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### **Journal of Nanotechnology**

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# Reduction of metals in production plant's effluents by applying air Micro-Nanobubbles in a factory of Lead Acid Batteries of the district of Puente Piedra, Lima

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#### Resumen

La ciudad de Lima tiene áreas industriales que generan muchos efluentes industriales que afectan la salud pública y el medio ambiente. El problema estudiado en una fábrica de baterías de plomo-ácido ubicada en Puente Piedra, Lima, es que genera y descarga aguas residuales ácidas (pH = 1,52). La investigación fue experimental, a nivel de laboratorio, para aplicar el tratamiento con Micro-Nanoburbujas de aire a estas aguas industriales, que contienen metales como el Aluminio (14.967 mg / L) y el Plomo (4.227 mg / L), fuertemente ácidas (pH= 0,55). A continuación, se ajustó el pH en dos muestras con Hidróxido de Sodio 1 M hasta obtener medio de pH ácido (6,01) y básico (8,92) para aplicar los Micro- Nanoburbujas (MNB) en estas muestras. Las Micro- Nanoburbujas fueron generadas por un dispositivo para la generación de Micro- Nanoburbujas patentado por el PhD. Jhonny Valverde Flores. La presión de aire fue de 90 PSI, el tamaño del MNB fue de 7 µm, el flujo de agua fue de 4,67 L/min. Tres muestras (S1, S2 v S3) se dosificaron en 1 L cada una. La proporción en volumen de agua efluente/agua con MNBs para S1 fue 3/7, para S2 fue 6/4 y para S3 fue 7/3. El tratamiento duró 8 minutos y como resultados de la investigación después de aplicar MNBs, la concentración de aluminio en S1 disminuyó a 1.176 mg/L, en S2 disminuyó a 1.421 mg/L y en S3 disminuyó a 11.996 mg/L, alcanzando una eficiencia de 92.14 %, 90,51% y 19,85%, respectivamente; La concentración de plomo en S1 disminuyó a 0.264 mg/L, en S2 disminuyó a 0.065 mg/L y en S3 disminuyó a 0.116 mg/L, alcanzando una eficiencia de 93.75%, 98.46% y 97.26%, respectivamente

Palabras clave: micro-nanoburbuja, metales, Plomo, Aluminio, aire.

#### Abstract

The Lima city has industrial areas that generate many industrial effluents that affect the public health and environment. The problem studied in a factory of Lead Acid Batteries located in Puente Piedra, Lima is, that it generates and discharges acidic wastewater (pH = 1.52). The research was experimental, at the laboratory level, to apply the treatment with Micro-Nanobubbles of air to these industrial waters, which contain metals such as Aluminum (14.967 mg / L) and Lead (4.227 mg / L), strongly acidic (pH 0.55). Then the pH was adjusted into two samples with Sodium Hydroxide 1 M until obtain acid (6.01) and basic (8.92) pH media in order to apply the Micro-Nanobubbles (MNBs) into these samples. Micro-Nanobubbles were then generated by a device for Micro-Nanobubbles generation patented by PhD. Jhonny Valverde Flores. The air pressure was 90 PSI, the size of the MNB was 7  $\mu$ m, the water flow was 4.67 L / min. Three samples (S1, S2, and S3) were dosed in 1 L each one. The volume ratio of water effluent / water with MNBs



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for S1 was 3/7, for S2 was 6/4 and for S3 was 7/3. The treatment lasted 8 minutes and as results of the research after applying MNBs, the Aluminum's concentration in S1 decreased to 1,176 mg / L, in S2 decreased to 1,421 mg / L and in S3 decreased to 11,996 mg / L, achieving an efficiency of 92.14 %, 90.51% and 19.85%, respectively; And the Lead's concentration in S1 decreased to 0.264 mg / L, in S2 decreased to 0.065 mg/L and in S3 decreased to 0.116 mg / L, achieving an efficiency of 93.75%, 98.46% and 97.26%, respectively.

Keywords: micro-nanobubbles, metals, Lead, Aluminum, air.

#### 1. Introduction

Lima owns industrial zones that use great amount of chemicals which generate many waste like industrial effluents that are discharged to a body of water or sewage network affecting public health and the environment.

Lead is found in the earth's crust naturally and is considered a toxic metal. The use of lead in lead-acid batteries increases the risk of high blood pressure and kidney damage; in pregnant women can cause abortion, fetal death and malformations in the fetus; in children can lead to death (WHO, 2015).

There are different alternatives to reduce pollution. Plants like Vetiver can reduce aluminum in waters (Aldana, 2014). Activated charcoal is also used to absorb up to 99.9% lead (Lavado and Sun, 2010). Clays can reduce up to 80% lead concentration in waters (Guerra and Hiyagon, 2012).

The environmental nanotechnology is a technological discipline which study properties of natural and man-made nanomaterials, applications, techniques for their characterization, integration processes and transformation into ecosystems (Valverde, 2016). Microbubbles have the ability to change the normal characteristic of water (Tsuge, 2014). The Microbubbles (MBs) have diameter more than 100  $\mu$ m, the micro-nanobubbles (MNBs) have diameter between 1 to 100  $\mu$ m and the nanobubbles (NBs) have diameter less than 1  $\mu$ m within the fluid field (Valverde, 2016). Microbubbles (MBs) possess special properties such as the capacity for generating free radicals (Sadatomi et al., 2007), self-pressurization, and carrying a negative charge. Such properties have attracted much attention in the fields of food science and agriculture (Takahashi and others 2007a). MNBs have now attracted attention for applications in engineering areas such as wastewater with coliforms in domestic residual water by Air-ozone micronanobubbles (Cruz & Valverde, 2016), Thermotolerant coliforms using air-ozone nanobubbles, (Abate and Valverde, 2017). The micro-bubble generation technology in water is also applied in Health, especially when person has cardiovascular problems (Valverde, 2016).

#### 2. Materials and Methods

#### i) Collection of wastewater sample

The wastewater samples were collected, following the indications of the Quality Monitoring National Protocol of Water from Peru.

#### ii) Sample analysis in laboratory

The Samples (initial and final Samples) were analyzed by an accredited laboratory. Physical (Temperature, Turbidity, and Electrical Conductivity), Chemical parameters (pH, Aluminum and Lead) and biological parameters (Dissolved Oxygen) were measured.



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#### iii) Fabrication of air-ozone micro-nanobubbles (MNBs)

The research was carried out ex-situ, in laboratory, where the whole system was first assembled to generate and to use the air micro-nanobubbles in wastewater. The patent obtained by Dr. Eng. Jhonny Valverde Flores was used to generate air MNBs. The schematic diagram of experimental apparatus for preparation of MNBs solutions is shown in Figure 1.

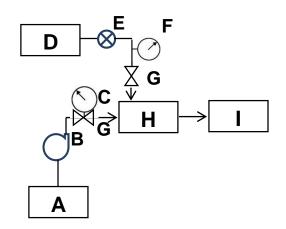


Figure 1. Schematic diagram for the wastewater treatment. Where, A: water tank, B: pump, C: flowmeter, D: air generator, E: pressure valve, F: pressure manometer, G: valve (general), H: MNBs generator, I: wastewater with air MNBs.

The obtained average diameter of a MNB was 7  $\mu\text{m},$  the water flow was 4.67 L/s, and the gas pressure was 90 PSI.



Figure 2. Average diameter of a MNB size is 7  $\mu m$ 





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#### iv) Treatment of the sample

Four samples (One initial sample and three samples after treatment) were dosed in order to evaluate the best reduction of metals into the wastewater. GMI is the initial Sample, GMA is called S1 [300 mL (wastewater) + 700 mL (water with MNB)], GMB is called S2 [400 mL (wastewater) + 600 mL (water with MNB)], and GMC is called S3 [600 mL (wastewater) + 400 mL (water with MNB)].

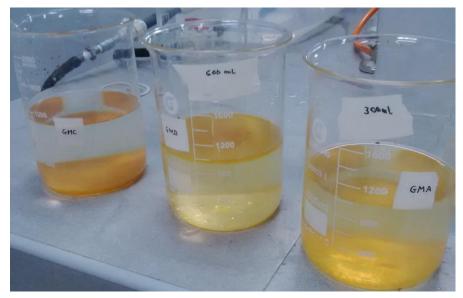


Figure 3. Treatment of Samples with air Nanobubbles.

#### v) Treatment's efficiency in laboratory

Results of the three samples in different concentrations were analyzed after of using air micronanobubbles.

To measure the MNBs treatment's efficiency on metals (Aluminum and Lead) was used the equations 1 and 2:

% Remotion(Aluminum) = 
$$\frac{[Aluminum]_{initial} - [Aluminum]_{end}}{[Aluminum]_{initial}} * 100$$
(1)

$$\% Remotion(Lead) = \frac{[Lead]_{initial} - [Lead]_{end}}{[Lead]_{initial}} * 100$$
(2)

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#### 3. Results and discussion

#### 3.1. Treatment of Samples

Physical, Chemical and Biological parameters from wastewater with metals before and after of treatment.

Table 1. Physical Parameters								
Parameters	Units	EQS*	Initial Sample	S1 300 mL (wastewater) + 700 mL (water with MNB)	S2 400 mL (wastewater) + 600 mL (water with MNB)	S3 900 mL (wastewater) + 100 mL (water with MNB)		
Temperature	°C	<35	21.8	25.5	24.8	25.3		
Turbidity	NTU	100	864	29.1	18.59	115		
Electrical Conductivity	µS/cm	1000	10.51	2.83	2.31	3.78		

Note: \*EQS is Environmental Quality Standard

The physical parameters measured were: temperature, Turbidity, and electrical conductivity. The temperature in S1 (25.5 °C) was a little higher than temperatures of S2 (24.8 °C) and S3 (25.3 °C). The turbidity in S2 (18.59 NTU) was lower than the initial turbidity (864 NTU). The electrical conductivity in S3 was higher (3.78  $\mu$ S/cm) than the initial electrical conductivity in (10.51  $\mu$ S/cm). See Table 1.

#### **Table 2. Chemical Parameters**

Parameters	Units	MAV*	Initial Sample	S1 300 mL (wastewater) + 700 mL (water with MNB)	S2 400 mL (wastewater) + 600 mL (water with MNB)	S3 900 mL (wastewater) + 100 mL (water with MNB)
рН	-	6 a 9	0.55	7.43	7.17	7.83
Aluminum (Al)	mg/L	10	14.967	1.176	1.421	11.996
Lead (Ld)	mg/L	0.5	4.227	0.264	0.065	0.116

Note: \* Maximum Admissible Value to discharge in sewage system.

The Chemical parameters measured were: pH, Aluminum and Lead. pH in S1, S2 and S3 have between 7.17 to 7.83. Aluminum metal in S1 (1.176 mg/L) was lower than initial sample (14.967 mg/L). Lead metal in S2 (0.065 mg/L) was lower than initial sample (4.227 mg/L). See Table 2.



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Parameters	Units	EQS*	Initial Sample	S1 300 mL (wastewater) + 700 mL (water with MNB)	S2 400 mL (wastewater) + 600 mL (water with MNB)	S3 900 mL (wastewater) + 100 mL (water with MNB)
Dissolved Oxygen (	<b>DO)</b> mg/L	>5	6.75	7.36	7.55	6.09

Note: \*EQS is Environmental Quality Standard

The Biological parameter measured was Dissolved Oxygen (DO). The Dissolved Oxygen (DO) in S2 (7.55 mg/L) was higher than in S1 (7.36 mg/L) and S3 (6.09 mg/L). See Table 3.

**Table 3. Biological Parameters** 

	Dose (mL)		Meta		
	wastewater	MNB	Aluminum (mg/L)	Lead (mg/L)	MAV*
initial sample			14.967	4.227	
S1	300	700	1.176	0.264	Yes
S2	400	600	1.421	0.065	Yes
S3	600	400	11.996	0.116	No

#### Table 4. Comparison from Dose vs. metals (S1, S2 and S3)

Note: \* Maximum Admissible Value to discharge in sewage system

At the beginning, the initial sample of Aluminum was 14.967 mg/L, after of applying air MNBs into the S1, S2 and S3, the results were 1.176 mg/L, 1.421 mg/L, and 1.421 mg/L, respectively. At the beginning, the initial sample of Lead was 4.227 mg/L, after of applying air MNBs into the S1, S2 and S3, the results were 0.264 mg/L, 0.065 mg/L, and 0.116 mg/L, respectively. S1 and S1 were within MAV. See Table 4.

#### 3.2. Treatment's efficiency in laboratory

To calculate the MNBs treatment's efficiency on metals in S1 as % Remotion was used the equation1:

% remotion (Aluminum) = (14.967 – 1.176)\*100/ 14.967 = 66.21 %

Then was calculated the S2 and S3. Also it was calculated efficiency on Lead. As a resume the efficiency is seen in table 5.



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	Dose (mL)		Met	als	— EF of AI	EF of Ld
	Sample	MNB	Aluminum (mg/L)	Lead (mg/L)	- EF 01 AI (%)	(%)
initial sample			14.967	4.227		
S1	300	700	1.176	0.264	92.14	93.75
S2	400	600	1.421	0.065	90.51	98.46
S3	600	400	11.996	0.116	19.85	97.26

#### Table 5. Efficiency of the Samples (1, 2 and 3)

The best Aluminum's efficiency in S1 was 92.14%, and the best Lead's efficiency in S2 was 98.46%.

#### 4. Conclusions

- There are reductions of Aluminum and Lead metals presents in sewage water. The initial sample had 14.967 mg/L of Aluminum. After applying the air micro-nanobubbles, the Aluminum concentration was reduced. The best reduction of Aluminum was in S1 (1.176 mg/L). Also, the initial sample had 4.227 mg/L of Lead. After applying the air micro-nanobubbles, the Lead concentration was reduced. The best reduction of Lead was in S2 (0.065 mg/L).
- The three treatments were obtained from different measures. The Aluminum in S1 and S2 were in of the Maximum Admissible Value. However S3 was out of the Maximum Admissible Value.
- The best treatment reduction Efficiency of Aluminum and Lead in sewage water were in S1 and S2 by applying air micro-nanobubbles. It was obtained 92.14% for Aluminum and 98.46% for Lead.

#### Acknowledgements

We gratefully acknowledge to the Department of Environmental engineering, University Cesar Vallejo – Lima Norte, for giving facilities in environmental issues. We also thank to the Institute of Nanotechnology, Centre of Research and Training to the Regional Development, (In Spanish, Centro de Investigacion y Capacitacion para el Desarrollo Regional-CINCADER) for allowing us to use the equipment to generate micro-nanobubbles and technical experiences.

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