Investigate the Possibility of Solid Waste Removing Fluoride Ions from Water

Luyi Wen

School of Resources and Environmental Engineering, Hefei University of Technology, Xuancheng, 242000, China

2022218628@mail.hfut.edu.cn

Abstract. With industrial development and the increase of human activities, the content of fluoride ions in water bodies is constantly rising, resulting in serious human health risks and environmental ecological pollution. Traditional methods for removing fluoride ions are usually costly and energy-intensive, making it difficult to apply them on a large scale. Therefore, finding low-cost, efficient, and environmentally friendly methods for removing fluoride ions has become one of the research focuses of various countries. However, due to their wide range of sources, low prices, and some unique pore structures and surface chemical properties, solid wastes can effectively adsorb fluoride ions. In order to explore the ability of solid waste to remove fluoride ions from water, this paper concludes that modified solid waste has a high fluoride ion removal rate under certain conditions, and also exhibits good reusability and stability. This paper not only provides a new way of thinking for the treatment of fluoride ion pollution but also achieves the secondary use of solid waste resources, which has good environmental and economic benefits.

Keywords: Fluoride ions, solid waste, adsorption, modified treatment.

1. Introduction

Fluoride ions are a common pollutant in natural water bodies. Sources include geological activity, industrial emissions and agricultural fertilisation. Fluorine is one of the essential trace elements for the human body, and an appropriate intake of fluorine is beneficial to human health. However, an excessive intake of fluorine can hurt human health and harm various organs and systems in the body [1]. In addition, the transfer of fluoride to soil, water bodies, and the atmosphere can pose a certain threat to the ecosystem, and once it enters the food chain, it can harm animals and plants [2]. Therefore, choosing a reasonable way to remove excess fluoride ions from water is of great significance for safeguarding public health and protecting the ecological environment.

Traditional methods of fluoride removal include chemical precipitation, adsorption, ion exchange, and electrocoagulation [3-6]. However, these methods have disadvantages such as high cost, limited treatment efficiency, and complex operation, so they are lacking in terms of economy and practicality. In recent years, the application of solid waste in water treatment has gradually attracted attention, especially in the removal of fluoride ions. Solid waste materials show great application potential due to their abundance, low cost, and porous structure. The use of solid waste to remove fluoride ions not only helps solve the problem of water fluorine pollution but also achieves the resource utilization of solid waste, which is in line with the concept of green and sustainable development. There are many types of solid waste, including industrial by-products, agricultural residues and waste materials. These materials often have good adsorption properties after appropriate modification or activation, and can effectively remove fluoride ions from water. Therefore, exploring the possibility of using solid waste to remove fluoride ions from water not only expands the ways to reuse solid waste but also provides new ideas for developing efficient and low-cost fluoride removal materials.

The purpose of this study is to explore the feasibility of using solid waste to remove fluoride from water by summarising and analysing existing relevant research results. After weighing the relevant properties, a suitable solid waste for adsorption research is identified, and the principle of the steps to improve the adsorption performance by modifying methods such as the synthetic zeolite method, salt fusion method, and thermal activation method is explained and analysed, the advantages and disadvantages are explained, and a theoretical basis and technical support for future fluoride removal technology is provided. This not only has a positive significance for the treatment of fluorine pollution but also promotes the green recycling of solid waste.

2. Fluorine Pollution

Fluorine pollution refers to the phenomenon in which fluorides (mainly including HF, NaF, CaF_2, etc.) enter the environment through various pathways, thereby negatively affecting ecosystems and human health. The industry is the main source of fluorine pollution, especially in the fields of metallurgy, aluminium electrolysis, glass, ceramics, chemical fertilisers, and the chemical industry. These industries produce a large amount of fluorine-containing gases and wastewater during the production process, which can cause pollution if discharged directly into the atmosphere or water bodies without treatment. Coal combustion is also a major source of fluorine pollution. Coal contains a certain amount of fluorine, which is released into the air during combustion. This is particularly the case in high-fluorine coal areas, where the long-term burning of coal with a high fluorine content can lead to increased fluorine pollution of the local air and soil. Fluorine pollution can also result from the use of pesticides and chemical fertilisers. Fluorine-containing compounds are widely used in pesticides and herbicides, and their long-term use can cause fluorine to enter the soil and groundwater, threatening the agricultural ecosystem and crop safety.

Fluorine pollution currently has a serious impact worldwide, especially in areas with developed industries and frequent coal combustion. China is one of the countries in the world most affected by fluorine pollution, especially in the coal-fired and industrial-intensive regions of the southwest and northwest. The concentration of fluoride in the air in these areas exceeds the standard, and fluoride accumulates in the soil and water bodies, posing a threat to residents and the ecosystem. For other countries in the world, the high fluoride content of groundwater due to geological processes poses a threat to the health of local residents if they drink water with too high a fluoride content for a long time, and improper treatment of industrial wastewater and waste gas also leads to fluorine pollution.

The impact of fluoride on human health is significant. As fluoride is a highly biotoxic element, long-term exposure to high fluoride environments can cause health problems such as fluorosis, dental fluorosis, damage to the nervous system and immune systems, and delayed intellectual development in children. Not only that, but fluoride can also have a number of impacts on the ecological environment. For example, fluoride can damage plant chloroplasts, inhibit the synthesis and decomposition of chlorophyll, and affect photosynthesis, causing plants to weaken or even die. Fluoride can also change the chemical properties of water bodies, affect the solubility of various ions, inhibit the reproductive capacity of aquatic organisms at certain concentrations, reduce the number of organisms, and threaten the stability of the ecosystem. Fluoride can inhibit the activity of soil microorganisms, affect their reproduction and growth, and disrupt the biological balance of the soil, which in turn affects the nutrient cycle of the soil [7].

3. Application of Solid Waste Adsorption of Fluoride Ions

3.1. Concept and Classification

Solid waste refers to materials that have lost their original use value or have been discarded during production, living, and other activities, and that are in solid, semi-solid, or gaseous form in containers, as well as materials that are regulated by laws and administrative regulations and are managed as solid waste. Countries classify solid waste from different perspectives and levels, and the classification methods and types are not consistent. At this stage, the most widely recognised classification method is based on the source, characteristics, form, size, and value of solid waste. The recycling of solid waste refers to the recovery and reprocessing of waste that has already been generated so that it can be used again. This process not only saves resources and reduces environmental pollution, but also promotes the development of a green economy.

3.2. Physico-Chemical Properties of Solid Waste

The adsorption capacity of some solid wastes is determined by their physicochemical properties.

3.2.1. Physical Adsorption

Physisorption is a phenomenon in which gas or liquid molecules and saturated molecules adsorb on the surface of a solid. It mainly relies on the relatively weak physical force of van der Waals' forces between molecules to adsorb molecules and capture them on the surface of the solid [8]. The advantages of physical adsorption are reflected in many aspects. For example, because van der Waals forces are weak interactions, the physical adsorption process is highly reversible, which is conducive to the repeated use of materials. Moreover, physical adsorption does not involve the breaking and forming of chemical bonds, so the process has low energy consumption, which is conducive to industrial energy conservation. Not only that, the physical adsorption process often occurs at the molecular level, with fast adsorption rates and rapid responses. More importantly, physical adsorption applies to a wide range of materials and can be described and quantified using models such as Langmuir and BET, which facilitates analysis and generalisation. However, physical adsorption also has some obvious limitations, such as weak adsorption capacity due to weak forces, and poor selectivity due to the influence of surface structure and physical properties. The adsorption capacity is limited by the surface area and pore structure of the material, and the adsorption effect is easily affected by the environment, and regeneration costs are high. Certain solid wastes, such as coal gangue and fly ash from industrial solid waste, and straw and rice husks from agricultural solid waste, have a certain physical adsorption capacity due to their porous structure and large specific surface area.

3.2.2. Chemisorption

Chemisorption is a process of adsorption involving the chemical bonding of molecules or atoms to a solid surface. This type of adsorption differs from physisorption in that it involves a strong chemical reaction [9]. Chemisorption is a strong form of adsorption because it involves the formation of chemical bonds. Moreover, only molecules or atoms that can react with the surface are effectively adsorbed, which makes chemisorption highly selective. Chemisorption also forms bonds with reactants and promotes their decomposition or transformation, improving reaction catalysis. Similar to physical adsorption, chemical adsorption can also be analysed in detail using various theoretical models, providing data support for further research. However, chemical adsorption, which achieves adsorption by forming chemical bonds, is also irreversible, which reduces its applicability in recycling applications. Moreover, chemical adsorption is sensitive to temperature and the environment, and achieving the desired adsorption effect is more costly. The presence of side reactions also makes chemical adsorption difficult to control, and greater care must be taken during the reaction process. A small number of solid wastes containing a variety of metal oxides, can chemically bind with fluoride ions to form relatively stable metal complexes, such as coal gangue. For another part of solid waste, the substances contained can form precipitates with fluoride ions and be stably precipitated, such as waste tiles and gypsum.

After considering the physicochemical properties, environmental hazard level, production volume and treatment cost of various solid wastes, it can be found that gangue, straw and waste tiles can all be used for the adsorption treatment of solid wastes. However, it is not environmentally friendly or efficient to directly use solid waste materials for the adsorption of fluoride ions. Therefore, solid waste should be modified and processed before being used in the adsorption process.

4. Modified Methods of Solid Waste Disposal

Modification generally refers to the treatment or modification of a substance or material to change its properties or characteristics [10]. In the treatment of fluorine-containing wastewater, modified solid waste can be used as an adsorbent, precipitant, and composite material to improve the removal rate of fluoride ions. Modification not only improves material properties and processability but also enhances the functionality and optimises cost-effectiveness. The following describes several methods for treating fluorine-containing wastewater using modified processed solid waste.

4.1. Novel Modification Methods

Hydrothermal synthesis is a method for synthesising inorganic materials under high temperature and pressure conditions using water or an aqueous solution as the reaction medium. It is generally carried out in a sealed high-pressure reactor. By adjusting the temperature and pressure, the dissolution and recrystallisation during the reaction can be controlled, so that specific compounds or materials can be crystallised at lower temperatures [11]. Hydrothermal synthesis is a method for preparing zeolites using modified solid waste. The selected solid waste, such as coal gangue, is mixed with a certain concentration of alkali solution. By controlling the reaction parameters and aging for some time, the mixture is transferred to a stainless steel autoclave for high-pressure reaction to obtain different types of zeolite molecular sieves. The process, shown in Fig. 1, involves three steps: dissolving Si^{4+} and Al^{3+} in the raw materials; polymerisation of the silicon and aluminium sources to form a gel; and crystallisation of the gel under appropriate conditions to obtain zeolite crystals. Type X, P and hydroxy zeolite can be obtained by adjusting the reaction conditions through the pretreatment of crushing, grinding, calcining and acid leaching of raw materials, followed by hydrothermal reaction. The traditional hydrothermal synthesis method is simple and easy to operate, but the synthetic product has low crystallinity and many impurities, and the particle size of the product is affected by the particles of solid waste.

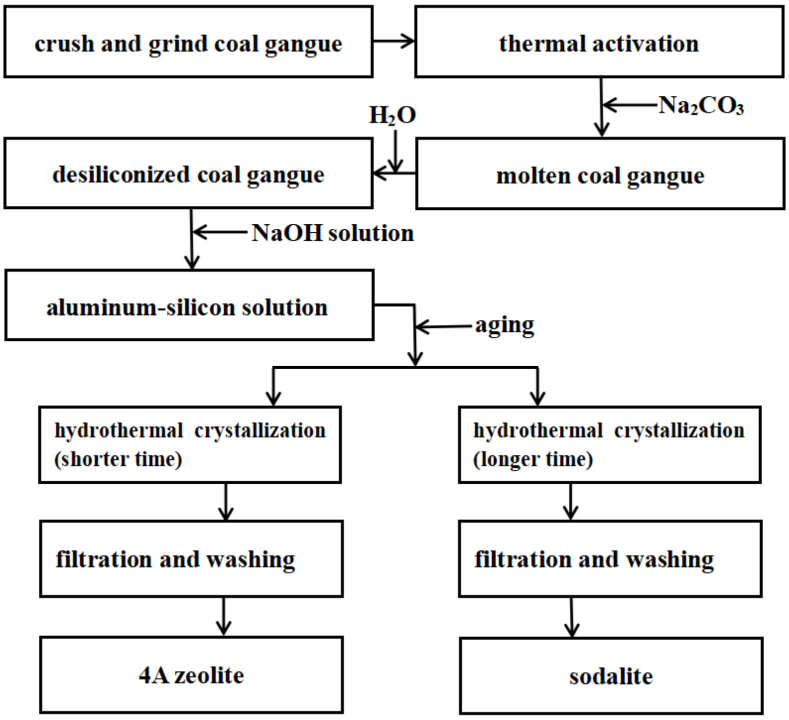

Fig. 1 Zeolite preparation process [12]

The salt fusion method is a high-temperature chemical reaction technology that uses molten salt as a reaction medium to cause raw materials to react at relatively low temperatures to prepare the target material. The salt fusion method has good thermal conductivity and stability. Molten salt can provide a uniform reaction environment for reactants and reduce the reaction temperature to increase the reaction rate [13]. Compared to the traditional hydrothermal synthesis method, which requires water as a reaction reagent, the salt fusion method replaces the hydrothermal method with water as the medium and instead uses a mixture of sodium hydroxide and sodium nitrate as the reaction medium. Among them, NaOH not only acts as a filler for the zeolite, but also affects the surface bonds of the split compound; while $NaNO_3$ can not only be used as a solvent to replace the water in the hydrothermal method, but also stabilize the porous structure of the zeolite. However, the ion exchange capacity of zeolites synthesized using the salt fusion method is relatively low, which places certain limitations on practical production.

The adsorption of fluoride ions in fluorine-containing wastewater by the zeolite prepared by the above two methods is very significant. The results of the change in the amount of fluoride ions adsorbed in water over time are shown in Fig. 2:

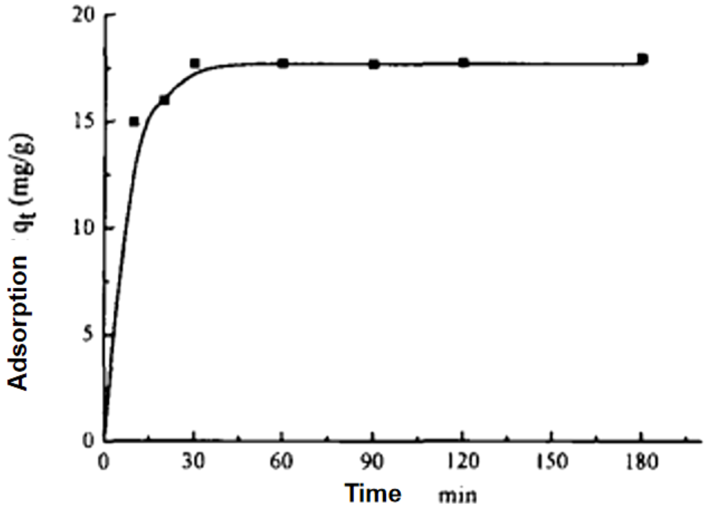

Fig. 2 Relationship between the amount of fluoride ions adsorbed by zeolite and time in water [12]

After the researchers used the Langmuir and Freundlich adsorption isotherm models to fit the experimental results of synthetic zeolite adsorbing F^- according to the isothermal equation, the linear fitting effect is shown in Fig. 3. It can be seen that the linear isothermal adsorption of synthetic zeolite adsorbing fluorine-containing solutions is more in line with the Freundlich isothermal adsorption model. After calculation, 1/n in the Freundlich model is 0.6916, which is less than 1, indicating that the adsorption of F^- on synthetic zeolite is a multi-molecular layer adsorption process and that the adsorption process is prone to occur.

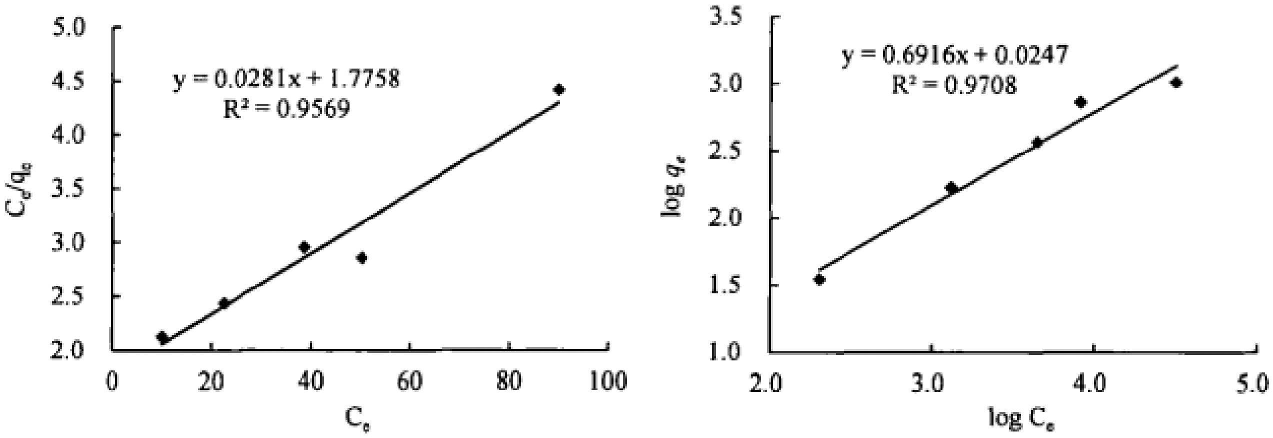

Fig. 3 Fitting results of the Langmuir and Freundlich isotherm adsorption models for synthetic zeolite adsorption and fluoride removal [12]

4.2. Traditional Modification Methods

There are various traditional modification methods, but relatively few of them are suitable for solid waste modification, including acid-base modification, thermal activation modification, organic modification, and biological modification. Among them, acid-base modification and thermal activation modification are the two most commonly used modification methods.

Acid-base modification refers to the process of improving the catalytic, adsorption, or other properties of a material by adjusting its surface acidity or alkalinity. This technology is widely used in fields such as chemistry, materials science, and environmental engineering. The surface acidity or alkalinity is mainly changed by introducing acidic or basic groups on the surface of the material, or by doping, impregnation, ion exchange and other methods. According to different modification methods, different surface pH values can be obtained, which affect the reactivity, adsorption capacity and selectivity of the material [14]. This method is widely used in waste modification, which can effectively remove surface impurities, improve the purity of the internal active ingredients, change the surface properties and enhance the adsorption activity. However, the modification process produces waste water and waste gas, introduces new harmful substances, poses potential environmental pollution risks and increases the cost of subsequent secondary removal.

Thermal activation modification is a method of improving the properties of materials or waste through heat treatment. This process mainly relies on the action of heat to change the physical and chemical properties of materials in order to improve their application value and performance [15]. Thermal activation modification can effectively improve the void structure and specific surface area of solid waste to enhance its adsorption capacity and chemical activity. However, the internal structure of some solid waste may be damaged during high-temperature treatment, affecting its adsorption performance, and the cost of modification is relatively high. For some solid wastes that can be used to adsorb fluoride ions, such as coal gangue and fly ash, the iron-based and aluminum-based oxides inside them account for a relatively high proportion and are key substances for adsorbing fluoride ions. Thermal activation can greatly enhance their adsorption performance, so it is a more ideal modification method for these types of solid waste.

5. Future Development Trends

The future development of the reuse of solid waste to remove excess fluoride ions from water is promising. Future research and applications may be further developed in many ways. The original solid waste often has problems such as insufficient adsorption capacity and low selectivity. In the future, the adsorption performance of solid waste may be improved by improving existing physical, chemical, or biological modification methods. For example, combining solid waste with metal oxides, magnetic materials, and nanomaterials can significantly enhance the adsorption capacity and regeneration performance of fluoride ions. In addition, functional surface treatment can also improve the selective adsorption of solid waste.

In the future, the application of nanotechnology may also have a positive impact on the removal of fluoride ions in water. Due to their large specific surface area and unique physicochemical properties, nanomaterials can adsorb fluoride ions to a certain extent. If they are further combined with solid waste for fluoride ion removal, not only can the adsorption efficiency be improved, but the reusability and stability of the material can also be optimised.

Sustainable treatment technology will also gradually develop over time. With the increasing demand for environmentally friendly technologies, greener and more efficient treatment methods will definitely be developed in the future for fluoride ion removal. Today's chemical modifications all use some chemicals, which may cause pollution to a certain extent. Future research will continue to explore how to reduce the use of chemicals in the modification process while ensuring the removal effect, so as to reduce secondary pollution to the environment.

Cost and large-scale applications are also one of the development directions. An important development direction for solid waste utilization and fluoride ion treatment technology is to reduce costs and improve economic efficiency. Future research may focus more on how to apply it on a large scale, develop low-cost production processes, and optimize the utilization efficiency of waste resources. In addition, policy support and increased social awareness of environmentally friendly technologies will also promote the widespread use of these technologies in industrial fluoride wastewater and rural drinking water treatment.

6. Conclusion

The harm caused by excess fluoride ions in water to the human body and the environment is very significant, so removing fluoride ions is already a cutting-edge research area that is of great significance for environmental protection and human health. After introducing the harm caused by excess fluoride ions in water and some existing treatment methods, this paper further refers to existing research results to analyse the physicochemical properties of solid waste and screen out solid waste with better fluoride ion removal capacity. It also reviews the impact of emerging and traditional modification methods on the adsorption properties of solid waste and finds that they can significantly improve the adsorption capacity of fluoride ions in fluoride-containing wastewater. It is proved that the use of solid waste to remove fluoride ions in water is a feasible method. This research can provide new methods for the removal of fluoride ions in water and new ideas for the treatment and disposal of micro-solid waste. For future development, researchers will focus on solving the steps in the modified treatment process of solid waste and finding and optimising modification methods. They will continue to innovate and optimise around the goals of high efficiency, low cost and sustainability to help achieve the dual benefits of environmental protection and resource recycling.

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