REMOVAL OF FLUORIDE FROM WATER BY ADSORPTION ONTO GAMMA ALUMINA, BAUXITE, CERIUM HYDRATE AND LANTHANUM OXIDE

SYNOPSIS

The presence of fluoride in drinking water supplies in quantities in excess of prescribed limits is a matter of serious concern from public health point of view and warrants removal prior to human consumption.

The present study was undertaken to investigate removal of fluoride from drinking water employing low cost and abundantly available Bauxite, rare earth materials, viz, Lanthanum oxide and Cerium hydrate and gamma Alumina.

All the four materials were initially screened for uptake of fluoride from a test fluoride solution employing batch adsorption experiments. Lanthanum oxide, Cerium hydrate and gamma Alumina exhibited good uptake whereas uptake by Bauxite was poor. The Bauxite was subjected to acid treatment with HCl acid and the acid treated Bauxite exhibited good uptake. Detailed experiments like adsorption kinetics, equilibrium adsorption, influence of pH and anions; desorption, interruption and regeneration studies and column studies were conducted and the results are discussed in the proceeding paragraphs. Further, Infrared spectral studies and X-ray Diffraction studies of loaded (sorbed) and unloaded (virgin) sorbents were conducted to study the nature of the adsorption reaction and probe into the mechanism aspects of adsorption interaction.

It follows from the batch adsorption experimental results that of all the sorbents, Cerium hydrate exhibited highest potential for fluoride removal followed by Lanthanum oxide, gamma Alumina and treated Bauxite. Adsorption was independent of system pH i.e., the pH of the solution has insignificant effect on adsorption in the pH range of 3.0 to 8.0, thus
indicating a good potential for field application. The pH sorption edges were typical of anionic sorption with sorption decreasing dramatically at high pH i.e., at pH above 9.0. The percentage of removal of fluoride increased with an increase in dose in all the cases with 100% removal achieved by Cerium hydrate at a dosage of 4 g.L⁻¹; however, in all the cases, the uptake of fluoride i.e., mg of fluoride sorbed per gram of sorbent decreased with increase in sorbent dose.

Study of kinetics of adsorption indicated that the adsorption process proceeded quite rapid initially and attained equilibrium gradually. The plot of the rate of uptake i.e., kinetics of the sorption constituted three distinct phases for all the sorbents; an initial steep portion denoting high rate of uptake; a transitional phase in which rate of uptake decreases gradually and approaches a more or less constant value denoted by curvilinear portion and a final equilibrium in which rate of uptake is almost constant, denoted by a straight line plateau.

Adsorption kinetic data fitted well to the pseudo second order model. Further processing of kinetic data suggested pore diffusion to be rate limiting though some film diffusion might occur overcoming the resistance offered by boundary layer because of agitation.

Isothermal equilibrium data of all the sorbent except treated Bauxite fitted well into the BET model. It may therefore be inferred that adsorption on a heterogeneous surface and resource in formation of multilayers. From the adsorption capacity and intensities the order of sorption is Cerium hydrate > Lanthanum oxide > gamma Alumina > Treated Bauxite. From the equilibrium data empirical adsorption isotherm models were obtained and are presented in the text.

Isothermal equilibrium adsorption curve (saturation curve) of Bauxite conform to Type I of BET classification, which is the Langmuir type, representing an adsorption that
presumably corresponds to a complete monolayer. Saturation curves of the remaining sorbents conform to Type IV, which are considered to reflect capillary condensation phenomenon in that they level off before the saturation is reached and may show hysteresis and specifically refer to porous solids.

Description studies are useful in elucidation of the mechanism of adsorption reaction and the amount of desorption provides an insight into the nature of sorbent-sorbate bonding and also of the ion-exchange property of the sorbent. Desorption studies conducted employing distilled water revealed insignificant desorption. The order of desorption of fluoride is (Cerium Hydrate and gamma Alumina) > treated Bauxite > Lanthanum oxide.

The results of desorption studies further indicated that the fluoride-sorbent sorption is mostly irreversible in nature with a chemisorption type interaction occurring between the fluoride and the sorbent surface.

In order to probe into the nature of the sorptive uptake of fluoride by various sorbent under study, interruption studies were conducted by interrupting the process of adsorption. Results of interruption tests indicate pore diffusion to be the rate limiting in the sorption process.

Regeneration studies with 0.1N HCl, 0.1N NaOH and 0.1N NaCl indicated insignificant regeneration with 0.1N HCl and 0.1N NaCl, whereas regeneration with 0.1N NaOH was significant (15-70%). Cyclic regeneration studies conducted using 1% Alum solution and it follows from these studies that all the sorbent under study could be regenerated for 10 cycles before the residual fluoride reaching $1.5 \text{ mgL}^{-1}$.

To investigate the engineering design aspects like contact time and optimum operating capacity, up flow column studies were conducted using a Perspex (polymethyl
methacrylate) column of 39 mm internal diameter having appropriate inlet and outlet arrangements. Fine size of the particles prevented down flow pattern. Three different weights of sorbents and three different linear flow velocities were used and the columns were run to exhaustion. Rate of appearance and breakthrough profile were recorded and the data fitted in to appropriate mass transfer models.

In real field environment a wide variety of anions like chlorides, carbonates, bicarbonates and sulphates may be present in aqueous phase in association with fluoride ions. In the present study, therefore, the effect of anions like $\text{SO}_4^{2-}$, $\text{Cl}^-$, $\text{CO}_3^{2-}$, $\text{HCO}_3^-$ on the adsorption of fluoride by various sorbents was studied. Chlorides, Sulphates and Bicarbonates influenced fluoride uptake beyond concentration of 500 mg of Chlorides/L, 150 mg of Sulphates/L and 50 mg of bicarbonates/L.

Infrared spectral analysis permits spectrophotometric observation of the solid surface in the Infrared range (4000 to 667 cm$^{-1}$) and serves as a direct means for identification of the organic functional groups on the surface. An examination of the sorbent surface before and after sorption reaction would possibly provide information regarding the surface groups that might have participated in the adsorption reaction and also indicate the surface site(s) at which sorption might have taken place.

In the present study, virgin (unloaded) sorbents and sorbent samples after adsorption (loaded) with fluoride were subjected to infrared spectral studies.

The spectrograms of loaded and unloaded sorbent samples compared in terms of the resultant changes in the finger print regions like appearance/disappearance of the bands, broadening/sharpening of the bands, shifting of the bands (spectral shifts) etc., and attempts were made to correlate these changes with the sorption interaction.
Pure i.e., unloaded Treated Bauxite, Cerium hydrate, Lanthanum oxide, gamma Alumina and loaded sorbents were also subjected to powder X-Ray diffraction (XRD) analysis. The X-Ray diffraction patterns of loaded sorbents exhibited some variations possibly due to Fluoride sorption.

From the above studies some key inferences were drawn like of all the sorbents studied Cerium hydrate exhibited the most rapid uptake and also maximum extent of uptake of fluoride followed by gamma Alumina, Lanthanum oxide and Treated Bauxite. The sorption interaction followed a pseudo second order reaction and sorption interaction was instantaneous and of the type Chemisorption with pore diffusion to be rate limiting. In the normal range of drinking water pH encountered, sorptive uptake of fluoride was not affected by pH of the water.