Removal of arsine by metal loaded γ-Al_2O_3 adsorbents

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Abstract. The modified γ-Al_2O_3 adsorbents were prepared by impregnation method has been studied for arsine (AsH_3) removal efficiency. The results show that γ-Al_2O_3 modified with $Cu(CH_3COO)_2$ (denoted as Cu/Al_2O_3) is found to have markedly enhanced adsorption purification ability. In the adsorption purification process, the Cu^{2+} impregnation concentration and calcination temperature are determined to be two crucial factors. The best breakthrough capacity was 28.9 mg AsH_3/g Cu/Al_2O_3 sorbent , which was prepared by calcining at 350ºC and the impregnation concentration of $Cu(CH_3COO)_2$ was 0.15mol/L. According to the current study results, the γ-Al_2O_3 impregnated with $Cu(CH_3COO)_2$ promises a good candidate for AsH_3 adsorbent.

Introduction

Arsine (AsH_3) is a hydrophobic, very volatile and highly poisonous gas, which can enter the body through the skin, respiratory tract or the digestive tract. Therefore, AsH_3 can easily induce several environmental hazards and serious health problems, including lung, respiratory tract, bronchus, kidney serious damage and even cancer [1]. AsH_3 is released to the air commonly arises from various sources, such as, the processes of arsenic-containing metals react with acids, the processes of coal gasification, yellow phosphorus tail gas, the burning of fossil fuels at high temperature, and so on[2-7]. Thus, removal of AsH_3 has a profound significance. At present, several treatment technologies for AsH_3 removal have been reported, including chemical absorption, catalytic decomposition, combustion, adsorption, etc. But catalytic decomposition and combustion are typically employed at high temperatures. Adsorption is one of the most mature and promising methods, because of its ease of operation, flexible design, employed at low temperatures and low-cost, and is more appropriate for the removal of low concentrations of AsH_3. Adsorption technology was chosen to accomplish the required contaminant removal. Although numerous materials have been reported as sorbents for effective removal of AsH_3, high operating temperatures are typically required [8-11]. For instance, S. Poulston et al. reported that Pd can be used to modify Al_2O_3 for the sorption of AsH_3 from simulated flue gas at temperatures of 204 ºC and 288 ºC [12]. M. Jiang et al. found that activated carbon modified with sulfonated cobalt phthalocyanine (CoPcS) and $Cu(NO_3)_2$ was able to adsorb AsH_3 efficiently [13]. But some shortcomings with present activated carbons have been identified, including thermal instability. In this work, a series of γ-Al_2O_3 loaded by different metal salts solutions has been prepared, and these systems show promise as AsH_3 sorbents operating at lower temperatures. Herein, sorbents were prepared by an impregnation method and the effects of impregnation concentration and calcinations temperature have been explored.

Materials and methods

Preparation of sorbents

All adsorbents have been prepared by impregnation method. Commercial γ-Al_2O_3 (99.99%, Nankai University Catalyst Co., Ltd., Tianjin, China) was used as support materials in the experiments. $Cu(CH_3COO)_2 \cdot H_2O$, $Zn(CH_3COO)_2 \cdot 2H_2O$ and $Pb(CH_3COO)_2 \cdot 2H_2O$ were used as impregnates in order to improve the adsorption performance of γ-Al_2O_3. The supports (10 g ± 0.1 g) were washed three times with 150 mL of distilled water at 70 ºC to remove soluble impurities，dried at 105 ºC for 12 h. Then the γ-Al_2O_3 was impregnated with $Cu(CH_3COO)_2 \cdot H_2O$ (0.1 mol/L, 50ml), $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.1 mol/L, 50ml), and $Pb(CH_3COO)_2 \cdot 2H_2O$ (0.1 mol/L, 50ml) at ambient temperature, respectively. The impregnation was stirred for 24 h, after that, the impregnation was filtrated and the adsorbent was dried for 12 h at 110 ºC, followed by calcination at the temperature of experiment designed for 6 h in a muffle furnace. Finally, samples modified with different metals were denoted as Cu/Al_2O_3, Zn/Al_2O_3 and Pb/Al_2O_3, respectively.

AsH_3 adsorption experiment

The AsH_3 adsorption tests were carried out in a fixed-bed quartz tube with 9 mm inner diameter and 60 mm in length under atmospheric pressure. The model gas flow was composed of 70ppm AsH_3 in N_2, which were mixed in a mixer with O_2 (99.999 % O_2) and introduced into the adsorption bed unit under the flow rate of 200 ml/min at 60 ºC. A total of 0.5 g of adsorbents was packed into the reactor for each test, and the experiment was stopped when the absorbent was saturated. AsH_3 concentration was measured by silver diethyl dithiocarbamate spectrophotometric method. In order to avoid safety problems, AsH_3 was absorbed readily in potassium permanganate. The ‘‘breakthrough time’’ is defined as the point at which the AsH_3 outlet concentration reaches 5 % of the inlet concentration according to breakthrough curves. After the end of the experiment, the AsH_3 adsorption capacity was calculated with the corresponding integral according to formula (1) under various conditions of the breakthrough curves [14].

$$X = (Qc_0 t - Q\int_0^t c dt) / m \tag{1}$$

Where X is the adsorption capacity in mg/g, m is mass of adsorption in g, Q denotes the flow rate in m^3/min, C_0 and C represent the initial and outlet concentration of AsH_3 in test times in mg/m^3, and t represent the test time in min, respectively, of the breakthrough curves.

Results and discussions

Effects of the types of modifiers

In this work, three metal precursors including $Cu(CH_3COO)_2 \cdot H_2O$, $Zn(CH_3COO)_2 \cdot 2H_2O$ and $Pb(CH_3COO)_2 \cdot 2H_2O$, with a concentration of 0.1 mol/L, were evaluated for their AsH_3 adsorption capacities on the Al_2O_3 adsorbents. The breakthrough curves of those adsorbents are plotted in Fig. 1, in which they seem to exhibit different AsH_3 adsorbing behaviors and clearly illustrate the efficiency of the treatment for the AsH_3 removal. One can see that the AsH_3 removal efficiency for the Cu-loaded Al_2O_3 adsorbent was much higher than those of Zn and Pb-loaded Al_2O_3. Therefore, Cu was chosen as the metal species for later study. The impregnation of $Cu(CH_3COO)_2$ led to increases in breakthrough time as well as AsH_3 breakthrough capacities which were 3.4, 9.1, 12.2, 24.3 mg AsH_3/g γ-Al_2O_3, Cu/Al_2O_3, Zn/Al_2O_3, Pb/Al_2O_3, respectively. The founding of above suggested that the improvement in the AsH_3 capacity is attributed to the active groups formed after the introduction of $Cu(CH_3COO)_2$ [15]. The Cu/Al_2O_3 adsorbent has better adsorption effect is because $Cu(CH_3COO)_2$ can get even distribution in the surface of γ-Al_2O_3 using developed pore

structure and large specific surface area. In addition to physical absorption, also occurred chemical adsorption process strongly.

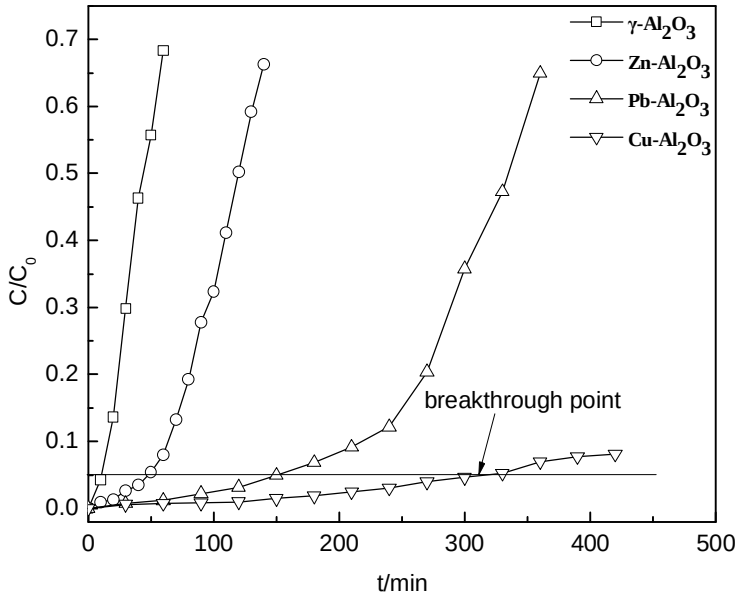

Fig.1. AsH_3 breakthrough curves on different sorbents (AsH_3 inlet concentration is 200 mg/m^3, calcination temperature is 350ºC, impregnation concentration is 0.1 mol/L).

Effects of Cu^{2+} impregnation concentration

The active component concentration in the process of preparing adsorbent is one of the important factors that affect adsorption effect. The relationship between the activity of adsorbing AsH_3 and the impregnation concentration of Cu^{2+} in this adsorbents was investigated, as shown in Fig 2. As seen, the AsH_3 removal efficiency initially increased and then decreased with the impregnation concentration of Cu^{2+} increasing, and the best impregnation concentration of Cu^{2+} was 0.15mol/L. The absorbents modified by different impregnation concentration of Cu^{2+} could enhance the adsorption activity of AsH_3 compared to fresh Al_2O_3 regardless of the Cu^{2+} impregnation concentration. The concentration of Cu^{2+} was low so cannot provide sufficient reaction active center. However, if the impregnation concentration of Cu^{2+} was above 0.15mol/L, Cu surface loading will occupy adsorption sites of the Al_2O_3 interface, and the adsorption efficiency cannot be enhanced. Thus, the surface adsorption sites or active sites of Al_2O_3 would be excessively overlapped when the Cu^{2+} concentration exceeds 0.15mol/L. Meanwhile, the microspores on the surface of Al_2O_3 could be blocked by the excessive metal oxide. The optimum Cu^{2+} impregnation concentration is 0.15mol/L for Cu/Al_2O_3 adsorbent.

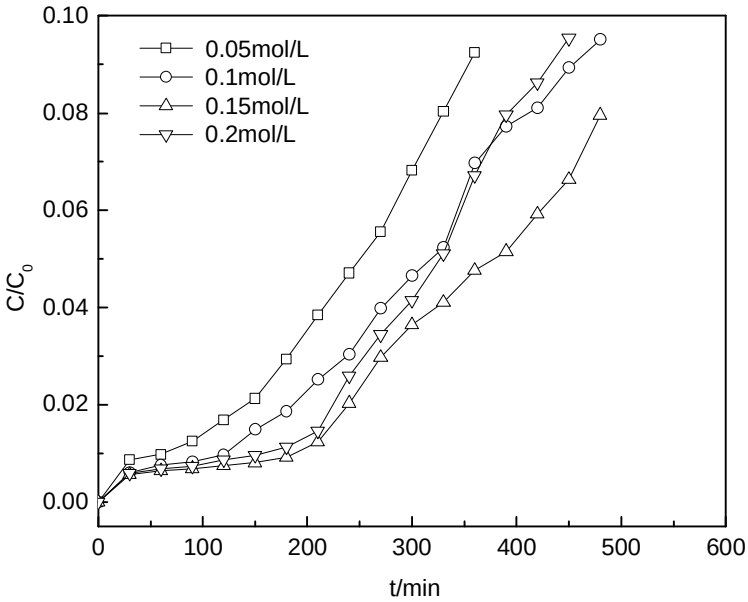

Fig.2. AsH_3 breakthrough curves on different concentration of $Cu(CH_3COO)_2$ loading Al_2O_3 (AsH_3 inlet concentration is 200mg/m^3, calcination temperature is 350ºC).

Effects of calcination temperature

The calcination temperature in the Cu/Al_2O_3 adsorbent preparation processes is one of the most important factors influencing the AsH_3 removal efficiency and adsorption capacity. The calcination temperature has a great effect on the activation, grain distribution, and formation of the absorbents [16-17]. The calcination temperature can influence the decomposition of metal salts and relate to the redistribution and aggregation of products on the Al_2O_3 surface. Fig. 3 shows the effect of calcination temperature on the AsH_3 removal efficiency of the absorbents. It can be seen that the breakthrough time for the sample calcined at 350ºC (Cu/Al_2O_3) was 380 min, longer than those of the samples calcined at 0, 250, or 450ºC. The calcinations temperature can affect the surface oxidation of transition metals. At low temperature (below 300°C in this work), it is not enough to make the active component surface changes and difficulty in forming the active group of effective. However, it may lead to sintering of active ingredient, adsorbent particles aggregation when temperature is high. In addition, it may destroy the pore and pore structure of Al_2O_3 which result in reducing the specific surface area and further affect adsorptive properties of modified Al_2O_3. Accordingly, the most appropriate calcination temperature is 350°C.

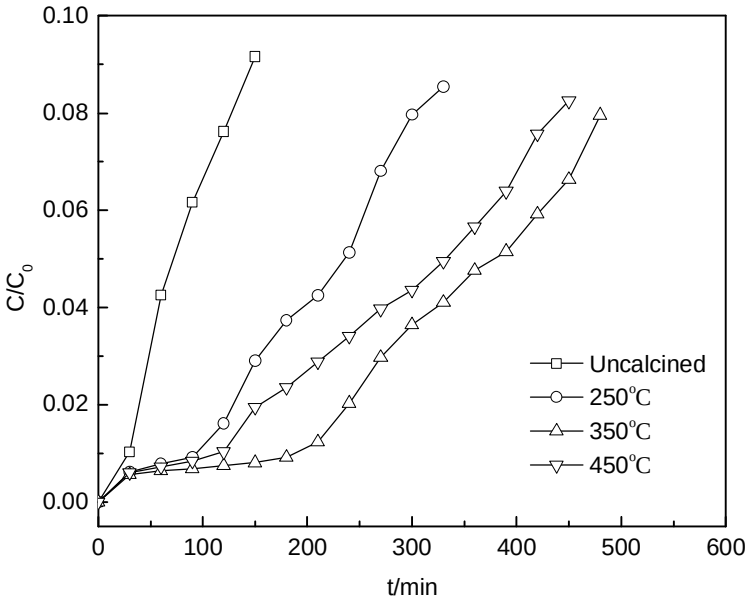

Fig.3. AsH_3 breakthrough curves on different calcination temperature (AsH_3 inlet concentration is 200 mg/m^3, impregnation concentration is 0.15 mol/L).

Conclusion

(1) For AsH_3 adsorption studies, four kinds of Al_2O_3 absorbents have been prepared and tested for AsH_3 removal. Breakthrough experiments have indicated that the Cu/Al_2O_3 is the most promising sorbent for AsH_3 removal.

(2) The Cu^{2+} impregnation concentration and calcination temperature play important roles in the AsH_3 removal by Cu/Al_2O_3. The results indicate that the best breakthrough capacity was 28.9 mg AsH_3/g Cu/Al_2O_3 sorbent, which was prepared by calcining at 350ºC and the impregnation concentration of $Cu(CH_3COO)_2$ was 0.15mol/L.

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Research Status and Prospect Of Micro-polluted Water Pretreatment With Biological Aerated Filter

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Abstract. Recently, with the rapid development of industry, the pollution of organic compounds and ammonia nitrogen is serious in source water. It is difficult to ensure the removal efficiency of ammonia nitrogen and organic compounds in effluent by conventional treatment technology. The article brings out the treatment of micro-polluted water by biological aerated filter. This article discuss the pre-treatment of micro-polluted water with biological aerated filter from following aspects:the principle of micro-polluted water's treatment by BAF, the advantages of pollutant removal ,and influencing factors of stable operation of BAF .In the end, this article introduces the practical application of the pre-treatment of micro-polluted water by biological aerated filter, and makes prospects for its development and application.

Introduction

In recent years, with the rapid development of industry, accelerated urbanization process and sharp increase in the use of agricultural chemicals, drinking water were polluted in different degree. Many rivers, groundwater and other water sources lose the function of being drinking water. But in the situation of shortage of water resources, micro-polluted water is still an important source of water. The species and quantity of organic compounds surge. And the phenomenon of eutrophication is aggravated. With the progress of science and technology, technology of analysis of water quality and the national drinking water standards is improving. The removal efficiency of dissolved organic compounds, ammonia nitrogen, iron and manganese is not ideal by using conventional water treatment. Addition of chemical reagents is easy to produce by-products. Aiming to solve this phenomenon, many scholars studied biological pre-treatment of micro-polluted water. With the help of the metabolism of the microbial population, the biological pre-treatment remove organic compounds, ammonia nitrogen, iron, manganese and other pollutants, and achieved considerable results. The removal rate of ammonia nitrogen reached more than 80%. And turbidity, chroma, iron, manganese and other pollutants are better removed [1].

The principle of micro-polluted water's treatment by BAF

The treatment medium of biological aerated filter is mainly the filter material of the reactor and the biofilm attached to the filter material. Pollutants were removed mainly through the filtration, adsorption and retention of filter material and biofilm, as well as the oxidation and decomposition of microorganism on biofilm. When the raw water containing the matrix passing through the filter material, the microorganism absorb nutrients in raw water. Microbes proliferate in the filler surface, after a certain period of time to form a biofilm. Mature biofilm surface contact with water, easy to absorb nutrients and dissolved oxygen, formed aerobic layer composed of aerobic and facultative microorganisms. Simultaneously, biofilm interior form anaerobic layer composed with Anaerobic and concurrent microorganisms [2]. At the same time, the proliferation of microorganisms and the accumulation of suspended substances, resulting in a gradual increase in the thickness of the biofilm, and the changes of biofilm structure. With the anaerobic layer aging, biofilm combined with filter

material loosening. Under the action of shear and back flushing of the water, the aging biofilm will fall off [3]. After falling off the biofilm, a new biofilm will grow up, which will be carried out repeatedly.

The advantages of pollutant removal

The Removal of Turbidity. Organic pollutants concentration is relatively low in micro-polluted water. Oligotrophic bacteria have a great advantage in nutrient competition. Therefore biofilm to with oligotrophic bacteria has larger specific surface area and have stronger adsorption and biological effects for suspended particles. According to microscope observation, the filter surface covered dough, flocculent biofilm. And across biofilm, there are still more biofilm covering the surface of filter [4]. Thus, the surface of the filter material can still play a role in the adsorption and retention of suspended particles in water. In addition, vorticellidae and shield worm on biofilm, feed with free bacteria and the sludge particle, also helped to reduce the turbidity [4]. Aging biofilms in the settlement process, can also contribute to the settling of fine suspended particles in water.

The Removal of Organic Compounds. The removal of organic compounds is mainly through the following aspects (1)the degradation of small molecule organic compounds by microorganisms;(2)the decomposition of macromolecular organic compounds by microbial extracellular enzymes; (3)biological adsorption flocculation. Biofilm with larger specific surface area, adsorb some organic compounds .Meanwhile, microbial extracellular enzymes, containing polysaccharide and other viscous substances, have the effect of chemical flocculation, and have strong adsorption and flocculation for organic compounds. Liu et al used bamboo charcoal as filler of BAF in treatment effect micro-polluted water, and found that the average removal rate of COD_{Mn} and ammonia nitrogen was 51.6% and 83.6% [5].

The Removal of Ammonia Nitrogen. The concentration of organic matrix, ammonia nitrogen and nitrite nitrogen in micro-polluted water, is lower relative to the corresponding substances in the sewage. Therefore, the oligotrophic bacteria have advantages in nutrient competition. Oligotrophic Bacteria has larger specific surface area, for matrix which it can make use of, has a strong affinity. The breathing rate of oligotrophic microorganism is low. Oligotrophic microorganism have relatively smaller maximum proliferation rate and Monod half rate constant. So it can adapt to low nutrient environments. Removal of ammonia nitrogen in micro-polluted water by biological method, achieve through the cultivation of oligotrophic microorganism such as the nitrite bacteria and nitrate bacteria [6]. Ammonia nitrogen under the action of nitrite bacteria transform into nitrite, and then in under the action of nitrifying bacteria into nitrate. The generation time of nitrifying bacteria is relatively long. Microorganism growth is immobilized in BAF. So microbial in the reactor can get a longer residence time, Nitrite and nitrification bacteria have enough time to accumulate. Therefore the removal of ammonia by BAF has great effect.

Influencing factors of stable operation of biological aerated filter

Hydraulic Load. Hydraulic load refers to the amount of water per hour of the unit area of the filter material. It is decided to the hydraulic retention time, effective volume and project investment important technical indicators of BAF. The size of the hydraulic load is directly related to the contact time of sewage with biofilm in BAF. Therefore, it is one of the significant factors that affect the treatment effect by BAF [7]. If the hydraulic load is too small, the hydraulic retention time is too long. It isn't conducive to microbial updates, and limit the improving of volume loading. Therefore, the function of BAF can't be utilized effectively ,leading to increasing the investment to the project. If the hydraulic load is too large, hydraulic residence time is too short. Contacting time of sewage and microorganism will be shortened, leading to pollutants removal capacity decreased. At the same time, too strong hydraulic erosion of the filter material, will make the loss of biofilm on the filter material.

Gas-Water Ratio. It is necessary to maintain a certain amount of dissolved oxygen (DO) in the reactor in order to degrading the pollutant by microorganism in the micro-polluted water. The ratio

can directly affect the concentration of DO in BAF. Usually, mass transfer resistance of the film will reduce with gas-water ratio increasing. Mass transfer coefficient of bubbles in the water also increase. Under similar conditions, the dissolved oxygen concentration in the biofilm increased, which resulted in the increase of the transmission and permeation rate of oxygen in the biofilm. The activity of aerobic heterotrophic bacteria and autotrophic nitrifier which can remove of organic compounds and ammonia nitrogen, also increased. Thus biological oxidation process will accelerate [8]. But the gas-water ratio can't be too large. Because of the limited solubility of oxygen, too large aeration rate can't be continued to improve DO concentration, instead of making power consumption and operating cost increase. In addition to excessive aeration, larger gas velocity produces stronger shearing force, leading to biofilm off [9].

Packing Height. Microorganisms on the filter with bottom-up show different distribution. It is mainly due to the different kinds and quantity of the microorganism along the water flow, and the thickness of the biofilm is also different [7]. When conditions (the type and quantity of filter, filling mode, particle diameter and inflow direction) are determined, the height of the filter plays a decisive role. If the filter is not high enough, it will affect the stable operation of biological aerated filter and water quality. If the filter material is too high, it will cause economic waste and other adverse effects.

Application of BAF in treatment of micro polluted water

Japan M.Takasaki et al began the research of BAF for micro-polluted water in 80 years of the last century. The research shows: BAF was used to treat micro-polluted water. Ammonia nitrogen removal rate is about 80%.even under extreme temperature conditions, the removal rate of ammonia nitrogen is in 60% - 80%. And compared with other packing processing system, BAF is not easy to be blocked [10]. Kyeong-Ho Lim from South Korea, in the 90s of the last century, began to research treatment by BAF for drinking water, efforts to control disinfection by-products formation and improve the safety of disinfection [11]. In China, although from the 90s of the 20th century ,we began extensive research on micro-polluted water by BAF pre-processing technology. But the research process also stay in production test research stage.

Department of environmental engineering of Tsinghua University and Bengbu water plant cooperate to research pre-treatment of micro-polluted water by BAF at home for the first time with the scale of production. The engineering manly apply biological ceramic filter, processing of raw water for the Huai River. The process flow chart is shown in Fig. 1.

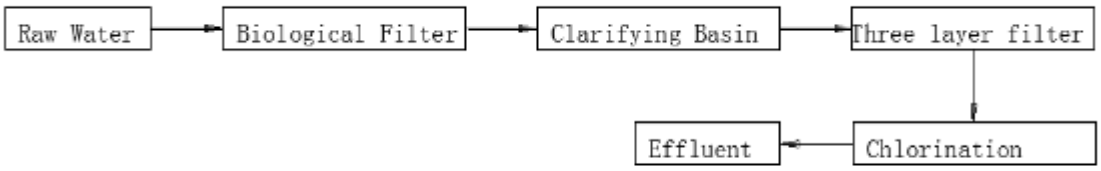

Fig.1. Treatment process of biological aerated filter

The results of the study show that biological pre-treatment in the conditions of gas water ratio of 1:1, the empty bed filtration velocity 3.6-6.0m/h, organics and ammonia nitrogen removal rate were separately 13.6%-20.5% and 70%-90%[12].

Conclusions

Pre-treatment of micro-polluted water by BAF can effectively remove biodegradable organic compounds, reduce bacteria in the water pipe network to breed, and improve the biological stability of drinking water. The pre-treatment process, in removal of organics and ammonia, can reduce the dosage of chlorine in disinfection process and disinfection by-products. Liu et.al research showed that BAF pre-treatment can reduce the zeta potential of the colloidal material in the water, and make

colloidal material easy to agglomerate, simultaneously reduce the dosage of coagulant and coagulant aid, thereby decreasing the treatment cost [13].

The BAF treatment of micro-polluted water extensively studied, but the production operation of BAF is not reported in China. Only Shanghai, Bengbu, several water plant run test. The process in some aspects still need to deeply explore: the process of long-term operation stability; running effect at low temperatures; inorganic sediment, shellfish , other aquatic organisms and algae breeding on the effect of the operation ; concentration of organisms and ammonia nitrogen seasonal changes greatly.

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