Electrolytic Treatment of Human Urine to Remove Nitrogen and Phosphorus

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Depending on the dilution ratio, nitrogen and phosphorus in human urine could be completely removed by electrolytic treatment using an iron electrode. Chemical oxygen demand (COD_{Mn}) could also be reduced by 85%. The treatment would decrease the nitrogen and phosphorus levels in domestic wastewater to 20 and 50%, respectively.

Water contamination by nitrogen and phosphorus is a serious concern worldwide. Nitrogen in the nitrate form in drinking water causes methemoglobinemia in infants and gastric cancer in adults,[1] and phosphorus has recently been reported to have a greater impact on endangered plants than nitrogen.[2] One of the effective ways to solve the problem of nitrogen and phosphorus contamination in water is nitrogen and phosphorus removal from human urine that is collected. This is because human urine contributes to approximately 80% of the nitrogen and 50% of the phosphorus present in domestic waste water,[3] although only 1.5 L of urine per adult is released in a day.[4] Therefore, a dramatic decrease in the nitrogen and phosphorus released into sewage would result in a suppression of the adverse environmental effects if urine can be separately collected from feces in toilets. However, current technologies to remove nitrogen and phosphorus cannot be applied to the urine treatment in toilets because biological methods require large facilities and physicochemical methods represented by ion exchange and reverse osmosis only concentrate nitrogen and phosphorus, but do not eliminate them. Addressing the problems, we have used an electrolysis method that uses Fe electrode[5] to treat both constituents. In this paper, we report an electrolytic treatment of human urine using the Fe electrolysis system that enables us to reduce the nitrogen and phosphorus levels by more than 95% in toilets.

A 2× stock solution of model urine (($(NH_2)_2CO$, 714 mM; KH_2PO_4, 16 mM; K_2HPO_4, 16 mM; NaCl, 260 mM; $CaCl_2$, 7.3 mM) was prepared. Various dilutions (1/2 to 1/20) of the model urine were prepared with 300 mM NaCl. An electrode system consisting of an iron (Fe) electrode sandwiched between platinum–iridium DSA® (PtIr) electrodes (Tanaka Kikinzoku, Japan) (PtIr/Fe/PtIr) was used. The diluted model urine solution (80 mL) was electrolyzed with a constant current of 0.8 A (40 mA/cm^2). The first round of electrolysis was performed with the PtIr/Fe/PtIr system where PtIr was set as the anode for 0.7 to 7 h depending on the dilution ratio. During the treatment, fractions of the solution were occasionally withdrawn and subjected to analytical measurements. Nitrogen from nitrate (NO_3^--N), nitrite (NO_2^--N), and ammonium (NH_4^+-N) were measured by ion chromatography (LC-10A, Shimadzu, Japan), and total phosphorus (T-P) and total nitrogen (T-N) were measured by colorimetry using a spectrophotometer (TNP-10, TOA-DKK, Japan). COD_{Mn} was measured by both colorimetry using a spectrophotometer (DR4000, Hach, U.S.A.) and UV absorption at 230 nm using a UV–vis spectrophotometer (V-560, Jasco, Japan). Figure 1 shows the time-dependent variation in the concentration of nitrogen compounds during the electrolytic treatment of the model urine that was diluted 10 times (the 10-times diluted sample was found to be the most efficient in nitrogen reduction; data not shown). As shown in Figure 1a, NH_4^+-N and NO_2^--N levels increased just after the start of the treatment; decrease in their levels was followed by an increase in NO_3^--N, although T-N steadily and considerably decreased with time (Figure 1b). Judging from the quantity of nitrogen removed, most of the urea in the diluted urine solution had decomposed to gaseous nitrogen compounds and only a fraction changed to ammonia (and isocyanic acid). Ammonia was then oxidized to nitrite or nitrogen gas via a reaction with electrolytically produced chlorines (hypochlorous acid and hypochlorite). The final product was nitrate and it remained constant. The existing nitrate concentration was a result of equilibration between reduction of nitrate to nitrite at the iron cathode and nitrite oxidation at the anode or by chlorines.[5]

A freshly collected urine sample (T-N, 5000 mg/L; T-P, 500 mg/L; chloride, 4000 mg/L) was diluted with 300 mM NaCl to prepare various diluted samples (1/1 to 1/20). The second round of electrolysis was performed using the same electrode system and the same current condition. First, Fe was used as the cathode for 3 to 9 h and later as the anode for 3 to 10 min. T-P in urine exists as PO_4^{3-}; therefore, anodically dissolved iron ions can form insoluble iron phosphate ($FePO_4$). Hence, T-P is removed. Figure 2 shows the nitrogen and phosphorus removal ratio as a function of T-N concentration. As shown in the figure, both nitrogen and phosphorus removal proceeded even when Fe was the cathode; however, the process was facilitated when Fe was switched to anode. During the electrolysis with Fe as the cathode, there was only a slight decrease in T-N removal at the beginning; however, when T-N reached a concentration of 250 mg/L, it could be completely removed only when Fe func-

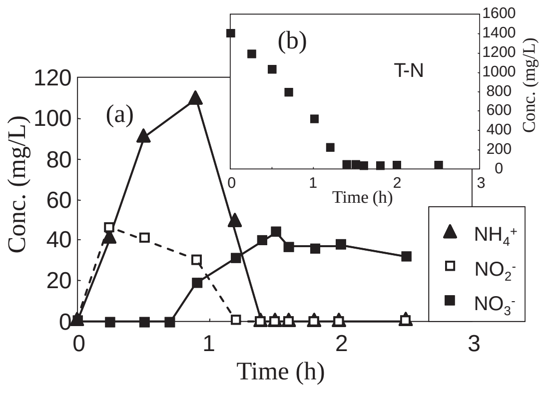

Figure 1. Nitrogen removal by iron electrolysis (model urine). Time-dependent variation in concentration of (a) ammonium, nitrite, and nitrate ions and (b) total nitrogen. Sample to be treated was prepared by diluting the model urine solution 10 times with 300 mM NaCl (see text).

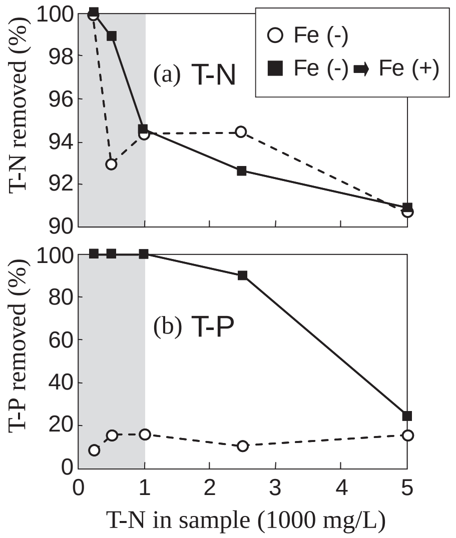

Figure 2. Nitrogen and phosphorus removal from urine by iron electrolysis. Dilution ratio-dependent variation in (a) Total nitrogen and (b) Total phosphorus. Sample to be treated was prepared by diluting a fraction of human urine collected prior to the experiment. ○, Treatment with iron cathode; ■, Treatment with iron cathode followed by iron anode. Complete removal of T-P is represented by dark area.

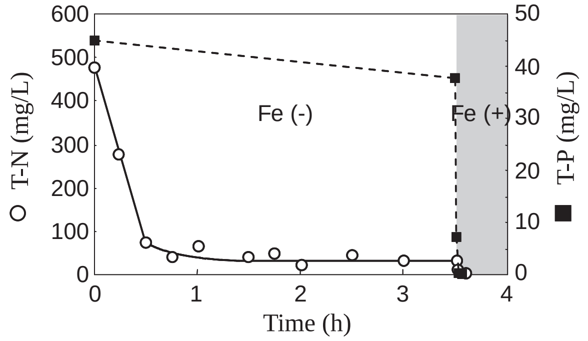

Figure 3. Trend in nitrogen and phosphorus removal from urine by iron electrolysis. Treatment was performend first by iron cathode and then by iron anode after switching the polarity at 3.5 h. Urine diluted 10 times was used. ○, Total nitrogen; ■, Total phosp horus.

tioned as the anode. This was believed to be due to the suppression of the cathodic function of the Fe electrode to reduce nitrate and nitrite to ammonia due to deposition of compounds present in the urine onto the Fe surface. During this deposition process, T-P removal to a small extent could occur if Fe was the cathode (Figure 2b). When Fe was switched to anode, T-N removal was slightly facilitated in a range less than 1000 mg/L (Figure 2a), whereas T-P removal was thoroughly accomplished in the same T-N range. A significant decrease in T-P removal with an increase in initial T-N concentration (Figure 2b) was possibly because Fe ion dissolution was hindered by the compounds deposited on the Fe electrode during the Fe cathode period. Removal of the residual T-N when Fe was the anode was possibly a result of co-precipitation of urea and its decomposed form with $FePO_4$ because T-N increases again if the electrolytic treatment with Fe anode was continued even after achieving the minimum residual T-N. From the above results, it can be concluded that as long as T-N is less than 1000 mg/L, 95% of T-N and 100% of T-P can be removed from urine using the iron electrolysis process. In most cases, the concentration of T-P in urine is less than one-tenth of that of T-N. Here, we used the urine sample with a T-P that was 10% of T-N; therefore, it was concluded that the results in Figure 2 represented a treatment process of a typical urine sample with T-P concentration of a highest range. The time-dependent variation in T-N and T-P during the electrolytic treatment of the 10-times diluted urine solution corresponded to a T-N: 500 mg/L in Figure 2 is shown in Figure 3. The figure indicates the progress of the treatment process—T-N decreased by 95% in approximately 45 min and thereafter remained unaltered, whereas not only T-P but also the residual T-N was almost completely removed when Fe was switched to anode. The initial T-N removal process followed the zeroth-order reaction irrespective of the dilution (data not shown), indicating that urea was decomposed by the electrolytically produced chlorine.

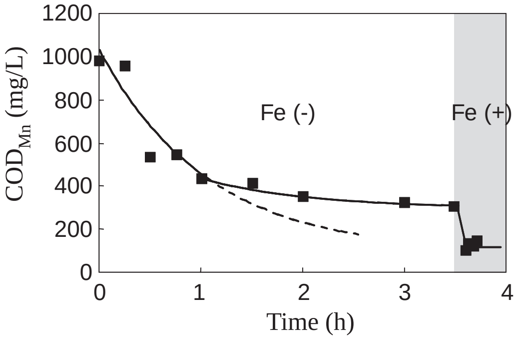

Figure 4. Time-dependent reduction in $\mathrm{COD_{Mn}}$ through iron electrolysis. Treatment was performend by iron cathode for 3.5 h and thereafter by iron anode. Urine diluted 10 times was used. $\mathrm{COD_{Mn}}$ was determined based on the absorbance readings at 230 nm.

Contrary to the T-N removal reaction, decrease in $\mathrm{COD_{Mn}}$ initially followed the first-order reaction followed by a very slow decrease (Figure 4). This indicates that COD was decomposed not only by the electrolytically produced chlorine but also by other processes such as a diffusion-controlled oxidation reaction at the surface of the anode. The slow decrease was possibly due to the formation of organic compounds that were not easily decomposed by chlorine oxidation. Nevertheless, Fe anode led to a further decrease in the residual COD to achieve 85% removal.

In summary, nitrogen and phosphorus in human urine could be thoroughly removed by electrolytic treatment using an iron electrode when the total nitrogen was adjusted (diluted) to less than 1000 mg/L. The chemical oxygen demand ($\mathrm{COD_{Mn}}$) could also be reduced by 85%. The treatment would be able to suppress nitrogen and phosphorus levels in domestic waste water to 20 and 50%, respectively. Using the treatment process mentioned here, a dramatic reduction in the environmental impact of water contamination can be achieved by removing nitrogen and phosphorus from human urine.

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