Transactions of the Materials Research Society of Japan 29[5] 1983-1986 (2004)

A removal process of phosphorus from waste water by using Calcium Sulfate

Takahashi Masaaki, Sato Kunihiko, Kato Susumu, Sasaki Kennichi*

Mie Pref. Science and Technology Promotion Center, Sakura 3690-1 Yokaichi, Mie, Japan

Fax; +81-593-29-2924, e-mail: takahm00@pref.mie.jp

* Ishihara Sangyo Kaisha Ltd. Ishihara1, Yokkaichi, Mie, Japan

Fax; +81-593-45-6182, e-mail: k-sasaki@iskweb.co.jp

Phosphorus removal from wastewater is very important subject of the water pollution control, and many methods for removals of phosphorus by using calcium compound with the exception of calcium sulfate have been developed. Calcium sulfate (gypsum) is widely produced as natural resources and also industrial by-product and waste, therefore, it can expected to be one of the cost-effective materials. Calcium sulfate dissolves slightly in water, calcium sulfate is expected to be calcium sources for the removal of phosphorus instead of other calcium compounds. In order to investigate the phosphorus removal effect, test solution (P=2mg/L) was employed for the basic test. Calcium sulfate was added to the test solution followed by the addition of NaOH. After 30 minute of stirring, test solution was settled for 30 minutes for precipitation. 90% to 95% of phosphorus in the solution was removed on this experiment, and these phosphorus could be recovered as phosphoric acid by using sulfuric acid. The result showed the availability of calcium sulfate for the phosphorus removal from wastewater.

Key words: Phosphorus, wastewater, Removal, calcium sulfate

1. INTRODUCTION

Removal of phosphorus from wastewater is becoming much more important subject to control eutropication of the river and sea. For phosphorus removal from wastewater, many methods using iron, aluminum, magnesium and calcium compound were already investigated[1-3]. Especially calcium chloride or calcium hydroxide has been used as absorbents on the viewpoint of the advantage of recovered calcium phosphate utilization. On the other hand, calcium sulfate (gypsum) is widely produced as natural resources and industrial by-product and waste plaster, and is regarded as one of the cost-effective materials. However phosphorus removal by using calcium sulfate were not reported as far as we know. Calcium sulfate dissolves slightly in water (about 0.5g/100g under room temperature), therefore, calcium sulfate is expected to be calcium sources like other calcium salts on the removal of phosphorus[4] in the wastewater. In this concept, basic studiy using calcium sulfate was carried out.

$$3CaSO_4 + 2NaOH + 2Na_2HPO_4 = Ca_3(PO_4)_2 + 3Na_2SO_4 + 2H_2O \quad \text{eq.1}$$

2. METHOD, RESULT AND DISCUSSION

2.1 Basic examination

Calcium sulfate (gypsum) can react with phosphorus in alkali condition as eq. 1, forms calcium phosphate. In this experiment, pure calcium sulfate 2 hydrate (assay maximum 99 %) was used for examining the basic phosphorus removal rate.

In order to confirm the phosphorus removing effect by calcium sulfate, test solution (PO_4-P 6 mg/L) was prepared. 5g of the calcium sulfate and 20mg of NaOH were added to the 500 mL of test solution (solution A, $CaSO_4$ $2H_2O$ 1%, NaOH 40mg/L), 5g of calcium hydroxide to the test solution (solution B, $Ca(OH)_2$ 1%), 5g of calcium chloride and 20mg of NaOH was added to the solution (solution C, $CaCl_2$ 1%, NaOH 40mg/L) respectively. The phosphorus concentration of the solution was analyzed by molybdenum-blue method after 30 minutes of stirring followed by 0.5 to 24 hours of settling. Sample A (Calcium sulfate) showed highest phosphorus removal rate after 0.5 hour of settling, on the other hand sample C (calcium chloride) showed 60% of removal rate (Table 1), however removal rate has increased at almost same as of the calcium sulfate after 24 hours settlement (Table 2). The difference of the phosphorus removal rate was regarded as derived from settling characteristics of the calcium phosphate formed by the reaction, and suggesting the availability of the calcium sulfate as phosphorus recovering agent. Therefore, we proposed basic procedure for phosphorus removal in the water as shown in Fig. 1. The wastewater is mixed with calcium sulfate (powder or water mixed slurry) and alkali. This mixture is stirred, and phosphorus can be separated by decanting processes in alkali condition (>pH 9). Phosphorus removed water can be discharged in environment after neutralization. Recovered phosphorus is expected to be calcium phosphate, or phosphoric acid by addition of sulfuric acid. $CaSO_4$ formed by the reaction of calcium phosphate and sulfuric acid, can be used as recycled for phosphorus removal processes.

2.2 Optimal NaOH concentration for removal of phosphorus

To confirm this process, 500ml of phosphorus solution (PO_4-P 2mg/l) was prepared for the test (as like basic examination), 5g of the calcium sulfate was added to this solution ($CaSO_4 \cdot 2H_2O$ concentration 1%), followed by the addition of NaOH. After 0.5 hour of stirring, test solution was settled for 0.5 hour to make precipitation. The phosphorus removal rate has increased with the concentration of NaOH and also pH value (Table 3), highest removal rate (over 90%) was observed at NaOH concentration 40mg/L.

2.3 Optimal calcium sulfate concentration for removal of phosphorus

To investigate the optimal calcium sulfate concentration, 500mL of phosphorus solution (PO_4-P 2mg/L), containing 20 mg NaOH (concentration 40mg/L) was prepared. Various amount of $CaSO_4 \cdot 2H_2O$ was added to them, after 0.5 hour of stirring, phosphorus concentration was analyzed as above mentioned way. The phosphorus removal rate has increased with addition of the $CaSO_4 \cdot 2H_2O$, and higher removal rate was observed at the CaSO4 concentration 1% (Table 4).

2.4 Phosphorus removal rate with various PO_4-P concentration

In order to investigate the phosphorus removal rate in many phosphorus concentrations, phosphorus solution (PO_4-P 2mg/L to 20 mg/L) was prepared. The phosphorus removal rates of these solutions were almost same (90% to 96%.) as shown in Table 5.

2.5 Application of this method for industrial wastewater

Three types of industrial wastewater were investigated for the phosphorus removal possibility. The phosphorus removal rate was 90 to 95 % on the sample A and B, however, lower removal rate was observed on the sample C. This cause is considered due to the lower PO_4-P concentration (Table 6).

2.6 Basic test for phosphorus recycling

To confirm the phosphorus recovering possibility, 20L of phosphorus solution (PO_4-P 20mg/L) was prepared. PO_4-P in the solution was decreased to 0.6 mg/L with addition of NaOH (20mg/L) and 200g of $CaSO_4 \cdot 2H_2O$ (10g/L) followed by 30 minute of settlement as above mentioned way. The residue (146g) was treated with aq. H_2SO_4 (H_2SO_4 3.6g+water 2.1L), phosphorus absorbed in the residue was regenerated in the acidic water (at pH 1.7), and phosphorus recovering rate was estimated as 92% (Table 7). The $CaSO_4 2H_2O$ that constitute the residue is expected to be recycled, and these processes water can also be discharged in environment after neutralization (pH adjustment).

These results showed that calcium sulfate can act as phosphorus absorbent, and expected to be a method for phosphorus removal from wastewater.

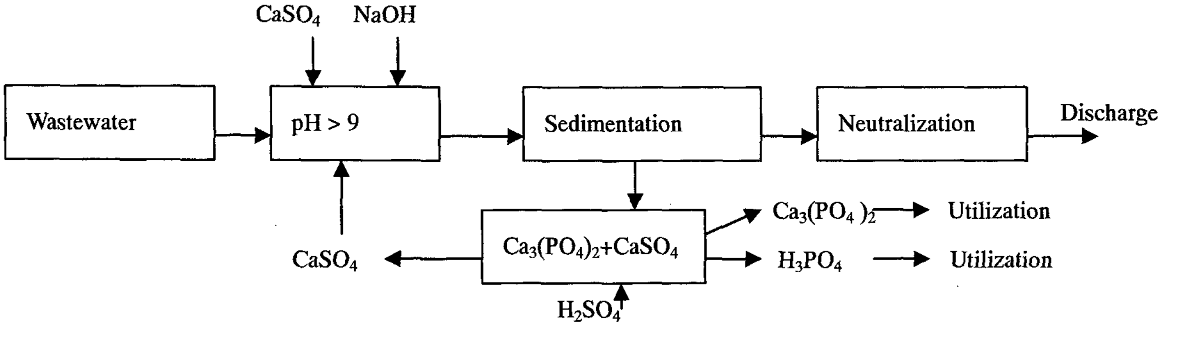

Fig. 1 Fundamental phosphorus removing process from wastewater

Table 1 Phosphorus removal rate at 0.5 hour of settling

	Calcium sulfate	Calcium hydroxide	Calcium chloride
Removal rate (%)	97	92	60
pH	10.5	11.5	10.4

Table 2 Phosphorus removal rate with settling time

	Phosphorus removal rate (%)				
Settling time	0.5h.	1h	2h	5h	24h
Calcium sulfate	97	97	98	99	99
Calcium hydroxide	92	94	95	98	99
Calcium chloride	60	67	74	90	98

Table 3 Phosphorus removal rate with NaOH concentration at $CaSO_4 2H_2O$ 1%

NaOH Conc.	0 mg/L	10 mg/L	20 mg/L	40 mg/L	100 mg/L
Removal rate (%)	0	75	90	96	98
pH	7.6	9.0	9.4	10.4	11.3

Table 4 Phosphorus removal rate with $CaSO_4$ concentration at NaOH 40mg/L

CaSO4 Conc. (%)	0.2	0.4	1.0	2.0
Removal rate (%)	45	85	96	98
pH	10.4	10.4	10.5	10.5

Table 5 Phosphorus removal rate with various PO_4-P concentration at NaOH 40mg/L, $CaSO_4$ $2H_2O$ 1%

PO_4-P Conc.	2 mg/L	5 mg/L	10 mg/L	20 mg/L
Removal rate (%)	96	97	97	96
pH	10.4	10.3	9.9	9.1

Table 6 Phosphorus removal rate of industrial waste water at $CaSO_4$ $2H_2O$ 1%, NaOH 40mg/L

.	Phosphorus Conc.		pH	
	Untreated	Treated	Untreated	Treated
Sample A	1.5	0.1	7.5	10.1
Sample B	5.5	0.4	6.7	10.4
Sample C	0.15	0.05	4.0	9.0

Table 7 The result of phosphorus recovering test

	Test water (20L)		$CaSO_42H_2O$	PO_4-P amount	Removal or recovered rate
	PO_4-P	pH			
Non treated	20 mg/L	---	200g	400mg	---
After treatment	0.6 mg/L	9.1	146g	388mg	97 %
Regenerated amount	---	1.7	146g	370mg	93 %

3. CONCLUSION

The phosphorus removal from wastewater is important technology, many studies has been carried out. As one of the method, phosphorus removal using calcium sulfate was investigated. The result showed, over the 90% of phosphorus in the water was removed in this experimental condition. Calcium sulfate showed higher phosphorus removal rate than calcium chloride, it showed effectiveness of calcium sulfate as calcium sources on water treatment. This result showed advantage of this method, because calcium is regarded as cost effective material. Further more, substituting calcium sulfate for calcium chloride do not need any reform of the water treatment equipment under operation, therefore, this proposed technology expected easily to get on the practical use. On this study, calcium sulfate 2 hydrate was used, however calcium sulfate has many forms as like 1/2 hydrate, anhydrite, industrial gypsum, gypsum waste etc, therefore much more studies are needed on such kinds of calcium sulfate.

4. REFERENCE

[1] Yukiko Miura, Kazuaki Shimamura and Toshihiro Tanaka: A Study of Phosphorus Recovery Method by MAP Reactor Setting up Aging Reactor, Proceeding of Japan Society on Water Environment No. 36, p-167 (2002) (in Japanese)

[2] Kazuyuki Tashiro, Hiromasa Iwata and Yutaka Sakakibara: Phosphorus Removal by Iron, Proceeding of the Japan Society on Water Environment, No. 37, p-218 (2003) (in Japanese)

[3] Kazuki Shimamura, Yukiko Miura, Toshiro Tanaka: Research on HAP recovery conditions using a Fluidized –bed Reactor, Proceeding of the Japan Society on Water Environment, No. 37, p-222 (2003) (in Japanese)

[4] Takahashi Masaaki, Sato Kunihiko, Kato Susumu, Saaki Kennichi: Phosphorus removal from wastewater by using calcium sulfate, Proceeding of the Japan Society on Water Environment, No. 37, p-220 (2003) (in Japanese)

(Received October 10, 2003; Accepted October 31, 2003)