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Progress of Technological Research on the Pharmaceutical Method in the Treatment of Fluoridated Wastewater

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Abstract

The treatment of fluorine-containing wastewater has been a hot topic in the field of water treatment, with the increasing emission standards, the current treatment of fluorine-containing wastewater has entered a policy and technology-driven phase, and the method of fluoride removal chemicals is simple and efficient in actual treatment, with significant advantages. This paper summarises the types and technological progress of fluoride removal agents in recent years, and puts forward the direction of future research and optimisation.

Keywords

Fluoride Removal Chemicals; Fluorinated Wastewater; Defluoridation.

1. Introduction

With the continuous development of social economy and human industry, the impact of human production and life on the environment is also increasing, the large-scale use of fluoride in industrial production, resulting in a large amount of fluoridated wastewater, fluorine is gradually enriched into the water environment, the need for proper treatment of fluoridated wastewater is becoming increasingly urgent. At present, the main agents for the treatment of fluoridated wastewater include chemical precipitation-type fluoride removal agents, coagulation precipitation-type fluoride removal agents, adsorption-type fluoride removal agents and compound-type fluoride removal agents, etc. Among them, the compound-type fluoride removal agents are free from the need to treat fluoridated wastewater[1]. Among them, the composite fluoride removal agent has got rid of all the limitations of single agent fluoride removal, and through the combination and matching of a variety of agents, it has been formulated into a high-efficiency fluoride removal agent, which can efficiently remove fluoride ions from wastewater, and it is a relatively novel and high development potential research field of fluoride removal technology at present.

2. Chemical Precipitation Type Fluoride Removal Agent

Chemical precipitation-type fluoride removal agents are mainly soluble calcium salts, including limestone, calcium chloride, calcium hydroxide and so on. The principle of chemical precipitation type fluoride remover is that calcium ions dissolved in water and fluoride ions undergo chemical precipitation reaction to produce CaF_2 precipitate, so that the fluoride ions in wastewater can be removed through solid-liquid separation. The reaction equation is as follows:

$$Ca^{2+}+2F^{-}=CaF_2 \quad (1)$$

The application process of chemical precipitation type fluoride removal agent is mature, with the advantages of convenient operation, convenient treatment, low cost, etc. However, a large amount of sludge will be produced, the sludge settles slowly, and it is difficult to dewater, resulting in extremely unstable effluent quality, and it is hard to meet the standard of the treated effluent, and the fluoride concentration of the effluent is not less than 20-30 mg/L,

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which is difficult to meet the discharge standard. At the same time, the surface of the agent is easily wrapped by the calcium fluoride generated by the reaction, resulting in the agent can not be fully utilised, resulting in the phenomenon of wastage of the agent. Therefore, in order to ensure the comprehensive economy, chemical precipitation type fluoride removal agent is usually used in the treatment of higher concentration of fluorine wastewater.

Peng et al. by exploring the various factors affecting the fluoride removal efficiency of chemical precipitation type fluoride removal agent, using the response surface analysis method to design the experimental scheme, to determine the optimal combination of parameters when the lime is added alone, in the lime dosage of 118%, the temperature of 62.25 ℃, the p H value of 8, can be reduced to the concentration of fluoride ions in the effluent water to 107.026 mg / L. At the same time, the establishment of the reaction model of the fluoride removal of lime, and found that the reaction model of fluoride in the At the same time, the reaction model of lime defluoridation was established, and it was found that the calcium fluoride precipitation generated by dissolved calcium ions and fluoride ions at room temperature and the small particles of dissolved lime could adsorb fluoride ions in the water, and the maximum adsorption capacity decreased with the increase of pH value when the pH was only greater than 10[2].

Chai et al. investigated the defluoridation process of high fluorine wastewater from nuclear fuel components by chemical precipitation type defluoridation chemicals, and determined that when lime is used alone for defluoridation, without controlling the reaction conditions, the dosage of 110% of the theoretical amount can make the defluoridation rate close to 90%, and based on the addition of 90% of the theoretical amount of calcium chloride, the wastewater can be up to the discharge standard. At the same time, it was clarified that when calcium hydroxide and calcium chloride are used together to remove fluorine, the wastewater can reach the discharge standard under the conditions that the dosage of calcium hydroxide is 110% of the theoretical amount, the dosage of calcium chloride is 95%, the dosage of aluminium sulphate is 600 mg/L, the temperature of the mixture is 50°C and the pH=8[3].

Feng et al. explored the influence of the type and dosage of chemical precipitation-type fluoride removing agent and the factors such as experimental pH, interfering ions and stirring speed on the experiments, and found that due to the solubility of calcium chloride is larger than that of calcium hydroxide, the fluoride removing effect of calcium chloride is better than that of calcium hydroxide during the experimental process. When controlling pH=10, stirring speed 400r/min, and calcium chloride was added according to the ratio of calcium to fluorine 1.5, the reaction was carried out for 40 minutes to reduce the fluoride ion concentration to 8.92mg/L, and the removal rate reached 98.51%[4].

3. Coagulation and Precipitation Type Fluoride Removal Agent

Coagulation and precipitation type fluoride removal agent is mainly some coagulants, commonly used coagulants can be divided into organic coagulants and inorganic coagulants, mainly including aluminium salt, iron salt and magnesium salt. Coagulation and precipitation type fluoride removal agents is the principle of aluminium, iron and magnesium salts and other coagulants dissolved in water, will hydrolyze to produce positively charged flocs, which can effectively adsorb negatively charged fluoride ions in the water to generate suspended particles or colloids, and then through the adsorption of bridging, net catching sweeping and other effects of rapid destabilisation, resulting in the formation of flocs with a larger size precipitation, and then the solid-liquid separation of fluoride ions in water to achieve the removal of the removal of the water.

Coagulation and precipitation type fluoride removal agent has the advantages of small dosage, high removal efficiency, simple dosage equipment, simple operation steps, large amount of treated water, etc. However, its fluoride removal effect is greatly affected by process conditions

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and water quality, and a large amount of sludge will be produced in the process of coagulation and precipitation, which will lead to the lack of stability of the effluent water quality, and further treatment is required to meet the discharge standards. In addition, due to the addition of a large number of metal salts, while removing fluoride ions, a large number of metal ions harmful to the body will be introduced, seriously affecting health, there is a need for secondary treatment.

Liu et al. investigated the efficacy of different properties of polymeric aluminium chloride in the process of fluoride removal, and studied the effects of alumina mass fraction, salinity, and the main coagulation parameters such as pH and aluminium morphology on the efficacy of fluoride removal, the results showed that the efficacy of fluoride removal varied greatly among different properties of polymeric aluminium chloride, and that the polymeric aluminium chloride with a higher mass fraction of alumina and salinity had a better effect of fluoride removal. At the dosage of 600-700 mg/L, the alumina mass fraction of 28%-35% and the salinity of 75%-89% of the polymeric alumina chloride could reduce the fluoride ion concentration in water to 1.28-1.40 mg/L. Compared with the alumina mass fraction, the salinity had a greater influence on the fluoride removal effect, and it was positively correlated with the removal of fluoride ions at the dosage of 100-900 mg/L. The study also showed that the removal efficacy of polymeric alumina chloride varied greatly among different properties. The study also showed that the suitable pH range of polymeric aluminium chloride coagulation for fluoride removal was between 6 and 8, in which the best effect was achieved around pH=7, and the percentage of polymeric aluminium state formed at this time reached 44.34%-55.26%, which was significantly and positively correlated with the fluoride ion removal rate[5].

Lu et al. investigated the mechanism of aluminium salt coagulation and precipitation type fluoride removal agent in the process of fluoride removal, and clarified that the main mechanisms of aluminium salt coagulation and precipitation type fluoride removal agent include adsorption, ion exchange, complexation and sedimentation, and netting and mechanical sweeping through the characterization tests of flocs such as ζ-potential measurement, X-ray powder diffraction, infrared spectroscopy and X-ray photoelectron spectroscopy, etc. The main mechanisms of aluminium salt coagulation and precipitation type fluoride removal agent are adsorption, ion exchange, complexation and sedimentation, and netting and mechanical sweeping. Comparing the two different forms of aluminium salts, aluminium chloride and polymeric aluminium chloride, the monomer $Al(H_2O)_6^{3+}$in aluminium chloride is better than the cationic form of polyhydroxyaluminium in polymeric aluminium chloride in the process and mechanism of fluoride removal, so aluminium chloride is better than polymeric aluminium chloride in the effect of fluoride removal[6].

Ma et al. investigated the fluoride removal efficiency of aluminium polysilicate as a coagulation and precipitation fluoride removal agent, and confirmed that the fluoride removal rate of aluminium polysilicate could reach 67.99% under the reaction conditions of pH=7, dosage of 4×10^{-4} mol/L, fast stirring rate of 260 r/min, fast stirring time of 2 min, slow stirring rate of 20 r/min, slow stirring time of 20 min, and precipitation time of 30 min. 67.99%, and the remaining fluorine concentration was 1.60 mg/L. Compared with aluminium sulphate and polymeric aluminium chloride, the fluorine removal effect of aluminium polysilicate was better than that of aluminium sulphate and polymeric aluminium chloride[7].

4. Adsorption-based Fluoride Removal Agents

Adsorption-type fluorine removal agents are mainly some adsorbents, including polymer adsorbents, natural mineral adsorbents, metal-based adsorbents, loaded adsorbents, rare earth-containing adsorbents and modified adsorbents, such as chitosan, diatomaceous earth, zeolites and modified zeolites, aluminium, iron and magnesium and other metals, oxides or hydroxides, hydroxyl lanthanum-modified resins and so on. The action mechanism of

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adsorption-type fluoride removal agent is mainly through the fluoride ions and adsorbent surface contact, with the help of its special pore structure and great specific surface area, through electrostatic action, complexation, ion exchange, etc. on the fluoride ion adsorption, so that the fluoride ions in the wastewater and its intermolecular force, so that the fluoride ions capture and adsorption on the surface of the adsorbent, and finally the solid-liquid separation process to remove fluoride ions from the wastewater. Finally, the solid-liquid separation process is used to remove the fluoride ions from the wastewater.

Adsorption-type fluoride removal agents have the advantages of reliable treatment effect, simple process operation, non-toxic and non-waste residue, strong ion selectivity, good removal effect, etc., and part of the adsorbent can be recycled through regeneration. However, the price of adsorbent is generally expensive and the regeneration process is cumbersome, and it is not suitable for large-scale industrial wastewater treatment, and in practical application, it is more suitable for fluoride removal from drinking water. Therefore, how to prepare the adsorbent with stable adsorption effect, simple regeneration and reuse, high economy and suitable for large-scale industrial wastewater fluoride removal needs to be further studied.

Zhao et al. prepared modified gangue by high temperature roasting of high silica and aluminium gangue loaded with zinc chloride, and investigated the adsorption kinetics and isothermal adsorption mechanism of fluoride, and the results showed that the activity of modified gangue was improved, the internal organic components were volatilised, and the pore and specific surface area increased, so that the adsorption capacity was greatly improved. Under the modified conditions of roasting temperature of 400°C, roasting time of 2h, and gangue:zinc chloride dosage ratio of 1:0.35, the removal rate of fluoride ions for fluoride-containing wastewater with a concentration of 10 mg/L reached 91.87%, and the adsorption capacity reached 91.87 mg/kg, and the adsorption process conformed to the quasi-secondary kinetic model and the Freundlich isothermal adsorption model[8].

Chen et al. used aluminium chloride hexahydrate and titanium trichloride to prepare Ti-Al hydrotalcites with different titanium-aluminium molar ratios as adsorbents, and explored their adsorption performance on fluoride ions in simulated wastewaters at low mass concentrations by controlling the dosage, initial solution pH and other factors. The results showed that the best fluoride ion adsorption performance of the prepared Ti-Al LDHs-1 was achieved when n(Ti):n(Al) = 2:8 and pH = 6. The fluoride ion adsorption capacity of Ti-Al LDHs-1 could reach 63.08 mg/g under the conditions of 0.1 g/L of Ti-Al LDHs-1, 25 ℃, and 200 r/min stirring speed for 12 h. The results showed that the fluoride ion adsorption capacity of the Ti-Al LDHs-1 could reach 63.08 mg/g. The results showed that the fluoride ion adsorption capacity of the Ti-Al LDHs-1 could reach 63.08 mg/g[9].

Shi et al. prepared MgO-10 with high crystallinity as the best loading material, and loaded La onto MgO-10 using isovolumetric impregnation method to prepare La/MgO adsorbent, and explored the adsorption performance of MgO adsorbent with different La loading through characterization and performance tests, which confirmed that the introduction of La improved the specific surface area of the material, and when the La loading reached 5%, its specific surface area reached 120.2 m2/g, the average pore size reached 27.92 nm, and the removal rate of fluoride reached 86.81%, which significantly enhanced the adsorption performance of MgO[10].

5. Complex Fluoride Removal Agents

Compound fluoride removal agent is a kind of efficient fluoride removal agent through the combination and matching of multiple agents, which can get rid of all the limitations of single agent fluoride removal, and can remove fluoride ions in fluoride wastewater efficiently, so as to achieve a more efficient, stable and economic fluoride removal effect, which is a relatively

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novel fluoride removal technology research field with high potential for development at present. Composite fluoride removal agents have achieved a breakthrough in fluoride removal efficiency due to the construction of a multi-component system and the combination of chemical precipitation, coagulation and adsorption, complexation and deposition and other multiple action mechanisms.

The performance advantages of the compound fluoride removal agent are closely related to its compounding system. Specifically, when the coagulant component is introduced into the compounding system, the agent shows the characteristics of coagulant such as easy process operation and large treatment scale; when the adsorbent component is introduced into the compounding system, it shows the advantages of adsorbent such as excellent ionic selectivity and stable and reliable treatment performance. In general, the compound fluoride removal chemicals have significant advantages in comprehensive performance through the synergistic effect of multiple components, which can meet the fluoride ion removal requirements under different water quality conditions and show broad application prospects in the field of fluoridated wastewater treatment.

Tang et al. optimized the composite defluorinating agents based on the coagulation and precipitation type of polymeric aluminium salts, and made the composite defluorinating agents according to the mass fractions of 70%-80% of polymeric aluminium chloride, 5%-10% of aluminium chloride hexahydrate, 5%-10% of aluminium sulphate, and 0.1%-1.0% of zinc sulphate. The results showed that within the above mass percentage range, the seven composite fluoride removers made according to different ratios could reduce the fluoride ion concentration in fluoridated wastewater from 10.6 mg/L to less than 1.0 mg/L when the dosage was 1400 mg/L[11].

Chen et al. studied the preparation of modified flocculant FCJZ-15 and its performance in the treatment of fluoridated wastewater, and found that the fluoride removal effect of this flocculant FCJZ-15 was not ideal when used alone, and better fluoride removal effect could be achieved when it was compounded with aluminium salt. The best effect was achieved by compounding the modified flocculant FCJZ-15: aluminium chloride hexahydrate = 16:9, and the fluoride removal effect of the modified flocculant FCJZ-15 was better than that of aluminium chloride hexahydrate when it was added first[12].

Jin et al. By studying a low-concentration coupled defluorinating agent and its preparation method, it was clarified that by polymeric aluminium iron sulfate 3-5%, magnesium oxide 2-4%, lanthanum nitrate 1-2%, cerium oxide-modified carbon nanotube complex 0.5-1.5%, Polyacrylamide 0.2-1%, calcium chloride 0.5-1.5%, hydrochloric acid 0.1-0.3%, the balance of the mass fraction of water produced by the composite fluoride removal agent, which has both adsorption, ion exchange, complexation and sedimentation of the three roles of fluoride ions have a very good removal effect, the fluoride ion can be controlled to the concentration of 2-6mg/L, while the treatment process produces a small amount of sludge, greatly reducing the Solid waste treatment costs, has a high degree of economy[13].

Shang et al. explored a new type of in-depth fluoride removal agent, and found that the composite fluoride removal agent made by the mass fraction of polymeric aluminium chloride 40%, polymeric aluminium sulphate 25%, polymeric ferric sulphate 16%, activated alumina 12%, coagulant booster 3%, carbon-based apatite 2.9%, calcium fluoride 1%, and nano iron 0.1%, which was used to treat the wastewater containing fluorine with low concentration, could reach more than 98% removal rate of fluoride ions by stirring and reacting for 15 minutes. When treating low concentration fluorine wastewater, the removal rate of fluoride ions can reach more than 98% in 15 minutes of stirring reaction, which has a good effect of fluoride removal at the same time of fast fluoride removal[14].

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6. Conclusion

In recent years, the production of fluoridated wastewater has continued to rise, and the restrictions on fluoride in environmental emission standards have become increasingly stringent. Although new fluoridated wastewater treatment technologies, such as membrane separation and electrochemical methods, are emerging, the fluoride removal agent method is still the most simple, efficient, economical and reliable way to remove fluoride in practical applications. However, practice has shown that there are significant limitations of a single agent system: chemical precipitation calcium-based fluoride removal agents are low-cost, but it is difficult to achieve a stable fluoride concentration in the effluent; coagulation and precipitation aluminium salts fluoride removal agents have rapid coagulation characteristics, but there are defects such as a large sludge production. Based on this, the development and research of multi-component composite fluoride removal agents with synergistic fluoride removal efficacy has become a hotspot in current research. In the future, by compounding multiple agents to build a multi-component system, and combining chemical precipitation, coagulation and adsorption, complexation and sedimentation and other multiple mechanisms, the development of cost-effective and efficient composite fluoride removal agents has great prospects for development.

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