Study on Recovery Source of Phosphorus from Toilet Water by Electrochemistry

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Abstract. The phosphorus resources in our country have accounted for second of the whole world, but it is predicted that the recoverable phosphorus resources can only be supplied by 2020. However sewage only account for about 1~ 2% in the entire volume of sewage waste , sewage contains 90% phosphorus.Electrolysis is a promising technology for simulated urine treatment,with adding magnesium source.In this way,it doesn’t have secondary pollution in case of recovery of phosphorus, while reducing the pressure on sewage treatment plant. Results show that the electrochemical recovery of phosphorus in urine is feasible, the phosphorus recovery rate increases over time. The velocity ratio and the magnesium source storage loading position can enhance the conversion capacity of magnesium to Mg2+, promote recycling of phosphorus, when flow ratio of cathode and anode water is 58:1, the recovery rate of phosphorus in the cathode is 70% above, the recovery rate of anode is more than 90%.

1. Introduction

The phosphorus resources in China are large, but the rich ore resources are few, and the recoverable deposits which more than 30% are only 7% of the total reserves. Phosphate rock difficult to mine, and the most are collophanite with harmful impurities.And it’s difficult to choose. [1] According to data of 2010 from the USGS, the recoverable amount of the global phosphate rock resources can only be supplied for 100~120 years. [2] In 2002, the Ministry of land and resources of China listed the phosphate rock resources as one of the 20 kinds of minerals which could not meet the requirements of the national economic development after 2010. [3] With the increase of population, the demand for phosphate (fertilizer, detergent, etc.)in daily life grows up.Discharging sewage into the water system makes eutrophication more and more serious (30% sewage was discharged without treatment in China), Pollution treatment needs high cost, but it is still difficult to achieve satisfactory results.Phosphorus is a kind of resource consumption whose natural ecological cycle has a feature of non-renewable cycle in a short term. [4] Therefore, phosphorus extraction from sewage can not only slow down the process of eutrophication of water source, but also reduce the pressure of phosphorus resources.Fecaluria accounted for only 1~2% of the volume of sewage, but 90% phosphorus in it, [5] it is necessary to explore the exploitation of phosphorus resources in our dynamic human body.Thus, the resources can be recycled and fully utilized.The general methods of removal of phosphorus from wastewater with Magnesium Ammonium Phosphate Crystallization (MAP),calcium phosphate

precipitation, hydroxyapatite (HAP) crystal, iron and aluminum salt precipitation method , and other new methods represented by ion exchange and adsorption / desorption methods.[6] Struvite crystallization method originated in 1960s. Hyperion found that sewage treatment equipment such as the pipeline of sewage treatment plants and valves are blocked due to scale formation ,which even affects the normal operation of the sewage treatment plant.The main component of this scale is struvite [magnesium ammonium phosphate (MAP)] [7]. Kim et al [8] found that among the different seeds of powdered slag, quartz sand, bone charcoal or phosphorite in crystallization of calcium hydroxy phosphate, it is better to set seed by powder of slag for phosphorus removal. Wang Lili et al [9] found that in the research of domestic wastewater with secondary treatment, polymeric ferric sulfate (PFS) is suitable for treating wastewater with low total phosphorus concentration, while polyaluminium chloride (PAC) is better in alkaline conditions and high content of total phosphorus. Mei Xiang et al [10] found that DSQ resin is efficient for separating phosphorus, with high selectivity and more than 96% elution rate. As the method of adsorption / desorption, Li et al [11] use natural magnetite to adsorb phosphorus in wastewater, but it is affected by temperature.

Electricity is a clean and green. Treatment of urine by electrochemical method without adding chemicals will not cause secondary pollution, and has the advantages of simple operation, small occupied area.The initial experiment shows that this method is feasible, and worth exploring deeply.
The characteristics of electrochemical oxidation technology: First,electron only transfer in electrode and wastewater, without addition of redox agents,which avoid the secondary pollution caused by the addition of chemicals.Second,the reaction conditions is mild, the process can be carried out under normal temperature and pressure.Third,the reactor equipment covers an small area, the operation is simple, the cost is not expensive if the design is reasonable.It can work separately, or combined with other treatment. [12]

2. Electrochemical detail

2.1. Experimental installation

The experimental setup used in this experiment is as follows:

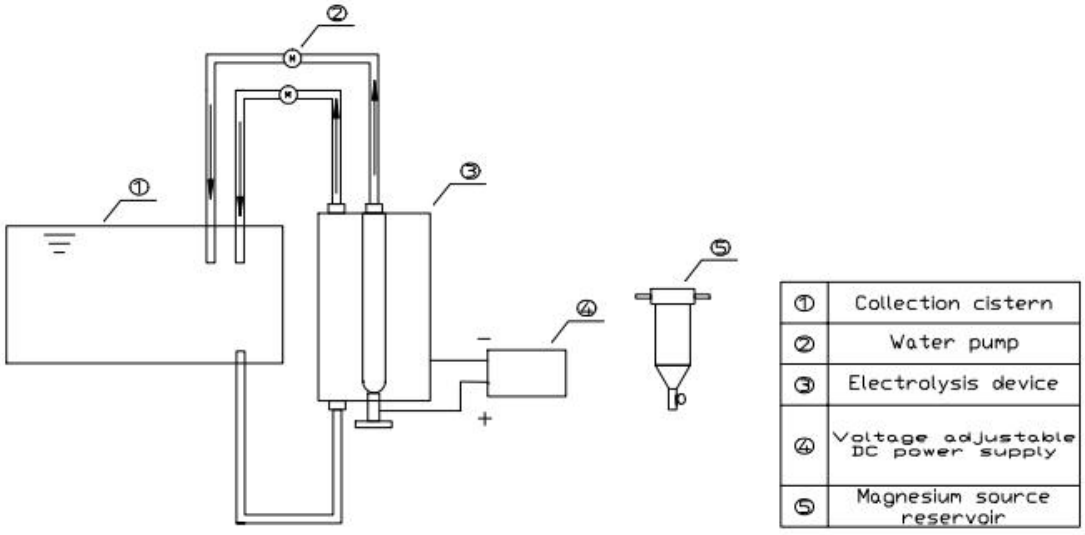

Figure 1. Electrochemical system device structure and magnesium source reservoir diagram

Table 1. The formula of simulated urine [13]

agentia	P/(g/L)	C/(mmol/L)
Na_2SO_4 (anhydrous)	2.3	16
KCl	3.4	46
NH_4Cl	3.9	73
NaH_2PO_4	2.6	17
NaCl	3.0	51
NH_2ONH_2	15.95	266

1. Main electrochemical devices:

Anode: Inert titanium microporous filter electrode made of titanium alloy (Φ=30mm, the porosity is 50%).The structure has a protective effect on the electrode, and at the same time, the porosity of 50% can make the reactant contact more fully, and the electrochemical reaction is more efficient.

Cathode: stainless steel shell, (Φ=100mm).

2. Magnesium reservoir: The magnesium source can be stored in it.Source can be managed well.

Self suction pipeline pump: 45W/12V, flow rate is 4L/min.

2.2. Experimental methods and testing methods

The average amount of each adult fecaluria is 550mL, using 6~ 13L water to flush.[14] Therefore, the mixture is 500ml simulated urine diluted 10 times by deionized water, then treated with electrochemical treatment system.

The phosphorus content in urine is mainly inorganic (salt phosphate).Magnesium storage provides magnesium ions. Mg^{2+} combines with free PO_4^{3-} and NH^{4+} or other ions to form magnesium ammonium phosphate or other precipitatesand.

In this experiment, determination of phosphorus content by molybdenum antimony spectrophotometry, the conductivity of the solution was measured by DDS-11A digital conductivity meter, and the pH value of the solution was determined by PHS-2S digital display acidity meter.

3. Result and discussion

3.1. Influence of voltage

The water flow controlled between anode and cathode is 1:1,the reaction is under different voltage range among 12~22V in 5 hours.The phosphorus content in the cathode and anode effluent was measured.The removal rate of the phosphorus between cathode with anode was calculated was shown in Figure 2. The treatment is best when the voltage is 18V.The reaction is promoted, because the current efficiency is improved due to the increase of voltage. The phosphorus removal rate under 18V is higher than the removal rate under the voltage of 22V, the reason is that at higher than 20V voltage, the degree of ionization of water is high, and Mg $(OH)_2$ was generated by combining $Mg^{2+}$with OH^-, which reduces the ability to combine with PO_4^{3-}.The effect between 20V and 18V has little difference, 18V voltage is smaller , more safe and energy-saving.Therefore, 18V is considered as the best treatment voltage.

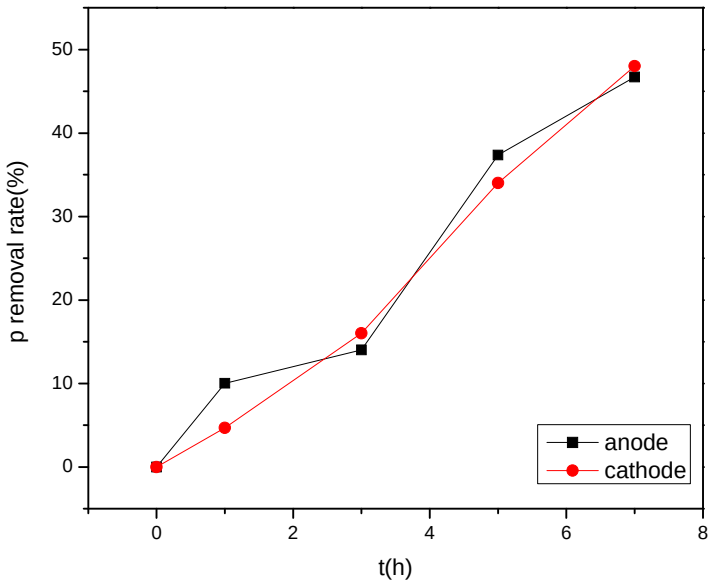

Figure 2. Removal rate of phosphorus

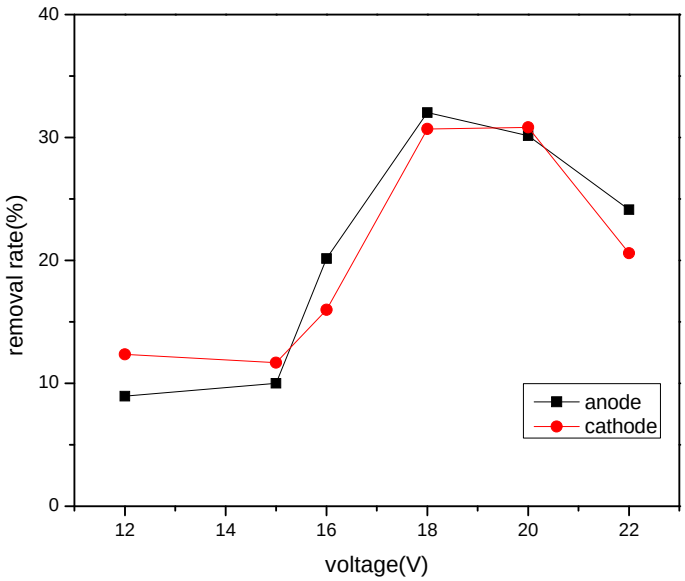

Figure 3. Phosphorus removal rate of urine in the cathode and anode water

The source storage is placed after the cathode outlet, the system works under 18V voltage in 7 hours.The result can be seen from Figure 3, with the passage of time, the phosphorus removal rate is almost increasing in the outlet water. This is because with the continuous entry of Mg^{2+} into the water treatment system, white precipitate is precipitated from solution by the combination of PO_4^{3-} and Mg^{2+}.

3.2. Influence of storage position of magnesium source

If the magnesium storage carrier after cathode outlet , the phosphorus removal rate was the highest in 50%~60%.In this case, it is observed that the corrosion degree of the magnesium is small, which indicates that the supply of magnesium ion is not enough to react fully. Therefore, by reducing the anode flow rate, the pH of anode water is fully reduced.And the magnesium storage device is placed

after the anode water which can improve the magnesium ion supply capacity. The anode flow rate is 0.6ml/s, and the cathode is 36ml/s.The method shown in Fig 4. which is compared with the case where the magnesium is placed at the cathode and the velocity ratio between the cathode and anode is 1:1.It seems that the phosphorus removal rate in the anode water reaches about 90%, twice as much as latter.Meanwhile, in the cathode water it also reaches about 70%.Thus, it is workable to recover phosphorus by electrochemical method.

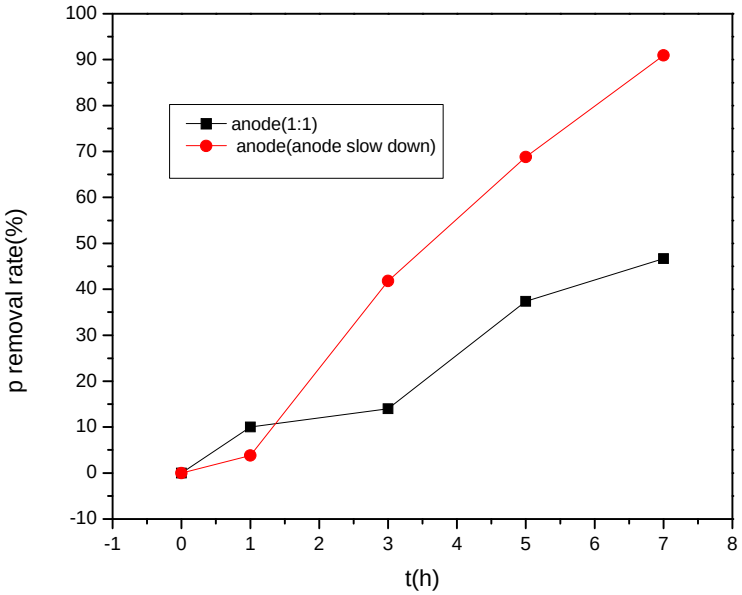

Figure 4. (a) Phosphorus removal rate of urine in the anode water

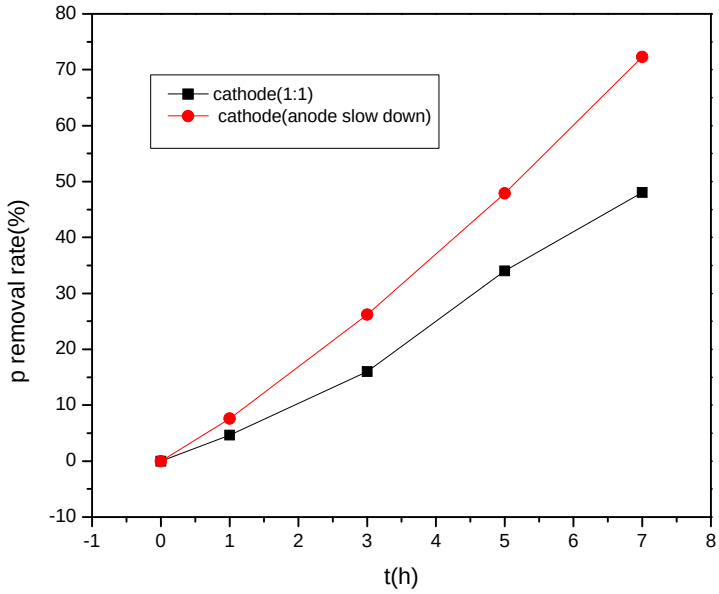

Figure 4. (b) Phosphorus removal rate of urine in the cathode water

pH of solution is shown in Fig 5. pH changes violently when the new treatment is working, especially within the first hour of the reaction.

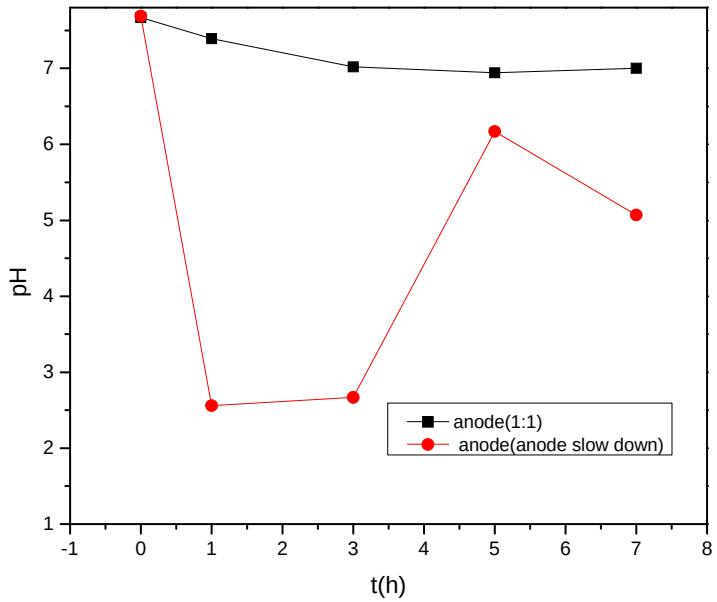

Figure 5. (a) Change of pH in the anode water

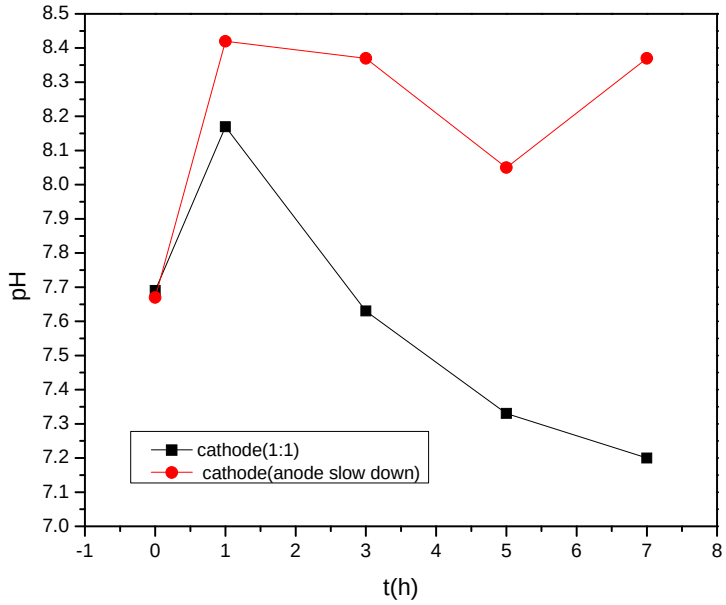

Figure 5. (b) Change of pH in the cathode water

Change of electrical conductivity is shown in Fig.6.Electrical conductivity in the anode water grows up rapidly when the new treatment is working,and it drops down after few hours.However,it always increases when the magnesium source storage carrier after cathode outlet.The factors causing the growth of conductivity can have the following points: Magnesium enters the solution.Urea is continuously decomposed in electrolysis process.In combination with Fig. 5 (a) and Fig. 6 (a) ,the solubility of magnesium increases with the decrease of anode pH.Therefore, the conductivity of the anode water rises rapidly.In combination with Fig. 5 (b) and Fig 6 (b),the decrease of conductivity of cathode water shows that the concentration of ion is decreased, and precipitation is easier to form under alkaline condition.

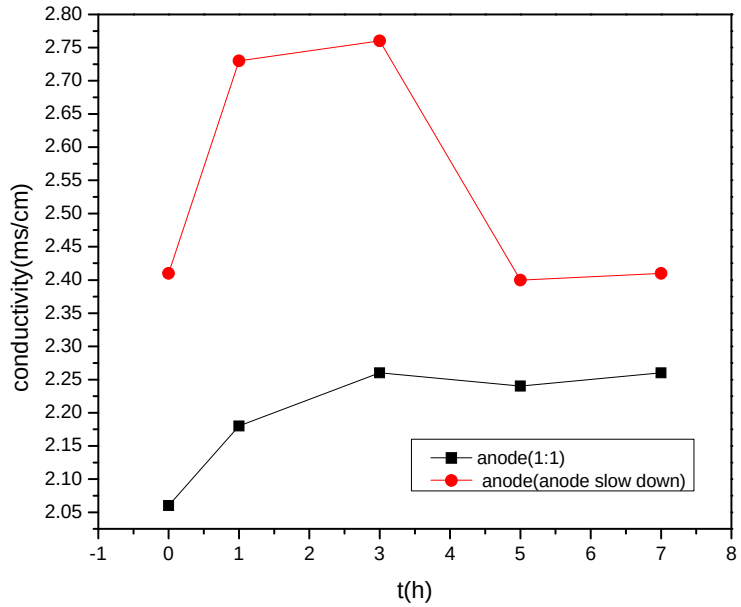

Figure 6. (a) Change of electrical conductivity in the anode water

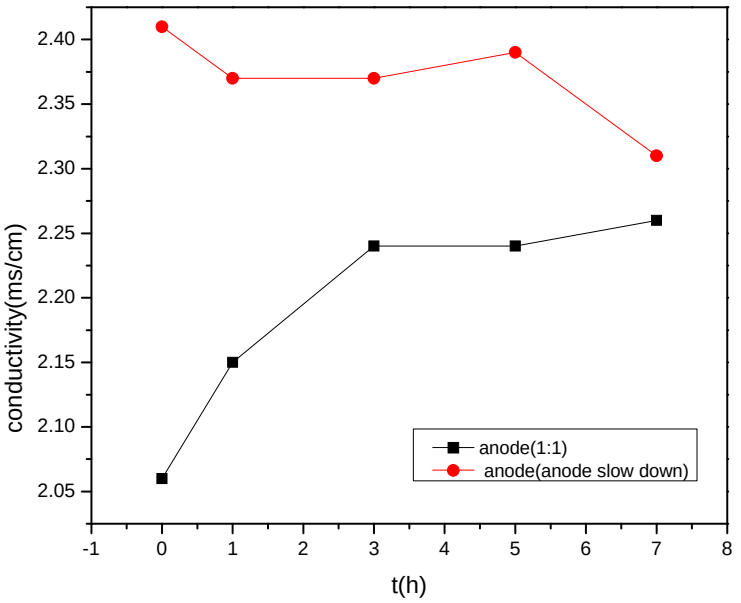

Figure 6. (b) Change of electrical conductivity in the cathode water

This situation can be explained as follows: The pH of anode water decreases with the decrease of flow rate. When the magnesium is placed at the anode, it is corroded in acidic condition and enters into the system with the form of ion. At this point, the cathode pH is increased, and phosphate is easier to combine with other ions such as magnesium ions to form precipitation which has good sedimentation and is easy to collect, and the supernatant with complete sedimentation has excellent clarity.

4. Conclusion

It seems that electrochemical oxidation of human waste is feasible, and the processing does not require very high voltages and much cost.This technology can not only recover the phosphorus resources, but also reduce the pressure of the sewage treatment plant. It meets the demand for phosphorus in human development and hopes to be used in reality.

Acknowledgments

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