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# Application of Air Micronanobubbles to Reduce Arsenic Present in an Effluent Generated at the Laboratory Level

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The objective of this research was applying air Micronanobubbles to reduce Arsenic present in an effluent generated at the laboratory level. In this research, an effluent with arsenic metal was used from a mixture of minerals with the presence of arsenopyrite with 19% As content. This mixture of minerals was stirred in a hot alkaline leaching medium at a temperature of 80 °C, with $Na_2S$ (1.5 M) and NaOH (1.0 M), then it was diluted with distilled water to obtain a volume of 100 L with a concentration of 150 ppm As. This effluent was treated with the air micronanobubble (MNB) generator equipment patented by Dr. Jhonny Valverde Flores. The variables of the pressure and the insufflation time of air as MNB in the effluent with content of the arsenic element were analyzed. A 40% decrease of As was obtained in the effluent. The results indicate that the use of MNB is promising in terms of the reduction of arsenic in solutions with concentrations of the same.

## 1. Introduction

Acid mine drainage (AMD) and mining effluents in general result in a very significant negative impact on water bodies and soil. It affects not only these environmental components but all biological activity that is comprised of these components (Hogsden and Harding, 2012; DeNicola and Stapleton, 2002). Although in some cases they are developed due to situations of natural leaching processes (Rodbell et al., 2014). The most worrisome cases are abandoned or inappropriately closed mining works at the national level, but above all Andean areas and those with difficult access, as well as El Faro Mining in Canada or mining companies in Alaska and the United States (Filion et al., 1992). The following elements are found in the water bodies from acid mine drainage (AMD) and mine effluents: mineralized rock, which has been exposed in its internal components usually iron sulfide, water, oxygen, bacteria such as Thiobacillus Ferrooxidans and Thibacillus Thioooxidans (Akcil and Koldas, 2006). As a consequence of the problem analyzed, there are the following factors: sulphide mineral, aqueous medium and bacteria, which influence the concentration of heavy metals, acidity or alkalinity of mine effluents (Kuyukac, 2021). In mining, cyanide leaching is one of the most widespread metallurgical processes and with a high polluting potential, therefore alkaline leaching emerges as an alternative due to its low toxicity and high efficiency (Sun et al., 2020). However, in some alkaline leaching processes, such as gold extraction with high arsenic content, these generate a high content of arsenate ions, which must be removed due to their high damage to the process and especially to the environment (Wang et al., 2019). It has been proven that arsenic can be adequately separated from other metals with optimal conditions of concentration, temperature and solid liquid ratio with NaOH-$Na_2S$ in a simple and efficient way (Guo et al., 2016). MNBs are characterized by their prolonged stability in aqueous media as charge, pressure and ionic absorption density (Koshoridze and Levin, 2019; Nirmalkar et al., 2018) as well as the size of their diameter, the nanobubbles being 150-200 nm, 70 µm microbubbles and 1 mm macrobubbles (Abate and Valverde, 2017; Rosa and Rubio, 2018). The insufflation of MNB, specific gases or air, into effluents contaminated with heavy metals is a technique that has been studied more frequently in recent years (Kyzas et al., 2021; Lee et al., 2020; Jin- Hee et al., 2017; Batagoda et al., 2019) and its use in environmental remediation has generated high expectations (Kyzasa et al., 2019)

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and the precision measurements are measured by scanning electron microscopy SEM, EDX, DLS (Jadhav and Barigou, 2020). Air (Huang et al., 2020), $O_2$ gas has been used to generate MNB, due to its great long-term stability (Wang et al., 2018; Khuntia et al., 2012) and also the use of nanobubbles of $CO_2$ gas bubbled for micro-extraction of heavy metals (Lee et al., 2020) is also an option. This is generated through an adjustment in the physicochemical properties of activated carbon fibers (ACF). In this experiment, the use of $CO_2$ nanobubbles could be a promising method in which case the physicochemical properties of an absorbent affect the overall microextraction performance. However, research using MNB directly as an alternative to reduce heavy metals from mine effluents has not been found. This study aims to find an alternative for environmental remediation by reducing arsenic metal with an effluent generated at the laboratory level in order to obtain a possible water remediation technique.

## 2. Materials and methods

### 2.2 Materials

One way to obtain samples is to collect directly from the natural source where the discharges or effluents are located (Chen et al., 2020). However, it is possible to carry out sample preparation in a controlled manner under laboratory conditions in order to study some specific characteristics. In this investigation, an alkaline leaching effluent containing various heavy metals was used, taking arsenic into consideration. Given this, the effluent generated in the laboratory was used with an initial concentration of 159.53 ppm of As in solution.

### 2.3 Preparation of sample

To obtain the solution that generates the effluent necessary to carry out this study, a ground sample of 1000 grams of arsenical sulfide mineral - arsenopyrite (19% As) was necessary until obtaining 80% - mesh # 400. With this ground mineral containing arsenic was leached with alkaline solutions of NaOH and $Na_2S$, in concentrations of 1 and 1.5 molar. The leaching reactor had a 3.8 L capacity. The alkaline solutions were then filtered using a 6-inch Denver brand filter press. Subsequently, the As concentration (ppm) was analyzed using ICP-OES Teledyne, Leeman Labs, Prodigy Spec model, N/S 3038. Regardless of the test performed, it is important to highlight that it was necessary to dilute with distilled water to obtain a concentration close to 150 ppm of As and a total of 100 liters of solution, with the purpose of expanding the range of tests.

### 2.3 Design of applications of MNB in the laboratory

The MNB application device used in this study is a gas micro-nano bubble generator equipment patented by Dr. Jhonny Valverde Flores (Patent no. PE20170424, 2017). The purpose of the device is to divide a jet of water under pressure and which goes through multiple holes (Sadatomi et al., 2012;) in a pipe specially designed to mix the gases that are to be insufflated which achieves diffusion of MNB throughout the solution evenly thanks to closed-loop flow (Valenzuela and Valverde, 2018). Figure 1 shows the diagram of the MNB insufflation process for liquid solutions.

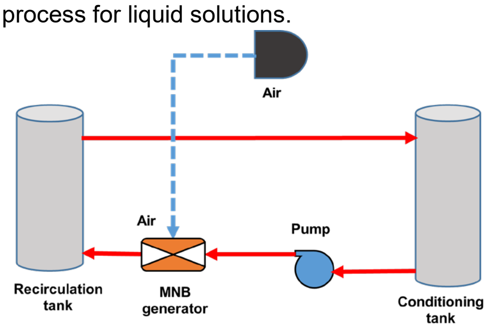


*Figure 1: Diagram of the MNB insufflation process for liquid solutions. Adapted from Garcia and Valverde (2017)*

### 2.4 Treatment description as MNB

For this investigation, 3 L of previously prepared solution of the mineral arsenical sulfide (arsenopyrite) was used, described in 2.2. This volume was added to the conditioning tank of the MNB generator equipment. Air was blown at pressures according to established levels: 10, 25, 40 and 55 psi provided by a 2 HP air compressor and volume flow of 0.17 $m^3$/min. The duration intervals of the experiment were 5, 15, 25 and 35 min. Then, the solutions were filtered and the arsenic concentration was analyzed using the ICP-OES equipment. Calculations of the arsenic removal percentage were made using the Minitab software version 19. Figure 2, represents the procedure carried out in the investigation.

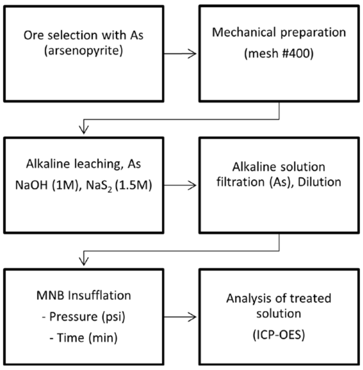


*Figure 2: Experimental Research Procedure*

## 3. Results and discussion

### 3.1 Aeration time and As reduction

Figure 3, shows the average values of the percentage decrease in arsenic as a function of aeration time, expressed in minutes, they were 55.80%, 48.96%, 27.68%, 25.16%, for values of 5 min, 15 min, 25 min and 35 min respectively. In addition, these values were statistically analyzed using a significance level of α = 0.05 and with F_0>F (∝,v1,v2) which determined that the aeration time (min) has a significant effect on the percentage decrease in arsenic, showing the highest value at a time of 5 min, with the percentage of arsenic decrease being 55.80%.

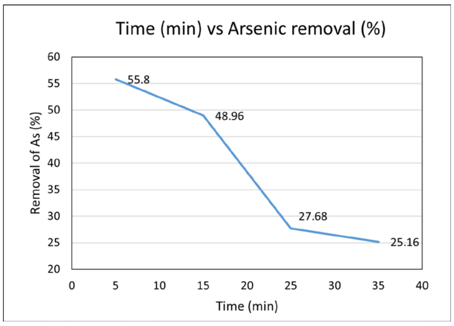


*Figure 3: Percentage´s variation of arsenic reduction vs. aeration time*

### 3.2 Air pressure and As reduction

Figure 4, shows the variation of insufflated air pressures vs. the As reduction of the study sample. It was determined that for the different pressures of insufflated air (psi) 10, 25, 40 and 55; the reduction percentages of As were 47.42%, 37.93%, 40.30% and 31.94% respectively. In addition, these values were statistically analyzed using a significance level of α = 0.05 and with F_0>F_(∝,v1,v2), managing to determine that air pressure (psi) has a significant effect on the percentage of arsenic reduction. It shows a higher value at a pressure of 10 psi, with the arsenic reduction percentage being 47.42%.

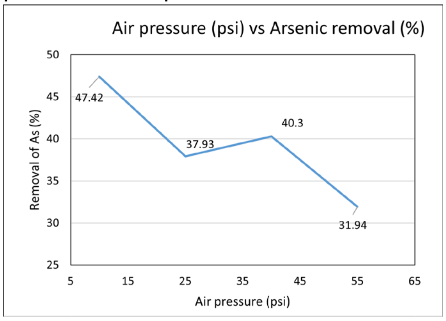


*Figure 4: Percentage´s variation of arsenic reduction vs. air pressure*

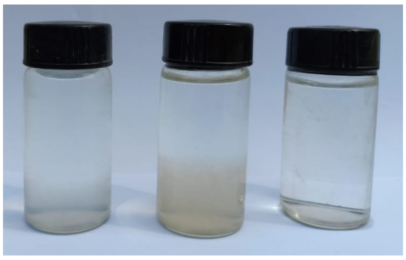

*Figure 5: Samples treatment process: Initial solution (left), solution with MNB (center), solution with MNB after 24 h (right)*

During the treatment of the solution, the formation of whitish precipitates was observed, and as the air pressure increases, it is divided into smaller parts that slow down its settling. It is likely that more precipitates that contain arsenic are being formed. However, their separation becomes more difficult, since they become colloids, and it is likely that for this reason the precipitates formed were taken at the time of obtaining the sample for analysis by ICP-OES. In the ICP-OES analysis procedure, hydrochloric, nitric and perchloric acids are added which, if there is arsenic in the precipitate, will dissolve it and the total arsenic content will increase as the air pressure increases.

*Table 1: Reduction percentage of arsenic, as a function of air pressure (psi) and aeration time (min)*

| Item N° | Air Pressure (Psi) | Time (min) | Initial As (ppm) | Final As (ppm) | As Reduction (%) |
|---|---|---|---|---|---|
| 1 | 10 | 5 | 159.63 | 71.5 | 55.21 |
| 2 | 25 | 5 | 159.63 | 63.075 | 60.49 |
| 3 | 40 | 5 | 159.63 | 70.35 | 55.93 |
| 4 | 55 | 5 | 159.63 | 78.77 | 50.65 |
| 5 | 10 | 15 | 159.63 | 71.93 | 54.94 |
| 6 | 25 | 15 | 159.63 | 89.45 | 43.96 |
| 7 | 40 | 15 | 159.63 | 75.47 | 52.72 |
| 8 | 55 | 15 | 159.63 | 95.73 | 40.03 |
| 9 | 10 | 25 | 159.63 | 96.12 | 39.79 |
| 10 | 25 | 25 | 159.63 | 127.25 | 20.28 |
| 11 | 40 | 25 | 159.63 | 114.04 | 28.56 |
| 12 | 55 | 25 | 159.63 | 135.75 | 14.96 |
| 13 | 10 | 35 | 159.63 | 100.75 | 36.89 |
| 14 | 25 | 35 | 159.63 | 119.71 | 25.01 |
| 15 | 40 | 35 | 159.63 | 127.74 | 19.98 |
| 16 | 55 | 35 | 159.63 | 129.3 | 19.00 |
| 17 | 10 | 5 | 159.63 | 69.81 | 56.27 |
| 18 | 25 | 5 | 159.63 | 65.36 | 59.06 |
| 19 | 40 | 5 | 159.63 | 68.46 | 57.11 |
| 20 | 55 | 5 | 159.63 | 77.16 | 51.66 |
| 21 | 10 | 15 | 159.63 | 70.14 | 56.06 |
| 22 | 25 | 15 | 159.63 | 86.31 | 45.93 |
| 23 | 40 | 15 | 159.63 | 72.33 | 54.69 |
| 24 | 55 | 15 | 159.63 | 90.41 | 43.36 |
| 25 | 10 | 25 | 159.63 | 93.64 | 41.34 |
| 26 | 25 | 25 | 159.63 | 117.39 | 26.46 |
| 27 | 40 | 25 | 159.63 | 108.15 | 32.25 |
| 28 | 55 | 25 | 159.63 | 131.23 | 17.79 |
| 29 | 10 | 35 | 159.63 | 97.54 | 38.90 |
| 30 | 25 | 35 | 159.63 | 124.11 | 22.25 |
| 31 | 40 | 35 | 159.63 | 125.82 | 21.18 |
| 32 | 55 | 35 | 159.63 | 130.8 | 18.06 |

### 3.3 Time and air pressure in the reduction of As

In Figure 6, the interaction of both variables is presented, showing that at 5 min of aeration and 25 psi of air pressure the highest arsenic decrease is obtained, being 59.77% and with a total arsenic concentration in the solution of 64.22 ppm.

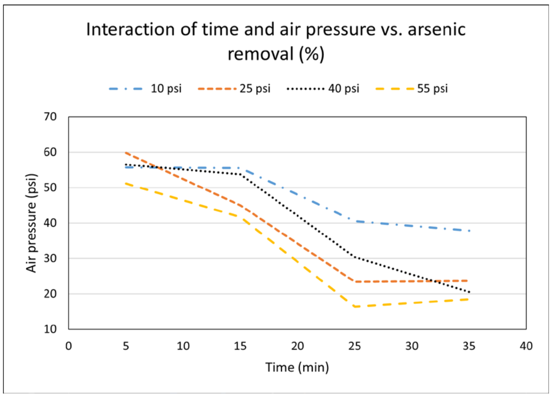


*Figure 6: Reduction percentage variation of arsenic as a function air pressure (psi) and aeration time (min).*

From the statistical analysis carried out at a significance level of α = 0.05 and with $F\_0>F\_(\propto,v1,v2)$ it was determined that the interaction between aeration time (min) and air pressure (psi) in the treatment of a solution containing arsenic (obtained by alkaline leaching with NaOH and $Na_2S$), by MNB, has a significant effect on the percentage of arsenic decrease, showing a higher value at a time of 5 min and 25 psi of air pressure.
Table 1 shows the results of the experimental tests, carried out with the MNB generator equipment at time of aeration of 5, 15, 25 and 35 min, and air pressure of 10, 25, 40 and 55 pounds per square inch (psi). The initial concentration of total As in the solution As was 159.63 ppm. After of the treatment with MNB the reduction was significant in different times. The lowest average concentration of total As was 64.22 ppm [result of [(63.075+65.36)/2]. The average reduction percentage of arsenic concentration was 59.77% [result of (60.49+59.06)/2].

## 4. Conclusions

The present study demonstrates that the use of MNB can be used as an alternative for the remediation of effluents contaminated with arsenic. In addition, the results suggest that both the application time and the pressure are two important factors to obtain positive and significant results in terms of reducing the arsenic concentration in the effluent with MNB.
In this sense, the study shows that the best operating parameters for the application of MNB are the interaction of air pressure and the time of air application have a significant influence at a significance level of 0.05, being the optimal value obtained. an air pressure of 25 psi and 5 min of air blowing, with a decrease of 59.77% and a concentration of 64.22 ppm of arsenic in the effluent.

### References

Abate B., Valverde J., 2017, Reduction of thermotolerant coliforms present in the sea water by means of micronanobubbles of air-ozone of the beach los pavos, Lima, Peru, Chemical Engineering Transactions, 60, 313-318. DOI: 10.3303/CET1760053.

Akcil A., Koldas S. ,2006. Acid Mine Drainage (AMD): causes, treatment and case studies. Journal of Cleaner Production, 14(12-13), 1139-1145. https://doi.org/10.1016/j.jclepro.2004.09.006.

Batagoda J., Aluthgun S., Meegoda J., 2019. Remediation of Heavy Metal Contaminated Sediments Using Ultrasound and Ozone Nano Bubbles. Journal of Environmental Engineering and Science, 130-138. https://doi.org/10.1680/jenes.18.00012.

Chen L., Joyanto R., Mårten D., Soumyajit S., Lezhang W., Dinggui L., Yu L., 2020. Distribution and mobilization of heavy metals at an acid mine drainage affected region in South China, a post-remediation study. Science of the Total Environment, 724, 138122. https://doi.org/10.1016/j.scitotenv.2020.138122.

DeNicola D., Stapleton M., 2002. Impact of acid mine drainage on benthic communities in streams: the relative roles of substratum vs. aqueous effects. Environmental Pollution, 119, 303-315. https://doi.org/10.1016/S0269-7491(02)00106-9.

Filion M., Sirois L., Ferguson K., 1992. Acid mine drainage research in Canada. Estados Unidos: Battelle Press.

García P., Valverde J., 2017. Reduction of metals in production plant's efluents by aplying air Micro-Nanobubbles in a factory of Lead Acid Batteries of the district of Puente Piedra, Lima. Journal of Nanotechnology, 1(1), 1-8.

Guo X.-Y., Yi, Y., Shi J., Tian Q.-H., 2016. Leaching behavior of metals from high-arsenic dust by NaOH-Na2S alkaline leaching. Transactions of Nonferrous Metals Society of China, 575-580. https://doi.org/10.1016/S1003-6326(16)64118-3.

Hogsden K., Harding J., 2012. Consequences of acid mine drainage for the structure and function of benthic stream communities: a review. Freshwater Science, 13(1), 108-120. https://doi.org/10.1899/11-091.1.

Huang X., Li Z., Deng Y., Cai W., Gu L., Lu H., 2020. Effect of Micro-Nano Bubble on the Crystallization of THF Hydrate Based on the Observation by Atomic Force Microscopy. The Journal of Physical Chemistry, 1-39. https://doi.org/10.1021/acs.jpcc.0c00181.

Jadhav A., Barigou M., 2020. Bulk Nanobubbles or Not Nanobubbles: That is the Question. Langmuir, 1699-1708. https://doi.org/10.1021/acs.langmuir.9b03532.

Jin-Hee J., Ho-Eun C., Byung-Gil J., Nak-Chang S., Gi-Chul Y., 2017. Heavy Metal Removal Efficiency in Accordance with Changes in Acid Concentrations in a Micro-nano Bubble Soil Washing System and Pickling Process. Journal of Environmental Science International, 23-28. https://doi.org/10.5322/JESI.2017.26.1.23.

Khuntia S., Majumder S. K., Ghosh P., 2012. Microbubble-aided water and wastewater purification: a review. Reviews in Chemical Engineering, 28(4-6), 191-221. https://doi.org/10.1515/revce-2012-0007.

Koshoridze S. I., Levin Y. K., 2019. Thermodynamic Analysis of the Stability of Nanobubbles in Water. Nanoscience and Technology: An International Journal, 21-27. 10.1615/NanoSciTechnolIntJ.2018028801

Kuyukac N., 2021. Water in Mining and Environment for Sustainability. Mine Water and the Environment. https://doi.org/10.1007/s10230-021-00814-x.

Kyzas G. Z., Mitropoulos A. C., Matis K. A., 2021. From Microbubbles to Nanobubbles: Effect on Flotation. processes, 8, 1287. https://doi.org/10.3390/pr9081287.

Kyzasa G., Bomisa G., Koshelevaa R., Efthimiadoub E., 2019. Nanobubbles effect on heavy metal ions adsorption by activated carbon. Chemical Engineering Journal, 91-97. https://doi.org/10.1016/j.cej.2018.09.019.

Lee J.-H., Lee S.-H., Suh D.-H., 2020. Using nanobubblized carbon dioxide for effective microextraction of heavy metals. Journal of CO2 Utilization, 101-163. https://doi.org/10.1016/j.jcou.2020.101163.

Nirmalkar N., Paceka A. W., Barigou M., 2018. Interpreting the interfacial and colloidal stability of bulk nanobubbles. Soft Matter, 9643-9656. https://doi.org/10.1039/C8SM01949E.

Rodbell D., Delman E., Abbott M., Besonen M., Tapia P., 2014. The heavy metal contamination of Lake Junín National Reserve, Peru: An unintended consequence of the juxtaposition of hydroelectricity and mining. The Geological Society of America, 24(8), 4-10. https://doi.org/10.1130/GSATG200A.1.

Rosa A., Rubio J., 2018. On the role of nanobubbles in particle–bubble adhesion for the flotation of quartz and apatitic minerals. Minerals Engineering, 127, 178-184. https://doi.org/10.1016/j.mineng.2018.08.020.

Sadatomi M., Kawahara A., Matsuura H., Shikatani S., 2012. Micro-bubble generation rate and bubble dissolution rate into water by a simple multi-fluid mixer with orifice and porous tube. Experimental Thermal and Fluid Science, 41, 23-30. http://dx.doi.org/10.1016/j.expthermflusci.2012.03.002.

Sun C., Zhang X., Kou J., Xing Y., 2020. A review of gold extraction using noncyanide lixiviants: Fundamentals, advancements, and challenges toward alkaline sulfur-containing leaching agents. International Journal of Minerals, Metallurgy and Materials, 417-431. https://doi.org/10.1007/s12613-019-1955-x.

Valenzuela L., Valverde Flores J., 2018, Reduction of lead and silicon in wastewater from gas scrubbing of a company using micronanobubbles of air-ozone, Chemical Engineering Transactions, 67, 517-522. DOI: 10.3303/CET1867087 5172.

Valverde-Flores J., 2017. Perú Patente nº PE20170424.

Wang Y., Lv, C., Xiao L., Fu G., Liu Y., Ye S., Chen Y., 2019. Arsenic removal from alkaline leaching solution using Fe (III) precipitation. Environmental Technology, 1714-1720. https://doi.org/10.1080/09593330.2018.1429495.

Wang L., Miao X., Ali J., Lyu T., Pan G., 2018. Quantification of Oxygen Nanobubbles in Particulate Matters and Potential Applications in Remediation of Anaerobic Environment. ACS Omega, 10624-10630. https://doi.org/10.1021/acsomega.8b00784.