

## Article

# Exploration and Optimisation of High-Salt Wastewater Defluorination Process

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**Abstract:** The typical lime precipitation method is used to treat high-concentration fluorine-containing wastewater. In this way, the fluorine in the wastewater can be removed in the form of CaF<sub>2</sub>. Thus, this method has a good fluoride removal effect. In this study, calcium hydroxide was used to adjust the pH and achieve a significant fluoride removal effect at the same time. The removal rate of fluoride ion decreases gradually with the increase in the concentration of sulphate in the raw water. When the synergistic defluorination cannot meet the requirements of water production, adding a step of aluminium salt flocculation and precipitation can further reduce the fluoride ion concentration. According to the feasibility of the actual project, this study improves the lime coagulation precipitation defluorination process on this basis, and the combined process is synchronised. In the process optimisation, barium chloride is added to remove the influence of sulphate radicals in the water, and then, the pH is adjusted to 5–6. The fluoride ion concentration in high-salt wastewater can be reduced from 446.6 mg/L to 35.4 mg/L by defluorination after pre-treatment whose removal rate was 92.1%. The combined process synchronously removes fluorine and purifies the water quality to a certain extent. Indicators such as COD, total phosphorus, ammonia nitrogen, and chloride ions in wastewater are reduced, and the removal rate is increased by 35.5% under the same conditions. This scheme improves the wastewater treatment effect without increasing the existing treatment equipment. Thus, it achieves a better defluorination effect and reduces the dosage of chemicals as much as possible, which is conducive to lowering the discharge of sludge after treatment.

**Keywords:** high-salt wastewater; fluorine removal; coagulation; precipitation; combined process



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## 1. Introduction

Fluoride ion (F<sup>-</sup>) pollution in water is recognised as a serious pollution [1]. Water pollution from natural and anthropogenic sources of fluoride has caused fluorosis in at least 25 countries worldwide [2,3]. Fluorine atom is the smallest halogen. A certain amount of fluorine and its organic compounds can prevent dental caries, but fluorine will cause great harm to the human body if the content exceeds the allowable range [4,5]. The continuous input of fluorine in the environmental water body and the excessive fluoride in the water body due to the dissolution of natural sources such as fluorine-rich minerals and the intensification of human activities are threatening the safety of drinking water quality for residents [6]. Excessive intake of fluoride will not only cause diseases such as dental fluorosis and bone fluorosis, but also adversely affect the body's immune system, kidneys, and gastrointestinal tract [7–9]. Excessive fluorine content will affect the metabolism of calcium and phosphorus in the human body. This phenomenon causes disorder in the metabolism and physiological functions of the human body, which results in a series of poisoning symptoms. Fluoride often appears in metallurgical industry, circuit board manufacturing, photovoltaic semiconductor, chemical industry, electric power industry, and silicate industry. The fluorine chemical industry is known as the modern 'gold industry'

and occupies an important position in the development of the country [10]. The problem of fluoride pollution in water bodies has received extensive attention. The current fluoride removal technology has no obvious effect on the removal of fluoride in natural water bodies, and it cannot be widely used. At present, the treatment of high-salt wastewater by evaporation and incineration technology has a good treatment effect, but the treatment process also has disadvantages [11]. Specifically, the corrosion problem of equipment is becoming increasingly prominent and the actual life of many equipment does not reach the design life, and the culprit is wastewater. In the reducing acid solution, fluoride is easily combined with hydrogen ions to form hydrogen fluoride, which is preferentially adsorbed on the surface oxide film. The expulsion of oxygen atoms also causes the passivation film on the surface of the alloy to form soluble fluoride and corrode. Amongst them, HF solution has the strongest corrosion effect on metals. At the beginning, the fluorine content is very low, which will not cause equipment corrosion. However, as the treatment time prolongs, the fluorine content after the concentration and enrichment continues to increase, exceeds the corrosion resistance of metal materials, and ultimately causes fluorine corrosion. Therefore, fluorine corrosion can be prevented in two ways: one is to reduce the fluorine content in industrial fluorine-containing wastewater, and the other is to solve the problem of fluorine corrosion of materials and equipment. The main tasks are to ensure proper equipment use environment, prolong equipment service life, reduce the cost of high-salt wastewater treatment, lower the risk of wastewater treatment accidents, and promote chemical safety production [12].

Commonly used methods for defluorination include chemical precipitation, adsorption, membrane filtration, and ion exchange. Amongst them, the adsorption method is often unsatisfactory in removing fluorine after regeneration. Furthermore, the membrane filtration and ion exchange methods have high costs and are difficult to maintain and manage [13]. The more mature lime precipitation method (CaO) will significantly increase the pH and become strongly alkaline [14]. Thus, it is unsuitable for natural water defluorination. CaCl<sub>2</sub> can also provide a large amount of Ca<sup>2+</sup> as a soluble calcium salt, which will theoretically promote the formation of CaF<sub>2</sub> precipitation. Adsorption and precipitation methods are currently the two methods commonly used in the treatment of industrial fluorine-containing wastewater in China [15]. Chemical precipitation is the most common and efficient treatment method to treat high concentrations of fluoride in wastewater [16]. The flocculated particles formed by the precipitation of CaF<sub>2</sub> and AlF<sub>3</sub> are used to remove the dissolved fluoride in the solution in the form of solid particles. When dealing with high-concentration fluorine wastewater, lime precipitation is an effective fluoride removal method, and it is simple, low cost, and effective. It uses calcium and fluoride ions in lime to precipitate CaF<sub>2</sub> for removing fluoride ions. Although the chemical precipitation method is simple and the treatment cost is low, it has the problem of secondary pollution and its treatment effect is not ideal [17]. It also has defects such as slow settling, long processing cycle for large flow of emissions, and unsuitability for continuous discharge. The coagulation sedimentation method can treat wastewater with high fluorine content, and it is economical, practical, it has simple equipment, and has easy operation. The root ions also tend to increase, and the treated water contains a large amount of dissolved aluminium. The adsorption method has a good effect in advanced treatment of fluorine-containing wastewater, but its practicality is limited due to problems such as bed loss, low adsorption capacity, bed regeneration, and complex treatment of regeneration liquid. In the future, the main direction of adsorption defluorination research is to develop high-efficiency new adsorbents to overcome the shortcomings of traditional adsorbents with small saturated adsorption capacity. Strengthening the research on the selectivity of the adsorbent, the regeneration of the adsorbent, and the adsorption mechanism is also necessary [18]. Reverse osmosis technology is widely used in seawater desalination and ultrapure water preparation, but few reports on its use in the treatment of fluorine-containing wastewater are available. The reason is that reverse osmosis technology is a molecular-level treatment technology, which needs to prevent the contamination of reverse osmosis membranes by

suspended solids. Moreover, complex pre-treatment is required before treatment because industrial wastewater has many impurities. Reverse osmosis equipment is costly and consumes a large amount of electricity. The electrocoagulation method is simple in equipment and easy to operate, but the cost of water production is high, and the treatment effect of wastewater with high fluorine content is not good. Thus, it is difficult to popularise at present. The ion exchange resin method uses the ion exchange between the resin and the solution to remove fluorine [19]. The exchange capacity and fluorine removal efficiency of the ion exchange resin method are low, and the resin is costly and the regeneration cost is high [20,21]. Thus, it has no industrialised example. Electrodialysis has a complex device, high power consumption, high maintenance intensity, and strict technical requirements for operators [22]. High-priced metal ions in the water can also easily cause membrane poisoning and damage to electrodes [23,24]. Several studies on fluoride removal technology have used simulated fluorine-containing solutions prepared in the laboratory, which have fewer impurities and are quite different from natural water bodies [25,26]. Thus, this method has been widely promoted.

For solving the difficulty in treating high-concentration fluorine-containing wastewater, this research aims to synchronously remove fluoride by combining processes on the basis of separate treatment processes whilst avoiding the phenomenon of low treatment efficiency, and increased cost caused by the addition of other pollutants. Through the mechanism comparison and research progress of various defluorination methods, the simple combined process defluorination technology can meet the increasingly stringent water quality standards and become the most promising method. A better agent is found through experiments and the optimal reaction time is confirmed. The pH value is also an important factor affecting the defluorination effect, and the proposed method has the best pH range with practical engineering value according to the experiments. From the comprehensive consideration of fluoride removal effect, material price, operating cost and secondary pollution, simple combined processes, especially the combined process of precipitation + coagulation and sedimentation, are undoubtedly the best choice for fluoride removal technology of drinking water.

In this study, industrial wastewater is taken as the research object, and the effects of materials such as  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCl}_2$  and PAC on the removal of fluoride ions in water samples under different dosing conditions are investigated. The raw materials and the water quality indicators after the treated water samples are analysed, and the possible mechanism of fluoride removal is explored, which provides a reference and basis for the control of fluorine pollution in water bodies. After the pre-treatment of chemical precipitation, coagulation precipitation, that is, calcium precipitation + coagulation precipitation combination, is conducted. In an alkaline environment, the colloid formed after the coagulant enters the water body is positively charged, and the fluoride ion has its own negative charge. Aluminium salt coagulants such as aluminium sulphate, polyaluminium chloride and polyaluminium sulphate are added to the water, and the complexation of  $\text{Al}_{3+}$  and  $\text{F}^-$  and the  $\text{Al}(\text{OH})_3$  alum produced after the hydrolysis of aluminium salt are used to remove the F in the wastewater. The effect of this method is good. The aluminium salt coagulation sedimentation method is widely used in industrial wastewater treatment because the dosage of chemicals is small, the cost is low, and the effluent can meet the national discharge standard after one treatment. The fluoride removal effect is modified by removing the common sulphate ions in the water body. The pH applicable range of  $\text{F}^-$  adsorption in the water body is explored to further reduce the concentration of fluoride ions in the treated effluent. On the basis of the stability of ion concentration, its adsorption mechanism is studied, which corresponds to the most commonly used defluorination technologies and methods. This work provides a reference for the understanding and development of defluorination technology and is important for the defluorination of high-salt wastewater and its process optimisation.

## 2. Materials and Methods

### 2.1. Materials

Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), polyaluminium chloride (PAC), barium chloride ( $\text{BaCl}_2$ ), calcium chloride ( $\text{CaCl}_2$ ), hydrochloric acid (HCl), and other reagents are purchased from Sinopharm Chemical Reagent Co., Ltd. They are analytically pure. The experimental water samples are taken from a sewage treatment plant in an industrial zone in Nanjing, Jiangsu. The basic water quality indicators of the experimental water samples are shown in Table 1. Compared with the standard limits in the Chinese national standard ‘Surface Water Environmental Quality Standard’ (GB 3838-2002) [27], the initial fluoride ion mass concentration of the experimental water sample is higher than the standard limit of Class V water, and it does not meet the discharge standard in the ‘Comprehensive Wastewater Discharge Standard’ (GB8978-1996) [28].

**Table 1.** Basic water quality of raw water.

Number	Water Sample	pH	COD (mg/L)	NH <sub>3</sub> -N (mg/L)	TN (mg/L)	TP (mg/L)	Inorganic Phosphorus (mg/L)	Conductivity ( $\mu\text{s}/\text{cm}$ )	Fluoride (mg/L)	Chloride (mg/L)
1	Regulation pool	9.8	451	29	50.3	29.4	28.8	37,120	308.5	7072.9
2	Intermediate pool	9.6	592	46.4	62.5	67.4	62.48	56,200	446.6	9787.8
3	Domestic sewage pool	8.6	114	7.1	11	3.94	3	10,620	113.2	2178.3
5	Neutralisation reaction tank A	10.8	575	1.9	19	24.5	21.8	68,400	236	4880.3
6	Neutralisation reaction tank B	10.9	542	2	19.6	23.5	21.2	65,600	242	5064.8

### 2.2. Experimental Method

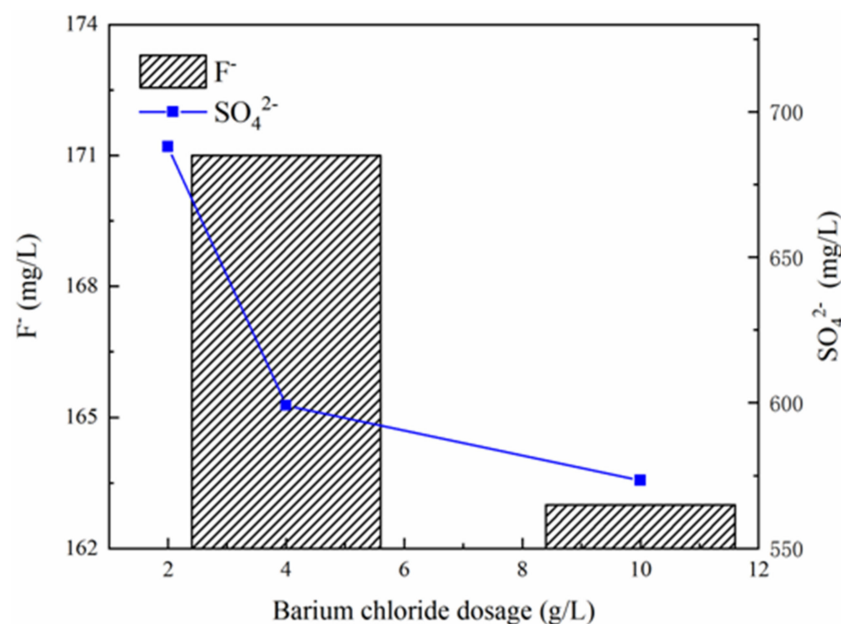
In this experiment, chemical precipitation method was used to remove fluoride ions, calcium precipitation + coagulation precipitation combination was utilised such that fluoride ions form  $\text{CaF}_2$  and the pH value of the solution was adjusted to achieve the best effect. The other group adds  $\text{CaCl}_2$  for comparison and provides remaining  $\text{Ca}^{2+}$ . In this study, PAC was used as a coagulant, and the general formula of polyaluminium chloride could be expressed as  $\text{Al}_n\text{Cl}_{3n}$ . Polyaluminium chloride could be regarded as an intermediate product of  $\text{AlCl}_3$ , which is gradually converted into  $\text{Al}(\text{OH})_3$  by hydrolysis. It is a compound composed of many different forms of hydrolysis products. As soon as polyaluminium chloride was added to the water, it could directly neutralise electricity, adsorb and bridge, and was less affected by the original water quality.

Raw water and experimental samples contain organic compounds with complex components and high chromaticity (greater than  $2500^\circ$ ), and the operability and accuracy of detection methods such as titration and spectrophotometry are seriously affected [29]. Thus, we refer to Chinese industry standards, national standards HJ776-2015, GB/T14642-2009, and the related literature reports [30]. The fluoride ion mass concentration is determined with reference to the standard curve method in ‘Determination of Fluoride in Water Quality’ (GB7484-87), and the determination of total phosphorus (TP) is based on ‘Ammonium molybdate spectrophotometric method for the determination of TP in water quality’ (GB11893-1989) [31]. The determination of total nitrogen (TN) refers to ‘Determination of total nitrogen in water quality by alkaline potassium persulphate digestion UV spectrophotometry’ (HJ636-2012). The determination of ammonia nitrogen ( $\text{NH}_3\text{-N}$ ) refers to photometric method in ‘Determination of ammonia nitrogen in water quality by Nessler’s reagent spectrophotometry’ (HJ538-2009). The determination of permanganate index (CODMn) refers to ‘Determination of permanganate index of water quality. (GB11892-89). The pH value is determined by glass electrode method, and conductivity (EC) is determined by conductivity ritual [32].

### 3. Results and Discussion

#### 3.1. Effect of Sulphate Radical on Fluoride Removal in Water

Figure 1 shows that with the increase in the dosage of barium chloride, the sulphate ions in the water are continuously precipitated and separated in the form of barium sulphate. The sulphate radicals decrease from 688 mg/L to 573.4 mg/L, and the fluoride ion concentration also decreases from 171 mg/L to 163 mg/L. The removal of fluoride ions is improved when sulphate ions are removed.



**Figure 1.** Effect of sulphate radicals on fluoride removal.

The main purpose of this experiment is to verify the fluoride removal effect after the sulphate radical is removed. The reason is that the sulphate radical also forms a precipitate with calcium ions. As the sulphate radicals in the raw water decrease, the fluoride ion concentration also decreases, and the removal of the sulphate radicals in the raw water helps improve the fluoride removal effect. This experiment confirms that the increase in sulphate concentration in raw water will strongly negatively impact the synergistic defluorination effect of chemical precipitation. When the sulphate concentration is high, the fluoride ion content in the produced water has difficulty meeting the standard requirements. The reason for this effect may be that calcium and fluoride ions can coexist at higher concentrations in the high-salt water system as affected by the salt effect [33,34]. For example, the calcium and fluoride concentrations in raw water have far exceeded the solubility product of calcium fluoride. The significant increase in the content of salt substances represented by sulphate will exacerbate this effect due to the limitation of the constant. Fluoride ions can exist more stably in a high-salt environment, and the residual amount after treatment increases.

#### 3.2. Impact of Dosage on Water Quality Treatment Effect

Table 2 shows that the concentrations of phosphorus and fluoride and chloride ions in water continue to decrease with the increase in calcium hydroxide dosage. As the dosage increases from 860 mg/L to 3440 mg/L, the pH increases from 10.9 to 12.5, TP decreases from 20.9 mg/L to 8.6 mg/L, inorganic phosphorus decreases from 19.8 mg/L to 8.3 mg/L, fluoride ion decreases from 231.8 mg/L to 205 mg/L, and chloride ion decreases from 6343 mg/L to 6057 mg/L. The water quality is also obviously improved with the increase in the dosage.

**Table 2.** Effect of dosage on phosphorus removal effect.

Number	Water Sample	pH	TP (mg/L)	Inorganic Phosphorus (mg/L)	Fluoride (mg/L)	Chloride (mg/L)
1	neutralisation tank + 860 mg/L Ca(OH) <sub>2</sub> + 200 mg/L PAC	10.9	20.9	19.8	231.8	6343
2	neutralisation tank + 1160 mg/L Ca(OH) <sub>2</sub> + 600 mg/L PAC	11.1	16.2	15.7	232	6327
3	neutralisation tank + 2320 mg/L Ca(OH) <sub>2</sub> + 600 mg/L PAC	12.2	14.1	13.3	214	6316
4	neutralisation tank + 3440 mg/L Ca(OH) <sub>2</sub> + 200 mg/L PAC	12.5	8.6	8.3	205	6057

Phosphate and fluoride ions in the water are both removed from the wastewater in the form of insoluble salts. Increasing the dosage of calcium hydroxide significantly improves the defluorination effect and plays a good role in promoting water quality treatment. However, the amount of sludge increases when the dosage is too large. Thus, the dosage cannot be increased blindly. In the treatment of fluorine-containing wastewater, the method of simply increasing the excess amount of lime cannot be used to improve the fluoride removal effect. In general, the remaining F<sup>-</sup> concentration in the water will gradually decrease with the gradual increase in the coagulant dosage. However, the dosage cannot be increased indefinitely during the operation of the project in practice considering the cost of the chemical [35]. Thus, finding an optimal dosage is necessary, which not only can meet the water quality treatment requirements but also can save the cost of the chemical. The two factors should be coordinated and considered to have better fluoride removal effect and as little lime as possible, which is also conducive to reducing the amount of sludge discharged after treatment [36].

### 3.3. Contrastive Experiment of Adding CaCl<sub>2</sub> Treatment Effect

Table 3 shows that the chloride ion content in calcium hydroxide and calcium chloride wastewater is significantly reduced. Moreover, the fluoride ion concentration of the calcium chloride group is 48% higher than that of the calcium hydroxide group. At the same time, the water quality treatment effect of the group with additional calcium hydroxide is better than that of the group with additional calcium chloride. Furthermore, the indexes of COD, TP, inorganic phosphorus, and electrical conductivity are all lower than those of the group with additional calcium chloride.

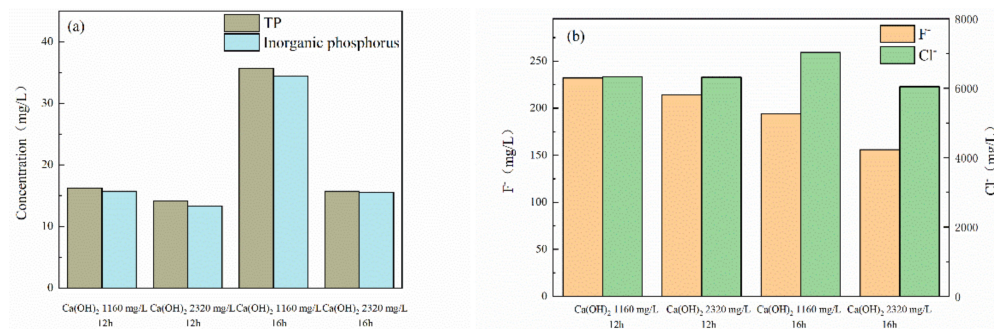
**Table 3.** Water quality comparison of adding CaCl<sub>2</sub> and lime.

Number	Water Sample	pH	COD (mg/L)	TP (mg/L)	Inorganic Phosphorus (mg/L)	Fluoride (mg/L)	Conductivity (µs/cm)
1	2000 mg/L Ca(OH) <sub>2</sub> + 600 mg/L PAC	8.3	1248	14.6	13.7	60.4	44,600
2	2800 mg/L CaCl <sub>2</sub> + 600 mg/L PAC	8.2	3121	15.5	15	89.3	45,600

The addition of calcium hydroxide and calcium chloride has a certain defluorination effect. When the water contains soluble calcium salts such as calcium chloride, the solubility of calcium fluoride will be reduced due to the same ion effect. The introduction of chloride ions into calcium will increase the solubility of calcium fluoride. Therefore, the mixture of calcium hydroxide and calcium chloride is added to the fluorine-containing wastewater. When the pH value is 7–8 after neutralisation and precipitation, the fluoride ion content in the fluorine-containing wastewater with calcium chloride is significantly higher than that with calcium hydroxide. The fluoride ion in the fluorine-containing wastewater and CaCl<sub>2</sub> provide an excess of Ca<sup>2+</sup>. Thus, reducing the fluoride ion content cannot be continued.

### 3.4. Effects of Different Reaction Times on Water Quality Treatment Efficiency

Figure 2 shows that the TP and inorganic phosphorus in the wastewater do not decrease after the reaction time is increased. On the contrary, the TP in the water after the reaction is completed is higher when the calcium hydroxide dosage is 1160 mg/L, and the reaction time is increased to 16 h. The concentration of inorganic phosphorus is much higher than that of other groups, and it is three times higher than the concentration of TP and inorganic phosphorus in the reaction time of 12 h. Specifically, it reaches 35.7 mg/L. The chloride ion concentration in the water does not change significantly when the reaction time is changed. By contrast, the fluoride ion concentration in the water decreases as the reaction time progresses. When the calcium hydroxide dosages are 1160 and 2320 mg/L, the reaction time for 16 h is faster than the reaction time for 12 h. The fluoride ion concentration decreases by 8.4% and 21.7% at 12 h.

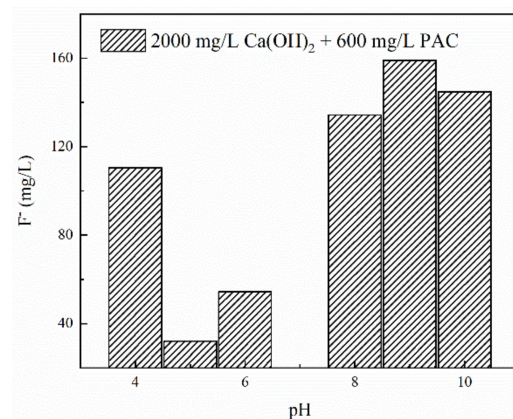


**Figure 2.** Effects of different reaction times on (a) phosphorus removal and (b) fluorine and chlorine removal efficiency.

When the reaction time is increased, the fluoride ion in the effluent decreases to some extent. However, the reaction time has no obvious effect on other water quality indicators. Nevertheless, the phosphorus content is improved by increasing the reaction time. Increasing the reaction time can improve the removal rate of fluoride ions, but it has no effect on other water quality indicators, especially the phosphorus removal effect is reduced. As time continues to change, the destabilised insoluble solids accumulate into larger insoluble solids and become stable colloids again. The impact of calcium hydroxide phosphorus removal is also affected by the pH value.

### 3.5. Effect of pH on the Defluorination

Figure 3 shows that the pH is adjusted to different levels by adding different amounts of calcium hydroxide and hydrochloric acid. The minimum fluoride ion concentration is 32.1 mg/L when the pH is 5, and the maximum fluoride ion concentration is 159 mg/L when the pH is 9. Ideal defluorination effect can be achieved between pH 5 and 6.

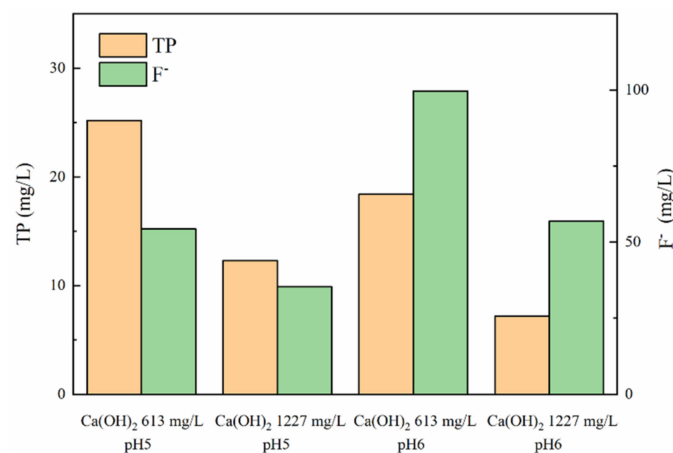


**Figure 3.** Effect of pH on the defluorination.

When adjusting the pH, more calcium ions are added to promote the formation of calcium fluoride, but the calcium concentration is no longer the main controlling factor. Specifically, the removal capacity of fluoride ions decreases with the increase in pH. pH will increase the solubility of calcium fluoride [37]. Thus, the effect is poor in an alkaline environment. Under acidic conditions,  $H^+$  and  $F^-$  form HF, which reduces the  $F^-$  concentration. When the pH value is too high,  $Ca^{2+}$  and  $OH^-$  form  $Ca(OH)_2$ , which reduces  $Ca^{2+}$ . This reduction increases the residual fluorine concentration. The precipitation effect of calcium ion and fluoride ion is good under neutral conditions. At this time, the pH is adjusted to about 7 with hydrochloric acid after adding calcium hydroxide and PAC. The pH is increased after the reaction.

### 3.6. Influence and Optimisation of Process Pretreatment on Defluorination Effect

Figure 4 shows that the fluoride ion concentration of the wastewater treated by the original scheme is 54.4 mg/L when the pH value is 5. The fluoride ion is reduced to 35.4 mg/L when the dosage of calcium hydroxide is increased to 1227 mg/L and the pH value is 5. At pH 6, increasing the dosage of calcium hydroxide to 1227 mg/L can also reduce the fluoride ion to below 56.9 mg/L. When the dosage of calcium hydroxide is 613 mg/L, the TP concentration is 25.2 mg/L when the pH is 6, and the TP concentration is 18.4 mg/L when the pH is 5. The TP concentration is further reduced to 7.2 mg/L with the increase in calcium hydroxide dosage.



**Figure 4.** Processing effects of different schemes.

The reason is that calcium hydroxide is alkaline and PAC is acidic. Calcium hydroxide can neutralise acidic wastewater, capture metal ions, remove fluoride ions, and neutralise acidic wastewater. It can help in the coagulation of colloidal particles in wastewater. Fluoride ions and many metal ions produce soluble substances. Calcium and fluoride ions can combine to form precipitates that are insoluble in water. The precipitate (calcium fluoride) and water can be separated by adding flocculants only when precipitates are formed. Polyaluminium chloride defluorination is a complex process [38]. When the pH value is about 7, the hydrolysed product of PAC coagulant has a high positive charge. With the increase in pH, the charge of the highly charged polynuclear complex in the hydrolysed product of PAC is reduced. Moreover, the form of aluminium is gradually transformed from a positive multinuclear complex to an amorphous aluminium hydroxide gel or an anion of tetrahydroxy aluminium. The direct adsorption capacity is also enhanced [39]. After the polyaluminium chloride is added to the water, the ion exchange, adsorption and sweeping of  $F^-$  through the complexation of  $Al^{3+}$  and  $F^-$ , the intermediate product of hydrolysis, and the final generated amorphous  $A(OH)_3(am)$  floc, the concentration of fluoride ions in the water gradually decreases [40,41]. The optimisation experiment is conducted under the experimental conditions with better effect, that is, pH 5 and 6. After sulphate is removed, the removal rate of fluoride ion and TP increases with the rise in the



dosage. Under the same dosage, the removal effect of fluoride ion of pH 5 is better than that of pH 6. In the meantime, the case for TP is the opposite. In addition to removing fluorine, the process is also very effective in removing phosphate radicals in wastewater and converting soluble phosphates into insoluble phosphates. This solution can simultaneously remove phosphorus whilst removing fluorine [42,43].

#### 4. Conclusions

The combined process simultaneously removes fluorine, adjusts the pH for precipitation, adds chemicals to reduce the influence of sulphate ions, adds sufficient calcium hydroxide for precipitation, and adds flocculant-assisted two-step chemical precipitation method. Thus, it can significantly remove fluoride ions. The fluoride removal effect of the combined process is affected by the sulphate concentration in the raw water. When the sulphate content is reduced, the fluoride ion concentration decreases significantly. As the sulphate concentration increases, the salt content of the raw water increases, and the removal rate of fluoride ions decreases significantly. Two-step chemical precipitation of 'calcium hydroxide + PAC' removes most of the fluorine, and then, it uses flocculation precipitation to remove the fluorine to the target value. The flocculation precipitation step is expected to be omitted when the raw water salt content is low. The combined process is intensive and efficient, and it has a good application prospect in the overall process of concentrated brine treatment and miscellaneous salt resource treatment. When removing fluoride by precipitation method, the dosage of chemical agent cannot be simply increased to improve the effect of fluoride removal. The efficiency of fluoride removal and economy should be considered in coordination to achieve better fluoride removal effect, and reduce the dosage of calcium hydroxide as much as possible. Reducing the discharge of sludge after treatment is beneficial. Thus, cost control and reasonable disposal of waste liquid are the guarantees for realising energy cycle and economical practicality.

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#### References

1. Choudhary, N.; Yadav, V.K.; Yadav, K.K.; Almohana, A.I.; Almojil, S.F.; Gnanamoorthy, G.; Kim, D.H.; Islam, S.; Kumar, P.; Jeon, B.H. Application of green synthesized MMT/Ag nanocomposite for removal of methylene blue from aqueous solution. *Water* **2021**, *13*, 3206.
2. Khan, S.H.; Pathak, B. Zinc oxide based photocatalytic degradation of persistent pesticides: A comprehensive review. *Environ. Nanotechnol. Monit. Manag.* **2020**, *13*, 100290.
3. Yadav, V.K.; Khan, S.H.; Choudhary, N.; Tirth, V.; Kumar, P.; Ravi, R.K.; Modi, S.; Khayal, A.; Shah, M.P.; Sharma, P.; et al. Nanobioremediation: A sustainable approach towards the degradation of sodium dodecyl sulfate in the environment and simulated conditions. *J. Basic Microbiol.* **2022**, *62*, 348–360. [[CrossRef](#)] [[PubMed](#)]
4. Mushtaq, F.; Zahid, M.; Bhatti, I.A.; Nasir, S.; Hussain, T. Possible applications of coal fly ash in wastewater treatment. *J. Environ. Manag.* **2019**, *240*, 27–46. [[CrossRef](#)] [[PubMed](#)]
5. Gupta, R.; Satyawali, Y.; Batra, V.S.; Balakrishnan, M. Submerged membrane bioreactor using fly ash filters: Trials with distillery wastewater. *Water Sci. Technol.* **2008**, *58*, 1281–1284. [[CrossRef](#)]
6. Liu, X. Online monitoring method of non-point source pollution of water resources in river scenic spots. *Arab. J. Geosci.* **2021**, *14*, 603. [[CrossRef](#)]

7. León, L.F.; Soulis, E.D.; Kouwen, N.; Farquhar, G.J. Nonpoint source pollution: A distributed water quality modeling approach. *Water Res.* **2001**, *35*, 997–1007. [[CrossRef](#)]
8. Boulkhessaim, S.; Gacem, A.; Khan, S.H.; Amari, A.; Yadav, V.K.; Harharah, H.N.; Elkhaleefa, A.M.; Yadav, K.K.; Rather, S.-U.; Ahn, H.-J.; et al. Emerging trends in the remediation of persistent organic pollutants using nanomaterials and related processes: A review. *Nanomaterials* **2022**, *12*, 2148.
9. Sharma, B. Microbes as indicators of water quality and bioremediation of polluted waters: A novel approach. In *Microbial Biotechnology in Environmental Monitoring and Cleanup*; Pankaj, Sharma, A., Eds.; IGI Global: Hershey, PA, USA, 2018; pp. 44–60.
10. Bilotta, G.S.; Brazier, R.E. Understanding the influence of suspended solids on water quality and aquatic biota. *Water Res.* **2008**, *42*, 2849–2861.
11. Wang, B.; Zhou, Y.; Li, L.; Xu, H.; Sun, Y.; Wang, Y. Novel synthesis of cyano-functionalized mesoporous silica nanospheres (MSN) from coal fly ash for removal of toxic metals from wastewater. *J. Hazard. Mater.* **2018**, *345*, 76–86. [[CrossRef](#)]
12. Yadav, V.K.; Yadav, K.K.; Gacem, A.; Gnanamoorthy, G.; Ali, I.H.; Khan, S.H.; Jeon, B.-H.; Kamyab, H.; Inwati, G.K.; Choudhary, N. A novel approach for the synthesis of vaterite and calcite from incense sticks ash waste and their potential for remediation of dyes from aqueous solution. *Sustain. Chem. Pharm.* **2022**, *29*, 100756. [[CrossRef](#)]
13. Dash, S.; Chaudhuri, H.; Gupta, R.; Nair, U.G. Adsorption study of modified coal fly ash with sulfonic acid as a potential adsorbent for the removal of toxic reactive dyes from aqueous solution: Kinetics and thermodynamics. *J. Environ. Chem. Eng.* **2018**, *6*, 5897–5905.
14. Cisneros, B.J. Safe sanitation in low economic development areas. *Treatise Water Sci.* **2011**, *4*, 147–200.
15. Adegoke, K.A.; Oyewole, R.O.; Lasisi, B.M.; Bello, O.S. Abatement of organic pollutants using fly ash based adsorbents. *Water Sci. Technol.* **2017**, *76*, 2580–2592. [[CrossRef](#)]
16. Inwati, G.K.; Kumar, P.; Roos, W.D.; Swart, H.C.; Singh, M. UV-irradiation effects on tuning LSPR of Cu/Ag nanoclusters in ion exchanged glass matrix and its thermodynamic behaviour. *J. Alloys Compd.* **2020**, *823*, 153820.
17. Malik, P.; Inwati, G.K.; Mukherjee, T.K.; Singh, S.; Singh, M. Green silver nanoparticle and Tween-20 modulated pro-oxidant to antioxidant curcumin transformation in aqueous CTAB stabilized peanut oil emulsions. *J. Mol. Liq.* **2019**, *291*, 111252.
18. Montes-Grajales, D.; Fennix-Agudelo, M.; Miranda-Castro, W. Occurrence of personal care products as emerging chemicals of concern in water resources: A review. *Sci. Total Environ.* **2017**, *595*, 601–614.
19. Daughton, C.G.; Ternes, T.A. Pharmaceuticals and personal care products in the environment: Agents of subtle change? *Environ. Health Perspect.* **1999**, *107*, 907–938. [[CrossRef](#)]
20. Geissen, V.; Mol, H.; Klumpp, E.; Umlauf, G.; Nadal, M.; van der Ploeg, M.; van de Zee, S.E.A.T.M.; Ritsema, C.J. Emerging pollutants in the environment: A challenge for water resource management. *Int. Soil Water Conserv. Res.* **2015**, *3*, 57–65. [[CrossRef](#)]
21. Chaukura, N.; Gwenzu, W.; Tavengwa, N.; Manyuchi, M.M. Biosorbents for the removal of synthetic organics and emerging pollutants: Opportunities and challenges for developing countries. *Environ. Dev.* **2016**, *19*, 84–89. [[CrossRef](#)]
22. Khan, M.; Khan, A.U.; Hasan, M.A.; Yadav, K.K.; Pinto, M.M.C.; Malik, N.; Yadav, V.K.; Khan, A.H.; Islam, S.; Sharma, G.K. Agro-Nanotechnology as an Emerging Field: A Novel Sustainable Approach for Improving Plant Growth by Reducing Biotic Stress. *Appl. Sci.* **2021**, *11*, 2282.
23. Gaur, N.; Flora, G.; Yadav, M.; Tiwari, A. A review with recent advancements on bioremediation-based abolition of heavy metals. *Environ. Sci. Process. Impacts* **2014**, *16*, 180–193. [[CrossRef](#)] [[PubMed](#)]
24. Bondi, C.A.M.; Marks, J.L.; Wroblewski, L.B.; Raatikainen, H.S.; Lenox, S.R.; Gebhardt, K.E. Human and environmental toxicity of sodium lauryl sulfate (SLS): Evidence for safe use in household cleaning products. *Environ. Health Insights.* **2015**, *9*, 27–32. [[CrossRef](#)] [[PubMed](#)]
25. Miller, R.G.; Kopfler, F.C.; Kelty, K.C.; Stober, J.A.; Ulmer, N.S. The occurrence of aluminum in drinking water. *J. Am. Water Works Assoc.* **1984**, *76*, 84–91.
26. Taylor, K.M.; Weisskopf, M.; Shine, J. Human exposure to nitro musks and the evaluation of their potential toxicity: An overview. *Environ. Health* **2014**, *13*, 14. [[CrossRef](#)]
27. Liyanage, C.P.; Yamada, K. Impact of population growth on the water quality of natural water bodies. *Sustainability* **2017**, *9*, 1405.
28. Shabir, M.; Muhammad, Y.; Hussain, M.; Shafiq, I.; Parveen, A.; Nizami, A.S.; Jeon, B.H.; Park, Y.K. A review on recent advances in the treatment of dye-polluted wastewater. *J. Ind. Eng. Chem.* **2022**, *112*, 1–19. [[CrossRef](#)]
29. Song, G.; Qin, F.; Yu, J.; Tang, L.; Pang, Y.; Zhang, C.; Wang, J.; Deng, L. Tailoring biochar for persulfate-based environmental catalysis: Impact of biomass feedstocks. *J. Hazard. Mater.* **2021**, *424*, 127663. [[CrossRef](#)]
30. Gnanamoorthy, G.; Ramar, K.; Ali, D.; Yadav, V.K.; Jafar ahamed, A.; Kumar, G. Synthesis and effective performance of Photocatalytic and Antimicrobial activities of Bauhinia tomentosa Linn plants using of gold nanoparticles. *Opt. Mater.* **2022**, *123*, 111945. [[CrossRef](#)]
31. Moussa, D.T.; El-Naas, M.H.; Nasser, M.; Al-Marri, M.J. A comprehensive review of electrocoagulation for water treatment: Potentials and challenges. *J. Environ. Manag.* **2017**, *186*, 24–41. [[CrossRef](#)]
32. Zylka, R.; Dabrowski, W.; Gogina, E.; Yancen, O. Trickling filter for high efficiency treatment of dairy sewage. *J. Ecol. Eng.* **2018**, *19*, 269–275.
33. Han, B.; Kyu Kim, J.; Kim, Y.; Seung Choi, J.; Young Jeong, K. Operation of industrial-scale electron beam wastewater treatment plant. *Radiat. Phys. Chem.* **2012**, *81*, 1475–1478. [[CrossRef](#)]

34. Xiong, J.Q.; Cui, P.; Ru, S.; Kurade, M.B.; Patil, S.M.; Yadav, K.K.; Fallatah, A.M.; Cabral-Pinto, M.M.S.; Jeon, B.H. A comprehensive review on the effects of engineered nanoparticles on microalgal treatment of pollutants from wastewater. *J. Clean. Prod.* **2022**, *344*, 131121. [[CrossRef](#)]
35. Yuan, P.; Wang, J.; Pan, Y.; Shen, B.; Wu, C. Review of biochar for the management of contaminated soil: Preparation, application, and prospect. *Sci. Total Environ.* **2019**, *659*, 473–490. [[CrossRef](#)]
36. Gul, E.; Alrawashdeh, K.A.B.; Masek, O.; Skreiberg, Ø.; Corona, A.; Zampilli, M.; Wang, L.; Samaras, P.; Yang, Q.; Zhou, H.; et al. Production and use of biochar from lignin and lignin-rich residues (such as digestate and olive stones) for wastewater treatment. *J. Anal. Appl. Pyrolysis* **2021**, *158*, 105263.
37. Guo, F.; Jia, X.; Liang, S.; Zhou, N.; Chen, P.; Ruan, R. Development of biochar-based nanocatalysts for tar cracking/reforming during biomass pyrolysis and gasification. *Bioresour. Technol.* **2020**, *298*, 122263. [[CrossRef](#)]
38. Gan, Y.Y.; Ong, H.C.; Show, P.L.; Ling, T.C.; Chen, W.H.; Yu, K.L.; Abdullah, R. Torrefaction of microalgal biochar as potential coal fuel and application as bio-adsorbent. *Energy Convers. Manag.* **2018**, *165*, 152–162. [[CrossRef](#)]
39. Sbizzaro, M.; Sampaio, S.C.; dos Reis, R.R.; de Assis Beraldi, F.; Rosa, D.M.; de Freitas Maia, C.M.B.; de Carvalho, C.; do Nascimento, C.T.; da Silva, E.A.; Borba, C.E. Effect of production temperature in biochar properties from bamboo culm and its influences on atrazine adsorption from aqueous systems. *J. Mol. Liq.* **2021**, *343*, 117667.
40. Dai, Y.; Zhang, N.; Xing, C.; Cui, Q.; Sun, Q. The adsorption, regeneration and engineering applications of biochar for removal organic pollutants: A review. *Chemosphere* **2019**, *223*, 12–27. [[CrossRef](#)]
41. Zhou, X.; Zhu, Y.; Niu, Q.; Zeng, G.; Lai, C.; Liu, S.; Huang, D.; Qin, L.; Liu, X.; Li, B.; et al. New notion of biochar: A review on the mechanism of biochar applications in advanced oxidation processes. *Chem. Eng. J.* **2021**, *416*, 129027. [[CrossRef](#)]
42. To-Hung, T.; Zhang, L.; Zhang, J.; Dai, Y.; WahTong, Y. Methodological framework for wastewater treatment plants delivering expanded service: Economic tradeoffs and technological decisions. *Sci. Total Environ.* **2022**, *823*, 153616.
43. To-Hung, T.; Zhang, L.; Zhang, J.; Dai, Y.; WahTong, Y. Engineering interface between bioenergy recovery and biogas desulfurization: Sustainability interplays of biochar application. *Renew. Sust. Energy Rev.* **2022**, *157*, 112053.