EVALUATION OF FLY-ASH BASED ZEOLITE AS AN ADSORBENT FOR REMOVAL OF LEAD IN AQUEOUS SYSTEMS

[1]**Varandani Sonia**　　[2]**Prabhu Pradnya**

Associate Professor,　Principal

[1]Department of Chemistry,

Smt. C.H.M College, Ulhasnagar, 421003, Mumbai, India

Abstract: The present study was initiated after the water catastrophe in Flint Michigan, USA (2014), when lead, a toxic metal seeped into drinking water and caused a massive health crisis and a state of emergency. The adsorption and treatment of lead in aqueous system was investigated using fly ash-based zeolite A sodalite (FAZAS). Fly ash, the starting material of FAZAS is inexpensive, abundant and currently underutilized. The fusion treatment of acidified fly ash with sodium hydroxide at 600ºC followed by hydrothermal treatment in presence of sodium aluminate results in formation of FAZAS. The FAZAS was characterized by XRD, SEM, FTIR spectroscopy and point of zero charge measurement. Modification of raw fly ash into FAZAS altered the ratio of Si: Al, increase the surface area and increase its utility as adsorbent. The adsorption capacity and estimation of efficiency of synthesized FAZAS for the removal of Pb was carried out in batch equilibrium wherein the influence of contact time, pH, and initial concentration of lead and FAZAS dosage on the adsorption process was investigated. It was found that the adsorption capacity of FAZAS increases with increase in concentration of Pb loaded on it. Removal efficiency was 99.88% at low concentration (20ppm) of lead solution and low dose ($0.4g/dm^3$) of the adsorbent. The moderate acidic condition (pH 3.0 to 5.00) had significant impact on adsorption capacity. The equilibrium data analyzed by two classical isotherm models, Langmuir and Freundlich, showed that the data agreed with both these isotherms. The maximum monolayer capacity of sodalite zeolite was found to about 100 mg per gram. The pseudo second order kinetic models helped to determine adsorption rate constants. Thermodynamic studies indicate that the adsorption process was spontaneous and adsorption was exothermic in nature. In the present studies, high temperature combustion at 823.15K for 3 hours has been used for regeneration of used FAZAS. The work concludes that sodalite could be effectively employed as an effective low-cost adsorbent for the removal of lead from aqueous solutions and the spent FAZAS can be recycled and reused for 5 cycles with decreasing efficiencies.

Index Terms: Fly ash, Zeolite, Adsorption Efficiency, Adsorption isotherms, Regeneration

Nomenclature		Abbreviations	
CFA	calcined acid treated fly ash	C_0	Concentration of lead (ppm) at beginning of batch equilibrium Experiment
FAZAS	Fly ash-based Zeolite A with Sodalite	C_e	Concentration (ppm) of lead metal at Equilibrium
FTIR	Fourier Transform Infra-Red	K	Kelvin
% R	Removal efficiency (%)	K_2	Adsorption rate constant for pseudo second-order (gm/mg min)
RFA	Raw fly ash	K_L	Constant for Langmuir isotherm model
SEM	Scanning Electron Microscope	m	Mass of synthesized zeolites (FAZAS) in grams
WHO	World Health Organization	Mg	Milligram
XRD	X ray diffraction	ppm	Parts per million
JCPDS	Joint Committee on Powder Diffraction	qe	Weight of Pb adsorbed (mg) per gram zeolites (FAZAS) at equilibrium (mg/gm).
		Q_o	- Maximum monolayer coverage capacity mg/gm
		R_L	Separation Factor for Langmuir isotherm model
		R^2	Coefficient of determination
		t	time in minutes
		V	Lead solution in dm^3 (L).

I. INTRODUCTION

Industrial revolution, the transition to new manufacturing process paved the way for modernization and urbanization. It has brought an extreme change from an agriculturally based economy to an industrial based economy. With so many benefits of the revolution, adverse effects predominate. The industries generate large quantity of effluent with variety of pollutants; which includes non-degradable chemicals, dyes, plastics and heavy metals[1,2]. The improper disposal of these waste commands industrial pollution and has adverse effects on environment and human beings too

Textile and pharmaceutical are the major industries of the developing countries and are responsible for global water pollution. The presence of toxic heavy metals in these industries are more notorious and hazardous. The unpleasant impact of the heavy metals on human health and ecosystem have led to concern about their influence on environment. Lead is the well-known toxic pollutant in industrial waste which is fatal and carcinogenic in nature. It taken into body through in inhalation, ingestion or skin adsorption. Exposure to lead cause detrimental and harmful effects on kidney, central nervous and reproductive system of human body with symptoms like headache, fever, fatigue, abdominal pain, joint pain, insomnia, irritability, altered consciousness, and hallucination

Numerous techniques are available for mitigation of lead from industrial waste[10,16]. Among all separation techniques, adsorption is most suitable, simple and effective technique for the removal of non-bio degradable pollutants including dyes and heavy metals from aqueous systems. Activated carbon, Clay minerals, biomaterials, Industrial solid waste and zeolites are significant and promising adsorbents for the removal of industrial pollutants. Zeolites, the group of crystalline hydrated aluminosilicates with clearly defined three-dimensional structure are captivating and enthralling adsorbent materials that have engrossed researchers and chemical industrialists. A Swedish mineralogist, Axel Fredrick Cronsted, discovered zeolite (stilbite) in 1756[11]. Zeolites swells and froth on heating (loose water and appears to boil), hence Cronsted called these minerals as "boiling stones". The several advantages of natural zeolites minerals are porous structure, high purity, thermally stable, ion exchange selectivity, decent resistance towards chemical substances and hence have plentiful and substantial applications in agriculture, water treatment, sewage treatment, laundry detergent, petrochemical refining etc. The wide applications and rarity of natural zeolites, chemist began to synthesize zeolites. Currently, there are more than 80 naturals zeolite minerals and more than hundred synthetic applications. The huge demand of natural and synthetic zeolites has increased its market value and the cost. It is essential to look for inexpensive resources to swap the natural as well as synthetic zeolites.

In India, more than 70% of power is generated thermally mainly using coal. Coal firing plants produces a fine, glass-like powder called fly ash. The X ray fluorescence (XRF) reveals that the chief components of fly-ash are of Si and Al in major amount and minor amounts of Na, K, Fe, Ca, Ti and S. The composition of fly ash varies from place to place. The X-ray diffraction (XRD) pattern and scanning electron microscopic (SEM) images exhibits the strongest peaks due to Mullite and quartz and mainly amorphous characteristic. [22,23,24]. A 2016-17 report on fly ash generation at coal/ lignite based thermal power stated that 169.25 million tons of fly ash was produced of which 62.15 million tons (36.72%) remained un-utilized. The unspent fly ash needs to be treated prior to disposing otherwise it may cause pollution and disruption in ecosystem. Keeping this in mind it is essential to place great emphasis on developing novel application for fly ash. Conversion of fly-ash to zeolite is highly perceivable strategy.

Several researchers [17,21] converted fly ash into diverse types of zeolites, characterized these using X ray diffraction, scanning electron microscope, FTIR and BET and studied the adsorption capacities of the modified fly ash for various cations and dyes. The cost of synthesized zeolite is estimated one fifth of the commercially available zeolites. Thus, conversion of fly ash into zeolite, partially resolve the problem of disposing fly ash and consequently minimize the impact of it on environment and provide cost effective adsorbent for pollutant in industrial effluent.

In the present study, the fly ash was collected from the Maharashtra state. The feasibility of lately developed synthesis protocols for designing novel zeolite material from fly ash was demonstrated. The product obtained was characterized using FTIR, XRF, XRD, SEM and BET surface area measurement. The adsorption capacity and removal efficiency of the zeolite material was studied for lead. The parameters influencing the adsorption such as, pH of lead solution, mass of zeolite material, initial concentration of lead solution, contact time and temperature were studied. The adsorption mechanism was described with the evaluation of adsorption isotherms, kinetics and thermodynamics study. The dispose of spent zeolite material is also a matter of concern. A protocol for regeneration of spent zeolite material was designed and the adsorption capacity of regenerated material was studied at optimum conditions

II. METHODS AND MATERIALS:

2.1 Raw Fly Ash:

Raw fly ash was collected from a thermal power plant located in Maharashtra, India. The RFA was sieved through a sieve of 80 mesh size. The fly ash with uniform size particles was used to synthesize fly ash-based zeolite A with sodalite (FAZAS)

2.2 Chemicals:

Analytical grade chemicals such as Sodium hydroxide (NaOH), Sodium aluminate (NaAlO$_2$), HCl, HNO$_3$, and Pb (NO$_3$)$_2$ sheets were purchased from S D Fine chemicals, Mumbai India. These were used without any additional refinement. Glassware used for this experiment was also cleaned and where required was calibrated by a standard procedure.

Stock solution of lead was prepared using analytical grade Lead (II) nitrate, propylene Erlenmeyer flasks were used for adsorption studies to avoid error due to adsorption loss on inner surface of glass container.

2.3 Synthesis of fly ash-based Zeolite A with sodalite (FAZAS):

The sieved RFA was calcined in a silica crucible by heating at 1173.15K for three hours in a muffle furnace to eradicate low boiling undesirable materials present in the raw fly ash. CFA was then treated with hydrochloric acid (1:3) at 363.15-373.15K for 120 minutes with constant stirring. Acid treatment was carried out in a controlled manner and it helped to remove iron (Fe) from CFA and also dealuminated the fly ash. The resultant solution was filtered to collect CFA on Whatman paper 41. The excess of acid associated with CFA was expelled using double distilled water and was oven dried at 363.15K for about 30 minutes. The washed and dried CFA was mixed uniformly with NaOH (1:1.2). The mixture was fused (873.15K) in a silica crucible in a muffle furnace for 180 minutes. The cooled fused mass was then mixed with equal amount of sodium aluminate. This mixture was stirred continuously at 363.15K in a thermostat with double distilled water. After stirring for two hours the reaction mixture was kept aside for six hours for ageing and was filtered to obtained residue. Double distilled water was used as washing liquid to remove excess of alkali. The washed residue was then dried in an oven at 333.15KC to obtain FAZAS. It was further stored in an air tight plastic container for experimental purpose.

2.4 Characterisation of FAZAS:

2.4.1. Spectroscopic Techniques:

X ray diffraction analysis was carried out to determine mineralogical composition of RFA and FAZAS, using Cu Ká radiation.The identification of the type of minerals present in both RFA and FAZAS was done by using JCPDS software. SEM micrographs were acquired to understand shapes and sizes of RFA and FAZAS by using Cumeca SU 30 models.FTIR analysis was carried out on Hyperion Microscope 3000 with Vertex 80 FTIR system, Bruker Germany available at SAIF. IR spectrum was recorded in the range between 4000 cm^{-1} to 400 cm^{-}

2.4.2. Point of Zero Charge::

The pH at which the surface of an adsorbent is globally neutral is known as the point of zero charge (pHZPC). The adsorbent is protonated at pH less than pHZPC and has positive charge. Above pHZPC, the surface of the adsorbent is negatively charged. The point of zero charge (pHZPC) for synthesised FAZAS was measured using the pH drift method[38].

0.01 M NaCl (50 cm^3) solution in 2-12 pH ranges were prepared in conical flasks using either HCl or NaOH. Nitrogen gas was bubbled in each solution to expel carbon dioxide and the flasks were closed firmly. Adsorbent FAZAS (0.15g) were added carefully to each flask. All flasks were kept in orbital shaker at 200 rpm for 24 hours at room temperature. The final pH was recorded at the end of 24 hours. The plots of final pH versus initial pH were used to determine the points of zero charge i.e. the point at which the initial and final pH values were equal.

III. Adsorption Experimental Programme:

3.1. Stock Solution of Lead (II) Nitrate (Pb (NO₃)₂):

100 ppm aqueous solution of lead was prepared by dissolving 159.8 mg of lead (II) nitrate (Analytical Grade) in 10 cm^3 of distilled water and 3cm^3 of high purity concentrated nitric acid, by gentle stirring. After complete dissolution of lead nitrate, the resultant solution was further diluted to 1000 cm^3 with distilled water.

3.2.: Batch Adsorption Experiment (For Lead) :

Lead (II) Nitrate stock solution was diluted to the required concentration for batch adsorption experiment. 0.1 M HNO$_3$ and 0.1M NaOH were used to adjust the pH of the lead solution using pH meter. Adsorption studies to evaluate the adsorption performance of FAZAS and to design adsorption system for the removal of lead were carried out in triplicate using a batch contact protocol. The experiments were carried out by stirring FAZAS with 50 cm^3 of lead metal solution, in a wide mouth polypropylene Erlenmeyer flask (125 cm^3 capacity) in an orbital shaker (Remi Electrotechnics) at 150 rpm. After the equilibrium, the solution was filtered through Nylon syringe filters, 0.22-micron pore size and 25 mm diameter. The filtrate was analysed for estimation of concentration of lead at equilibrium by using ARCOS, Simultaneous ICP spectrometer (SPECTRO Analytical instruments GmbH, available at SAIF. Experiments were performed to investigate the influence of pH (1.5-9.0), loading dose (5mg/l-80mg/l), initial concentration of lead metal solution (5ppm -160ppm), on adsorption of lead on FAZAS. The adsorption equilibrium data obtained for these parameters were studied for best fitting of Langmuir and Freundlich isotherm models.

Percentage metal removed and metal adsorption capacity was calculated using following mass balance equations (1) and (2) respectively:

% metal removed (%R) $=\frac{(Co-Ce)}{Co} \; x \; 100$.   .. (1)

Metal adsorption capacity qe $= \frac{(Co-Ce)}{m} \; x \; V$ ... (2)

3.3. Adsorption Equilibrium isotherms [3, 15]

Langmuir isotherm and Freundlich isotherms are the most common isotherm models that can be obtained by plotting the quantity of adsorbate adsorbed per unit mass of adsorbent against the concentration of dissolved adsorbate, at constant temperature. These isotherms corelate the adsorbate uptake per unit mass of adsorbent (qe) with the equilibrium adsorbate concentration in the bulk aqueous phase (Ce). The applicability of the isotherm equation to the adsorption study can be judged on the basis of correlation coefficients.

3.3.1. Langmuir Isotherms:

Langmuir isotherm describes the formation of mono layer adsorbate on the outer surface of adsorbent and represents the equilibrium distribution of copper metal between the solid and liquid phase. This isotherm is expressed by equation (3)

$$q_e = \frac{Q_o K_L C_e}{1 + K_L C_e}, \qquad\qquad (3)$$

On linearization Langmuir equation can be expressed as equation (4)

$$\frac{Ce}{q_e} = \frac{1}{Q_0\ KL} + \frac{Ce}{Q_0} \qquad\qquad (4)$$

The slope and intercept of the plot of Ce/qe versus Ce assist to determine maximum adsorption capacity (Q$_O$) and Langmuir isotherm constant (K$_L$). K$_L$ characterises the ability of the given surface to adsorb the given solute from the mixture of solvent. The confirmation of Langmuir isotherm model depends upon the coefficient of determination, R^2

Additionally, separation factor RL is also calculated by equation (5)

$$R_L = \frac{1}{1 + (1 + KlQ0)} \qquad\qquad (5)$$

The R$_L$ value indicates whether adsorption is unfavourable (RL> 1), linear (RL= 1), favourable (0 < R$_L$< 1) or irreversible (R$_L$ = 0)

3.3.2 Freundlich Isotherm:

Freundlich isotherm describes the adsorption on heterogenous surface and is given by equation (6).

$$Logqe = LogK_f + 1/n\ log\ Ce \qquad\qquad (6)$$

The slope of the plot logqe vs log Ce provides the value of 1/n, that indicates the adsorption intensity of the adsorbate onto the adsorbent surface. The value of 1/n ranges from 0-1. The closer the value is to zero, the more is the homogeneity. The rate of adsorption and spontaneity of the adsorption of copper on FAZAS and FBZ were studied using kinetic isotherms and thermodynamic-isotherms.

3.4 Kinetic Adsorption Studies (Effect of Contact Time)

Effect of contact time was investigated by shaking 50 cm^3 of 20 ppm lead solution with 20mg of sodalite between 15 to 120 minutes, at the initial pH of 5.0 and at constant temperature of 30°C. Kinetics of adsorption was determined by analysing the amount of lead adsorbed per unit weight of sodalite (qt) at different time intervals. (15-120 minutes).

3.5 Thermodynamic Adsorption Studies (Effect of Temperature)

Effect of temperature on adsorption of lead on FAZAS were studied by estimating adsorption of 50 cm^3 of 20 ppm lead solution on 20 mg of FAZAS at different temperature (303-333K).

3.6 Regeneration of FAZAS[12,20]:

The desorption of Lead from spent zeolites to regenerate the active zeolites can be accomplished by altering the equilibrium conditions, either pH or temperature. In the present studies the regeneration of spent FAZAS was attained by heating the spent zeolite in a muffle furnace at 823.15K for three hours. At higher temperature the moisture of zeolites along with other volatile material and captured lead element vaporised out and the entire adsorbent surface was available for re-adsorption. The efficiency of regenerated zeolites for the adsorption of lead was investigated at optimum adsorption conditions.

IV RESULTS AND DISCUSSION[4,14,18,19]

4.1 Surface Morphology (Scanning Electron Microscopy) :

Figure 1 shows the shape of RFA as spherical beads while FAZAS occurs as mixture of spherical beads and cubic shape particles. The transformation of spherical particles into cubic particles indicates conversion of amorphous original fly ash to partially crystalline fly ash zeolites

Figure 2 depicts the particle size of RFA and FAZAS. The particle size of RFA ranges from 0.36 μm to 7.79 μm whereas the particle size of FAZAS range from 0.40 μm to 1.77 μm. The decrease in particle size confirms increase in surface area and signifies conversion of fly ash into zeolite. The conversion of amorphous character of original fly ash to crystalline nature in FAZAS further confirmed by XRD and FTIR studies.
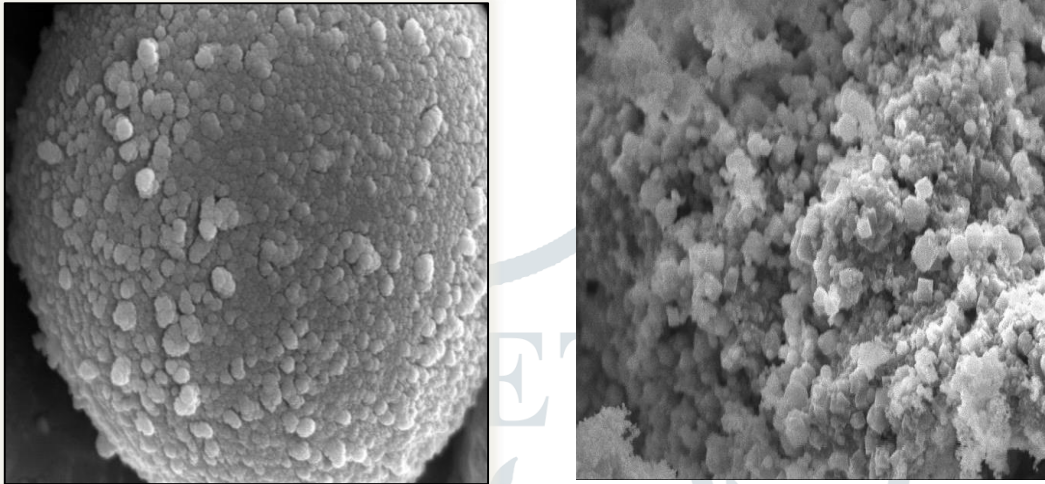
Figure 1 SEM images, L-R RFA (spherical) and FAZAS(Cubic)
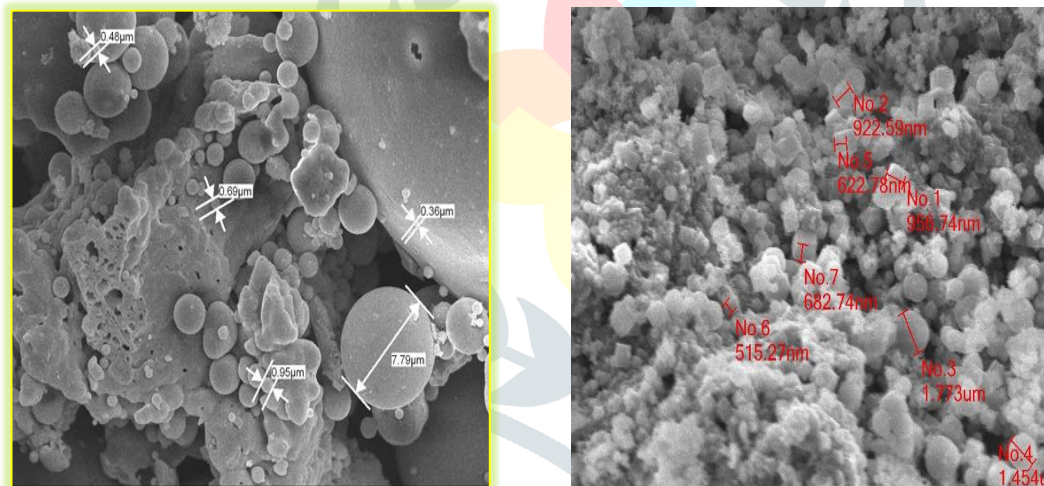
Figure 2 SEM Images L – R Particle size RFA (0.36μm -7.79 μm) and FAZAS (0.4μm -1.4μm)

4.2 Mineralogy (X-Ray Diffraction Spectroscopy – XRD)

The X- ray diffractogram (XRD) patterns of RFA and FAZAS are presented in Fig. 3A and 3B respectively. X'pert high score plus software was used to analyse XRD data of RFA and FAZAS. The XRD pattern of original fly ash depicts strong peaks of Quartz and Mullite and these peaks are almost absent in synthesised fly ash-based zeolite. The FAZAS exhibits the peak due to crystalline sodalite and zeolite A. This confirms the conversion of RFA into FAZAS. The increase number of sharp peaks in FAZAS indicates increase in crystallinity.
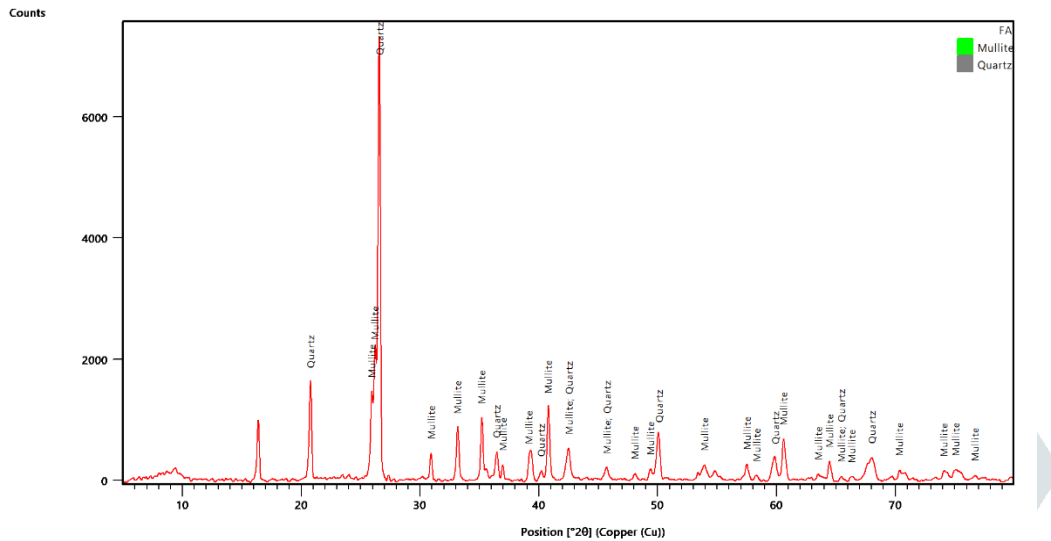
Figure 3A XRD Pattern of Raw Fly Ash (RFA)
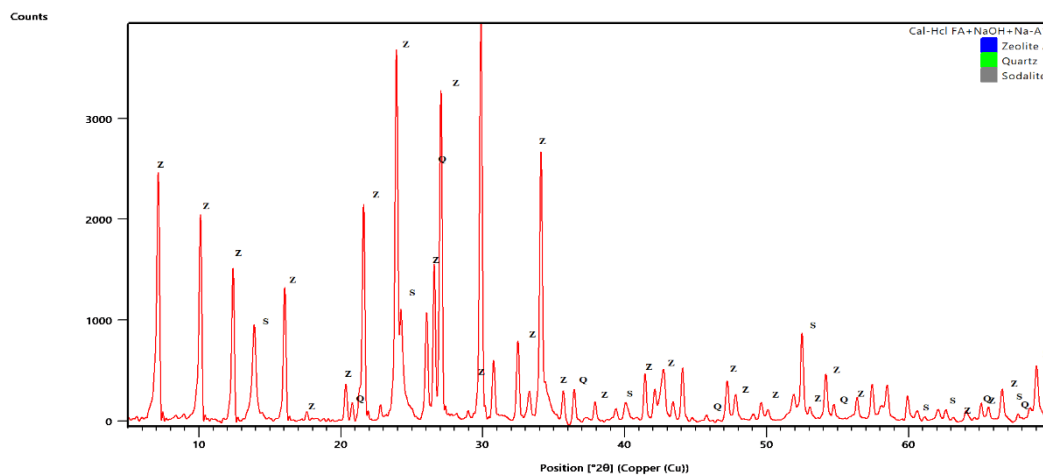
Figure 3B -XRD pattern of FAZAS

4.3 Structural Information (Fourier Transform Infrared Spectroscopy – FTIR[9,6]):

The FTIR spectra of RFA, Zeolite sodalite (FAZAS) are presented in Fig.4, The O-H stretching region (3200cm^{-1} to 3649cm^{-1}) provides information of hydroxyl groups attached to zeolite structure. The appearance of broad peak at 3353.57cm [-1] in FAZAS indicates strong hydrogen bonding in fly ash-based zeolites and signifies an asymmetrical stretching of OH group linked to Na^{+} and / or Al[+3] available on the surface of synthesised zeolites. The weak band at 1617.7 cm^{-1} in RFA is shifted to 1647.12 cm^{-1} in FAZAS and can be attributed to gain of Si[+4] during interaction of RFA with NaOH and synthesis of silicates. RFA and FAZ spectrum exhibit sharp peaks around 1000 cm^{-1}, i.e. peaks at 1091.69cm^{-1} in RFA and 971.96 cm^{-1} in FAZAS signifying asymmetrical stretching of Si-O-Si. The increase in sharpness in FAZAS confirms synthesis of silicates and change in its acidic characteristics. The appearance of weaker bands in between 800 cm^{-1} and 400cm^{-1} (667.02, 557.39, 465.75 and 414.6 cm^{-1}) in FAZAS corresponds to inter-particle pores and confirmation of crystalline silicates. The various peaks in the finger print region (1200- 900 cm^{-1}) show that FAZAS have multiphase mineral-logical　composition and possess polycrystalline silicates.
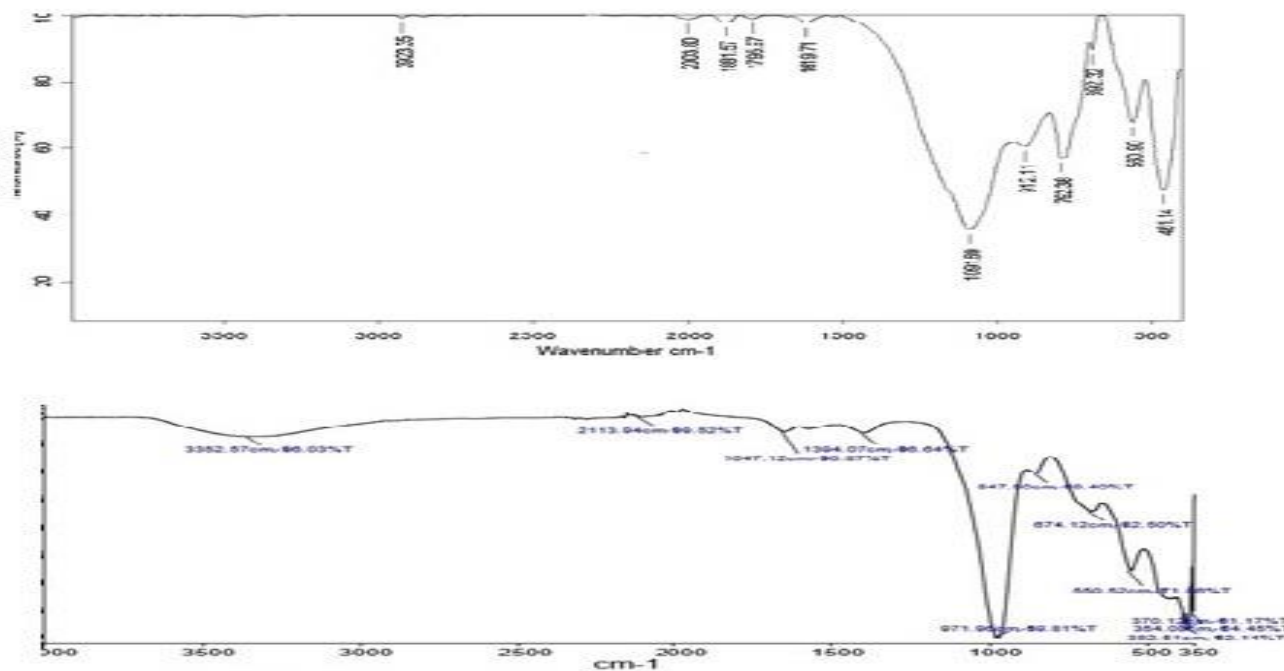

Figure 4 : FTIR Spectra of RFA(top) and FAZAS (Bottom)

4.4 Point of Zero Charge (pHZPC)

Figure 5 is the Plot of Final pH vs Initial pH of FAZAS in NaCl solution. From the Plot , pHZpc of FAZAS was found to be 4.5. At this point the surface of FAZAS is globally neutral. Below these values the surface is positively charged whereas, above this value, the surface of FAZAS is negatively charged.
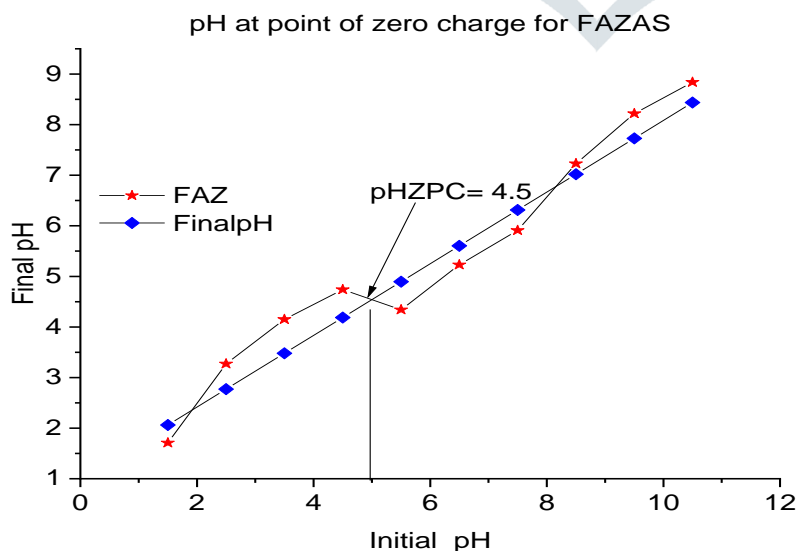

Figure 5: Point of zero charge, FAZAS

4.5 Effect of Variable parameters on Removal Efficiency (%) and Adsorption Capacity (mg / gm) of FAZAS :

4.5.1 Effect of Initial pH:

The solubility of metal ions and the stability of the adsorbent depends upon the initial pH of metal ion solution, during the adsorption process. The effect of pH on adsorption of Lead metal ion was studied by stirring 50 cm^3 of 20 ppm lead solution with 20 mg of FAZAS, in an orbital shaker at 150 rpm, at different pH (1.5 to 9) ranges and at 35°C. At the adsorption equilibrium, the concentration of lead metal in the aqueous phase was determined by inductively coupled emission spectroscopy.

Figure 6 exhibits the Plot of Amount of Lead Adsorbed per unit Weight of Adsorbent (mg/gm) (qe) and Removal Efficiency of Lead (RE%) against the pH of lead solution. The Fig 6 indicates that the adsorption capacity of FAZAS and Removal Efficiency of Lead increases when the pH changes from 1.5 to 3. The RE% and qe is approximately constant between pH 3 to 5. The maximum Adsorption capacity of FAZAS is 49.98 mg/gm and percentage Removal Efficiency are 99.96%. at pH approximately 4.5 (Table 1)

The surface FAZAS is highly protonated at lower pH. At lower pH the competition at adsorption sites for proton and lead metal is significant and thus the electrostatic repulsion between adsorbent and adsorbate is remarkable, that lowers the adsorption. As the pH increases from 3 to 5, the electrostatic repulsion decreases thus enhancing the percentage Adsorption capacity of FAZAS. At higher pH (>5.5), where the concentration of hydroxide ions is substantial, the precipitation of lead as lead hydroxide occurs significantly and percentage efficiency and adsorption capacity drop down vividly. The results indicate that the optimum pH for the removal of lead is 4.5, due to ion exchange and electrostatic phenomenon. Several researchers (M.K. Mondel (2008), Naeema H. Yarkandi (2014))[13,25] have reported similar observations.
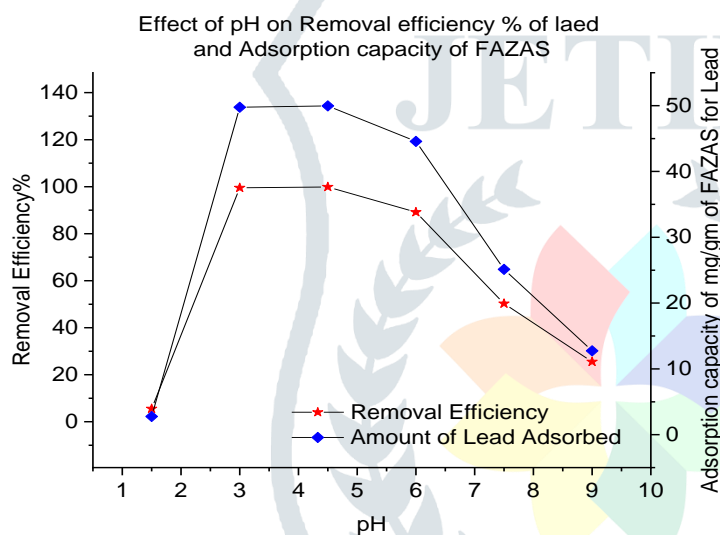

Figure 6: Effect of pH for removal of lead

Table 1, Effect of pH for removal of lead

pH	Removal Efficiency RE%	Adsorption Capacity qe (mg / gm)
1.5	5.55	2.78
3	99.91	49.96
4.5	99.96	49.98
6	94.15	47.08
7.5	50.25	25.13
9	25.5	12.75

4.5.2 Effect of Mass of FAZAS

The effect of Mass of FAZAS on the Removal Efficiency of Lead (RE%) and Amount of Lead Adsorbed (mg / gm) on FAZAS was investigated and is shown in Fig 7 and Table 2. In this study, 50 cm^3 of 20 ppm of lead solution was shaken separately with different doses of FAZAS, for 60 minutes at pH 4.5 at 150 rotations per minute. From Table 2 and fig 7 indicates that increase in FAZAS dose from 0.005 g to 0.080 g results in rise of Lead removal that is a result of increase in number of sites on adsorbent.

The decrease in the amount of lead adsorbed per gram of adsorbent mg/gm (qe (adsorption capacity)) with increasing adsorbent loading is due to the concentration gradient between lead in the solution and its concentration on the adsorbent surfaces. It has been reported that at higher dosage, the driving force due to adsorbate decreases and adsorption capacity also decreases. A similar trend is observed in the present study wherein the adsorption capacity decreases as the adsorbent dosage increases. The optimum dose of FAZAS for further studies is 0.4 gm / dm^3.
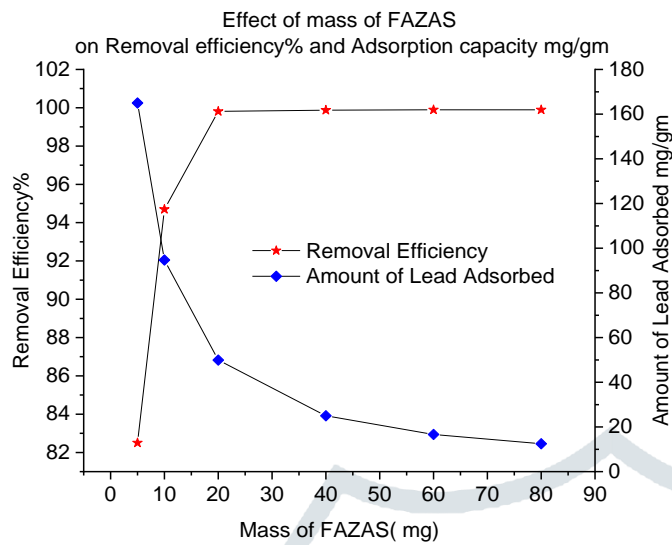

Figure 7: Effect of mass of FAZAS on Removal Efficiency (RE%) and Amount of Lead Adsorbed (mg / gm)

Table 2 : Effect of Mass of FAZAS

Dose (mg)	Removal-Efficiency (%RE)	Adsorption Capacity qe (mg / gm)
5	82.50	165.00
10	94.70	94.70
20	99.51	49.76
40	99.88	24.97
60	99.90	16.65
80	99.90	12.49

4.5.3 Effect of Initial concentration of Lead metal:

Adsorption of metal on adsorbent mainly depends upon availability of active sites on it. The number of sites on adsorbent are substantial when the concentration of the adsorbate is low. At higher concentration of the metal, the number of sites is not sufficient to adsorb the adsorbate significantly. This is clearly evident from the Fig 8 and Table 3. Removal efficiency of lead onto FAZAS, decreases with increase in concentration of lead metal. An increase in amount of lead adsorbed per unit mass FAZAS is observed with increase in initial concentration of lead. The increase in adsorption capacity can be attributed to high potential driving force of lead that overcome all mass transfer resistance between the aqueous and solid phase.
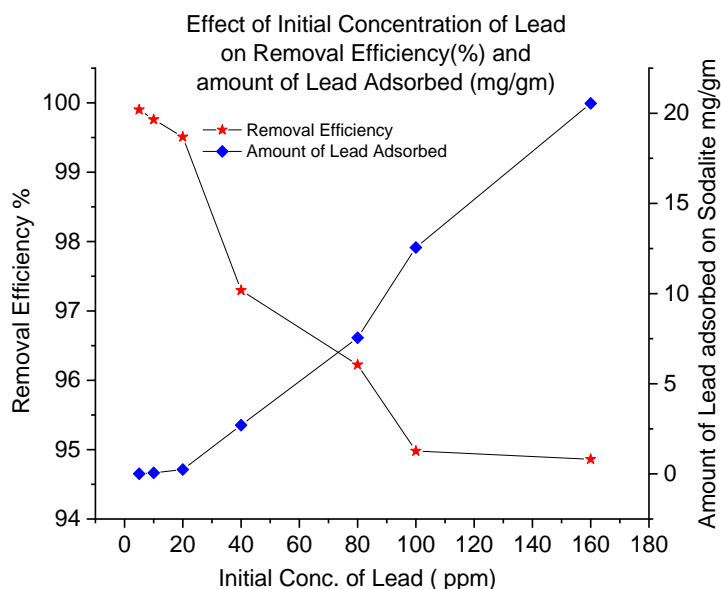
Figure 8 : Effect of initial concentration of Lead (ppm)

Table 3 : Effect of initial concentration of Lead (ppm)

Initial Concentration of Lead ppm	05	10	20	40	80	100
Removal Efficiency %	99.9	99.76	99.51	97.30	96.22	94.98
Amount of lead Adsorbed mg/gm	0.01	0.06	0.25	270	7.55	12.55

4.6 Modelling and Interpretation of Adsorption Isotherms[8]:

4.6.1 Adsorption Equilibrium Isotherms:

The Experimental Adsorption data for lead were fitted by Langmuir and Freundlich models These models explain the Adsorption mechanism and the intensity of Lead - FAZAS interactions. The plots for Langmuir and Freundlich isotherms in Fig. 9 and Fig. 10 and the Values of Parameters and Correlation Coefficient for each Isotherm model is shown in Table 4.

The data on Adsorption Isotherm studies evidently specify that the adsorption behavior of Lead on FAZAS fits on Langmuir Isotherms as well as on Freundlich Isotherms.   The correlation coefficient (R^2) value of Freundlich Isotherm (0.9833) is higher than Langmuir isotherms (0.904). This suggest that the adsorption data for lead fits more to Freundlich model. The maximum monolayer capacity for FAZAS is 100 mg/gm. The value of n is greater than unity (2.31) that indicates adsorption intensity is favourable at high concentration.
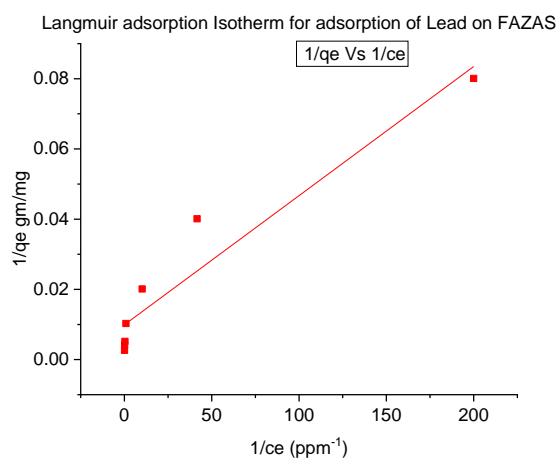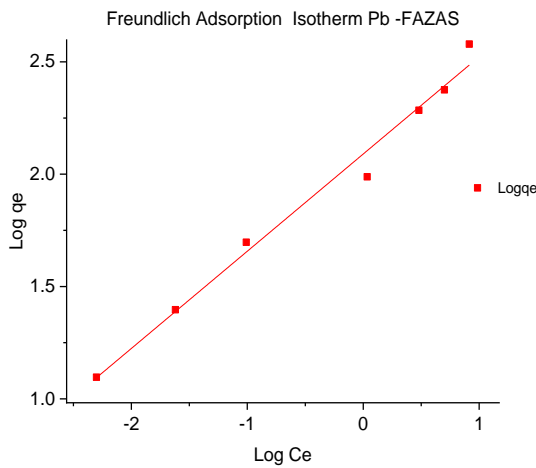

Figure 9: Langmuir Adsorption Isotherm Pb – FAZAS

Figure 10: Freundlich Adsorption Isotherm Pb – FAZAS

Table 4 Values of different Langmuir and Freundlich Adsorption Isotherm Pb- FAZAS

Values for Langmuir Model		Values for Freundlich Model	
Parameters	Pb- FAZAS	**Parameters**	Pb- FAZAS
Q_0 **(mg/gm)**	100	**N**	2.31
R_L	0.9898- 0.752	K_f**(mg/gm)**	122.99
R^2	0.904	R^2	0.9833

4.6.2 Kinetics Studies: (Time dependency Studies)[5]

Effect of contact time was investigated by shaking 50 cm^3 of 20 ppm lead solution with 20mg of FAZAS between 15 to 120 minutes, at the initial pH of 5.0 and at constant temperature of 30°C. Kinetics of adsorption was determined by analysing the amount of lead adsorbed per unit weight of FAZAS (qt) at different time intervals. (15-120 minutes). The amount of lead adsorbed per unit weight of FAZAS at different time is presented in Fig. 11
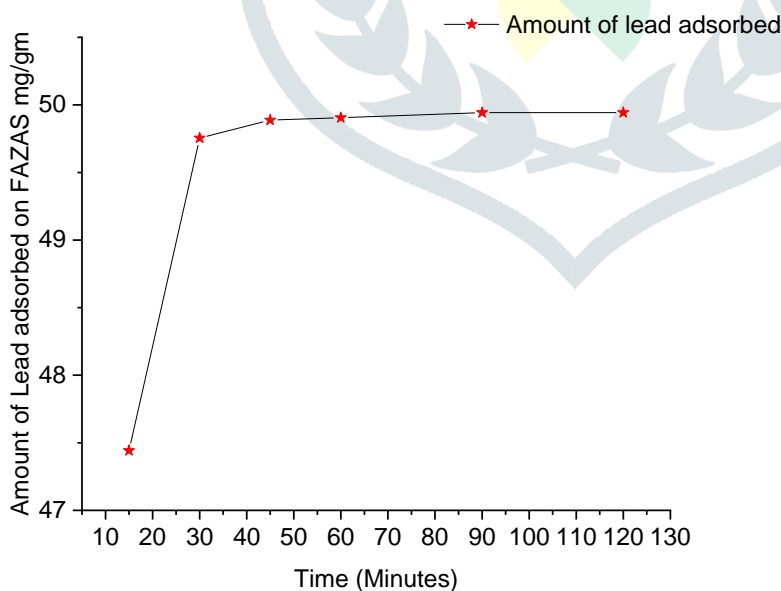

Figure 11: Effect of Contact Time (minutes) on Amount of Lead Adsorbed (mg/gm)

From Fig. 11, it is confirmed that the adsorption process depends upon time. The amount of lead adsorbed increases rapidly between 15 minutes to 30 minutes and remains approximately constant beyond 30 minutes.

The reaction was found to follow Pseudo Second Order Kinetics, the Linearized form of Pseudo Second Order equation is expressed as equation (7),

$$\frac{t}{qt} = \frac{1}{K_2 qe^2} + \frac{1}{qe}t, \qquad\qquad ... \qquad\qquad (7)$$

The Pseudo Second Order plot (t/qt against t) is presented in Fig. 12 and Rate Constant, Adsorption Capacity at equilibrium and Correlation Coefficient for FAZAS is presented in Table 5. The Calculated values of Adsorption Capacity (qe_{Cal}) are very close to Experimental values of Adsorption Capacity (qe_{exp}). Thus, the Adsorption of Lead on FAZAS is described Pseudo Second Order with Strong Positive Correlation (0.999)
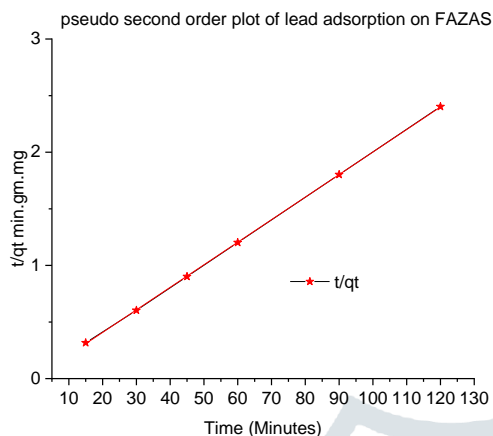

Figure 12: Pseudo Second Order plot of Lead Adsorption on FAZAS

Table 5 : Pseudo Second Order parameters of Lead Adsorption on FAZAS

Adsorbent	Pseudo Rate Constant K2 min^{-1}	Adsorption Capacity mg/gm	Correlation coefficient
FAZAS	9.5×10^{-2}	50.2	0.999

4.6.3 Thermodynamics Studies[7]

In the present work, Adsorption behaviour of Lead on FAZAS was studied at different temperatures. Thermodynamic parameters ΔG^o (KJ/mole), change in Standard Gibbs Free Energy, ΔH^o Change in Enthalpy (KJ/mole) and ΔS^o change in Entropy (KJ/mole/K), were calculated using equation (8) and Gibb's free Energy equation (9)

$$\Delta G^o = - RT \ln K_D, \qquad\qquad\qquad ... (8)$$

Where R is the universal gas constant (8.314×10^{-3} KJ/mol K), T is the temperature in kelvin (K) and K_D is the thermodynamic distribution coefficient, $K_D = \frac{Co - Ce}{Co}$

And Gibb's Free Energy equation, $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$ $\qquad\qquad$ ... (9)

Combining equation (8) and (9), we get

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad\qquad\qquad ... (10)$$

Figure 13 shows the Vant' Hoff plot of ln K_D against 1/T which shows an excellent linearity. The Enthalpy change, ΔH° (KJ/mole), and the Entropy change, ΔS° (KJ/mole/K), for the adsorption processes were obtained from the intercept and slope of Equation (10) and are presented in the Table 6.
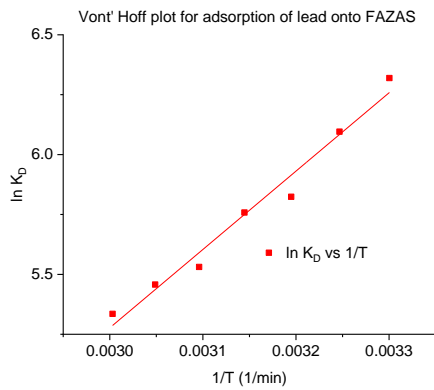
Figure 13: Vant' Hoff Plot for Adsorption of Lead on FAZAS

Table 6: Thermodynamic Parameters for Adsorption of Lead on FAZAS.

Temperature K	ΔG° - Change in Gibbs' Free Energy	ΔH° Change in Enthalpy	ΔS° Change in Entropy
303	-15919.2		
308	-15609.3		
313	-15155.8		
318	-15223.9	-27.2	-0.037
323	-14853.3		
328	-14882.7		
333	-14771.1		

The Negative values of ΔG° confirm the Feasibility of the Process and the Spontaneous nature of Adsorption of Lead on FAZAS.

The Increase in the Negative value of ΔG° with an increase in Temperature indicates that the Adsorption process of Lead on FAZAS is more Favourable at Lower Temperature.

The Negative value of ΔH° (27.195KJ Mole^{-1}) indicates that the Adsorption process with FAZAS is Exothermic. ΔS° values enlightens the disorder at solid/liquid interface in the adsorption system. Negative value of ΔS° (0.037) , reveals that the System gets Disordered to Less Extent.

4.7 Adsorption studies on regenerated FAZAS:

The removal efficiency and adsorption capacity of regenerated FAZAS were studied for the lead metal. Herein 50 cm^3 of 20 ppm lead solution was stirred with 20 mgs of regenerated zeolites in an orbital shaker for 60 minutes at 303.15K.. After 5 cycles removal efficiency of FAZAS decreased from 99.81% to 12.2 %. The FAZAS was heated at 823.15K for three hours to remove lead from FAZAS surface. Removal Efficiency of FAZAS for removal of lead metal, for every cycle is shown in fig.14.
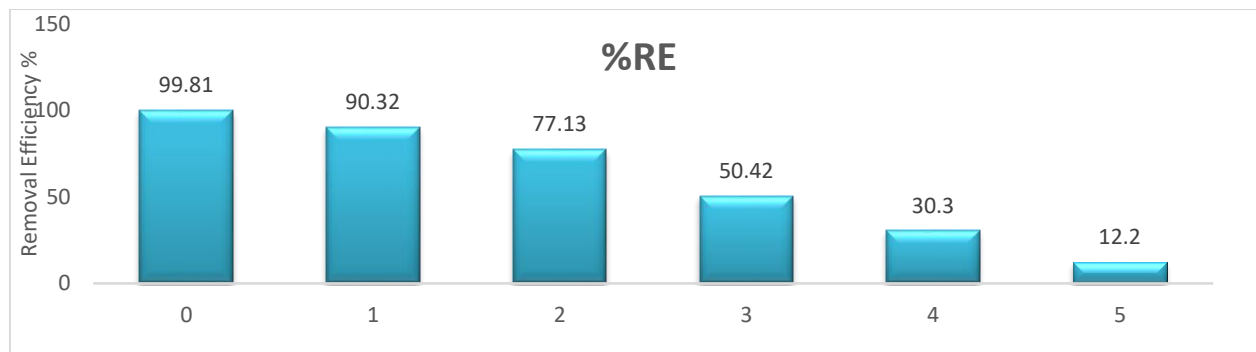

Figure14 Removal efficiency (%) after every cycle of Regenerated FAZAS

V. CONCLUSION:

The Hydrothermal Treatment to fused mass of RFA and NaOH, in presence of Sodium Aluminate results in formation of FAZAS. The cubic structure, FTIR, SEM, and XRD studies reveals the conversion of raw fly ash into FAZAS.

Adsorption studies for the removal of lead showed that optimum adsorption can be achieved at pH 4.5, when 20 ppm of lead solution was shaken with 0.4gms/dm^3 of zeolite for 60 minutes. The adsorption data fitted most to Freundlich adsorption isotherm when compared with Langmuir adsorption isotherm. The maximum monolayer capacity of FAZAS was 100 mg/gm. The adsorption proceeds according to the pseudo-second-order model. Negative $\Delta H°$ and $\Delta S°$ values of Pb-FAZAS system indicated that the adsorption of lead on FAZAS was Exothermic and structural changes are minimum.

Combustion process was employed to regenerate the used FAZAS . The removal efficiency of the regenerated zeolite decreased to 12% after 5 cycles. Finally, it can be concluded that synthesized zeolites from fly ash are novel, inexpensive green adsorbent for removal of lead metal ions from aqueous solutions

VI. ACKNOWLEDGMENT:

REFERENCES:

[1] Abbas, M.,Aksil,T,and, Trari, M. 2017. Isotherm and thermodynamic study of the adsorption of Toxic metals by the Apricot stone. Environ Anal Eco Stud. 1(1) : 1-3

[2] Arbabi, M. and Golshani,N. 2016. Removal of copper ions from industrial waste water: A review of removal methods. International journal of Epidemiological Research. 3(3) : 283-293

[3] Arivoli, S., Asthuni, A. K, Pandian, P., Partasarathy, S. and Venkatraman, B.R., Adsorption dynamics of copper ions by Acid Activated low cost carbon, Kinetic, thermodynamic and Equilibrium Studies. 2008.*Rasayan J Chem*, 1 (2), 276-287.

[4] Arshadi, M., Amiri, M.J.and Mousovi, S.2014 Kinetic, Equilibrium and Thermodynamic investigations of Ni (II), Cd (II), Cu (II) and Co (II) adsorption on barley straw ash, *Water, Resources and Industries*, 6,1-17.

[5] Aseel, M. ,Aljeboree, A., Alshirifi,N,and Ayad F. Alkaim. 2017.Kinetics and equilibrium study for the adsorption of textile dyes on Coconut shell activated carbon. Arabian Journal of Chemistry. 10(2).3381- 3393.

[6] Byrappa, K., and Suresh Kumar, B.V.,2007. Characterisation of Zeolite by Infra-red Spectroscopy. Asian Journal Of Chemistry. (6) . 4933-5935.

[7] Dar, B . Taher, A. Wani,A. and Farouqui, M. 2013.Isotherms and thermodynamics studies on adsorption of copper on powder of shed pods pf Acacia nicotica. Journal of Environmental chemistry and Ecotoxicolgy. 5(2)17-20

[8] G.Vijayakumar 1, R.Tamilarasan 2, M. Dharmendirakumar. 2012. Adsorption, Kinetic, Equilibrium and Thermodynamic studies on the removal of basic dye Rhodamine-B from aqueous solution by the use of natural adsorbent perlite. J. Mater. Environ. Sci. 3 (1) (2012) 157-170

[9] Gonghu Li.2005 FTIR studies of zeolite material: Characterisation and Environmental Application. PhD (Doctor of Philosophy) thesis, *University of lowa*

[10] Gunatilake, S.2015.Methods of removal of Heavy metals from industrial waste water.Journal of multidisciplinary Engineering Science studies, 1(1)12-18.

[11] Jha,B. and Singh.D. 2012.Zeolitization characteristics of a fly ash from wet and dry disposal system. Acta Geotechnica Solvenica.4.263-273
Journal of Clean Energy Technologies, 2(2),

[12] Kulkarni,S.and Kaware, J.2015. Desorption studies for low cost adsorbents. International Journal of chemical studies. 3(2) 38-41.

[13] Mondal,M.2008. Removal of Pb(II) from industrial wastewater by using various natural materials – a review.Int. J. Sus. Dev. Plann. 3(4). 377–393

[14] Nath, K., Ghor,J Shah,N. and Modi,K. 2007.Physico Chemical Parameters, isotherms, sorption Kinetics and column operation for adsorption of copper (II) from waste water using fly ash. Journal of Scientific & Industrial Research. 66.170-177.

[15] Newton, E., Azibaola, I. Nimibofa ,A.and Donbebe,W.2017. Modeling of Adsorption Isotherms for Methylene Blue Sorption onto Fly Ash Modified with Hydrochloric acid. Journal of Chemical Science and Technology.6(1) 1

[16] Oghenerobor, B., Gladys, O and Tmilola, O.2014. Heavy metal pollutants in wastewater effluents: Sources effects and remediation. Advances in Bioscience and Bioengineering 2(4): 37-43.

[17] Ojha,K.,Pradhan,N. and Samanta, A. 2004,. Zeolite from Fly Ash: Synthesis and Characterization. Bull. Mat. Sci., 27 (6) 555– 564.

[18] Penpun ,T. 2014. Adsorption of Copper Using Pomelo Peel and Depectinated Pomelo Peel

[19] Praseetha P. and Krishnaveni M. Methylene blue adsorption from aqueous solution using activate carbon – a review . Research Journal of Chemistry and Environment. 23 (4) April (2019 Research Journal of Chemistry and Environment 23 (4). 109-116 .

[20] Sayilgan,S.Mobedi,M., Ulku,S. 2016. Effect of regeneration temperature on adsorption equilibria and mass diffusity of zeolite 13X- Water pair. Microporous and mesoporous materials. 224: 9-16.

[21] Taamneh,Y and Sharadqas,S.2017.The removal of heavy metals from aqueous solution using natural Jordanian zeolite.Applied Water Science.7(4): 2021-2028

[22] Varandani, S.and Prabhu,P. 2016.Zeolite-A from fly ash: Synthesis and Characterization, International Journal of Chemistry. 5 (3&4) :313-323

[23] Visa, M.Bogatu C. and Duta, A. 2009. Simultaneous adsorption of dyes and heavy metals from multicomponent solutions using fly ash . Advanced Materials Research. 247. 79-82

[24] Woolard, C.D., Petrus, K. and Vander Horst,M. 2000. The use of a modified fly ash as an adsorbent for lead. Water SA 26(4)

[25] Yarkandi.N. 2014.2014. Removal of lead (II) from waste water by adsorption , Int.J.Curr.Microbiol.App.Sci 3(4): 207-228.