

Calcite-Seeded Crystallization Technique for Phosphorous Removal from Waste Water and Waste Sediment

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Abstract

Induced crystallization of calcium phosphate was carried out by using calcite obtained from Kyaukse. The bismuth phosphomolybdate complex method was used for the determination of phosphorus. At first, preliminary investigation on phosphorous removal from model phosphorus solutions was carried out to understand the nature of calcite seeded crystallization process. The characterization of fresh calcite (before use) and used calcite was carried out by using ED-XRF and XRD techniques. Crystallization processes were studied with batch and column experiments. Calcite seeds were also reused several times for phosphorus removal. Application of calcite seed materials for the removal of phosphate in waste water samples was carried out. The maximum phosphorus removal percent was found at 91.41% for fish aquarium water, 93.73% for agricultural run-off water and 96.22% for waste water from fertilizer factory by using 4g calcite seed, the solution of pH 9 and 24 hours contact time. Removal of phosphate and recovery of calcium phosphate from waste sediment of fertilizer plant that has high content of phosphorus (153.27 ppm) were carried out.

Key words: Bismuth phosphomolybdate, calcite, crystallization, phosphorus removal, calcium phosphate, column experiment

Introduction

Phosphate that enters water from sources such as phosphorus-containing waste is one of the greatest pollution problems facing freshwater systems today. Extensive use of phosphate, mainly due to increasing agricultural needs, has resulted in high phosphate level in surface water (eutrophication), which contributes to environmental problems (Wallingford, 2001). Thus, phosphate pollution within the aquatic environment is of national and international importance in relation to ecological status (Jarvie *et al.*, 2007).

So removal of phosphorus from waste water has been also attracting attention (Yoshino, 2003). For this reason, the removal of phosphorus from waste water is being very common, to meet water quality targets, and avoid environmental problems related to eutrophication (Lesjean *et al.*, 2003).

The treatment of waste water effluents is an increasing demand not only to protect the limited water resource but also to minimize the cost (Smethurst, 1979). Crystallization process is one of the classical fields of application of water treatment. The technical utilization of the crystallization phenomena mainly depends on the availability of suitable and cheap seed materials (Sawada, 1997). Calcite is an inexpensive and readily available. In this research, induced crystallization of calcium phosphate was carried out by using calcite seed materials.

Materials and Methods

The chemicals used in this research work were purchased from "British Drug House" (BDH) Chemical Ltd., Poole, England, "Kanto" Chemical Co, Inc., Japan, "Hopkins and Williams" Co., Ltd, England, "Merck" Darmstadt, Germany, "Sigma-Aldrich" Co., Germany and England.

Determination of Wavelength of Maximum Absorption (λ_{\max}) of Bismuth-Phosphomolybdate Complex

A 2.5 mL of 5 M HClO₄ solution, 1 mL of 0.12 M ammonium molybdate solution and 2 mL of 0.001 M bismuth solution were placed in a 50 mL volumetric flask. Then 2.5 mL of 2% ascorbic acid solution was added and the resulting mixture was diluted with distilled water

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up to 50 mL. The solution mixture gave a blue colour after 10 min. The absorption spectrum of bismuth phosphomolybdate complex was recorded between the wavelength range of 600-900 nm. The wavelength of maximum absorption was found at 716 nm.

Effect of pH, Calcium Concentration and Contact Time on Phosphorus Removal Percent

A 4 mL of 500 ppm phosphorus solution and 96 mL of tap water were taken into separate glass stoppered bottles. Then 2 g of calcite-seed were added to each bottle and formed 100 mL of 20 ppm phosphorus solution. The solutions were agitated in shaker. After 6, 12, 24 and 48 h, the solutions in the respective bottles were removed and filtered. Similarly, the solution in the respective bottles for Inya-water and different contact times for 6, 12, 24 and 48 h were filtered. The phosphorus contents in the resultant filtrates were measured at 716 nm.

Determination of Phosphorus Removal Percent by Column Technique

A glass column (2.5×50 cm) was taken and the glass wool was introduced at the bottom of the glass column by means of a glass rod. Then the column was packed with 50 g of calcite. The sufficient volume of water was passed to wash the calcite. After that, the 25 ppm of phosphorus 50 mL solution was poured into the column. The solution was collected in the beaker. Then the phosphorus content of the collected solution was measured by using bismuth phosphomolybdate complex method and measured the absorbance at 716 nm.

Effect of pH, Calcium Concentration and Weight of Calcite on Removal of Phosphorus from Waste Water Samples

Three different waste water samples were collected and calcite seeded crystallization experiments were carried out. A 100 mL of three different waste water sample and 2 g calcite were added to six separate glass stoppered bottles. The pH of the solution in three bottles was adjusted to 9 using 1 M NaOH solution. Then these six prepared solutions were agitated in the shaker. After 24 h, the solutions in the each bottle were removed and filtered. The same experiments were done by using 4 g calcite seed. The phosphorus contents in the resultant solutions were measured by using the bismuth phosphomolybdate complex method and measured absorbance at 716 nm.

Semi-pilot Scale Process for Phosphorus Removal

Semi-pilot scale experiments were carried out for removal of phosphorus from waste water samples obtained from No. 1 Fertilizer Factory, Chauk Township, Magway Region. In four experiments, 60 and 120 g of calcite seeds were used in 3 L of the waste water solution with and without pH adjustment. Without pH adjustment, initial pH of the sample solution was 7.5. In the case of pH adjustment, pH was adjusted to 9 by using 1 M NaOH solution. The contact time was 24 h.

Determination of Phosphorus Content in Waste Sediment of Fertilizer Plant

A 50 g of waste sediment was dissolved in 20 mL of conc. HCl and stirred with a glass rod in a beaker. Then the solution was transferred to 1000 mL volumetric flask and made up to the mark with distilled water. This solution was adjusted to pH 7 using 1 M NaOH solution. The resultant solution was measured for phosphorus by applying bismuth phosphomolybdate complex method absorbance measured at 716 nm.

Phosphorus Removal from Waste Sediment of Fertilizer Plant

These waste sediment solutions were added into separated glass bottles and calcites were added as presented below. The mixtures were stirred magnetically for 24 hours. Then the solutions were removed and filtered. The phosphorus contents in the resultant solutions were measured as described above.

- (A) 2 g calcite + 100 mL waste sediment solution
- (B) 4 g calcite + 100 mL waste sediment solution
- (C) 6 g calcite + 100 mL waste sediment solution
- (D) 12 g calcite + 100 mL waste sediment solution
- (E) 6 g calcite + 10 mL of 1000 ppm calcium solution + 90 mL waste sediment solution
- (F) 12 g calcite + 10 mL of 1000 ppm calcium solution + 90 mL of waste sediment solution

Results and Discussion

The bismuth phosphomolybdate complex method was used for the determination of phosphorus in the solution (Mihajlovic *et al.*, 2007). The wavelength of maximum absorption of the complex was found at 716 nm (Figure 1). The standard calibration curve was constructed at λ_{\max} 716 nm by using different phosphorus concentrations (0.04 to 0.6 ppm). Tap water sample (pH 5.31, 32.26 ppm calcium concentration) showed 70.45% of phosphorus removal percent, that is lower than Inya water 73.19% (pH 7.45, 41.61 ppm calcium concentration) for 48 h contact time (Table 1 and Figure 2).

Column technique was also used for the phosphorus removal. By applying the repeated use of calcite seed sample, phosphorus removal percent increased gradually 79.82%, 80.57% and 82.5% for fresh calcite (1st time), used calcite (2nd time) and used calcite (3rd time) respectively (Table 2). Three different waste water samples were collected and calcite seeded crystallization experiments were carried out. Experimental results (Tables 3 and 4) revealed that phosphorus removal increased with an increasing dosage of calcite and pH of the solution. The maximum phosphorus removal percent was found at 91.41% for fish aquarium water (Twantay Township), 93.73% for agricultural run-off water (Mingalardon Township) and 96.22% for waste water from fertilizer factory (Chauk Township) by using 4g calcite seed, the solution of pH was adjusted to 9 and 24 hours contact time. In semi-pilot scale experiment, phosphorus removal percent increased to 90.23% (pH 9) from 86.93% (pH 7.5) by using 60 g calcite seed (Table 5). When the dosage of calcite seed increased to 120 g, phosphorus removal percent also increased to 97.12% (pH 9) from 90.65% (pH 7.5) (Figure 3).

In the characterization of fresh calcite and used calcite seeds, the increase in relative abundance (%) of the phosphorus was found in ED-XRF spectrum of used calcite. The phosphorus content increased to 15.538% (used calcite) from 1.037% (fresh calcite). The relative abundance (%) of calcium decreased from 98.369% (fresh) to 82.399% (used) due to the involvement of phosphate in used calcite seed (Table 6).

The XRD diffractogram (Figure 4) of fresh calcite seed well matched with calcium carbonate data from standard library software. By using the Scherrer equation, average crystalline size of the calcite was calculated to be 55.68 nm. The XRD diffractogram of calcium phosphate coated calcite seed (used calcite) (Figure 5) well matched with the calcium phosphate data from standard library software. Average crystalline size of the calcium phosphate coated calcite seed was 57.06 nm. Therefore after coating of calcium phosphate on calcite seed, the average crystalline size increased from 55.68 nm to 57.06 nm.

For phosphorus removal from waste sediment in fertilizer plant, removal percent of phosphorus increased from 72.56% (pH 7) to 77.23% (pH 9) for sample A. When the dosage

of calcite increased from 2 g to 4 g, 6 g and 12 g, phosphorus removal percent also increased. Removal percent of phosphorus was found 84.83% at pH 7 and 89.14% at pH 9 by using 12 g calcite seed. By adding appropriate amount of calcium and using 6 g calcite seed, the removal percentage was found 85.46% at pH 7 and 90.23% at pH 9. In this situation, when 12g of calcite seed was used, the removal of phosphorus was also increased to 91.42% at pH 7 and 97.58% at pH 9. Removal of phosphate and recovery of calcium phosphate from waste sediment of fertilizer plant that has high content of phosphorus (153.27 ppm) was carried out (Table 8 and Figure 6).

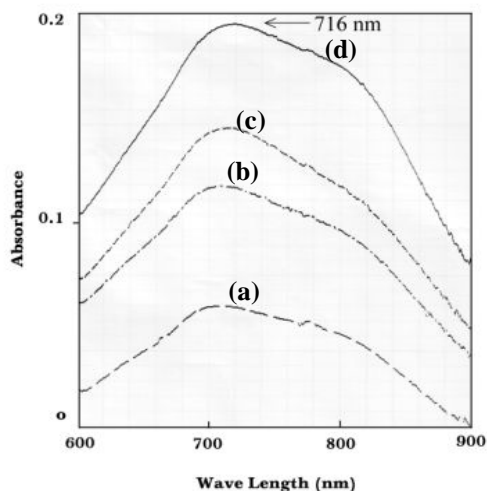


Figure 1. Visible absorption spectrum of Bismuth-Phosphomolybdate complex
(a) 0.12 ppm, (b) 0.16 ppm, (c) 0.20 ppm,
(d) 0.24 ppm

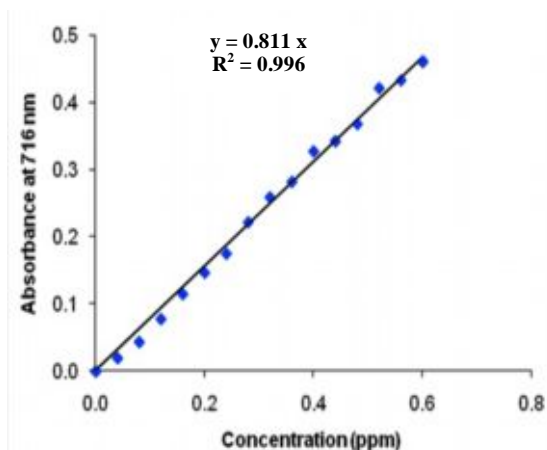


Figure 2. Standard calibration curve for Phosphorus determination

Table 1. Effect of pH, Calcium Concentrations and Contact Time on Phosphorus Removal

Water Sample	pH*	[Ca ²⁺] ppm	Phosphorus removal %			
			6h	12h	24h	48h
Tap water	5.31	32.26	27.69	41.34	69.82	70.45
Inya-water	7.45	41.61	30.06	44.06	72.13	73.19

*Original pH of the soln. Vol. of the soln. = 100 mL. Vol. of water sample = 96 mL
Vol. of phosphorus soln. (500 ppm) = 4 mL. Wt. of calcite seed = 2g

Table 2. Phosphorus Removal by column technique with calcite seed

Calcite	Absorbance	Residual phosphorus (mg)	Phosphorus removal %
Fresh (1 st time)	0.198	0.2523	79.82
Used (2 nd time)	0.190	0.2429	80.57
Used (3 rd time)	0.176	0.2219	82.25

50 mL of 25 ppm original concentration of phosphorus soln. was used (1.25 mg).
Wt. of calcite seed = 50 g

Table 3. Comparison of phosphorus removal % among concentration of calcium and pH of the solution (using 2g calcite seed)

Water sample	[Ca ²⁺] (ppm)	pH	Initial phosphorus conc: (ppm)	2g calcite use and 24 h contact time					
				Absorbance	Residual phosphorus ⁺ (ppm)	removal (%)	Absorbance	Residual phosphoru* (ppm)	removal (%)
Fish aquarium water	80.43	6.9	1.5073	0.221	0.2815	81.32	0.177	0.2253	85.05
Agricultural run-off water	88.21	6.4	3.5073	0.449	0.5727	83.67	0.381	0.4871	86.11
Waste water (Fertilizer Factory)	84.08	7.5	23.7091	2.764	3.5279	85.12	1.948	2.4870	89.51

⁺original pH of the sample *pH adjusted to 9

Table 4. Comparison of phosphorus removal percents among concentration of calcium and pH of the solution (using 4g calcite seed)

Water sample	[Ca ²⁺] (ppm)	pH	Initial phosphorus conc: (ppm)	4g calcite use and 24 h contact time					
				Absorbance	Residual phosphorus ⁺ (ppm)	removal (%)	Absorbance	Residual phosphoru* (ppm)	removal (%)
Fish aquarium water	80.43	6.9	1.5073	0.174	0.2226	85.23	0.101	0.1294	91.41
Agricultural run-off water	88.21	6.4	3.5073	0.371	0.4734	86.50	0.172	0.2199	93.73
Waste water (Fertilizer Factory)	84.08	7.5	23.7091	1.907	2.4349	89.73	0.702	0.8962	96.22

⁺original pH of the sample *pH adjusted to 9

Table 5. Removal of phosphorus from 3 L of waste water using 60 and 120 g calcite

Use calcite (g)	Original pH 7.5			pH adjusted to 9		
	Absorbance	Residual phosphorus (ppm)	Removal (%)	Absorbance	Residual phosphorus (ppm)	Removal (%)
60	2.427	3.0987	86.93	1.815	2.3163	90.23
120	1.737	2.2168	90.65	0.535	0.6828	97.12

Vol. of the waste water = 3L. Contact time = 24h. Initial phosphorus concentration = 23.7091 ppm

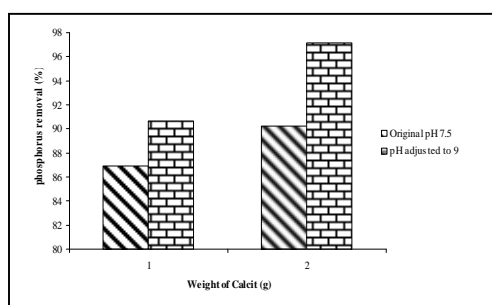


Figure 3. Histogram of phosphorus removal percent with weight of used calcite

Table 6. Relative abundance (%) of trace elements of fresh calcite and used calcite

No.	Element	Relative abundance (%)*	
		Fresh Calcite (before use)	Used Calcite
1.	Ca	98.369	82.399
2.	P	1.097	15.533
3.	K	0.454	1.561
4.	Fe	-	0.258
5.	Cu	-	0.129
6.	Sr	0.140	0.119

*EDXRF

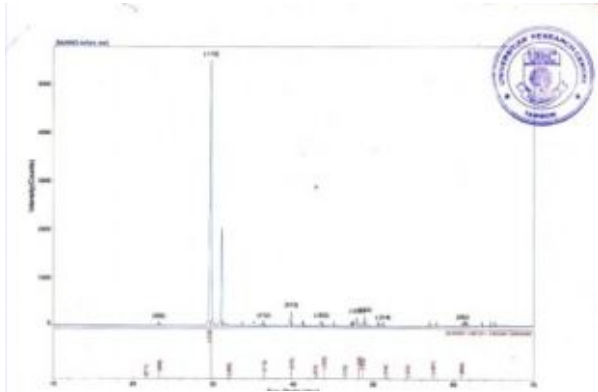


Figure 4. XRD pattern of fresh calcide seed (after used)

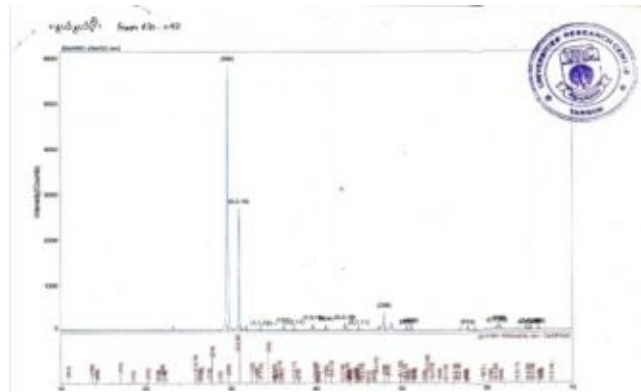


Figure 5. XRD pattern of fresh calcide seed (before used)

Table 7. Phosphorus content in waste sediment from fertilizer plant

Sample	Absorbance	Phosphorus content (ppm)	Mean ± SD
Waste sediment	119.572	152.8755	153.2685 ± 0.9689
	119.892	153.0571	
	120.529	153.8729	

Table 8. Phosphorus removal from fertilizer waste sediment by using calcite seeded crystallization of calcium phosphate

Sample	Initial phosphorus (ppm)	pH 7			pH adjusted to 9		
		Absorbance	Residual phosphorus (ppm)	Removal (%)	Absorbance	Residual phosphorus (ppm)	Removal (%)
A	153.2685	32.947	42.0568	72.56	27.340	34.8992	77.23
B	153.2685	28.540	36.4319	76.43	22.189	28.3240	81.52
C	153.2685	24.410	31.1594	79.67	18.779	23.9711	84.36
D	153.2685	18.214	23.2508	84.83	13.039	16.6449	89.14
E	137.9416	15.712	20.0567	85.46	10.557	13.4768	90.23
F	137.9416	9.272	11.8353	91.42	2.615	3.3381	97.58

Initial concentration of Calcium (Sample A, B, C, D) = 500.7 ppm

Sample	Waste sediment solution (mL)	+ Calcite (g)	
A	100	+ 2	2
B	100	+ 4	4
C	100	+ 6	6
D	100	+ 12	12
E	100	+ 6	1000 ppm 'Ca' 10 mL
F	100	+ 12	1000 ppm 'Ca' 10 MI

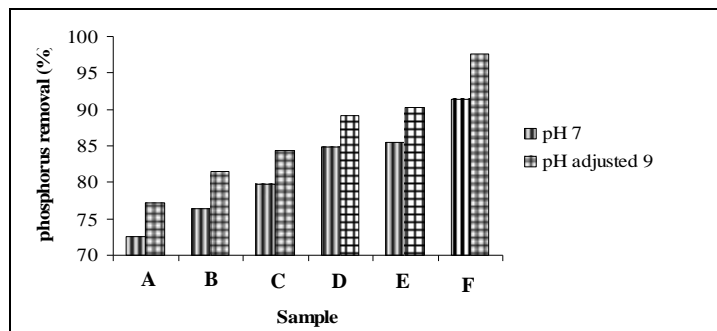


Figure 6. Histogram of phosphorus removal with sample (original pH 7 and pH adjusted to 9)

Conclusion

The visible spectrophotometric method was used for the determination of phosphorus in the solution. The wavelength of maximum absorption of the bismuth phosphomolybdate complex was found at 716 nm. In the construction of the standard calibration curve, the straight line passed the origin and Beer's Law was obeyed.

Column technique was also used for the removal of phosphorus. By using calcite seed samples, phosphorus removal percent increased gradually 79%.82%, 80.57% and 82.5% for fresh calcite (1st time), used calcite (2nd time) and used calcite (3rd time), respectively.

Three different waste water samples were collected and phosphorus removal experiments were carried out. The maximum phosphorus removal percent was found at 91.41% for fish aquarium water, 93.73% for agricultural run-off water and 96.22% for waste water from fertilizer factory by using 4g calcite seed, solution pH 9 and 24 h contact time. In semi pilot scale study, phosphorus removal percents were 90.23% (pH 9) and 86.93% (pH 7.5) using 60g calcite seed for 3L of waste water from No.1 Fertilizer Factory Chauk Township. When the dosage of calcite seed increased to 120 g, phosphorus removal percent also increased to 97.12%(pH 9) from 90.65% (pH 7.5). Removal of phosphate and recovery of calcium phosphate from waste sediment of fertilizer plant that has high content of phosphorus (153.27 ppm) was carried out.

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References

- Jarvie, H.P., Withers, J.A., Hodgkinson, K.I., Wicelham, H.D. and Harmom, S.A. (2007). "Influence of Rural Land Use on Stream water Nutrients and their Ecological Significance", *Journal of Hydrology*, **350**, 166-186
- Lesjean, B., Gnirss, R., Adam, C., Kraume, M. and Luck, F. (2003). "Enhanced Biological Phosphorus Removal Process Implemented in Membrane Bioreactors to Improve Phosphorus Recovery and Recycling", *Water Science Technology*, **8(1)**, 87-94
- Mihajlovic, R. P., Kaljevic, V. M., Vukasinovic, M. P., and Pantic, L. D. (2007). "Spectrophotometric Method for the Determination of Phosphorus in Natural Waters Using the Bismuth-phosphomolybdate Complex", *Water Science Association*, **33(4)**, 513-517
- Sawada, K. (1997). "The Mechanism of Crystallization and Transformation of Calcium Carbonate", *Pure and Applied Chemistry*, **69**, 921 – 928.
- Smethurst, G. (1979). "Basic Water Treatment", First Edition, Thomas Telford Ltd., London, 22-35
- Wallingford, O. (2001). "The Potential for Phosphorus Pollution Remediation by Calcite Precipitation in UK Freshwaters", *Hydrology and Earth System Science*, **5**, 119–131
- Yoshino, M., Yao, M., Tsuno, H. and Somlyna, I. (2003). "Removal and Recovery of Phosphate and Recovery of Phosphate and Ammonium as Struvite Digestion," *Water Science and Technology*, **48**, 171-178