

Removal of Phosphate from Aqueous Solution by Crystallization Using Coal Fly Ash

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ABSTRACT

The removal of phosphate from aqueous solutions by crystallization using coal fly ash has been studied in order to establish a simple and inexpensive wastewater treatment system. Coal fly ash samples obtained from coal fired power plants in Japan, Philippines and Thailand were used in this study. Phosphate ion is removed from an aqueous alkaline solution as hydroxyapatite by crystallization reaction with calcium and hydroxide ions when seed crystalline substance coexists in the solution. All the coal fly ashes used conducted itself as calcium ion supplier, pH controller and seed crystal when added into the aqueous phosphate ion solution. To determine the optimal conditions for an effective removal of phosphate, sets of 50-ml of 10 mg L⁻¹ phosphate solutions were stirred with 1 g of each coal fly ash. Water-soluble calcium content of coal fly ash, pH of the solution, reaction time and reaction temperature was major operating parameters in removal of phosphate. A phosphate removal efficiency of 90 % was easily achieved at pH 10 for all the coal fly ashes studied. The rate of phosphate removal depended on the kind of coal fly ash. The phosphate removal capacity of the ash was calculated between 3.2 mg g⁻¹ and 15.6 mg g⁻¹ from the adsorption isothermal plots according to the Langmuir adsorption equation at 25 °C. Although, most of diverse ions such as Cl⁻, NO₃⁻, SO₄²⁻ did not affect the removal efficiency of phosphate, the interference of CO₃²⁻ ion was significant. Typically, the phosphate removal efficiency of 99.6 % at pH 11.29 with Philippine fly ash was decreased to 83.9 % when 120 mg L⁻¹ of carbonate ion coexisted. Phosphate removal efficiency was enhanced by increase of the reaction temperature. Continuous removal of phosphate by a column method has also been performed with some coal fly ashes.

INTRODUCTION

Water pollution in lakes and inland seas by phosphate becomes serious in recent years especially in the developing countries. For example, findings in a study conducted from 1990 to 1995 revealed a significant deterioration of water quality and aquatic habitat in major surface of water in Metro Manila, Philippines, e.g., Laguna Lake, Manila Bay, Pasig River etc¹. The level of phosphate concentration in the Laguna Lake has increased steadily in the past decade to a high of 10 mg/L in 1999². Excessive phosphorous fertilization enhances overgrowth of aquatic plants and algae, which cause local oxygen shortage, seriously affecting fish farming and other aquatic inhabitants. It is, therefore, desired immediate establishment of simple and economic methods to remove phosphate from contaminated water.

It is possible to remove phosphate from an aqueous alkaline solution as hydroxylapatite by crystallization reaction with calcium ion when seed crystalline substance coexists in the solution³. Coal fly ash, which is a massive waste product of coal fired thermal power generating plants and has a major disposal problem in itself, is a good candidate for the crystallization removal of phosphate. Because coal fly ash generally contains much water-soluble calcium which reacts with phosphate to give insoluble crystalline compounds as well as it can be a seed crystal for its fine particle size.

Although the phosphate removal capabilities of coal fly ash have been studied previously by several authors⁴⁻⁶, the mechanism of phosphate removal has not been understood in detail yet.

In this work, the mechanism of crystallization removal of phosphate from aqueous solutions using coal fly ashes has been studied in order to find out the capability of coal fly ash for a simple and inexpensive wastewater treatment system.

EXPERIMENTAL

Materials

Coal fly ash samples used in this study were obtained from different coal fired power plants, Isogo and Takehara (Japan), Calaca U-1 and U-2 (Philippines) and Mae Moh U-1 and U-5 (Thailand). Among the power plants, Calaca U-2 and Mae Moh plants use local coal produced in respective country, while Japanese plants use mainly imported coal and Calaca U-1 uses mixed Australian and local coal. Two standard reference materials of fly ash distributed by Geological Survey of Japan (JCFA-1) and National Institute of Standard Technology, USA (1633a) were employed for the confirmation of the chemical composition analysis. The fly ashes were dried over night at 105 °C and stored in a desiccator before use.

Characterization of coal fly ashes

Chemical composition of ash samples was determined by ICP-AES after microwave digestion with HNO₃ and HF mixed acid. The reliability of the analyses were confirmed by two standard reference materials of fly ash, 1633a and JCFA-1.

Leaching test was performed as follows. Five gram of coal fly ash was dispersed into 50 mL of water and was stirred for a desired time at constant rate and at 25 °C. Then the suspended solution was vacuum filtered and the eluted elements were measured by ICP-AES.

Phosphate removal experiments

Experiments were carried out using 200 mL grass flasks. One gram of coal fly ash was added to 50 mL of 10 mgL⁻¹ of aqueous PO₄³⁻ solution. The suspended solution was continuously stirred at constant speed (c.a. 250 rpm) with magnetic stirrer at constant temperature in a thermo-regulating water bath. If necessary, the pH of the solution was adjusted by adding H₃BO₃/NaOH buffer solution. Furthermore, necessary ions were added when the effect of the coexisting ions is determined. After the stirring for the required time, the solution was vacuum-filtered. Then the pH of the filtrate was determined and PO₄³⁻ concentration was determined by spectrophotometric analysis with molybdenum blue method.

Removal of phosphate by column method

The continuous column method for the removal of PO₄³⁻ was carried out with the use of a glass column (i.d.: 25 mm, length: 150 mm) packed with 25 g of coal fly ash. The column was connected to a peristaltic pump and 20 mg L⁻¹ of PO₄³⁻ solution was passed through the column at flow rate 3 mL h⁻¹ and temperature at 25 °C. The solution passed through the column was collected and determined the residual PO₄³⁻ concentration. In his experiment, the ash particle size of 75 – 150 μ m was employed.

RESULTS AND DISCUSSION

Characterization of coal fly ashes

The major element composition of the respective coal fly ashes is shown in Table 1. The result indicates that coal fly ashes contain mostly SiO₂, Al₂O₃, Fe₂O₃ and CaO. The CaO content varied from 3 to 11 wt. % depends on the kind of coal fly ash. The leaching experiments have been done for stirring time from 10 min to 3 days. The result of 1 day stirring for Philippine and Thailand coal fly ashes is shown in Table 2.

Table 1. Major element composition of coal fly ashes

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
	(wt. %)						
Isogo	54.01	25.38	6.01	4.63	1.00	0.32	0.60
Takehara	51.42	26.16	6.74	4.93	1.09	0.55	0.91
Calaca U-1	47.07	30.01	4.87	4.50	1.37	1.15	0.79
Calaca U-2	54.34	23.83	3.78	3.06	2.06	0.94	1.58
Mae Moh U-1	47.53	20.32	9.37	11.33	2.72	0.61	1.77
Mae Moh U-5	53.70	24.54	7.55	4.72	1.72	0.33	2.85

As shown in Table 2, the aqueous extracts of the coal fly ashes were strongly alkaline. The rapid dissolution of minerals during the initial leaching period has observed for all the fly ashes tested. All the coal fly ashes appear to have water-soluble calcium as the most abundant mineral in them.

Table 2 pH and major element concentration of the solutions after 24 h stirring with Philippine and Thailand coal fly ashes

Sample	pH	Si	Al	Fe	Mg	Ca	Na	K
(mg L ⁻¹)								
Calaca U-1	9.9	6.0	1.0	5.0	132	77.0	7.0	
Calaca U-2	12.2	2.2	1.7	4.0	351	42.0	7.0	
Mae Moh U-1	11.7	2.3	13.0	4.7	2.3	310	28.0	11.7
Mae Moh U-5	11.1	2.7	14.5	4.7	2.5	240	16.9	17.5

Removal of phosphate

Effects of reaction time, pH and Ca²⁺ concentration

In general, a higher removal efficiency of PO₄³⁻ can be obtained at longer reaction time. The removal efficiency also increases with increasing Ca²⁺ concentration and /or pH of the reaction solution. For example, the removal efficiency was increased with increasing the pH from 30 % at pH 7.03 to 90 % at pH 11.28 with Calaca U-1 fly ash. Experimental result revealed that 90 % removal was attained at pH 11.28, reaction time of 120 min for Calaca U-1 fly ash, and for Calaca U-2 fly ash, a removal efficiency of 99.6 % was obtained at pH 11.02, reaction time of 100 min. Similar tendency was obtained with other coal fly ashes used in this study. The experimental results showed that 20 mg L⁻¹ of Ca²⁺ is enough at pH 11.20 to remove more than 99.5 % of PO₄³⁻ from its 10 mg L⁻¹ solution.

Theoretical calculations on the correlation between pH and PO₄³⁻ concentration for solubility of hydroxylapatite (Ca₅(PO₄)₃(OH)) tell that the crystallization reaction occurs pH region around 8 and 11 when available seed crystal is coexists. From the prediction and the experimental results mentioned above, PO₄³⁻ removal provably proceeds by crystallization and precipitation of hydroxylapatite where coal fly ash conducts itself as supplier, pH controller and seed crystal.

Effect of diverse ions

The effect of diverse ions on the removal of PO₄³⁻ was investigated. Anions such as Cl⁻, NO₃⁻ and SO₄²⁻ gave no significant effect on the PO₄³⁻ removal. However, the interference of carbonate ion (CO₃²⁻ and HCO₃⁻) was serious. Table 3 gives the effect of carbonate ion on the PO₄³⁻ removal by Philippine coal fly ashes at various pH. The serious interference on the PO₄³⁻ removal by other coal ashes was also observed. This serious interference is caused by some extent of Ca²⁺ supplied from coal fly ash is consumed by the reaction with carbonate ion to produce CaCO₃.

Table 3 Effect of carbonate on the removal of PO_4^{3-}

Coal Fly Ash	pH	PO_4^{3-} Removal Efficiency (%)	
		No Carbonate	with Carbonate*
Calaca U-1	8.72	48.5	0.0
	9.43	57.8	44.5
	11.28	88.8	63.0
Calaca U-2	8.98	50.1	34.9
	10.22	73.5	54.2
	11.29	99.6	83.9

* Initial carbonate concentration: 120 mg L^{-1}

Effect of temperature

The effect of temperature on the PO_4^{3-} removal was determined between 10 and 40 °C with Philippine and Thailand coal fly ashes. The removal efficiency was found to be 65 % at 10 °C and 98 % at 30 °C for Calaca U-1 coal fly ash at pH 9.95 and contact time of 120 min. Furthermore, the linear relationship between the removal efficiency and temperature was found for this fly ash. For other coal fly ashes, however, temperature effect on the removal efficiency was not significant.

Calculation of PO_4^{3-} removal capacity of coal fly ashes

The isothermal adsorption experiments have performed to calculate the PO_4^{3-} removal capacity of individual coal fly ash. The plots of the experimental data of PO_4^{3-} removed by per unit weight of coal fly ash ($\text{mg PO}_4^{3-} / \text{g ash}$) versus residual PO_4^{3-} concentration in the solution (mg L^{-1}) showed straight line for all the coal fly ashes examined.

Assuming that the PO_4^{3-} removal reaction is in accord with the Langmuir adsorption isotherm, maximum PO_4^{3-} removal capacity of coal fly ashes was calculate from the lines of the plots. The result is shown in Table 4.

Table 4 Calculated PO_4^{3-} removal capacity of coal fly ashes

Coal Fly Ash	Removal Capacity (mg g^{-1})
Isogo	15.6
Takehara	7.1
Calaca U-1	15.6
Calaca U-2	4.0
Mae Moh U-1	14.4
Mae Moh U-5	3.2

Removal of PO_4^{3-} by column method

Removal of PO_4^{3-} with Calaca U-1 coal fly ash by the column method has tested. High removal efficiency of 94 – 99 % was achieved at pH 11.8 – 12.0 until it reached to near the breakthrough point. The removal efficiency gradually decreased near the

breakthrough point. Total PO_4^{3-} removal capacity was found to be 0.84 mg g^{-1} . This value is smaller than that obtained by calculation from the isothermal plot.

REFERENCES

- [1] Annual Water Quality Report on the Laguna de Bay and its Tributary Rivers, Laguna Lake Development Authority (Philippines), 1996
- [2] K. Yamada, C. M. Shilverio, K. Haraguchi, L. S. Salinas, C. C. Gacho and R. K. Adan, Removal of phosphate and heavy metals in aqueous solution by fly ash, Report of international research development cooperation, 2001
- [3] H. Sunahara, Phosphorous removal process by using crystallization (in Japanese), *Suishitsu-odaku-kennkyu*, 11, 617-622(1988)
- [4] N. Gangoli and G. Thodos, Phosphate adsorption studies, *J. Water Poll. Control Fed.*, 45, 842-849(1973)
- [5] B. P. J. Higgins, S. C. Mohleji and R. L. Irving, Lake treatment with fly ash, lime and gypsum, *J. Water Poll. Control Fed.*, 48, 2153-2164(1976)
- [6] D. L. Vinyard and M. H. Bates, High-calcium fly ash for tertiary phosphorous removal, *Water and Swage Works*, 62-104(1979)