_e$ is the equilibrium adsorption capacity

(mg/g), $q_m$ is the maximum adsorption capacity (mg/g) and $K_L$ is the Langmuir constant (L/g).

Table 2

Adsorption isotherm model data for the adsorption of MG on Na-Zeolite and Li-Zeolite

| Na-Zeolite | Parameters | 293 /K | 303 /K | 313/K |
|---|---|---|---|---|
| | $Q_m$/ mg.g$^1$ | 1104.84 | 1039.18 | 871.54 |
| Langmuir Model | $K_L$/ L.mg$^{-1}$ | 0.0204 | 0.0647 | 0.1119 |
| | $R^2$ | 0.9481 | 0.9562 | 0.9429 |
| | $K_f$/ mg.g$^{-1}$ (mgL$^{-1}$)$^{-1/n}$ | 51.185 | 99.973 | 129.86 |
| Freundlich Model | N | 1.6675 | 1.7429 | 2.009 |
| | $R^2$ | 0.9501 | 0.9782 | 0.9806 |
| Li-Zeolite | Parameters | 293 /K | 303 /K | 313 /K |
| | $Q_m$/ mg.g$^1$ | 481.48 | 509.33 | 608.61 |
| Langmuir Model | $K_L$/ L.mg$^{-1}$ | 0.0199 | 0.0563 | 0.0673 |
| | $R^2$ | 0.9668 | 0.9453 | 0.8495 |
| | $K_f$/ mg.g$^{-1}$ (mgL$^{-1}$)$^{-1/n}$ | 30.169 | 76.157 | 111.48 |
| Freundlich Model | N | 2.0126 | 2.6702 | 2.8933 |
| | $R^2$ | 0.9675 | 0.9670 | 0.9296 |

Freundlich isotherm model is used to explain that the adsorption takes place on diversified surfaces

of adsorbent [8]. Freundlich isotherm model is:

$$q_e = K_f C_e^{1/n} \qquad (8)$$

where $q_e$ indicates the adsorption capacity (mg/g), $C_e$ represents concentration of adsorbate in solution at stability (ppm), $K_f$(mg.g$^{-1}$(mgL$^{-1}$)$^{-1/n}$) &$n$ are Freundlich constant associated with adsorption capacity and adsorption intensity of adsorbent. The equilibrium saturation capacities of MG dye for each temperature is established in fig.10, showing the applicability for both CFA based zeolites for each isotherm model. If $n>1$, it shows the favorability for the adsorption system that adsorption the multilayer adsorption procedure[48]. Differentiating parameters for both CFA based zeolites on diff. temperatures are presented in table 1 obtained from the graphical sketches in fig.10 between $C_e$ vs. $Q_e$. The high values of relative coefficient for Freundlich model illuminates that the adsorption of MG dye occurs at heterogeneous active surfaces of both zeolites which is already confirmed by the adsorption intensity constant ($n$). Kinetic studies were also in the favor of heterogeneous adsorption process with the validity of elovich model that is confirmed here that the adsorption of MG is taking place on different active surfaces of Na/Li-Zeolites.
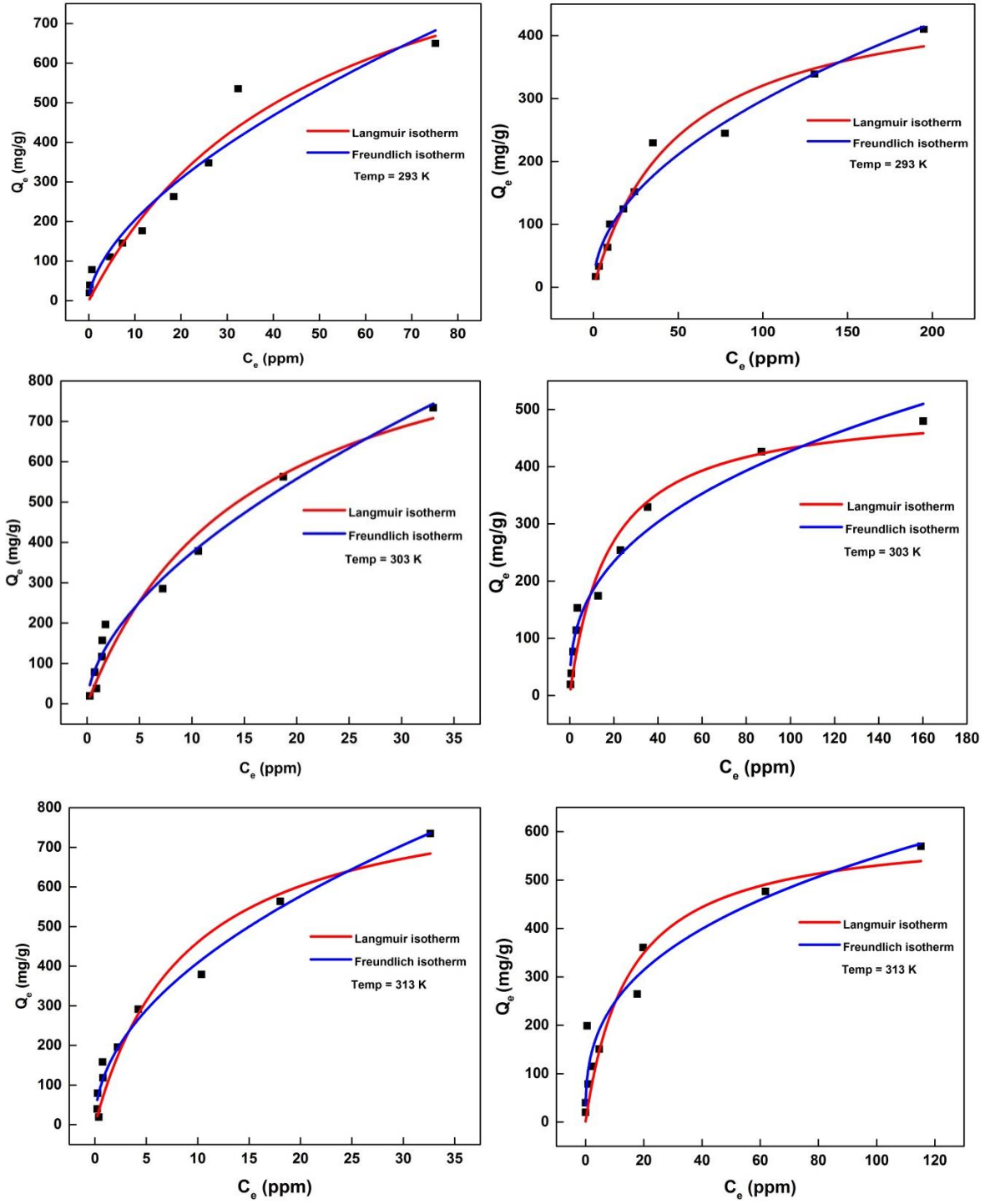
Li- Zeolite            Na-Zeolite

Fig.10- Langmuir and Freundlich plots for the adsorption of MG on Li-Zeolite & Na-Zeolite at 293K, 303K, 313K

## 3.2.6 Thermodynamic study

The thermodynamic performance of adsorption of MG dye on Na/Li-Zeolites was investigated at 293K, 303K, and 313K. Thermodynamic constraints such as Gibbs free energy ($\Delta G^0$), enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) were estimated to comprehend the effect of temperature on adsorption process. The mathematical expressions for these thermodynamic parameters are assumed by the subsequent equations [49]:

$$K_c = C_{AD}/C_{SD} \qquad (9)$$

$$\Delta G^0 = -RT\ln K_c \qquad (10)$$

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (11)$$

where $K_c$ is the equilibrium constant which is the ratio of adsorbed dye by adsorbent at equilibrium ($C_{AD}$) & the remaining quantity of dye in aqueous solution at equilibrium ($C_{SD}$). T (K) is operating temperature and R is gas constant (8.3144 J/mol.K). The plot between $\ln K_C$ and 1/T lead to a straight line having the slope of $\Delta H^0$ (KJ/mol) and intercept of $\Delta S^0$(J/molK) is shown in fig.11 for both zeolites. The obtained value of $\Delta H^0$ from the slope was negative, which indicates that the adsorption system is feasible at low temperature. By increasing in temperature, the adsorption capacity is increasing but the efficiency for the deduction of MG dye decreases by adsorbents at high temperature. The change in entropy is positive affinity of adsorbent surfaces towards the MG dye molecules which leads to the randomness of the whole adsorption system [50].

Table 3

Thermodynamic parameters for the adsorption of MG on Na-Zeolite and Li-Zeolite

| Temp / K | Na-Zeolite | | | | Li-Zeolite | | | |
|---|---|---|---|---|---|---|---|---|
| | $K_c$ | $\Delta G^0$ / KJ mol$^{-1}$ | $\Delta H^0$ / KJ mol$^{-1}$ | $\Delta S^0$ / J mol$^{-1}$K$^{-1}$ | $K_c$ | $\Delta G^0$ / KJ mol$^{-1}$ | $\Delta H^0$ / KJ mol$^{-1}$ | $\Delta S^0$ / J mol$^{-1}$K$^{-1}$ |
| 293 | 4.32198 | -3.566 | -4.434 | 16.74 | 1.051 | -0.121 | -3.912 | 13.374 |
| 303 | 11.11387 | -6.066 | | | 1.496 | -1.015 | | |
| 313 | 11.2549 | -6.230 | | | 2.472 | -2.355 | | |
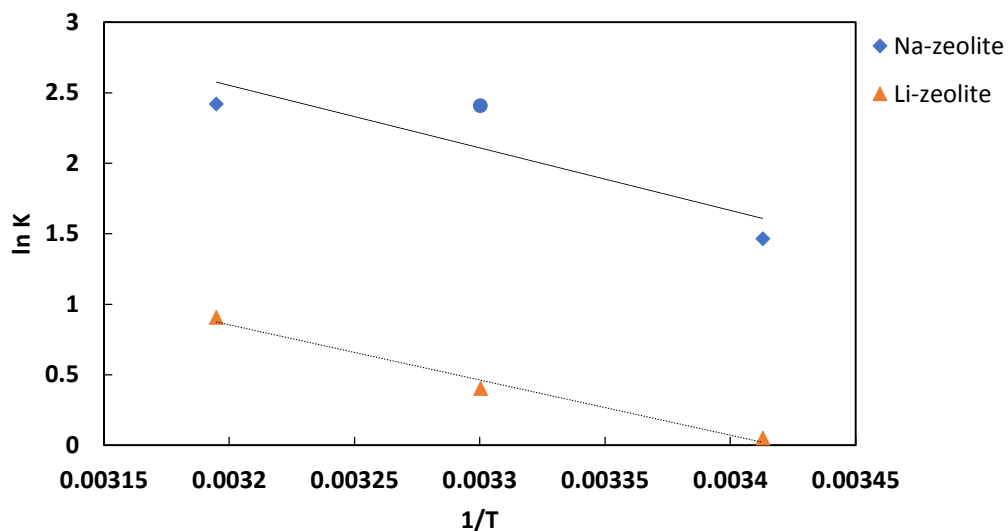


Fig.11- von't Hoff plot of adsorption equilibrium constant *K*

The system's entropy can also be responsible if there are some chances of increase in entropy of the universe because the adsorption system is not an isolated process, but this effect is on lighter side. The Gibbs free energy with negative sign reflects the possibility and spontaneity of adsorption of MG dye against both zeolites [51]. The decreasing trend of Gibbs free energy by increasing in temperature shows that the adsorption becomes less satisfactory at elevated temperatures. All thermodynamic parameters are listed in table 3.

# CHAPTER # 4
# CONCLUSION

## 4. Conclusion

The research study justified the useful alteration of raw CFA to Na-zeolite and Li-zeolite for the removal of MG dye from aqueous solution. Adsorbent dosage study confirmed that the raw CFA has not enough prospective to absorb the MG dye from aqueous solution. So, further research work was accomplished only by considering the modified raw CFA i.e. Na-zeolite and Li-zeolite. A comparative study was done between Na-zeolite and Li-zeolite that showed that the Na-zeolite has the most promising results. Contact time study was also in the favor of Na-zeolite. Kinetic adsorption was performed by applying four kinetic models. Intra particle diffusion model explained that rate controlling step was intraparticle diffusion step. Elovich model was the best fitted model that was further confirmed by isotherm study where Freundlich model explained the adsorption process. Elovich and Freundlich models verified the adsorption process that it occurred on multilayers of adsorbent. According to thermodynamic studies, the removal of MG dye is feasible a low temperature and spontaneous. The negative of Gibbs free energy exposed that the adsorption phenomena is less favored by increasing the temperature.

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