2024年臺灣國際科學展覽會
優勝作品專輯

作品編號　030030

參展科別　化學

作品名稱　Resolving the Phosphate Fertilizer Dilemma through Progressive Wastewater Treatment

得獎獎項　一等獎

就讀學校　Shizuoka Kita High School
指導教師　Yuta Fuchigami
作者姓名　Hayato Yamashita;Kento Hagiwara;Kaede Honda

作者照片



Summary

The study aimed to resolve global phosphate scarcity by developing a cost-effective method for phosphorus recovery from industrial wastewater. In existing wastewater treatment, oxidizing phosphite ions (PHO_3^{2-}) posed a significant challenge. However, our research aimed to develop an effective method for this oxidation process, crucial for phosphorus recovery in industrial wastewater treatment. By utilizing low-cost iron compounds and innovative catalysts, such as iodine obtained from seawater and copper, we achieved remarkable success. Our method demonstrated the ability to oxidize over 80% of PHO_3^{2-} into phosphate ions (PO_4^{3-}) within 120 minutes, overcoming the limitations of existing costly methods involving palladium catalysts or high-voltage conditioned ozone (O_3). Moreover, the process exhibited profitability, with a gross profit of $1.84 per kilogram of phosphorus, presenting a drastic reduction in cost compared to conventional methods using palladium catalysts. This breakthrough not only offers sustainable wastewater purification but also promises a pathway for resource recovery. Additionally, our future prospects involve refining this method into a device capable of purifying industrial wastewater and recovering phosphorus, emphasizing sustainability and reduced power consumption through innovative techniques like using iron and carbon plates forming a battery. This novel technology represents a sustainable solution utilizing abundant resources such as iodine from seawater, iron, and calcium, paving the way for sustainable phosphorus resource recovery.

1. Purpose

In wastewater treatment, developing phosphorus recovery technology is crucial. Phosphate deposits are scarce globally, except in the United States, China, and Morocco. This scarcity forces many nations to heavily rely on importing phosphate as fertilizer, a depleting resource. For the reason, we conducted an experiment using low-cost iron plate to recover phosphorus from industrial wastewater rich in phosphite ions (PHO_3^{2-}). After leaving iron in the PHO_3^{2-} solution for a week, white crystals formed on the iron plate. Initially, we thought they were just PHO_3^{2-}. But we accidentally dropped the crystals into the measurement solution during cleanup. Suddenly, the unexpected change in color from colorless to blue surprised us!

The solution turned blue only with phosphate ions (PO_4^{3-}) present, sparking our realization about whether iron might be helping the oxidation of PHO_3^{2-}, emphasizing that he oxidation of PHO_3^{2-} triggered our investigation. We conducted control experiments under conditions (I) to (IV) using a 1.0 mmol/L PHO_3^{2-} solution of 50mL each, and the concentration of PO_4^{3-}(as PO_4-P) was measured by using the molybdenum blue method[1] .

1) 1.0 mmol of $Fe(NO_3)_3 \cdot 9H_2O$
2) O_2 removal and 1.0 mmol of $FeSO_4 \cdot 7H_2O$
3) 1L/min air
4) 1.0 mmol of $FeSO_4 \cdot 7H_2O$ and 1L/min air

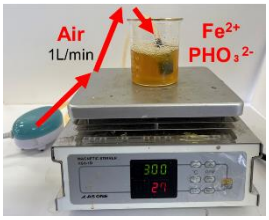


Fig.1 Confirmed PHO_3^{2-} oxidation setup

None of 1), 2), or 3) detected PO_4^{3-}, while 4) had a PO_4-P conc. of 0.064 mmol/L.

These results suggest that both Fe^{2+} and air are necessary for the oxidation of PHO_3^{2-}. So, we began studying method to oxidize PHO_3^{2-} furthermore, while there are existing methods (Table 2, page 10), such as expensive palladium catalysts or high-voltage conditioned O_3. These existing methods are impractical for recycling PHO_3^{2-} into PO_4^{3-} in industrial wastewater, especially for use as fertilizer. In this report, we present the development of a cost-effective method for oxidizing PHO_3^{2-} and recovering PO_4^{3-} using iodine catalyst that meets Japan's wastewater standards.

Our approach resolves issues such as uneven phosphate distribution, self-sufficiency and eutrophication. Eutrophication occurs when runoff of excessive agricultural nutrients or wastewater causes an overgrowth of planktons, depleting oxygen levels and harming aquatic life. Based on these findings, we aimed at Resolving the Phosphate Fertilizer Dilemma through Progressive Wastewater Treatment.

2. Method and Results

Development of a cost-effective PHO_3^{2-} Oxidation and Recovery Method consists of three stages:

I) PHO_3^{2-} Concentration Process, II) PHO_3^{2-} Oxidation Process, and III) PO_4^{3-} Recovery Process (Fig. 2).

I) In the PHO_3^{2-} concentration process, we confirmed PHO_3^{2-} recovery by adding iron compounds to the aqueous solution.

II) In the PHO_3^{2-} oxidation process, we discovered that hydroxyl radicals derived from Fe^{2+} and reducing agents oxidize PHO_3^{2-}, but the consumption of reducing agents became an issue. We uncovered that iodine ion I^- obtained from seawater, along with iron or copper, acts as a catalyst for PHO_3^{2-} oxidation, and we validated this (Fig. 3).

III) In the PO_4^{3-} recovery process, we confirmed the dissolution of PO_4^{3-} from iron phosphate (III) $FePO_4$ generated in the oxidation process, and their recovery as calcium dihydrogen phosphate fertilizer $Ca(H_2PO_4)_2$ using calcium chloride $CaCl_2$.

The verification of the continuity in the all process of I), II) and III), along with the reusability of Fe^{3+} and I^-.

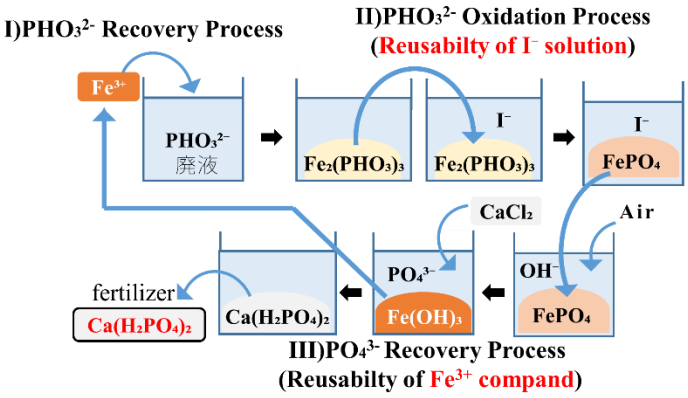


Fig. 2

I) PHO_3^{2-} Recovery Process

Exp. 1: Recovery of PHO_3^{2-} by Iron compounds

5 mmol of Sodium dihydrogen phosphite pentahydrate $Na_2PHO_3 \cdot 5H_2O$ was dissoloved in 50mL of water, creating a 100 mmol/L(mM) PHO_3^{2-} solution. Additionally, 0, 0.5, 2.5 and 5.0 mmol of iron(III) nitrate nonahydrate $Fe(NO_3)_3 \cdot 9H_2O$ were separately added to a 100 mM PHO_3^{2-} solution in 50 mL at pH5 and each was stirred for 30 minutes. The Total Phosphorus (TP) concentration was measured. The recovery rate was calcurated as 87.6%, defined by the following equation.

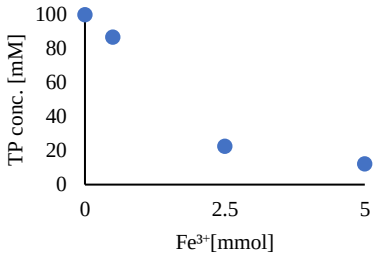


Fig.3

Recovery rate of PHO_3^{2-} = Total Phosphorus conc. after addition of Fe^{3+} / Initial Total Phosphorus conc.

The recovered product, iron phosphite $Fe_2(PHO_3)_3$, allowed the generation high-concentrated PHO_3^{2-} solution. This concenrated solution, in the oxidation process, high-concentrated solution accelerates the reaction and enables the treatment of more wastewater using minimal agents.

Exp. 2: Measurement of the Total Phosphorus content in the precipitate generated in Exp. 1

The precipitate primarily composed of $Fe_2(PHO_3)_3$, obtained from Experiment 1 and weighing 0.50 g (dry weight), was mixed with 1M of NaOH solution in 50 mL. After stirring for 10 minutes, the Total Phosphorus (TP) concentration was measured, resulting in a TP concentration of 314 mmol/L. This shows the presence of **3.14 mmol/g of phosphorus in the form of PHO_3^{2-}-P, within the precipitate**.

II) PHO_3^{2-} Oxidation Process

Exp.3: Discovery of PHO_3^{2-} oxidation by $Fe^{2+}$and air

0, 1.0, 2.5, 5.0, and 7.5 mmol of $FeSO_4 \cdot 7H_2O$ and 1L/min air were added to a 100 mM PHO_3^{2-} solution in 50 mL at pH9. After 30 minutes, the PO_4-P conc. was measured.

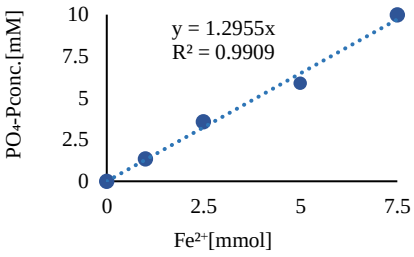


Fig.4

In the presence of oxygen, the promotion of PHO_3^{2-} oxidation is proportional to the amount of Fe^{2+}. This is thought that Hydroxyl radicals (OH・) generated by the reaction of Fe^{2+} and oxygen as shown in equations 1 and 2. Based on equation 3, it is believed that hydroxyl radicals oxidized PHO_3^{2-}.

$2Fe^{2+} + O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O_2$ [2] … equation 1

$H_2O_2 + Fe^{2+} \rightarrow OH\cdot + Fe^{3+} + OH^-$ [2] … equation 2

$PHO_3^{2-} + 2OH\cdot \rightarrow PO_4^{3-} + H^+ + H_2O$ … equation 3

We discovered that PHO_3^{2-} oxidation in the presence of Fe^{2+} was possible, although PHO_3^{2-} oxidation by air alone was not achievable.

Exp.4: PHO_3^{2-}oxidation stopped due to Fe^{2+}exhaustion

7.5 mmol of $FeSO_4 \cdot 7H_2O$ and 1L/min air were added to a 100 mM PHO_3^{2-}solution in 50 mL at pH9. The PO_4-P conc. was measured.

The exhaustion of Fe^{2+} halted the oxidation of the PHO_3^{2-}. Therefore, we considered that reducing Fe^{3+} to Fe^{2+} might restart the oxidation.

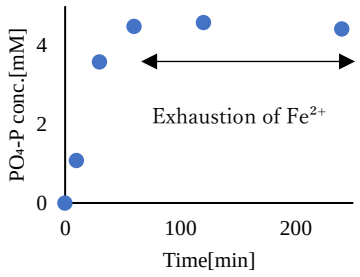


Fig.5

Exp.5: PHO_3^{2-}oxidation resumed due to ascorbic acid(AsA)

15 mmol of $FeSO_4 \cdot 7H_2O$ and 1L/min air were added to a 100 mM PHO_3^{2-} solution in 50mL at pH9. After the reaction had stopped, at 90 minutes, 7.5 mmol of AsA was added.

Between 30 to 90 minutes, the exhaustion of Fe^{2+} halted the oxidation of PHO_3^{2-}. Additionally, at the 90-minute mark, the addition of the reducing agent, AsA, generated Fe^{2+} from Fe^{3+}, which enabled the restart of the oxidation of PHO_3^{2-}.

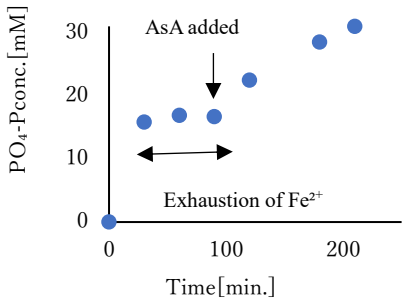


Fig.6

Exp.6: The oxidation stopped due to AsA exhaustion

7.5 mmol of $FeSO_4 \cdot 7H_2O$, 7.5 mmol of AsA and 1L/min air were added to a 100 mM PHO_3^{2-} solution in 50mL at pH5.

Even with the additional AsA, finally, exhaustion of it also halted the oxidation of PHO_3^{2-}. Therefore, we should search the reducing agent, unlike AsA.

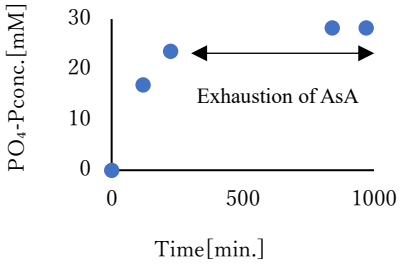


Fig.7

Exp.7: Time- Dependent Effects during addition of KI as a catalyst

6.0 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ and 3.0 mmol of KI were added to a 100mM PHO_3^{2-} solution in 10mL at pH 0 and 90 degrees. It was stirred for 120 minutes, after which the PO_4-P concentration was measured.

94% of the initial concentration of PHO_3^{2-} was oxidized according to the follow defined equation.

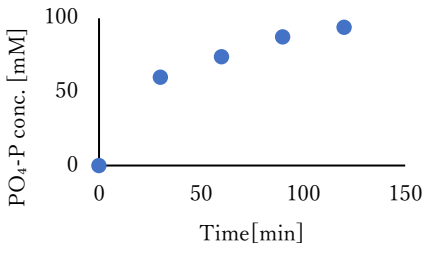


Fig.8

Oxidation Rate = PO_4-P Concentration after oxidation / Initial Total Phosphorus concentration

The I_2 generated from Equation 4 oxidized PHO_3^{2-} according to Equation 5. Subsequently, **the regeneration of I_2 by I^- from Equation 5 constituted a catalytic process**, as described in Equation 4 (Fig.9).

$2I^- + 2Fe^{3+} \rightarrow I_2 + 2Fe^{2+}$ … Equation 4

$PHO_3^{2-} + I_2 + H_2O \rightarrow PO_4^{3-} + 3H^+ + 2I^-$ … Equation 5

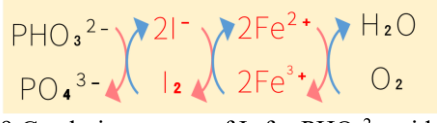


Fig.9 Catalytic process of I_2 for PHO_3^{2-} oxidation

Exp.8: Temperature effectiveness during the addition of KI as a catalyst

6.0 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ and 3.0 mmol of KI were added to a 100mM PHO_3^{2-} solution in 10mL at pH 0 and 25, 40, 50, 60, 70 and 90 degrees. It was stirred for 120 minutes, after which the PO_4-P concentration was measured.

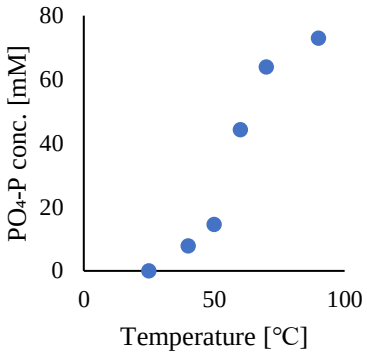


Fig.10

Exp.9: Optimal ratio of Fe^{3+} / KI

0, 0.25, 1.5, 3.0 and 6.0 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ and 3.0 mmol of KI were individually added to a 100mM PHO_3^{2-} solution, each contained within 10mL at pH 0 and 90 degrees. It was stirred for 30 minutes, after which the PO_4-P concentration was measured.

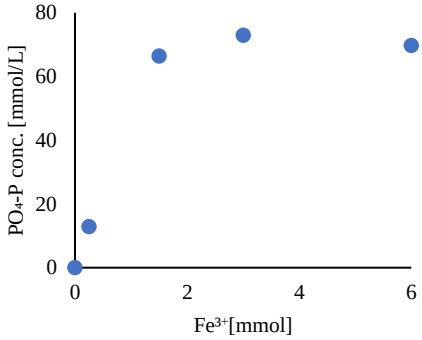


Fig.11

Exp.10: Time-course oxidation of PO_2^{3-} during the addition of KI as a catalyst

1.0 mmol of sodium phosphinate monohydrate $NaPH_2O_2 \cdot H_2O$ was dissoloved in 10 mL of water, creating a 100 mM PO_2^{3-} solution. 3.0 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ and 3.0mmol of KI were added to a 100 mM PO_2^{3-} solution at pH 0 and 90 degrees. After stirring for 120 minutes, PO_4-P concentration was measured.

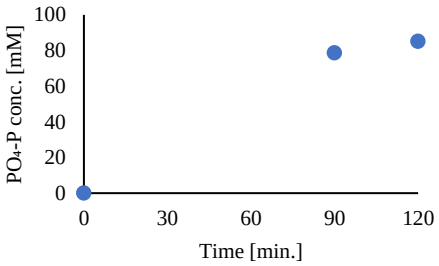


Fig.12

Oxidation rate of PO_2^{3-} was 85.1%= Total Phosphorus conc. after oxidation / Initial Total Phosphorus conc.

The oxidation of PO_2^{3-} sequence: $PO_2^{3-} \rightarrow PHO_3^{2-} \rightarrow PO_4^{3-}$

This method has been confirmed to enable the oxidation of even PO_2^{3-}.

Exp.11: Application to Wastewater Samples

6.0 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ and 3.0 mmol of KI were added to a 15 mL wastewater sample containing 59.8 mM of TP and 0 mM of PO_4-P at pH 0 and 90 degrees. After stirring for 30 minutes, the PO_4-P concentration was measured at 46.1 mmol/L, indicating the **Oxidation Rate of 77%. This suggests the method's applicability to the wastewater sample.** Additionally, it was confirmed that **coexisting substances such as citric acid were not affected.**

III) PO_4^{3-} Recovery Process

Exp.12 Recovery of PO_4^{3-} by $CaCl_2$

0, 1.0, 2.5 and 5.0 mmol of $CaCl_2$ were added to 100 mM PO_4^{3-} solution at pH5. The solution was stirred for 30 minutes. Approximately 98.8% of PO_4^{3-} were recovered as calcium dihydrogen phosphate $Ca(H_2PO_4)_2$.

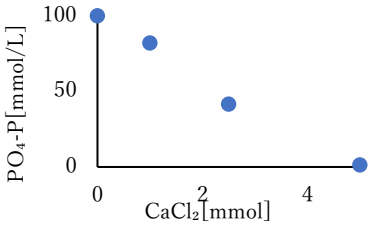


Fig.13

Recovery Rate of PO_4^{3-} = PO_4-P concentration after calcium addition / initial PO_4-P concentration

The verification of the continuity in the concentration process of PHO_3^{2-}, the oxidation process, and the recovery process of generated PO_4^{3-}, along with the reusability of Fe^{3+} and I^-.

The solutions and precipitates containing phosphorus generated in each step recovered to confirm the sequence of processes by utilizing them in subsequent steps (Experiments 13, 14, 15, 16). Additionally, we verified the reusability of the I^- solution used in the oxidation step as a catalyst again in the PHO_3^{2-} oxidation process (Experiment 17) and confirmed the reusability of iron compounds generated in the recovery process, in the PHO_3^{2-} concentration step (Experiment 18).

Exp. 13: Oxidation of $Fe_2(PHO_3)_3$ generated in Exp.1

1.0 g of precipitate obtained from Experiment 1 (main component: $Fe_2(PHO_3)_3$, PHO_3-P quantity 3.14 mmol) and 3.0 mmol of KI added to 15mL of water at pH 0 and 90 degrees. After 120-minute stirring and centrifugation, the measured PO_4-P concentration reached 246 mM, almost 1.2 times more due to evaporation, resulting in 12.5 mL of obtained solution. This value aligns with the theoretical concentration indicating **complete oxidation of all PHO_3^{2-}.**

Exp. 14: Precipitation of $FePO_4$ from PO_4^{3-} generated in Exp. 13

12.5 mL of the solution obtained from Exp. 13 (PO_4-P 246 mM, PO_4-P quantity 3.07 mmol) and 2.5 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ were stirred for 30 minutes at pH 2.3 before centrifugation. The supernatant solution had 1.88 mM of PO_4-P concentration, indicating **the precipitation of 99.2% of free PO_4^{3-} as $FePO_4$** (dry weight 1.72 g, PO_4-P quantity 3.05 mmol). Additionally, 10 mL of the supernatant solution containing I^- was obtained.

Exp. 15: Dissolution of PO_4^{3-} from $FePO_4$ generated in Exp. 14 by NaOH

1.72 g of precipitate obtained from Exp. 14 (main component: $FePO_4$, PO_4-P quantity 3.05 mmol) were added to 1.0 M of sodium hydroxide NaOH solution in 50 mL and stirred for 10 minutes before centrifugation. The supernatant solution had 54.2 mM of PO_4-P concentration, indicating **the dissolution of 88.9% of PO_4^{3-} as its free form**. Additionally, a precipitate was obtained (main component: iron(III) hydroxide $Fe(OH)_3$, dry weight 0.3 g).

Experiment 16: Recovery of PO_4^{3-} generated in Exp. 15 by $CaCl_2$

The 50 mL of solution obtained from Exp. 15 (PO_4-P concentration 54.2 mM, PO_4-P quantity 2.71 mmol) and 10 mmol of $CaCl_2$ were stirred for 30 minutes at pH 5 before centrifugation. The supernatant solution had a 2.76 mM of PO_4-P concentration, indicating **the recovered precipitate of 94.9% of PO_4^{3-} as $Ca(H_2PO_4)_2$** (PO_4-P quantity 2.57 mmol).

Hence, 81.9% of PO_4-P as fertilizer was recovered through oxidation from initial 1.0 g of precipitate $Fe_2(PHO_3)_3$ as a concentrated PHO_3-P of wastewater in all the process.

Exp. 17: The verification of PHO_3^{2-} Oxidation Process using reused I^- solution from Exp. 14

The 10.7 mL of the solution containing I^- obtained from Exp. 14 (PO_4-P 1.88 mM) and 1.0 g of the precipitate obtained from Experiment 1 (main component: $Fe_2(PHO_3)_3$, PHO_3-P quantity 314 mmol/g) and hydrochloric acid HCl were stirred in 15mL for 120 minutes at pH 0 and 90 degrees. The measured PO_4-P concentration was 355 mM, almost 1.1 times more due to evaporation, indicating complete oxidation of PHO_3^{2-}. Therefore, **the I^- obtained from Exp. 14 was successfully verified for reuse as a catalyst.**

Exp. 18: The verification of PHO_3^{2-} Concentration Process using reused $Fe(OH)_3$ from Exp. 15

The 0.30 g of precipitate obtained from Exp. 15 (main component: $Fe(OH)_3$) was dissolved in HCl, added to the 100mM PHO_3^{2-} solution in 50mL at pH 5. After stirring for 30 minutes and centrifugation, the supernatant solution reached the detection limit, indicating complete recovery as $Fe_2(PHO_3)_3$. Therefore, **the $Fe(OH)_3$ obtained from Exp. 15 was successfully verified for reuse.**

Additional a mild-condition Experiment for PHO_3^{2-} Oxidation Process by copper

PHO_3^{2-} Oxidation Process by iron requires temperature of 90 degrees to accelerate the reaction. According to Table2, **a temperature of 90 degrees is commonly used in existing methods for the PHO_3^{2-} Oxidation Process** due to the difficulty of oxidizing PHO_3^{2-}.(Table 2) But, we believed that **there is need to search for substance with reactivity even at lower room temperatures**. Therefore, we conducted experiment of the PHO_3^{2-} Oxidation Process to be mild condition a pH higher than 0 and temperature lower 90 degrees.

Exp.19: Comparison of iron and copper for PHO32- oxidation at 25 degrees

1.0 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ or $CuSO_4 \cdot 5H_2O$ was added to a 100 mM PHO_3^{2-} solution in 50 mL at pH 3 and 25 degrees. The mixture was added 2.0 mmol of KI and was stirred for 30 mintues.

The oxidation of PHO_3^{2-} does not occur with iron and KI at 25 degrees and pH 0. However, **copper and KI enable the reaction even at room temperature and pH 3, leading to a PO_4-P concentration of 9.7 mM. (Fig.14)**

Additionally, **this treated wastewater safe for release**. The solubility of Cu^+ at 0.067 mg/L meets Japan's discharge limit of 3.0 mg/L for copper and the fertilizer standard of 300 mg/kg in Japan.

$[Cu^+]$=0.067 mg/L was calucrated as $K_{sp} = [Cu^+][I^-] = 1.1\times10^{-12}$ mol^2/L^2 [3].

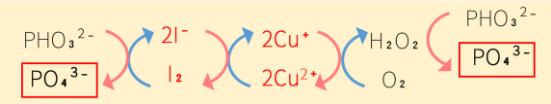


Fig.14 The Mechanism of I^- Catalytic Reaction

Exp.20: Time-Dependent Effects in copper for oxidation

12 mmol of $CuSO_4 \cdot 5H_2O$, 60 mmol of KI and 1L/min air were added to 100 mM PHO_3^{2-} solution in 50 mL at pH3 and 25 degrees.

Oxidation Rate of PHO_3^{2-} was calculated as 58.4%

Since $E^0_{Cu+/Cu2+}$= +0.16 V and $E^0_{Fe2+/Fe3+}$= +0.77 V, Cu^{2+} is more readily reduced by I^- than Fe^{3+}, thus more easliy generating I_2 and H_2O_2 oxidize PHO_3^{2-}.

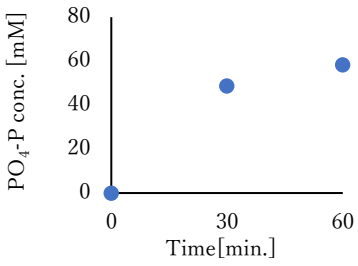


Fig.15

Exp.21: Application of oxidation and recovery by using a device

4 mmol of $CuSO_4 \cdot 5H_2O$, 20 mmol of KI and 1L/min air were added 100 mM PHO_3^{2-} solution at pH3 and 25degrees. After 42 hour, PO_4-P conc. was measured.(PHO_3^{2-} Oxidation Process) The solution was transported for reaction with 5 mmol of $CaCl_2$. And PO_4-P conc. was measured.(PO_4^{3-} Recovery Process)

The Oxidation Proccess : 53.2mM of PO_4-P conc.

The Recovery Proccess : 0.15mM of PO_4-P conc.

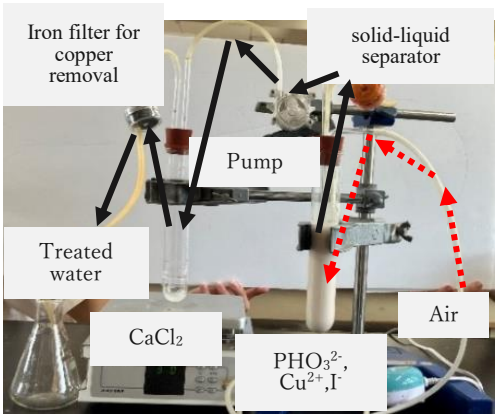


Fig.16 Device

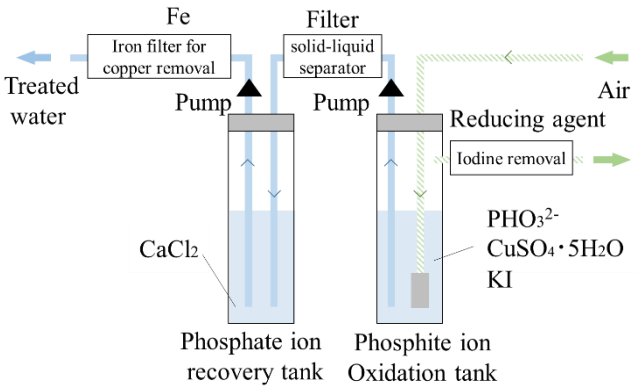


Fig.17 Structure of device

3. Discussion

The oxidation costs per 1 kg of PO_4-P, as shown in Table 1, were calculated for Exp. 4, Exp. 6, existing method, and the newly developed method, assuming the catalyst is reused 1000 times.

The newly developed method in this study achieved a cost for the PHO_3^{2-} Oxidation Process that is 1/2500th compared to the cost of the existing method using a Pd catalyst , such as the one using a Pd catalyst as in JP-A-Hei-6-279009 patent.

Table 1 The oxidation costs per 1 kg of PO_4-P

Agent	The cost of oxidation per 1kg of phosphorus
$FeSO_4$(Exp. 4)	USD $45.55
AsA(Exp. 6)	USD $166.92
Pd catalyst※(existing method)	USD $958.49
KI,Fe,Cu catalyst※ (Newly method)	**USD $0.34**

Ministry of Finance,Trade Statistics of Japan,(2022)

Moreover, an approximate estimation of **the running cost for the entire process yields a rough profit of around $1.84 per 1 kg of phosphorus, indicating financial profitability.**

Rough Profit $1.84 /1 kg of Phosphorus = Selling Price $3.05 - (Oxidation Cost $0.34 + Recovery Cost $0.58+ Electricity Cost $0.30+ Others)

Selling Price $3.05/kg of Phosphorus = Selling Price of $Ca(H_2PO_4)_2$ $0.81/kg[3] × 234/(31×2)

Oxidation Cost $0.34 = (KI $11.06/kg[3] × 5 w% + $Fe(NO_3)_3$ $2.51/kg[3] × 20 w%) × 1000/3.1/1000

Recovery Cost $0.58/kg = $CaCl_2$ $0.32/kg3) × 111/(31×2)

Electricity Cost $0.30/kg = 4.2 kJ/kg℃ × 75℃ × 32.3 kg Solution × Chubu Electric Power $0.1/kWh[6] / 3600s/h

Additional Information: As a solution of 32.3 kg (equivalent to $Fe_2(PHO_3)_3$ concentration in Exp. 13 as 1.0 g/15 mL), containing 1 kg of phosphorus, without any heat exchange

Molar mass: $Ca(H_2PO_4)_2$ = 234, $CaCl_2$ = 111, P = 31

As indicated in Table 2 and Exp.7, **the new method successfully achieved the oxidation of PO_2^{3-} and PHO_3^{2-}**, which was considered a challenging task for the existing method. Additionally, this new method demonstrates superiority in profitability, reusability, reactionability, and eco-friendliness compared to any methods, as shown in Table 2.

Table 2: Overview of oxidation techniques for hypophosphite ions and PHO_3^{2-}

Japanese Patent Application Publication	Method	Problem
JP-A-Hei-6-279009	Using Pd catalyst	Oxidizing PHO_3^{2-} is impossible, but only PO_2^{2-} can be done
JP-A-Hei-6-263414	Using B-Ni compound catalyst	The same as above.
JP-A-Sho-58-119389	Using Cu compound as oxidation agent	The same as above.
JP-A-2019-118908	Using Iron-Nickel compound catalyst	The same as above.
JP-A-Hei-10-85769	Under Ni^{2+}, hydrothermal reaction at 160°C in a heat-resistant and pressure-resistant vessel even for 6 hour.	The initial cost of the device and the cost of treating wastewater are high
JP-A-Hei-11-226596	Irradiation in the presence of O_3 with UV.	The same as above.
JP-A-2010-100875	At 100°C, using a catalyst made of amorphous compounds from dimethyl-amineborane, B and Ni	Drying deactivates the catalyst, and reagents are costly. Separating the resulting dimethylamine is difficult, carrying toxicity and environmental damage.
JP-A-Hei-1-310793	At 90°C, a large amount of H_2O_2 as the oxidizing agent, along with the catalyst of W or Mo compounds.	The cost of treating wastewater is extremely high.
JP-A-Hei-4-338284	Irradiation with a large amount of H_2O_2 as the oxidizing agent, using UV	The same as above.

4. Conclution

I) The verification confirmed the successful establishment of the concentration of PHO_3^{2-}, oxidation of PHO_3^{2-}, and recovery of PO_4^{3-} as a complete process, enabling the oxidation and recovery of over 80% of PHO_3^{2-} in wastewater as PO_4^{3-}.

II) With a gross profit of USD $1.84 per 1 kg of phosphorus, it demonstrates profitability. This equals 1/2500th of the cost compared to using the Pd catalyst.

III) Under the coexistence of Fe^{2+}, the air oxidation of PHO_3^{2-} was achieved.

IV) The discovery of oxidation catalysts involving Fe^{3+} or Cu^{2+} and I^- enabled the oxidation of 94% of 100mM PHO_3^{2-} and 85.1% of 100mM PO_2^{3-} ions within 120 minutes.

V) Application to wastewater confirmed a 77% oxidation rate in 30 minutes, unaffected by coexisting substances such as citric acid.

VI) The reusablity of recycling Iron and Iodine was confirmed.

VII) Successful device demonstration using copper as a catalyst was achieved.

This novel technology represents a sustainable industrial wastewater purification method, solely utilizing abundant resources such as iodine extracted from seawater, calcium, and iron. It promises sustainable phosphorus resource recovery. Conclusively, the goal of this research, the development of PHO_3^{2-} oxidation and recovery method, has been achieved.

5. Future prospects

Future prospects involve developing a device capable of purifying industrial wastewater and recovering phosphorus using iron and carbon plates to form a battery, adjusting pH through iron plate dissolution, and recovering hydrogen H_2 or electricity to reduce power consumption.

6. Refurence

1) JSAC and Hokkaido Branch, Analysis of Water - 4th Edition -, p269, Kagakudojin (1999)

2) K. Tamura and others, The air oxidation of ferrous ions in aqueous solution, JSCM, 45,(1972)

3) H. Freiser, Q. Fernando (T.Fujinaga, E.Sekido), Ion equilibrium, p.250, Kagakudojin (1967)

4) Chubu Electric Power Miraize Co., Ltd., for Retail and Small-Scale Factories, https://miraiz.chuden.co.jp/business/electric/menu/pricelist/smallscale/index.html,(2023-10-1)

【評語】030030

Recycle, reduce and reuse of chemical waste holds the key for sustainable society. In this research, the students produce phosphate-containing fertilizer from electrochromic wastes. Therefore, it is ideal for the regeneration of economic value and protect the environment. The presentation is really interesting and the students showed great enthusiasm.