Study on the Action Process and Mechanism of Fluorine between Reservoir Water and Bottom Sediments

Qing Liu¹, 2, 3, 4, *

¹Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd. Xi’an, China
²Shaanxi Provincial Land Engineering Construction Group Co., Ltd. Xi’an, China
³Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natural Resources, Xi’an, China
⁴Shaanxi Provincial Land Consolidation Engineering Technology Research Center. Xi’an, China

*Corresponding author e-mail: 553664133@qq.com

Abstract. The surface sediments in the control of pollutants in surface water fluoride fate plays a key role and effectiveness, to reveal the process and mechanism of action, the dynamic test and the adsorption and desorption experiment, combining with the pseudo two order kinetics equation, isothermal adsorption equation, simulation of reaction process between three springs reservoir sediment and reservoir water fluoride. The results showed that: (1) by fluorine ion dynamics in the process of chemical reaction control in surface sediments, can be described by the pseudo two order kinetics equation, the fitting equation is \( t/qt= 0.7401t + 0.1266 \), the correlation coefficient \( R^2 = 0.9985 \); (2) the linear adsorption isotherm of \( F^- \) in surface sediments, the regression equation is \( Qe=0.0047Ce+0.0115 \) that decision coefficient of \( R^2 \) reached 0.99, the saturated adsorption amount of \( F^- \) in the sediments of 30.56 mg/g.

1. Introduction
Fluoride ion (\( F^- \)) is an important anionic water pollutant. At present, China is one of the countries with more serious \( F^- \) pollution in the world [1]. As a pivot of the \( F^- \) environment system, surface soil has a direct impact on the distribution and migration of \( F^- \) in the environment [2]. The study of dynamic adsorption characteristics of \( F^- \) in sediments will help us to understand the migration and transformation of \( F^- \). So far, there have been many studies on the adsorption analysis of \( F^- \) at home and abroad [3-9], and different isothermal adsorption types have been proposed for different background conditions. Among them, Wang Qingwen et al [5] studied the reaction mechanism of soil on \( F^- \) in mine water, and obtained that the soil adsorption of \( F^- \) and the Freundlich type adsorption isotherm fit better; Liang Peng et al [6] adsorption test shows MCLB the amount of \( F^- \) adsorption is higher than that of MCLRB. The experimental results are consistent with the adsorption isotherms Langmuir and Freundlich models. Yan Jianyun et al [7] believe that the adsorption rate of fluorine is obviously affected by the change of fluorine concentration. The higher the concentration, the more easily the fluoride is resolved. The tea garden soil is \( F^- \) adsorption simulation equations by Freundlich, Langmuir equation applies only to a low concentration (0.5-2.0 mmol/L). Peek [8] studied the adsorption and analytical reactions of fluoride in.
10 soils. It is believed that the Langmuir adsorption isotherm conforms to the concentration range of all soils. The Freundlich adsorption isotherm is suitable for the initial F-concentration range of 0.0-2.5 mmol/L. ZHU [9] and other batch treatment techniques were used to study the combined adsorption of fluorine and phosphorus in acid red soil. It is believed that the increase of F-concentration inhibits the absorption of phosphorus. Throughout the previous studies, the influence of coexisting ions on the adsorption process of F- and the related chemical reaction mechanism were less considered.

According to the investigation report on the scope and artificial increase route of the Gudui spring water supply area, it is indicated that since the Sanquan Reservoir is located in the drainage area of the Gudui Spring Area, the landing funnel appears in this area at present, and the reservoir water will inevitably pass through the silt layer during the leakage process. Vertical supply of karst water may have an impact on groundwater. In this paper, the sediments in the vicinity of the Sanquan Reservoir water channel are used to carry out the F-kinetic test and the static adsorption chamber test. The reaction kinetics, F-adsorption characteristics and the chemical reaction mechanism are studied. The accumulation, migration and transformation of F- in sediments of the reservoir are obtained, which provides theoretical support for the treatment of water pollution.

2. Materials and methods

2.1. Test materials

Soil samples for testing: Sediments were taken from the vicinity of the water inlet of Sanquan Reservoir in Xinyi County, Yuncheng City, Shanxi Province on August 13, 2016, and soil samples of 0 to 10 cm were taken. The sediments were subjected to the removal of impurities-air drying-sieving, and the physical and chemical properties were measured as shown in Tables 1 to 3.

| Sampling point | Particle size of different particle sizes (%) | Classification of soil |
|----------------|---------------------------------------------|------------------------|
| Depth of sediment 0-10(cm) | >2mm | >0.5 | >0.25 | >0.075 | <0.002 | Sandy soil |
| 0.06 | 0.45 | 1.04 | 20.00 | 9.77 |

Remarks: Adopt international soil quality grading standards

| Sampling point | Natural dry bulk density/(g·cm⁻³) | Natural moisture content/ (%) | Dry density/(g·cm⁻³) | Wet density/(g·cm⁻³) |
|----------------|-----------------------------------|-------------------------------|---------------------|---------------------|
| Depth of sediment 0-10(cm) | 1.44 | 0.08 | 0.14 | 0.15 |

| Sampling point | pH | TDS/(g·kg⁻¹) | Organic compound/(g·kg⁻¹) | F-/(g·kg⁻¹) | Cl-/(g·kg⁻¹) | SO₄²⁻/(g·kg⁻¹) | Fe/(g·kg⁻¹) | Mn/(g·kg⁻¹) | NH₄⁺/(g·kg⁻¹) | CO₃²⁻/(g·kg⁻¹) |
|----------------|----|-------------|-------------------------|------------|------------|---------------|------------|------------|----------------|----------------|
| Depth of sediment 0-10(cm) | 8.21 | 200 | 12.45 | 1.22 | 15.59 | 147.14 | 0.2512 | 0.076 | 3.73 | 122.23 |

Water sample: The water sample in the kinetic test is based on the water sample of the reservoir collected by the monitoring, and the concentration of each ion in the reservoir is obtained as C(F⁻)=0.5 mg/L and C(SO₄²⁻)=150 mg/L respectively. /L, C(Fe)=0.4 mg/L, C(Mn)=0.15 mg/L, C(Na⁺)=120 mg/L, C(Ca²⁺)=30 mg/L, C(Mg²⁺)=60 mg/L. The ion concentration in the reservoir solution is configured according to the monitoring value of the reservoir water. The isothermal adsorption test was configured with 8 groups of water samples, wherein the concentration of F⁻ was set at different concentrations (0.5 mg/L, 1 mg/L, 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L, 10 mg/L, 12 mg/L), the concentration of other ions was
configured according to the monitoring value of the reservoir water, and the concentrations of other ions in the test remained unchanged.

2.2. Test methods
Kinetic test: We use the quartering method to take about 120 g of soil sample, weigh 10 soil samples, each soil sample weighs 10 g, and the soil samples are placed in a 250 ml triangular conical flask, according to the measured water content of the reservoir. Proportional configuration of the aqueous solution of the library. We mix the soil sample and the water sample and shake it at room temperature at a temperature of 250 r/min. The interval is 0.5, 1, 1.5, 2, 3, 4, 6, 8, 12, 16, 20 and 24 h. A sample was taken and the sample was centrifuged-filtered-measured.

Isothermal adsorption test: At room temperature, we took 10.0 g of 1 mm sieve soil sample in a numbered conical flask, and added 8 different concentrations of F-solution to the soil sample, pH=7. The soil sample was shaken in a water bath shaker at 250 r/min for 8 h to reach the adsorption equilibrium. The soil sample taken out immediately was centrifuged at 5000 r/min for 8 minutes in a centrifuge, filtered, and the supernatant was taken. We determined the water sample. The equilibrium concentration of the corresponding ions is Ce (mg/L), and the adsorption amount per unit mass of soil Cs (mg/g) is calculated [10].

All water samples were measured in the laboratory of indoor water chemistry instruments. The measurement items included pH, fluoride ion, sulfate ion, iron, manganese, calcium ion and magnesium ion. The pH was measured by lightning magnetic ZDJ-4A automatic potentiometric titrator and pH composite electrode. The fluoride ion and sulfate ion were determined by 883 Basic IC plus ion chromatograph. The iron, manganese, calcium and magnesium ions were analyzed by TAS-990 atomic absorption spectrometry. Photometric measurement.

We used the widely used pseudo first-order kinetics, pseudo-secondary kinetics, intraparticle diffusion, particle surface diffusion, and five dynamic models of Elovich dynamics [11] to simulate the adsorption process of ions in the reservoir water on the sediment. The adsorption kinetic equation is finally obtained. We used linear regression equations and nonlinear Langmuir equations, Freundlich empirical formulas and Temkin equations to fit the isothermal adsorption test data.

We used an ion chromatograph to measure the F-concentration in the solution after the end of the test, and calculated the adsorption amount (Qe) according to the formula (1), and calculated the mass (mg/g) of the adsorbed F- per unit mass of the deposit.

\[ Q_e = \frac{(C_e - C_0)V}{m} \]  

In the formula, Qe represents the amount of adsorption of F- on the equilibrium (mg/g), C0 represents the concentration of F- in the initial solution (mg/L), Ce represents the volume of liquid in equilibrium (L), and m represents sediment. Quality (g).

3. Results and analysis

3.1. Adsorption kinetics of fluoride on sediments
At present, the most widely used soil chemical kinetic model is the adsorption kinetic equation [11]. Based on the results of chemical kinetics and kinetic experiments, we established a model describing the long-term release characteristics and regularity of F- in sediments of Sanquan Reservoir, and applied five commonly used kinetic equations to fit the F- acting process. The fitting results are shown in Table 4.
Table 4. F⁻ five kinds of adsorption kinetic model fitting

| Model type                      | Pseudo-primary adsorption model | Pseudo-secondary adsorption model | Intraparticle diffusion model | Particle surface diffusion model | Elovich dynamics model |
|---------------------------------|---------------------------------|-----------------------------------|------------------------------|---------------------------------|------------------------|
| Related parameters              | k₁                              | R²                               | kₚ                            | R²                              | αₑ                     |
|                                 | 0.89                            | 0.78                             | 0.62                          | 0.998                           | 6.59                   |
|                                 |                                 |                                  |                               |                                 | 0.87                   |
|                                 |                                 |                                  |                               |                                 | 10.66                  |
|                                 |                                 |                                  |                               |                                 | 0.71                   |
|                                 |                                 |                                  |                               |                                 | 3.66                   |
|                                 |                                 |                                  |                               |                                 | 7.35                   |
|                                 |                                 |                                  |                               |                                 | 0.93                   |

Based on the above analysis, it can be seen that the correlation of the five kinetic models is good, the correlation coefficient reaches the significant level, and the pseudo second-order dynamic equation is the optimal model. See Figure 1 for details. Using the empirical formula, we can indirectly prove the kinetic mechanism. The adsorption of F⁻ in the sediment of the reservoir is the result of the interaction of different processes, and the equilibrium adsorption amount calculated by the equation is very sensitive to the random error of the test. Therefore, we believe that the long-term release of sediment is regular and can be expressed by the pseudo second-order dynamic equation \( \frac{t}{q_t} = 0.74t + 0.1266 \). The reaction process of F-genesis may be dominated by the chemical process controlled by chemical reaction.

\[ t/qt = 0.7401t + 0.1266 \]
\[ R² = 0.9985 \]

**Figure 1.** Pseudo-second-order kinetic fit

3.2. Isothermal adsorption characteristics of sediments to fluoride ions

Figure 2(a) is a linear regression equation for fitting the relationship between the initial mass concentration of F⁻ in solution and the mass concentration of solution F⁻ after equilibrium. The fitted equation is: \( Q_e = 0.0047C_e + 0.0115 \), relevant the determination coefficient \( R² \) is as high as 0.99, indicating that the two are extremely significant. The fitting results show that with the increase of F⁻ in the solution, the F⁻ which is resolved from the bottom sediment is gradually increased, showing a linear positive correlation level. This is because the clay content in the sediment is low, the clay has a small specific surface, it is not suitable to adsorb F⁻, and the soil with low clay content is generally low in weathering and oxide content, resulting in F⁻ The adsorption is reduced. According to the measured physical and chemical properties of the soil samples, the surface soil of the inlet of Sanquan Reservoir is silt, and the clay content is not high, and its water-soluble F-background value is 1.22g·kg⁻¹.

In addition, we also use the nonlinear Langmuir equation, the Freundlich empirical formula and the Temkin equation to fit the experimental data. Fig. 2(b)(c)(d) are the obtained fitting results, which are arranged from good to bad according to the correlation coefficient \( R² \): Langmuir equation <Freundlich equation <Temkin equation.
It can be seen from the nonlinear adsorption characteristic curve of F\(^-\) that the adsorption curve shows a steep rise at low concentration, indicating that the sediment has a higher F\(^-\) adsorption capacity, and the rate of increase of the adsorption amount decreases as the solution F-concentration increases. It tends to be flat and the adsorption capacity is gradually weakened. The sediment has a high adsorption rate when the concentration of F\(^-\) is low. The reason may be that at low concentration, the surface active sites of the sediment are more, and Mg\(^{2+}\) and Ca\(^{2+}\) easily reach the adsorption site and adsorb to the surface, with the F-concentration. Increasingly, the surface active sites of the deposits are less and less, and the Mg\(^{2+}\), Ca\(^{2+}\) adsorbed to the surface and the F\(^-\) in the solution have an electrostatic repulsion, which weakens the adsorption of F\(^-\), thereby reducing the adsorption rate of F\(^-\)[15].

4. Conclusion
We used kinetic experiments to study the F\(^-\)adsorption performance of reservoir sediments in reservoir water. The adsorption rate can be described by pseudo-second-order kinetic equation. The fitting equation is \(\frac{t}{q_t} = 0.7401t + 0.1266\), correlation coefficient \(R^2 = 0.9985\).

We obtained the linear equation of fitting of F\(^-\) by isothermal adsorption test: \(Q_e=0.0047C_e+0.0115\), the correlation coefficient \(R^2\) reached 0.99, and the F-saturated adsorption capacity was 30.56 mg /g.

References
[1] Cao Chun, Kang Hongliang, Li Pingping, et al. Adsorption and Mechanism of Fluoride Ion in Polyacrylamide Amidoxime Modified Wool [J]. Journal of Polymer Science, 2016 (4): 486-493.
[2] Jing Xiuyan, Yuan Zhouyan, Yang Hongbin, et al. Static adsorption characteristics of soil fluorine and its influencing factors [J]. Journal of Eco-Environment, 2008, 17 (5): 1818-1821.

[3] YANG Junyao. Analysis of factors affecting fluorine migration in water-soil system [J], 1998 (3): 42-44.

[4] Jiang Shuangying, Gao Tingyao. Study on the mechanism of adsorption and removal of fluoride ion in water by clay [J], 2003, 23 (4): 204-208.

[5] Wang Qingwen. Adsorption kinetics and adsorption mechanism of soil on F- in mine water [J]. Journal of Henan Polytechnic University(Natural Science), 2009, 28 (6): 807-810.

[6] Liang Peng. Preparation, Characterization and Adsorption Characteristics of Rare Earth Modified Chitosan Resin [D]. Ocean University of China, 2013.

[7] Zhai Jianyun, Ma Lifeng, Shi Yuanzhi, et al. Adsorption and Desorption Characteristics of Fluoride in Tea Garden Soil [J]. Tea Science, 2001, 21 (2): 161-165.

[8] Peek D C, Volk V V. Fluoride Sorption and Desorption in Soils [J]. Soil Science Society of America Journal, 1985, 49 (3): 583-586.

[9] Mao-Xu Zhu, Kui-Ying Ding, Xin Jiang, Hai-Hua Wang. Investigation on Co- sorption and Desorption of Fluoride and Phosphate in a Red Soil of China [J]. Water, air, and soil pollution, 2007, 183 (1-4): 455-465

[10] Chen Nan. Adsorption of Fluoride in Groundwater by Natural and Synthetic Porous Clay Materials [D]. China University of Geosciences (Beijing), 2012.

[11] Han Degang, Gao Panliang. Fundamentals of Chemical Dynamics [M]. Peking University Press, 1987.

[12] Deng Hui, Liao Xuepin, Shi Bi. Study on Adsorption of Fluoride by Metal Ions Loaded on Collagen Fiber [J]. Journal of Sichuan University (Engineering Science Edition), 2006, 38 (3): 76-80.

[13] Dong Suiming. Study on the migration mechanism of fluorine in soil-water system and the treatment of fluorine-containing water [D]. Chang'an University, 2004.

[14] Liang Xiujuan. Study on the mechanism of fluorine migration and transformation in the water and soil environment of Yangshapao Reservoir in western Jilin [D]. Jilin University, 2008.

[15] Nur T, Loganathan P, Nguyen T C, et al. Batch and column adsorption and desorption of fluoride using hydrous ferric oxide: Solution chemistry and modeling [J]. Chemical Engineering Journal, 2014, 247 (7): 93-102.