Bioleaching kinetics of trace metals from coal ash using *Pseudomonas spp.*

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Abstract. The kinetics of bioleaching of chromium, copper, manganese and zinc from coal ash using Pseudomonas spp. isolated from coal ash pond was investigated. From the previous study, parameters used for bioleaching were 1% pulp density, 90 rpm, 37°C and 5 ml inoculum was placed in a 100 ml fresh medium with the ash. These conditions were used for bioleaching of coal ash for 30 days. Moreover, the initial pH of the solution is 8.20 and decreases to 8.61. After 30 days of bioleaching, the maximum metal leached were 13.77% Cr, 14.61% Cu, 6.33% Mn and 12.18% Zn. Assuming that the coal ash will shrink uniformly with respect to time using Shrinking Core Model, the kinetic data showed linear plot for percent metal leached versus time, suggested that diffusion through ash layer control was the rate controlling mechanism.

1 Introduction

Coal is the most abundant, affordable and easy to transport and store fossil fuel used in the world. Coal is still the major source of raw material for power and heat generation **[1-2]**. Upon the combustion of coal, 80% of fly ash and 20% of bottom ash were produced. As of today, more than 39% of the world's global electricity is produced using coal with an annual production of 800 million tons of coal ash **[3-4].**

According to the Department of Energy (2017), the Philippine consumed more than 20 million metric tons of coal wherein 47% were used by power plants for the production of electricity **[5-6].** Due to increasing industrial and economic growth demand for electricity would increase, thus, increasing production of coal ash is expected **[4,7-8].**

The common disposal method of coal ash is via ash pond or lagoons that pose significant health and environmental problems **[9-10].** Since coal ash is produced in large quantities, it is considered as a secondary waste material that can be used in different applications such as road base construction, soil amendments and stabilizer, light weight aggregates, mine backfill, zeolite synthesis, fillers in polymer, adsorbent and scrubber, manufacture of construction materials, wastewater treatment and geopolymer **[9-11]**.

In the technological era where metal is an important commodity, metal processing and recovery is focused in a low cost, environmental friendly method in developing this secondary waste material such as bioleaching **[12-13].** Bioleaching is an innovative low-carbon and green technology, low cost and energy efficient technique for metal extraction from secondary waste material using microorganism via the production of organic and/or inorganic acids **[12-15]**.

This research used *Pseudomonas spp.* which was isolated in a coal ash pond. The indigenous microorganism is a heterotrophic microbes that relies on organic compounds as a source of energy for their metabolism which results in the production of organic acids such as citric, gluconic and oxalic acid **[13-14,16]**.

Kinetic study was used to analyze the mechanism of trace metals extraction via bioleaching process. The Shrinking Core Model is used to determine the rate controlling mechanism of the bioleaching process. Moreover, assuming that the coal ash is spherical, the material will shrink over time through bioleaching. Shrinking core model follows three scenarios namely: diffusion through the liquid film controls, diffusion through ash layers control and chemical reaction controls. Different studies were done using different secondary material such as: waste printed circuit board, spent refinery catalyst, copper smelter dust, sphalerite and spent hydro-processing catalyst **[17-19]**. However, mechanism for extraction of trace metals from coal ash has not been investigated.

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The focus of this study is to investigate the rate controlling mechanism using Shrinking Core Model of trace metal extraction from coal ash using Pseudomonas spp. Based on the previous study **[20]**, optimum conditions were used in the bioleaching process to obtain maximum extraction of trace metals.

2 Materials and methods

2.1 Coal ash from coal ash lagoon

A combination of fly and bottom ash was used in the research was collected in the coal ash lagoon. The coal ash was provided by the private coal-fired power plant that uses Circulating Fluidized Bed (CFB) Boiler. The coal ash was oven dried at 105°C for 24 hours, passed though sieve #200 mesh (0.075 microns) particle size. The particle size was held constant. The coal ash has a pH value of 10-11.5 making it alkali in nature.

2.2 Microorganism

The microorganism used in the experiment was *Pseudomonas spp.* This microorganism was indigenous in the coal ash pond in one of the power plants in the Philippines. *Pseudomonas spp.* was isolated by the University of the Philippines – Los Baños (UPLB), Department of Microbiology and identified using TaKaRa PCR thermal Cycler Dice TP600 at the Nakasaki Laboratory of Tokyo Institute of Technology (Tokyo, Japan).

2.3 Growth of *Pseudomonas spp.*

Pseudomonas spp. was cultured using a Nutrient Broth Medium consisting of 1 g/L yeast, 2 g/L peptone and 5 g/L glucose. 8 grams of nutrient broth medium was dissolved in 1 liter of deionized water. The solution was autoclaved at 121°C for 15 minutes **[21].** The resulting solution has a pH of 7.2. Then the inoculum was placed in a water bath shaker (Visio VS-1205SW1) at 90 rpm and 37°C. *Pseudomonas spp.* were incubated for 5 days prior to bioleaching **[22-23]**.

2.4 Bioleaching using *Pseudomonas spp.*

The bioleaching experiment was done in a 250 mL Erlenmeyer flask with the following conditions: 1% pulp density (1 g of ash per 100 ml medium), 90 rpm and 37ºC. The solution was autoclaved at 121°C for 15 minutes and cooled. 5 ml of the inoculum was placed in a 100 ml fresh medium with the ash. The bioleaching experiment was for 30 days **[24]**. The extracted solution was filtered using a 0.45 micrometer cellulous acetate filter. Few drops of concentrated nitric acid were used to acidify the solution and stored at 4°C prior to metal analysis using ICP-OES. The loss culture media was replenished every sampling. The experiment was done in duplicate runs. Table 1 shows the experimental model for the acquisition of data for Shrinking Core Model. This data will determine the controlling mechanism for bioleaching.

Table 1. Shrinking Core Model Experimental Run

Days	% Metal Leached
1	
6	
11	
16	
21	
26	
30	

2.5 Analytical methods

X-ray Diffraction (XRD) analysis was performed using Bruker D8 Advance diffractometer equipped with copper radiation Sol-X detector (CuKα, λ = 0.15406 nm). The data were recorded with a 1s step time and 0.02° scan step between 2° to 80°. On the other hand, X-ray Fluorescence (XRF) analysis was conducted using Pananalytical Xflourescence spectrometer equipped with 150 eV (Mn Ka) resolution Energy Dispersive Minipal 4 tube (Rh X Ray tube – 30 kV –9W). All samples were dried at room temperature.

Also, metal analysis was done using Shimadzu AA-6300 AAS analysis. Different wavelength were used namely: 267 nm for Cr, 324 nm for Cu, 257 nm for Mn and 213 nm for Zn were used to detect the concentration of the trace metals in the solution, reported as mg/kg or ppm. To preserve the samples, few drops of concentrated nitric acid was added.

3 Results and Discussion

3.1 XRD: Mineralogical composition

Figure 1 confirmed the mineral composition of the coal ash namely: quartz-SiO_2, lime-CaO, anhydrite, melilite, mullite, periclase, rutile and tricalcium aluminate. These minerals were detected by the different researchers **[25-26].**

3.2 XRF: Elemental composition

Table 2 shows the major and trace elements in the coal ash. The highest elemental composition is calcium which is accounted due to the addition of limestone prior to combustion process **[27-28]**. The mineralogical structure and elemental composition coincide with the XRD and XRF analyses. Furthermore, total metal contents in the ash are 0.96 mg/kg Zn, 4.13 mg/kg Mn, 0.81 mg/kg Cr and 2.22 mg/kg Cu.

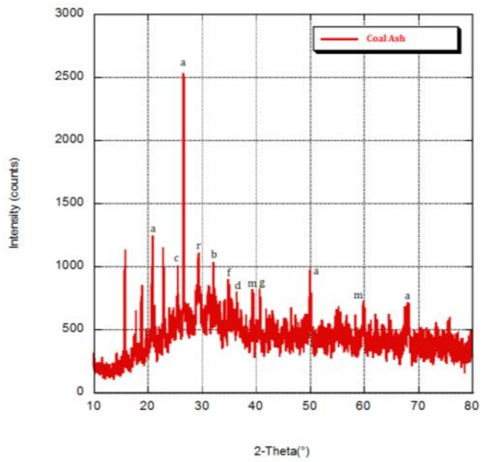

Fig. 1. XRD Analysis for Coal Ash (a: Quartz-SiO2, b: Melilite, ‘c: Anhydrite, d: Tricalcium aluminate, f: Lime-CaO, g: Periclase, m: Mullite, r: Rutile).

Table 2. XRF analysis of ash samples.

Element	% by weight
Calcium	39.46
Silicon	25.70
Aluminum	10.62
Iron	6.20
Sulfur	5.98
Sodium	3.99
Chlorine	2.11
Potassium	1.83
Magnesium	1.67
Titanium	1.51
Strontium	0.43
Barium	0.22
Zirconium	0.05
Tin	0.035
Vanadium	0.034
Chromium	0.033
Nickel	0.025
Manganese	0.023
Tellurium	0.021
Copper	0.020
Zinc	0.011
Bromine	0.011
Yttrium	0.007

3.3 Bioleaching experiment using *Pseudomonas spp.*

At the start of the bioleaching experiment, the pH value is 8.20 and 0.88% Cr, 0.96% Cu, 0.52% Mn and 0.71% Zn were leached in the coal ash. After 30 days, the pH value increase to 8.61 with 13.77% Cr, 14.61% Cu, 6.33% Mn and 12.18% Mn were leached as seen in Figure 2. The final pH of the solution increased in the addition of the coal ash having high buffering capacity of the material and its toxicity to the bacteria in the presence toxic metals. The decrease in pH was due to the excreted metabolites, which include H^+ from organic acids, amino acids and other metabolites. These metabolites dissolve metals by displacement of metal ions from the solid materials by hydrogen ion or by the formation of soluble metal complexes and chelates. Moreover, the bacteria undergo microbial oxidation which resulted in the production of organic acids that plays an important role in the environmental mobility of the metal ions **[29-30].**

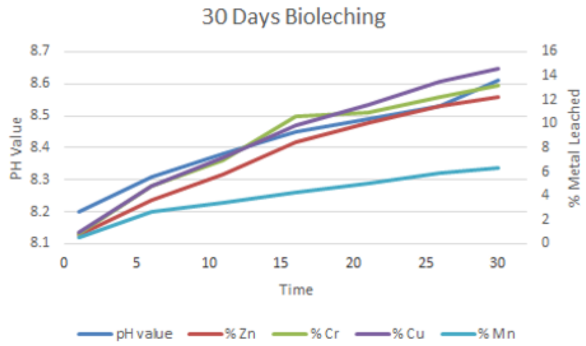

Fig. 2. pH profile vs. percent metal leached after 30 days bioleaching.

3.4 Bioleaching kinetics: Shrinking core model

From the previous study **[20]**, the optimum parameter obtained were 1% pulp density, speed of 90 rpm at 37°C and 5 mL initial inoculum. After 30 days of bioleaching, the maximum trace metal extracted were 13.77% Cr, 14.61% Cu, 6.33% Mn and 12.18% Mn. For the extraction of zinc, chromium, copper and manganese using *Pseudomonas spp.* follows the different shrinking core equations:

$$\frac{t}{\tau} = 1 - \left(\frac{r_c}{R}\right)^3 = X_B \quad (1)$$

$$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \quad (2)$$

$$\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_B)^{1/3} \quad (3)$$

Eq. 1 follows the diffusion through the liquid film control. Then **Eq. 2** follows the diffusion through ash layers control and **Eq. 3** follows the chemical reaction controls.

Figs. 3-6 show the bioleaching kinetics of chromium, copper, manganese and zinc. Based on the result, diffusion though ash layers control is the rate determining step in all of the metal extracted. The R^2 values are 0.9718, 0.9873, 0.9928 and 0.9844 for chromium, copper, manganese and zinc respectively. This can be associated by the production of biofilms and organic complexing agent of *Pseudomonas spp*. that can interfere in the bioleaching process. The extraction of the trace metals in the surface of the coal ash diminishes as the formation of biofilm increases over time. Moreover, the penetration of the organic acid produced by the bacteria decreases due to this interference **[30-31].**

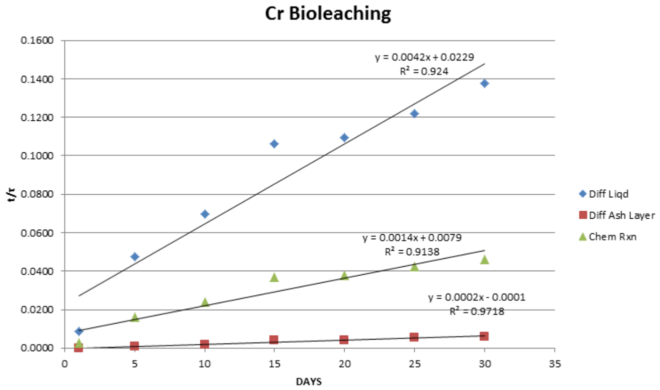

Fig. 3. Shrinking core model for Cr bioleaching.

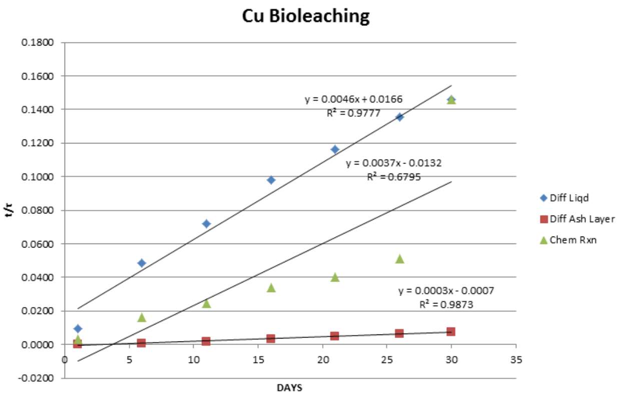

Fig. 4. Shrinking core model for Cu bioleaching.

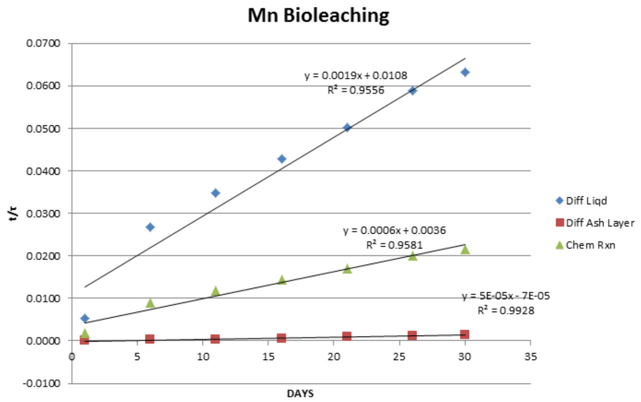

Fig. 5. Shrinking core model for Mn bioleaching.

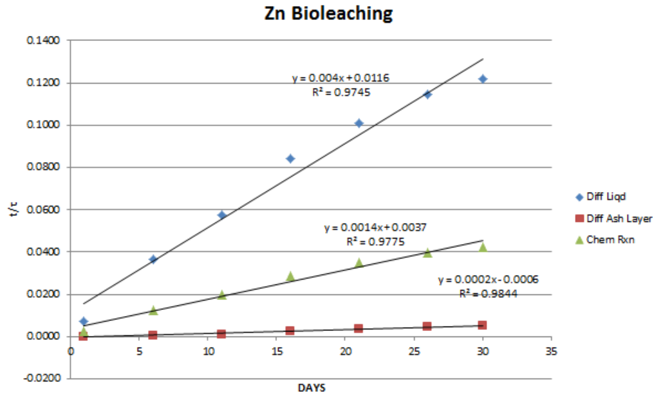

Fig. 6. Shrinking core model for Zn bioleaching.

4 Conclusion

Bioleaching kinetics of coal ash using *Pseudomonas spp.* was investigated. Total metal content, mineral and elemental composition was determined using ICP-OES, XRD and XRF respectively. Based on the result, the total metal contents of the coal ash are 0.81 mg/kg Cr, 2.22 mg/kg Cu, 4.13 mg/kg Mn and 0.96 mg/kg Zn. Also, the minerals detected are quartz-SiO2, lime-CaO, anhydrite, tricalcium aluminate, periclase, melilite, mullite and rutile and the major elemental composition are calcium, silicon, aluminum, iron and sulfur with conincide with the XRD result. High calcium oxide contributed to the alkalinity of the ashes. Using the optimum parameters, percent metal leached and rate controlling mechanism were determined. After 30 days of bioleaching, the maximum trace metal extracted were 13.77% Cr, 14.61% Cu, 6.33% Mn and 12.18% Mn. And the pH value increased from 8.20 to 8.61 after 30 days bioleaching. Based on the Shrinking core model the rate controlling mechanism for all metal leached is diffusion though ash layers control.

This research is funded by Engineering Research and Development for Technology (ERDT) – Department of Science and Technology (DOST), Philippines, Campus France, Republic of France, Japan International Cooperation Agency (JICA) Project Office for the ASEAN University Network/Southeast Asia Engineering Education Development Network (AUN/SEED-Net) under the Collaborative Research Program for Common Regional Issues (CRC) with De La Salle University. Furthermore, we would like to thank the partner coal fired power plant and Tokyo Institute of Technology, Tokyo, Japan. Also, we like to thank the private coal fired power plant and Ile de France Region for the ICP-OES analysis.

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