ABSTRACT

Fluoride ingress in sub surface water resources is widely found in many parts of world including India. Concentration in groundwater over and above 1.5 mg/L- 2 mg/L is considered to be unsafe for human consumption. Dental carries, Skelton fluorosis are the common health issues for fluoride uptake in drinking water. Fluoride contamination of groundwater is also an important global water quality issue. Approximately 200 million people in 29 counties are suffering from fluoride contamination. Fluoride contamination through wastewater discharge s also found in some industrial effluent that releases from industries of fertilizer manufacturing, glass processing units, semiconductor manufacturing industries, etc.

In this connection various technologies are used presently for removal of fluoride from water environment. Among all available technologies, use of adsorption is very common. Adsorption is a technologically friendly and easily applicable engineering method for fluoride removal from water environment. Activated alumina is an excellent material for elimination of Fluoride from water, however this material is costly and is availability is also a concern. Moreover, it is efficient technique at lower pH (5-6). The most important fact that, disposal of used Activated alumna is a cumbersome process. Due to limiting usage of activated alumina, scientist and engineers are actively exploring for easily available low-cost absorbent particularly deriving from waste materials for removal of fluoride from water environment.

Earlier, Bhaumik *et al*., (2017) used fish scale powder material for removal of fluoride. In India, many markets produce huge amount of fish scale waste and dispose them off indiscriminately causing aesthetics and physical pollution of soil and other environment. Moreover, fish scale derived active carbon contained some useful sorption site for removal of the above solute material. With this viewpoint a research study is undertaken to examine the potential application of fish scale derived activated carbon as biochar (FSB) with some surface modification for removal of Fluoride from water environment.

Successful use of Fish scale biochar (FSB) as an absorbent material is considered to be novel and not only groundwater treatment to be done by this material but at the same time solid waste problem to is curbed down particularly from fish market area. In the present research Fish scales in sizeable amount was collected from a local fish market and sundried in openly in air with subsequent heating at 600^0C in muffle furnace to remove moisture, volatile matter reduced for converting to carbonaceous material. The biochar thus formed is named as Fish Scale Biochar (FSB). This material was subsequently washed in ammonia free distilled water and exposed to acidic solution to remove fine foreign materials and other impurities. This acid laden Fish scale biochar was named as Acid modified fish scale biochar (AMFSB). FSB and AMFSB are tested with Fourier-transform infrared spectroscopy (*FTIR*) scanning electron microscope (SEM) Energy Dispersive X-ray and X-Ray Diffraction Analysis (XRD)to characterize its chemical and structural composition. A pre-determine amount of both the material have been taken in Fluoride spiked solution of known fluoride concentration is with varying adsorbent dose and stirred 150 rpm for contact time of 150 minute to examine its fluoride removal capacity.

To determine the feasibility and fluoride uptake capacity of absorbent batch Kinetic studies are conducted with the different initial fluoride concentration, pH, absorbent dose, contact time and agitation speed, as per standard absorption experiment flowed by previous researchers. The effect of various influencing parameters on fluoride removal efficiency of AMFSB are also observed. Various types of isotherm studies are carried out and plotting was done based on experimental data. Kinetic Data reveals that it follows pseudo first order kinetic rate and Langmuir adsorption isotherm model, was reasonably fitted for FSB (R^2 =0.984) and AMFSB (R^2 =0.985). The result demonstrated that fish scale derived biochar is able to remove fluoride up to 92.2 % corresponding to an initial concentration 5mg/L and adsorbent dose of 6 gm/L. Both the materials followed adsorption phenomenon. It is also found that adsorption capacity of FSB and AMFSB is about 2.12 and 5.16 mg/g respectively. Which is comparable with many other adsorbents investigated earlier by other researchers for fluoride removal.

The batch experimental data also indicates that pH of the solution contributes maximum effect on removal mechanism. It was observed that for FSB maximum removal taken place at pH 5.5. Whereas, for AMFSB pH value was found to be 6.5 for optimum removal. Other parameter effects are not very predominant as compared to pH. It was found by various earlier researchers that percent fluoride removal by activated alumina took place at pH less than 4, i.e., in acidic condition.

After kinetic studies, fixed bed column study is conducted with perplex short column with column of 2 cm diameter and 40 cm length for different initial concentration of fluoride such as 5, 7, 10 mg/L. The bed height of column was varied between 1, 2 and 3cm, the application flow rate was also allowed to vary. The breakthrough service time was noted and plotted with c/co value. Column study results are also employed to examine validity of Thomas model, Yoon-Nelson and BDST model. The column study plot exhibit BDST model reasonably fitted well with service time 674 minutes for column of adsorbent depth of 3cm.

Some optimization too has been also exercised to predict the optimum condition for fluoride removal of AMFSB application for batch treatment. This optimization analysis was done by applying RSM analysis with Box-Behnken design model. The F-test ANOVA is used for explaining the significance of the regression model equations. The F-values and P-values gave the significance of each variable. The RSM analysis predicted maximum fluoride % removal efficiency of AMFSB to be 85% at optimum pH of 7.1, contact time of 156.9 min, initial fluoride concentration of 5.3 mg/L. and adsorbent dose of 6.21 mg/L.

This present research investigation exhibits both Fish scale biochar (FSB) and Acid modified fish scale biochar (AMFSB) are significantly efficient for removal of fluoride from water environment and perhaps be new adsorption material for groundwater and wastewater.