

# Adsorption Behaviour of Modified Zeolite as Novel Adsorbents for Fluoride Removal from Drinking Water: Surface Phenomena, Kinetics and Thermodynamics Studies

Sanghratna Waghmare, Tanvir Arfin, Sadhana Rayalu, Dilip Lataye, Samujjwala Dubey, Sangeeta Tiwari

**Abstract**— The present study is showing the improved removal of fluoride from water with the help of zeolite, a modified form of calcium and aluminum (CAZ) for consumption, characterized as XRD, FTIR and SEM – EDAX and BET surface area analysis along with the Batch adsorption studies were done which include the effect of dose, contact time, pH, initial fluoride concentration and effect of other competing co – anions on the adsorption capacity of CAZ. According to the Langmuir adsorption capacity, was noticed as  $8.03 \text{ mg g}^{-1}$  for an initial concentration of  $10 \text{ mg l}^{-1}$ . It was later found that the data were suitable for Freundlich adsorption isotherm following the pseudo second order kinetics when the optimum pH range of removal was 4 to 8. It was also observed that the presence of anions such as nitrate, sulphate and chloride had no effect on the adsorption process. WHO relates to shows that leaching of aluminum could be permissible and CAZ would be significantly used for removing fluoride from drinking water without any hazardous effects.

**Index Terms**— Defluoridation, zeolite, Kinetic, adsorption isotherm

## I. INTRODUCTION

The most significant source of drinking water is the ground water which is consumed in large amount of all living organisms. It seems to be polluted by both the organic and inorganic agents [1]. The most serious threat to the ground water is the contamination by fluoride ion [2]. The various sources of fluoride are rocks, minerals such as fluorite, Phosphorite, Cryolite and Topaz etc., even the industrial

*Sanghratna Waghmare, Environmental Materials Division, National Environmental Engineering Research Institute, Nehru Marg, Nagpur, India, 07122247828.*

*Tanvir Arfin, Environmental Materials Division, National Environmental Engineering Research Institute, Nehru Marg, Nagpur, India, 07122247828.*

*Sadhana Rayalu, Environmental Materials Division, National Environmental Engineering Research Institute, Nehru Marg, Nagpur, India, 07122247828.*

*Dilip Lataye, Civil Engineering Department, Visvesvaraya National Institute of Technology, Nagpur, India, 07122801081.*

*Samujjwala Dubey, Amity Institute of Applied Science, Amity University, Noida, India, 01204713600.*

*Sangeeta Tiwari, Amity Institute of Applied Science, Amity University, Noida, India, 01204713600.*

products like glass and ceramic industries, semiconductor manufacturing, coal-fired power stations, brick and iron works, fertilizers production, aluminum smelters etc. [3].

According to the various level of fluoride as well as useful effects of it on human life [4]. When the fluoride is present in less amount it helps in strengthening of bones and prevention of tooth decay [5]. However, if it is present in large amount there are various hazardous diseases taking place such as osteoporosis, arthritis [6], neurological damage [7], Alzheimer's Syndrome [8], thyroid disorder [9], infertility and cancer [2] and even the fluoride are having strong interaction with positive charge ions and responsible for dental and skeletal fluorosis [10]. The various organisation such as WHO vs public health standard has undergone through the health problems and they have limited the amount of fluoride in the drinking water as 1.5 mg/l and 1.2 mg/l because BIS has set the limit of 1.0 mg/l [5]. Considering the severity of health problems various agencies like WHO and US public health standards has set the permissible limit of fluoride in drinking water as 1.5 mg/l and 1.2 mg/l.

The chemical methods included for defluoridation are precipitation, coagulation, ion exchange, electrolytic defluoridation, adsorption, reverse osmosis, electro dialysis, nanofiltration etc. [10]. Most of the above methods are responsible for removing fluoride from the water as such, it's costly where the secondary waste is important [5]. Therefore, the less expensive methods are to be employed for removing the excess amount of fluoride from drinking water. Those methods include absorption based process which has a large number of properties such as simplicity, versatility, high efficiency, low cost [11] and capable enough to discard ion at a wide range of pH [12]. The various adsorbent are utilized for removing fluoride namely activated alumina [13], activated carbon [14], mixed metal oxides [15], LDH [16], clays [17], industrial wastes [18], zeolite [19] etc.

Zeolites, hydrated alumina silicates [20] are less expensive having a large surface area [21] and is possessing permanent negative charge on their surface, due to which they have low adsorption capacity for anions [22]. The adsorption capacity can be raised by changing the surface of the zeolite with the cationic surfactants or the metallic

cations [23]. When  $\text{Na}^+$  in zeolite is exchanged with metallic ion, it become active sites for fluoride adsorption. The properties such as small size, hard base nature, high electro negativity makes the fluoride compatible with metal ions [24].

The natural and synthetic zeolite were used for adsorption of various health hazard elements from water and other resources like removal of arsenic from drinking water [25], removal of brine by Zeolite Y synthesized by fly ash [26], removal of cadmium from aqueous solution by Na-A and Na-X zeolites synthesized by rice husk ash [27], removal of heavy metals like Cadmium, copper and nickel from aqueous solution by zeolite synthesized by fly ash [28], removal of cadmium and cobalt by Zeolite-A and Zeolite-X [29], removal of cadmium ions by Zeolites (ZAM and ZMB) from rice husk ash [30], removal of Cr(III) by zeolite NaY synthesized by rice husk ash [31], removal of Cu(II) from aqueous solution by coal fly ash derived zeolite [32], removal of malachite green dye by zeolite-iron oxide magnetic nanocomposites that was prepared by combination of zeolite derived from fly ash and iron oxide [33], removal of heavy metals like iron, chromium, aluminium, bismuth, cadmium, magnesium, silver, nickel, zinc, copper and lead from drinking water by surfactant (HMNDA) modified natrolite zeolite [34], removal of anatomy and manganese by  $\text{HNO}_3$  and NaOH pretreated natural zeolite [35], removal of heavy metals (Cadmium, copper, lead and zinc) by natural Jordanian zeolite [36] and similarly by natural zeolite [36-38], removal of lead by fly ash based zeolite [39-40], removal of manganese by manganese oxide coated zeolite [41], removal of strontium and potassium ions by synthetic zeolite 4A [42], removal of nickel ions, Ni(II) from aqueous solution by zeolite-X [43], removal of nitrate from groundwater and drinking water by natural zeolite [44-45], removal of nitrate by HCl treated Clinoptilolite zeolite [46], removal of ammonium and nitrate from aquatic solution by natural zeolite clinoptilolite [47], phosphate removal from hybrid adsorbent prepared by lanthanum hydroxide modified zeolite from coal fly ash [48], removal of uranium from aqueous solution by ammonium modified zeolite [49], removal of ammonium by low and high calcium fly ash derived zeolite [50] and adsorption of natural organic matter by surfactant modified zeolite [51]. Apart from these, the various types of natural, synthetic and modified zeolites were also used for defluoridation of water and wastewater [52].

The main purpose of the study is to generate an absorbent possessing cost-effective quality of removal of fluoride. The adsorption capacity of synthesized RHAZ - A and CAZ was done and briefly discussed in the following paper. The defluoridation capacity of CAZ was done with the help of different parameters such as doses, contact time, pH of solution, presence of other co anions and initial fluoride concentration. To investigate the best and suitable model for adsorption system, the comparative study was done that suggested about equilibrium absorption data onto different isotherm.

## II. MATERIALS AND METHODS

### A. Chemical Used

Rice husk ash used for synthesis of zeolite was obtained from Purti Power and Sugar Limited Khursapar (Bela), Nagpur. NaOH,  $\text{NaAlO}_2$ ,  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ ,  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ , HCl,  $\text{HNO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{HPO}_4$ , NaCl,  $\text{Na}_2\text{SO}_4$ , KBr, KOH,  $\text{KNO}_3$  used were of analytical grade (Merck, India). Total ionic strength adjustment buffer (TISAB III) solution and fluoride standard solution (100ppm) were purchased from Thermo fisher scientific, Mumbai, India. Stock solution of fluoride was prepared by dissolving NaF in deionized water from a Milli-Q water system and working solution was obtained by suitable dilutions of the stock solution. Fluoride concentration of solution was measured by Orion star - A214 fluoride ion selective electrode. pH measurements were carried out with Eutech – 06 pH meter.

### B. Synthesis of Materials

Zeolite was synthesized by grinding and mixing of rice husk ash with sodium hydroxide in the ratio of 1:1.2. The mixture was heated to 550-600°C for about 90 minutes in muffle furnace to obtain fused mass. To this fused mass, 200 ml of 1M  $\text{NaAlO}_2$  and 100 ml of DI water were added and it was then stirred by mechanical stirrer at room temperature for 8 – 10 hours. After stirring the slurry was kept in a teflon pot for hydrothermal crystallization at 110°C for 4 hours in oven and then obtained material was filtered by vacuum filter, subsequently washed with DI water and dried at 70°C for 2 hours [53]. This zeolite is named as rice husk ash zeolite (RHAZ-A).

The rice husk ash zeolite (RHAZ-A) was further modified with aluminium sulphate and calcium sulphate. For modification of RHAZ-A, it was soaked in 0.01N HCl for 6 – 7 hours and then washed with DI water for several times followed by drying in oven at 110°C. This acid treated zeolite was added to  $\text{Al}_2(\text{SO}_4)_3$  solution and the slurry so formed was added to  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$  solution [w/w ratio of zeolite,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$  were taken as 1:1:1, 1:1.5:1 and 1:2:1 respectively. Then the pH of this slurry was maintained in the range of 7 – 8 by the addition of NaOH solution and it was stirred for 3 hours at room temperature by magnetic stirrer. After stirring the slurry was filtered and material obtained was washed with DI water for 4 times. Then the material was dried at 70°C for 2 hours in oven. The best result for adsorption has obtained at mix ratio of 1:2:1.

### C. Optimization of Zeolite/Aluminium/Calcium Ratio in CAZ

The optimization of the zeolite/ aluminium sulphate/ calcium sulphate molar ratio of the adsorption capacity is shown in Fig.1. It shows that the adsorbent reaches the highest adsorption capacity of 8.62 mg/g when the amount of zeolite/ aluminium sulphate/calcium sulphate is in the ratio of 1:2:1. This states that the ratio of 1:2:1 was used in the optimized adsorbent preparation.

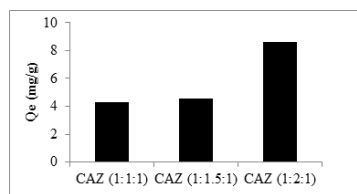


Fig.1 – Optimization of ratio of aluminium in CAZ

### III. RESULTS AND DISCUSSION

#### A. XRD Analysis

The powder XRD patterns were recorded using Rigaku desktop X-ray diffractometer (mini flex). The operating target voltage was 30 kV and the current was 15 mA. The radiations of Cu K $\alpha$  were generated using X-ray generator. The samples were powdered and scanned for diffraction angle of 2 $\theta$  ranging between 5° to 80° with the scan speed of 5° per minute. XRD of synthesized zeolite, acid-treated zeolite, and modified zeolite were done to predict changes in the crystal structure of the zeolite. The X-ray diffraction (XRD) technique has been one of the most prominent for the identification of crystal study and becomes an important field for the scientific community in the last few decades [54]. Fig.2 shows the XRD patterns of the (a) bare zeolite, (b) acid treated zeolite (c) modified zeolites before and (d) after fluoride adsorption. The following samples are in the pure phase without any mineral impurity. When (a) bare zeolite and (b) the acid treated zeolite is compared, they retain high crystallinity. The position of diffraction peaks is not changing which shows that crystalline transformation does not occur to the treatment. (c) The Modified zeolite before the fluoride adsorption is genuinely showing the sharp and symmetric peaks that is crystalline in nature, whereas (d) after fluoride adsorption, there is no formation of peaks, which resembles about that it's an amorphous structure.

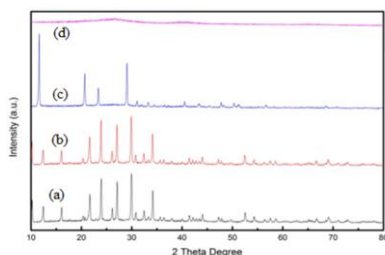


Fig.2 – XRD of (a) bare zeolite, (b) acid treated zeolite, (c) modified zeolite before adsorption and (d) modified zeolite after adsorption

#### B. FRIT Analysis

The FTIR spectra were recorded by using Bruker – Vertex 60. FTIR of bare and modified zeolite were done to understand the concept of bonding between the metal with zeolite by doing the comparison of the position of different peaks and their intensities in the spectra. The natural behaviour of samples is shown with the help of IR spectra and is said to be highly diverse molecular spectroscopy technique and it is a chemical analyzed method. Fig. 3 shows the comparative studies of FTIR (a) bare zeolite, (b) acid treated

zeolite (c) modified zeolites before and (d) after fluoride adsorption. Fig. 3(a) is showing a slight increase in the intensity of peak at 1657 cm<sup>-1</sup> designating the incorporation of H<sup>+</sup> ions into the framework of zeolite. The loading of aluminum in zeolite are signified by the intense peak found in bare zeolite than the peak shown is Fig.3(c) at 460 cm<sup>-1</sup>. The combination of calcium in zeolite is signified by the formation of new peak found at 1169 cm<sup>-1</sup> that is less intensity. The peak at 441.60 cm<sup>-1</sup> shown in Fig. 3(d). It shows the presence of fluoride ion on the surface of CAZ. The peaks at 1096.94 cm<sup>-1</sup>, 488.59 cm<sup>-1</sup> and 543.01 cm<sup>-1</sup> corresponds to Ca-F stretching, Ca-F bending and Al-F bending respectively [55].

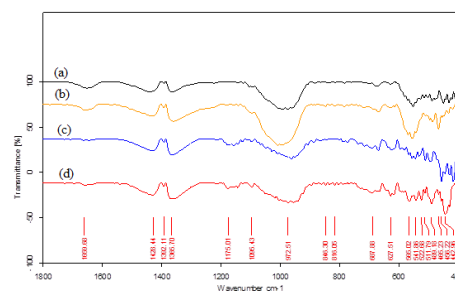


Fig.3 – FTIR of (a) bare zeolite, (b) acid treated zeolite, (c) modified zeolite before adsorption and (d) modified zeolite after adsorption

#### C. SEM-EDAX Analysis

SEM – EDAX was done by Zeiss (EVO 40) scanning electron microscope equipped with energy dispersive X – ray (EDAX) analyzer to study the surface morphology of bare and modified zeolite. The surface morphology is possible due Scanning Electron Microscopy-Energy dispersive X-ray spectroscopy. Fig.4 shows the SEM images of (a) bare zeolite, (b) modified zeolite before adsorption and (c) modified zeolite after adsorption. Fig.4(a) clearly shows the cubic shaped crystals of zeolite with smooth surface. The tiny particles attached to the surface of crystal are found to be seen in Fig. 4(b).The inter-granular cavitation with clearly formed cavities evident on the grain surfaces of CAZ is shown in Fig. 4(c) [56]. The percent composition of different elements present in bare and modified zeolite is analyzed by the EDS.

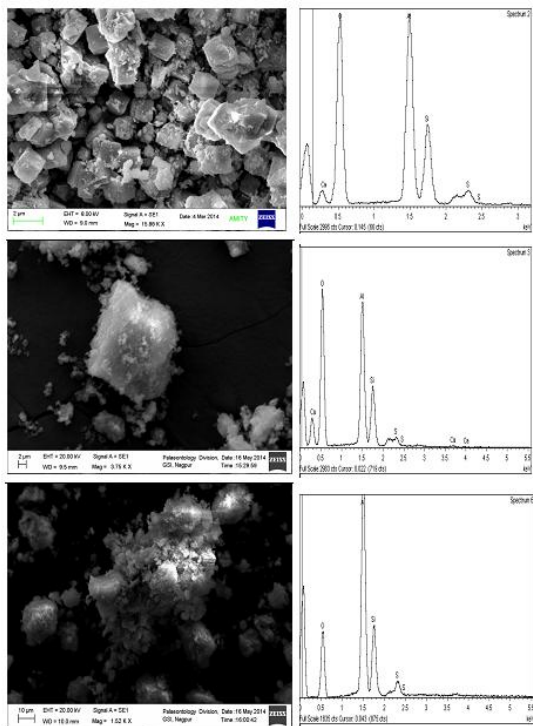


Fig. 4 – SEM-EDAX of (a) bare zeolite, (b) modified zeolite before adsorption and (c) modified zeolite after adsorption

**D. BET Surface Area**

BET surface area analysis was done for understand the concept of change in surface area of bare and modified zeolite. The surface area before adsorption occurring through BET is noticed to be  $30.097 \pm 1.909 \text{ m}^2/\text{g}$ , which is suggesting about the development of porous structure of the adsorption process. Later on the BET surface was found to be  $65.693 \pm 5.918 \text{ m}^2/\text{g}$  occurring due to increase in surface area with decrease in pore radius [57]. The change in structure is supported by increase in surface area which took place at the adsorption of fluoride ions [58].

**E. ICP-OES Analysis**

Inductively coupled plasma with optical emission spectroscopy (ICP-OES) was performed using Thermo Fischer iCAP 6300 for checking the amount of metal ion loaded on zeolite. For analysis by ICP-OES, 3ml  $\text{HNO}_3$  and 5ml  $\text{HCl}$  were added to 0.150 g of zeolite and then it was kept for digestion in Mars –6 microwave acid digester. After digestion, it was diluted about 1000 times and analyzed by ICP-OES.

The ICP-OES quantify the amount of metal ion is loaded with zeolite and it was noticed that out of 269.7 mg Al and 828.3 mg Ca only 62.63 mg of Al and 7.27 mg of Ca were loaded on 3g of acid treated zeolite. On the analysis with ICP – OES, the following results were obtained and listed in Table 1.

Table 1 – Results for metal loading obtained by ICP – OES

Metal	Amount of metal tried to load	Actual Loading (in 3g of Zeolite)	% metal loading
Al	269.7 mg	62.637mg	23.22
Ca	828.3 mg	7.27mg	0.877

**F. Zero Point Charge**

The Zero point charge is referred as the pH value at which the net charge on the surface of adsorbent is found to be zero. 10 different flasks with the 25 ml of 0.1M  $\text{KNO}_3$  solution for the determination of zero point charge and the pH of each flasks were maintained between the range of 1 – 10 with the addition of either 0.1M  $\text{KOH}$  or by 0.05M  $\text{HNO}_3$  solution [59]. Later on the optimized doze of adsorbent was added to each flask and kept on shaker incubator for 24 hours at 150 rpm and  $27^\circ\text{C}$ . Then the pH of filtered solutions was measured and the difference between initial and final pH was also calculated.

Fig.5 shows the graph plotted between initial pH of the solution and the variation on the initial and final pH. The zero point charge of CAZ was estimated at 5.6 that refers the occurrence of change in surface charge. Therefore, it is noticed that CAZ shows more adsorption for the fluoride ion at less pH than  $\text{pH}_{\text{ZPC}}$  and less adsorption at  $\text{pH}_{\text{ZPC}}$ . The occurrence is due to the fact that, at  $\text{pH}_{\text{ZPC}}$ , the net charge of CAZ surface was zero and less than that the surface shows positive charge. It states that the adsorption of fluoride ion on the surface is favoured for experimentation and when the surface is negative charged at  $\text{pH}_{\text{ZPC}}$  more, the fluoride adsorption is not favoured.

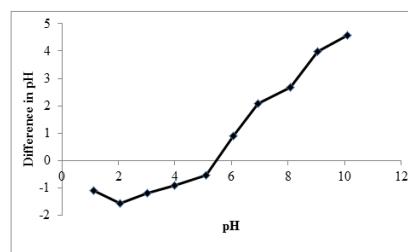


Fig.5 – Zero point charge of CAZ

**G. Zeta Potential**

Zeta potential indicates the stability of adsorbent. A high value of zeta potential indicates the higher stability of adsorbent. After analysis for zeta potential of CAZ – A following parameters were obtained as shown in Table 2.

Zeta potential value of CAZ was found to be +5.0 V. The stability of adsorbents at different Zeta potential values and their stability are as shown in Table 3. CAZ was found to undergo rapid coagulation which suggests higher instability of CAZ.

Table 2 – Zeta potential values for CAZ Metal

S. No.	Parameter	Value
1	Zeta potential	+5.0 V
2	Electrophoretic Mobility Mean	0.000039 $\text{cm}^2/\text{Vs}$
3	Conductivity	0.318 $\text{ms}/\text{cm}$
4	Dispersion medium viscosity	0.893 $\text{mpa.s}$

Table 3: Stability of adsorbents at different Zeta Potential values

S. No.	Value of Zeta Potential	Remarks
1	0 to $\pm 5$	Rapid coagulation
2	$\pm 10$ to $\pm 30$	Incipient stability
3	$\pm 30$ to $\pm 40$	Moderate stability
4	$\pm 40$ to $\pm 60$	Good stability
5	$> \pm 61$	Excellent stability

**H. Adsorption Experiments**

Concentration of fluoride ion in solution before and after adsorption was measured by using Orion star – A214 fluoride ion selective electrode. Standards of different range such as 1ppm, 10ppm and 100ppm were prepared for calibration of fluoride ISE and TISAB III were used as the buffer to maintain the pH and background ion concentrations during measurement. The various factors included for adsorption studies are optimization of doze, time, effect of pH, initial concentration, and various competing co – anions on fluoride adsorption capacity of CAZ. The pH of filtrate was measured with the help of pH meter.

**I. Optimization of Dose**

For optimization of dose, different doses of adsorbent (CAZ) ranging from 0.5 – 3.5 g L<sup>-1</sup> were added to the flasks containing 25 ml of 10 ppm fluoride ion solution and the flasks were kept in shaker incubator for 24 hours at 150 rpm and 25°C. Then the solutions were filtered where the fluoride concentration was measured by fluoride ISE. Fig.6 shows the graph plotted between various doze of adsorbent, % removal and adsorption capacity (Q<sub>e</sub>), which resembles that % removal increases in an increase in adsorbent doze due to the number of active adsorption sites present at high doses and is capable to accommodate fluoride ions [52] whereas the adsorbent doze increases, the adsorption capacity goes on decreasing. Fig.6 also refers that the two lines are intersecting with point 0.0375. So, 0.0375 g per 25 ml was fixed as optimum doze for further studies.

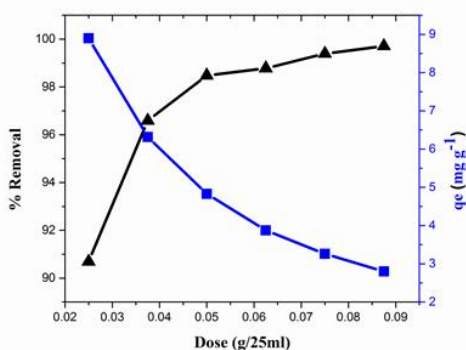


Fig.6 – Optimization of Doze for CAZ

**J. Optimization of Contact Time**

For optimization of contact time, optimized dose of adsorbent was added to the flasks containing 25 ml of 10ppm fluoride ion solution and then the flasks were kept in shaking incubator for different time intervals ranging from 1 min – 24 hours at 150 rpm and 25°C. Then the solutions were filtered where the fluoride concentration was measured by fluoride ISE. A graph was plotted between contact time and adsorption capacity (Q<sub>e</sub>) as shown in Fig.7. It was found that at initially staging the adsorption of fluoride increases in an

increase in contact time whereas after some duration the significant change was not noticed in fluoride concentration of solution. Therefore, the equilibrium was achieved in 6 hrs, which are attributed that the adsorption of fluoride took place because of the diffusion occurring in the pores on the surface of the adsorbent [2].

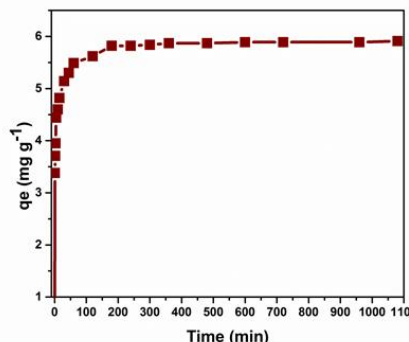


Fig.7 – Optimization of Contact Time for CAZ

**K. Effect of pH**

The pH of solution is an important factor of the adsorption process. Therefore, the determination of pH at maximum adsorption phase has become obligatory. For the study of pH effect on the adsorption capacity of CAZ, fluoride ion solution to 25 ml of 10ppm was taken in flasks where the pH was balanced between 3 to 11. To the respective flask, optimized doze of adsorbent was added and later on kept on shaker incubators for 150 rpm and 25°C. Then the solutions were filtered and fluoride concentration was measured by fluoride ISE. Fig.8 shows the graph plotted between pH and adsorption capacity. The result of the graphs reveals that CAZ has high adsorption capacity for the pH ranging from 4 to 8. The same pattern was seen for RHAZ – A. The H<sup>+</sup> ions present in the solution reacts with the fluoride ions leads to weak ionized HF formation at the pH less than 4. Therefore, it is frequently noticed that at low pH, the adsorption of fluoride ion decreases. The removal capacity of fluoride decreases in pH above 8, which is generally due to the adsorbent surface tending to behave is negatively charged one where the concentration of hydroxyl ions increase and they compete with fluoride ions for adsorption [60].

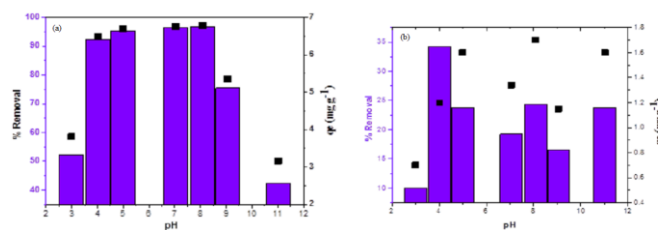


Fig.8 – Effect of pH on fluoride removal capacity of (a) CAZ and (b) RHAZ – A

**L. Effects of Co-anions**

Along with the fluoride ion present in drinking water, the effect of different other co – anions such as NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>,

CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> and PO<sub>4</sub><sup>3-</sup> on the adsorption capacity of CAZ was also determined. For the experimental study of the effect of co-anions, the fluoride ion solution to 50 ml at 10ppm was taken in flasks where the sodium salts of different co – anion was added respectively. It was noticed that the concentration of different anions added was double than the limit prescribed by WHO. After that the optimized doze of adsorbent was added and the flask was kept on shaker incubators for the contact time of 150 rpm and temperature of 25°C. Lastly, the solution was filtered and fluoride concentration was measured as given in Table 4.

The effect of various coexisting ions on fluoride removal of CAZ and RHAZ – A in shown in Fig.9. It was observed that adsorption capacity of CAZ and RHAZ – A decreased due to the existence of bicarbonate, carbonate and phosphate, which is mainly due to the competitive effects of anions along with the change in pH of solution. However, it was found that there was no effect on adsorption CAZ and RHAZ – A due to the presence of chloride, sulphate, and nitrate [61]. Therefore, in the presence of all the co anions, the value of adsorption capacity trends to decreases downs by 40%.

Table 4 – Various Co – anions and their amount added

S.No.	Name of Anion	Name of Salt	Permissible limit (ppm)	Weight of salt added (in g)	Concentration (ppm)
1.	Cl <sup>-</sup>	NaCl	250	0.0412	500
2.	HCO <sub>3</sub> <sup>-</sup>	NaHCO <sub>3</sub>	200	0.0276	400
3.	CO <sub>3</sub> <sup>-</sup>	Na <sub>2</sub> CO <sub>3</sub>	200	0.0354	400
4.	NO <sub>3</sub> <sup>-</sup>	NaNO <sub>3</sub>	50	0.00685	100
5.	SO <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> SO <sub>4</sub>	500	0.0739	1000
6.	PO <sub>4</sub> <sup>3-</sup>	Na <sub>2</sub> HPO <sub>4</sub>	5	0.00063	10

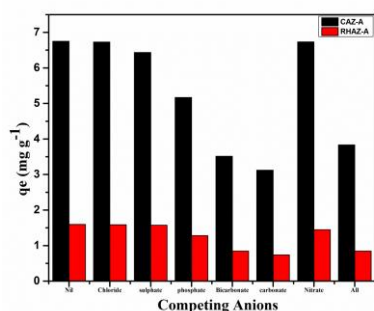


Fig.9 – Effect of various competing co – anions on fluoride removal capacity of CAZ and RHAZ – A

M. Effect of Initial Concentration

25 ml of different fluoride ion concentration ranging between 2ppm – 50ppm was taken in the flasks for the study of the effects of initial concentration of fluoride ion solution to adsorption capacity of adsorbent. The optimize doze of adsorbent was added and the flask was kept on shaker incubators for contact time of 150 rpm and temperature of 25°C. Then the solution was filtered and fluoride concentration was measured by fluoride ISE. Fig.10 shows the effect of initial concentration on fluoride removal

capacities of CAZ and RHAZ – A. From the graph, it was noticed that adsorption capacity increases with an increase in fluoride concentration attributed by the increased diffusivity. But later on it was observed that adsorption capacity decreases after certain concentration [62].

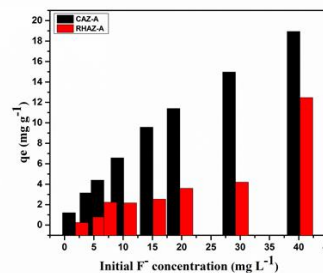


Fig.10 - Effect of initial fluoride concentration on adsorption capacity of CAZ and RHAZ – A

N. Adsorption Isotherm Study

The interaction of adsorbate with adsorbent is very well explained by isotherm study. The equilibrium data were interrelated by Langmuir and Freundlich models. Langmuir isotherms depends on the presumption that uptake happens on a homogenous surface by monolayer sorption without collaboration between adsorbed particles. The Freundlich adsorption isotherm is based on the equilibrium sorption on heterogeneous surfaces.

The linear isotherm equations for Langmuir and Freundlich are shown in equations (1) and (2) respectively [63-64].

$$\frac{1}{q_e} = \frac{1}{(q_{max} K_L) C_e} + \frac{1}{q_{max}} \tag{1}$$

Where q<sub>e</sub> is the amount of fluoride adsorbed capacity (mg/g); q<sub>max</sub> is the maximum amount of adsorbent that can be adsorbed pe unit mass adsorbent (mg/g); C<sub>e</sub> is equilibrium concentration of F<sup>-</sup> (mg/L); K<sub>L</sub> is Langmuir isotherm constant (L/mg).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{2}$$

Where C<sub>e</sub> (mg/L) and q<sub>e</sub> (mg/g) are the equilibrium concentration of F<sup>-</sup> in the solution and the amount of F<sup>-</sup> adsorbed at equilibrium respectively; K<sub>F</sub> is the empirical Freundlich constant (mg/g) and 1/n is Freundlich exponent.

The Langmuir isotherm application was indicated by the linear plot of  $\frac{1}{q_e}$  vs.  $\frac{1}{C_e}$  in Fig.11. The value calculated

for  $q_{max}$  and  $K_L$  is given in Table 5. The linear plot of  $\log q_e$  vs.  $\log C_e$  shows the application of Freundlich equation in Fig.12. Table 5 shows the value obtained for  $\frac{1}{n}$ , n and  $K_F$  respectively. The value of  $\frac{1}{n}$  ranges between 0

and 1 and for n ranges between 1 and 10 which shows the favourable conditions for sorption. The value of correlation coefficients for Freundlich isotherm is higher in comparison to that obtained for Langmuir isotherm. Hence, it can be concluded that Freundlich isotherm is the best suited for adsorption of fluoride ion than Langmuir isotherm on the basis of the experimental study and finally can be predicted that the surface adsorbent was heterogeneous in nature. For the Langmuir model, the value of correlation coefficient ( $R^2$ ) was 0.80. The maximum adsorption capacity of the adsorbent for Langmuir isotherm is 8.03 mg/g. It has been found from experiment Langmuir isotherm model is not suitable for adsorption process.

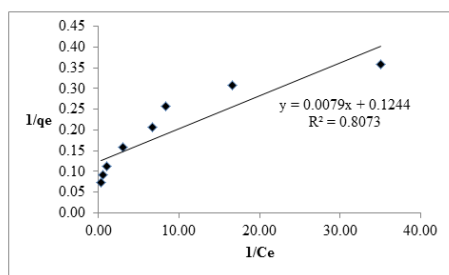


Fig.11 – Langmuir adsorption isotherm for CAZ

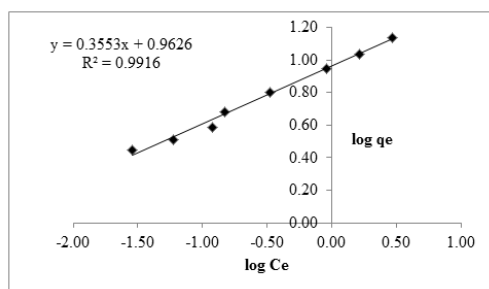


Fig.12– Freundlich adsorption isotherm for CAZ

Table 5 – Values of constants and coefficient of determination for adsorption isotherm data

Langmuir adsorption isotherm			Freundlich adsorption isotherm		
$q_{max}$ (mg g <sup>-1</sup> )	$K_L$ (L g <sup>-1</sup> )	$R^2$	n	$K_F$ [(mg g <sup>-1</sup> ) (L mg <sup>-1</sup> ) <sup>1/n</sup> ]	$R^2$
8.0385	15.7468	0.8073	2.8145	2.6184	0.9916

*O. Adsorption Kinetics Study*

Adsorption kinetics is referred as the most significant characteristics representing adsorption efficiency of the adsorbent. The certain factors on which the adsorption kinetics of the process depends are structural features of adsorbent, characteristics and concentration of adsorbate and interaction between adsorbent and adsorbate. Kinetic study is done for calculating the fastness of the reaction taking place during the process. Again for kinetic experiment, the optimize doze of adsorbent was added and the flask was kept on shaker incubator for contact time at 150 rpm and temperature of 25°C. The solutions were collected at time intervals of 1, 2, 3, 5, 7, 10, 15, 30, 45, 60, 120, 180 and 240 minutes. Then the solution was filtered and fluoride concentration was estimated by fluoride ISE.

Three models were employed for understanding the concept of kinetics of adsorption process. They are pseudo first-order equation, pseudo second-order equation and intra-particle diffusion models.

For more frequently used rate equation for assigning the adsorption process is Pseudo-first-order kinetic model [65]. The linear form of pseudo-first-order model is given by Eq. (3)

$$\log(q_e - q_t) = \log q_e - \frac{K_{ads}}{2.303} t \tag{3}$$

Where  $q_e$  (mg g<sup>-1</sup>) and  $q_t$  (mg g<sup>-1</sup>) are the amounts adsorbed at equilibrium and time t respectively, and  $K_{ads}$  (min<sup>-1</sup>) is the pseudo-first-order rate constant.

The pseudo second order kinetic order equation [66] is expressed by Eq. (4)

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \tag{4}$$

Where  $h = Kq_e^2$

Where K is pseudo second order rate constant (g mg<sup>-1</sup> min) and  $q_e$  is equilibrium adsorption capacity (mg g<sup>-1</sup>).

Weber-Morris intra-particle diffusion model is used to determine the limiting step of adsorption state and the linear form of Intra-particle diffusion model is given by Eq. (5)

$$q_t = K_p \cdot t^{1/2} + C \tag{5}$$

Where  $K_p$  and C are intra-particle diffusion rate constant (mg/g/min<sup>1/2</sup>) and constant (mg/g) respectively. The value of C gives the information about the thickness of boundary layer.

The linear plots of first-order, second-order and intra-particle diffusion kinetic models are shown in Fig.13, 14 and 15 respectively and the summary of the parameters estimated in the kinetic data models are represented in Table 6.

The adsorption process cannot be explained through the pseudo-first-order kinetic model since the value of pseudo-first-order kinetic model is obtained as low correlation coefficient ( $R^2$ ). The above statement reveals that pseudo-first-order kinetic model is applicable only in the initial stage [67]. So, it is assumed that it will not be appreciate for the whole adsorption process. The value of correlation coefficient ( $R^2$ ) is high in the pseudo-second-order kinetic model which reveals that pseudo-second-order kinetic model is genuine and is predicted as well suited for whole adsorption process. As such the value of correlation coefficient ( $R^2$ ) for pseudo-first order and pseudo-second-order kinetic models are 0.9305 and 0.9996 respectively. The value  $K_{ad}$ , K and  $K_p$  are 0.01566 min<sup>-1</sup>, 0.065 g.mg<sup>-1</sup>.min<sup>-1</sup> and 1.407 mg.g<sup>-1</sup>.min<sup>-1/2</sup> respectively.

The linear portion of the curves do not pass through the origin indicating that the fluoride adsorption mechanism of PBA was rather complex process and both intra-particle

diffusion and surface diffusion was involved in the rate-limiting step [68].

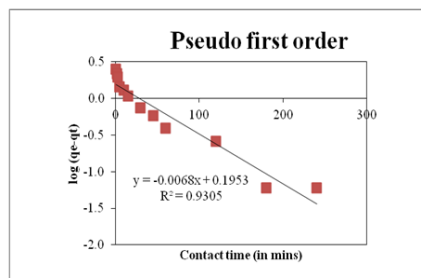


Fig.13: Pseudo first order plot for kinetic data for fluoride removal with CAZ

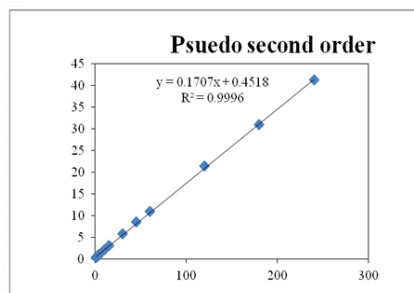


Fig.14: Pseudo second order plot for kinetic data for fluoride removal with CAZ

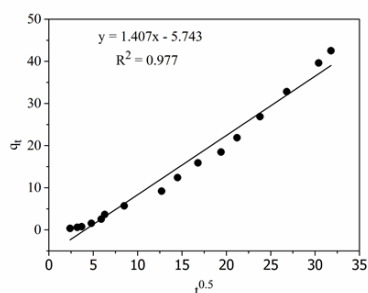


Fig.15: Intra-particle diffusion kinetic plot for fluoride removal using CAZ

Table 6: Kinetic and statistical parameters of the three kinetic models

C <sub>0</sub> (mg l <sup>-1</sup> )	Pseudo first order			Pseudo Second Order Parameters			Particle Diffusion Model		
	q <sub>e</sub> (mg g <sup>-1</sup> )	K <sub>d</sub> (min <sup>-1</sup> )	R <sup>2</sup>	q <sub>e</sub> (mg g <sup>-1</sup> )	K (g mg <sup>-1</sup> min <sup>-1</sup> )	h (mg g <sup>-1</sup> min <sup>-1/2</sup> )	R <sup>2</sup>	Kp (mg g <sup>-1</sup> min <sup>-1/2</sup> )	R <sup>2</sup>
10	1.2156	0.0156	0.9385	5.8582	0.065	2.2134	0.9996	1.407	0.977

P. Thermodynamics Study

In order to see the effect of temperature on adsorption of fluoride by CAZ, thermodynamic parameters associated with the adsorption process, viz. standard free energy change ( $\Delta G^\circ$ ) (kJ mole<sup>-1</sup>), standard enthalpy change ( $\Delta H^\circ$ ) (kJ mole<sup>-1</sup>) and standard entropy change ( $\Delta S^\circ$ ) (J mol<sup>-1</sup> K<sup>-1</sup>) were calculated using the following equations (6, 7 and 8)

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \tag{6}$$

$$\Delta G^\circ = - RT \ln K_c \tag{7}$$

$$\ln K_c = \ln \frac{q_e}{C_e} = \frac{\Delta S}{R} - \frac{\Delta H^\circ}{RT} \tag{8}$$

where  $K_c$  is sorption equilibrium constant;  $R$  is universal gas constant (8.314 J mol<sup>-1</sup>K<sup>-1</sup>);  $T$  is temperature in Kelvin;  $q_e$  is amount of  $F^-$  adsorbed (mg/g) and  $C_e$  is equilibrium concentration of  $F^-$ .

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  can be obtained from the slope and intercept of a plot of  $\ln(q_e/C_e)$  Vs  $1/T$  as shown in Fig. 16. The values of  $K_c$ ,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  are represented in Table 7. The negative  $\Delta G^\circ$  value confirms the feasibility of the sorption process and the spontaneous nature of adsorption. The standard free energy change ( $\Delta G^\circ$ ) of the adsorption process decreases (-4.014 to -3.058 KJ/mol.) with an increase in temperature and it shows that the process is spontaneous and the adsorption process is decreased at high temperature. The positive value of enthalpy change ( $\Delta H^\circ$ ) obtained indicate the endothermic nature of the process [69]. The positive value of standard entropy change ( $\Delta S^\circ$ ) shows the increase in randomness at the solid/liquid interface during the absorption of fluoride ion solution, i.e. it indicated the affinity of the adsorbent for fluoride removal as replacement of fluorine and the release of hydroxyl groups from the adsorbent surface into the bulk solution.

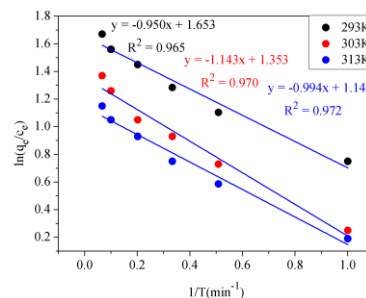


Fig.16: The plot of  $\ln(q_e/C_e)$  against  $1/T$  for thermodynamic parameter

Table 7: Thermodynamic parameters for fluoride adsorption onto CAZ

Temperature (K)	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol.K)	$K_c$
293	-4.018	0.007	13.743	1.0017
303	-3.398	0.009	11.248	1.0014
313	-3.058	0.008	9.494	1.0011

Q. Reuse and Regeneration

An adsorbent would be cost effective and vitality compelling on the off chance that it can be reused [70-73]. The reusability experiment was carried out by repeating the adsorption experiment with used and oven dried sample under similar condition used for the first cycle and is shown in Fig 17. The fluoride removal of fresh adsorbent (CAZ) is 96% whereas its removal efficiency gradually decreases from 71% to 20% in first and third reuse cycles respectively. This indicates that the adsorbent do not exhaust its fluoride uptake capacity in one cycle and oven drying of the used sample results in significant fluoride adsorption in subsequent cycles. After complete saturation adsorbent was subjected to regeneration using different regeneration media such as



sodium hydroxide, alum, hydrochloric acid and combination of them as shown in Fig 18.

The CAZ regenerated with 2% of alum - 2% of NaOH-HCl show good result in comparison to others and 90% regeneration was achieved. Regenerated adsorbent was subjected for fluoride adsorption experiment to determine the fluoride removal efficiency and the results are shown in Fig 19. To test the adsorption efficiency of regenerated adsorbent, two more cycles of adsorption-desorption cycles were carried out. The fluoride removal efficiency of get reduced from 85% to 22% in first to third desorption-adsorption cycles. From the study, it was expected that the CAZ has somewhat recycling and regeneration capacity for defluoridation.

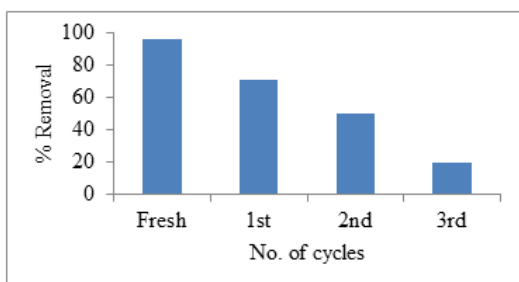


Fig 17: Reuse study of CAZ [Conditions: Initial fluoride concentration = 10 mg/L; adsorbent dose = 0.0375g/ 25 mL; contact time = 6 h; temperature = 25±1°C; shaking speed = 150 rpm].

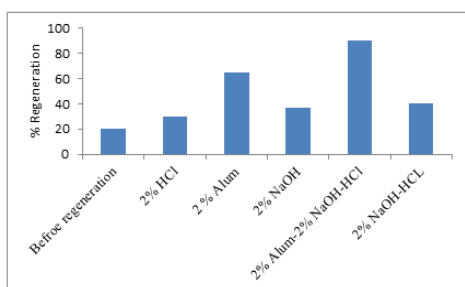


Fig 18: Regeneration of CAZ using different regeneration media.

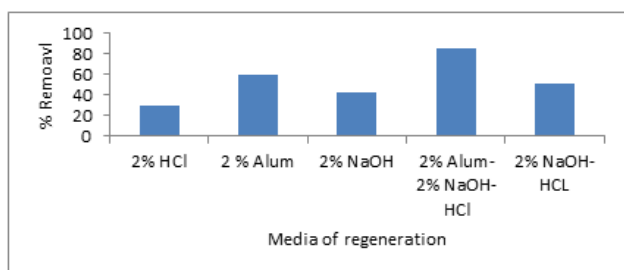


Fig 19: Effect of regeneration on fluoride removal efficiency [Conditions: Initial fluoride concentration = 10 mg/L; adsorbent dose = 1.5 g/L; shaking speed = 150 rpm; volume of fluoride solution = 50 mL, temperature = 25±1°C]

R. Field Study

Four field samples were collected from different locations of Bhandara district, Maharashtra with fluoride ion

concentration of 5.6mg/l, 4.5mg/l, 3.7mg/l, and 4.8mg/l, which was more than permissible limit of WHO. After adsorption the fluoride ion concentration of all four samples were measured and it was found that CAZ decreases the fluoride concentration below the permissible limit of WHO in all the four samples (Conditions – dosage 0.0375g/25 ml of sample, temperature of 25°C, rotation speed of 150 rpm and contact time of 6hrs) as shown in Fig. 20. CAZ showed almost three times more removal efficiency for field samples than bare zeolite derived from rice husk ash. The result so obtained shows that CAZ performed well even in presence of high concentration of other anions like HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> etc. The final pH of treated water is found in the range of 6.8 to 7.8.

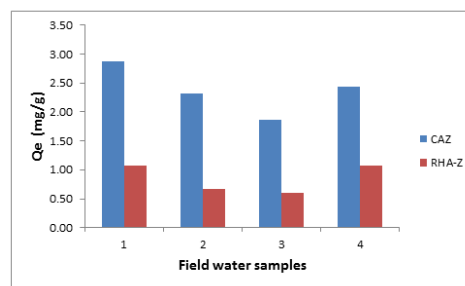


Fig. 20: Evaluation of adsorbent in field sample

IV. CONCLUSION

The developing countries like India depends on ground water as natural resources for the drinking water and similarly most bit of the universe are unreasonably depended on it [74–84]. In this paper, the best suited results for fluoride ion was presented with the help of zeolite modified with aluminium sulphate and calcium sulphate in the ratio as 2:1. The XRD, ICP-OES and FTIR represent the ubiquitous incorporation of aluminium and calcium on zeolite surface. SEM – EDAX results shows that it is heterogeneous. Kinetic study reveals about the fluoride removal capacity to be rapid which was carried out in approximately 60 min with maximum adsorption of 96% at 6 h. It also refers that the kinetic study was favoured by pseudo-second-order adsorption kinetic model. The fluoride was removed from drinking water at the wide range of pH between 4 and 8. The adsorption isotherm was fitted well by Freundlich model and the maximum adsorption capacity of CAZ was found to be 8.0385 mg g<sup>-1</sup> from Langmuir isotherms. The sorption process is spontaneous, endothermic and increase in interface at solid/liquid interface during adsorption. The investigation and examination done for the treated water states that leaching of aluminium and calcium is extensively below the permissible limit as prescribed by WHO. Therefore, the process can be employed for fluoride removal from the drinking water. Hence, the field trial afforded as results of CAZ materials captivated that it can be agitatedly used for defluoridation technique. The CAZ material generally possesses some characteristics such as low cost and eco-friendly adsorbents for the removal of fluoride.

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## REFERENCES

- [1] S. Jagtap, M. K. Yenkie, N. Labhsetwar, and S. Rayalu, "Fluoride in Drinking Water and Defluoridation of Water," *Chemical Review*, vol. 112, pp. 2454-2466, 2012.
- [2] S. S. Tripathy, J. L. Bersillon, and K. Gopal, "Removal of fluoride from drinking water by adsorption onto alum-impregnated activated alumina," *Separation and Purification Technology*, vol. 50, pp 310-317, 2006.
- [3] M. Mohapatra, S. Anand, B. K. Mishra, D. E. Giles, and P. J. Singh, "Review of fluoride removal from drinking water," *Journal of Environmental Management*, vol. 91, pp. 67-77, 2009.
- [4] S. Peng, Q. Zeng, Y. Guo, B. Niu, X. Zhang, and S. J. Hong, "Defluoridation from aqueous solution by chitosanmodified natural zeolite" *J Chem Technol Biotechnol*, vol. 88, pp.1707-1714, 2013.
- [5] P. Loganathan, S. Vigneswaran, J. Kandasamy, and R. Naidu, "Defluoridation of drinking water using adsorption processes," *Journal of Hazardous Materials*, vol. 248- 249, pp. 1- 19, 2013.
- [6] P. K. Pandey, M. Pandey, and R. Sharma, "Defluoridation of Water by a Biomass: *Tinospora cordifolia*," *Journal of Environmental Protection*, vol. 3, pp. 610-616, 2012.
- [7] V. Sivasankar, S. Marriages, S. Rajkumar, and A. Darchen, "Cerium dispersed in carbon (CeDC) and its adsorption behavior: A first example of tailored adsorbent for fluoride removal from drinking water," *Chemical Engineering Journal*, vol. 214, pp. 45-54, 2013.
- [8] A. Bansiwala, P. Pillewan, R. B. Biniwale, and S. S. Rayalu, "Copper oxide incorporated mesoporous alumina for defluoridation of drinking water," *Microporous and Mesoporous Materials* 2010, 129, 54-61.
- [9] N. Gandhi, D. Sirisha, and K. B. C. Shekar, "Adsorption of fluoride from aqueous solution by using chalk powder," *World Journal of Pharmacy and Pharmaceutical Sciences*, vol. 2, Issue5, pp. 3897-3914, 2013.
- [10] Meenakshi, and R. C. Maheshwari, "Fluoride in drinking water and its removal," *J. Hazard. Mater.*, vol. 137, pp. 456-463, 2006.
- [11] V. Ganvir, and K. Das, "Removal of fluoride from drinking water using aluminum hydroxide coated rice husk ash," *Journal of Hazardous Materials*, vol. 185, pp.1287-1294, 2011.
- [12] S. M. Maliyekkal, S. Shukla, L. Philip, I. M. Nambi, "Enhanced fluoride removal from drinking water by magnesia-amended activated alumina granules," *Chemical Engineering Journal*, vol. 140, pp. 183-192, 2008.
- [13] S. Jagtap, M. K. N. Yenkie, N. Labhsetwar, and S. Rayalu, "Defluoridation of drinking water using chitosan based mesoporous alumina," *Microporous and Mesoporous Materials*, vol. 142, pp. 454-463, 2011.
- [14] V. Veeraputhiran, and G. Alagumuthu, "Treatment of High Fluoride Drinking Water Using Bioadsorbent," *Research Journal of Chemical Sciences*, Vol. 1(4), pp. 49-54, July 2011.
- [15] B. Zhao, Y. Zhang, X. Dou, X. Wu, and M. Yang, "Granulation of Fe-Al-Ce trimetal hydroxide as a fluoride adsorbent using the extrusion method," *Chemical Engineering Journal*, vol. 185- 186, pp. 211- 218, 2012.
- [16] L. Lv, J. He, M. Wei, and X. Duan, "Kinetic Studies on Fluoride Removal by Calcined Layered Double Hydroxides," *Ind. Eng. Chem. Res.*, vol. 45, pp. 8623-8628, 2006.
- [17] G. Karthikeyan, A. Pius, and G. Alagumuthu, "Fluoride adsorption studies of montmorillonite clay" *Indian Journal of Chemical Technology*, vol. 12, pp. 263-272, 2005.
- [18] G. Lv, L. Wu, L. Liao, Y. Zhang, Z. Li, "Preparation and characterization of red mud sintered porous materials for water defluoridation," *Applied Clay Science*, vol. 74, pp. 95-101, 2013.
- [19] Z. Zhang, Y. Tan, and M. Zhong, "Defluorination of wastewater by calcium chloride modified natural zeolite," *Desalination*, vol. 276, pp. 246-252, 2011.
- [20] R. Terzano, M. Spagnuolo, L. Medici, F. Tateo, and P. Ruggiero, "Zeolite synthesis from pre-treated coal fly ash in presence of soil as a tool for soil remediation," *Applied Clay Science*, vol. 29, pp. 99-110, 2005.
- [21] S. Wang, and Y. Peng, "Natural zeolites as effective adsorbents in water and wastewater treatment," *Chemical Engineering Journal*, vol. 156, pp. 11-24, 2010.
- [22] S. Nasserli, and M. Heidari, "Evaluation and comparison of aluminum-coated pumice and zeolite in arsenic removal from water Resources," *Iranian Journal of Environmental Health Science & Engineering* 2012, vol. 9, pp.1-7.
- [23] S. Samatya, U. Yuksel, M. Yuksel, and N. Kabay, "Removal of Fluoride from Water by Metal Ions (Al31, La31 and ZrO21) Loaded Natural Zeolite," *Separation Science and Technology*, vol. 42, pp. 2033-2047, 2007.
- [24] S. Xingbin, X. Chengju, and H. Zhaochao, "The fluoride-adsorption capacity and influencing factors study of Zeolite," *International Conference Challenges in Environmental Science and Computer Engineering*, Wuhan, China, vol. 2, pp. 358-361, 6-7 March 2010.
- [25] M. B. Baskan, and A. Pala, "Removal of arsenic from drinking water using modified natural zeolite," *Desalination*, vol. 281, pp. 396-403, 2011.
- [26] T. Sonqishe, G. Balfour, E. Iwouha and L. Petrik, "Treatment of Brine using commercial zeolites and zeolites synthesized from fly ash derivative," *International Mine Water Conference*, , Pretoria, South Africa, pp. 695 - 702, 19<sup>th</sup> -23<sup>rd</sup> October 2009.
- [27] C. Santasnachok, W. Kurniawana, and H. Hinodea, "Kinetic and Thermodynamic Studies of Removal of Cadmium Ion onto Synthetic Pure Zeolite from Rice Husk Ash Thailand," *Global Journal of Researches in Engineering: J General Engineering*, vol. 15, Issue 2, pp. 1 - 11, 2015.
- [28] M. Visa and N. Popa, "Adsorption of Heavy Metals Cations onto Zeolite Material from Aqueous Solution, *Journal of Membrane Science & Technology*," vol. 5, Issue 1, pp. 1-8, 2015.
- [29] I. Garcia-Sosa, and M. Solache-Rios, "Cation-exchange capacities of zeolites A, X, Y, ZSM-5 and Mexican erionite compared with the retention of cobalt and cadmium," *Journal of Radioanalytical and Nuclear Chemistry*, vol. 250, no. 1, pp. 205-206, 2001.
- [30] G. W. Mbugua, H. M. Mbuvi and J. W. Muthengia, "Rice Husk Ash Derived Zeolite Blended with Water Hyacinth Ash for Enhanced Adsorption of Cadmium Ions," *Current World Environment*, vol. 9(2), pp. 280-286, 2014.
- [31] N. A. N. N. Malek and A. M. Yusof, "Removal of Cr(III) from aqueous solutions using zeolite NaY prepared from rice husk ash, *The Malaysian Journal of Analytical Sciences*," vol. 11, no 1, pp.76-83, 2007.
- [32] S. Huiping, C. Huaigang, Z. Zepeng and C. Fangqin, "Adsorption properties of zeolites synthesized from coal fly ash for Cu (II)," *Journal of Environmental Biology*, vol. 35, pp. 983-988, Sept. 2014.
- [33] N. Jain, M. K. Dwivedi, R. Agarwal and P. Sharma, "Removal of Malachite Green from Aqueous Solution by Zeolite-Iron Oxide Magnetic Nanocomposite," *Journal of Environmental Science, Toxicology and Food Technology*, vol.9, Issue 6, pp. 42 - 50, June 2015.
- [34] G. B. Gholikandi, M. M. Baneshi, E. Dehghanifard, S. Salehi, A. R. Yari, "Natural Zeolites Application as Sustainable Adsorbent for Heavy Metals Removal from Drinking Water," *Iranian Journal of Toxicology*, vol. 3, no. 3, pp. 302 - 310, Autumn 2010.
- [35] P. Zhang, W. Ding, Y. Zhang, K. Dai and W. Liu, "Heavy metal ions removal from water using modified zeolite," *Journal of Chemical and Pharmaceutical Research*, vol. 6(11), pp.507-514, 2014.
- [36] H. M. Baker, A. M. Massadeh, H. A. Younes, "Natural Jordanian zeolite - removal of heavy metal ions from water samples using column and batch methods, *Environmental Monitoring and Assessment*," vol. 157, pp. 319-330, 2009.
- [37] D. N. Paithankar, and V. B. Kokate, V. S. Chaudhari, "Removal of Heavy Metals from synthetic wastewater using Peanut Husk Charcoal, Fly ash and Zeolite as adsorbents," *International Journal of Modern Trends in Engineering and Research*, vol. 2, Issue 7, pp. 633 - 641, July 2015.
- [38] M. Nigam, N. Dubey, S. Khan, Beena and A. Kumar, "Heavy Metal Removal from Aqueous Solution Using Zeolite (A Review)," *International Journal of Scientific Research and Reviews*, vol. 4(2), pp. 17 - 27, 2015.
- [39] S. M. Kanawade, "Removal of Heavy Metals from Wastewater by Using Natural Zeolites as Adsorbent," *International Journal of Engineering Studies and Technical Approach*, vol. 1, no. 1, pp. 30 - 38, Jan. 2015.
- [40] P. Kumar, S. Rayalu and S. M. Dhopte, "Fly ash based zeolite-A : A suitable sorbent for lead removal," *Indian Journal of Chemical Technology*, vol. 11, pp. 227 - 233, March 2004.
- [41] S. R. Taffarel, and J. Rubio, "Removal of Mn2+ from aqueous solution by manganese oxide coated zeolite," *Minerals Engineering*, vol. 23, pp. 1131-1138, 2010.
- [42] M. do Rosario T. de Abreu, F. C. de F. Barros, G. S. C. Raulino, C. P. Moura, and R. F. do Nascimento, "Metal Ions Removal From Synthetic Solutions and Produced Water Using Activated Zeolite," *International Journal of Civil & Environmental Engineering*, vol. 12, no. 3, pp. 20 - 25, June 2012.
- [43] S. Singh, L. K. Verma, S. S. Sambhi, and S. K. Sharma, "Adsorption Behaviour of Ni (II) from Water onto Zeolite X: Kinetics and Equilibrium Studies," *Proceedings of the World Congress on Engineering and Computer Science*, San Francisco, USA, pp. 1-6, October 22 - 24, 2008.
- [44] S. M. Kanawade, "Removal of Nitrate from Groundwater by using Natural Zeolite as Adsorbent," *International Journal of Multidisciplinary Research and Development*, vol. 2, Issue 10, pp. 125 - 132, Oct. 2015.
- [45] S. M. Kanawade, "Use of natural zeolite for treating drinking water containing excess amount of nitrate," *International Journal of Multidisciplinary Research and Development*, vol. 2, Issue 4, pp. 336 - 345, April 2015.

- [46] A. Azari, A. H. Mahvi, S. Naseri, R. R. Kalantary, and M. Saberi, "Nitrate Removal from Aqueous Solution by Using Modified Clinoptilolite Zeolite," *Archives of Hygiene Sciences*, vol. 3(1), pp. 21–29, 2014.
- [47] M. Murkani, M. Nasrollahi, M. Ravanbakhsh, P. Bahrami, N. J. H. Fard, "Evaluation of natural zeolite clinoptilolite efficiency for the removal of ammonium and nitrate from aquatic solutions," *Environmental Health Engineering and Management Journal*, vol. 2(1), pp. 17–22, 2015.
- [48] J. Xie, L. Lai, L. Lin, D. Wu, Z. Zhang, and H. Kong, "Phosphate removal from water by a novel zeolite/lanthanum hydroxide hybrid material prepared from coal fly ash," *Journal of Environmental Science and Health, Part A*, vol. 50, pp. 1298–1305, 2015.
- [49] E. N. Bakatula, A. K. Mosai and H. Tutu, "Removal of Uranium from Aqueous Solutions using Ammonium-modified Zeolite," *South Africa Journal of Chemistry*, vol. 68, pp. 165–171, 2015.
- [50] M. Zhang, H. Zhang, D. Xu, L. Han, D. Niu, L. Zhang, W. Wu, B. Tian, "Ammonium removal from aqueous solution by zeolites synthesized from low-calcium and high-calcium fly ashes," *Desalination*, vol. 277, pp. 46–53, 2011.
- [51] M. V. Niri, A. H. Mahvi, M. J. Mohammadi, A. Takdastan, A. Zahedi, B. Hashemzadeh, "Kinetic Study of the Adsorption of Natural Organic Matter From Aqueous Solution by Surfactant Modified Zeolite," *Jundishapur Journal of Health Science*, vol. 7(3), pp. 20-25, July 2015.
- [52] Y. Sun, Q. Fang, J. Dong, X. Cheng, J. Xu, "Removal of fluoride from drinking water by natural stilbite zeolite modified with Fe(III)," *Desalination*, vol. 277, pp. 121–127, 2011.
- [53] S. Rayalu, N.K. Labhsetwar, P. Khanna, "Process for the synthesis of flyash based zeolite-A", US 5965105 A, pp. 1-10, Oct. 1999.
- [54] F. Mohammad, L. Plessis, T. Arfin, K. Shih (Eds.), In "X-Ray Diffraction: Structure, Principles and Applications", Nova Science Publishers Inc, New York, 161-181, 2013.
- [55] C.N.R. Rao, "Chemical Applications of Infrared Spectroscopy", Academic Press, New York, 1963.
- [56] T. Arfin, A. Falch, and R.J. Kriek, "Evaluation of charge density and the theory for calculating membrane potential for a nano-composite nylon-6,6 nickel phosphate membrane," *Phys. Chem. Chem. Phys.*, 14, pp. 16760 – 16769, 2012.
- [57] V. Tomar, S. Prasad, and D. Kumar, "Adsorptive removal of fluoride from water samples using Zr–Mn composite material," *Microchemical Journal*, vol. 111, pp. 116-124, 2013.
- [58] G. E. J. Poinern, M. K. Ghosh, Y. J. Ng, T. B. Issa, S. Anand, P. Singh, "Defluoridation behavior of nanostructured hydroxyapatite synthesized through an ultrasonic and microwave combined technique," *Journal of Hazardous Materials*, vol. 185, pp. 29–37, 2011.
- [59] R. Bhaumik, N. K. Mondal, B. Das, P. Roy, K. C. Pal, C. Das, "Eggshell Powder as an Adsorbent for Removal of Fluoride from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Studies," *E - Journal of Chemistry*, vol. 9, pp. 1457-1480, 2012.
- [60] B. Shimelis, F. Zewge, and B. S. Chandravanshi, "Removal of excess fluoride from water by aluminium hydroxide," *Bull. Chem. Soc. Ethiop.*, vol. 20, pp. 17-34, 2006.
- [61] L. Chai, Y. Wang, N. Zhao, W. Yang, and X. You, "Sulfate-doped Fe<sub>3</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> nanoparticles as a novel adsorbent for fluoride removal from drinking water," *Water Research*, vol. 47, pp. 4040-4049, 2013.
- [62] W. Nigussie, F. Zewge, and B.S. Chandravanshi, "Removal of excess fluoride from water using waste residue from alum manufacturing process" *Journal of Hazardous Materials*, vol. 147, pp. 954-963, 2007.
- [63] Langmuir, "The constitution and fundamental properties of solids and liquid," *I J. Am. Chem. Soc.* 1916, 38, 2221.
- [64] H.M.F. Freundlich, "Uber die adsorption in losungen," *Z. Phys. Chem.*, 57A, pp. 385–470, 1906.
- [65] Y.S. Ho, J.C.Y. Ng, G. McKay, "Kinetics of pollutant sorption by biosorbents: review," *Separation & Purification Reviews*, vol. 29(2), pp. 189-232, 2000.
- [66] V. Chandra, J. Park, Y. Chun, J. W. Lee, I. C. Hwang, and K. S. Kim, "Water-Dispersible Magnetite-Reduced Graphene Oxide Composites for Arsenic Removal," vol. 4(7), pp. 3979-3986, 2010.
- [67] Y. S. Ho, and G. McKay, "The Sorption of Lead(II) Ions on Peat," *Water Research*, vol. 33 (2), pp. 578-584, 1999.
- [68] M. Jerold, C. Vigneshwaran, and V. Sivasubramanian, "Macrophytes: A Potent Bio - Sorbent for the Sequestration of Heavy Metals," *International Advanced Research Journal in Science, Engineering and Technology*, vol. 2, Issue 10, pp. 16-26, Oct. 2015.
- [69] A. Dhillon, and D. Kumar, "Development of a nanoporous adsorbent for the removal of health-hazardous fluoride ions from aqueous systems," *Journal of Materials Chemistry A*, vol. 3, pp. 4215-4228, 2015.
- [70] N. Sakhare, S. Lunge, S. Rayalu, S. Bakardjiva, J. Subrt, S. Devotta, and N. Labhsetwar, "Defluoridation of water using calcium aluminate material," *Chemical Engineering Journal*, vol. 203, pp. 406–414, 2012.
- [71] G. Alagumuthu, V. Veeraputhiran, and R. Venkataraman, "Adsorption Isotherms on Fluoride Removal: Batch Techniques," *Archives of Applied Science Research*, vol. 2 (4), pp. 170-185, 2010.
- [72] A. K. Shrivastava, and M. K. Sharma, "An Innovative Technique for Removal of Fluoride from Drinking Water," *Scientific Review & Chemical Communications*, vol. 2(2), pp. 133-140, 2012.
- [73] M. V. B. Rao, M. Subba Rao, V. Prasanthi, and M. Ravi, "Characterization and Defluoridation Study of Activated Dolichos Lab Lab Carbon," *Rasayan Journal of Chemistry*, vol.2, no.2, pp. 525-530, 2009.
- [74] S. S. Waghmare, T. Arfin, N. Manwar, D. H. Lataye, N. Labhsetwar, and S. Rayalu, "Preparation and Characterization of Polyalthia longifolia Based Alumina as a Novel Adsorbent for Removing Fluoride from Drinking Water," *Asian Journal of Advanced Basic Sciences*, vol. 4(1), pp. 12-24, 2015.
- [75] D. Thakre, P. Dixit, S. Waghmare, N. Manwar, N. Labhsetwar, and S. S. Rayalu, "Synthesis Optimization and Fluoride Uptake Properties of High Capacity Composite Adsorbent for Defluoridation of Drinking Water," *Environmental Progress & Sustainable Energy*, pp. 1-10, 2015.
- [76] S. S. Waghmare, and T. Arfin, "Fluoride Removal from Water by Calcium Materials: A State-Of-The-Art Review," *International Journal of Innovative Research in Science, Engineering and Technology*, vol. 4(9), pp. 8090-8102, 2015.
- [77] S. S. Waghmare, and T. Arfin, "Fluoride Removal from Water by Mixed Metal Oxide Adsorbent Materials: A State-Of-The-Art Review," *International Journal of Engineering Sciences & Research Technology*, vol. 4(9), pp. 519-536, 2015.
- [78] S. S. Waghmare, and T. Arfin, "Fluoride induced water pollution issue and its health efficacy in India- A review," *International Journal of Engineering Research & General Science*, vol. 3(5), pp. 345-358, 2015.
- [79] S. S. Waghmare, and T. Arfin, "Fluoride Removal from Water by various techniques: Review," *International Journal of Innovative Science, Engineering & Technology*, vol. 2(9), pp. 560-571, 2015.
- [80] S. S. Waghmare, and T. Arfin, "Fluoride removal from water by carbonaceous materials: Review," *International Journal of Modern trends in Engineering and Research*, vol. 2(9), pp. 355-361, 2015.
- [81] S. S. Waghmare, and T. Arfin, "Fluoride Removal from Water by Aluminium Based Adsorption: A Review," *Journal of Biological and Chemical Chronicles*, vol. 1(1), pp. 1-11, 2015.
- [82] S. S. Waghmare, and T. Arfin, "Fluoride Removal from Industrial, Agricultural and Biomass Wastes as Adsorbents: Review," *International Journal of Advance Research and Innovative Ideas in Education*, vol. 1 (4), pp. 628 – 653, 2015.
- [83] S. S. Waghmare, and T. Arfin, "Defluoridation By Adsorption With Chitin - Chitosan-Alginate – Polymers – Cellulose – Resins – Algae And Fungi - A Review," *International Research Journal of Engineering and Technology*, vol. 2 (6), pp. 1179 – 1197, 2015.
- [84] S. S. Waghmare, and T. Arfin, "Fluoride Removal by Clays, Geomaterials, Minerals, Low Cost Materials and Zeolites by Adsorption: A Review", *International Journal of Science, Engineering and Technology Research*, vol. 4(11), pp. 3663 – 3676, 2015.