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BIOLOGICAL PHOSPHATE REMOVAL USING A DEGRADABLE CARBON SOURCE PRODUCED BY HYDROTHERMAL TREATMENT OF EXCESS SLUDGE

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Abstract - The possibility of reusing excess sludge treated by hydrothermal reaction for the purpose of improving the efficiency of the enhanced biological phosphate removal (EBPR) process was investigated. Excess sludge from a fish-processing industry located in Japan was treated in high-temperature and high-pressure water, at a reaction temperature ranging from 200 to 400°C, a pressure of 1.8 to 30MPa and a constant reaction time of 7 min. For the conditions tested, the results showed that when the reaction temperature was increased the content of readily biodegradable substrate in the total COD_{Cr} increased. In addition, the amount of some volatile fatty acids (VFAs) produced by the hydrothermal reaction increased as reaction temperature increased. From the phosphate release tests under anaerobic conditions, it was possible to demonstrate that not only the VFAs, but also the readily and slowly biodegradable substrates are used as potential carbon source by the phosphate-accumulating organisms (PAOs).

Keywords: COD_{Cr} characterization enhanced biological phosphate removal (EBPR); Excess sludge; Hydrothermal reaction; Readily biodegradable substrate.

INTRODUCTION

The control of excess sludge produced in industrial and domestic wastewater treatment plants has been a matter of considerable concern. The discharge of excess sludge poses significant risks to the environment, and the development of new technologies that are capable of decreasing the pollution has challenged many research projects.

The principal methods still used in most countries are landfill and incineration. But problems such as the decline in available land for construction of new landfills and the generation of ash with a high content of heavy metals and general toxicity by the incinerators have made these methods impracticable (Wei et al., 2003). Some new technologies, such as thermal processes (Neyens and Baeyens, 2003), ozonation (Ahn et al., 2002), chlorination (Saby et al., 2002), bead mill processes (Jung et al., 2001) and reactions in high-temperature and high-pressure (HTHP) water (Shanableh, 1999), have been studied with a view to solubilizing and mineralizing the

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*To whom correspondence should be addressed excess sludge.

Reactions in HTHP water have attracted the attention of many researchers because of the unique properties of water at elevated temperatures and pressures as reaction medium. Under HTHP conditions, the static dielectric constant of water decreases and the water becomes an excellent solvent for organic compounds. In addition, the ion product of water decreases, favoring hydrolytic reactions (Savage et al., 1995). However, HTHP water has been studied just from the viewpoint of solubilization and COD reduction of the treated excess sludge (Shanableh, 1999). Evaluations of the change in content have not yet been reported.

On the other hand, the release of some nutrients, such as nitrogen and phosphorus, has increased the problem of eutrophication in many rivers around the world. The enhanced biological phosphate removal (EBPR) process is currently considered one of the most economical ways to remove phosphate from wastewaters. The EBPR process is characterized by cycling anaerobic and aerobic conditions. In this process, phosphate removal occurs when the content of volatile fatty acids (VFAs), such as acetic and propionic acids, in the wastewater is sufficient. Under anaerobic conditions, these acids are used as carbon source by the phosphate-accumulating organisms (PAOs) to synthesize poly-β-hydroxyalkanoate (PHA), an internal storage compound. To obtain energy for PHA synthesis, the PAOs degrade the intracellular polyphosphate (polyP) granulates in the form of orthophosphate and release it into the bulk liquid. Under subsequent aerobic conditions, the PAOs use the stored PHA as carbon and energy sources and polyP is formed in excess of the levels normally required to satisfy the metabolic demand. This synthesis results in the uptake of higher levels of phosphate than that released under anaerobic conditions. Thus, a net phosphate removal can be obtained (Mino et al., 1998; Morse et al., 1998; Seviour et al., 2003). However, the VFA content in the wastewaters is not sufficient to achieve a stable phosphate removal. It is also known that only a small quantity of readily biodegradable substrate that can be easily fermented to VFAs under anaerobic conditions is present. In order to achieve stable biological phosphate removal and therefore an efficient phosphate recovery, the development of a new treatment system is required.

The objective of this work was to evaluate the feasibility of reusing the excess sludge treated in HTHP water as carbon source for the purpose of increasing the efficiency of EBPR process. In previous work (Kim et al., 2003, 2004; Quitain et al., 2002), the production of biodegradable substrates through hydrolysis of non biodegradable substrates was reported. Making use of this knowledge, excess sludge is treated in HTHP water for the purpose of obtaining biodegradable substrates through change in content of the treated excess sludge. Due to this change in content, the treated excess sludge can be recycled in the biological processes and used as carbon source for biological phosphate removal.

MATERIALS AND METHODS

Sludge Samples

Excess sludge obtained from a local fish-processing industry in Japan was used as the raw material due to its high organic content. The COD_{Cr} and concentration of mixed-liquor suspended solids (MLSS) were 32000 mg/L and 25000 mg/L, respectively. Activated sludge from an aerobic reactor was used as inoculate for water quality analysis and a phosphate release test. The concentration of MLSS and total phosphorus (TP) were 2100 mg/L and 54 mg/L, respectively.

Batch Reactor Apparatus

Hydrothermal reaction was carried out using a batch reactor apparatus (TSC-006, Taiatsu Glass Corp.) that consists mainly of a stirrer, a pressure gauge, a reactor and a molten salt bath containing a mixture of potassium nitrate and sodium nitrate (Quitain et al., 2002). The batch reactor is made of hastelloy C22 (Ni, Cr, Mo alloy) and has a total inner volume of 65.9cm^3. The maximum operational conditions of the reactor are 450^{o}C and 45MPa.

Hydrothermal Treatment of Excess Sludge

Excess sludge was treated at reaction temperatures of 200, 250, 300, 350 and 400^{o}C and pressures of 1.8, 4.0, 9.0, 17.0 and 30.0MPa, respectively. Reaction time, defined as the time required to raise the temperature up to 90% of the reaction temperature (Kim et al., 2003), was 7 minutes for all temperatures and pressures used. Below the critical point of water (374^{o}C, 22.1MPa), saturated vapor pressures at the specific temperature were selected as liquid-phase reaction pressure. The desired pressure was obtained by adjusting the initial amount of sample, and during hydrothermal reaction, it was read with a pressure gauge located in the batch reactor. In each run, a sample was placed inside the reactor, the reactor was sealed and residual air was purged using a pure nitrogen gas stream. The reactor was placed in the preheated molten salt bath during the predetermined reaction time. Afterwards, the reactor was immediately quenched with a water bath, effectively stopping any ongoing reactions.

Phosphate Release Test

For the phosphate release test under anaerobic conditions, excess sludge treated by hydrothermal reaction was used as carbon source. Prior to the test, the treated excess sludge was diluted. This dilution is necessary because the high concentration of acetic and propionic acids in the treated excess sludge would rapidly exhaust the intracellular polyP and the ability to use S_S or X_S as carbon source could not be addressed. The dilution factor was calculated in order to obtain 100 mg-BOD_5/L of the treated excess sludge. In this situation, the concentration of VFAs is low enough to release less than 5% of the TP contained in the seeding activated sludge. The mixture of treated excess sludge and the seeding activated sludge was adjusted to a specific concentration with dechlorinated tap water, and 300mL of the mixed solution was placed in a flask. The air inside the flask was replaced with pure nitrogen gas and the flask was sealed. At this moment, the phosphate release test was initiated, and during 5 hours samples were taken at prescribed time intervals. A control test was also carried out using sodium acetate as sole carbon source. In this case, the carbon source was diluted in order to obtain 100 mg/L of BOD_5. It was assumed that the value of the BOD_5 was 90% of the value of the theoretical oxygen demand (ThOD).

Analytical Methods

For evaluation of the products, the treated excess sludge was analyzed using an organic acid analyzer (LC-10A, Shimadzu Corp.) with two ion-exclusion columns (Shim-park SCR-102H, Shimadzu Corp.) connected in series and an electroconductivity detector (CDD-6A, Shimadzu Corp.). Total organic carbon (TOC) and dissolved organic carbon (DOC) were measured with a TOC analyzer (TOC-5000A, Shimadzu Corp.). Chemical oxygen demand (COD_{Cr}) was analyzed with a COD analyzer consisting of a COD reactor (P/N 45600-00, HACH Corp.) and a spectrophotometer (DR/3000, HACH Corp.). Biological oxygen demand (BOD_5) was determined with a BOD tester (BOD Tester 200F, Taitec Corp.). TP, soluble phosphate (PO_4-P) and MLSS were analyzed following the standard method (American Public Health Association, 1995). Before analysis of organic acid, soluble phosphate and DOC, all samples were filtered to separate solid parts using syringes and filters with a pore size of 0.45μm.

For characterization of the total COD_{Cr}, the fraction of readily biodegradable substrate (S_S) was based on the respirometric test, conducted in accordance with the method reported by Kappeler and Gujer (1992) and Henze et al. (1995). The fraction of slowly biodegradable substrate (X_S) was defined as the difference between the value of BOD_5 and the value of S_S. The fraction of soluble non biodegradable substrate (S_I) was measured following this procedure: the activated sludge used as inoculate and the treated excess sludge were mixed in order to obtain a concentration of F/M = 0.1 and placed in a flask. The tests were carried out under aerobic conditions during 8 hours. After this period of time, it was expected that all of the S_S and X_S content would have been completely consumed, with only the non biodegradable substrates remaining. The solution was then filtered and the COD_{Cr} of the liquid phase was measured. The value of S_I was defined as the difference between the COD_{Cr} of the liquid phase and the BOD_5. Finally, the value of particulate non biodegradable substrates (X_I) was defined as the difference between the total COD_{Cr} of the treated excess sludge and the sum of S_S, X_S and S_I.

RESULTS AND DISCUSSION

Improvement in Biodegradability

Figure 1 shows the variations in the ratio of TOC to BOD_5 for the excess sludge treated by hydrothermal reaction and the respective values for the raw material, TOC_i and BOD_{5i}.

The value of TOC at a reaction temperature of 200°C practically remained constant in relation to that of TOC_i, but the value of BOD_5 was 3.8 times higher than the respective value for the raw material. In other words, after hydrothermal reaction, some non biodegradable substrates present in the raw material were degraded into biodegradable substrate.

At this reaction temperature, the increase in biodegradability was obtained without mineralization of the organic compounds. In the case of the reaction temperature of 250°C, in spite of a higher degree of mineralization, the BOD_5 did not show a significant variation. Increasing the reaction temperature to 300, 350 and 400°C, the BOD_5/BOD_{5i} ratio remained practically constant at 3.4. On the other hand, a considerable decrease in the value of the TOC/TOC_i ratio was obtained. Values of 0.44 and 0.22 were obtained for reaction temperatures of 350 and 400°C, respectively. This means that when the reaction temperature was increased, mineralization of the excess sludge occurred faster than the formation of biodegradable substrates.

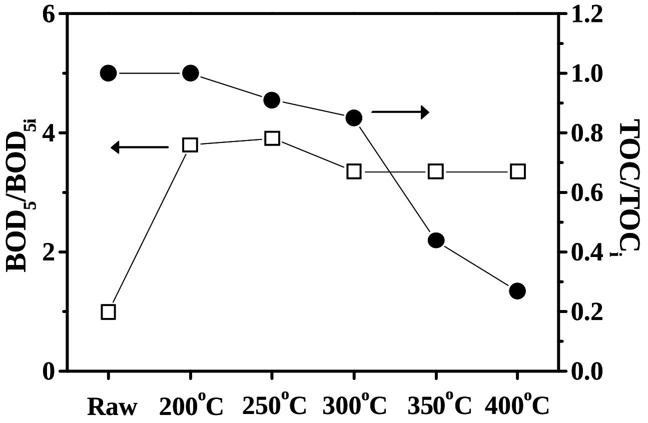

Figure 1: Effect of TOC reduction on improvement of BOD_5 in excess sludge treated at 200, 250, 300, 350 and 400oC and pressures of 1.8, 4.0, 9.0, 17.0 and 30.0MPa, respectively.

Characterization of the Total COD_{Cr}

Figure 2 shows the characterization of the total COD_{Cr} of the raw material and the treated excess sludge. This characterization expresses the change in content after hydrothermal reaction. Here the total COD_{Cr} was classified into four categories: readily biodegradable substrate (S_S), slowly biodegradable substrate (X_S), soluble non biodegradable substrate (S_I) and particulate non biodegradable substrate (X_I).

In the raw sample, approximately 90% of the total COD_{Cr} was non biodegradable substrates, with approximately 85% being X_I and only 5%, S_I. As the reaction temperature was increased, the S_I and X_I fractions were hydrolyzed into biodegradable substrates. Although the total fraction of non biodegradable substrates (S_I+X_I) continuously decreased, the S_I fraction increased up to a reaction temperature of 300°C. At reaction temperatures of 350 and 400°C, the S_I fraction decreased to approximately 20 and 3% of the total COD_{Cr}, respectively. The presence of S_I in wastewaters is undesirable because this fraction cannot be separated from the water in the settling stage and will be released into the environment. In some cases, some of the S_I can be a precursor of compounds that are carcinogenic for human beings. Thus, a further stage in the wastewater treatment process needs to be created in order to reduce the S_I fraction.

On the other hand, the fraction of X_S increased to 34% of the total COD_{Cr} at a reaction temperature of 200°C and did not change significantly when the reaction temperature was increased to 300°C. However, at 350 and 400°C, not only X_S, but also S_S were obtained, particularly in the case of 400°C, 67 and 31% of the total COD_{Cr} was S_S and X_S, respectively.

In the case of excess sludge treated at 200, 250 and 300°C, where a relatively low TOC reduction was obtained, the S_I and X_I fractions represented more than 65% of the total COD_{Cr}. On the other hand, at 350 and 400°C, where a relatively large TOC reduction was obtained, the S_I and X_I fractions were reduced to less than 40% of the total COD_{Cr}. Moreover, the S_S fraction was produced only at reaction temperatures higher than 350°C.

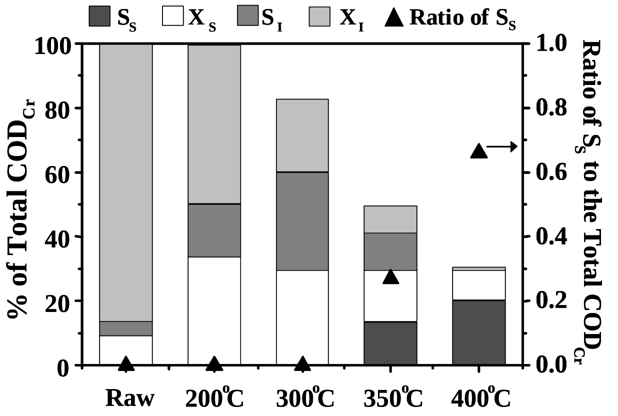

Figure 2: Change in content of the total COD_{Cr} of the excess sludge treated by hydrothermal reactions.

Table 1: Variation in acetic and propionic acids in the treated excess sludge

Specification	Raw	200°C	250°C	300°C	350°C	400°C
Acetic acid	0	50	300	420	560	720
Propionic acid	0	0	250	350	170	50

Unit: [mg/L]

Effect of S_S on the Phosphate Release Activity

Table 1 shows the results on acetic and propionic acid concentrations in the excess sludge before and after hydrothermal reaction.

In the raw material, a zero concentration was observed for both acetic and propionic acids. However, when the reaction temperature was increased, the concentration of these acids increased, reaching a concentration of 720 mg/L at 400°C, which is 16% of the S_S fraction. On the other hand, the concentration of propionic acid increased up to a reaction temperature of 300°C, but at higher temperatures it started to decrease. This decrease was caused by the degradation of propionic acid by hydrolytic reaction into a simpler molecular structure, i.e., acetic acid. From these results, it could be demonstrated that hydrothermal reaction can successfully produce VFAs, a carbon source essential for EBPR.

The importance of VFAs to the EBPR processes has been exhaustively studied (Mino et al., 1998). It is clear that VFAs, such as acetic and propionic acids, are directly used as carbon source by the PAOs. However, the ability to use S_S or X_S as carbon source to obtain stable phosphate removal has not yet been elucidated. In the S_S fraction, not only the VFAs, but also other substrates that can be readily fermented into VFAs by the microorganisms, are included. On the other hand, the X_S fraction cannot be directly consumed by the microorganisms, but it is known that it can be used as carbon source after extra cellular hydrolytic reactions. These reactions transform X_S into S_S, and the latter is then fermented to form VFAs. Therefore, the capacity of PAOs to use S_S or X_S as carbon source needs to be studied.

Figure 3 shows the results of phosphate release tests under anaerobic conditions. The treated excess sludge was used as carbon source.

A control test was also carried out using sodium acetate as sole carbon source in order to verify the EBPR activity of the activated sludge. From the results of phosphate release in the first half hour of the test, the phosphate release rate was estimated at 3.7 mg-P/g-SS.(1/2 hr). This suggests that the activated sludge had sufficient EBPR activity. The overall phosphate released in the tests using the treated excess sludge as carbon source was lower than that released in the control test. However, the initial concentration of VFAs in the treated excess sludge is different from that in the control, and thus the results cannot be directly compared.

From the results, the highest overall phosphate release was obtained for the excess sludge treated at 400°C, followed by that treated at 300°C. In addition, an appreciable difference in the slope of the phosphate release trend was obtained in the first half hour of the test. For the excess sludge treated at 400°C, the slope obtained was higher than those for the sludge treated at 300 and 200°C. In this time period, the PAOs used the VFAs as carbon source and released phosphate into the bulk liquid. The VFAs were completely consumed from the medium, as can be observed in Figure 4, which shows the variation in concentration of acetic acid in the medium during the phosphate release test.

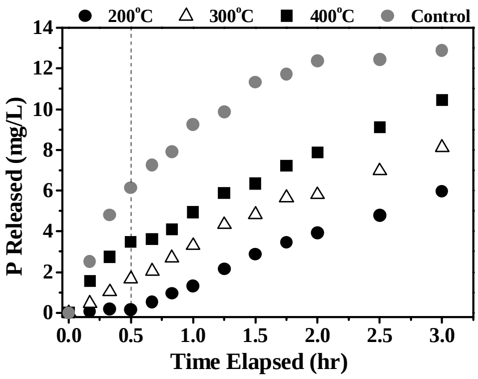

Figure 3: Phosphorus release tests under anaerobic conditions using treated excess sludge as carbon source.

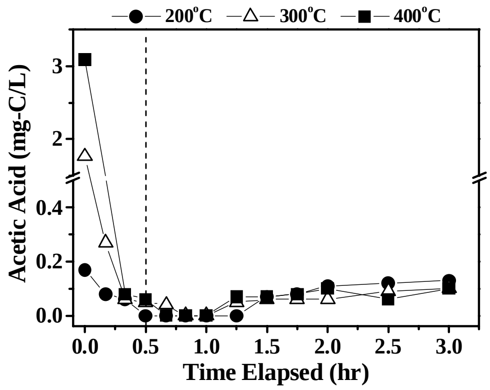

Figure 4: Consumption of acetic acid in the phosphorus release tests using the treated excess sludge as carbon source.

In the first half hour, the concentration of acetic acid dropped to a value near zero as a result of its consumption by the PAOs. However, after this time period, phosphate was still being released. It is suggested that the fermentation of S_S to acetic acid caused a continuous release of phosphate. In other words, as the S_S was fermented, the acetic acid produced was mostly used as carbon source and phosphate continued to be released. The excess acetic acid produced was then released into the bulk liquid.

Using excess sludge treated at 200°C, only 0.14 mg/L of phosphate was released in the first half hour, since the concentration of VFAs in the medium was very low. After this time period, phosphate release by hydrolysis of X_S started. Lower overall phosphate release was then obtained, since the hydrolysis of X_S took place in two steps. First, the X_S was hydrolyzed into S_S and then the S_S was fermented and the acetic acid formed was used as carbon source by the PAOs.

The results obtained in the phosphate release tests demonstrate that the S_S and X_S fractions produced by hydrothermal reaction can be a potential carbon source for the PAOs.

CONCLUSIONS

The possibility of reusing excess sludge treated by hydrothermal reaction as carbon source for EBPR processes was studied. Excess sludge obtained from a fish-processing industry located in Japan was treated in HTHP water and the improvement in biodegradability and the change in content of the total COD_{Cr} were addressed. The results showed that when the reaction temperature was increased, the X_S and S_S fractions increased, reaching values of 31 and 67% of the total COD_{Cr}, respectively, for the excess sludge treated at 400°C. In the S_S fraction, 16% were composed of acetic acid, an essential carbon source for the PAOs. In addition, phosphate release tests were carried out under anaerobic conditions. The results demonstrated that not only are VFAs used as carbon source, but also that phosphate release occurred by fermentation of S_S or hydrolysis of X_S in the absence of VFAs in the medium. These results provide important evidence that encourages the reuse of treated excess sludge as carbon source for EBPR processes.

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