



**EFFECT OF DIFFERENT PARAMETERS FOR THE REMOVAL OF FLUORIDE FROM WATER AND WASTEWATER USING INDUSTRIAL SOLID WASTE LIKE CHINACLAY.**

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**ABSTRACT**

Exposure to fluoride beyond the recommended level for longer duration causes both dental and skeletal fluorosis. Thus, the development of cost-effective, locally available, and environmentally benign adsorbents for fluoride removal from contaminated water sources is absolutely required. Presence of fluoride in low concentration ( $< 1.5 \text{ mg L}^{-1}$ ) is beneficial to the people for the calcification of dental enamel and maintenance of healthy bones. Fluoride presence in higher concentration become a monster and can cause dental, skeletal fluorosis and also non-skeletal problems. Among several treatment technologies applied for fluoride removal, adsorption process has been explored widely and offers satisfactory results especially with surface modified adsorbents. It is evident from the literature survey that various adsorbents have shown good potential for the removal of fluoride. Batch adsorption experiments were conducted to obtain the optimum conditions for fluoride removal. Effect of parameters like contact time, pH, temperature and adsorbent dose were also determined.

**KEYWORDS:** Adsorption, China clay, Fluoride, Human health, pH.

**INTRODUCTION**

Water is a source of life, a fundamental requirement for health and main need for industrialization. It is essential for all forms of growth and development of humans, animals and plants. However, the suitability of water for a specific purpose can be affected by other substances dissolved or suspended in it. Contamination of drinking water by fluoride is one such example. In addition to arsenic and nitrate, which cause large-scale health problems, fluoride is classified as one of the contaminants of water for human consumption by the World Health Organization (WHO).<sup>[1]</sup> Fluoride ion exists in natural waters and it is an essential micronutrient in humans in preventing dental caries and in facilitating the mineralization of hard tissues if taken at a recommended range of concentration. Higher level of fluoride in groundwater is a worldwide problem.<sup>[1-3]</sup> The World Health Organization (WHO) has set a guideline of 1.5mg/L for fluoride in potable water.<sup>[4]</sup> Concentration higher than this value can lead to fluorosis and several types of neurological damage in severe cases.<sup>[5]</sup> Many methods have been developed for fluoride removal from water such as adsorption<sup>[6]</sup>, ion exchange<sup>[7]</sup>, membrane processes such as reverse osmosis and nanofiltration<sup>[8,9]</sup> electro-dialysis<sup>[10,11]</sup> and precipitation.<sup>[12]</sup> Among these methods, adsorption is widely used method for defluoridation which depends on ions in fluid diffusing to the surface of a solid when they are bound to the solid

surface or are held there by weak intermolecular forces.<sup>[13]</sup> Adsorption is recognized as the most efficient, promising, and widely used fundamental approach in water and wastewater treatment processes.<sup>[14]</sup> Different adsorbents such as activated alumina<sup>[15]</sup>, bleaching earth<sup>[16]</sup>, iron oxide<sup>[17]</sup>, activated titanium rich bauxite<sup>[18]</sup>, activated carbon<sup>[19]</sup>, red mud<sup>[20]</sup>, and clay<sup>[21, 22]</sup> were tested to find out efficient and economically viable defluoridating ones. Among these adsorbents, clay and clay minerals are naturally abundant, renewable, and environmentally sustainable.<sup>[23-25]</sup> They are considered robust adsorbents<sup>[24]</sup> due to their low cost, adsorption properties, and ion exchange potential. In recent years, considerable amount of work has been done on activation of clay and clay minerals to improve the adsorption capacity and hence removal efficiency.<sup>[26, 27]</sup> The main objective of this investigation is to study the removal efficiency of China clay as a potential adsorbent for fluoride removal under different physicochemical conditions.

**Preparation of Adsorbent**

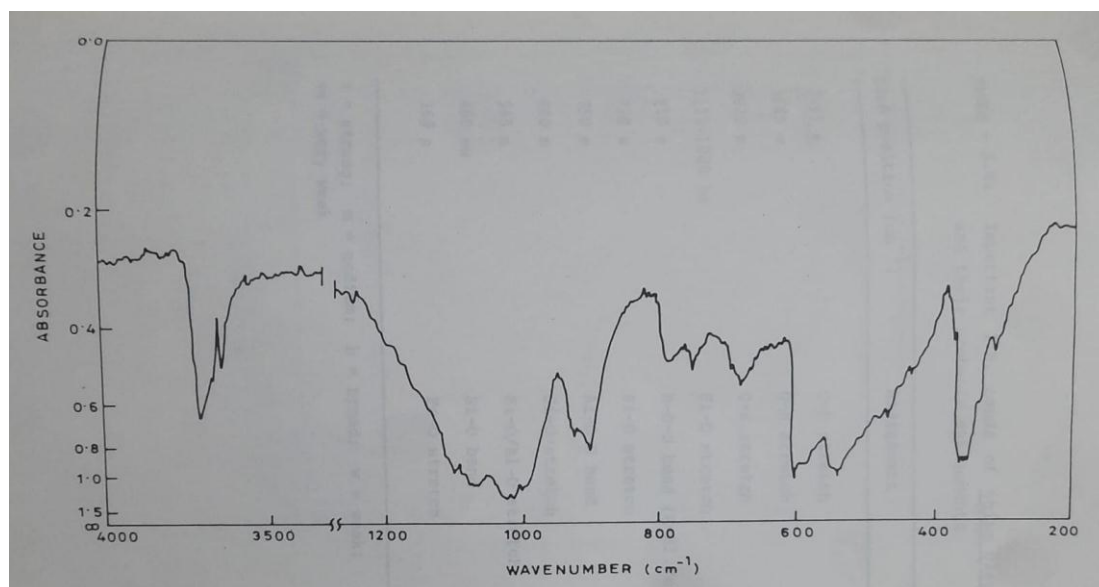
China clay is a mineral of kaolinite group. It does not swell with addition of water. The alumina content present in it does not form isomorphous series with any other metallic compounds. It is generally used in the manufacture of different types of ceramic goods. It has been used by several workers<sup>[28-32]</sup> as an adsorbent for

water and wastewater treatment by adsorption process. It was collected from Patharghatt village of Bhagalpur district, Bihar (India).

The Infra-red spectrum of adsorbent was recorded in KBr and nujol null using Perkin Elmer Spectrophotometer, Model 783 and 621 in the range of 4000-200  $\text{cm}^{-1}$ .

**Table 1: Chemical analysis of China clay as Adsorbent.**

Constituents	Percentage by weight
SiO <sub>2</sub>	46.22
Al <sub>2</sub> O <sub>3</sub>	38.40
CaO	0.86
Fe <sub>2</sub> O <sub>3</sub>	0.68
MgO	0.37
Loss of ignition	13.47
Particle size	53 $\mu\text{m}$
Mean Particle size diameter	$51 \times 10^{-4}$ cm
Surface area	$13.52 \text{ m}^2 \text{ g}^{-1}$
Porosity	0.330
Density	$2.692 \text{ gcm}^{-3}$



**Figure1 : Infra red spectrum of China clay.**

#### Adsorption method :

In the adsorption method, raw water is passed through a bed containing defluoridating material. The material retains fluoride either by physical, chemical or ion exchange mechanisms. The adsorbent gets saturated after a period of operation and requires regeneration. A wide range of materials has been carried out for fluoride uptake such as Bauxite, magnetite, kaolinite, serpentine, various types of clays and red mud are some of the naturally occurring materials were studied. The general mechanism of fluoride uptake by these materials is the exchange of metal lattice hydroxyl or other anionic groups with fluoride. Fluoride uptake capacity can be increased by certain pre-treatment like acid washing, calcinations, etc.

#### Experimental Method

The Corning glassware was washed off with nitric acid and distilled water before use. First, a stock solution of  $100 \text{ mg L}^{-1}$  was prepared by dissolving appropriate

amount of sodium fluoride (NaF) in distilled water and desired concentrations of working solutions were then prepared from stock solution. H<sub>2</sub> SO<sub>4</sub> (0.1N) and NaOH (0.1 N) were used for adjusting the pH values either acidic or alkaline conditions. Low cost material like China clay were utilized (Table 1 and Figure 1). China clay was sieved through IS sieves of 53  $\mu\text{m}$  was used in all experiments. Non-flow batch adsorption studies were conducted to study the effect of controlling parameters like contact time, adsorbent dosage, solution pH etc. Continuous down flow column studies were also conducted to study the practical applicability of China clay for removal of Fluorides from water. All the experiments were conducted at room temperature (25<sup>o</sup> C). Fluoride concentration was estimated by SPADNS method (APHA) using a SYSTRONICS-105 spectrophotometer.

The amount of fluoride adsorbed ( $qt$ ) was calculated as the change in the aqueous phase concentration from

initial value according to the equation,  $qt = \left[ \frac{C_0 - C_t}{m} \right] V$  .....(1)

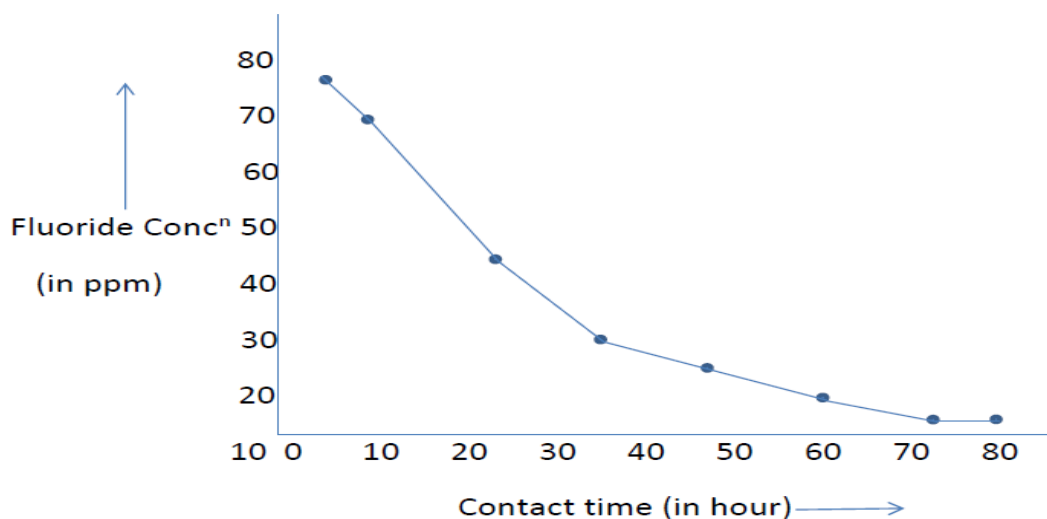
where,  $C_0$  and  $C_t$  ( $\text{mg L}^{-1}$ ) are the initial fluoride concentration and at contact time  $t$ ,  $V$  (L) is the volume of solution, and  $m$  (mg) is the amount of adsorbent added. The fluoride removal efficiency (percent fluoride removal) was calculated using the following equation.<sup>[33]</sup>

Percent fluoride removal (% removal) =  $\left[ \frac{C_0 - C_e}{C_0} \right] 100$  ..... (2)

**RESULTS AND DISCUSSION**

**1: Effect of contact time.**

The effect of contact time on the removal of Fluoride using China clay is presented graphically in Figure 2. It may be observed that as contact time increases, ppm removal also increases initially and reduces gradually with time and attains almost an equilibrium condition in nearly 72 hours and remains constant thereafter. A maximum of 85% removal could be accomplished by China clay.



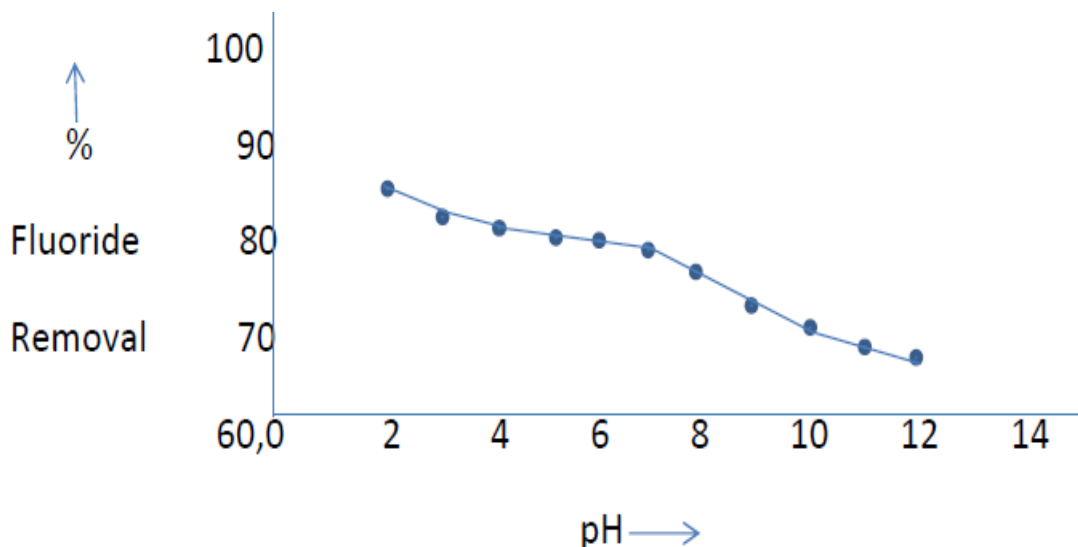
**Figure 2 : fluoride removal at different contact time.**

**2: Effect of Solution pH**

Removal of Fluoride by China clay decreased continuously as pH was increased from 2.0 to 12.0 (Figure 3). Decrease in percentage removal of Fluoride in pH range of 2 to 10 was low i.e., 12.5% whereas removal of Fluoride decreased significantly from pH

10 to..

12. Marginal variation in Fluoride removal by China clay over pH range of 2 to 10 indicates its usefulness for removal of Fluoride in the pH range normally encountered in ground waters laden with Fluoride.



**Figure 3: Fluoride removal at different pH.**

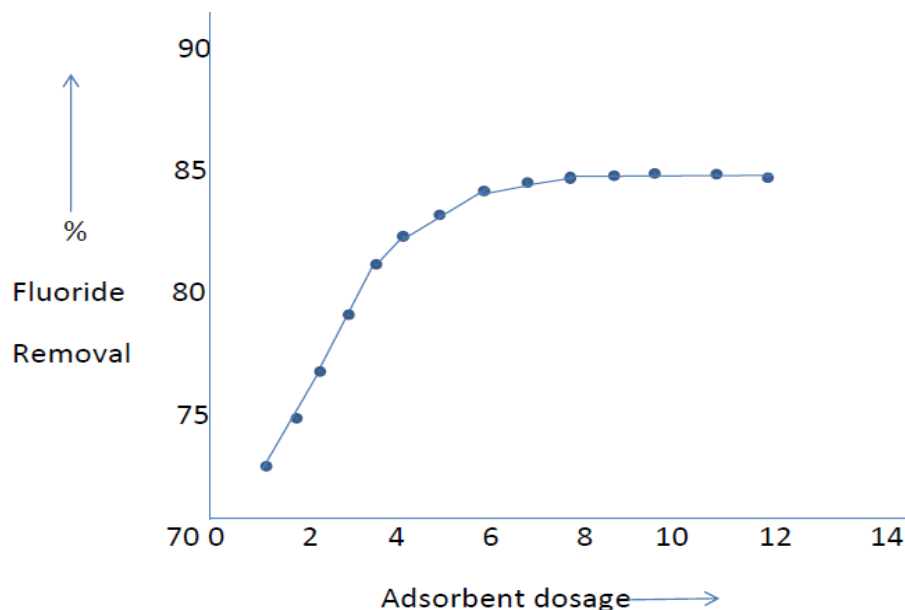


Figure 4: Effect of adsorbent dose on fluoride removal.

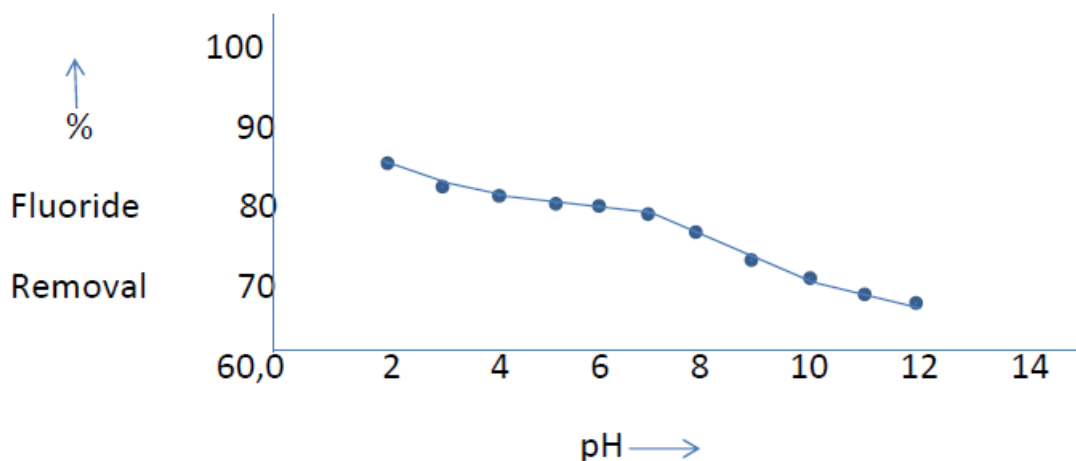
### 3: Effect of adsorbent Dose.

Results of equilibrium adsorption experiments conducted with a test Fluoride solution of concentrations  $10 \text{ mg L}^{-1}$  (Figure 4). The amount of Fluoride adsorbed increased with increase in dose and 84% removal was accomplished at a dosage of 9 gm. At higher doses than 9gm there is no increase in Fluoride removal perhaps due to non-absorbability of Fluoride ions.

### 4: Effect of temperature

The effect of temperature was studied by conducting the experiment at different temperatures of 303,313,323 and

333K ( $30^{\circ} \text{C}$  to  $60^{\circ} \text{C}$ ). The percentage removal of the fluoride ion vs temperature (figure 5). It was observed that with an increase in the temperature from 303K to 333K ( $30^{\circ} \text{C}$  to  $60^{\circ} \text{C}$ ) the percentage removal of fluoride ion increases from 63.5% to 83.5%. As the temperature increases, the thickness of the outer surface of the adsorbent decreases and the kinetic energy of the fluoride ion decreases across the external boundary layer and also internal pores of the adsorbent. The increase in the percentage of fluoride adsorption at higher temperatures confirms the endothermic nature of the process.<sup>[34]</sup>



### CONCLUSION

The experimental investigations clearly suggest that abundantly available and low-cost materials like China clay, is effective in removing fluoride from water to acceptable levels. Equilibrium isothermal adsorption experiments suggested that adsorbent dosages of 9 gm of adsorbent accomplished a removal of 85% of fluoride. The time to reach equilibrium was observed to be 72

hours. pH does not have any significant impact in the range of 2 to 10, whereas pH of more than 10 resulted in a steep decrease in fluoride removal. The study revealed that the percentage removal of fluoride increases with the increase in temperature for the adsorbent.

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