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Removal and recovery of phosphorus during anaerobic digestion of excess sludge by the addition of waste iron scrap

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Abstract: In the current investigation, the feasibility of phosphorus removal in the anaerobic digestion of excess sludge by the addition of waste iron scrap (WIS) was studied. The results showed that the removal efficiency of phosphorus increased with increasing amount of WIS, and the maximum removal efficiency of 39, 93 and 99 % could be reached at WIS dosages of 1, 2 and 3 g L^{-1}, respectively. Sterilization greatly decreased the removal efficiency of phosphorus, being only –6, 53 and 64 % at WIS dosages of 1, 2 and 3 g L^{-1}, respectively. This means that iron-reducing bacteria and hydrolytic bacteria enhance 45 , 40 and 35 % of the phosphorus removal at WIS dosages of 1, 2 and 3 g L^{-1}, respectively. The first and most important mechanism of phosphorus removal using WIS involves hydrolytic bacteria, which reduce the pH of the sludge to corrode the WIS, followed by precipitation of phosphorus by ferrous iron generated by iron-reducing bacteria. Phosphorus adsorption onto the WIS is the second probable mechanism. The removed phosphorus is recovered by up to 56 % using magnet. This method is characterized by high removal efficiency, easy and steady operation, low cost, recovery and reuse, making it better than other physical and chemical treatments.

Keywords: waste iron scrap; phosphorus removal; excess sludge; anaerobic digestion.

INTRODUCTION

An excessive presence of phosphate in freshwater affects the water quality and the ecosystem balance negatively through a process known as eutrophication. To diminish the negative effects of phosphorus in effluents from municipal wastewater treatment plants (MWWTP), treatment processes are becoming more stringent. Today, the main commercial processes for phosphorus removal from

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wastewater effluents are chemical precipitation with iron, alum, lime and magnesium[1–6] and, to a lesser extent, biological removal.[7]

An efficient phosphate removal technique is precipitation involving struvite;[8] however, the crystallization rate of struvite is low. Another method, chemical precipitation, is a very flexible and speedy process for phosphorus removal using ferric chloride and ferrous sulfate.[9] However, this process is not generally favored because of high costs.[10]

In contrast to the majority of research dedicated to the removal of phosphorus, including chemical[11–14] and biological methods,[15–20] phosphorus is removed from the aqueous phase to the solid phase, especially in biological methods. Phosphorus is transferred from the water to the sludge, and in the process of sludge treatment, abundant phosphorus is released from the sludge to the aqueous phase. The whole process consumes large amounts of energy and cannot fundamentally solve the problems.

Currently, the removal of phosphorus in the process of sludge digestion has not yet been studied. In the present study, investigated the feasibility of phosphorus removal in the process of excess sludge digestion using waste iron scrap (WIS) was investigated. The effects of sterilization and adsorption were also studied to understand the mechanisms of phosphorus removal. The phosphorus recovery was also investigated.

MATERIALS AND METHODS

Composition of anaerobic sludge and WIS

The anaerobic sludge used in this study was obtained from a MWWTP in Changsha, China. The sludge was filtered through a 1×1 mm metal sieve and stored at 4 °C for later use. The total solids (TS) content, total volatile solids (TVS), dissolved phosphate, total iron ions, and pH were 11.1, 7.5, 93.6 and 125 mg L^{-1} and 6.8, respectively. The WIS, which was collected from a grinding workshop near Hunan University, China, was 4–8 mm in length and 3 mm in width. The WIS was first degreased in 10 % NaOH solution and then cleaned using deionized water.

Experimental setup

Experiments on the influence of dosage of WIS on phosphorus removal were performed in 10 identical glass reactors, each having a liquid volume of 500 mL. The WIS was added into the reactors (*i.e.*, unsterilized, sterilized sludge and prepared phosphate solution) at dosages of 0, 1, 2 and 3 g L^{-1}. Subsequently, the reactors were air-bath mixed at 120 rpm to blend the contents, at a temperature maintained at 25±1 °C. Each reactor was purged with nitrogen gas for 5 min and sealed to ensure anaerobic conditions. To investigate the adsorption performance of WIS onto phosphorus, a phosphate solution of definite concentration was prepared to which WIS at the above-mentioned dosages was added. All the reactors were run for 10 d. At predetermined time intervals, samples were collected and analyzed. All tests were performed in triplicate and the average results are presented in this study.

Analytical methods

The values of TS, TVS, and dissolved phosphate were determined according to standard methods.[21] The pH was determined using a Multiline 330i pH meter standardized using buffer solutions of different pH values. The concentration of total iron was measured using the phenanthroline spectrophotometric method.[22]

The volatile fatty acids (VFAs) were analyzed using an Agilent 6890N GC with a flame ionization detector and equipped with a 30 m×0.25 mm×0.25 µm DB-FFAP column. Nitrogen was used as the carrier gas at a flux of 5.6 mL min^{-1}. The injection port and the detector were maintained at 250 and 300 °C, respectively. The oven of the GC was programmed to start at 70 °C for 3 min, then to increase at a rate of 20 °C min^{-1} to 250 °C, at which temperature, it was held for 3 min. The sample injection volume was 1.0 µL.

RESULTS AND DISCUSSION

Effect of WIS dosage

The amounts of phosphorus removed as a function of the amount of WIS are shown in Fig. 1. The amount removed increased with increasing amount of WIS, except for the control test because of the phosphorus released in the process in excess of the sludge digestion. The highest phosphorus removal efficiency at WIS dosages of 1, 2 and 3 g L^{-1} were 39, 93 and 99 %, respectively, because higher dosages of WIS have larger surface areas available for reaction with phosphate. The chemical removal of phosphate was accompanied by the adsorption of phosphate ions and dissolved organic phosphorus on ferric hydroxide flocs.[13,23] The

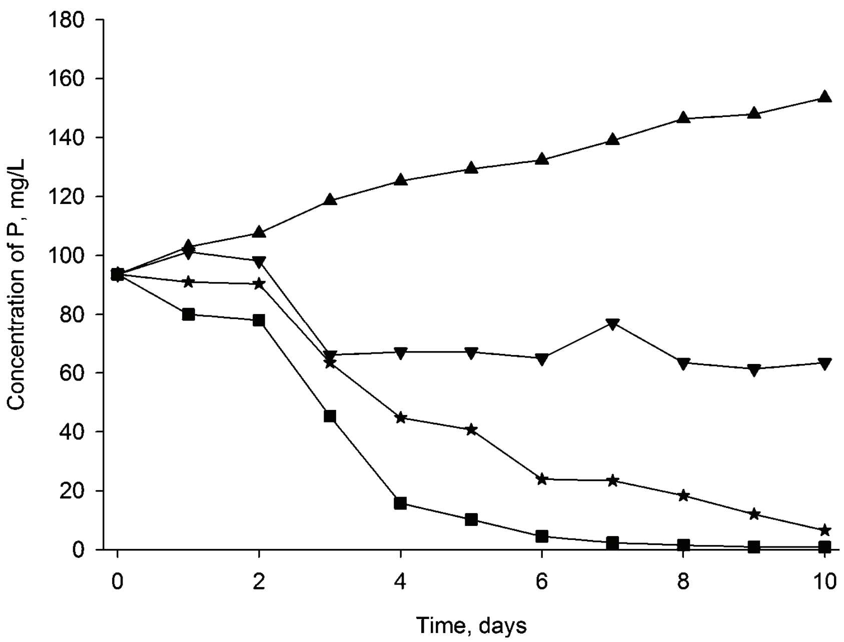

Fig. 1. Effect of WIS dosage on the removal of phosphorus (▲, 0; ▼, 1; ★, 2; ■, 3 g L^{-1}).

removed phosphorus, Fig. 1, was not released with extended time, indicating that the WIS had a high affinity for phosphorus. The final concentration of phosphate at a WIS dosage of 3 g L^{-1} was 0.8 mg L^{-1}, which is lower than the permitted level of phosphate in MWWTP effluent in China.

The removal of phosphorus from excess sludge prior to supernatant recycling in aerobic tanks can significantly reduce the phosphorus load in the main stream of the MWWTP effluent, thereby preventing the eutrophication of aquatic systems and deterioration of water quality.[13,24] Another benefit of this technology is that it can recover phosphorus used as a fertilizer in agriculture.

pH Variation and total production of volatile fatty acids

The pH variations at different WIS dosages during sludge digestion are shown in Fig. 2, from which it can be seen that the pH of the sludge in the presence and absence of WIS exhibited a similar trend: an initial decrease followed by an increase. This trend is caused by the production of organic acids during the digestion of the excess sludge and the bacterial conversion of the organic acids into methane and carbon dioxide. Higher WIS dosages can shorten the time during which the pH decreases, which may be attributed to the bioreduction of WIS (Eqs. (1) and (2)) and the corrosion of WIS (Eqs. (3)and (4)).

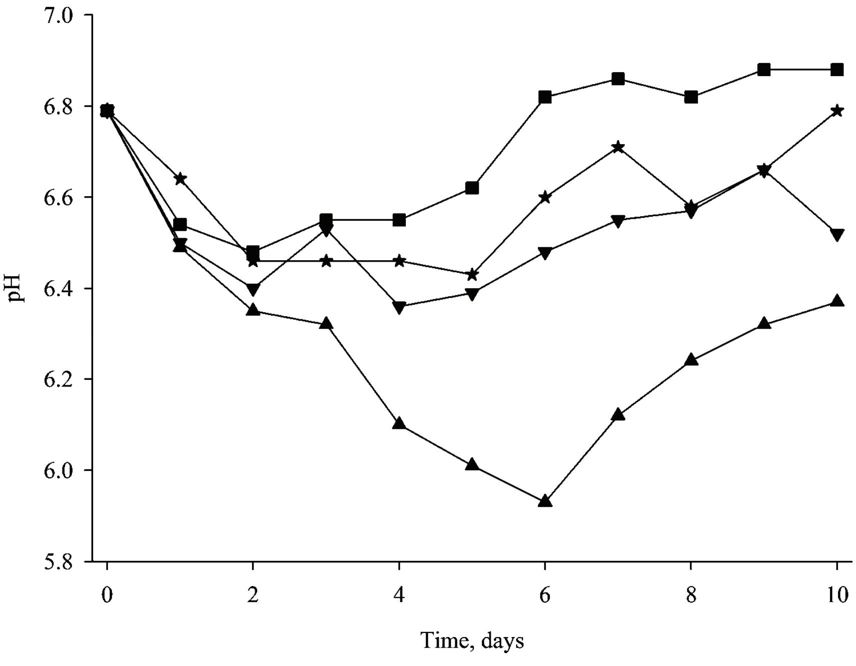

Fig. 2. Variation in pH at different WIS dosages during sludge digestion (▲, 0; ▼, 1; ★, 2; ■, 3 g L^{-1}).

An anaerobic digester contains many types of iron-reducing bacteria.[25] With acetate as the electron donor, the reduction of WIS, which is mainly composed of Fe_2O_3 and Fe_3O_4, and the precipitation of phosphorus by ferrous irons can be described by the following equations:

$$4Fe_2O_3 + CH_3COOH + 16H^+ \rightarrow 8Fe^{2+} + CO_2\uparrow + 10H_2O \quad (1)$$

$$4Fe_3O_4 + CH_3COOH + 24H^+ \rightarrow 12Fe^{2+} + 2CO_2\uparrow + 14H_2O \quad (2)$$

$$Fe_2O_3 + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O \quad (3)$$

$$Fe_3O_4 + 8H^+ \rightarrow Fe^{2+} + 2Fe^{3+} + 4H_2O \quad (4)$$

$$3Fe^{2+} + 2PO_4^{3-} \rightarrow Fe_3(PO_4)_2\downarrow \quad (5)$$

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4 \quad (6)$$

However, Ca^{2+} and Mg^{2+} are released in the process of excess sludge digestion. The results of Gao and Mucci[26] further indicated that the formation of Mg^{2+}, Ca^{2+} and ternary cation–phosphate surface complexes ($\equiv FeOMg^+$, $\equiv FeOCa^+$, $\equiv FeOMgHPO_4^-$, $\equiv FeOMgH_2PO_4^0$, $\equiv FeOCaHPO_4^-$ and $\equiv FeOCaH_2PO_4^0$) affect phosphate adsorption by WIS.

The effects of WIS dosage and hydrolysis time on the total production of VFAs are shown in Fig. 3. The individual VFAs were converted to chemical oxygen demand (*COD*) values using appropriate conversion factors. The total VFA concentration was greatly affected by the WIS dosage. The fermentation time to

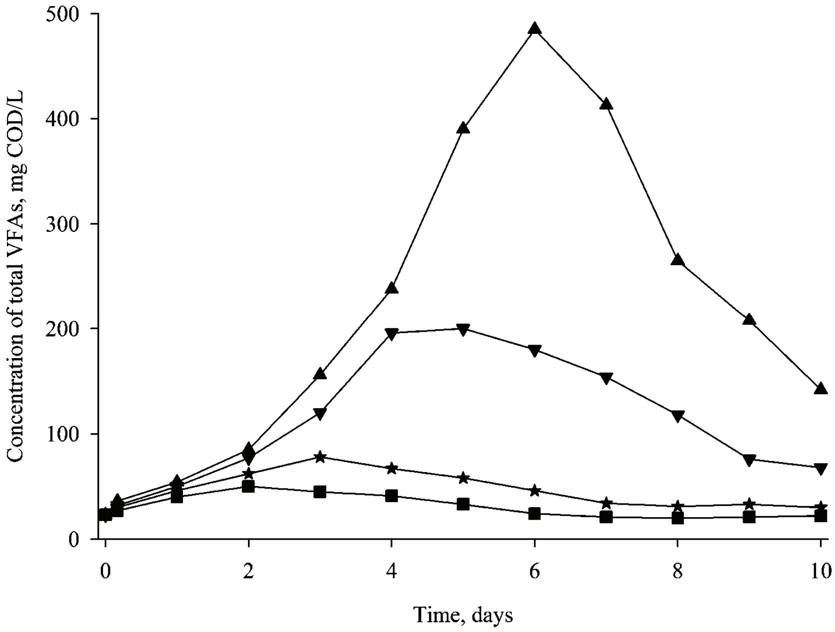

Fig. 3. Production of VFAs at different WIS dosages during sludge digestion (▲, 0; ▼, 1; ★, 2; ■, 3 g L^{-1}).

reach the maximum VFA concentration was also affected by the WIS dosage. For example, the maximum VFA concentration was 485 mg COD L^{-1} on the 6th day in the blank test, 200 mg COD L^{-1} on the 5th day at a WIS dosage of 1 g L^{-1}, 78 mg COD L^{-1} on the 3rd day at 2 g L^{-1} and 50 mg COD L^{-1} on the 2nd day at 3 g L^{-1}. Moreover, as shown in Fig. 3, the concentration of the VFAs decreased with increasing WIS dosage because the VFAs were consumed, according to Eqs. (1)–(4).

Effect of adsorption

The important mechanisms involved in phosphorus removal using steel slag are specific adsorption on metal hydroxides and precipitation.[27] To determine the effect of adsorption, three 140 mg L^{-1} phosphorus solutions were prepared. The phosphorus removal efficiency by WIS as function of the WIS dosage and contact time are presented in Fig. 4, which shows that phosphorus removal first increases with the increasing contact time, then there was no obvious increase when the contact time was longer than 9 and 7 d at WIS dosages of 3 or 2 and 1 g L^{-1}, respectively. This finding indicates that the adsorption reaction of phosphorous onto WIS mainly occurred within the first 9 and 7 d, respectively. When the contact time reached 9 and 7 d, phosphorus removal was 38, 34 and 16 % at WIS

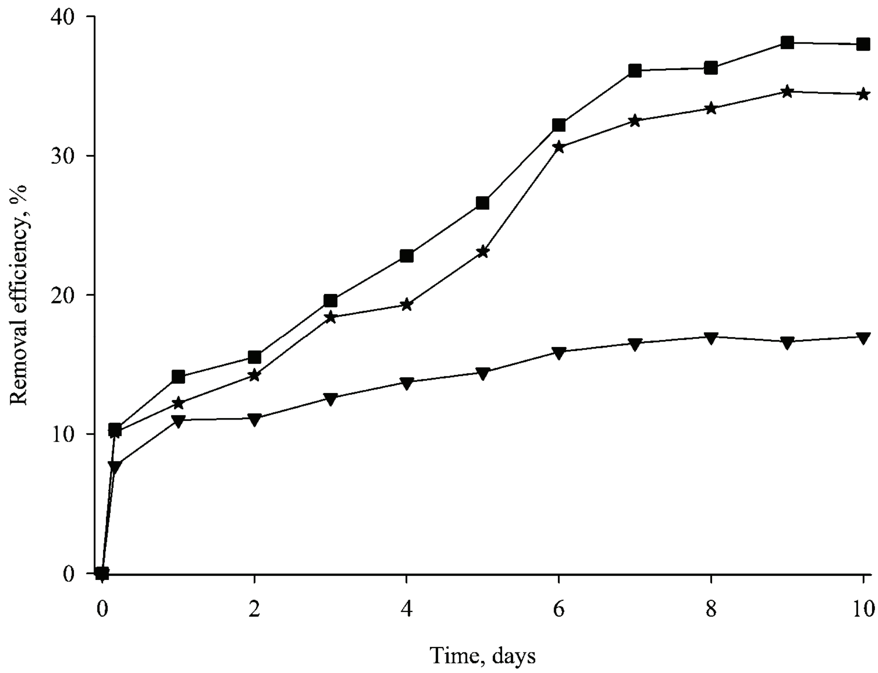

Fig. 4. Effect of the adsorption of phosphorus at different WIS dosages (▼, 1; ★, 2; ■, 3 g L^{-1}).

dosages of 3, 2 and 1 g L^{-1}, respectively. The presence of Ca^{2+}, Mg^{2+} and other heavy metals in the excess sludge led to decreases in phosphorus removal by the sludge phase. Thus, adsorption removal of phosphorus in the process of excess sludge digestion was less than 16, 34 and 38 % at WIS dosages of 1, 2 and 3 g L^{-1}, respectively. The contribution of iron-reducing bacteria and hydrolytic bacteria (hyrolyze complex organics (carbohydrates, proteins and lipids to monosaccharides, amino acids, higher fatty acids and alcohols) in phosphorus removal was more than 32, 61 and 61 % at WIS dosages of 1, 2 and 3 g L^{-1}, respectively.

Effect of sterilization

Sterilization was used to determine the effect of iron-reducing bacteria and hydrolytic bacteria. As shown in Fig. 5, the concentration of phosphorus first increases and then decreases. However, the concentration of phosphorus in the reactor of unsterilized sludge decreases with the increase in time at all WIS dosages (Fig. 1). This finding indicates that sterilization can inhibit phosphorus removal, especially at the low WIS dosages. As shown in Figs. 1 and 5, the removal efficiencies of phosphorus are –6, 53 and 64 % in sterilized sludge and 39, 93 and 99 % in unsterilized sludge at WIS dosages of 1, 2 and 3 g/L, respectively. This finding indicates that iron-reducing bacteria and hydrolytic bacteria enhance 45, 40 and 35 % of phosphorus removal at WIS dosages of 1, 2 and 3 g/L, respectively.

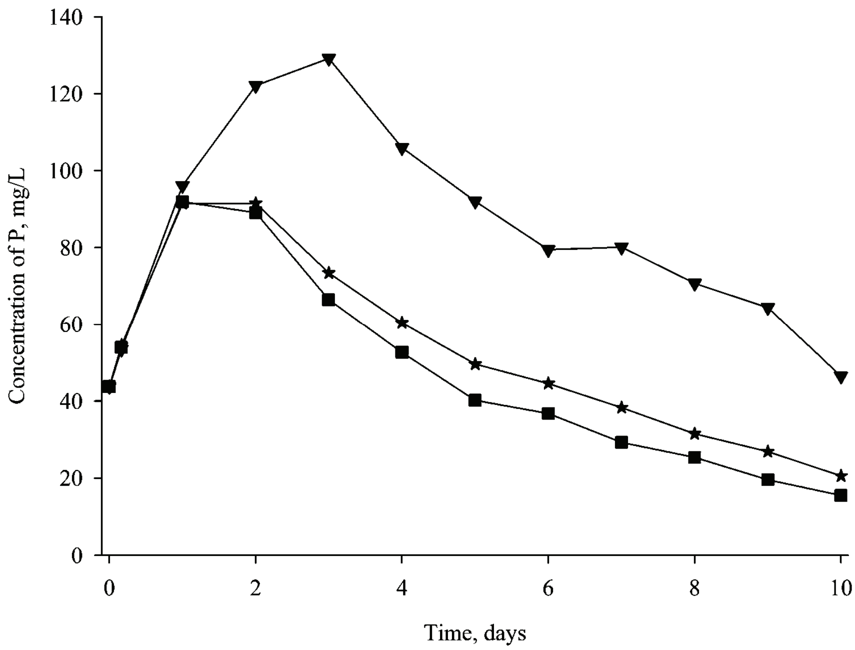

Fig. 5. Effect of sterilization on the removal of phosphorus (▼, 1; ★, 2; ■, 3 g L^{-1}).

Recovery of phosphate

Currently, fertilizer utilizes 80 % of the world's phosphate production. The production of phosphorus fertilizer from ores is non-renewable and should be considered unsustainable.[28] Thus, recycling phosphorus resources and gaining political and economic priority are important in the long term. A magnet is used for the removal of phosphorous from the sludge (3g L^{-1}) *via* three cycles of attraction for a 10-day treatment. During this process, WIS and the adsorbed phosphate can be fully attracted, while $Fe_2(PO_4)_2$ and $FePO_4$ are partially attracted due to their weak magnetism. The attracted substance was cleaned using distilled water and then transferred to a clean beaker. The attracted substance was dissolved using hydrochloric acid (1 mol L^{-1}). The results show that 56 % of phosphate was recovered. The attraction between the magnet and the removed phosphorus was (P+WIS) > $Fe_3(PO_4)_2$ > $FePO_4$. Thus, the recovered phosphorus was mainly in the form of phosphate adsorbed by WIS and partially in the form of $Fe_3(PO_4)_2$ and $FePO_4$.

Economic estimation

The iron scrap in the present study was waste and obtained free. No reagents were added in the entire process, except WIS. This method is characterized by high removal efficiency, easy and steady operation, low cost, recovery and reuse, making it better than other physical and chemical treatments.

CONCLUSIONS

The results of the current study indicate that WIS could effectively remove phosphorus from excess sludge. The highest phosphorus removal efficiencies at WIS dosages of 1, 2 and 3 g L^{-1} were 39, 93 and 99 %, respectively. The mechanisms of phosphorus removal by WIS were surface adsorption onto WIS, hydrolysis and bioreduction of WIS and precipitation of phosphorus by ferrous ions resulting from the action of hydrolytic and iron-reducing bacteria. The first and the most important mechanism of phosphorus removal using WIS is hydrolytic bacteria, which reduce the pH of the excess sludge that corrodes the WIS, followed by precipitation of phosphorus using ferrous ions. Phosphorus adsorption to WIS is the second mechanism, which is less than 16, 34 and 38 % at WIS dosages of 1, 2 and 3 g L^{-1}. This type of material may have broader applications because of its high phosphorus removal efficiency, abundant supply, and low cost. Using a magnet, 56 % of the removed phosphorus is recovered. This method is characterized by high removal efficiency, easy and steady operation, low cost, recovery and reuse, making it better than other physical and chemical treatments.

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И З В О Д

УКЛАЊАЊЕ И САКУПЉАЊЕ ФОСФОРА ТОКОМ АНАЕРОБНЕ ОБРАДЕ ОТПАДНОГ МУЉА ДОДАВАЊЕМ ОТПАДА ГВОЖЂА

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У овом истраживању проучавана је изводљивост уклањања фосфора при анаеробној преради отпадног муља додавањем отпада гвожђа (ОГ). Резултати показују да се ефикасност уклањања фосфора побољшава са количином ОГ, достижући ефикасност од 39, 93 и 99 % при дозама ОГ од 1, 2, односно 3 g L^{-1}. Стерилизација знатно умањује ефикасност уклањања фосфора, достижући само 6, 53 и 64 % при дозама ОГ од 1, 2, односно 3 g L^{-1}. Ово значи да бактерије које уклањају гвожђе и хидролитичке бактерије побољшавају уклањање фосфора за 45, 40 и 35 % при дозама ОГ од 1, 2, односно 3 g L^{-1}. Први и најважнији механизам уклањања фосфора помоћу ОГ су хидролигичке бактерије, које смањују pH муља да би нагризла ОГ, након чега следи таложење фосфора феро-јонима које генеришу бактерије које редукују гвожђе. Други могућ механизам је адсорпција фосфора на ОГ. До 56 % уклоњеног фосфора се сакупи помоћу магнета. Овај метод карактерише висока ефикасност уклањања, лак и континуалан рад, економичност и рециклабилност, што га чини бољим од других физичких и хемијских поступака.

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