ZEOLITE SYNTHESIS AND ITS APPLICATION AS ADSORBENT

A Thesis report submitted in partial fulfillment of the requirement for the award of degree of

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In

Chemical Engineering

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CERTIFICATE

This is certified that the thesis entitled ***"Zeolite Synthesis and its application as adsorbent",*** *is an authentic record of my own work carried out as requirements for the award of the degree of M.Tech (Chemical Engineering) at Thapar University, Patiala, under the guidance of Dr. Sanghamitra Barman (Assistant Professor, ChED) and Mr. Sanjeev Ahuja (Assistant Professor, ChED) during January to June 2010.*

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ABSTRACT

The present environmental concerns over fly ash disposal have sparked a resurgent interest in its conversion to value added product such as zeolites. Fly ash derived from coal residues has a tremendous potential for conversion to zeolites. Still more remarkable is the subsequent utilization of theses zeolites synthesized from fly ash as adsorbent for removal of dye in the industry. In the present study the coal based fly ash was used to synthesis X-type and A-type 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). Particle Size, surface area and pore volume of the synthesized zeolites were also being measured. The synthesized zeolite was then used as adsorbent for removal of different dyes such as methyl orange, methylene blue and safranine T from the aqueous solution.

Dyestuff production units and dyeing units have always had a pressing need for techniques that allow economical pre-treatment for colour in the effluent. At present, there is a growing interest in using low-cost, commercially available materials for the adsorption of dyes. Zeolite synthesized from fly ash was found to be a good adsorbent for removal of Methylene blue, Methyl Orange and Safranine T. Various types of materials such as silica gel, alumina, bentonite, perlite and clays have already been used as adsorbent to removal of these dyes. Zeolites are interesting materials because of their intrinsic properties to removal of these dyes. The adsorption of basic and acid dyes from aqueous solution onto zeolite synthesized from fly ash has been studied using an agitated batch adsorber. Physical regeneration of used adsorbent was studied at higher temperature. Combustion at higher temperature produced effective adsorbents for further adsorption. Several factors have been studied: initial dye concentration, adsorbent mass and contact time. For adsorption of methyl orange experimenal data was fitted to the Freundlich isotherm better than Langmuir isotherm. Correlation coefficient was found to be 0.998.

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CHAPTER 1

INTRODUCTION

1.1 Zeolite from fly ash

The disposal of coal fly ash from coal based power plants is a problem of global concern today. In India, most of the utility thermal power and sub-bituminous coal with high ash content (30-50%) resulting in the production of a huge quantity of fly ash. Only a small portion of this huge quantity is used as a raw material for concrete manufacturing and construction purposes, remainder being simply dumped on the landfill sites. Currently, more than 90 million tons of fly ash is being generated annually in India, with 65000 acres of land being occupied by ash ponds. Without proper disposal options, such a huge quantity of ash has posed a great threat to the environment.

The possibility of using waste coal fly ash in synthesizing zeolite molecular sieves is very much attractive for its widespread applications in diversified fields. In fact, high content of reactive materials like aluminosilicate make fly ash an interesting starting material for the synthesis of zeolite (Shigemoto et al.,1993; Chang & Shih, 1998). Converting fly ash into zeolites not only eliminates the disposal problem, but also turns an otherwise waste material into a marketable commodity.

Fly ash, an oxide-rich waste product of thermal power plants, can be used as raw material for different industries on proper treatment. In India, a little effort has been paid on proper utilization of fly ash. However, only three percent of fly ash is being utilized, mostly in the manufacture of pozzolonic cement, ready-made hollow blocks, and asbestos sheets and in road embankment and agricultural purpose. Two classes of fly ash are defined by American Society of Testing Material (ASTM):

- Class F fly ash
- Class C fly ash

Class F fly ash:

The burning of harder, older anthracite and bituminous coal typically produces Class F fly ash. This fly ash is pozzolanic in nature, and contains less than 20% lime (CaO). Possessing pozzolanic properties, the glassy silica and alumina of Class F fly ash requires a cementing agent, such as Portland cement, quicklime, or hydrated lime, with the presence of water in order to react and produce cementitious compounds. Alternatively, the addition of a chemical activator such as sodium silicate (water glass) to a Class F ash can leads to the formation of a geopolymer.

Class C fly ash:

Fly ash produced from the burning of younger lignite or sub bituminous coal, in addition to having pozzolanic properties, also has some self-cementing properties. In the presence of water, Class C fly ash will harden and gain strength over time. Class C fly ash generally contains more than 20% lime (CaO). Unlike Class F, self-cementing Class C fly ash does not require an activator. Alkali and sulfate (SO_4) contents are generally higher in Class C fly ashes.

The types of zeolites formed on treatment are very much selective to reaction parameters and also the raw material compositions. The synthesis of various zeolites from fly ash and their properties mainly depend on the effect of reaction time, reaction temperature, alkalinity and fly ash composition.

Zeolites are crystalline, micro-porous, hydrated aluminosilicates that are built from an infinitely extending three dimensional network of $[SiO_4]^{4-}$ and $[AlO_4]^{4-}$ tetrahedral linked to each other by the sharing of oxygen atom. Generally, their structure can be considered as inorganic polymer built from tetrahedral TO_4 units, where T is Si^{4+} or Al^{3+} ion. Each oxygen (O) atom is shared between two T atoms.

$M_{x/n}$ $[(AlO_{2x}(SiO_2)_y]$ · wH_2O, where M is an alkali or alkaline earth cation, n is the valence of the cation, w is the number of water molecules per unit cell, x and y are the total number of tetrahedra per unit cell, and the ratio y/x usually has values of 1 to 5, though for the silica zeolite, y/x can be raging from 10 to 100.

The adsorption of dyes onto zeolites has been extensively investigated by some researcher but only a few studies have been reported about the adsorption of dye onto fly ash-based zeolites .A comparison of the adsorption capabilities of methyl orange with other larger dyes over zeolites may provide valuable information about adsorption mechanisms and the structure of the zeolites.

Structure of Zeolite:

The primary building unit for zeolites is the tetrahedron and the secondary building units (SBUs) are the geometric arrangements of tetrahedra. The SBUs may be simple polyhedra such as cubes, hexagonal prisms, or cubo-octahedra. The structures can be formed by repeating SBUs.

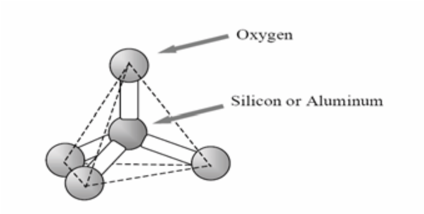

Figure 1.1 Primary building unit of zeolite structure.

Types of zeolite:

Zeolites	Typical oxide formula
Zeolites A	$Na_2O.Al_2O_3.2SiO_2.4.5H_2O$
Zeolites X	$Na_2O.Al_2O_3.2.5SiO_2.6H_2O$
Zeolites Y	$Na_2O.Al_2O_3.4.8SiO_2.8.9H_2O$

Table 1.2 Typical oxide formula of some synthetic zeolites

1.2 Application of Zeolites for the adsorption of Dyes:

Adsorption and adsorption processes are important fields of study in physical chemistry. They form the basis for understanding phenomena such as heterogeneous catalysis, chromatographic analysis, dyeing of textiles, and clarification of various effluents.

Dyes are defined as colored substances which when applied to fibers give them a permanent color, i.e. resistant to action of light, water and soap. Practically every dyestuff is made from either one or more of the compounds obtained by the distillation of the coal tar. The chief of these are Benzene (C_6H_6), Toluene ($C_6H_5.CH_3$), Naphthalene ($C_{10}H_8$), Anthracene ($C_{14}H_{10}$), Phenol (C_6H_5OH), Cresol (C_7H_7OH), Acridine ($C_{13}H_9N$), and Quinoline (C_9H_7N).

The present investigation describes the adsorption of methylene blue, methyl orange and safranine T over zeolite catalysts. 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 industry are generally high in both color and organic content. 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 existing technologies have certain efficiency in the removal of dyes but their initial and operational costs are very high. On the other hand, low cost technologies do not allow the desired degree of color removal or have certain disadvantage.

Oxidation and adsorption are two major technologies that are used for wastewater treatment in the textile industry. Among oxidation methods, UV/Ozone and UV/H_2O_2 treatments are technologies for decolorizing waste water. Adsorption is rapidly becoming a prominent method of treating aqueous effluents and has been extensively used in industrial processes for a variety of separation and purification purposes. Adsorption of dyes by zeolites has evolved into one of the most effective physical process for the decolorization of textile wastewater. This process 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.

1.2.1 Methyl Orange Dye:

A basic azo dye having the molecular formula $C_{14}H_{14}N_3NaO_3S$ that is used chiefly as an acid-base indicator and whose dilute solution is yellow when neutral and pink when acid. The structure of. Methyl orange dye is given below.

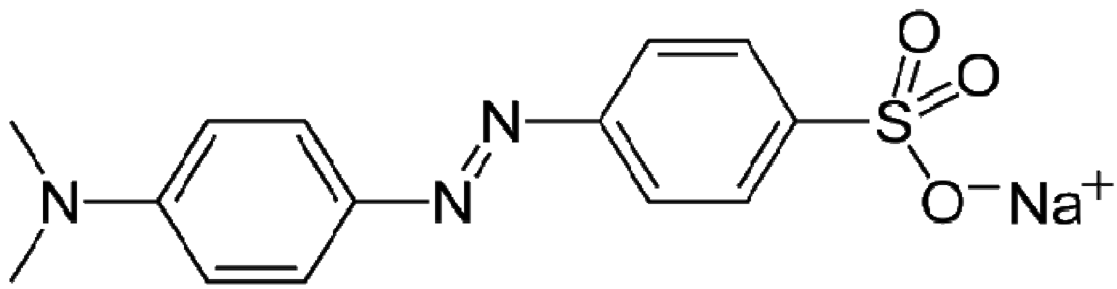

Figure 1.2 Structure of Methyl orange dye

1.2.2 Methylene Blue:

Methylene blue is a heterocyclic aromatic chemical compound with the molecular formula$C_{16}H_{18}N_3SCl$. It has many uses in a range of different fields, such as biology and chemistry. At room temperature it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water. The structure is given below.

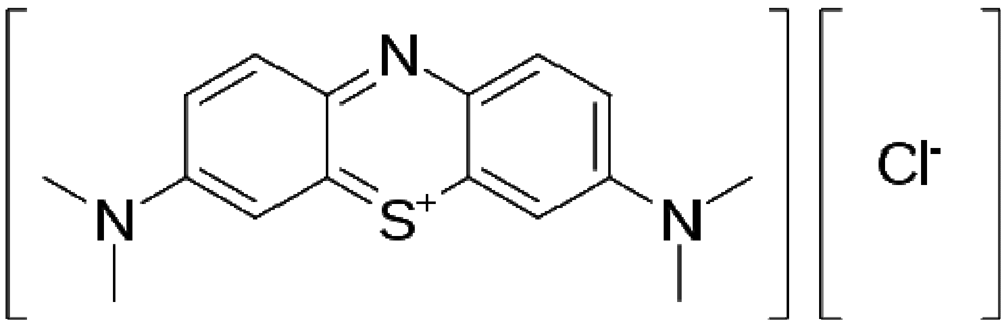

Figure 1.3 Structure of Methylene blue dye

1.2.3 Safranines Dyes:

Safranines are the azonium compounds of 3,7-diamino-phenazine. They are obtained by the joint oxidation of one molecule of a *para*-diamine with two molecules of a primary amine; by the condensation of *para*-aminoazo compounds with primary amines, and by the action of *para*-nitrosodialkylanilines with secondary bases such as diphenylmetaphenylenediamine. The structure of safranines dyes is given below.

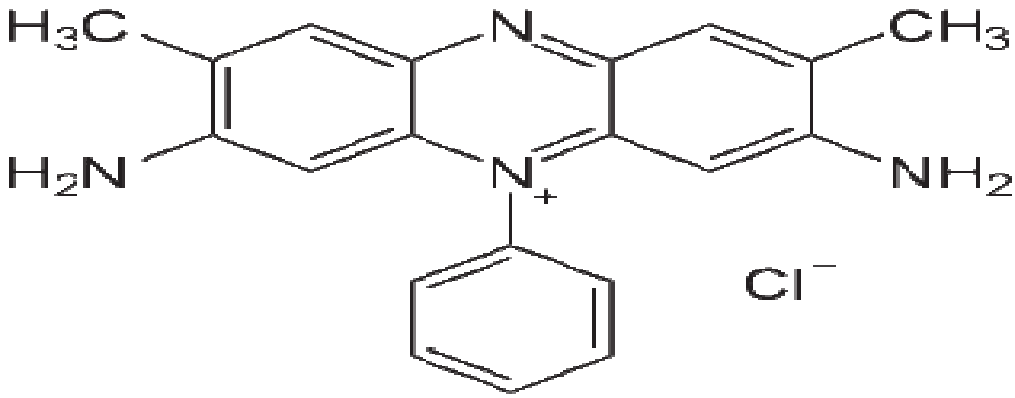

Figure 1.4 Structure of saffranine dye

Zeolitized fly ash products was successfully used as low cost adsorbents for cationic and anionic dyes. Equilibrium and kinetic results obtained in this study may be useful for designing a treatment plant for dye removal from industrial colored effluents.

1.3 The objectives of the present investigation are:

- Synthesis of zeolite-X, and A from fly ash
- Characterization of synthesized zeolite
- Application of synthesized zeolite as an adsorbent for removal of dyes.

CHAPTER 2

LITERATURE REVIEW

Recent investigations have shown the potential of fly ash as a raw material for synthesis of various types of zeolites. The conversion of fly ash to zeolite has gained importance due to intensive research on zeolite growth in geological materials such as volcanic rock and clay minerals. High content of reactive materials like alumino silicate makes it interesting starting material for the synthesis of zeolite with a wide range of applications. Various methods of synthesis of zeolite from fly ash have, so far, been invented and patented. Some of the important techniques are alkali fusion followed by hydrothermal treatment (Shigemoto et al., 1993), slurry method (Grutzeck & Siemer, 1997), molten salt method (Park et al., 2000a, 2000b). Fusion method is found to be the most efficient and a general method for synthesis of X-type, Y-type, and A-type from a large variety of fly ash.

A modified fusion process to synthesize zeolites A and X from fly ash was studied by Chang et al. (2000). It was found that the addition of aluminium hydroxide to the fused fly ash solution followed by hydrothermal treatment at 60 ^{0}C produced single –phase zeolite A and X depending on the source of the ash received fly ash. The result confirms that the quantity of dissolved aluminium specie is critical for the type of zeolite formed from fused fly ashes.

Sutarno et al. (2007) synthesized faujasite from fly ash and its application for hydrocracking catalyst of heavy petroleum distillates has been studied. Faujasite was synthesized from fly ash by hydrothermal reaction in alkaline solution via combination of reflux treatment of fly ash with HCl and fusion with NaOH.

Ojha et al. (2004) synthesized X-type zeolite by alkali fusion followed by hydrothermal treatment. The synthesized zeolite was characterized using various techniques such as X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy.

Querol et al. (2002) synthesized zeolitic material from fly ash using two different methodologies.(a) impure zeolitic material obtained by direct conversion from different fly ashes, and (b) a high purity 4A-X zeolite blend synthesized from the silica extracts obtained from the Meirama fly ash.

Lu et al. (2010) synthesized zeolite NaPI by a hydrothermal method from coal fly ash, the possibility of using modified zeolite NaPI as a material for removing fluorine from drinking water was studied.

Fukui et al. (2003) studied the effects of NaOH concentration on the crystal structure and the reaction rate of zeolite synthesized from fly ash with a hydrothermal treatment.

Rungsuk et al. (2006) synthesized zeolite by fusion method. The synthesis conditions were optimized to obtain the product with high cation exchange capacity (CEC). CFA was mixed with NaOH at various ratios and the results revealed that the optimal ratio between CFA and NaOH.

Vadapalli et al. (2010) studied solid residues resulting from the active treatment of acid mine drainage with coal fly ash were successfully converted to zeolite-P under mild hydrothermal treatment conditions. Scanning electron microscopy showed that the zeolite-P product was highly crystalline. The product had a high cation exchange capacity (178.7 meq / 100 g) and surface area (69.1 m^{2}/g) and has potential application in waste-water treatment.

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Mondragon et al. (1990) investigated on possible use of coal fly ash, in general and synthesis of zeolitic material from it, in particular. But like most other investigators, they also tried the hydrothermal method.

Lin et al (1995) extensively investigated the effects of the hydrothermal reaction parameters such as temperatures, molarity of caustic reagents and reaction time on the properties of the treated fly ash and also optimized the reaction parameters to obtain the product of the best quality.

Park and coworkers (2000b) developed a new method for synthesizing zeolite under molten conditions without any addition of water. This is a new and alternative approach for massive zeolitisation of various mineral wastes at low cost. However, complete zeolitisation of fly ash could not be accomplished by this molten salt method, probably due to low temperature and in sufficient contact of NaOH with raw materials.

Adsorption of dyes over zeolite: Although the adsorption of dyes onto zeolites has been extensively investigated only a few studies have been reported about the adsorption of dye onto fly ash-based zeolites .

O.Ozbayrak et al. (2004) studied the adsorption conditions of Toluidine Blue-O, which is phenothiazine derivative.. The adsorption time, pH, concentration range and temperature were optimized and amount of loaded dyes were calculated. Langmuir and Freundlich isotherms were also studied.

Gülten Atun et al (2011) investigated the adsorption characteristics of two basic dyes, thionine (TH) and safranine T (ST), onto fly ash (FA) and its three zeolitized products prepared at different hydrothermal conditions.

Shaobin Wang et al (2006) studied adsorption over natural zeolite and synthetic zeolite such as MCM-22, as effective adsorbents for the removal of a basic dye, methylene blue, from wastewater. Two methods, fenton oxidation and high temperature combustion, have been used for regeneration of used materials.

L.Markovska et al (2005) studied the adsorption of basic and acid dyes from aqueous solution onto natural zeolite using an agitated batch adsorber. Several factors had been studied such as agitation, initial dye concentration and adsorbent mass. The adsorption isotherms parameters for Langmuir, Freundlich,combined Langmuir-Freundlich and Redlich-Peterson were determined using the adsorption data.

A. Bhatnagar et al (2006) studied the suitability of activated carbon and other alternative adsorbents for wastewater treatment .

J.H.Potgieter (1991) studied the adsorption of methylene on activated carbon and different type of isotherm (Langmuir,Freundlich,and Frumkin adsorption isotherms) had been studied.

E.Voudrias et al (2002) investigated the removal of various reactive dyes from aqueous solutions over activated carbon. Batch kinetic and isotherm experiments were conducted to determine the sorption-desorption behavior of the examined dyes from aqueous solutions and wastewaters by different sorbents, including activated carbon, fly ash, bentonite and bleaching earth.

CHAPTER 3

EXPERIMENTAL SECTION

3.1 Materials:

The Catalysts were 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, Methylene blue, Safranine T, were procured from Puja Chemical, Patiala. All reagents were analytically pure (99%) and used without purification.

The fly ash samples contained both amorphous (mainly SiO_2, Al_2O_3) and crystalline components (mainly quartz and mullite). Table 3.1 presents the physico-chemical properties of the fly ash samples used in the present investigation.

Table 3.1 Composition (wt %) of fly ash

Components	NTPC	BTPS
Na_2O	1	0.7
Al_2O_3	27.86	29.1
SiO_2	60.03	55.6
K_2O	0.0	1
CaO	0.5	3
TiO_2	4.2	2
Fe_2O_3	4.0	4
BaO	0.2	0
MgO	1.8	2
Surface area (m^2/g)	1.	3
Mean particle size	26 .08	13

Depending upon the source and makeup of the coal being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline) and calcium oxide (CaO). Microscopic structure of fly ash is given below.

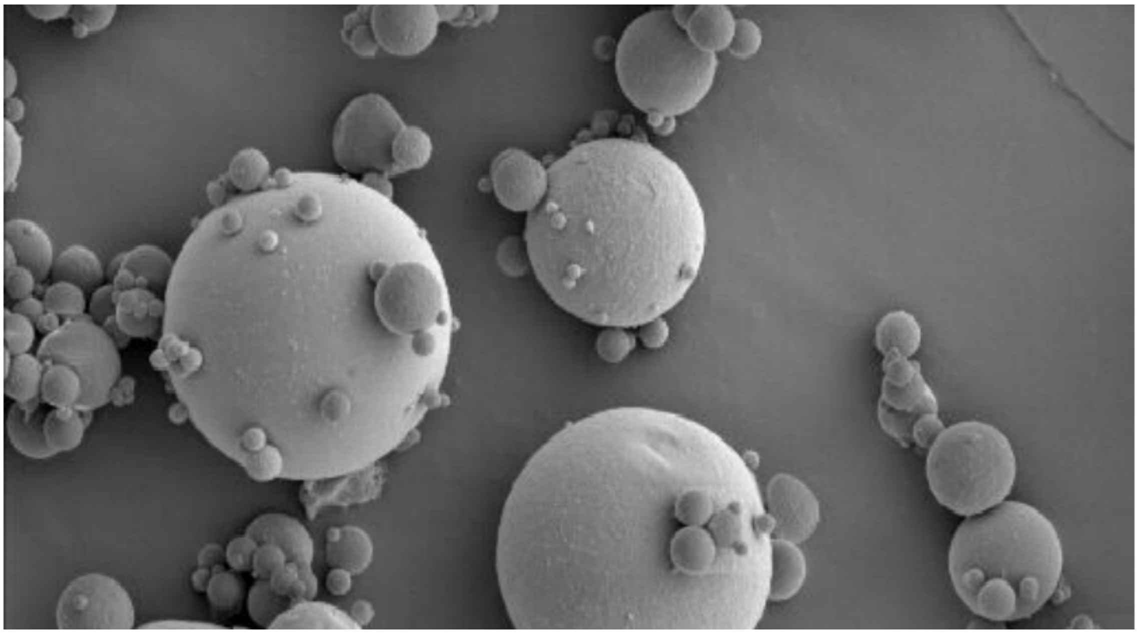

Figure 3.1 Microscopic spherical structure of fly ash

3.2 Zeolite Synthesis Method:

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. Fly ash samples were further treated with hydrochloric acid to increase their activity in zeolite formation. The acid treatment helped to dealuminate the fly ash and removed iron to a certain extent, thereby increasing the activity, thermal stability and acidity of the zeolite, all aiming for better catalytic applications. 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 flow diagram of the synthesis process is shown in figure 3.2. The resultant precipitate was then repeatedly washed with distilled water to remove excess sodium hydroxide, filtered and dried. The sodium hydroxide added to the fly ash not only works as an activator, but also adjusts the sodium content in the starting material. Mullite and α- quartz present in the fly ash are the sources of aluminum and silicon, respectively, for zeolite formation. The steps for synthesizing zeolites from fly ash are given below.

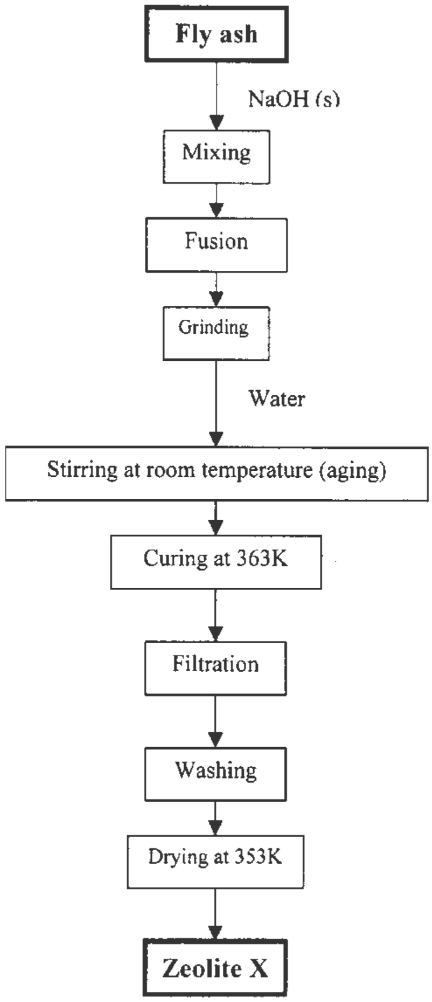

Figure 3.2 Process flow diagram for synthesis of zeolite X type from fly ash

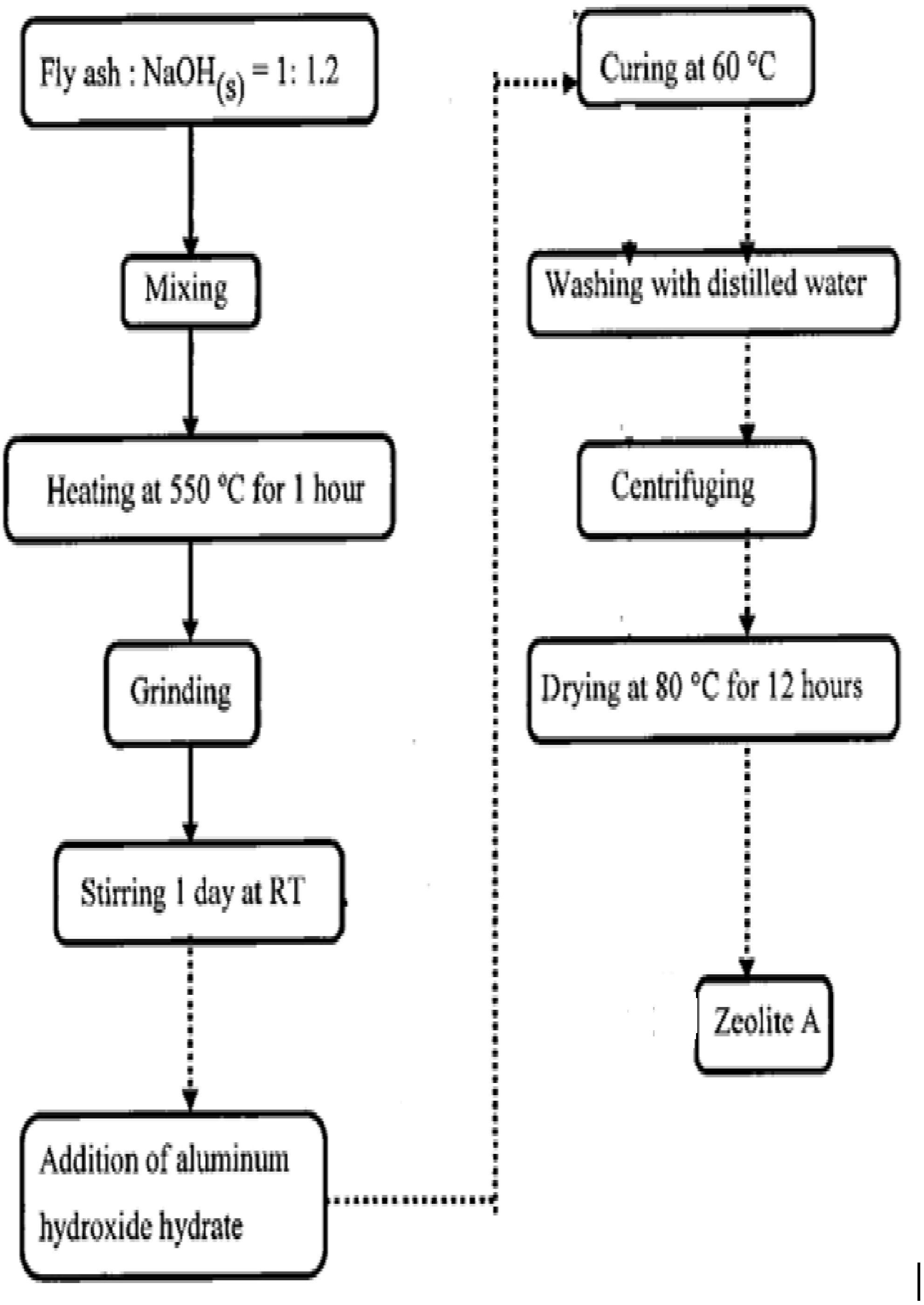

Figure 3.3 Process flow diagram for synthesis of zeolite A type from fly ash

3.3 Regeneration of zeolite (ZX_1):

Regeneration of zeolite (ZX_1) was done by keeping the used zeolite (ZX_1) in the furnace around 550^{0}C for 5 hours **.** Catalyst is regenerated by calcination at higher temperature. By calcination adsorbent structure becomes stable. At higher temperature moisture with other volatile matters goes out and also the adsorbed compounds are desorbed so that the entire surface of the catalyst becomes available for re-adsorption.

3.4 Adsorption of different dyes over zeolite (ZX_1).

The adsorbent used in the experiment was zeolite (ZX_1) synthesized from fly ash. A methyl orange solution with a concentration of 5 mg/L was prepared from analytical-grade reagent and distilled water..

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 500 rpm at different temperatures. The determination of dye concentration was done spectrophotometrically on a Spectrophotometer (USA) by measuring absorbance at λ_{max} of 464 nm, 630 nm and 560 nm for Methyl Orange, Methylene Blue and Safranine-T respectively. The data obtained from the adsorption tests were then used to calculate the adsorption capacity, q_t (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 ^{0}C.

3.5 Adsorption analysis was done by the Spectrophotometer: A spectrophotometer is a photometer (a device for measuring light intensity) that can measure intensity as a function of the light source wavelength. Important features of spectrophotometers are spectral bandwidth and linear range of absorption or reflectance measurement. The spectrophotometer is commonly used for the measurement of transmittance or reflectance of solutions, transparent or opaque solids, such as polished glass, or gases. However they can also be designed to measure the absorbance on any of the listed light ranges that usually cover around 200nm - 2500nm using different controls and calibration. Within these ranges of light, calibrations are needed on the machine using standards that vary in type depending on the wave length of the photometric determination.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Properties of Zeolite

Zeolite was synthesized from fly ash using hydrothermal treatment. The synthesized Zeolite ZX_1 is having the following properties given below.

- Particle size- 1-1.5 mm
- Porosity- 0.28
- Surface area- 425 m^2 / g

Surface area of fly ash was found to be 3.5 m^2/g, mean Particle size 24.90 µm.

4.2 The synthesis conditions of different type of zeolites X, Y and A prepared from fly ash.

Table 4.1 Zeolite synthesis condition

Zeolite Designation	**Source of fly ash**	**Zeolite synthesis condition**				
		NaOH/Fly ash ratio	**Fusion Temp (K)**	**Aging Time (h)**	**Hydrothermal Treatment**	
					Temp (K)	**Time (h)**
ZX_1	NTPC	1.2	823	24	363	6
ZX_2	NTPC	1.3	823	24	363	6
ZX_3	NTPC	1.4	823	24	363	6
ZA_1	BTPS	1.2	823	24	353	6
ZA_2	BTPS	1.4	823	24	353	6

4.3 Effect of Hydrochloric (HCl) treatment:

Alongwith SiO_2 and Al_2O_3, fly ash contains several other components that are undesirable in synthesized zeolite. Some of these components act as a poison during catalytic applications of zeolite. Some of these unwanted materials could be removed by acid treatment. In the present study, HCl was used to reduce the concentration of iron and alkali oxide present in fly ash. Thus, it helped in increasing the SiO_2 content of the reaction mixture. On acid treatment, iron oxide present in the original fly ash was removed in some extent.

Table 4.2 Composition of fly ash (SEM) without HCl treatment

Element	Weight (%)
Al_2O_3	25.46
SiO_2	58.84
K_2O	9.36
TiO_2	2.84
FeO	3.50

Table 4.3 Compositon of fly ash (SEM) with HCl treatment

Element	Weight(%)
Al_2O_3	26.46
SiO_2	60.84
K_2O	10.01
TiO_2	2.95
FeO	0.50

4.4 Thermal stability of zeolites

Crystalline zeolites are more resistive to heat than amorphous materials, the main reason being the geometrical structure of the crystalline framework. However, the effects of silica/alumina ratio and level of cation exchange on thermal stability also cannot be denied. The commercial zeolites having high (SiO_2/Al_2O_3) ratio can resist much higher temperature. The zeolite presently prepared was observed to lose its crystallinity beyond 973 K and the crystalline structure was mostly collapsed above 1073 K (figure 4.4).

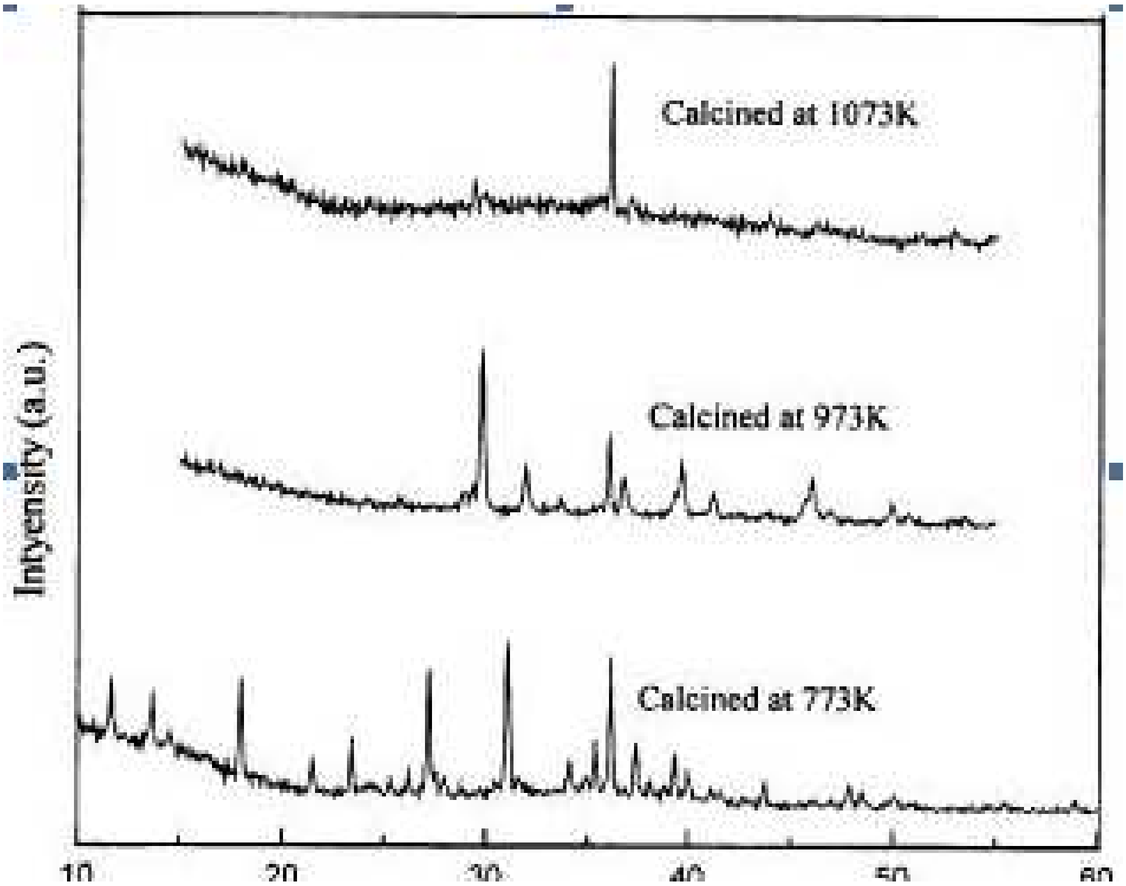

Fig 4.1 Thermal stability of synthesized zeolite

4.5 Characterization:

4.5.1 X-ray diffraction

The X-ray (powder) diffraction (XRD) patterns of different fly ash samples and synthetic zeolitic materials were obtained using a Philips X-ray diffractometer (Philips BW1710). Operating conditions involved the use of CoK*a* radiation at 4 kV and 30 mA. The samples were scanned from 10–50° (2*q*, where *q* is the angle of diffraction). Various crystalline phases present in the samples were identified with the help of JCPDS (Joint Committee on Powder Diffraction Standards) files for inorganic compounds. Quantitative measure of the crystallinity of the synthesized zeolite was made by using the summed heights of major peaks in the X-ray diffraction pattern (Szostak 1976). The major peaks were selected specifically because they are least affected by the degree of hydration of samples and also by others. The percentage crystallinity was taken as the sum of the peak heights of the unknown materials divided by the sum of the peak heights of a standard material that has been assume to be 100% crystalline i.e.

% Crystallinity = (sum of the peak heights of unknown material) × 100/ (sum of peak heights of standard material).

4.5.2. Particle size and surface area:

The average particle sizes of various samples were determined by particle size analyzer (Malvern Instruments M7).BET method is used to measure specific surface area of the samples (Flowsorb-II, Micromeritics).

4.5.3 Morphological analysis by scanning electron microscope (SEM):

The morphological structure of the raw fly ash, treated fly ash and synthesized zeolitic materials were obtained by using scanning electron micrograph (Jeol, JSM 5800). The bulk composition was also estimated from SEM/EDXS by indirect method. The elemental composition of the samples was first determined from the SEM/ EDXS, and from these data, the percentages of oxides were calculated. The results were further verified by X-ray fluorescence (XRF) data.

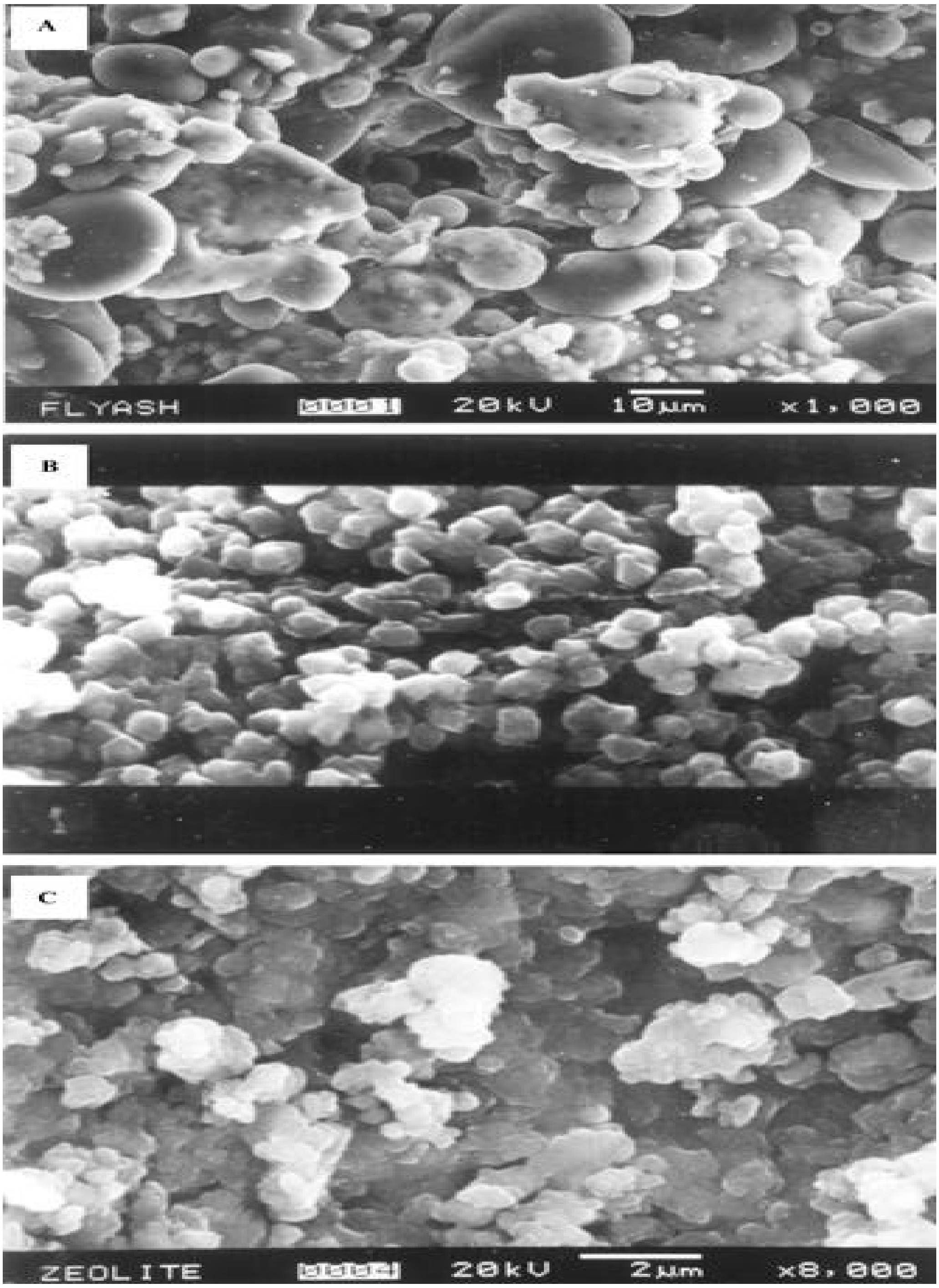

Figure 4.2

Scanning electron micrographs of (**A**) Fly ash, (**B**) Synthesized ZX_1 and (**C**) commercial 13X zeolite.

4.6 Application of synthesized zeolite as adsorbent for the removal of dyes.

The present investigation describes the adsorption of Methylene Blue, Methyl Orange, and Safranine T, the organic dyestuffs commonly used for tracer studies over different type of zeolite synthesized from fly ash. 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 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 dyes were measured with spectrophotometer at a wavelength corresponding to the maximum absorbance for each dye, 464 nm, 630 nm and 560 nm for respectively Methyle Orange, Methylene Blue and Safranine T. In accordance with the Lambert- Beer law the adsorbance was found to vary linearly with concentration and dilutions were undertaken when adsorbance exceeded 0.6.

4.6.1 Kinetic experiments over zeolite ZX_1, ZA_1 and Fly ash 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°C. From the initial concentrations of sorbents (g l^{-1}) and dyes (mg l^{-1}) the amount adsorbed in the sorbent were measured. Percent removal of dyes over zeolite ZX_1, ZA_1 and Fly ash as a function of contact time, are shown in Fig. 4.2, Fig 4.3 and Fig 4.4 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_1 was higher due to larger pore size and surface area compared to ZA_1 and Fly ash. Molecular size of Methyl Orange facilitate the adsorption, resulting in higher adsorption capacity than Methylene Blue and Safranine T. Reduced adsorption in ZA_1 is due to the inability of the molecule to penetrate all the internal pore structure and less available surface.

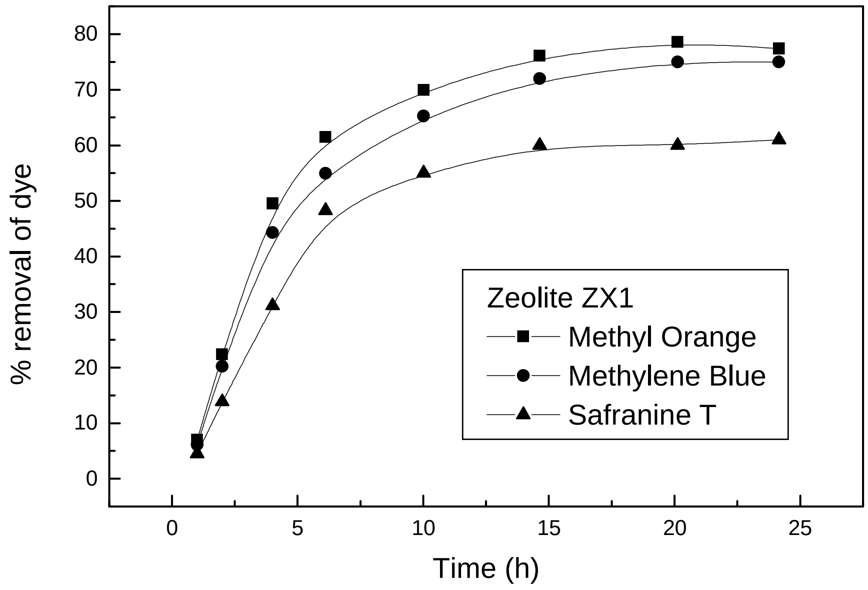

Figure: 4.3 Adsorpton of dyes over ZX_1

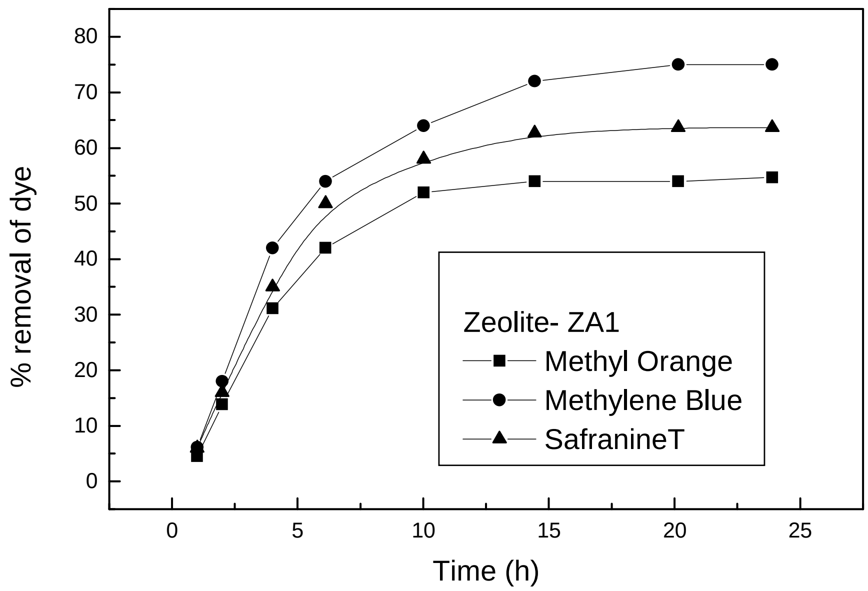

Figure: 4.4 Adsorption of dyes over ZA_1

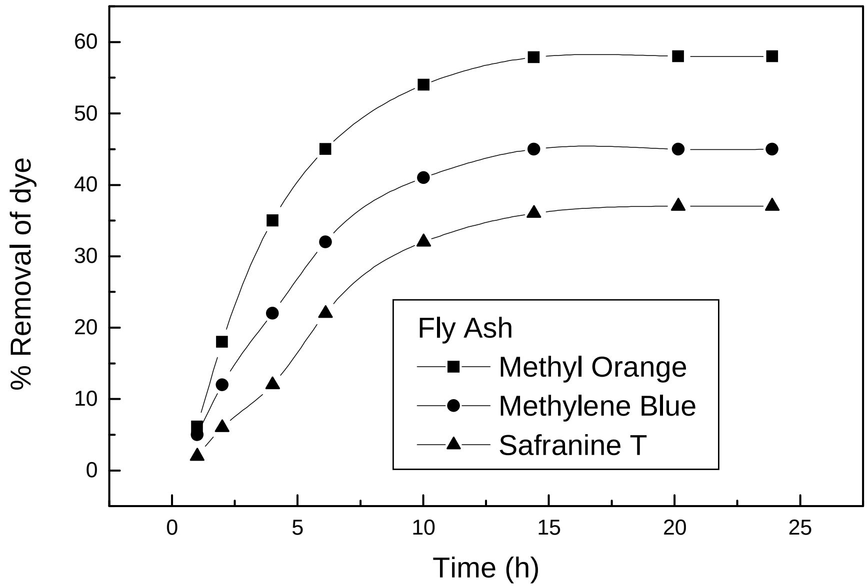

Figure: 4.5 Adsorption of dyes over fly ash

4.6.2 Effect of pH on dye removal

The pH values of Methyl orange, Methylene Blue and Safranine T solutions were measured as 8.92, 6.32 and 6.34, 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. Fig. 4.5 shows the dynamic adsorption of Methyl Orange, Methylene Blue and Safranine T on zeolite ZX_1 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 MB adsorption will have higher adsorption at higher pH values (Al-Ghouti et al., 2003; Singh et al., 2003; Gupta et al., 2004; Wang et al., 2005a,b). For cationic dyes like Methylene Blue, lower adsorption of MB at acidic pH is probably due to the presence of excess H^+ 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 (MB) 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, excess H+ ions balances the anionic charge of the dye. The excess anionic part of the Methyl Orange get attracted to the cationic adsorption surface and thereby enhances adsorption. With increase in solution pH due to the reduction of H^+ ion more anionic dyes can be adsorbed on the cationic surface of the adsorbent.

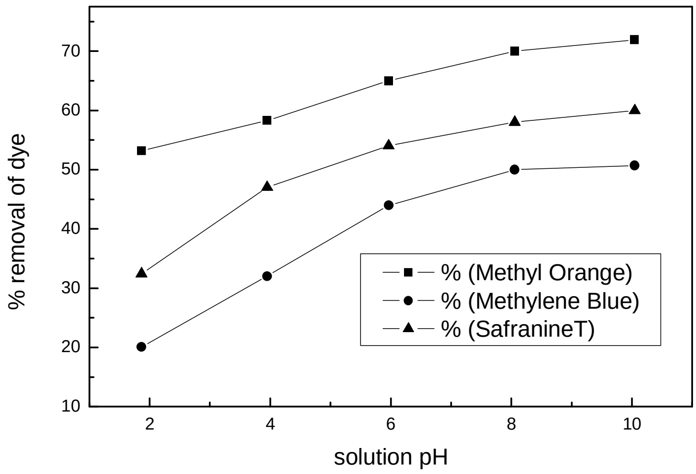

Fig. 4.6 Effect of solution pH on adsorption of different dyes

4.7 Adsorption behavior of regenerated adsorbents

The high temperature regeneration was conducted at 540^0C for 5 h. The regenerated zeolite ZX_1 was tested again for Methyl Orange and Methylene Blue adsorption. Fig. 4.6 and Fig 4.7 represents the comparison of the performance of fresh and regenerated ZX_1 for the adsorption of Methyl Orange and Methylene Blue 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.

Further investigations of calcination temperature and time on adsorption recovery were conducted and the results are shown in 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.

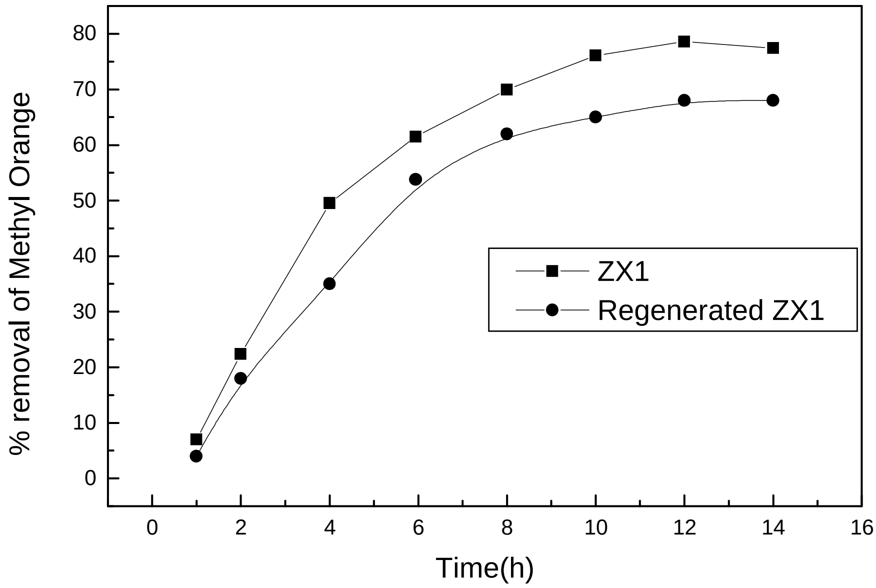

Figure 4.7 Adsorption over fresh and regenerated zeolite ZX_1 on Methyl Orange

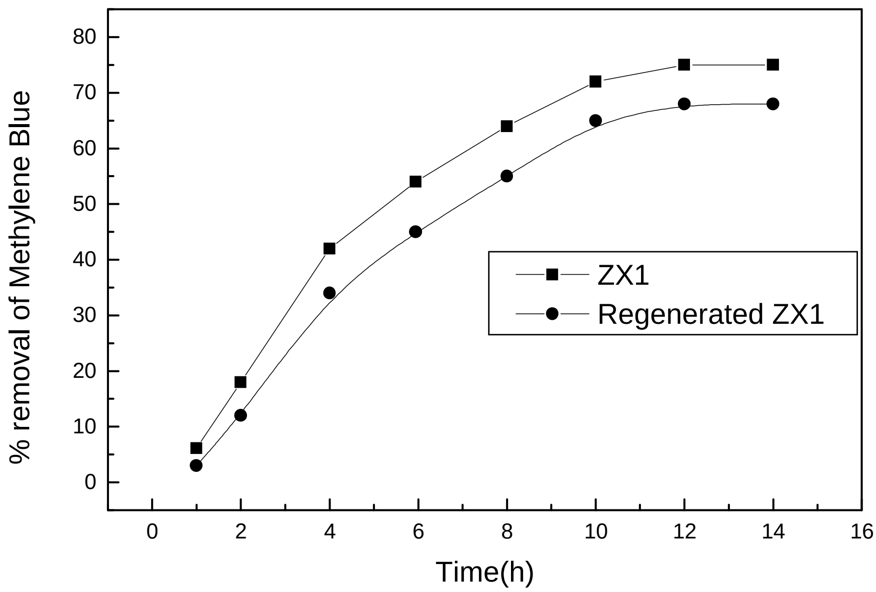

Figure 4.8 Adsorption over fresh and regenerated zeolite ZX_1 on Methylene blue

4.8 Isotherms:

Langmuir and Freundlich isotherms are used for fitting the experimental data in adsorption studies to understand the extent and degree of favorability of adsorption. The two isotherms depend on temperature and they have two constants each in their general form given respectively by equations (1) and (2), indicating

- Adsorption capacity: b of Langmuir equation and k of Freundlich equation
- Energy of adsorption: a of Langmuir equation
- Intensity of adsorption: (1/n) of Freundlich equation

$$q_e=b\,(aC_e)/(1+C_e) \qquad (1)$$

$$q_e=k\,(C_e)^{1/n} \qquad (2)$$

The Freundlich constant, n also indicates the degree of favorability of adsorption (Treybal, 1981). 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 a and k are used to estimate the enthalpy of adsorption (Singh and Srivastava, 2001). From the enthalpy of adsorption, the spontaneity (Patnaik and Das, 1995) and nature of adsorption as to whether it is exothermic or endothermic is predicted (Singh and Srivastava, 2001; Ajmal et al., 1998; Manju and Anirudhan, 1997; Raji and Anirudhan, 1997). A smaller value of (1/n) indicates a stronger bond between adsorbate and adsorbent (Ramu et al., 1992), while a higher value for k indicates rate of adsorbate removal is high (Ajmal et al., 1998). 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 paramaters. They are dependent on temperature since temperature is an important parameter in estimating the thermodynamic parameters.

4.8.1 Freundlich Isotherm

Table 4.4 The experimental data for freundlich isotherm are given below :

Zeolite Mass (mg)	Initial MO mass before adsorption (mg)	Final MO mass after adsorption (mg)	Mass of MO adsorbed (mg)	MO after adsorption (mg/dm^3)	Q=(X/m)	log C	log(X/m)
1	0.5	0.42	0.08	4.2	0.42	0.623	-0.376
5	0.5	0.28	0.22	2.8	0.056	0.447	-1.251
10	0.5	0.16	0.34	1.6	0.016	0.204	-1.795
12	0.5	0.07	0.43	0.7	0.00583	-0.154	-2.234
100	0.5	0.02	0.48	0.2	0.0002	-0.698	-3.698

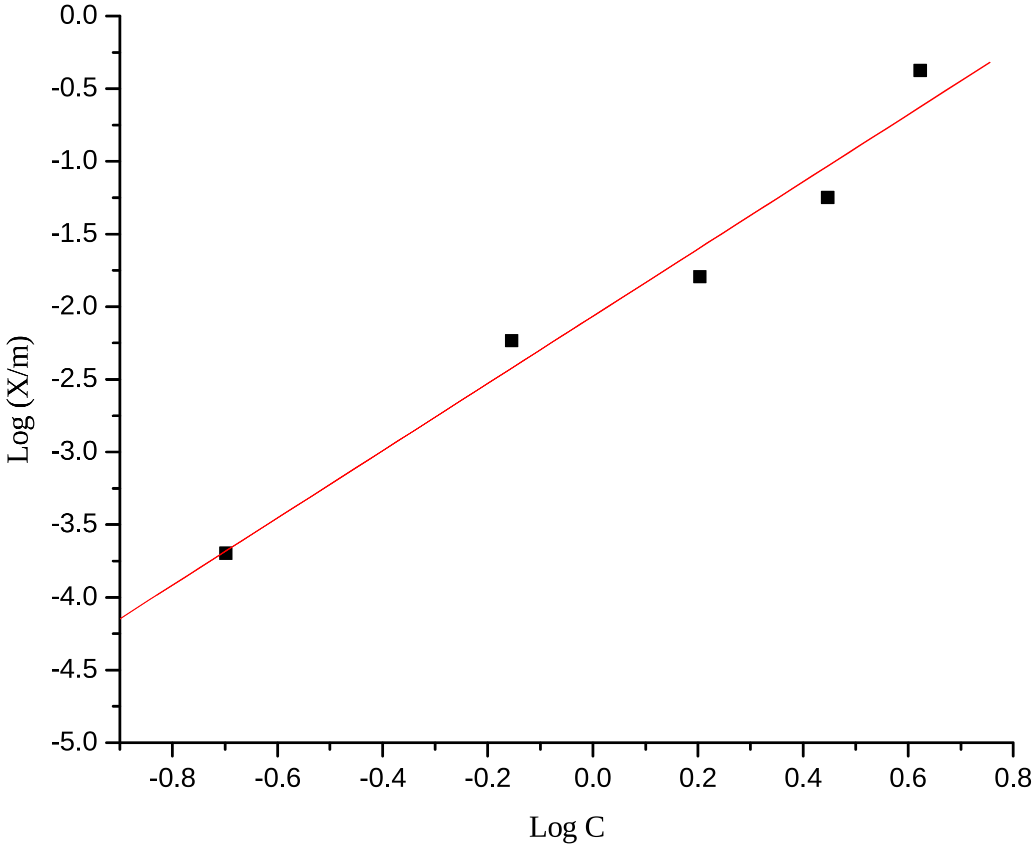

Fig 4.9 Freundlich isotherm curve

From the above graph, the adsorption coefficient K is 0.01266 and n is 1.43. The Freundlich constant, *n* should have values lying in the range of *1 to 10* for classification as *favorable* adsorption (Rao and Bhole, 2001; Raji et al., 1997).Hence the above data fit the freundlich isotherm. The Correlation coefficient was found to be 0.998.

4.8.2 Langmuir isotherm:

Table 4.5 The experimental data are given below for Langmuir isotherm:

C	1/C	X	1/X
4.2	0.238	0.42	2.38
2.8	0.3571	0.056	17.857
1.6	0.625	0.016	62.5
0.7	1.428	0.00583	171.52
0.2	5	0.0002	5000

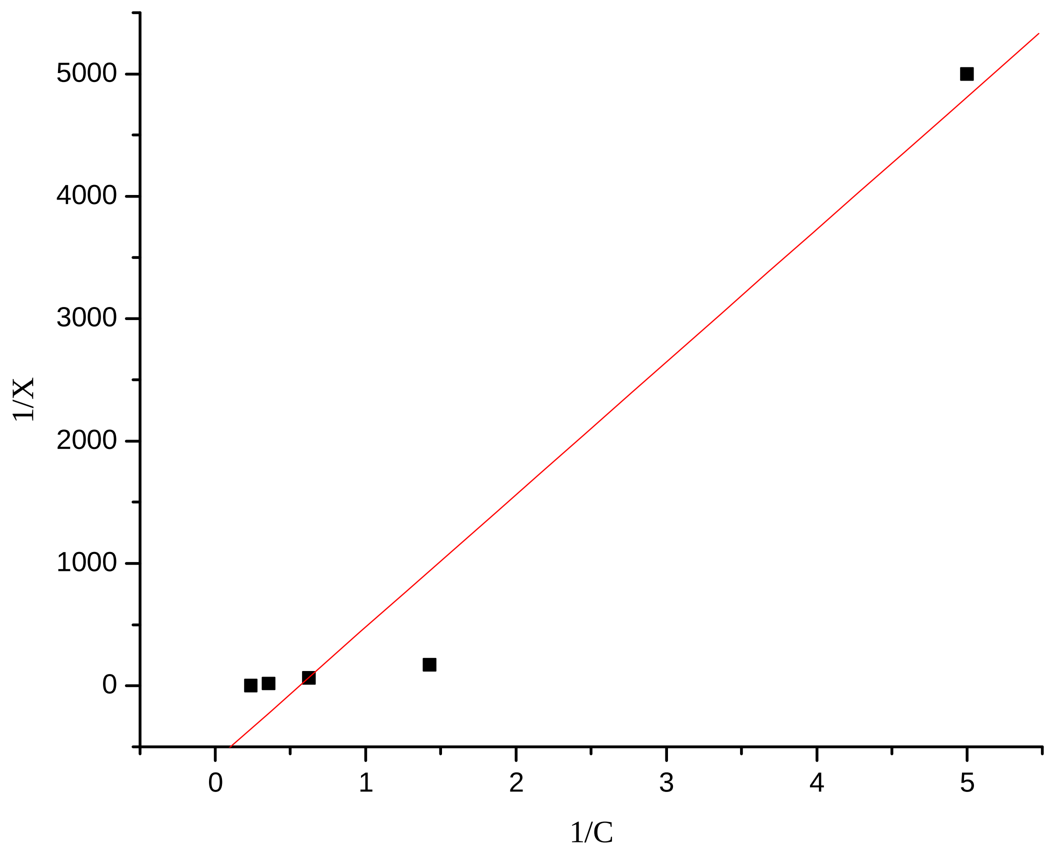

Fig 4.10 Langmuir isotherm curve

The above graph shows that, experimental data doesn't fit the Langmuir isotherm.

CHAPTER 5

CONCLUSIONS

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 different types of pure zeolites at suitable treatment conditions. The properties of zeolites material formed strongly depended upon the treatment conditions and composition of the raw materials. Zeolites of varying surface area, silica/alumina ratio, and crystallinity were obtained by changing the reaction parameters such as aging time, fusion temperature and fly ash/ NaOH ratio**.** 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. It can also be applied to wastewater treatment and ion exchange applications . This work, therefore, shall be very much useful to synthesize zeolites at low cost and apply it in commercially important fields. 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. The % removal with increase in the pH of the solution increases is almost constant within the range of of solution pH 8-10 . The high temperature regeneration was conducted at 540^0C for 5 h. which shows that regenerated catalyst has adsorption capacity slightly less than the fresh catalyst.

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