Advances in the treatment of phosphorus-containing wastewater

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Abstract. In recent years, many rivers, lakes and oceans around the world have exposed to diverse contaminants or red tides due to excessive discharge of nutrients such as nitrogen and phosphorus. The high content of phosphorus often leads to the nutrition of water body. Water resources have been seriously threatened, which has brought great impact on environment and public health. Therefore, the removal of phosphorus from wastewater attracts more and more attention. This work reviewed the forms, hazards and treatment of phosphorus in wastewater, and focuses on the methods of phosphorus-containing wastewater such as chemical precipitation, adsorption, ion exchange, membrane separation and biological methods. With the current economic and development of world, the bio-treatment of phosphorus-containing wastewater will become a research trend in the future, and the research and development of new technologies for phosphorus-containing wastewater will be an important topic for the treatment of phosphorus-containing wastewater in the future.

1. Introduction

With the urbanization, industrial and agricultural production is developing rapidly. Due to outdated technology, environmental damage and consumption of resources, resource shortage and environmental pollution attract more and more attention, especially water pollution. According to the data [1], many rivers in the world are affected to varying degrees, and red tides occur frequently in diverse sea areas. The main reason for water pollution in China's oceans, lakes and rivers is the nutrient-rich water body. The main factors leading to the nutrient-rich water body are phosphorus and nitrogen in untreated or incomplete [2].

The phosphorus contained in water body can be divided into insoluble phosphorus and soluble phosphorus according to physical form and divided into organophosphorus and inorganic phosphorus according to chemical properties. The most of which are colloidal and granular, while inorganic phosphorus is almost always in the form of soluble phosphate, including orthophosphate and polyphosphate [3]. There are two main sources of nitrogen and phosphorus in water, one is ammonia nitrogen produced by animal and plant decomposition of some organic matter, animal excrement and dissolved phosphorus-containing minerals in water [4]. But the process of this happening is very slow. More due to human overuse of fertilizers, pesticides and phosphorus-containing detergents [5]. Industrial wastewater containing large amounts of nitrogen and phosphorus and domestic sewage is discharged into the water. Algae in water are multiplying rapidly due to the increase of nitrogen, phosphorus and other nutrients, resulting in less and less transparency of water, which in turn destroys...
the ecological balance. The high content of phosphorus in the water body has caused serious damage and threat to water resources, public property losses, and brought great environmental problems to human health and urban development. Therefore, it is particularly important to develop the treatment of phosphorus in sewage and control the content of phosphorus discharged [6].

2. chemical precipitation

The basic principle of chemical precipitation method is to add soluble chemical reagents into the water, so that they react with phosphate roots in sewage to produce insoluble phosphates, and remove phosphorus from sewage by the method of solid separation. Common precipitants are lime, aluminum salt, iron salt [7].

2.1. The lime precipitation

The principle of lime precipitation is that calcium salts and phosphates in sewage produce hydroxyphosphorus insoluble lime precipitation in water, which in turn removes phosphorus from water. Lime precipitation can be expressed in the following chemical equations:

\[5\text{Ca}^{2+}+4\text{OH}^-+3\text{HPO}_4^{2-} \rightarrow \text{Ca}_5(\text{OH})(\text{PO}_4)_3 \downarrow+3\text{H}_2\text{O}\]  

(1)

\[\text{Ca}^{2+}+\text{HCO}_3^-+\text{OH}^- \rightarrow \text{CaCO}_3 \downarrow+\text{H}_2\text{O}\]  

(2)

Lime added to phosphorus-containing sewage can react with both HCO\text{\textsubscript{3}}-reactive and HPO\text{\textsubscript{4}}\text{\textsubscript{2}}-present in sewage. From the above equation, it can be learned that lime firstly produces calcium carbonate precipitation with HCO\text{\textsubscript{3}}-reaction in water, and excess Ca\text{\textsubscript{2}}+ reacts with phosphate in water to produce hydroxyphosphorus lime precipitation. When the higher the OH-content in the solution, the higher the corresponding PH, the lower the solubility of hydroxyphosphorus lime, the more precipitation, the higher the removal rate of phosphorus. Therefore, PH in phosphate can be converted to hydroxyphosphorus. Lime precipitation play a major role. In order to achieve a better phosphorus removal effect, PH is generally more than 10.0.

2.2. Metal salt precipitation

Metal salts used are iron salts and aluminum salts, and the principle of phosphorus removal is that metal salts react with phosphate roots in water to form large particles that are insoluble in water, thereby removing phosphorus. Commonly used aluminum salts are aluminum sulfate and polymerized aluminum chloride, iron salts are iron sulfate, iron sulfate, iron chloride and iron chloride. Iron salt and aluminum salt precipitation characteristics, the reaction equation is as follows:

\[\text{Fe}^{3+}+\text{PO}_4^{3-} \rightarrow \text{FePO}_4 \downarrow\]  

(3)

\[3\text{Fe}^{2+}+2\text{PO}_4^{3-} \rightarrow \text{Fe}_3(\text{PO}_4)_2 \downarrow\]  

(4)

\[\text{Al}^{3+}+\text{PO}_4^{3-} \rightarrow \text{AlPO}_4 \downarrow\]  

(5)

Above main reaction will also occur competitive reaction:

\[\text{Fe}^{3+}+3\text{OH}^- \rightarrow \text{Fe(OH)}_3 \downarrow\]  

(6)

\[\text{Al}^{3+}+3\text{OH}^- \rightarrow \text{Al(OH)}_3 \downarrow\]  

(7)

In the process of the above reaction, Fe\text{\textsuperscript{3+}} and Al\text{\textsuperscript{3+}} of salt mainly react with phosphate roots in phosphorus-containing sewage to produce insoluble phosphate precipitation. Due to the presence of sewage alkalinity, metal salt ions and OH\text{\textsuperscript{-}} reaction in sewage to produce a gel state Hydroxide, which adsorptions phosphates to the surface to form a flocculation. It is very beneficial to the precipitation of flocculation, but also adsorption of some tiny suspended particles. Therefore, metal salt precipitation is not a simple precipitation process [8]. During the whole reaction process, PH value not only affects the precipitation effect, but also affects the dissolution of metal phosphate. In order to minimize the dissolution of phosphate, the optimal pH range of iron salt and aluminum salt is 5.0 to 5.5, 6.0 to 7.0 [9].

Chemical precipitation of phosphorus removal has the advantages of simple operation and excellent phosphorus removal effect, and the recovery can reach about 75%. pH has a greater impact on phosphorus removal, resulting in increased operating costs, in the process of phosphorus removal needs to invest a large number of chemical reagents, not only will produce a large number of difficult to deal with chemical sludge, but also cause secondary pollution to the environment. Although there are
methods to achieve the reuse of phosphorus, the utilization rate is relatively low, which is difficult to meet the application of practical industry [10].

3. Adsorption

Adsorption method mainly utilizes adsorption agent to attract phosphorus in solution, and then separates from the liquid phase, so as to achieve the purpose of phosphorus removal. Adsorbent has a large surface area, the adsorption ability of phosphorus in water is strong, which can effectively achieve adsorption and removal of phosphorus in water. There are many commonly used phosphorus adsorbents, many industrial waste, low-cost minerals can also be used as adsorbents [11]. For example, benthic soil, activated carbon, zeolite, slag, etc. The aperture size of adsorbent has a great impact on the adsorption volume and adsorption rate. Many researchers are working on the development of modified adsorbents to improve phosphorus removal efficiency and reduce costs, but also through some technical means to replace the adsorbent after use, so as to achieve the recycling of adsorbents [12]. He et al. [13] used NaOH and LaCl$_3$ modified zeolite to adsorb phosphate in wastewater. The results showed that the adsorption capacity of zeolite before and after modification increased from 0.2mg/g to 8.96mg/g, and the adsorption process was in line with quasi-secondary kinetics equation.

Adsorbents have the advantages of low cost, wide range of sources, simple equipment and less sludge when absorbing phosphorus from water. However, the adsorption capacity is low, the replacement cost of adsorbent is too high, the process of adsorption regeneration and adsorption will also produce a certain amount of sewage, these shortcomings lead to the use of adsorption agent to remove phosphorus in water is difficult to obtain a promising application.

4. Ions exchange technology

The ion exchange method is to exchange porous anions with phosphate roots in wastewater, so as to remove phosphorus from water. Studies such as Awual [14] and Chen's [15] have shown that the pH of the solution plays an important role in removing phosphates from water, and that higher pH is beneficial to the removal of phosphorus. However, the presence of certain ions in the solution affects the phosphorus removal, such as Cl$^-$, CO$_3^{2-}$, SO$_4^{2-}$, etc.

The capacity of ion exchange resin to phosphate root ions is relatively stable. After many exchange regenerations, the exchange capacity of ion exchange resin can still maintain a high exchange capacity. However, there are a series of problems, such as synthetic ion exchange resin and regeneration cost is high, resin drugs are susceptible to poisoning, poor selectivity, so this method is difficult to get industrial application.

5. Membrane separation technology

Membrane separation technology is the removal of specific substances in water according to the different aperture sizes on the membrane by a thin film with selective separation. Membrane bio-reactive device (MBR) is usually used in wastewater phosphorus removal, which combines membrane separation with biological method, replacing the traditional sedimentation pool with membrane separation technology for solid fluid separation and avoiding the loss of microorganisms, which greatly improves the efficiency of phosphorus removal. Huang and others [16] can make 96% removal rate of phosphorus by using permeable membrane bio-reactive device, and the system can also use the resulting phosphorus-rich liquid for phosphorus recovery.

Membrane bio-reactive device can improve the volume load, further reducing the footprint, and the water quality is relatively stable, so the amount of sludge produced is less. Due to the high investment and operating costs of equipment, so the application of wastewater phosphorus removal has greater limitations.
6. Biological methods

6.1. Traditional methods

At present, it is generally believed [17-19] that the mechanism of biophosphorus removal is the release of phosphorus and microbial phosphorus removal. Under anaerobic conditions, polyphosphates break down polyphosphates (Poly-P) in their own cells and produce ATP at the same time, and utilize ATP to ingest volatile fatty acids in water or from fermentation processes in cells to PHB (poly β-hydroxybutyric acid) is stored in the form of phosphorus for energy reserves in an aerobic environment, while the poly-P decomposition of phosphoric acid excreted from the cells, this stage is mainly manifested in the release of PAOS phosphorus. That is, phosphate is transferred from microorganisms to sewage. Under aerobic conditions, polyphosphorus bacteria use O$_2$ as an electronic receptor, oxidize and store the PHB of cells to produce energy, and ingest phosphates from sewage in large quantities to synthesize Poly-P. This stage is manifested in the excessive absorption of phosphorus by polyphosphorus bacteria, i.e. the transfer of phosphates from sewage to microorganisms. The content of phosphorus in ordinary bacteria is about 2%-3%, while PAOS in aerobic conditions, due to excessive intake of external phosphorus, polyphosphorus bacteria can absorb phosphorus up to 12%. Finally, by way of dredging, the bacteria from the sewage excessive intake of phosphorus with the remaining sludge discharge system, it is generally believed that polyphosphorus bacteria absorb more phosphorus than the release of phosphorus, so as to achieve the effect of efficient removal of phosphorus in sewage.

6.2. Denitrification

With the further research of sewage phosphorus removal technology, it has been found that specific aerobic bacteria are not the only bacteria that can release and ingest phosphorus [19]. Under the condition of oxygen insufficiency, the bacteria can take nitrate as the final electron subject to achieve excessive ingestion of phosphorus in water, which is named denitrifying phosphate removal bacteria (DPB).

The principles of anti-nitrification phosphorus removal and PAOS phosphorus removal are similar, except that their electrons in PHB (poly β-hydroxybutyric acid) stored in cells are not the same, and the final electron subject of anti-nitrosification phosphorus bacteria is NO$_3^-$, while the final electrons of PAOS are O$_2$ [20]. During the anaerobic phase, anti-nitrosined phosphorus bacteria multiply in large numbers by absorbing small molecular compounds produced by BOD decomposition in water, while hydrolysis cell polyphosphates (Poly-P) produce inorganic phosphates and ATPs. Inorganic phosphate is discharged outside the cell, and the resulting ATP is used to synthesize PHB stored in bacteria to complete phosphorus under anaerobic conditions. During the hypoxia phase, anti-nitrosification phosphorus bacteria take NO$_3^-$as the final electron subject of PHB, degrade PHB stored in cells, and produce ATP. Most of the ATP produced is used for the synthesis of in-cell substances and the maintenance of their own life activities. A small portion of the phosphate used in excess intake of water is stored in cells in the form of polyphosphate (Poly-P), and NO$_3^-$ is reduced to N$_2$. Under the alternating operation conditions of anaerobic and hypoxia, the anti-nitrification effect of anti-nitrification phosphorus bacteria can be achieved [21-25].
Cloete et al. [27] demonstrated that phosphorus-accumulating cells contain 57-59% phosphorus, and extracellular polymers generally contain about 27-30% phosphorus. Xiao et al. [28] considered that in the biological dephosphorization process, the removal rate of total phosphorus can reach 97%, and the effluent concentration is about 0.32mg/L. Cassidy et al. [29] used an SBR reactor containing granular sludge to treat slaughterhouse wastewater, and the removal rate of COD and total phosphorus could reach 98%, and the removal rate of ammonia nitrogen exceeded 97%.

Microbial phosphorus removal is not only simple to operate, but also does not require the consumption of chemicals, and will not produce new secondary pollution. The amount of sludge produced is less, so it is more economical and environmentally friendly.

7. Conclusion and overlook
In sewage phosphorus removal technology, there are mainly physical chemistry and biological methods. Although the simple chemical method is simple, but with the disadvantage of complex operation, high cost and easier to cause secondary pollution.

Although the adsorbent has a wide range of sources, low price and other advantages. However, adsorbent adsorption capacity is low, replacement cost is too high, regeneration and adsorption process will also produce a certain amount of sewage. These shortcomings make the adsorption method difficult to be widely used.

The exchange capacity of ion exchange resin to phosphate root ions is stable. After exchange regeneration, the exchange capacity of ion exchange resin can still maintain a high exchange capacity. However, the cost of resin regeneration is high, resin drugs are susceptible to poisoning, poor selectivity, so this method is difficult to get practical application.

Membrane separation can reduce the footprint, and the water is relatively stable, resulting in less sludge. However, due to the high cost of equipment investment and operation, there are fewer types of phosphate removed, so the application of wastewater phosphorus removal has great limitations.

Biological cause process is simple, easy to operate, the resulting secondary pollution and other advantages, has become a hot research at home and abroad, has been widely used. Anti-nitrification phosphorus removal technology is developed in the traditional biological phosphorus removal technology, is a kind of high-efficiency, low-consumption, economical biophosphorus removal technology, with broad research prospects.

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