

Article

Kinetic Adsorption of Fluoride from an Aqueous Solution onto a Dolomite Sorbent

Aunnop Wongrueng^{1,2,a,*}, Benja Sookwong^{2,3}, Pharkphum Rakruam^{1,2},
and Suraphong Wattanachira^{1,2}

1 Department of Environmental Engineering, Faculty of Engineering, Chiang Mai University, Chiang Mai, Thailand

2 Center of Excellence on Hazardous Substance Management (HSM), Bangkok, Thailand

3 International Postgraduate Programs in Environmental Management, Graduate School, Chulalongkorn University, Bangkok, Thailand

*E-mail: aunnop@eng.cmu.ac.th (Corresponding author)

Abstract. The adsorption of fluoride from an aqueous solution onto a dolomite sorbent was studied. The surface morphology of the dolomite sorbent was evaluated, and it was found to have an un-smooth porous structure. The point of zero charge (PZC), specific surface area, and average pore size of the dolomite were observed at approximate pH 8.0-9.5, 1.17 m²/g, and 105.7 Å, respectively. The major mineral components of the dolomite sorbent were dolomite, calcite, and quartz. From a kinetic adsorption test, the dolomite sorbent required 12 hours of contact time to reach equilibrium with a fluoride adsorption capacity of 0.000581 mM/g, and the kinetic adsorption fitted well with a pseudo-second order kinetic reaction with a rate constant of 21.07 g/mM·min.

Keywords: Dolomite sorbent, fluoride, point of zero charge, pseudo-second order.

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1. Introduction

Many countries such as India, Sri Lanka, Pakistan, China and parts of East Africa have been faced with a fluorosis problem due to high fluoride concentrations in groundwater [1]. Exposing humans to high fluoride levels in water, which is used for cooking and drinking, can cause dental and skeletal fluorosis [2]. In the Thai Provinces of Chiang Mai and Lamphun, the populations have been exposed to high amounts of fluoride through their fluoride-rich groundwater [3]. The influence of the high fluoride content in the Chiang Mai Basin has been observed in alluvial plain aquifers. The highest fluoride concentration was recorded at 16.1 mg/L [4], which far exceeds the World Health Organization's maximum drinking water limit of 1.5 mg/L [5]. The Ministry of Public Health in Thailand set the fluoride concentration in drinking water standard at 0.7 mg/L [6].

Child-education program was implemented to reduce health risks from fluoride in their groundwater in the area [2]. Not only the child-education program but also fluoride removal technology should be considered. Several technologies have been applied for fluoride removal (e.g., membrane filtration and bone char adsorption). Adsorption is a physicochemical treatment and provides a high removal efficiency of the polluting component. Adsorption works without the addition of excessive chemicals, which is different from the use of precipitation-coagulation technologies. Thus, it has a smaller footprint and the absence of sludge generation in the process [7]. Many materials have been utilized as an adsorbent in various applications. For example, removal of free fatty acid by magnesium silicate derived from rice husk, using of activated carbon for residual aluminium-dye complex reduction, and application of organo-rice straw for yellow20-dye removal [8–10]. Dolomite is a low cost material that contains a magnesium carbonate and calcium compound. The properties of dolomite are similar to limestone, which is known as magnesium limestone in the industry. Several researchers have used dolomite to treat many heavy metal ions such as Cd^{2+} and Pb^{2+} in water [11]. Furthermore, calcined dolomite could be applied to remove phosphate (PO_4^{3-}) from solutions in which the adsorption of phosphate occurs through physical interactions [12]. The objectives of this study are to characterize a dolomite sorbent and to investigate the kinetic adsorption of fluoride from an aqueous solution onto the dolomite sorbent. In addition, actual groundwater defluoridation by the dolomite sorbent was examined.

2. Materials and Methods

2.1. Dolomite Sorbent

Dolomite rock was collected from the P.C. Nisith mine at Suratthani Province, Thailand. Before being used in the experiments, the dolomite rock was crushed into small pieces by a disc mill and put through sieves of different sizes (0.420-0.074 mm) to investigate the dolomite's properties. The 0.42 mm size pieces of the dolomite sorbent were selected for this experiment. The dolomite was then washed in deionized water and dried at room temperature.

2.2. Water Samples

Water samples for this experiment included synthetic water and actual groundwater. Synthetic water was prepared from NaF (10 mg/L). Actual groundwater containing 15 mg/L of fluoride was taken from a high fluoride area in Lamphun Province, Thailand.

2.3. Determination of the Point of Zero Charge (PZC) of the Dolomite Sorbent

The method used to determine the point of zero charge (PZC) was adapted from the proposed procedures [13, 14]. Before the experiment, the dolomite sorbent was washed in pure water. Then, it was dried in an oven for 12 hours. A NaCl solution 0.01 mol/L was prepared. HCl and NaOH (0.01 mol/L) were used to adjust the pH of the NaCl solution to a pH range of 2-10. One gram of dolomite sorbent was immersed in each volumetric bottle, which contained the adjusted pH (2-10) solution. Then, all the volumetric bottles were shaken for 24 hours at 100 rpm at room temperature. Afterwards, the pH of each bottle was measured again. The initial and final pH values were taken to plot the graph, and the PZC was identified.

2.4. Surface Characterization of Dolomite Sorbent

The specific surface area and pore size of the dolomite sorbent was analyzed using a nitrogen adsorption isotherm (BET). The mineral composition of the dolomite sorbent was determined by an X-ray diffraction spectrometer (XRD). The chemical composition of the dolomite sorbent was investigated using an X-ray fluorescence spectrometer (XRF). The surface morphology of the dolomite sorbent was detected by a scanning electron microscope (SEM).

2.5. Kinetic Adsorption of Fluoride onto the Dolomite Sorbent

Synthetic water containing fluoride (10 mg/L) was used in the batch adsorption experiments. Before the experiment, the pH of the synthetic water was adjusted to 7.0. The experiment was carried out in a 100 mL Erlenmeyer flask containing 5 g of the dolomite sorbent in 50 mL of synthetic water at room temperature. Then, it was shaken at 200 rpm on a rotary shaker. Kinetic adsorption was then determined and observed over a 24-hour period at 10 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, 12 hours, and 24 hours. At each time, 2 mL of the synthetic water was collected and filtered through a nylon syringe filter with a pore size of 0.45 μm . The concentrations of fluoride were analyzed by ion chromatography (IC).

2.6. Adsorption of Fluoride from Actual Groundwater by the Dolomite Sorbent

1000 ml of groundwater containing a high fluoride concentration from Lamphun Province, Thailand, was poured into an Erlenmeyer flask. The water sample was adjusted to pH 7. Then, 100 g of the dolomite sorbent was added. With the groundwater at room temperature, it was put on a rotary shaker at 200 rpm, until equilibrium was reached. After the shaking phase was complete, the groundwater was filtered and placed in a 10 mL flask to measure the concentration of fluoride using ion chromatography (IC).

3. Kinetic Adsorption Model

Different kinetic models, such as first-order, second-order, pseudo-first order and pseudo-second order equations, are applied to describe the rate constant of a reaction.

3.1. The First-Order Equation

The first-order equation [15] is shown as Eq. (1).

$$\ln q = -kt + \ln q_0 \quad (1)$$

where q_0 and q are the amounts of fluoride adsorbed (mM/g of dolomite) at the initial time and time t (min), and k is the rate constant of adsorption (min^{-1}).

3.2. The Second-Order Equation

The second-order equation [16–18] is shown as Eq. (2).

$$\frac{1}{q} = k_2 t + \frac{1}{q_0} \quad (2)$$

where q_0 and q are the amounts of fluoride adsorbed (mM/g of dolomite) at the initial time and time t (min), and k_2 is the rate constant of adsorption ($\text{g}/\text{mM}\cdot\text{min}$).

3.3. The Pseudo-First Order Equation

The pseudo-first order equation [19] is shown as Eq. (3).

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (3)$$

where q and q_e are the amounts of fluoride adsorbed (mM/g of dolomite) at time t and at equilibrium, k_1 is the rate constant of adsorption (min^{-1}).

Equation (3) is called Lagergren's first-order (LFO) equation [19]. Generally, k_1 is obtained by plotting $\ln(q_e - q)$ versus t . To express the adsorption characteristics, Eq. (3) is rewritten as Eq. (4).

$$\ln\left(1 - \frac{q}{q_e}\right) = -k_1 t \quad (4)$$

3.4. The Pseudo-Second Order Equation

The pseudo-second order equation [16–18] is shown as Eq. (5).

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where q and q_e are the amounts of fluoride adsorbed (mM/g of dolomite) at time t and at equilibrium, k_2 is rate constant of adsorption (g/mM·min).

4. Results and Discussion

4.1. Point of Zero Charge (PZC) of the Dolomite Sorbent

The point of zero charge (PZC) of the dolomite sorbent was found at approximate pH 8.0-9.5, as shown in Fig. 1, which was close to the 1999 results of Pokrovsky and co-workers [20]. It meant that at the solution pH of 8.5, the dolomite surface was neutral or had a near zero charge. When the solution pH was below the PZC of dolomite (pH < 8.0-9.5), the dolomite surface was positively charged, and when the pH of the solution was above the PZC of dolomite (pH > 8.0-9.5), the dolomite surface was negatively charged.

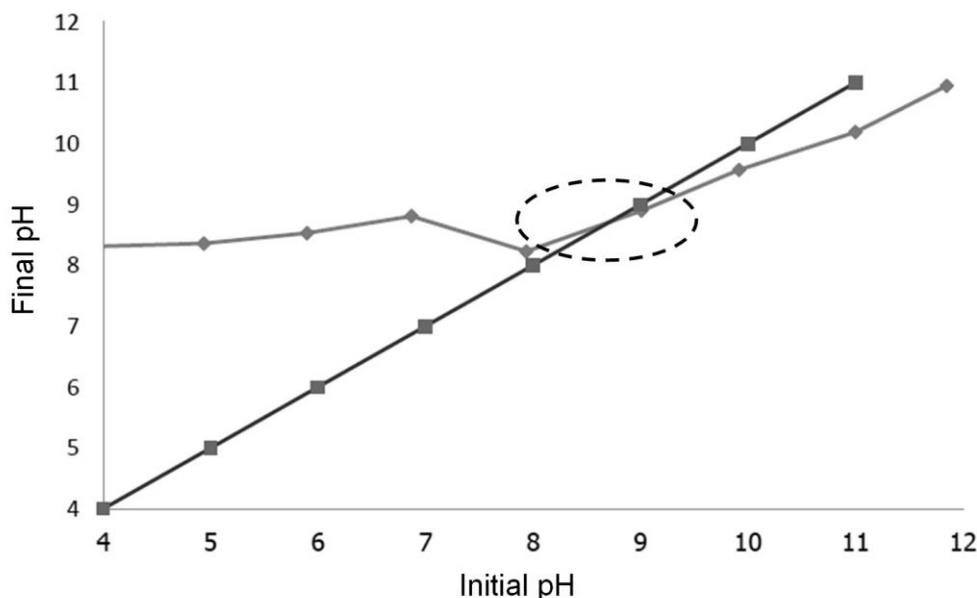


Fig. 1. Point of zero charge (PZC) of dolomite sorbent.

When cations of dolomite (Mg^{2+} , Ca^{2+}) and anions (CO_3^{2-}) diffused into the aqueous solution, the resulting hydrolysis and proton reactions can generate HCO_3^- and MOH^+ in the dissolution process. After the dolomite surface reacted with water molecules, HCO_3^- and MOH^+ were produced and a surface charge resulted from the unequal composition of HCO_3^- and MOH^+ . When the pH was below the PZC of dolomite (pH < 8.0-9.5), the dolomite surface was positively charged because $[MgOH^+] + [CaOH^+] > [HCO_3^-]$. When the pH was above the PZC of dolomite (pH > 8.0-9.5), $[MgOH^+] + [CaOH^+] < [HCO_3^-]$, thus giving the surface a negative charge [21].

In this study, dolomite was used to adsorb fluoride ions, which are negatively charged. The adsorption process could thus only occur when the solution pH was lower than the pH at the PZC because the dolomite's surface had a positive charge.

4.2. Specific Surface Area

Even when same materials have the same volumes and weights, their surface activities and adsorption volumes can vary. Thus, it is important to measure the specific area of interest to evaluate the activity and adsorption capacity of a material. The specific surface area, average pore diameter, and total pore volume of the adsorbent were determined using the BET technique, an important analysis technique for the measurement of a specific surface area of a material [22]. The specific surface area was investigated and the results of that area and the total pore volume of the dolomite sorbent are shown in Table 1. The specific surface area, total pore volume, and average pore size of dolomite were observed at 1.17 m²/g, 0.0031 cc/g, and 105.7 Å, respectively.

Table 1. Characteristics of the dolomite sorbent.

Dolomite sorbent	Value
Specific surface area (m ² /g)	1.17
Total pore volume (cc/g)	0.0031
Average pore diameter (Å)	105.7

4.3. Mineral Composition

The mineral composition of the dolomite sorbent was investigated by X-ray diffraction (XRD) analysis and the results show that the dolomite sorbent consisted of calcite and dolomite. Moreover, it contained some quartz, as illustrated in Fig. 2. In Fig. 2, the peaks of its three main minerals are illustrated: dolomite CaMg(CO₃)₂, calcite (CaCO₃) and quartz (SiO₂). The areas under the peaks of the graph were calculated to find the percentage of each mineral. It was found that the percentages of dolomite, calcite, and quartz were 89.1%, 6.8%, and 4.1%, respectively.

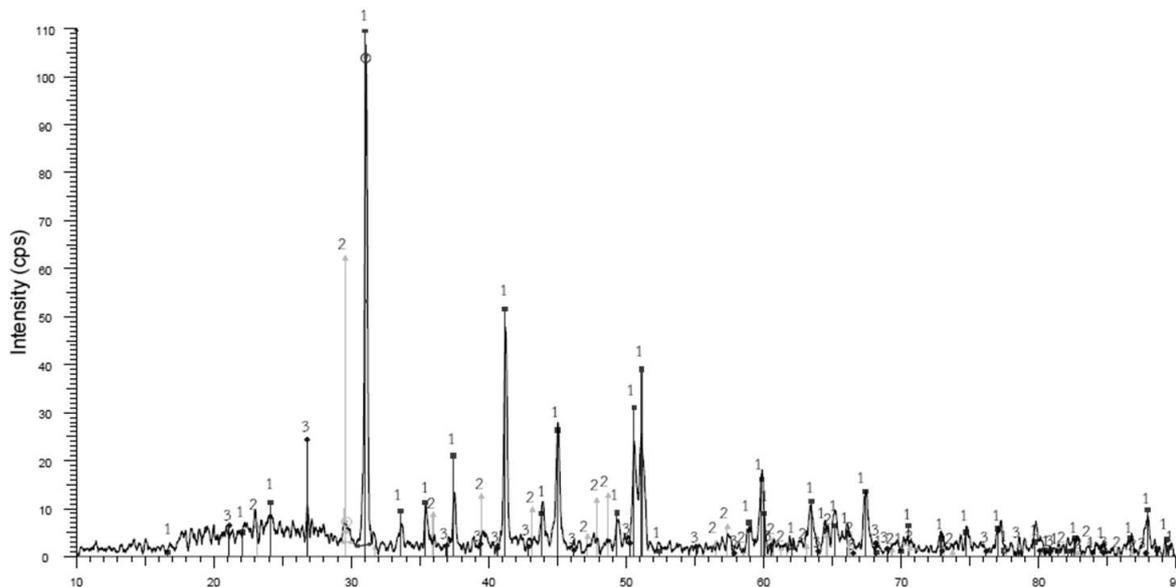


Fig. 2. Mineral compositions of dolomite sorbent.

4.4. Chemical Composition

The chemical composition refers to the identities and relative numbers of elements that form any particular compound. A chemical compound may consist of two or more chemical elements and is a pure chemical substance. The chemical composition of the dolomite sample was investigated using an X-ray fluorescence spectrometer (XRF) and the chemical components of the dolomite sorbent are shown in Table 2.

Table 2. Chemical compositions of the dolomite sorbent.

Compound	Percent composition (%)
CaO	72.19
MgO	22.61
SiO ₂	2.35
Al ₂ O ₃	1.31
Fe ₂ O ₃	0.771
K ₂ O	0.295
TiO ₂	0.063
P ₂ O ₅	0.051
Na ₂ O	0.058

4.5. Surface Morphology

Surface morphology is the study of the form or shape of a material. In this study, the structure of the dolomite's surface was investigated by SEM analysis. Figure 3 shows the SEM images of the dolomite sorbents at each magnifying power, which brought to light dolomite's un-smooth surface with its porous structure.

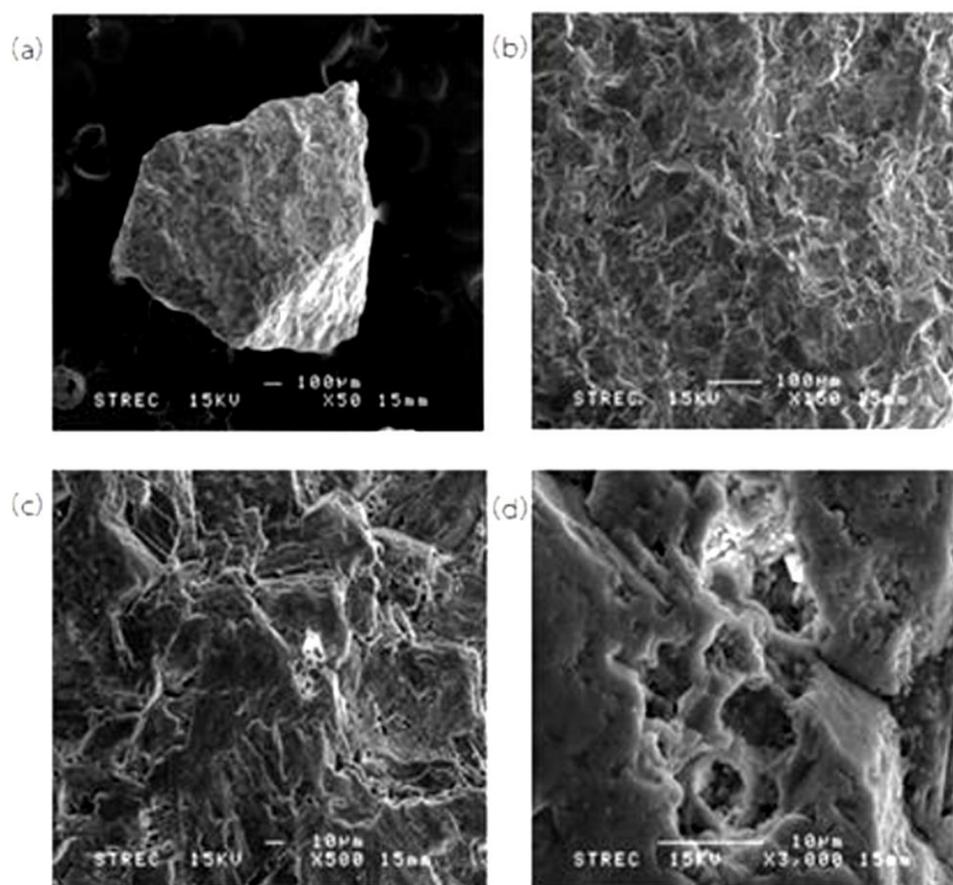


Fig. 3. Surface morphology of dolomite sorbent.

4.6. Kinetic Adsorption of the Dolomite Sorbent

A kinetic adsorption experiment was performed to obtain the time needed for equilibrium of fluoride adsorption by the dolomite sorbent. Kinetic adsorption of fluoride by dolomite was carried out at a solution pH of 7.0, to aid the electrostatic interactions between the dolomite surface and fluoride ions.

Figure 4 illustrates the amount of fluoride adsorbed with time by dolomite sorbent at a solution pH of 7.0. The dolomite adsorbed fluoride rapidly in the first hour. Then, the adsorption gradually slowed until it reached equilibrium after 12 hours. At equilibrium, dolomite could adsorb fluoride by 0.000581 mM/g of the dolomite sorbent.

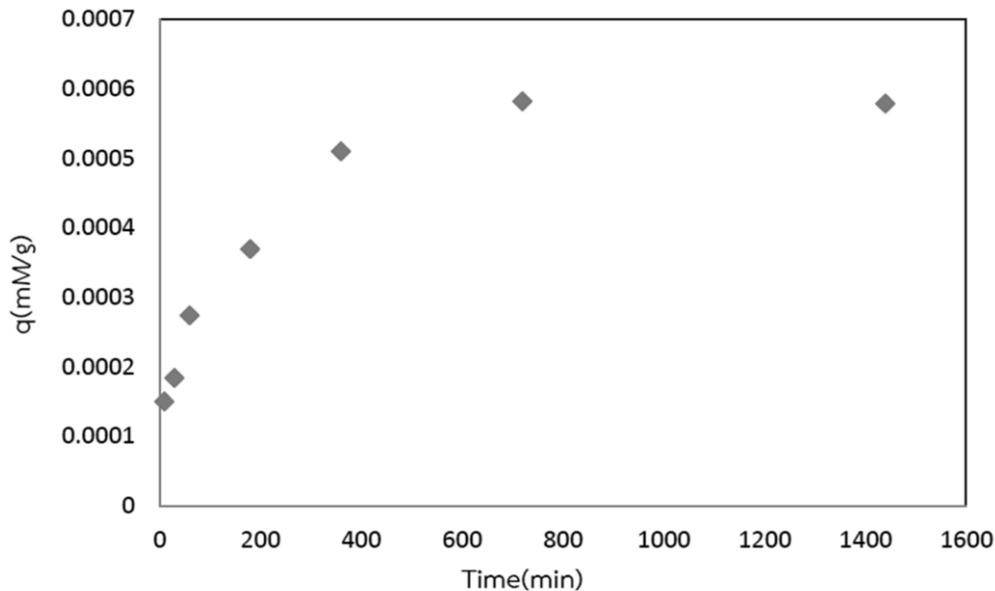


Fig. 4. Amount of fluoride adsorbed with time by dolomite sorbent.

In order to investigate the rate constant of fluoride adsorption on dolomite, the data obtained from the experiments were fitted to four kinetic models. The constant (k) values of first-order, second-order and pseudo-first order models were calculated from the slope of each regression line. The constant (k) of the pseudo-second order kinetic model was calculated from the square of the slope divided by the intercept of the regression line. In this study, the correlation coefficient, R^2 , was used to test which kinetic model had the best fit. The correlation coefficients for the linear graph of the pseudo-second order model were higher than those of the other models. Thus, it could be concluded that the pseudo-second order kinetic model was what kinetically controlled the reaction rate of fluoride adsorption by dolomite, as shown in Fig. 5. The pseudo-second order kinetic model indicated chemisorption, which an electrostatic interaction between fluoride and dolomite sorbent might possibly take place.

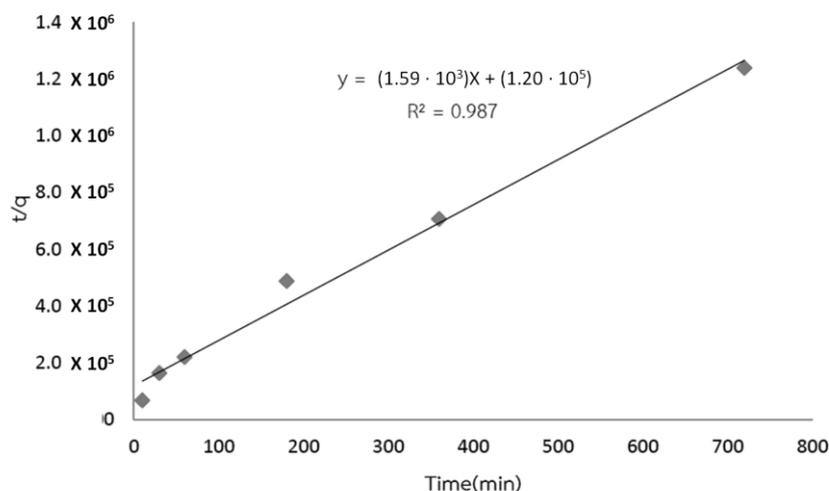


Fig. 5. Pseudo-second order kinetic model.

Figure 5 shows the correlation coefficient (R^2) of 0.987 for the linear graph of the pseudo-second order model. The pseudo-second order rate constant of fluoride adsorption on dolomite was calculated as follows.

$$k_2 = \text{slope}^2 / \text{intercept} \quad (6)$$

From Eq. (6), the pseudo-second order rate constant (k_2) of fluoride adsorption on dolomite was calculated to be 21.07 g/mM·min.

4.7. Groundwater Defluoridation

Groundwater containing fluoride (15 mg/L) was adjusted to pH 7.0, which aided the electrostatic interactions between the dolomite surface and fluoride ions. Adsorption occurred over a period of 12 hours. It was observed that groundwater pH increased from pH 7.0 to pH 9.0 and the results showed 9% fluoride removal, which is quite low as same as nirmali seeds and lignite in another study [23]. Nirmali seeds and lignite showed a removal of 6-8%, but removal by kaolinite clay was 18.2%. Charfines and bentonite provided the highest removal efficiencies of 38 and 46%, respectively depending on pH, dose, and size of these adsorbents. The low fluoride removal efficiency of dolomite might have been due to the large amount of OH^- ions, which may have hindered the diffusion of the fluoride ions [24]. Thus, enhancing the efficiency of fluoride adsorption on the dolomite sorbent could be achieved at a low pH. Large amounts of H^+ altered the neutralization of the negative charge (OH^-) on the dolomite sorbent's surface and changed it to a positive charge. As a result, increased fluoride adsorption was accomplished.

5. Conclusion

The adsorption of fluoride in an aqueous solution onto a dolomite sorbent was investigated. The dolomite sorbent in this study showed a point of zero charge (PZC) at approximate pH 8.0-9.5. This indicated that the electrostatic interaction between the dolomite surface and fluoride ion was preferred when the water had a pH of less than 8.0-9.5. The dolomite sorbent required 12 hours of contact time to reach equilibrium and had a fluoride adsorption capacity of 0.000581 mM/g. It proved to be a pseudo-second order kinetic reaction with a rate constant of 21.07 g/mM·min. Low fluoride removal efficiency was observed when actual groundwater was used. However, a low pH level was found to enhance the fluoride adsorption efficiency of the dolomite sorbent.

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