Adsorption of Heavy Metals from Small-Scale Gold Processing in Baguio Mining District, Philippines

Jyra Rancel Banta

Saint Louis University

Marcelino Jr Lunag (✉ mnlunagjr@slu.edu.ph)

Saint Louis University <https://orcid.org/0000-0002-4073-2850>

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Abstract

Small-scale mining in the Philippines lacks research and technologies for the application of an inexpensive and environmentally sound treatment of its wastewaters. Hence, laboratory-scale fixed-bed column tests were carried out to test and evaluate the sorbent adsorption performance of the Philippine Natural Bentonite (PNB) and the Philippine Natural Zeolite (PNZ) against the heavy metals present in the ball mill facilities within the Baguio Mining District. Results showed that removal percentages of PNB and PNZ in terms of lead (Pb) concentrations are 50.43% and 26.90%, respectively. Moreover, the dynamic uptake capacity and maximum adsorption capacity values of PNB showed greater values than PNZ and the sorption models, Bohart-Adams, Wolborska, Thomas, and Yoon-Nelson models, which displayed a good fit for the breakthrough curves. Furthermore, the effect of varied flow rate and bed height manifested that an increase in flow rate yields a lesser saturation time while the rise in bed height increases uptake capacity, saturation time, and removal percentage of the system. Regarding the cost-efficiencies of the sorbents, the study revealed that PNB is more cost-efficient than PNZ since only 1.13 Philippine pesos of PNB is required to remove a gram of Pb compared to PNZ, which cost 3.30 pesos. Therefore, this research concluded that PNB could be a better sorbent of Pb in terms of removal percentage and cost-efficiency. The study recommends more regeneration studies for the reusability of the sorbents after exhaustion and hopes that this research will be a springboard for further environmental studies.

1. Introduction

The Philippines is a significant gold producer which ranks 24th in gold production in 2018 (Rashotte 2019). The majority of the gold production is in the five well-known gold mining districts, namely the districts of Baguio and Paracale, which is located on the island of Luzon, while the remaining three: Masara, Surigao, and Masbate, are situated in the Mindanao islands. These mining locations comprise more than 60% of gold produced, all of which are small-scale mining operations (Simeon 2019). The Republic Act 7076, also known as the People's Small-scale Mining Act of 1991, has allowed these small-scale mines (SSM) to be operated in areas declared by the law as "Minahang Bayan or Peoples small-scale mining area." Although lawfully recognized, a great majority of SSM operations have been running illegally for decades, wherein licenses are only temporary permits that are valid for less than a year. Most of the miners practice their gold extraction processes using harmful chemicals such as mercury and cyanide due to their high gold recovery and low-cost characteristics. With these, there is an unregulated and widespread small-scale mining operation that dumps untreated toxic wastewater directly into the environment (Mendoza 2014).

The non-compliance of SSM operators to environmental laws and regulations is one of the main reasons the approval rate of permits is very low and the biggest obstacle in obtaining an Environmental Compliance Certificate (ECC) (Simeon 2019). In small-scale mines, the waste disposal system is one of the major issues impeding the approval of the eleven applications for SSM permits in Tuba, Benguet. The study of Macasieb et al. (2014) detected traces of heavy metals such as arsenic (As), mercury (Hg), and lead (Pb) in the sediments of Bued River, which primarily covers the provinces of Benguet, Pangasinan, and La Union. Despite the consequences of improper wastewater disposal, which causes pollution to the Bued river and its tributaries, small-scale miners continue their gold processing operations. The need for intervention for this kind of undertakings is paramount for environmental protection.

Over the years, numerous treatment processes were developed to remove heavy metals from polluted waters. These include reverse osmosis, ultrafiltration, ion exchange, and electrodialysis; however, these technologies are costly, which most SSM industries cannot afford. One of the least expensive methods is adsorption, which depends on the sorbent material used (Acheampong et al., 2010), such as the naturally occurring clay minerals and zeolite. These minerals have small particle sizes and are mainly composed of silica, alumina, water, and weathered rocks. The adsorption capabilities of clay minerals and zeolite are owed to their complex porous structures and high specific surface area, allowing physical solid and chemical attractions with species dissolved in solutions such as heavy metals (Uddin 2017).

The Philippines is known to bear mineralization of clay minerals zeolite and bentonite, which are found to adsorb heavy metals such as the study of Gili et al. (2019). Zeolite and bentonite are locally found in regions of Pangasinan (Region I), and Albay (Bicol) (PSA 2013). The Philippine natural bentonite (PNB) is predominantly composed of mordenite, hectorite, and montmorillonite with kaolinite, feldspar, mica, and nontronite traces. It is chemically composed of 47.9% SiO_2 and 14.02% Al_2O_3 (Olegario and Gili 2021). On the other hand, the Philippine natural zeolite (PNZ) comprised of mordenite followed by clinoptilolite and chabazite has a chemical composition of PNZ is 73.20% silica and 10.72% alumina, with a calculated Si/Al ratio of 3.67, which is higher than the Si/Al ratio of PNB (Olegario-Sanchez and Pelicano 2017). According to literature, these adsorption materials, specifically the use of natural zeolite and bentonite, have not been fully employed in the Philippine Small-Scale Mining operations. Hence, this study aims to evaluate the adsorption capability or removal efficiency and cost-effectiveness of natural zeolite and bentonite as an alternative wastewater treatment method to remove heavy metals found in SSM wastewater so that the Minahang Bayan or the so-called small-scale mining areas will have a higher approval rate due to its improved wastewater treatment method.

2. Materials And Methods

2.1 Study Area and Wastewater Sampling

The study was conducted in Barangay Loacan, Itogon, Benguet among the SSM processing facilities under Loacan, Itogon Pocket Miners Association (LIPMA) since the area is declared as a Minahang Bayan in 2019. However, the facilities still practice direct dumping untreated wastewater into the environment. Nevertheless, wastewater samples were collected from the five disposal points along with the ball mills of the LIPMA area. A total of 10 L wastewater discharge was collected from a full 24 hour-operation, not including cleaning activities and downtime. The water samples were then characterized using X-ray Fluorescence (XRF) Vanta M Series. According to Zhou et al. (2018), the XRF device is an effective alternative and portable method of analyzing polluted waters caused by heavy metals.

2.2 Preparation of Sorbents

The PNB and PNZ materials were acquired from LITHOS Manufacturing, which was then ground with a ceramic mortar and pestle and sieved to 0.25-0.40 mm particles using stainless steel test sieves. No further treatment was applied to maintain the as-purchased properties of the sorbent's materials. The samples of the PNB and PNZ were again analyzed for their chemical composition using the Vanta M Series XRF Analyzer in the Department of Chemical and Mining Engineering, Saint Louis University, Baguio City. The water sample and sorbents were measured in analyzed in triplicate analysis.

2.3 Experimental Set-up

Adsorption was studied by employing a laboratory scale fixed-bed column setup for natural zeolite and natural bentonite, as shown in Fig. 1. A fixed-bed column setup is preferred because the effect of operational parameters such as the amount of sorbent and feed flow rate may be investigated, compared to batch sorption tests that only analyze a sorbent's adsorption capacity (Sazali et al. 2020). A standard borosilicate glass chromatography column of 11 mm inner diameter and 200 mm high was used to house the media sorbent. The bottom of the column includes a sintered glass disk to support the adsorbent bed and minimize the loss of adsorbent mass. A slurry of the sorbents was then added into the glass column to achieve uniform packing. The stationary phase (sorbent) was allowed to settle up to a specific depth. Then, the mobile phase (solvent) will be drained only up to the level of the stationary phase to avoid displacement of the packed sorbent when the feed water comes into the system. A peristaltic dosing pump with an adjustable flow rate was used to maintain the desired feed flow rate. The experiment was held at room temperature 22°C-23°C.

The effects of the process parameters were studied by varying the sorbents bed's depth and the system's feed flow rate. The samples were collected at regular intervals from the outlet of the column. After that, the concentration of the samples was analyzed using the XRF Analyzer. The varied operational parameters per column setup are shown in Table 1.

Table 1
Operational parameter per column setup

Sorbent	Bed height (mm)	Feed flow rate (mL·min ⁻¹)
PNZ	10	1
PNZ	15	1
PNZ	20	1
PNZ	10	3
PNB	10	1
PNB	15	1
PNB	20	1
PNB	10	3

2.4 Data processing and analysis

The performance of each column setup with varied sorbent type, amount, and the feed flow rate was determined by plotting the breakthrough curves for Pb adsorption. The dimensionless concentration of C/C₀ is plotted against time, where C is the effluent concentration at any time t, and C₀ is the feed concentration. The total adsorbed species, q_{total} in mg, is calculated as the area above the breakthrough curve times the feed flow rate as shown in equation one below adapted from Karimi et al. (2012):

1

$$q_{total} = \frac{Q}{100} \int_0^{t_{total}} (C_o - C) dt$$

Where Q is the volumetric flow rate (mL·min⁻¹), (C₀-C) is the adsorbed metal concentration represented by the equation of the breakthrough curve (mg/L), and t is the total time of flow (min).

The dynamic uptake capacity of the columns at exhaustion point is calculated from equation two based on the study of Chittoo and Sutherland (2020):

2

$$q_e = \frac{q_{total}}{m}$$

Where q_e is the mass of adsorbate adsorbed per mass of adsorbent at equilibrium ($\text{mg}\cdot\text{g}^{-1}$) and m is the mass of adsorbent packed in the column, g.

The total removal percentage of metal was calculated from the following equation 3 below:

$$R_E(\%) = \frac{q_{total}}{m_{total}} \times 100$$

3

Where m_{total} (mg) is the total amount of metal entering the column at t_{total} , which is calculated by the following equation 4 (Karimi et al. 2012):

$$m_{total} = \frac{C_o Q t_{total}}{1000}$$

4

The simulation of an adsorption column was achieved by fitting the experimental data into empirical sorption models as specified below and by calculating corresponding model parameters. The determined parameters are used to predict the adsorption performance given new operational conditions to facilitate the up-scale design of column systems.

Bohart-Adams Model

The Bohart-Adams model was based on the assumption that the adsorption rate is proportionate to the adsorbate initial concentration and the remaining capacity of the adsorbent (Bohart and Adams 1920). The model was used to describe the portion of the breakthrough curve where C/C_o is less than 50%. The Adams-Bohart model is expressed as:

$$\frac{C}{C_o} = e^{\left(k_{AB} C_o t - k_{AB} N_o \frac{Z}{u} \right)} \quad (5)$$

Where k_{AB} is the Bohart-Adams constant ($\text{L}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$), Z is the bed height (cm), u is the linear flow rate (cm/min), and N_o is the volumetric adsorption capacity ($\text{mg}\cdot\text{L}^{-1}$) (Zhang et al. 2019). The k_{AB} and N_o are empirical constants of the Bohart-Adams model, which values are characteristics of a specific column system. These constants are applied in scale-up studies wherein the desired column system is reproduced into a larger column.

Wolborska Model

The Wolborska model was a mathematical model that illustrates the lower concentration region of the breakthrough curve (Wolborska 1989). The model is established on the general equation of mass transfer accounting for the diffusion mechanism of the breakthrough curve (Trgo et al., 2011). It is expressed as:

$$\frac{C}{C_o} = e^{\left(\frac{\beta C_o t}{N_o} - \frac{\beta Z}{u} \right)} \quad (6)$$

Where β is the kinetic coefficient of external mass transfer, min^{-1} (Chittoo and Sutherland 2020), similar to the Bohart-Adams constant, β is a constant empirical characteristic of a specific Wolborska model of a particular column system. Also, it is applicable in scaling up laboratory-scale columns.

Thomas Model

The Thomas model was used to estimate the maximum adsorption capacity of a system based on the mass-transfer theory (Thomas, 1948). It was established to represent adsorption without the consequences of intraparticle mass transfer resistance and external film resistance. The model assumes that the adsorption rate depends on the surface interaction between the adsorbate and the unused adsorbent capacity (Chittoo and Sutherland 2020). The model is expressed as:

$$\frac{C}{C_o} = \frac{1}{1 + e^{\frac{k_{TH}}{Q}(q_o m - C_o V)}} \quad (7)$$

Where q_o is the maximum adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$), K_{TH} is the Thomas rate constant, V is the volume of effluent (L), m is the adsorbent mass (g), and Q is the feed flow rate ($\text{L} \cdot \text{min}^{-1}$) (Zhang et al. 2019).

Yoon-Nelson Model

Yoon and Nelson (1984) developed a simple empirical model which assumes that the rate of decrease of the likelihood of adsorption of adsorbate is proportionate to the probability of adsorption and breakthrough of an adsorbate and is expressed as:

$$\frac{C}{C_o} - C = e^{(K_{YN}t - K_{YN}\tau)} \quad (8)$$

Where k_{YN} is the Yoon-Nelson rate constant (min^{-1}) and τ is the time at $C/C_o=50\%$ (Chittoo and Sutherland 2020).

3. Results And Discussion

3.1 PNB and PNZ Characterization

The elemental composition of the sorbents is summarized in Table 2 below. The results indicated that PNZ comprises 46.52% silica (SiO_2) and 9.00% alumina (Al_2O_3), while PNB shall consist of 30.66% SiO_2 and 8.69% Al_2O_3 . Based on the elemental analysis of the sorbents, the Si/Al ratio of PNB and PNZ are 3.53 and 5.17, respectively. The Si/Al ratio affects natural bentonite and zeolite adsorption performance. Higher adsorption is achieved at higher CEC, which is usually associated with a lower Si/Al ratio (Gili and Hila 2021). From this data, it is expected that PNB will yield higher adsorption performance than PNZ. The adsorption performance of bentonite is attributed to its predominant composition of clay minerals belonging to the smectite group, usually montmorillonite. Smectites are hydrous aluminosilicates with a 2:1 Si/Al ratio structure of interlayers giving the bentonite a high specific surface area, porosity, water, compound retention capability, and cation-exchange capacity. In aqueous solutions, bentonite can exchange its cations with the ones present in the solution (Belbachir & Makhoukhi, 2017).

Table 2
Elemental composition of PNZ and PNB

PNZ		PNB	
Element	Concentration (%)	Element	Concentration (%)
LE	73.055	LE	77.28
Si	15.505	Si	10.22
Fe	4.273	Fe	7.77
Al	3.615	Al	3.475
Ca	2.621	Ca	0.5445
K	0.3535	Ti	0.474
Ti	0.341	Mn	0.0914
Mn	0.16	P	0.036
Sr	0.02525	Cu	0.01675
Zr	0.0091	Zn	0.0155
Zn	0.009	Sr	0.0147
Cu	0.0078	Ni	0.0099
Y	0.0033	Zr	0.0077
Ni	0.0033	V	0.0067
Th	0.0031	Y	0.0051
Mo	0.0021	Th	0.0033
Nb	0.00135	Nb	0.00245
Rb	0.0013	Mo	0.00255
Pb	0.00125	Rb	0.0004
V	ND	K	ND
P	ND	Pb	ND

On the other hand, Zeolite is characterized as a crystalline tectosilicate structure interconnected with tetrahedra of silicon, aluminum, and oxygen atoms. The bonding of the tetrahedra to ordinary oxygen atoms prevents dense packing of the layers, leaving open pores or cavities in its framework. The open cavities in zeolite are often occupied by H₂O molecules and cations commonly exchangeable (Ramesh and Reddy, 2011). The isomorphous substitution between the Si⁴⁺ and Al³⁺ ions in bentonite and zeolite crystal lattices results in a negative net charge. This negative charge is neutralized by the exchangeable cations such as Na⁺, K⁺, and Ca²⁺. These cations can be exchanged with heavy metal ions during adsorption. The released ions from the trading of cations in the bentonite and zeolite adsorption are relatively safe, which is advantageous in choosing these materials in wastewater treatment for heavy metals (Olegario-Sanchez and Pelicano, 2017).

3.2 Wastewater Characterization

The heavy metal concentration of the wastewater composite is composed mainly of lead, cadmium, and iron, as shown in Table 3. Results showed that mercury (Hg) and arsenic (As) were below the limits of detection of the Vanta M Series XRF Analyzer. In contrast, a high amount of Pb, Cd, and Fe were detected, exceeding the Class D standard set by DAO 2016-08 (DENR 2016). Hence, the wastewater quality of the samples indeed contained harmful heavy metals, which need to be treated.

Table 3
Wastewater concentration and standard limits

	Pb (ppm)	Cd (ppm)	Fe (ppm)	Hg (ppm)	As (ppm)
Ave Concentration	82.8	19	432.4	ND	ND
Effluent Standard (Class D)	<0.2	<0.02	<35	<0.008	<0.08

3.3 Removal efficiency

The performance of each column setup, with varied sorbent type, sorbent amount, and feed flow rate, were determined by plotting the breakthrough curves for Pb adsorption as shown in Fig. 2. Results showed that the removal percentage values between natural zeolite and natural bentonite are 26.90% and 50.43%, respectively, as shown in the statistical hypothesis testing for the difference of two means for independent groups in Table 5. The degrees of freedom are calculated using a 2-sample t-test with unequal variances (Welch's t-test). The test shows a significant difference with a p-value of 0.02518 ($p < 0.05$) in the removal percentage between PNB and PNZ as sorbent for Pb. These results suggest that the mean removal percentage of PNB is greater than that of PNZ.

On the other hand, the total adsorbed species are presented in Table 4, in which the breakthrough curves do not follow a smooth curve. In terms of total adsorbed species, q_{total} , the adsorption of each setup shows that PNB yields higher performance than PNZ. As determined in the Si/Al ratio calculation, PNB indeed showed a higher experimental adsorption performance based on the removal percentage owing to its lower Si/Al ratio, consequently a higher CEC, as compared to PNZ.

Table 4
Breakthrough parameters

Sorbent	BH (mm)	FR (mL·min ⁻¹)	Area	q_{total} (mg, Pb)	m (g)	q_e (mg Pb/g sorbent)	t_{total} (0.9)	m_{total} (mg Pb)
PNB	10	3	82.37	20.46	0.41	49.90	178.08	44.24
PNZ	10	3	42.03	10.44	0.73	14.30	210.4	52.26
PNB	10	1	74.28	6.15	0.41	15.00	226.08	18.72
PNZ	10	1	51.69	4.28	0.73	5.86	254.08	21.04
PNB	15	1	195.08	16.15	0.61	26.48	336.22	27.84
PNZ	15	1	114.13	9.45	1.09	8.67	376.6	31.18
PNB	20	1	326.08	27.00	0.82	32.93	504.77	41.79
PNZ	20	1	195.65	16.2	1.45	11.17	529.2	43.82

Table 5. Comparison of Mean Removal Percentage

	R_E PNB	R_E PNZ
$\bar{x}$	50.43	26.90
sd	13.96	8.25
df	4.87 $\approx$ 5	
α	0.05	
$t_{5,0.025}$	2.57	

3.4 Application of Fixed Bed Adsorption Models

Linear models were initially obtained as a prerequisite of the non-linear models. Logarithms were used to linearize the experimental data to estimate characteristic parameters of the different adsorption models. The experimental data were fitted into the Bohart-Adams and Wolborska models for adsorption. Characteristic parameters were estimated by linear models $\ln(C/C_0)$ versus t in regions where the relative concentration $C/C_0 < 0.75$ at $Q = 1$ mL·min⁻¹. The respective values of parameters K_{AB} , N_0 , and β_a are shown in Table 6, wherein the parameters K_{AB} and β_a increase with decreasing bed height while the N_0 values increase with increasing bed height. In general, K_{AB} and β_a values are greater in PNB than in PNZ, whereas N_0 values are greater in PNZ than in PNB.

Table 6
Bohart-Adams and Wolborska model parameters

Sorbent	Z (mm)	Equation by $\ln(C/C_0)$ versus t	R^2	Bohart-Adams model		Wolborska model
				$K_{AB} (10^{-5} \text{ L}\cdot\text{mg}^{-1}\cdot\text{min}^{-1})$	$N_0 (\text{mg}\cdot\text{L}^{-1})$	$\beta (\text{min}^{-1})$
PNB	10	$y = 0.0034x - 0.8032$	0.95	4.11	20582.58	0.85
PNB	15	$y = 0.0033x - 1.1684$	0.96	3.99	20565.6	0.82
PNB	20	$y = 0.0012x - 0.9482$	0.84	1.45	34422.61	0.50
PNZ	10	$y = 0.0022x - 0.5791$	0.93	2.66	22934.33	0.61
PNZ	15	$y = 0.0013x - 0.6224$	0.93	1.57	27809.3	0.44
PNZ	20	$y = 0.0009x - 0.8018$	0.92	1.09	38810.45	0.42

In the Thomas model summarized in Table 7, parameters were estimated from the linear plot $\ln[(C_0/C)-1]$ versus V_{eff} at $Q = 1 \text{ mL}\cdot\text{min}^{-1}$. The column data was fitted within the breakthrough curves' $0.1 < C/C_0 < 0.9$ regions. Results show that K_{TH} increases and q_0 decrease with the decreased mass of sorbent.

Table 7
Thomas model parameters

Sorbent	m (g)	Equation by $\ln[(C_0/C)-1]$ versus V_{eff}	R^2	$K^{\text{TH}}(10^{-5} \text{ L}\cdot\text{mg}^{-1}\cdot\text{min}^{-1})$	$q_0(\text{mg}\cdot\text{g}^{-1})$
PNB	0.41	$y = -0.0143x + 0.7374$	0.92	17.3	10.41
PNB	0.61	$y = -0.0071x + 0.9376$	0.96	8.57	17.93
PNB	0.82	$y = -0.0069x + 1.2511$	0.82	8.33	18.31
PNZ	0.73	$y = -0.0075x - 0.1571$	0.95	9.06	2.38
PNZ	1.09	$y = -0.0067x + 0.3316$	0.91	8.09	3.76
PNZ	1.45	$y = -0.0059x + 1.2613$	0.82	7.13	12.21

The Yoon-Nelson parameters were estimated by plotting $\ln[C/(C_0-C)]$ versus t. Table 8 shows constant rate values, K_{YN} , and time at 50% concentration, τ . As the bed height increases, K_{YN} decreases while τ increases.

Table 8
Yoon-Nelson model parameters

Sorbent	Z (mm)	Equation by $\ln[C/(C_0-C)]$ vs t	R^2	$K_{\text{YN}} (\text{min}^{-1})$	$\tau (\text{min})$
PNB	10	$y = 0.0143x - 0.7374$	0.92	0.0143	65.57
PNB	15	$y = 0.0071x - 0.9376$	0.96	0.0071	132.06
PNB	20	$y = 0.0069x - 1.2511$	0.82	0.0069	181.32
PNZ	10	$y = 0.0075x + 0.1571$	0.95	0.0075	20.95
PNZ	15	$y = 0.0067x - 0.3316$	0.91	0.0067	49.49
PNZ	20	$y = 0.0059x - 1.2613$	0.82	0.0059	213.7797

The fit of the non-linear models and the actual plot of C/C_0 versus time are shown in Fig. 3 Column systems, and its parameters are summarized in Table 9 ($Q=10\text{mL}\cdot\text{min}^{-1}$). The Bohart-Adams and the Wolborska models follow the same upward curve for each system, while the Thomas model follows a downward curve. These three models have y-intercept values greater than zero. The Yoon-Nelson model closely follows the actual plot of C/C_0 versus time, including an estimated curve beginning from $t=0$. The different adsorption models obtained provide valuable information for assessing the movement or the retention of metal ions from the liquid phase to the solid phase. Each column system may now be described by a specific adsorption model whose characteristic parameters be used in replicating the desired column behavior based on a chosen model. The information from the models is significant for the reproduction, scaling up, and improvement of a column system.

Table 9
Non-linear sorption models

SYSTEM	Sorbent	Z, mm	Bohart-Adams	Wolborska	Thomas	Yoon-Nelson
A	PNB	10	$\frac{C}{C_o} = \exp[0.0034t - 0.8032]$		$\frac{C}{C_o} = \left[\frac{1}{1 + \exp[0.73474 - 0.0143t]} \right]$	$\frac{C}{C_o} = \left[1 - \frac{(C_o - C) \exp[0.73474 - 0.0143t]}{C_o} \right]$
B		15	$\frac{C}{C_o} = \exp[0.0033t - 1.1684]$		$\frac{C}{C_o} = \left[\frac{1}{1 + \exp[0.9376 - 0.0071t]} \right]$	$\frac{C}{C_o} = \left[1 - \frac{(C_o - C) \exp[0.9376 - 0.0071t]}{C_o} \right]$
C		20	$\frac{C}{C_o} = \exp[0.0012t - 0.9482]$		$\frac{C}{C_o} = \left[\frac{1}{1 + \exp[1.2511 - 0.0069t]} \right]$	$\frac{C}{C_o} = \left[1 - \frac{(C_o - C) \exp[1.2511 - 0.0069t]}{C_o} \right]$
D	PNZ	10	$\frac{C}{C_o} = \exp[0.0022t - 0.5791]$		$\frac{C}{C_o} = \left[\frac{1}{1 + \exp[0.1571 - 0.0075t]} \right]$	$\frac{C}{C_o} = \left[1 - \frac{(C_o - C) \exp[0.1571 - 0.0059t]}{C_o} \right]$
E		15	$\frac{C}{C_o} = \exp[0.0013t - 0.6224]$		$\frac{C}{C_o} = \left[\frac{1}{1 + \exp[0.3316 - 0.0067t]} \right]$	$\frac{C}{C_o} = \left[1 - \frac{(C_o - C) \exp[0.3316 - 0.0067t]}{C_o} \right]$
F		20	$\frac{C}{C_o} = \exp[0.0009t - 0.8018]$		$\frac{C}{C_o} = \left[\frac{1}{1 + \exp[1.2613 - 0.0059t]} \right]$	$\frac{C}{C_o} = \left[1 - \frac{(C_o - C) \exp[1.2613 - 0.0059t]}{C_o} \right]$

3.5 Effect of varying flow rate

The results of varying the flow rate from $1\text{ mL} \cdot \text{min}^{-1}$ to $3\text{ mL} \cdot \text{min}^{-1}$ on both PNB and PNZ sorbents with a constant bed height of 10 mm are shown in Fig. 4. In this result, increasing the flow rate leads to a faster uptake (lesser saturation time) of both sorbents at 90% of the initial concentration. The plot of each sorbent in an increased flowrate is moving upward, resulting in a smaller area above the curve which translates into lower uptake capacity. This is explained by the accelerated movement of Pb in the system resulted in less sufficient residency time in the column. These results agree with the study by Chittoo and Sutherland (2020), where increased flow rates resulted in lessened contact time between the sorbent and sorbate.

3.6 Effect of bed height

Figure 5 below shows the effect of bed height relative to dynamic uptake capacity, saturation time, and removal percentage. The bed height of the columns was varied at 10mm, 15mm, and 20 mm for both PNB and PNZ sorbents with a constant flow rate at $1\text{ mL} \cdot \text{min}^{-1}$. Results showed that increasing the bed height yielded a more uptake capacity, saturation time at $C/C_o=90\%$, and removal percentage against Pb. These results coincide with the adsorption study by Zhang et al. (2019), where the increase of bed height resulted in a slower breakthrough that translates into higher saturation time. The gradual addition of sorbent in an increased bed height supports the idea that it takes longer to saturate the sorbent thoroughly. Hence, an increased amount of sorbent will have more adsorption sites available, resulting in capacity uptake improvement and a higher removal percentage of lead in the system.

3.7 Cost-efficiencies

The prices of the sorbents per kilogram are 17.5 Philippine peso (PHP) for PNB and 16.5 pesos for PNZ. The cost-efficiencies of each sorbent as cost per amount of Pb removed (PHP/g Pb) were calculated using the mass of Pb adsorbed per mass of adsorbent as summarized in Table 10. Results show that PNB can remove a gram of lead 2.17 PHP cheaper than PNZ. A unit of PNB is more expensive than a unit of PNZ; however, PNB removes a gram of lead for a much more affordable price than PNZ.

Table 10
Cost and cost efficiencies of PNB and PNZ

Sorbent	PHP/kg	$q_{e,ave}$ (g Pb/g sorbent)	PHP / g Pb
PNB	17.50	0.031	1.13
PNZ	16.5	0.010	3.30

4. Conclusions And Recommendations

This study was carried out to evaluate and compare the utilization of PNZ and PNB sorbents in removing potentially toxic chemicals in the wastewater from small-scale mines. The wastewater from the ball mill facilities contained average heavy metal concentrations of 82.8 ppm, 19 ppm, and 432.4 ppm for Pb, Cd, and Fe, respectively. Column studies were conducted to evaluate the adsorption performance of the PNZ and PNB against Pb at varied flow rates and bed heights. Key findings of the study showed that PNB is a better adsorbent against heavy metals due to a lower experimental Si/Al ratio than PNZ. This is

confirmed by comparing the removal percentages of the two sorbents in terms of Pb removal. The removal percentage of PNB was 50.43% which is significantly greater than PNZ with 26.90%. The significant difference between PNB and PNZ was further confirmed by determining the dynamic uptake capacity and maximum adsorption capacity, wherein PNB yields higher values than PNZ. In applying empirical sorption models, the Yoon-Nelson model visually shows the closest estimation of actual values; however, the curves produced are not smooth.

Nevertheless, the effect of flow rate for the two sorbents showed that an increase in flow rate results in a lesser saturation time at 90% initial concentration. Meaning, the faster the inlet flow rate, the higher it takes for the sorbent to be spent. Moreover, varying the bed height of the columns showed that the more bed height, the higher the uptake capacity, saturation time, and removal percentage for both sorbents. Furthermore, in terms of the cost-efficiencies of the sorbents, it revealed that PNB could remove a gram of lead 2.17PHP cheaper than PNZ; thus, PNB is more cost-efficient. To further investigate the adsorption performance of the PNB and PNZ sorbents, it is recommended to study the effect of sorbent particle sizes on the adsorption capacity. Additionally, the study only investigates the sorption properties of virgin PNB and PNZ sorbent. It is recommended to study the reusability of the sorbents after exhaustion. Regeneration studies to minimize the demand for virgin sorbents, reduce secondary pollution, and address the disposal problem.

5. Declarations

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Ethics approval and consent to participate

Not applicable.

Consent to publication

Not applicable.

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Authors Contribution

All authors contributed to the study. Material preparation, data collection and analysis were performed by Jyra Rancel Banta. The first draft of the manuscript was edited and approved by Marcelino Lunag Jr. All authors read and approved the final manuscript.

Availability of Data and Materials

Not applicable.

6. References

1. Acheampong MA, Meulepas RJW, Lens PNL (2010) Removal of heavy metals and cyanide from gold mine wastewater. *J Chem Technol Biotechnol* 85:590–613. <https://doi.org/10.1002/jctb.2358>
2. Bohart GS, Adams EQ (1920) Some Aspects of the Behavior of. Charcoal With Respect to Chlorine
3. Chittoo BS, Sutherland C (2020) Column breakthrough studies for the removal and recovery of phosphate by lime-iron sludge: Modeling and optimization using artificial neural network and adaptive neuro-fuzzy inference system. *Chinese Journal of Chemical Engineering* 28:1847–1859. <https://doi.org/10.1016/j.cjche.2020.02.022>
4. DENR (2016) Water Quality Guidelines and General Effluent Standards of 2016. DENR Administrative Order 2016-08
5. Gili MB, Olegario-Sanchez L, Conato M (2019) Adsorption uptake of Philippine natural zeolite for Zn 2+ ions in aqueous solution. *Journal of Physics: Conference Series* 1191:12042. <https://doi.org/10.1088/1742-6596/1191/1/012042>
6. Gili MBZ, Hila FC (2021) Characterization and Radiation Shielding Properties of Philippine Natural Bentonite and Zeolite. *Philippine Journal of Science* 150:1475–1488
7. Karimi M, Shojaei A, Nematollahzadeh A, Abdekhodaie MJ (2012) Column study of Cr (VI) adsorption onto modified silica-polyacrylamide microspheres composite. *Chem Eng J* 210:280–288. <https://doi.org/10.1016/j.cej.2012.08.046>

8. Macasieb RQ, Tapales BJM, Orozco CR, Resurreccion AC (2014) Characterization and Heavy Metal Contamination Assessment of Sediments in Bued River. 11th Engineering Research and Development for Technology Conference, UP Diliman, Philippines
9. Mendoza HD (2014) ECO-FRIENDLY Recovery of GOLD and COPPER. for the Small-Scale Mining Industry
10. Olegario EM, Gili MBZ (2021) Characterization of Philippine natural bentonite. *Experimental Results* 2:1–10. <https://doi.org/10.1017/exp.2021.16>
11. Olegario-Sanchez E, Pelicano CM (2017) Characterization of Philippine Natural Zeolite and its Application for Heavy Metal Removal from Acid Mine Drainage (AMD). *Key Eng Mater* 737:407–411. <https://doi.org/10.4028/www.scientific.net/KEM.737.407>
12. PSA (2013) *Mines and Minerals: Philippine Yearbook 2011*
13. Rashotte N (2019) Mining for Gold in the Philippines. *Gold Mining Companies*
14. Sazali N, Harun Z, Sazali N (2020) A Review on Batch and Column Adsorption of Various Adsorbent Towards the Removal of Heavy Metal. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* Journal homepage 67:66–88
15. Simeon LM (2019) Mining group renews call for crackdown on small-scale operations. *The Philippine Star*
16. Trgo M, Vukojević Medvidović N, Perić J (2011) Application of mathematical empirical models to dynamic removal of lead on natural zeolite clinoptilolite in a fixed bed column
17. Uddin MK (2017) A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. *Chem Eng J* 308:438–462. <https://doi.org/10.1016/j.cej.2016.09.029>
18. Wolborska A (1989) ADSORPTION ON ACTIVATED CARBON OF p-NITROPHENOL. FROM AQUEOUS SOLUTION
19. Zhang Y, Jin F, Shen Z et al (2019) Adsorption of methyl tert-butyl ether (MTBE) onto ZSM-5 zeolite: Fixed-bed column tests, breakthrough curve modelling and regeneration. *Chemosphere* 220:422–431. <https://doi.org/10.1016/j.chemosphere.2018.12.170>
20. Zhou S, Yuan Z, Cheng Q et al (2018) Rapid in situ determination of heavy metal concentrations in polluted water via portable XRF: Using Cu and Pb as example. *Environmental pollution (Barking, Essex: 1987)* 243:1325–1333. <https://doi.org/10.1016/j.envpol.2018.09.087>

Figures

Figure 1

Figure 2
Breakthrough curves of lead adsorption of PNZ and PNB (a) $Z=10\text{mm}$, $Q=3\text{mL}\cdot\text{min}^{-1}$, (b) $Z=10\text{mm}$, $Q=1\text{mL}\cdot\text{min}^{-1}$, (c) $Z=15\text{mm}$, $Q=1\text{mL}\cdot\text{min}^{-1}$, and (d) $Z=20\text{mm}$, $Q=1\text{mL}\cdot\text{min}^{-1}$

Figure 3

Actual and mathematical breakthrough curves of (a) Systems A-C and (b) Systems D-F

Figure 4

Breakthrough curves at a varied flowrate

Figure 5

Effect of bed height to (a) dynamic uptake capacity, (b) saturation time at $C/C_0=90\%$, and (c) removal percentage