

Fluoride removal from water by adsorption on acid activated kaolinite clay

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Received 19 April 2007; revised 14 May 2008

When drinking water contains excess fluoride it causes health hazards to human beings. In the present investigation the removal of fluoride has been attempted using acid activated kaolinite clay obtained from local traditional potter of Majuli river island, Assam. The clay was characterized by chemical analysis, IR, XRD data and thermal analysis. The clay was activated with conc. H_2SO_4 . The fluoride removal studies were done by adsorption method on raw clay and acid activated clay. The effects of contact time, approximate particle size, pH and temperature were investigated. The adsorption followed Langmuir isotherm. The results show that acid activated kaolinite clay is effective for defluoridation of water while raw kaolinite has very low defluoridation capacity due to low adsorption.

Keywords: Fluoride removal, Activated kaolinite, Majuli clay, Adsorption isotherms

It is now well known that the fluorosis disease caused by consumption of excess fluoride from drinking water is a major health problem in some parts of India¹. Fluorosis is a dangerous disease which is characterized by mottled teeth in dental fluorosis and brittle bones in severe skeletal fluorosis. The fluorosis is caused by oral intake of fluoride when drinking water contains more than the permitted² concentration of fluoride (1.5 mg/L). Fluorosis may be life threatening in particular fluoride effected area if proper defluoridation techniques are not employed to defluoride the drinking water. Similar health problems due to high fluoride content in ground water have also been reported from China, Sri Lanka, Spain, Holland, Italy, Mexico and North and South American countries.

In recent years defluoridation of water has been tried by using the adsorbents like activated carbon³, coconut shell carbon, natural zeolites, illite-zeolite soils⁴ and other low cost adsorbents^{5,6}. In kaolinite, the silicon ions are found to be surrounded by four oxygen⁷ ions, but each aluminium ion is coordinated with four hydroxyls and two oxygens. These

hexagonally shaped crystals carry a negative charge on the basal surface. It is generally assumed to be due to the substitution of aluminium for silicon in tetrahedral layer with a consequent imbalance of negative charge. The edges of crystal, where imperfections necessarily occur because of bond breakage, carry⁸ a positive charge at low pH and this decreases to zero as the pH is raised to 7. Though the surface area of kaolinite clay is comparatively lower than other clay minerals, it increases after leaching⁹ with acid. High grade kaolinite find uses in making ceramic materials in industry as well as in petroleum reservoir engineering. In the present work the study of defluoridation of water by adsorption method using acid treated kaolinite clay has been done. The effects of contact time and temperature on the defluoridation property of acid activated clay have been experimentally studied. The adsorption process is explained in terms of the Langmuir and Freundlich isotherms. Further, the nature and morphology of the adsorbent are discussed on the basis of XRD studies.

Experimental Procedure

The clay sample was obtained from local traditional potter of Majuli river island, Assam, India. The sample was dried, grounded in a mortar and then sieved as to pass through 200 mesh ASTM sieve and retain on 300 mesh. For experiments, 20 g of the clay sample was stirred well in a 1000 mL sedimenting cylinder with 1000 mL distilled water. It was allowed to stand for 3 h and 27 min and 250 mL of the suspension was removed and evaporated¹⁰. The sample was grounded and heated in an air oven at 60°C. The clay was characterized by chemical analysis (SiO_2 , 49.11; Al_2O_3 , 36.34; Fe_2O_3 , 5.15; CaO , 0.92; MgO , 7.34; K_2O , 0.15; Na_2O , 0.35 and loss on ignition, 12.33%), IR spectroscopy, thermal and XRD studies. The acid activated clay was prepared by treating the clay sample with concentrated H_2SO_4 in the clay/acid ratio of 0.30 (w/w) heated in a water bath with constant stirring. Stock solution of NaF (3 mg/L) was prepared and this was used throughout the experiments. The adsorption experiments at room temperature and at higher temperatures were performed by mixing 10 g of acid activated clay with 100 mL of NaF in Eltek magnetic stirrer MS203. The residual fluoride concentration in

each sample was determined by gravimetric estimation¹¹. The percentage adsorption¹² was calculated from the residual fluoride concentration using the formula:

$$\% \text{ adsorption} = 100 \times (3 - [F]_{\text{residual}}) / 3$$

where $[F]_{\text{residual}}$ is the concentration of fluoride ion after adsorption which is subtracted from the initial concentration of fluoride ion (3 mg/L). The experiments were carried out in neutral aqueous medium. The extent of adsorption on raw Majuli clay was also evaluated. The effects of contact time on defluoridation were studied for 25, 50, 75, 100 and 150 min. The adsorption behaviour was also examined with different particle sizes and different temperatures as parameters. The extent of adsorption with the variation of pH at 4, 5, 10 and 12 was also determined. The pH of the solution was measured with Elico India LI pH meter. The pH was varied by using standard HCl and NaOH solution. The experiments were carried out at 25, 40, 50 and 60°C. The nature and morphology of the adsorbent was studied by taking XRD using Philips PW 1700 APD at University Science Instrumentation Centre, Guwahati University, Guwahati. Thermal analysis was done with Perkin-Elmer Pyris-Diamond TG/DTA and IR spectrum was recorded as KBr pellets with Perkin-Elmer spectrophotometer, model No. 883 at Dibrugarh University, Dibrugarh.

Results and Discussion

Characterization of Majuli clay

The differential thermal analysis done at 10°C/min in static air condition shows an endothermic peak at 83.94°C which may be ascribed to kaolinite. Differential thermal analysis curve (Fig. 1) also shows an endothermic deflection between 450 and 600°C with peak temperature at 480.1°C due to the dehydration and decomposition of crystal structure of the clay¹³. This peak temperature is indicative of kaolinite¹⁴ mineral. The IR band near 441 cm⁻¹ may be attributed to kaolinite clay. The medium band near 914 cm⁻¹ is also significant band for kaolinite. The strong bands at 3616 and 3687 cm⁻¹ arise principally from OH-stretching vibration¹⁵. The broad band near 3423 cm⁻¹ is ascribed to absorbed H₂O molecules and therefore, has a large spreading. Such type of band is sometime exhibited by kaolinite clay mineral also. The two characteristics XRD peaks are obtained at the d-value 7.24 and 3.35Å. The XRD of Majuli clay

shows a weak peak at 1.50Å for (060) reflections which is also characteristic for kaolinite¹⁶.

Adsorption studies

The adsorption rate of fluoride for the initial 150 min was studied. The percentage of fluoride removed increased linearly in the early stages up to 100 min and thereafter remained static. The extent of adsorption was plotted against time at room temperature. The extent of adsorption on kaolinite clay was found to be very poor which is almost 19% due to its low surface area and low ion exchange capacity. The adsorption rate of fluoride by acid activated clay was studied in terms of its intra-particle diffusion within the pores of adsorbent. Figure 2 shows the extent of adsorption of fluoride as a function of square root of time at room temperature. The plot is linear for a wide range of contact time but it does not pass through the origin which implies that the defluoridation mechanism on clay is both by surface adsorption and through intra-particle diffusion¹⁷. The experiments were conducted with

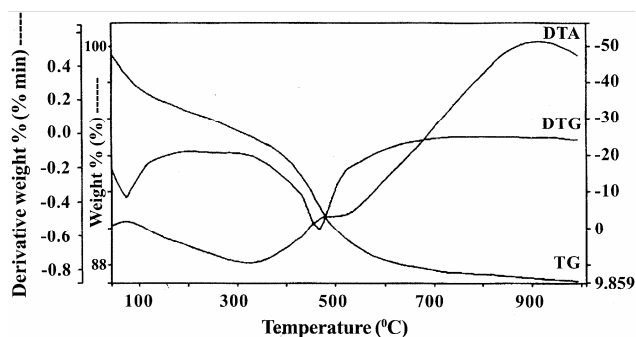


Fig. 1—TGA/DTA of Majuli clay.

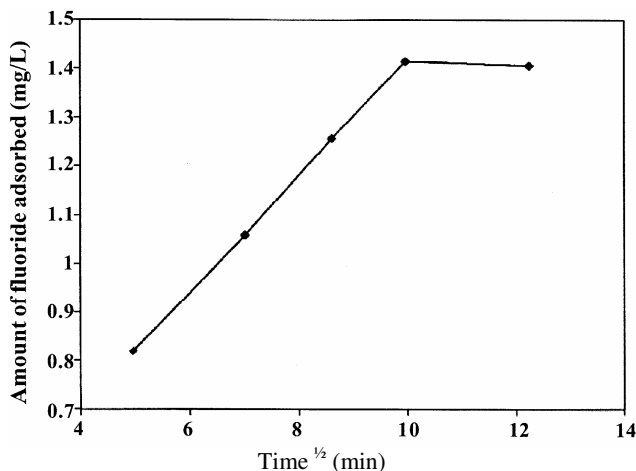


Fig. 2—Plot for intraparticle diffusion at room temperature.

three different approximate particle sizes *viz.* 150 (passed through 150 mesh and retained on 200 mesh), 200 (passed through 200 mesh and retained on 300 mesh) and 300 meshes (passed through 300 mesh and retained on 400 mesh). The clay of 300 mesh size showed the maximum adsorption of fluoride, which is due to the availability of more specific surface area on the adsorbent surface. The lowest adsorption was 28% for 150 mesh sized particle while 32% adsorption was found for 200 mesh sized particle.

The adsorption increases with decrease of pH as it increases the positively charged sites¹⁸. The optimum adsorption was obtained at the pH value of 4. The temperature dependence of fluoride adsorption by acid activated clay was studied at 25, 40, 50 and 60°C. The percentage of adsorption of fluoride ion at 100 min was found to be 47.3, 50.11, 50.62 and 55.23 respectively at 25, 40, 50 and 60°C. From the plot of time against fluoride adsorbed by the acid activated kaolinite clay at four different temperatures, it was found that the extent of adsorption increased with increase in temperature. It revealed the endothermic nature of the process and is in perfect agreement with earlier findings¹⁹.

Adsorption isotherm

The Langmuir and Freundlich adsorption isotherms are evaluated for the adsorption of fluoride. The Langmuir constant Q^0 and b were obtained from the linear regression analysis of the Langmuir equation^{19,20}.

$$C_e/q_e = 1/Q^0 b + C_e/Q^0$$

where Q^0 and b represent adsorption capacity and energy of adsorption respectively, C_e is the concentration of fluoride at equilibrium (mg/L) and q_e is the amount of fluoride adsorbed per unit weight (mg/g). The values of Q^0 and b were calculated from the slopes and intercepts of the linear plots of C_e/q_e versus C_e respectively (Table 1). The plot at 40°C is shown in Fig. 3. The values of b increases with increase in temperature and

Table 1—Values of Langmuir and Freundlich constants					
Temp. (°C)	Q^0 (mg/g)	b (dm ³ /mg)	m	k_f	n
25	0.0450	2.7	22.030	1.2870	0.5182
40	0.0470	2.83	20.9850	1.4960	0.6720
50	0.0528	3.084	18.900	1.6100	0.7211
60	0.0557	3.282	17.9460	1.4000	0.8750

the values of m decrease with increase in temperature which implies favourable adsorption¹⁹.

The Freundlich equation for the system can be given as¹⁹

$$\log q_e = \log k_f + 1/n \log C_e$$

where k_f and n are adsorption capacity and intensity of adsorption. The plots of $\log q_e$ versus $\log C_e$ are shown in Fig. 4. As the values of n are <1, it indicates unfavourable adsorption condition¹², the adsorption of fluoride does not fit well with the Freundlich adsorption isotherm.

The XRD of acid activated kaolinite clay is different from raw Majuli kaolinite clay due to the broken lamellar structure on heating with acid (Fig. 5). A small structural change occurred for

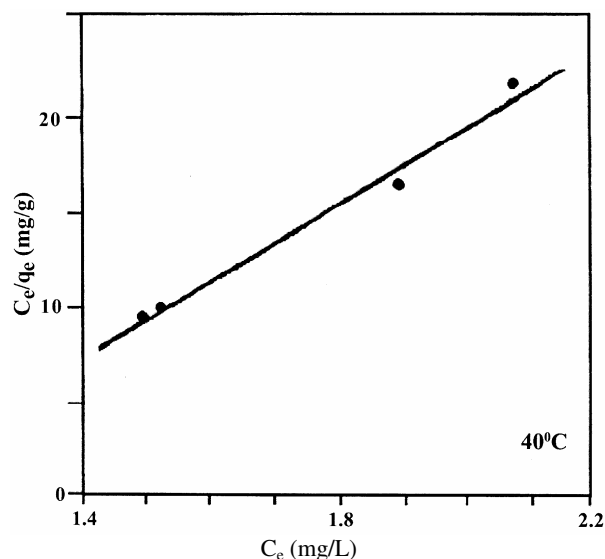


Fig. 3—Effect of temperature: Langmuir's plot

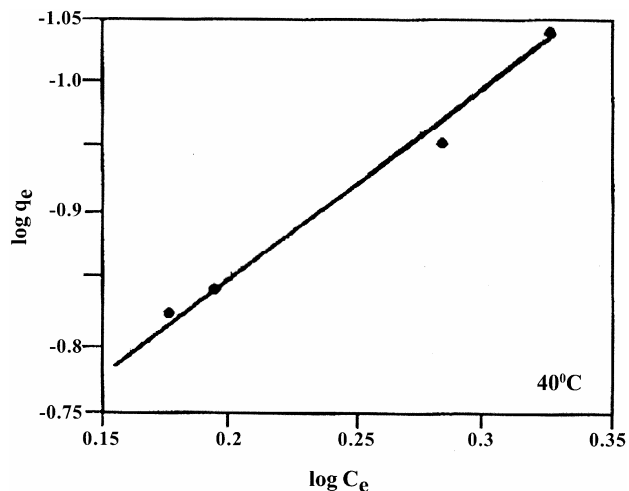


Fig. 4—Effect of temperature: Freundlich's plot

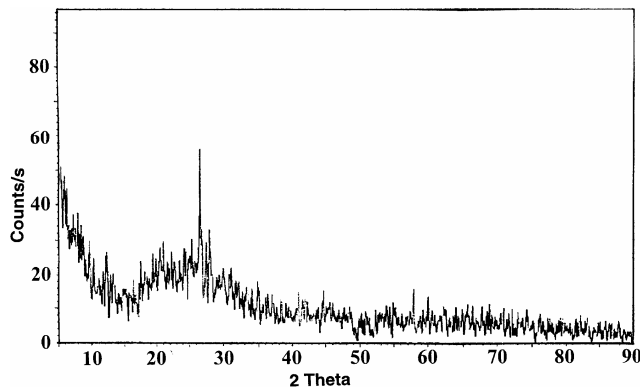


Fig. 5 — XRD of acid activated Kaolinite clay.

fluoride adsorption on acid activated kaolinite clay. The weak peak due to 060 plane disappeared completely after fluoride adsorption.

Conclusion

The study indicates that though raw kaolinite has low defluoridation capacity yet kaolinite clay may be helpful for defluoridation if it is activated with acid. In addition, small particle size and low pH can improve the defluoridation capacity of acid activated kaolinite.

Acknowledgement

Authors thank Dr. S. Karmaker, Scientist in charge, USIC, Gauhati University Guwahati, Assam for recording XRD.

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