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The study on the separate collection and nutrients recovery of urine in municipal wastewater

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ABSTRACT

In consideration of the high N and P contents of urine in municipal wastewater, a technical idea of collecting urine separated from municipal wastewater for recovery of N and P is put forward to enhance the poor performance of sewage treatment plants in N and P removal due to high contents of N and P in municipal wastewater, the relatively low content of organic carbon source as well as the unbalanced ratio of C/N. By adding activated sludge in the collected urine, the decomposition of urea and polyphosphates in urine and their transformation to ammonia nitrogen and phosphate is highly promoted, which provides basic conditions for collecting N and P from urine through magnesium-ammonium-phosphate precipitation (also known as struvite formation). Under the conditions where pH = 5 and sedimentation time = 5 min, $MgCl_2$ and sodium dihydrogen phosphate are added as magnesium salt and phosphorous source with Mg:N:P proportion of 1.4:1:1 (molar ratio); the best recovery efficiency is obtained at which the recovery rate of N and P are nearly 95 and 98%, respectively. According to the analysis result of X-ray diffraction, the main precipitate is $NH_4MgPO_4{\cdot}6H_2O$ with a fraction of 70% among all recovery products with excellent values as fertilizers.

Keywords: Municipal wastewater; Urine; Nitrogen and phosphorus recovery; Magnesium ammonium phosphate (MAP)

1. Introduction

In general, there are high concentration of nitrogen and phosphorus in urine [1]. For urine just excreted from human bodies, nitrogen exists in the form of urea with a content of 8,000–10,000 mg/L, while phosphorus exists in the form of polyphosphate with content of 700–2,000 mg/L [2,3]. Most N and P nutrients in municipal wastewater are from urine. According to related data, 88–98% of nitrogen and 65–71% of phosphorus [4] come from urine in toilet wastewater, while in municipal wastewater this ratio comes to 80 and 50%, respectively [5].

Currently, N and P are hard to be removed completely through secondary biological treatment

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due to high loads of N and P in mixed municipal wastewater containing manure and urine, especially when there is a lack of carbon source in the raw water [6]. N and P nutrients are important components in fertilizers. Once these nutrients can be recycled, not only the high N and P loads in sewage inflow can be solved and the quality of effluent can be improved but also certain economic benefits can be obtained because recycled nutrients can be processed into fertilizers for agricultural production [7]. Therefore, the treatment of separately collected urine and study on effective methods for N and P recycling are of great significance in improving effluent quality, decreasing the emission loads of N and P nutrients into natural water as well as reducing the risk of water eutrophication. Therefore, separate collection of urine and recovery of N and P become one of the best ways to solve those problems.

By now, the study on urine nutrients recycling has been mainly focused on three aspects: recovery of phosphorus alone, recovery of nitrogen alone, and simultaneous recovery of N and P [2]. A study from Udert [8] indicated that magnesium ammonium phosphate (MAP) precipitation is effective to recover urine phosphorus alone. By adopting ion exchange method, Liberti [9] successfully recovered 95% ammonia nitrogen from wastewater. Iso-butyl diurea method is effective in recovering urine separately, but the method is limited by its low recovery quality and higher requirements for conditions [10,11]. Struvite formation could recover about 90 and 98% of nitrogen and phosphorus [5,12] but this result can be only achieved under the condition of complete decomposition and transformation of urine urea.

How to accelerate the conversion of urea into ammonia nitrogen is becoming the key step of recovering N and P in urine by MAP precipitation. It is an effective approach to promote the urea decomposition by adding urease to urine [13]. However, the method is limited by the high price of the urease. The operating conditions of adding chemicals reagent method are tough and the conversion rate is low [14]. In nature, most fungi and bacteria could generate urease [15]. Hence, promoting the urea decomposition under microbial actions is a promising technology. So far, there has been no relevant report about this area.

In this paper, the urine is collected separately from pipe network. An experimental study on the promotion of microorganism in degrading urea was carried out. When urea and polyphosphates are, respectively, converted into ammonia nitrogen and phosphate completely, MAP is employed for further study on recovery of N and P and the operational conditions of MAP precipitation are optimized, which is of practical significance in decreasing N and P emission and reducing the operating load in wastewater treatment [15].

2. Materials and experimental methods

2.1. Materials and reagents

2.1.1. Collection of urine samples

Nitrogen content in morning urine is higher than that in urine excreted at any other time of the day. To guarantee a better representativeness of the urine used in this study, a mixture of morning and noon urine from a specific group of people collected in real time is adopted as the urine sample. After uniformly mixing, the urine sample is immediately put into PTFE laboratory bottles (with stoppers) from the same batch. All samples are stored in 4℃ and avoid direct sunlight. All laboratory bottles have been sterilized beforehand to protect the samples from being polluted.

2.1.2. Experimental reagents

Activated sludge used in this study to promote urea decomposition is taken from Beishiqiao wastewater treatment plant in Xi'an. The moisture content of the activated sludge is 80 and the sodium hydroxide, hydrochloric acid, magnesium chloride, and potassium dihydrogen phosphate are analytically pure.

2.1.3. Analysis and testing methods

The total nitrogen in urine is represented by TN and the urea decomposition is determined by analyzing NH_3-N. The precipitation and recovery effects of N and P are determined by analyzing NH_3-N and TP in the liquid. Analysis of TN, NH_3-N, and TP is carried out by employing peroxide potassium sulfate-ultraviolet spectrophotometry, Nessler's reagent spectrophotometry, and ammonium molybdate spectrophotometric methods, respectively [16].

SP-500UZ(C)-C digital camera (OLYMPUS, Japan) is used in achieving sharp pictures for identifying and analyzing participates and the MAP content of the participates is determined through X-ray differaction analysis by D/amx 2400X (Rigaku, Japan).

2.2. Experimental methods

2.2.1. Effect of pH value on the forms of nitrogen and phosphorus in urine

Since only N in NH_3-N and P in PO_4^{3-} can be recovered when MAP precipitation is adopted, authors have studied the transformation effects of urea and phosphate in urine with different pH values firstly. Three groups of 100 mL PTFE laboratory bottles (with stoppers) were filled with the collected urine sample and the pH was adjust to 2.5, 6.5, and 10, respectively by adding in hydrochloric acid and sodium hydroxide. The bottles were placed in an incubator at 20℃. Each batch of sample (of the three) contains 20 small bottles where one small bottle of each kind is used only once for analysis each day.

2.2.2. Promotion of urea decomposition and nitrogen transformation

Three groups of 100 mL PTFE laboratory bottles (with stoppers) were filled with the collected urine sample and activated sludge was added to each group of sample with dosages of 10, 20, and 50 g/L. Each batch of sample contains 20 small bottles where one small bottle of each kind is used only once for analysis each day.

2.2.3. Synchronous recovery of nitrogen and phosphorus from urine

Theoretically, 1 mol of Mg^{2+} is required to recover 1 mol of NH_4^+ and 1 mol of PO_4^{3-}. However, in urine, ion composition is complex and there may be anions which react with Mg^{2+} and consume Mg^{2+}. Therefore, dosage of Mg^{2+} should be greater than the theoretical one in experiment. In this paper, magnesium chloride and potassium dihydrogen phosphate are added as magnesium salt and phosphorous source to study the synchronous recovery effects of N and P in different ratios of Mg:N, P:N (molar ratio) and determine the optimal reaction condition.

3. Results and discussion

3.1. Effect of pH value on the variation of ammonia nitrogen and TP in urine

The fresh urine samples with pH values of 2.5, 6.5 and 10 are well-sealed, respectively, in a constant temperature box of 20℃. The varying patterns of ammonia nitrogen and phosphate in the samples with time are shown.

As shown in Fig. 1, the content of ammonia nitrogen under three different pH values increases slightly and sustains at a relatively low level for which the content of ammonia nitrogen is far from that of TN. The content of ammonia nitrogen reaches its lowest value when pH = 2.5, while remains highest at normal condition (pH = 6.5). Some data show that under acid condition, the components of urine tend to be more stable [17]. Fig. 2 shows that under different pH values, the content of TP in the urine increases greatly and reaches its maximum after 1 d. Then it remains steady at pH = 2.5. While when pH equals to 6.5 and 10, the TP decreases rapidly. After 3 d, it remains relatively stable. It can be seen from the data that the polyphosphate in urine can be rapidly hydrolyzed into phosphate group and the higher of the pH value, the easier that phosphate group reacts with calcium and magnesium ions to form precipitates [18,19]. Therefore, how to improve the hydrolysis degree and rate of the urea is the key factor to increase the efficiency of N and P synchronous recovery by MAP precipitation.

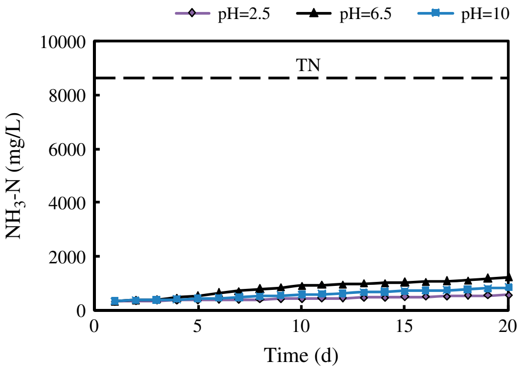

Fig. 1. Effect of pH value on content of NH_3-N in urine.

3.2. Promotion of NH_3-N transformation in urine

In this study, activated sludge is added into urine (from Bei Shiqiao sewage in Xi'an) under at T = 20℃ and pH = 6.5 to promote the hydrolyzing of urea. The result is shown in Fig. 3. Meanwhile, the nitrogen content of added activated sludge is observed to determine the authentic promoting efficiency of urea hydrolysis as shown in Fig. 4.

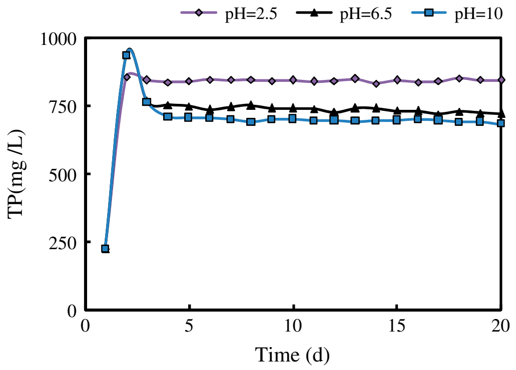

Fig. 2. Effect of pH value on content of TP in urine.

It can be concluded from Fig. 3 that when the activated sludge dosage comes to 10, 20, and 50 g/L, the hydrolysis conversion rate of urea in urine increases rapidly to about 82% in 2, 4, and 6 d, respectively. It can be seen from Fig. 4 that the content of TN and ammonia nitrogen in the added activated sludge can be neglected as compared with that in the urine. Therefore, the rapid increasing content of ammonia nitrogen shown in Fig. 3 is caused by the promoting effect of urease on hydrolysis rate of urine.

From the above experiments, we can conclude that by adding certain quantity of activated sludge, a quick and complete transformation of urea into ammonia nitrogen can be achieved and the polyphosphate will be rapidly hydrolyzed into phosphate as well. The N and P synchronous recovery in urine by MAP precipitation can be expected on the basis of the urine decomposition and polyphosphate hydrolysis.

3.3. Recovery of N and P from urine

3.3.1. Determination of composite ratio of N and Mg

$MgCl_2$ and NaH_2PO_4 are added to the sample with a composite ratio [Mg]:[N] of 0.8:1, 1:1, 1.2:1, 1.4:1, and 1.6:1, respectively (molar ratio) to conduct the experiment of N and P recovery from urine on the basis that urea is catalyzed by activated sludge (sedimentation time is 5 min). The result is shown in Fig. 5. It can be seen that the recovery rates of N and P vary under different composite ratios. When the composite ratio is 1:1, the recovery rates of TP and TN are 84 and 78.5%, respectively. When the ratio is increased to 1.4:1, the recovery rates of TP and TN increase to 97.5, 93.8% accordingly. After that, the recovery rate shows little increase with the ever-increasing composite ratio. Considering to reduce the dosage of drugs to avoid introducing new contaminants and to guarantee the purity of recovered products, [Mg]:[N] = 1.4:1 is determined as the composite ratio.

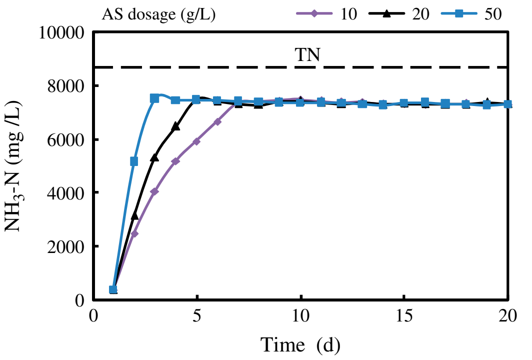

Fig. 3. Variation of decomposition efficiency of urea under different activated sludge dosage.

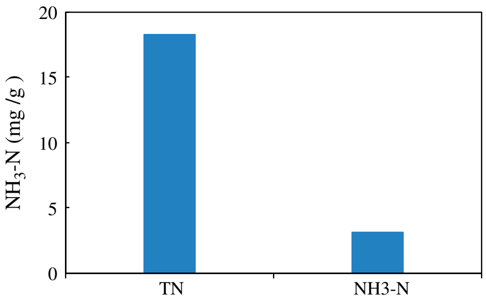

Fig. 4. Content of nitrogen in activated sludge.

3.3.2. Determination of composite ratio of N and P

$MgCl_2$ and NaH_2PO_4 used as added sources of magnesium and phosphorus with fixed composite ratios [Mg]:[N] = 1.4:1 and [N]:[P] are 1:1 and 1:0.8 (mole ratios). The pH values are adjusted to 7, 8, 9, 10, 11, and 12, respectively. The experiment of N and P synchronous recovery from urine is conducted on the basis that urea is decomposed and catalyzed by activated sludge (sedimentation time is 5 min). The results of residual determination of ammonia nitrogen and total phosphorus are shown in Figs. 6 and 7.

It can be seen from Fig. 6 that the variations of residual ammonia nitrogen and total phosphorus in urine under two different n(N):n(P) composite ratios are similar. When pH < 10, the residual ammonia nitrogen decreases as the pH increases. When pH = 10, the residue reaches the lowest with a maximum recovery rate of 94.1%. When pH > 10, the residue begins to increase which is mainly because in higher pH condition, NH_4^+ will separate from NH_4MgPO_4 to form a less soluble $Mg_3(PO_4)_2$.

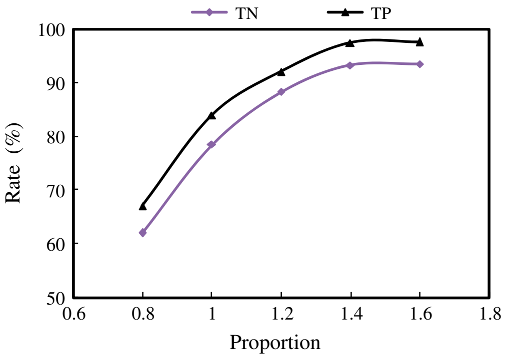

Fig. 5. Experiment on composite ratio of N, Mg.

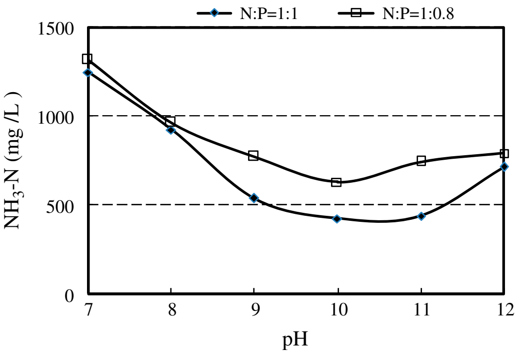

Fig. 6. Variation of ammonia nitrogen residue in urine under different pH.

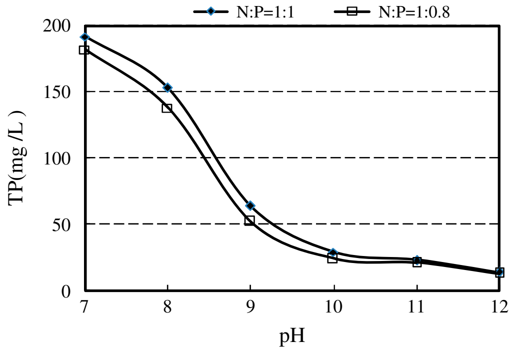

Fig. 7. Variation of total phosphorus residue in urine under different pH.

Fig. 7 indicates that the residual phosphorus decreases as the pH increases. When pH = 12, the total phosphorus reaches the lowest with a recovery rate above 98%. This is because in higher pH condition, the less soluble $Mg_3(PO_4)_2$ will be formed and the PO_4^{3-} consumption by excess Mg^{2+} will decrease the concentration of the total phosphorus.

It can be concluded from the experimental results that the variation of ammonia nitrogen is not consistent with that of the total phosphorus. Therefore, the pH, composite ratio, and other influencing factors shall be considered in determination of optimal N and P recovery condition. Analyzing the experimental results, the optimal operating condition is determined as: pH = 10.5 and the composite ratio of added magnesium and phosphorus sources is [Mg]:[N]:[P] = 1.4:1:1.

3.3.3. *Identifying the recovery products*

The research result indicates that taking NaH_2PO_4 as added phosphorous source under the condition that [Mg]:[N]:[P] = 1.4:1:1 and pH = 10.5, the best recovery result for nutrients in urine after being promoted by activated sludge can be obtained. The precipitates picture is taken by SP-500UZ(C)-C digital camera (OLYMPUS, Japan) and the recovery product morphogram under the optimal condition is shown in Fig. 8.

To further determine the components of precipitates, D/amx2400X (Rigaku, Japan) is adopted to analyze MAP content in precipitates by X-ray diffraction. The result is shown in Fig. 9.

It can be seen that the diffraction peak when $2\theta = 16.2^\circ, 19.7^\circ, 30.2^\circ, 32.0^\circ$, and 33.5° belongs to the crystal faces (020), (111), (040), (120), (212) of hexahydrate and MAP (ASTM No.: 15-0762). According to the results, the main component of precipitate is $NH_4MgPO_4{\cdot}6H_2O$ with content about 70% and the remaining part may be attributed to the impurities induced by dosing activated sludge.

3.4. *Dispose of residual urine*

After the N and P in urine sample are recovered by MAP precipitation, the compositions of dominant contaminant in urine sample under optimal operational condition are analyzed. The result is shown in Table 1.

Table 1 indicates that after N and P synchronous recovery by MAP precipitation, contents of TN, urea, and TP decreased sharply with a removal rate above 90%, respectively. While NH_3-N shows little variation.

Fig. 8. Morphogram of precipitates.

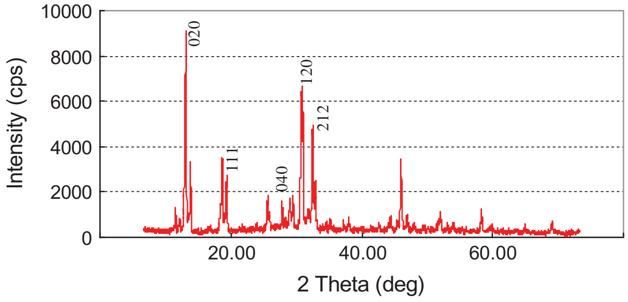

Fig. 9. Analytical graph of precipitates diffracted by X-ray.

Table 1
Main components and contaminant index after N and P synchronous recovery from urine

Parameter (mg/L)	Value
TN	940–1,050
NH_3-N	405–430
Urea	140–175
TP	32–38
COD	6,300–7,500

The reduction in COD is not great but still as high as 7,000 mg/L. As the proportion rate of urine in municipal wastewater is less than 1%, the treated urine can be discharged into sewage networks directly. It will mix with wastewater from other sources and flow to wastewater treatment plants finally for ultimate treatment to prevent pollution to the environment.

4. Conclusion

(1) The experimental results indicate that it is feasible to add activated sludge into urine to hydrolyze urea into ammonia nitrogen by the indirect catalyzing effect of microorganisms. When the dosage of the activated sludge is 50 mg/L, the decomposition transformation rate of urea can reach 82% within 2 d.

(2) With activated sludge promoting the urea decomposition, NaH_2PO_4 is adopted as the phosphorous source. Under the condition that a composite ratio of [Mg]:[N]:[P] = 1.4:1:1 and pH = 10.5, more than 95% of N and P can be recycled synchronously by MAP precipitation.

(3) After identified by X-ray diffraction, the $NH_4MgPO_4 \cdot 6H_2O$ shares 70% in precipitate composition and has an excellent practical value as fertilizer.

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