Treatment of High Fluorine Surface Water by Crystal Seed Method

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Abstract. In view of the current defluorination process of surface water mainly concentrated on the treatment of reduce the concentration of fluoride to less than 10 mg/L, but less research on the treatment of reduce the concentration of fluoride less than 1.0 mg/L, the existing technology are complex process, and the cost is high. High concentration fluoride surface water was treated by crystal seed process which high-purity calcium fluophosphate and calcite as seed crystal. The best operation conditions for fluoride removal were confirmed through the single factor experiments and orthogonal test: adding seed crystal(Calcite: calcium fluophosphate is 1:4) of 8 g/L with Na₃PO₄ and CaCl₂ to make molar ratio of the calcium ion, phosphate ion and fluorin ion be 12:6:1, the reaction time was 1 h, and the stirring rate was 200 r/min. High removal rate of fluorine ion and utilization rate of phosphate ion were also achieved during the reaction (higher than 94% and 97%, respectively). This research proved that the crystal seed process could reduce the concentration of fluoride in surface water from 15 mg/L to less than 1 mg/L which meets the standard of surface water environment quality.

Keywords: Calcium Fluophosphate, Fluoride Removal from Surface Water, Seed Crystal

1. Introduction
Fluorine is an essential trace element for human body [1]. When the mass concentration of fluorine ion in drinking water is between 0.5 and 1.0 mg/L, human can prevent dental and skeletal diseases. However, long-term drinking water with fluorine content greater than 1.0 mg/L will cause dental fluorosis, and fluoride in drinking water greater than 4 mg/L will cause skeletal fluorosis [2]. With the development of modern industry, the production of fluorine and its compounds is increasing day by day. The mining and processing of fluorine-containing ores, metal smelting, aluminum electrolysis, coke and other industries emit a large number of high-concentration fluorine-containing wastewater, caused environmental pollution, and the surface water such as rivers also appear excessive fluorine [3].

At present, the f-concentration limit of the first-level standard in China's comprehensive sewage discharge standard [4] is 10 mg/L, so the main treatment method is to treat the high-concentration industrial wastewater containing fluorine to 10 mg/L. The main methods include chemical precipitation, adsorption, coagulation precipitation, ion exchange, electrocoagulation and reverse osmosis et. al [5,6,7,8,9]. However our country...
"surface water environment quality standard" [10] IV class water health standards in the F - concentration limit is 1.0 mg/L, though ion exchange method, electrocoagulation method and reverse osmosis method can reduce fluoride wastewater treatment to 1.0 mg/L, but complex process, high cost, large excess fluorine cannot be applied to flow the processing of surface water, how to quickly and efficiently from high fluorine surface water treatment reduce to 1.0 mg/L still not have good solution [11, 12].

In this paper, high purity calcium fluorophosphate was used as seed to remove fluoride ions from water. This method uses the principle of adding crystal seeds to accelerate precipitation and crystallization [13], and uses the known calcium fluoride (Ca10(PO4)6F2) + calcite with the minimum solubility product (1.44×10-119) in fluoride as the seed material for removing fluoride. An appropriate amount of calcium fluorophosphate + calcite, phosphate and calcium salt was added to the high-fluorine water to form calcium fluorophosphate crystals on the surface of the seed [14, 15, 16, 17]. In this study, the composition and purity of homemade crystal seeds, the effects of crystal seeds, phosphate and calcium salt on fluoride removal were investigated, in order to explore a more rapid and effective method to remove fluoride from surface water.

2. Test Part

2.1. Preparation of high purity calcium fluorophosphates crystal seeds

There are many impurities in natural fluorapatite, and the effect of fluorine removal is not good. In this experiment, use self-made high purity fluorapatite as crystal seed to reduce the interference of impurities and improve the effect of fluorine removal. 2.5 g CaCl2 was dissolved in 100 mL deionized water, and 1.78 g (NH4)2HPO4 and 0.17 g NH4F were respectively dissolved in 5 mL deionized water, mix (NH4)2HPO4 solution with NH4F solution and add it to CaCl2 solution; Stir for 1 h at 150℃ and 100 r/min; filter the stirred solution and then bake the solids for 6 h in an oven at 100-105℃. Shimazu X-ray diffractometer was used to analyze the self-made crystal seeds to determine their specific composition and purity and reduce the interference of impurities.

2.2. Test method

The simulated fluorine-containing wastewater in this experiment was prepared from superior pure sodium fluoride (NaF) and deionized water [18] to eliminate interference from other ions.

Analysis method: In this experiment, fluorine ion was measured by fluorometer. After the water sample was filtered through 0.45µm microporous membrane and diluted to a certain multiple, the phosphate ions were determined by molybdate antimony antispectrophotometry. Use an acidity meter to determine PH. Fluorometer is pfs-80; Uv spectrophotometer is hashes DR5000; PHS-3C acidity, X - ray diffraction (XRD) instrument for shimazu products.

2.2.1. Screening of phosphate types. In the experiment, 100ml of prepared raw water containing fluorine was separated, and 0.6g calcium fluoride phosphate and 0.4g calcite were added as crystal seeds after the actual concentration was detected; Adding the same pitch doubling number (10 times of fluorine ion concentration Moore) of sodium dihydrogen phosphate, disodium hydrogen phosphate and trisodium phosphate, and amount of adding the calcium chloride, with 200 r. min 1 h - 1 speed mixing, reaction after filtering, respectively analyzing the residual fluorine ion and phosphate ion, contrast effect on the efficiency of the fluoride in phosphate type, and through the influence of different phosphate on the fluoride in efficiency to obtain the optimal phosphate.

2.2.2. Effect of crystal seeds on fluoride removal. Separate 100ml of the prepared water containing fluorine, after testing the actual concentration, crystal seeds (calcite + calcium fluorophosphate) with different proportions (0+1, 0.2+0.8, 0.4+0.6, 0.6+0.4, 0.8+0.2 and 1+0 g) were added respectively, add phosphate and calcium chloride with the same doubling (10 times the molar concentration of fluoride) after the reaction was finished, the remaining fluoride ions and phosphate ions were analyzed respectively. The fluoride removal rate of the system was investigated with the change of crystal seed ratio to obtain the appropriate crystal seed ratio. After the seed proportion is determined, the amount of seed addition should be determined. In the
experiment, the prepared water containing fluorine was separated, the actual concentration was detected, and
the crystal seeds of 0, 2.0, 4.0, 6.0, 8.0 and 10.0 mg/L were added in the optimal proportion, add phosphate
and calcium chloride with the same doubling (10 times the molar concentration of fluoride). Stir at the speed
of 200 r•min\(^{-1}\) for 1 h, after the reaction was finished, the remaining fluoride ions and phosphate ions
were analyzed respectively. The effects of addition amount of crystal seeds on the removal efficiency were
compared, and the optimal addition amount of crystal seeds was determined according to the effects of
different addition amount of crystal seeds on the removal efficiency.

2.2.3. Optimization of dosage of precipitant. (1)Phosphate dosage is preferred 100ml of prepared raw water
containing fluorine was separated, the actual concentration was detected, and then the optimal amount of
crystal seeds was added, separately add Phosphate so that the molar ratios of phosphate to fluorine are 3:1,
4:1, 5:1, 6:1, 8:1, and 10:1, add the same amount of calcium chloride (10 times the molar concentration of fluorine),
Stir for 1 hour at the speed of 200 r•min\(^{-1}\), after the reaction was finished, the remaining fluoride
ions and phosphate ions were analyzed respectively. Investigate the change of the removal rate of fluorine
in the system with the amount of phosphate. (2)Optimal dosage of calcium fluoride 100ml of prepared raw
water containing fluorine was separated, detected the actual concentration, and then added the optimal
amount of crystal seeds and phosphate, added calcium salts respectively make the molar ratios of calcium
ions to fluorine were 5:1, 8:1, 10:1, 12:1, 15:1, and 20:1, at the speed of 200 r•min\(^{-1}\), stirred the mixture for
1 h and filtered after the reaction. The residual fluorine ions and phosphate ions were analyzed respectively.

2.2.4. Orthogonal test. In the experiment, the prepared fluorine-containing raw water was divided into 9
beakers, detect the actual concentration, and then respectively added crystal seeds, phosphate and calcium
chloride according to table 1. After stirring for 1 h at the rotating speed of 200 r•min\(^{-1}\), filtration was
performed after the reaction, respectively analyze residual fluorine ions and phosphate ions, and investigate
the change of fluoride removal rate of the system to obtain the optimal process parameters.

| seed proportion | seed addition amount (g L\(^{-1}\)) | dosage of phosphate (Multiple of F\(^{-}\)) | dosage of calcium salt (Multiple of F\(^{-}\)) |
|-----------------|-------------------------------|---------------------------------|---------------------------------|
| 1               | 2:3                           | 6                               | 4                               | 10                             |
| 2               | 2:3                           | 8                               | 5                               | 12                             |
| 3               | 2:3                           | 10                              | 6                               | 15                             |
| 4               | 3:2                           | 6                               | 5                               | 15                             |
| 5               | 3:2                           | 8                               | 6                               | 10                             |
| 6               | 3:2                           | 10                              | 4                               | 12                             |
| 7               | 4:1                           | 6                               | 6                               | 12                             |
| 8               | 4:1                           | 8                               | 4                               | 15                             |
| 9               | 4:1                           | 10                              | 5                               | 10                             |

3. Result Analysis and Discussion

3.1. Analysis of crystal composition of high purity calcium fluorophosphate
In this experiment, X-ray diffractometer was used for phase analysis of self-made high-purity calcium
fluorophosphate, and the results were shown in figure 1. After analysis and comparison, the self-made crystal
seeds were monophasic materials with Ca\(_5\) (PO\(_4\)) \(_3\) F composition and 100% purity.
3.2. Effect of different phosphates on fluoride removal

The effect of different phosphates on fluoride removal is shown in table 2. The initial fluoride concentration was 15.275 mg/L. As can be seen from table 2, under certain reaction conditions, after successively adding calcium fluoride phosphate, Na₃PO₄ and CaCl₂ to the fluoride-containing water, the concentration of fluoride in the effluent decreased to below 1.0mg /L, and the maximum removal rate of fluoride ions could reach 96.39%. However, change Na₃PO₄ into NaH₂PO₄ or Na₂HPO₄, which could not reduce the concentration of fluoride ions in the water sample reduce to below 1.0mg /L. The removal rates of fluoride ions were respectively 71.49% and 89.88%. At the same time, by comparing the phosphate ion concentration after reaction among the three groups, it was found that the phosphate ion concentration was the lowest in the water sample added with Na₃PO₄, and its utilization rate reached 99.04%, while the utilization rate of phosphate ion in the water sample added with NaH₂PO₄ and Na₂HPO₄ was only 77.39% and 88.45%.

Table 2. Influence of different phosphate on fluoride ion removal effect

|                          | NaH₂PO₄ + CaCl₂ | Na₃HPO₄ + CaCl₂ | Na₃PO₄ + CaCl₂ |
|--------------------------|----------------|----------------|---------------|
| F⁻ in raw water(mg/L)    | 15.275         | 15.275         | 15.275        |
| F⁻ in water after reaction(mg/L) | 4.355         | 1.546          | 0.551         |
| Removal rate of F(%)     | 71.49          | 89.88          | 96.39         |
| PO₄³⁻ in water after reaction(mg/L) | 172.699       | 88.203         | 7.329         |
| Utilization ratio of PO₄³⁻(%) | 77.39         | 88.45          | 99.04         |

3.3. Effect of crystal seeds on fluoride removal

3.3.1. Optimization of seed proportion. Due to the constant amount of crystal seeds (10g/L), the amount of calcium fluorophosphate decreased with the change of the ratio. The initial fluoride concentration was 15.275 mg/L. As can be seen from figure 2, the addition of calcium fluorophosphate can effectively reduce fluorine ions in water samples. The concentration of fluorine ions in groups (0.2+0.8) and (0.4+0.6) (calcite + calcium fluorophosphate, the same as below) all dropped below 1mg/L, with removal rates respectively is 96.47% and 96.39%. In contrast, the utilization rate of PO₄³⁻ decreases with the increase of the proportion of calcite, because calcite has certain adsorption effect on phosphate ions in water. Therefore, on the premise of high removal fluorine efficiency, in order to better reduce phosphate ion concentration, should appropriately increase the calcite dosage.
3.3.2. Optimization of seed addition amount after. Selecting the seed proportion, the amount of addition need further determined. The experimental results are shown in figure 3. The initial fluorine ion concentration was 15.344 mg/L, and the crystal seed ratio (calcite: calcium fluorophosphate) was 2:3. With the increase of seed mass, the removal effect of fluoride ion in water was improved. When the dosage was about 10g/L, the concentration of residual fluorine ion will decreased to 0.989mg/L, and the removal rate of fluorine ion reached more than 93%. With the increase of seed addition, the efficiency of fluoride removal was further improved. However, the more phosphate ions in the water sample, the lower the utilization rate. Therefore, the amount of crystal seeds added in water is not too large, first it will reduce the utilization rate of phosphate ions, and second it will cause too much precipitation.

3.4. Effect of dosage of precipitant on removal efficiency

3.4.1. Optimization of phosphate dosage. In theory, the molality ratio of calcium ions, phosphate ions and fluorine ions needed to form calcium phosphate precipitation is 5:3:1. However, due to the slow formation of fluorine-containing crystals and the difficulty of fine precipitation and deposition, the actual addition amount of calcium ions and phosphate ions is much larger than the theoretical value. The effect of phosphate dosage on the removal efficiency of induced crystallization is shown in figure 4. The initial fluoride concentration was 17.182 mg/L. As can be seen from figure 4, when the molar ratio of phosphate ion of fluorine ion exceeds 3, the concentration of the remaining fluorine ion will decreases with the increase of phosphate dosage. When the molar ratio of phosphate ion to fluorine ion is 4, 5 and 6, the concentration of the remaining fluorine ion drops below 1 mg/L, with removal rates respectively is 94.85%, 95.16% and 95.64%. However, when the molar ratio exceeds 6, the residual fluoride concentration is inversely proportional to the amount of phosphate added. The utilization rate of phosphate ions is above 96%. However, with the increase of phosphate dosage, the more phosphate ions remaining in the water sample, the lower the utilization rate.
According to the experimental results, 4, 5 and 6 times of the concentration of fluoride ion added to phosphate ion is a better choice, which not only ensures that the removal of fluorine meets the standard of surface water, but also reduces the residual amount of phosphate ion.

![Figure 4. Influence of phosphate dosage on fluorine ion removal effect](image)

3.4.2. Optimization of dosage of calcium salt. The effect of calcium salt dosage on fluoride removal is shown in figure 5. The initial fluoride concentration was 16.098 mg/L. As can be seen from figure 5, with the increase of calcium salt dosage, the concentration of residual fluorine ions gradually decreased. When the molar ratio of calcium ions and fluorine ions was greater than 10, the change of fluorine removal efficiency tended to be flat. When the molar ratio of calcium ion and fluorine ion was higher than 20, the concentration of the remaining fluorine ion dropped to below 1 mg/L, and the removal rate reached more than 93%. The utilization rate of phosphate ions is above 90%, and with the increase of calcium salt dosage, the less phosphate ions remaining in the water sample, the higher the utilization rate. Considering that the residual calcium ions after the reaction should not be too much, it is better to add calcium ions as 10, 12, 15 times of the concentration of fluoride ions.

![Figure 5. Influence of calcium ion dosage on fluorine ion removal effect](image)

3.5. Orthogonal test

After the optimal process conditions were determined by the single factor experiment, the optimal process combination was selected through the orthogonal experiment, crystal seeds and precipitants were added according to table 1, and the initial fluoride concentration of raw water was 16.564 mg/L. The experimental results are shown in table 3. Best group 7 fluorine ion concentration reaches the surface water environment quality standard “remaining IV class water standard of 1 mg/L, removal rate is 94.07% ; The experiment showed that the utilization rate of phosphate in all groups was above 94%, among which group 7 had the highest utilization rate, and the residual concentration of phosphate was 13.620 mg/L. By comprehensive comparison, the test condition of group 7 is the optimal process condition. That is the ratio (calcite: calcium fluorophosphate) was 6 g/L of 1:4 seed, adding trisodium phosphate and calcium chloride make the molar
ratio of calcium ion, phosphate ion and fluorine ion was 12:6:1.

Table 3. Orthogonal experimental results

|   | 1       | 2       | 3       | 4       | 5       | 6       | 7       | 8       | 9       |
|---|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| F in raw water(mg/L) | 16.564  | 16.564  | 16.564  | 16.564  | 16.564  | 16.564  | 16.564  | 16.564  | 16.564  |
| F in water after reaction(mg/L) | 5.519   | 3.305   | 2.843   | 2.155   | 2.774   | 1.668   | 0.983   | 2.103   | 3.212   |
| Removal rate of F(%) | 66.68   | 80.05   | 82.84   | 86.99   | 83.25   | 89.93   | 94.07   | 87.30   | 80.61   |
| PO₄³⁻ in water after reaction(mg/L) | 14.43   | 14.63   | 12.818  | 14.830  | 21.972  | 9.499   | 13.623  | 14.931  | 23.380  |
| Utilization ratio of PO₄³⁻(%) | 95.65   | 96.47   | 97.42   | 96.42   | 95.58   | 97.13   | 97.26   | 95.49   | 94.35   |

4. Conclusion

Self-made high purity calcium fluoride phosphate, through XRD analysis, self-made calcium fluoride phosphate purity is 100%.

The optimal reaction conditions were as follows: add 6 g/L of crystal seeds with a ratio (calcite: calcium fluorophosphate) of 1:4, add trisodium phosphate and calcium chloride, make the molar ratio of calcium ion, phosphate ion and fluorine ion is 12:6:1, and stir for 1 h at the speed of 200 r•min⁻¹. Under the best condition, the removal rate of fluoride ion can reach 94.07%, and the utilization rate of phosphate ion is above 97%.

Use high purity calcium fluoride phosphate + calcite as crystal seed, and trisodium phosphate and calcium chloride are used as precipitators to remove fluorine ions from surface water. The high fluorine water with fluorine concentration of about 15 mg/L can be reduced to less than 1.0 mg/L within 1 h, which meets the environmental quality standard of surface water.

5. Prospect

In this study, use self-dispensing water samples from the laboratory to simulate high-fluorine surface water, which was conducive to the exploration of the reaction mechanism. However, the water quality was quite different from that of the actual high-fluorine surface water. Therefore, need further studies on de-fluoridation of the actual high-fluorine surface water.

During the test, the residual phosphate ion concentration is large, so other reaction conditions need to be further optimized to reduce the residual phosphate ion.

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