Study the Comparison of Defluorination Capacity of processed Ores & Coal-based Sorbent through Column Technique

Rubina Sahin, Ashish Kumar Tiwari, Kavita Tapadia

Abstract- **Fluoride more than permissible limit (< 1.5 mg/l, WHO) in water cause health hazards to the human health. The removal of fluoride was attempted using natural ores such as, Dolomite, Limonite, or coal-based sorbent such as Lignite and Coke. Each material was set up in a column for a known volume and the defluorination capacities of these materials were studied with respect to time. According to the maximum defluorination capacity these materials were added proportionally to the vertical column. 10 mg/l of fluoride was passed through the column and the variation of fluoride removal for a known rate of flow was studied. Correlation analysis of defluorination capacity with time was done and an attempt has been made to classify them accordingly. At neutral pH defluorination efficiency is more in Dolomite as compared to other three sorbent.**

Keywords terms: **Solid-sorbent, Removal, Defluorination, Column technique, Adsorption**

1. INTRODUCTION

Fluoride is a natural constituent of natural water resources. Its concentration in water resources varies region to region. The major source of fluoride constituent in the groundwater are the fluoride bearing rocks such as fluorspar, cryolite [1,2]etc. The fluoride content in the groundwater is a function of factors such as availability of fluoride minerals, velocity of flowing water, pH, and temperature, concentration of calcium & bicarbonate ions in water [3] etc. Fluoride is an essential constituent for both humans & animals depending on the total amount ingested or its concentration in drinking water. The presence of fluoride in drinking water within permissible limits of 0.5- 1.5 mg/l [5]is beneficial for the production and maintains of healthy bones and teeth; excessive fluoride in drinking water causes harmful effects such as dental fluorosis and skeletal fluorosis.[5-6]

Adsorption is a surface phenomenon where is the dissolved substances in polluted water are attached to and adhere to the surface of the adsorbent. The amount of material adsorbed depends on a number of factors including: the degree of attraction of surface area exposed to mobile particles, the concentration of the contaminants, pH and temperature of the liquid, the strongest adsorbed are microspores or finally divided solids (clays, charcoal powdered metals); and liquids (fine droplets like aerosols and sprays). Basically, the adsorption mechanism is described by three consecutive steps [7] namely

1. External mass transfer of solute molecules from the solution bulk to the sorbent particles surface.
2. Diffusion within the particle internal structure to the sorption sites where.
3. Rapid uptake occurs.

Step 3 is immediately fast and therefore contributes no resistance to the adsorption process, so film mass transform and intra particle diffusion remain the rate determining step.

The adsorbent consists highly of porous particles characteristic by a large surface area and a highly developed internal structure[8]. The lattice contains a complex network of pores and channels inter spaced throughout the particle diffusion which depends on the internal structure of the sorbent[10,11].

Present study aimed to find a low-cost environmental friendly method for the removal of fluoride in the groundwater that is used by common man. Therefore, few natural ore and coal based solid fuels such as Dolomite, Limonite, Lignite & Coke used. The ability of natural materials adsorbents adsorb fluorine from solution has been studied by earlier researchers[12,13]. The capacity of fluoride removal by the individual materials was studied and accordingly two columns were set up and studied for the removal of fluoride from rural water supply scheme, basically in Chhattisgarh because this state is enriched of different type of minerals or ores.

MATERIALS AND METHODS

Fluoride removal was done by passing water through column as earlier studies or stirring methods has confirmed that an increase in stirring rate increase the fluoride removal for a given temperature[9,10].This study is an attempt to remove fluoride by column methods using natural ores and solid fuels. The removal rate of fluoride was tested using 25 g of the materials (Dolomite, Lignite, Limonite & Coke collected in different flasks. The Dolomite is basically ore of magnesium & calcium. The chemical composition of Dolomite was used having Cao-51.03%, MgO- 20.60%, CO_2-24.23%, NO- 3.38&& SiO_2– 0.1%.The limonite were obtained from Iron Ore Mines, NMDC Ltd. Bacheli and its consist of Fe_2O_3 -51.62%, MnO_2 -3.32% , Al_2O_3- 37% & SiO_2-8.36%. Coke from Coal Washeriey of B.C.C.L Dhanbad. Lignite from CFRI,(Central fuel Research Institute), Dhanbad containing C-59.5%, H-5.9%, O-15.6%, S-0.2%, Volatile matter-29.2% and other impurities 0.6%. the mentioned all four adsorbents taken in powdered form with size 60 mesh in initial step

of the experiment. The image of all is shown in fig.1. AllIII. the materials used for defluorination were not pre-treated only washed with distilled water and dried for 2 hrs. at 110° C and the size fraction were of 1mm and 60 ϕ mesh fraction. The surface character of solid material is not considered here. The standard solution of 10mg/l fluoride capacity of each solid sorbent was calculated by taking treated samples were collected at intervals of 0-15, 15-30, 30-60, 60-90 and 90-120 min. The collected solution was analysed for fluoride using Nova 60 Photometer of Merck and Ion Selective Electrode (Model 94-09, Orion USA). The column setup has been shown in fig. 2. According to fluoride removal capacity, two columns were set up in different proportion of mentioned solid adsorbent and standard solution of fluoride 10 mg/l were allow to pass through it in order to determine the adsorption capacity of these four naturals materials and the eluent was collected at a rate of 1.5 ml/min. The removal rate of the collected solution and their fluoride content was determined in Table 1. the flow rate was found to be satisfactory during preliminary trials. Larger flow rate was within ± 20%. Hence the 1 ml/min flow rate was maintained for this study. The validity of maintaining this flow rate needs further investigation.

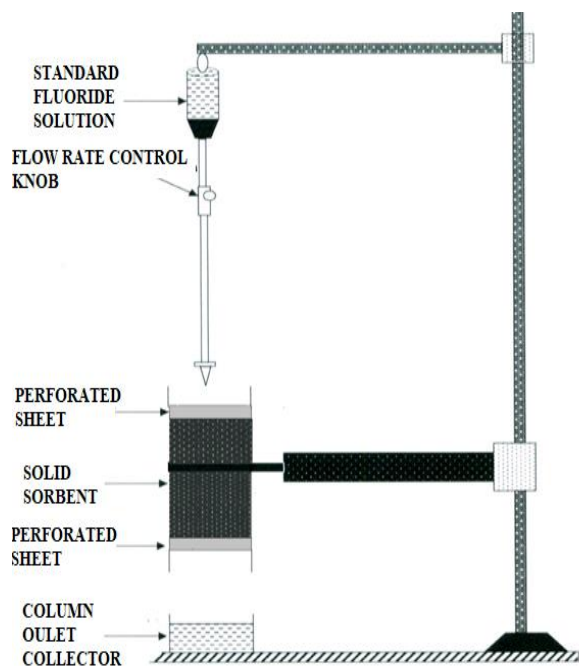Fig. 1 Image of all sorbent used for defluorination.

Fig. 2. Schematic diagram of experimental setup for Column Study.

RESULTS & DISCUSSION

Every solid material is potential adsorbent. It is also reasonable to utilise the naturally occurring fluoride-seeking minerals since the minerals can provide a number of fluoride-seeking cations such as Ca(II), Mg(II), Al(III), etc. Besides these cations, exchangeable anions such as OH$^-$ are present in many minerals and the proxy of F$^-$ for would serve as one of the principals contributing factors for defluorination due to the similar charge and size of these anions[15]. Therefore, such natural materials were used to remove the excess fluoride concentration in the natural freshwaters and were found to be effective. Untreated coke (Fig. 3) seems to have very less effect on the concentrations of fluoride with time and it adsorbed 1.21 mg/l of fluoride. The Dolomite show typically a sudden removal of fluoride from 10 mg/l to 3.59 mg/l. 64% reduction of concentration take place within 45min. Lignite adsorbed 37.1% of fluoride. Maximum adsorption had seen till 60 min after that gradual decrease in defluorination capacity from 90 to 120 min.

A functional relationship common to most treatment of inter-particle diffusion is that uptake varies almost proportionately with half the power of time $\sqrt{t}$ (min), rather than t. Figure 4 shows the amount of fluoride (in moles) removed per gram of the material. It clearly shows that in the case of Lignite & Limonite the amount removed per gram progressively decreases with half the power of time. The removal capacity of coke remains almost constant. But in the case of Dolomite initial time fraction shows a progressive increase of the fluoride removed per gram but later it remains constant. The maximum removal per gram is therefore at the beginning and later there is a gradual movement towards equilibrium. Many linear variations of amounts adsorbed with $\sqrt{t}$ is predicted for large initial fraction, which might be controlled by rates of inter-particulate diffusion. (Fig. 4)

The plot against ratio Ct/Co and reaction time in minutes (Fig. 5) shows that the untreated coke show weak fluoride removal capacity and it is almost constant over time. In case of Lignite& Limonite ore removal is initially strong and at the later stages fluoride removal progressively decreases. This is evident from the increases of the C_t/C_o ratio toward the maximum time fractions. Dolomite shows similar trends exhibiting a maximum removal up to 60 min where after the ratio tends to move gradually toward equilibrium.

The observation reveals that after a period of 30 min removal of fluoride is reduced, Perhaps due to saturation of the anion exchange site and hence the concentration of fluoride shoots up. This is also evident in the increase of the HCO$_3$ content in water (from Dolomite & Limonite ore), which increases along with pH.[11] The removal of fluoride ion with pH variation was found to be very effective by various workers [11]at lower ranges. As the decreases of pH probably results in the reduction of negative charges which are more at the surface of the

material, adsorption is enhanced. It is interesting to note that Dolomite has the highest capacity to remove fluoride. The main factors here are the dominance of Ca^{2+} ion which binds the fluoride ion on its surface, organic matter also promotes to hold the fluoride ions[12,13]. Similarly, Limonite ore is rich in iron & aluminium oxide in composition and has good anion exchange capacity. In general Calcium compound are found to be good fluoride removers because of the reaction between calcium and fluorine molecule. Similarly, reaction between Al and F also be takes place in case of Limonite ore. Several fluoride removal methods were carried out by using calcium compound[14]and aluminium-based compounds**[9]** natrolite, sitilbite, aphophyllite[15] and aluminiumphosphate[13].Adsorption studies carried out**.**[14] attributed the release of OH^- (ionic radii of 1.40° A), release to the exchange of minerals from ore, lattice by F^- (ionic radii 1.36 ° A). The exchange of F^- for OH^- has been studied [15,16]. Samson (1952) has reported fluoride removal, when the F ion attacks the lattice Al of ore minerals causing minerals decomposition, formation of complex solid F phases and release of OH^- into the solution. Since the Limonite, is one of the iron ore and contain Al. Since both Al & Fe ions goes into solution with the stoichiometric release of OH^-. But the replacement of OH^- by F is minor significance [17] pH shoots up to 8.0 with HCO_3 concentration going to 250 mg/l. The surface in the Fe-rich materials can enter into complexation reaction [18,19] with ionium solution.

Time (min)	15	30	60	75	90	120
Dolomite	3.99	3.54	3.09	2.93	3.56	4.06
Lignite	6.58	5.98	6.13	5.87	6.06	7.13
Limonite	5.41	5.04	4.11	5.03	6.86	6.99
Coke	9.05	8.49	8.23	8.85	9.01	9.06

Table I. Fluoride removal in time interval.

$$Fe\,(OH)_3 + M^{n+} / A^{n-} + mH_2O\,(aq) = FeO\,-M\,(OH)_m\,^{(n-m-1)}\,(s) + (m+1)\,H^+\,(aq)$$
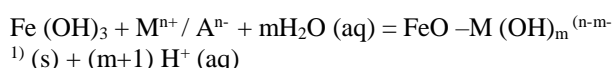
M and A represent cationic and anionic adsorbates, respectively $(OH)_m\,^{(n-m-1)}$ refers to the hydrolytic species of the metal. In general, the positively charged sites and negatively charged F ion is also possible. Dolomite & Limonite have good removal capacity because it contains both the oxide of iron, aluminium and calcium which are good fluoride removers. Lignite has a moderate to fluoride-removal capacity since it mostly contains carbon compound, organic matter.

It is evident from (Figure 4) that the rapid rate of removal of fluoride decreases markedly within 60 min or so to gradually approach equilibrium which is attained almost completely after 90 min of contact between the solution and the material. The rate of adsorption / absorption or ion exchange is controlled by the rate of diffusion of fluoride in the inter-capillary pores of the particles. The mathematical treatment of inter-particulate diffusion does not lead to a simple algebraic relationship between the external solute concentration and time of the reaction event when a constant saturated external layer is maintained.

The dilution methods can be adopted to reduce the F^- concentration in groundwater but lack of water resources is the main constraint. Our preliminary experiments indicate that almost all the naturally occurring materials are used here to remove excess fluoride in water are suitable. Some have the ability to remove F over short periods of time and need regeneration immediately after 15 min. So, approximately 25 ml can be treated within 30 min using 25 g volume of material. After this, two-cylinder columns each of 20 cm in height were set up containing a combination of different materials in order to determine the efficiency of F^- removal materials. Two columns were setup to determine the fluoride removal capacities for different anisotropic ratios [18,19] for a layered sequence of same materials of different thickness. The thickness of the layers in the different columns is displayed (Fig. 6). Of the two columns prepared, the first column has a higher F^- removal rate than the other[20]. In the first column excess of Dolomite & Limonite were used whereas it amounts reduced in second column which have considerable defluorination capacity[20]. Due to that reason first column has most effective in removal of F^- in water.

The contaminated water of 6.2 mg/l was passed through both the columns at the same time and collected effluent was tested for fluoride ions. Column I was found to be more effective than Column II. Equilibrium was attained in Column I earlier than Column II. When the amount of material used varies, the capacity of fluoride removal also varies along with the equilibrium time[21,22]. The quantities of the materials were used in the order of removal capacities to get good result (Fig. 7).
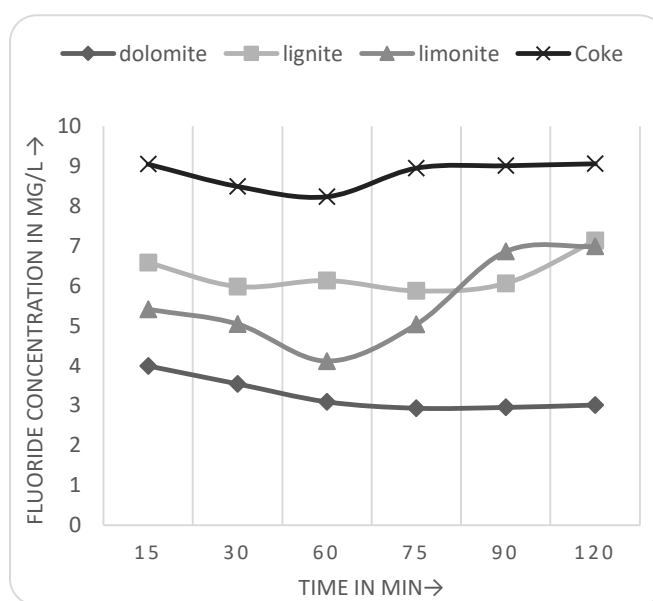

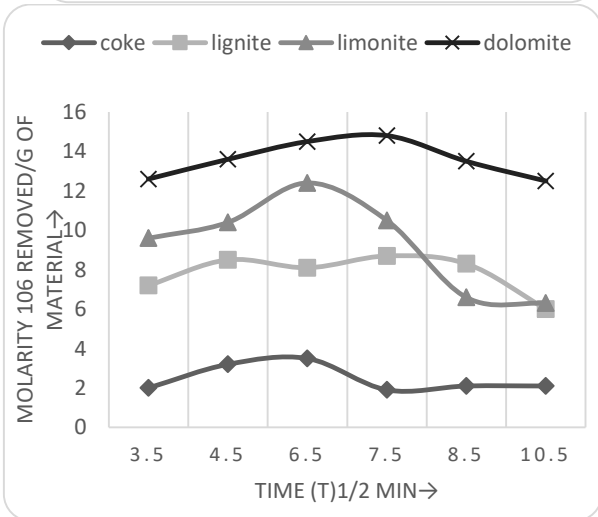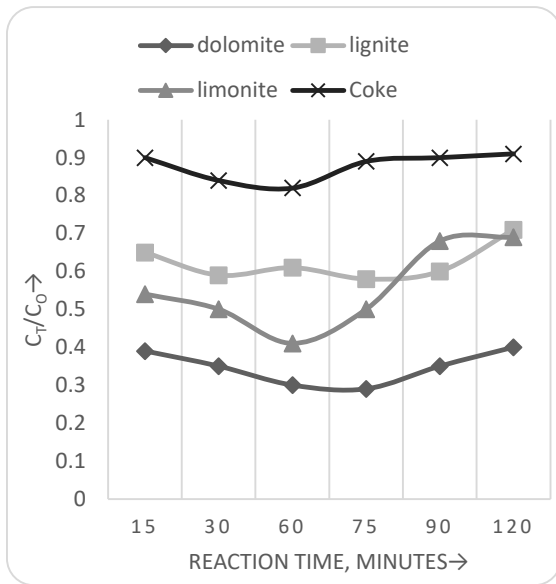Fig. 3.Fluoride removal capacities by solid-sorbent .

Fig. 5. Fluoride removal by natural ores.

The correlation coefficient (Table II) between the materials and time indicates negative correlation by all adsorbent but good relation showed by Limonite.

II. CONCLUSION

The Column study reveals that of four materials used for defluorination. Dolomite has a good defluorination capacity followed by Limonite, Lignite and Coke. Near equilibrium is attained after 60 min of the experiment. Maximum defluorination occurs immediately after the experiment has started. The molarity of fluoride removed per gram is more in dolomite when compared to other

materials[23]. Dolomite and Limonite have the highest fluoride removal capacity because it has oxide of Calcium, Aluminium and Iron as its major components. The column study reveals that use of materials according to fluoride removal capacity seems to be very effective. Our study gives hope for using low- cost locally available natural ores for removing excess fluoride from drinking and domestic water. In order to improve on these techniques, further detailed investigations are needed and are being undertaken. In spite of certain technical drawbacks among the method, application of column technique is going to be very significant to rural population. In this respect our study will be of great relief to those drinking-water supply systems where F^- is reported to be very high.
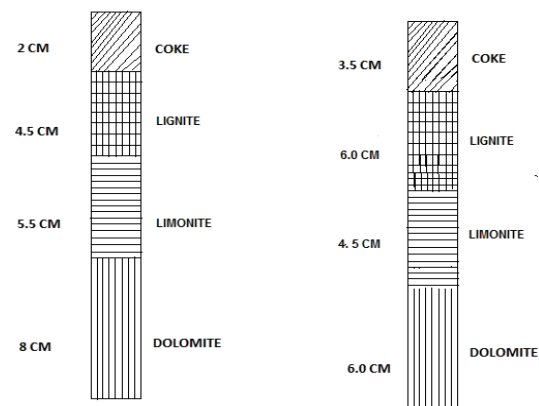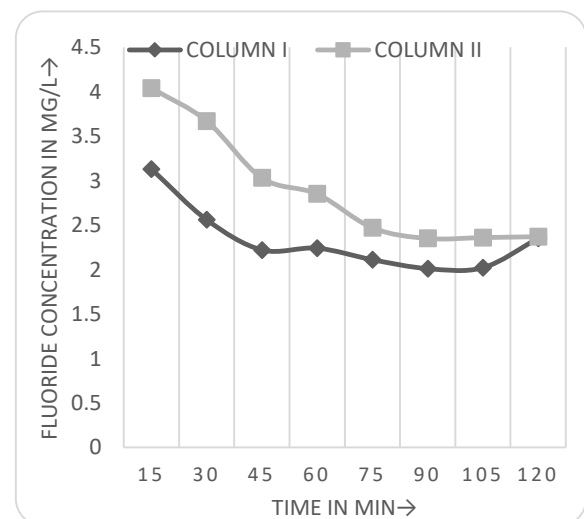

Fig 6. Thickness of layers in different columns

Fig. 7 Efficiency of two columns

Correlation matrix of the materials used with time					
	Coke	Limonite	Lignite	Dolomite	Time
Coke	1				
Limonite	0.93	1			
Lignite	0.55	0.77	1		
Dolomite	0.81	0.66	0.82	1	
Time	-0.47	-0.61	-0.36	-0.02	1

Table 2. Showing Correlation of four sorbent with time

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