Study on Fluoride Removal from Aqueous Solutions by a Novel Defluoridation Adsorbent NEWDEF®

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Abstract. Batch experiment was carried out to determine the effectiveness of the novel composite defluorinating agent NEWDEF® for fluoride removal from aqueous solution. The results showed that the maximum adsorption capacities for F⁻ were 4.09 mg·g⁻¹. Kinetics data obtained for the adsorption process fitted the Lagergren First-order equation. The adsorption kinetics and isotherm were found well fitted by Langmuir isotherm models and a pseudo-second-order kinetic, showing F⁻ removal belonged to monolayer adsorption process. The reaction of F⁻ adsorption from aqueous solutions by NEWDEF® was an endothermic process. Micro-column and home-used equipment defluoridation test indicated that NEWDEF® can be perfectly suitable defluorinating agent in F⁻ removal for drinking water in small towns.

1. Introduction
Because of a shortage of freshwater, it’s the major, important and preferable source of drinking water in developing countries especially, while ground water only makes up 0.6% of the total water resources on the earth [1]. Fluoride removal from drinking water has become an urgent task all around the world, particularly in China, owing to the wide distribution and high concentration in groundwater. There are more than 20 nations which are suffering from endemic fluorosis, for example, China, Africa, India, Spanish and the Middle East in particular [2]. In China, which has a large area with fluoride, fluorosis were found prevalently in 29 provinces, municipalities and autonomous regions. According to the investigation results by the Ministry of Health and the Ministry of Water resources in China, there were 81.41 million people suffered from fluorosis. There were about 100 million people drinking water with fluorine content had over 1.0 mg/L and approximately 5 million people whose potable water with fluorine exceed 5.0 mg/L [3]. Fluoride is one of the necessary microelement for human body. However, its excessive intake could be harmful to human health, which may result in detrimental physical effects include dental fluorosis, skeletal fluorosis etc, such as hypersensitivity reactions and kidney disease.

The mainly methods to remove excess fluoride from water including ion-exchange, adsorption, chemical precipitation, electro dialysis, ultra filtration, reverse osmosis, membrane separation treatment and so on. Adsorption was one of the most extensive application and the commercially
viable technology. The commonly used defluoride adsorbents include alumina, bone char, zeolite, gypsum material, kaolinite, cement clay, montmorillonite and rare earth metal [4-8]. However, the adsorbents have been restricted due to their unfeasibility, inoperability, expensive price, unsafety or not widely adaptability. Therefore, a novel adsorbent with high efficiency, practically, economical and safety was developed for defluoridation in our study.

2. Materials and methods

2.1. Materials

NEWDEF® is a new high efficiency drinking-water defluoridation media, which was natural mineral and insoluble in water. The particle size of the media was 0.5mm-1.5mm and bulk density was 1.33g/ml.

2.2. Methods

2.2.1. Batch adsorption experiments. NEWDEF® was sieved firstly, and then agitated with 1.0 g in 100 ml beaker of fluoride aqueous solution of desired concentration in triplicate by stirring with speed of 150 rpm. At the end of predetermined time intervals, NEWDEF® defluorinating agent was removed from the solutions by centrifugation at 10000 rpm for 5 min, and finally determining the residual concentration of F⁻. The adsorption capacity (q) and the percentage removal (%) by NEWDEF® were calculated by using the following equation:

\[
q = \frac{(C_i - C_e)}{1.0} \times V
\]

The percentage removal (%) = \[
\frac{(C_i - C_e)}{C_i} \times 100\%
\]

Where q (in mg/g) was capacity, the Ci and Ce were the initial and equilibrium concentrations of F⁻ in aqueous solution (mg/L), V was the solution volume(L).

2.2.2. Micro-column experiments. 30 g NEWDEF®, 30 g activated alumina, 30 g activated zeolite was added to three 50ml acid burettes respectively, with 2ml/min-2.5ml/min flow of raw water. Then the fluoride content was determined until more than 1.0mg/L. The fluoride content of raw water was 2.4mg/L, which was from a water plant in Puyang City in China.

2.2.3. Home-used defluoridation equipments. 30 kg filter were filled in the household defluoridation equipment with 2.0 L/min flow of fluoride water, and the water fluoride content was determined until the fluoride content over 1.0 mg/L. Then the flow rate mode was changed to 1 hour per day intermitted flow, the effluent fluoride concentration was measured and the flow volume was recorded simultaneously.

2.2.4. Statistical analysis. Descriptive statistics, analysis of variance and treatment group comparisons were calculated using the computer program, GraphpadPrizm (Version4) at 0.05 and 0.01 significance level.

3. Results

3.1. Effect of particle size and contact time on fluoride removal

The effect of particle size and contact time was conducted by the experiments on the fluoride removal. The NEWDEF® adsorbent media size was range from at 0.2-0.5, 0.5-1.0 and 1.0-1.5mm diameter, and the result was displayed in Fig.1. It is evident that there was a sharply rising in fluoride removal in the
initial stages. The effect of particle size on the defluorinating efficiencies was limited, of which maybe the smaller particle sizes has the relatively higher external surface area. But the efficiency of F removal was no significantly different (P>0.05) as particle size increase, that showed particle size has no obvious effect on F removal.

![Fig. 1. Effect of particle size and contact time on fluoride removal](image)

3.2. Determination of adsorption kinetic constants of NEWDEF® in defluorinating process

The adsorption kinetic was determined by using Lagergren first-order rate at room temperature 25°C (±1°C), and the rate constants of adsorption (K_ad) by NEWDEF® were obtain by the following equation expression [9]:

$$
\log(q_e - q_t) = \log q_e - \left(\frac{K_{ad}}{2.303}\right)t
$$

(3)

Where $q_e$ and $q_t$ (both in mg/g) were the amount of F adsorbed at equilibrium and any time ‘t’, respectively. $K_{ad}$ (h⁻¹) was the kinetic rate constants of adsorption. The value of $k_{ad}$ was determined by ‘log ($q_e-q_t$)’versus time as shown in the graph. The correlation coefficient of Lagergren’s plot for kinetic modeling was 0.9902 (Fig. 2). The results reveal that the adsorption process fitted the Lagergren kinetic modeling better and the rate constant of adsorption was 14.28 h⁻¹ for F.

![Fig. 2. Lagergren’s plot for kinetic modeling for fluoride removal](image)
3.3. Adsorption isotherm
The distribution of F in aqueous solution by NEWDEF® were determined by Freundlich or Langmuir, which indicate the distribution equilibrium of F between the solid phase or the liquid phase in the adsorption process.

The Langmuir adsorption isotherm is expressed in a linear form, which demonstrated a monolayer sorption. The Langmuir adsorption assumes that maximum adsorption occurs when the surface is covered by defluorinating agents, and the adsorption onto a surface with identical sites of the media.

The equations are given as following:

\[ q_e = \frac{abC_e}{1 + bC_e} \]  \hspace{1cm} (4)

\[ \frac{C_e}{q_e} = \frac{1}{a} \frac{C_e}{q} + \frac{1}{ab} \]  \hspace{1cm} (5)

The Langmuir and Freundlich adsorption isotherms of F adsorption were displayed in Fig.3. From the graph (Ce/qe) vs. Ce showed a straight line and the empirical constant could be obtained from the kinetic data. Which ‘Ce’ (mg/L) represents the equilibrium concentration, ‘qe’ (mg/g) represents the amount adsorbent at equilibrium, ‘a’ represents the constant related to adsorption capacity, and ‘b’ is the constant about the energy of adsorption.

Fig.3. The Langmuir and Freundlich adsorption isotherms of F adsorption

From the correlation coefficient of both equations with the experimental data (as shown in Fig.3), it was found that Langmuir adsorption isotherm (\( R^2 \approx 0.9992 \)) fitted the experimental data better than that of the Freundlich adsorption isotherm (\( R^2 \approx 0.9507 \)). The adsorption capacity of NEWDEF® was 4.09mg/g.

3.4. Micro- column fluoride removal experiment
The results in Table 1 and Fig. 4 illustrate the treated water was only 0.97L and 2.23L by activated zeolite and the activated alumina respectively, while treatment by NEWDEF® was 11.35 L of raw water. The amount of water treated by NEWDEF® is 11.7 times that of activated zeolite and 5.09 times that of activated alumina in the same condition.
Table 1 Flow testing results by micro-column defluoridation

| Material Flow rate | NEWDEF® (30g) | Activated alumina (30g) | Activated zeolite (30g) |
|--------------------|---------------|-------------------------|------------------------|
| 43ml/min           | Fluorine content in effluent 0.20mg/L | Fluorine content in effluent 0.90mg/L | Fluorine content in effluent 1.0mg/L |

Fig. 4. The volume of water treated by different media under the same condition

3.5. Removal of F⁻ by home-used defluoridation equipment
The results from Fig. 5 showed that NEWDEF® filter in the home-used equipment can still maintain the same fluoride removal capacity as the micro-column test. It can still restore part of the fluoride effect by replace continuously flow with intermitted flow as the material saturated with the raw water, and NEWDEF® can maintain a more stable effect.

Fig. 5. The fluoride removal by home-used equipment
4. Conclusions
The effectiveness and capacity of defluorinating agent NEWDEF® was investigated, and the conclusions are made as follows:

(1) The adsorption process by NEWDEF® attain equilibrium in 6 h, and F⁻ removal was no significantly different (P>0.05) as particle size increase.

(2) The removal of F⁻ by NEWDEF® was found to fit Langmuir adsorption isotherm models ($R^2=0.9992$).

(3) The adsorption kinetics data indicated a pseudo-second-order kinetic, showing F⁻ removal belonged to monolayer adsorption process and the reaction of F⁻ adsorption by NEWDEF® was an endothermic process.

(4) Micro-column and home-used defluoridation tests indicated NEWDEF® is 11.7 times that of activated zeolite and 5.09 times that of activated alumina in removal F⁻ and can maintain a more stable effect.

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