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Reduction of Lead and Silicon in Wastewater from Gas Scrubbing of a Company using Micronanobubbles of Air-Ozone

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The research's goal was to reduce the concentration of Lead and Silicon through the application of air-ozone micro-bubbles in gas scrubbing's wastewater of a company. The micronanobubbles generator was used to reduce heavy metals. A preliminary analysis of wastewater was carried out to confirm Lead concentration of 32.26 mg/L and Silicon of 70.49 mg/L. Then the treatment with micronanobubbles generator was carried out for three times of 8, 16 and 24 minutes, with a pH of 6, 8 and 10 until achieving a Lead reduction of 0.088 mg/L, with a reduction percentage of 99.7% and of silicon of 12.97 mg/L, with a percentage of reduction to 81.6% of residual water.

1. Introduction

Water pollution is one of the most alarming problems that is present worldwide. The growth of the population is generating shortages of water resources as consumption doubles more and more, and this has generated concern and interest for governments, scientists and technicians and in general for all inhabitants (UN, 2012). In Peru, the contamination of water by heavy metals is one of the socio-environmental problems, in most are the mining industries that discharge their effluents to the rivers (OEFA, 2014). The generation of massive quantities of flue gas scrubber sludge containing hazardous heavy metals such as lead posing a potential environmental threat. The amount of sludge can be reduced by NaCl and calcium oxide (Xing et al, 2017).

Nanotechnology is the field of applied sciences that studies the manipulation of matter at the nanoscale. There is a new concept to deal with pollution to the environment called environmental nanotechnology. Environmental nanotechnology is a technological discipline that studies properties of natural and artificial nanomaterials, applications, techniques for their characterization, process of integration of transformation in ecosystems (Valverde, 2016). The Micro-Nanobubbles are submicron cavities containing gas in aqueous solution. The Microbubbles (MBs) have a diameter from 10 to 100 µm, the micro-nanobubbles (MNBs) have a diameter between 0.1 to 100 µm and the Nanobubbles (NBs) have a diameter of less than 0.1 µm inside the fluid (Valverde, 2017). Microbubbles have the ability to change the normal characteristic of water (Tsuge, 2014).The micro-nanobubbles generation technology in water is applied in: sea water, water bodies, groundwater, domestic wastewater and industrial wastewater (Valverde, 2017).

There are reductions of: thermotolelant coliforms presents in marine water after applying the air-ozone micro-nanobubbles (Abate and Valverde, 2017), fecal and total coliforms present in domestic wastewater after applying the airozone micro-nanobubbles (Cruz and Valverde, 2016), BOD5 in river's water applying ozone micro-nanobubbles (Salguero and Valverde, 2017), The Chemical Oxygen Demand of water with Amoxicillin applying air micro-nanobubbles (Mendez and Valverde, 2017), total coliforms presents in domestic wastewater applying air micro-nanobubbles (Reyes and Valverde, 2017), Sanguaza applying air micro-nanobubbles (Ventura and Valverde, 2017).

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2. Materials and Methods

The sample is industrial wastewater from a gas scrubber equipment containing Lead and Silicon that is part of the process of a battery factory. The stages of the investigation were the following:

Step I: Collection of the sample
A sample of 40 L water was taken of gas scrubbing taking into consideration the National Protocol of Quality Monitoring.

Figure 1: Sampling of gas scrubber.

Step II: Initial analysis of the sample
The residual water sample is found with a pH equal to 6 at a temperature of 20 ºC. Then the sample was preserved by adding 5 mL of nitric acid (HNO_3) to the residual water to bring it to a pH of less than 2.
The initial sample was analyzed to determine the physical parameters (turbidity, electrical conductivity, Dissolved Oxygen, pH, temperature) and chemical parameters (concentration of Lead and Silicon) in the laboratory.

Stage III: Water treatment through the use of air-ozone MNBs
The water treatment was carried out with the generating equipment of MNBs with continuous system. For this, air-ozone micro-nanobubbles with the following features were used:

Table 1. Results of MNBs characterization

Characterístics	Results
Contact time (min)	8 min,16 min, 24 min
Diameter of MNB(μm)	0.024
Internal Pressure (atm)	120.95
Ascent Speed (cm/h)	3.15

It was used 39 liters of waste water (sample of 13 liters with a pH equal to 6, sample of 13 liters with a pH equal to 8 and sample of 13 liters with a pH equal to 10) up to 24 minutes of treatment. Subsamples were taken during the treatment of the samples in 8 minutes, 16 minutes and 24 minutes.

a) Titration with sodium hydroxide
The sample with pH equal to 6 was not subjected to titration with NaOH. To achieve pH 8 and 10, the other samples were increased by titration with NaOH 1 M.
The procedure for the increase to pH equal to 8 is as follows: 100 mL of residual water was taken in a 250 mL beaker. NaOH was added dropwise by means of a burette until achieve a pH equal to 8. The amount consumed by weight of NaOH was 0.056 g. making a simple conversion we obtain that for 7.2 L, 7.28 g should be added of NaOH.

The procedure for the increase to pH equal to 10 is as follows: 100 mL of residual water was taken in a 250 mL beaker. NaOH was added dropwise by means of a burette until achieve a pH equal to 10. The amount consumed by weight of NaOH was 0.138 g. making a simple conversion, we obtain that 17.94 g must be added NaOH.

b) Water treatment with Micro-nanobubbles
For the treatment of samples with pH 6, 8 and 10 with micronanobubbles of ozone air, a water flow rate of 8 L/min, an air pressure of 30 PSI, and an O^3 generator with a concentration of 1000 mg/h.

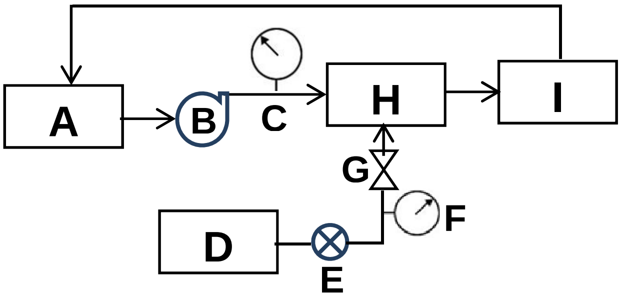

Figure 2. Presentation of the micro-nano bubble generating equipment. Where, A: water tank, B: pump, C: flowmeter, D: air generator, E: pressure valve, F: pressure manometer, G: valve (general), H: MNBs generator, I: wastewater with air MNBs.

After the treatment of the residual water with air-ozone micro-bubbles, the analysis of physical parameters (electrical conductivity, dissolved oxygen, turbidity, pH, temperature) and chemical parameters (Lead and Silicon) were carried out. A total of nine samples were taken: three subsamples of the sample with pH 6 (time of 8min, 16 min and 24 min.), Three subsamples of the sample with pH 8 (time of 8min, 16 min and 24 min.), and three subsamples of the sample with pH 10 (time of 8 min, 16 min and 24 min).

Step IV: Calculation of efficiency in the reduction of Lead and Silicon
The efficiency's determination of the physical and chemical parameters in the laboratory was carried out using the following equations.

Air MNBs treatment's efficiency on Lead (Pb) was used the equation 1:

$$\% \, Reduction(Pb) = \frac{[Pb]_{initial} - [Pb]_{end}}{[Pb]_{initial}} * 100 \quad (1)$$

Air MNBs treatment's efficiency on Silicon (Si) was used the equation 2:

$$\% \, Reduction(Si) = \frac{[Si]_{initial} - [Si]_{end}}{[Si]_{initial}} * 100 \quad (2)$$

3. Results

3.1 Preliminary results of the sample

The initial sample of wastewater was analyzed, obtaining results in the following table.

Table 2. Physical- and chemical parameters from Initial Sample

Parameter	Unit	Value
Lead	mg/L	32.26
Silicon	mg/L	70.49
pH	-	6
Disolved Oxygen	OD	6.13
Electrical Conductivity	ms/cm	4.28
Turbidity	NTU	50
Temperature	^{0}C	20

As shown in Table 2, the initial parameters values of Lead was 32.26 mg/L and Silicon was 70.49 mg/L.

3.2. Wastewater treatment with MNBs

Wastewater with pH equal to 6 reduced the Lead concentration from 32.26 mg/L to 1,519 mg/L at 24 minutes of treatment and reduced the Silicon concentration from 70.49 mg/L to 29.70 mg/L. Wastewater with pH equal to 8 reduced the Lead concentration from 32.26 mg/L to 0.088 mg/L at 24 minutes of treatment and reduced the Silicon concentration from 70.49 mg/L to 13.42 mg/L. Wastewater with pH equal to 10 reduced the Lead concentration from 32.26 mg/L to 0.563 mg/L after 24 minutes of treatment and reduced the Silicon concentration from 70.49 mg/L to 12.97 mg/L.

Table 3. Results of Silicon and Lead concentrations (in mg/L) at pH 6, 8 and 10.

	Time (min)	**Lead(mg/L)**	**Silicon(mg/L)**
Initial	**0**	32.26mg/L	70.49mg/L
pH=6	8	2.311	30.20
	16	1.909	30.10
	24	1.519	29.70
pH=8	8	0.121	13.69
	16	0.113	13.47
	24	0.088	13.42
pH=10	8	0.798	13.11
	16	0.778	13.09
	24	0.563	12.97

Table 4. Results of physical parameters of wastewater

	Time(min)	**Temperature**	**Electrical Conductivity (ms/cm)**	**Turbidity(NTU)**	**Disolved Oxygen (mg/L)**
pH= 6	8	20,4	3,08	12,47	8,17
	16	20,5	3,01	11,94	8,06
	24	21,7	3,01	11,28	8,05
pH=8	8	21,4	3,07	22	8,31
	16	20,6	2,88	22,4	8,29
	24	21,2	2,85	22,1	8,28
pH=10	8	21,3	3,05	19	8,25
	16	21,2	2,5	18,89	8,26
	24	21,1	2,01	18,22	8,28

Wastewater with pH equal to 6 slightly reduced electrical conductivity (from 4.28 ms/cm to 3.01 ms/cm), turbidity (from 50 NTU to 11.28 NTU) and dissolved oxygen increased (from 6.13 mg/L to 8.05 mg/L) at 24 minutes of treatment. Wastewater with pH equal to 8 reduced electrical conductivity (from 4.28 ms/cm to 2.85 ms/cm), turbidity (from 50 NTU to 22.1 NTU) and dissolved oxygen increased (from 6.13 mg/L to 8.28 mg/L) to 24 minutes of treatment. Wastewater with pH equal to 10 reduced electrical conductivity (from 4.28 ms/cm to 2.01 ms/cm), turbidity (from 50 NTU to 18.22 NTU) and dissolved oxygen increased (from 6.13 mg/L to 8.28 mg/L) to 24 minutes of treatment. In figure 2, the treated subsamples are appreciated. Subsequently the sediments were analyzed by fluorescence X-rays to determine the concentrations of Lead and Silicon.

The measurement and analysis of the sample by X-ray fluorescence was performed with a BRUKER Total X-Ray Fluorescence Spectrometer, model S2-PICOFOX. The X-ray source is a Molybdenum Tube, the international standard for quantification is Gallium (Ga), at a concentration of 1 g / L and the time of 500 sec.

The comparison of the spectrum of the sample analyzed with the characteristic energies of the elements from periodic table for Sodium (Na), indicate presence mainly of: Magnesium (43610 mg/kg), Silicon (12650 mg/kg), Potassium (188.6 mg/kg), Calcium (80660 mg/kg), Manganese (72.3 mg/kg), Iron (439.2 mg/kg), Nickel (4.46 mg/kg), Copper (144.1 mg/kg), Zinc (284.8 mg/kg), Strontium (435.8 mg/kg), Cadmium (400 mg/kg), Barium (445 mg/kg) and Lead (17184 mg/kg).

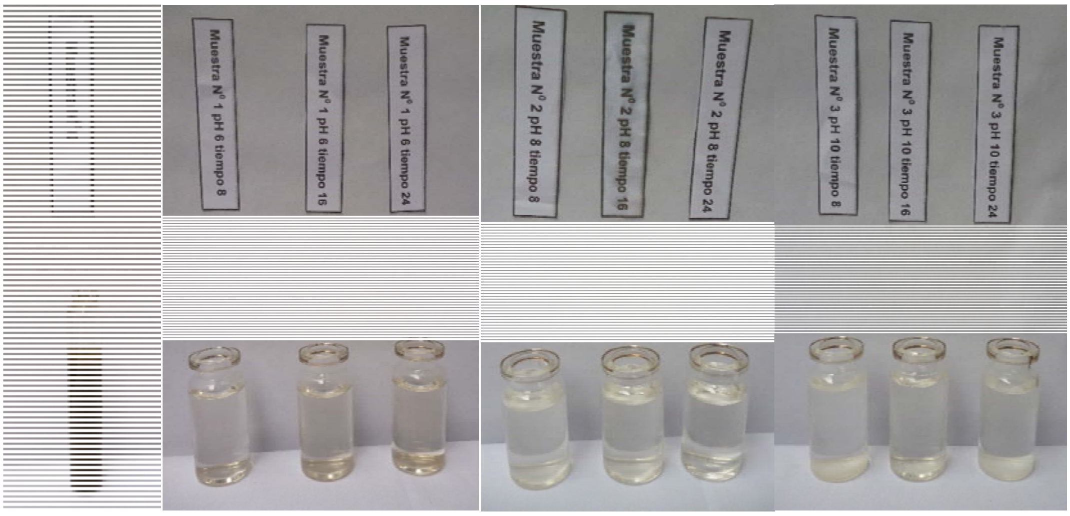

Figure 2. Samples with pH 6, 8 and 10

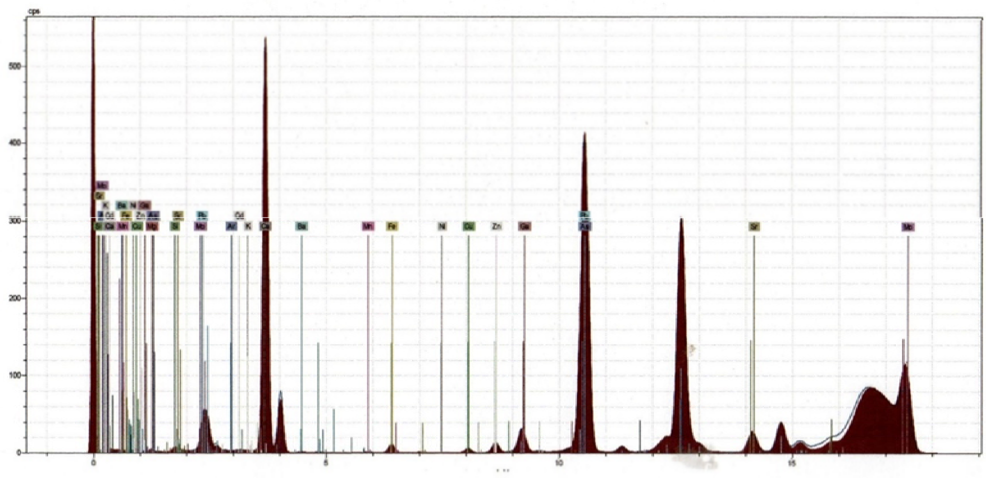

Figure 3. Spectrum of the analyzed sample with the corresponding detected elements

3.3. Calculation of efficiency in the reduction of Lead and Silicon

After using the air-ozone micronanobubbles, in a continuous system and for different times of 8,16 and 24 minutes it has been verified that the concentrations of Lead and Silicon have been reduced in each time and by the different pH (6, 8 and 10), as well as the physical characteristics.

To measure the air MNBs treatment's efficiency on Lead (Pb) was used the equation 1:

$$\% \, Reduction(Pb) = \frac{32.26-0.088}{0.088} * 100 = 99.7\%$$

To measure the air MNBs treatment's efficiency on Silicon (Si) was used the equation 2:

$$\% \, Reduction(Si) = \frac{70.49-12.97}{70.49} * 100 = 81.6\%$$

4. Conclusions

It is concluded that the wastewater from the company's gas scrubbing water exceeds the Environmental Quality Standards, having the parameter of Lead and Silicon, in category 3 being the irrigation of vegetables with 0.05 mg/L, having the initial sample of residual water with 32.26 mg/L of Lead, taking 70.49 mg/L of Silicon.

The final concentration of Lead and Silicon, after the application of air-ozone micronanobubbles at a pH equal to 8 achieved a percentage of removal of 99.7%. In the case of Silicon at pH equal to 10, a removal percentage of 81.6% was achieved.

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