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Clean Up of Fluoride Rich Effluents by the China Clay

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Fluoride concentration in water has significant importance. Fluoride is beneficial when present in concentration of 0.5-0.8 ppm. But fluoride has been associated with mottled enamel of the teeth in concentrations in excess of 1.5 mg/L. The adsorption of fluoride on China clay was investigated in the present study. The parameters studied include the contact time, setting time, pH, dose of absorbent, rate of stirring and initial adsorbate concentration of fluoride removal efficiency. The optimized sorbent dose was found to be 1.5 g/100 mL equilibrium was achieved in 2 h and maximum adsorption was obtained at pH 3. Freundlich adsorption isotherms were plotted and kinetic constants were determined.

Key Words: Fluoride, Adsorption China clay, Freundilich isotherm.

INTRODUCTION

Fluoride is mroe aboundant in nature. It is recognized as an element of public health concern[1]. It occurs in pharmaceutical compounds, tooth paste, drugs, cosmetics, chewing gums *etc.* A small amount of it is beneficial for human health for preventing dental carries. It is very harmful when present in excess of 1 mg/L. World health organization (WHO) and IS:10500 recommended that fluoride content in drinking water should be in the range of 1.0-1.5 mg/L. The high fluoride concentration results in dental skeletal fluorosis and neurodegenerative effect on brain[2-4].

The high fluoride concentration in water is a problem in India. India is one among the 23 nations in the world, where fluoride contaminated ground water is creating health problems. The state of art report of UNICEF confirms the problem in 177 districts of 20 states in India. The high fluoride levels in drinking water and its impacts on human health have increased the importance of defluordation studies[7]. The magnitude of the problem made towards defluoridation of drinking water, combating the debilitating fluorosis and taking steps to prevent and control the disease.

Nalgonda technique developed by NEERI is commonly perferred at all levels because of its low price and ease of handling[5]. Various processes tried so far for the removal of fluoride from water are adsorption ion exchange, precipitation and membrane process. These methods have high operational and maintenance low cost fluoride removal capacities, lack of selectivity for fluoride, undesirable effects on water quality, complicated procedures involved in the treatment. Adsorption process is more efficient for defluoridation. Researches were carried out on different adsorbents like activated carbon, processed bone char powder, activated alumina, activated bauxite, fly ash alum lime hydrated zirconium oxide[5-14].

The aim of the research is to demonstrate the use of adsorbent China clay to gain an understanding of adsorption process. The adsorbent is in abundance and easy availability makes them a strong choice in the investigation of an economic way of fluoride removal. They can be easily solidified after the pollutants are adsorbed.

In the present study various parameters affecting adsorption like contact time between waste water and the adsorbent, adsorbent dose, setting time, stirring rate, pH and initial fluoride concentration have been investigated and the data of adsorption isotherms have been presented.

EXPERIMENTAL

Water sample were collected near Koradi thermal power palnt. The pH and EC of the sample were measured on the site and other parameters were analyzed in the laboratory according to the APHA[1] samples were stored at temperature below 5 ºC to avoid any change in the physical and chemical characteristics.

The stock solution of 5.1 mg/L of fluoride was prepared by adding appropite quantity of NaF with the water sample keeping in view that the maximum concentration of fluoride normally report around 5 mg/L.

Batch adsorption studies were conducted using shaking machine. A spectrophotometer (Systronics 105) was used to analyze fluoride content of water at a wavelength of 570 nm.

The experiments were carried out in batch mode. the batch adsorption experiments were carried out by shaking adsorbent with the sample in plastic bottle using average speed shaker. Each bottle was filled with a known volume of sample having desired pH. The plastic bottles containing sample was withdrawn from the shaker at the predetermined time interval and kept for setting about 24 h. After 24 h the sample is filtered through filter paper No. 42 and analyzed for residual fluoride by SPADNS method using SPANDS solution and zirconyl acid regent as per the procedure of standard methods for examination of wastewater.

RESULTS AND DISCUSSION

Characterization of the adsorbent: X-Ray analysis of the adsorbent was carried out and it showed that the adsorbent is amorphous thus indicating that the adsorbent is adequately porous in nature. Further an elemental analysis of the adsorbent was carried out indicating the chemical compositions percentage of the adsorbent used. The elemental analysis of the adsorbent showed the presence of 43.049 % of oxygen, 21.411 % silicon, 20192 % aluminum and 0.567 % of iron and 0.542 % of titanium.

With the knowledge of the optimal conditions the understanding of adsorption technique is possible. Thus the effect of some major parameters like pH, contact time, dose of adsorbent and initial concentration of fluoride ions of the uptake on adsorbent materials were investigated from kinetic view point (Table-1). Adsorption studies were performed by batch technique to obtain the equilibrium data. All the experiments were conducted at room temperature.

TABLE-1

Parameters	Observed value	Maximum permissible limit
pH	8.3	6.8-8.5
BC (mmhos)	031	0.1
Temperature (ºC)	29	16-32
Turbidity	80	5-10
TDS	580	450
Fluoride	3.1	1.0-1.5 mg/L

Effect of pH: In the adsorption process, pH is the controlling factor. The effect of pH at 2-8 was observed. The pH was maintained value with ± 0.2 by adding 0.5 N HCl or 0.1 NaOH. The influence of pH shown in Fig. 1. It was observed that the maximum adsorption of 86.44 % at pH 3 by China clay. A decrease in the extent of removal of fluoride ion was observed with increase in the pH of the solution. At low pH large numbers of H^+ ions are present.

Effect of adsorbent dose: studies on effect of adsorbent doses were conducted between 0.25-2.00 g/100 mL. The pH was maintained at 3. While the fluoride ion concentration was 5.1 mg/L and contact time was kept 2 h.

The effect of adsorbent dose on the removal of fluoride is presented in Fig. 2. The observations reveal that an increase in the adsorption occurs with the corresponding increase in the amount of adsorbent. The increase in the removal efficiency with simultaneous increase in adsorbent dose is due to the increase in surface area. Hence more active sites were available for the adsorption of fluoride.

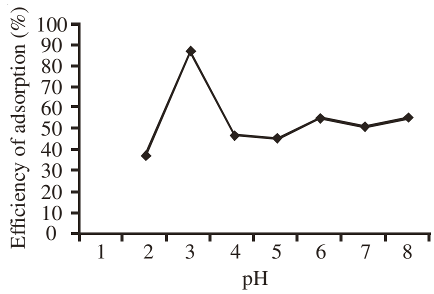

Fig. 1. Effect of pH on fluoride removal. Initial F^- concentration of 5.1 mg/L; adsorbent dose of 0.6 g/100 mL, contact time of 2 h, stirring rate was 50 rpm and setting time 24 h

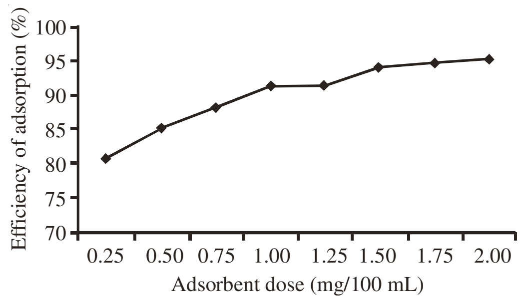

Fig. 2. Effect of adsorbent dose on fluoride removal. Initial F^- concentration of 5.1 mg/L; pH 3 contact time of 2 h, stirring rate was 50 rpm and setting time 24 h

The results showed that China clay adsorbs 80 % removal of fluoride ions at the lowest dose of 0.25 g/100 mL and 94.5 % at maximum dose of 2 g/100 mL, respectively at room temperature.

The adsorption extent for adsorbent dose of 1.5 g/100 mL to 2 g/100 mL does not show any significant increase. Hence 1.5 g/100 mL was selected for further study.

Effect of stirring rate: The effect of stirring rate was studied by varying speeds from 25-100 rpm at optimum pH of 3 with adsorbent dose of 1.5 g/100 mL and contact time 2 h. The influence of stirring rate on the extent of adsorption is shown in Fig. 3.

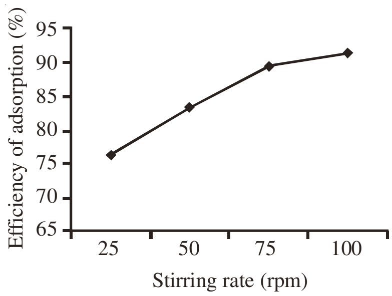

Fig. 3. Effect of stirring rate on fluoride removal. Initial F^- concentration of 5.1 mg/L; pH 3 contact time of 2 h, adsorbent dose 1.5 g/100 mL, setting time 24 h

It is observed that fluoride removal is a function of stirring rate. At a given time fluoride removal increases with the increase in the rate of stirring.

The removal is 76.4 % at 25 rpm and attains 91.2 % at 100 rpm for China clay adsorbent. The percentage adsorption is less at lower stirring rate and increases with the stirring rate up to 75 rpm and thereafter remains more or less constant. The reason for the increase in efficiency is that at higher speeds better contact between the adsorbate and adsorbent take place. The adsorption extents for stirring rate of 75-100 rpm dose not show any significant increase. Hence stirring rate of 75 rpm was considered for further study.

Effect of contact time: The effect of contact time was studied by varying it from 30-150 min keeping adsorbent dose of 1.5 g/100 mL, pH of 3 and stirring rate of 75 rpm.

Fig. 4 shows the progression of adsorption reaction and the percentage removal of fluoride for different contact times. It is found that the removal of fluoride ions increases with increase in contact time but after some time it gradually attains as constant value denoting attainment of equilibrium. Further increase in contact time does not increase uptake due to deposition of fluoride ions on available adsorption sites on adsorbent material. The changes in the extent of removal might be due to the fact that initially all adsorbents sites were vacant and the solute concentration gradient was high. Later the fluoride uptake by adsorbent decreases significantly due to the decrease in the number of adsorption sites. Decreased extent adsorption towards the end of experiment, indicates the possible monolayer of fluoride ions on the outer surface, pores of the adsorbent and pore diffusion onto inner surface of adsorbent particles through the film due to continuous mixing maintained during the experiment. It was assumed that the equilibrium time is at which curves appear nearly asymptotic to the time axis[2]. In present case the equilibrium time was obtained at 2 h and hence considered for further study.

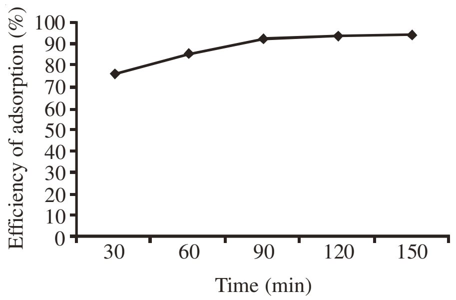

Fig. 4. Effect of contact time on fluoride removal. Initial F^- concentration of 5.1 mg/L, pH 3 adsorbent dose 1.5 g/100 mL, setting time 24 h stirring rate 75 rpm

Effect of initial concentration: The effect of initial fluoride concentration was studied by varying it from 5-25 mg/L keeping adsorbent dose 1.5 g/100 mL at pH 3, stirring rate 75 rpm, contact time 2 h and setting time of 24 h. Fig. 5 indicates that the percentage removal of fluoride ion decreases with increase in initial fluorde ion concentration. The percentage removal of fluoride was observed to be 86 % at 5.1 mg/L and 61 % at 25 mg/L.

This is probably due to the fact that for a fixed adsorbent dose the total available adsorption sites are limited thereby adsorbing almost the same amount of fluoride, a decrease in percentage of removal of fluoride corresponding to an increased initial fluoride ion concentration was observed.

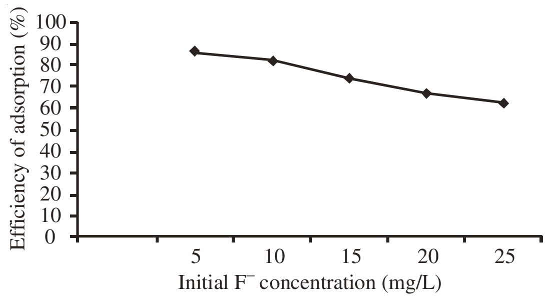

Fig. 5. Effect of initial fluoride concentration on fluoride ion removal. Contact time 2 h, pH 3 adsorbent dose, 1.5 g/100 mL, stirring rate 75 rpm, setting time 24 h

Effect of setting time: The effect of setting time was studied by varying it from 4-24 h, with adsorbent dose 1.5 g/100 mL, contact time of 2 h, stirring rate of 75 rpm at pH 3 with initial concentration 5.1 mg/L. The influence of setting time on the extent of adsorption is shown in Fig. 6.

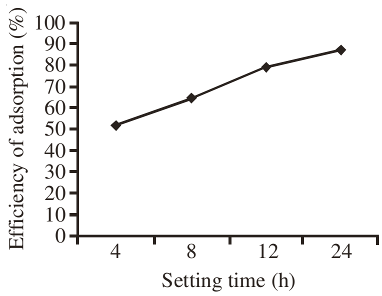

Fig. 6. Effect of setting time on fluoride ion removal. Contact time 2 h, pH 3 adsorbent dose 1.5 g/100 mL, stirring rate 75 rpm, Initial F^-, concentration of 5.1 mg/L

It reveals that the fluoride removal is a function of setting time. At a gtiven time fluoride removal increases with the increase in the setting time. The result indicates that there is definite improvement in the extents of adsorption with increase in setting time and then equilibrium was set up after 24 h.

Adsorption mechanism: Adsorption isotherms helps in determining the feasibility of China clay for treating fluoride ion in water. Freundilich isotherms is plotted. The isotherm not only provides the general idea of the effectiveness of the China clay in removing fluoride ion, but also indicates the maximum amount of fluoride ions that can be adsorbed by it. This adsorption isotherms is equilibrium test. It does not indicate the actual performance of the adsorbents.

The Freundilich expression is an empirical equation based on adsorption on heterogenous surface. The Freundilich equation is commonly represented as

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C_0$$

C_0 = equilibrium concentration (mg/L), x = amount of fluoride adsorbed (mg), m = weight of the adsorbent used (g), K and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity. Linear plots of $\log \frac{x}{m}$ *versus* log C_0 shows that the adsorption follows Freundilich isotherm model; log K and 1/n are calculated from the intercepts and slop of the plot, respectively.

Freundilich isotherm was plotted with $\log \frac{x}{m}$ *versus* log C_0 as shown in Fig. 7. From the graph the value of log k is 0.63 and 1/n = .40 and thus Freundilich isotherm is x/m = $0.63 + C_0^4$.

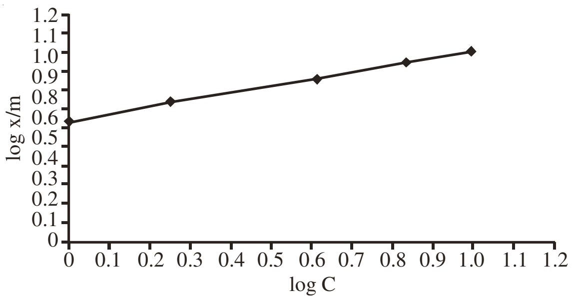

Fig. 7. Freundlich isotherm

A smaller value of 1/n points out better absorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent.

Conclusion

China clay showed 93 % adsorptive removal of fluoride ion under optimized conditions of pH 3 and dosage 1.5 g/100 mL in 2 h contact time. The adsorption is pH dependent and maximum adsorption occurs at pH 3. The experimental data on the adsorptive behaviours of fluoride on China clay follow Freundilich model.

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