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Reduction of Salinity from sea water using air micronanobubbles and graphene in laboratory scale

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Resumen

El objetivo de la investigación fue reducir la salinidad de las aguas de mar de San Pedro, Lurín, Peru. El método propuesto fue un pre tratamiento con Micro-Nanoburbujas (MNBs) de aire en diferentes tiempos y un post-tratamiento con grafeno a diferentes concentraciones, a esto se le denominó Grafenano. La primera etapa consistió en pasar primero las muestras recolectadas por el generador de MNBs, que permitió reducir los parámetros físicos y químicos; la segunda etapa consistió en filtrar el agua tratada con MNBs utilizando grafeno en tres proporciones 5g, 10g y 15g, que permitió reducir la concentración de sales disueltas. La salinidad del agua de mar se determinó así como los parámetros físico-químicos antes y después del tratamiento. Se caracterizaron las micronaburbujas y el grafeno. Los resultados obtenidos fueron: remoción de Turbidez en 96% (de 27.57 NTU a 1.06 NTU), de conductividad en 65% (de 49.01 mS/cm a 17.04 mS/cm), de DBO5 en 70% (de 2.42 mg/L a 0.72 mg/L) y una remoción de sales de 47% (de 34.46 g/L a 18.41 g/L).

Palabras clave: agua de mar, salinidad, grafeno, Micronanoburbuja, tratamiento

Abstract

The objective of the research was to reduce the salinity of the waters of San Pedro, Lurín, Peru. The proposed method was a pre-treatment with Micro-Nanobubbles (MNBs) of air at different times and a post-treatment with graphene at different concentrations, this was called Grafenano. The first stage was to first pass the samples collected by the MNBs generator, which allowed to reduce the physical and chemical parameters; The second stage consisted of filtering the water treated with MNBs using graphene in three proportions 5 g, 10 g and 15 g, which allowed to reduce the concentration of dissolved salts. The salinity of the seawater was determined as well as the physical-chemical parameters before and after the treatment. The air micronabubbles and graphene were characterized. The results obtained were: removal of Turbidity in 96% (from 27.57 NTU to 1.06 NTU), conductivity in 65% (from 49.01 mS/cm to 17.04 mS/cm), of BOD5 in 70% (from 2.42 mg/L to 0.72 mg/L) and a salt removal of 47% (from 34.46 g/L to 18.41 g/L).

Keywords: seawater, salinity, graphene, Micronanobubble, treatment.

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1. Introduction

Fresh water is a scarce resource and a fundamental factor for global sustainability and economic, environmental and social development. This resource is essential in all activities, both agricultural, domestic and industrial. Today, the increase in water demand has been increasingly prominent due to demographic and economic growth.

According to the UN, areas that are below 1700 m^3 (annual water supply per person) experience water stress and if it falls below 1000 m^3 there is talk of water scarcity. In relation to this, Peru has a population of 31,448,625 people, with 64,000 m^3 of water per capita per year. On the other hand, Lima hosts 9 million 985 thousand 664 people with 125 m^3 of water per capita per year (Chillón, Rímac and Lurín). This situation shows that thousands of Peruvians are experiencing great tension due to the availability of drinking water (AQUAFONDO, 2016). This problem occurs throughout Peru, since there are different factors that reduce the availability (quantity and quality) of this water resource, such as climatic conditions, geographic distribution, population growth, extractive activities, increased droughts and desertification, and so on.

Although Peru is considered as one of the main countries with the largest water reserve, there are 2.7 million Peruvians who do not have drinking water services, Lima exceeds 700 thousand people (SUNASS, 2016). This reality faces 16 districts between Lima and Callao, where 88% of water is distributed through cisterns. One of them includes the district of Lurin, whose population centers, such as San Pedro, are supplied with groundwater by a system of tubular wells without a storage system for housing with distribution by pumping, providing high costs of 2 to 10 soles per liter. (INTEGRATION, 2017).

Researches have been conducted to reduce the salinity of marine waters to obtain drinking water such as: reverse osmosis system and photovoltaic energy (Soto G., Soto M., 2013), crystallization treatment using chitosan to reduce the amount of salinity of seawater (Chacón, 2016); the solar treatment of seawater (Aylas, 2017); electromagnetic irradiation (solar and artificial) using water surfaces coated with graphite (Rainer et al., 2016), and capillary flows (Garcia, 2013).

Graphene is an atomically thick, two dimensional sheet composed of sp^2 carbons in a honeycomb structure. It can be viewed as the building block for all the other graphitic carbon allotropes. The are many potential applications for graphene, including but not limited to: additive for mechanical, electrical, termal, barrier and fire resistant properties of a polymer; surface area component of an electrode for applications such as fuel cells, super-capacitors and lithium ion batteries; conductive, transparent coating for the replacement of indium tin oxide; and components in electronics.

The Micronanobubbles (MNBs) are characterized by: their size, shape, contact angle, surface tension and internal pressure, the rate of rise of the Micronanobubbles, the pressure of the Micronanobubbles, the temperature, is altered according to the change in properties of Micronanobubbles so if the conductivity increases the viscosity of the liquid and the surface tension decreases (Tsuge, 2014).

The Microbubbles (MBs) have diameter more than 100 μm, the micro-nanobubbles (MNBs) have diameter between 1 to 100 μm and the nanobubbles (NBs) have diameter less than 1 μm within the fluid field (Valverde, 2016). The micro-nanobubbles generation technology in water is applied in: sea water, water bodies, groundwater, domestic wastewater and industrial wastewater (Valverde, 2017).

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2. Materials and Methods

The design is pre-experimental at the explanatory level. The study population was represented by the marine waters that circulate in the San Pedro de Lurín Beach, with a coastal extension of 5 meters deep. With an area it is comprised between the limits of: Mamacona beach (298078 E- 8639537 S) and Arica beach (293335 E- 8642017 S) in Lima, Peru.

The stages of the investigation are described below:

Step 1: Diagnosis of the study area.

The control points (P1, P2 and P3) for the sampling of the coastal marine waters of San Pedro beach were established by the location and delimitation of the study area through the Google Earth program. One in the area with the highest incidence of visitors, and two at both ends to determine the concentration variation of the physical and chemical parameters. The division of the area was carried out in accordance with the National Protocol for the monitoring of water quality of surface water resources No. 010-2016-ANA. (See Figure 1).

Figure 1. Map of the study area
Source: Google Earth. 2017

Step 2: Initial analysis of the sample

A preliminary preliminary analysis was carried out. The samples obtained were placed in 1 L plastic containers labeled and labeled according to the parameters analyzed for their conservation and subsequent analysis in the laboratory. Subsequently, the samples collected were taken to the laboratory where their physical parameters (temperature, turbidity, and conductivity) and chemical parameters (BOD5, COD, chloride ions, and hydrogen potential) were analyzed and evaluated.

Step 3: Water treatment with air Micronanobubbles and Graphene

Air Micro-Nanobubbles

The representative samples were transported to the laboratory for further treatment, where the MicroNanobubbles equipment was first used. The treatment time was 20, 40 and 60 minutes. For the generation of Micronanobubbles, air was used at a pressure of 80 PSI, a flow of 7.05 L/min. The average value of the diameter of the MNBs of the 3 repetitions performed is 1.65 µm.

Then these samples were subjected to a filtering system using graphene that acted as a filter for the separation of ions.

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Characterization of Graphene

The analysis to determine the characterization of graphene was carried out using the Raman spectroscopy method.

Figure 2 shows the Raman spectra of representative graphite and graphene powder samples measured at a range of 1000 to 3200 cm^{-1} with excitation wavelength of 514 nm. Where the G and 2D bands present significant changes in the shape, line width and intensity of graphite peaks compared to graphene. The most intense characteristics are in the G peak that oscillate from 1500 to 1600 cm^{-1} and a second band observed in the 2D peak whose frequency values are higher than those of the D peak, these range between 2650 to 2800 cm^{-1}

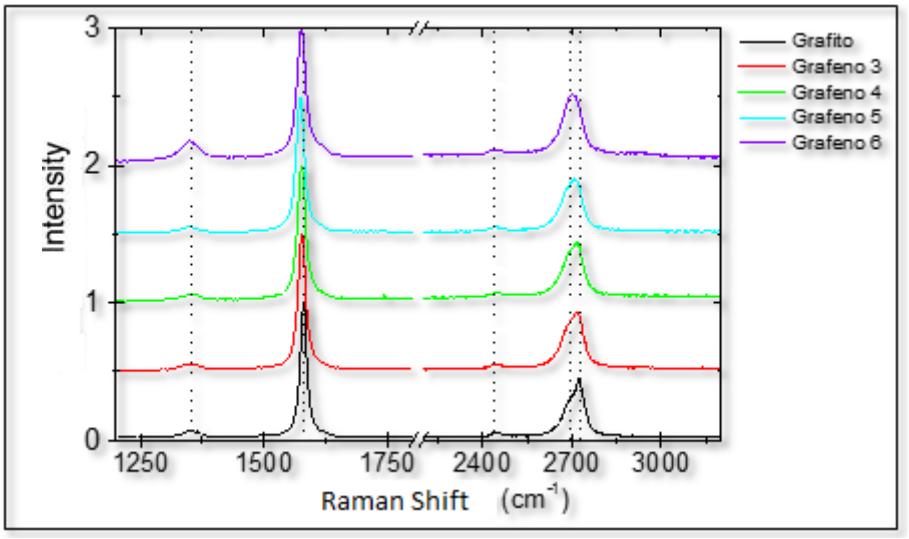

Figure 2. Raman spectra of Graphite and Graphene
Source: Service made from Centro de caracterización de materiales, PUCP, 2017

The process of reducing salts is shown in the following figure

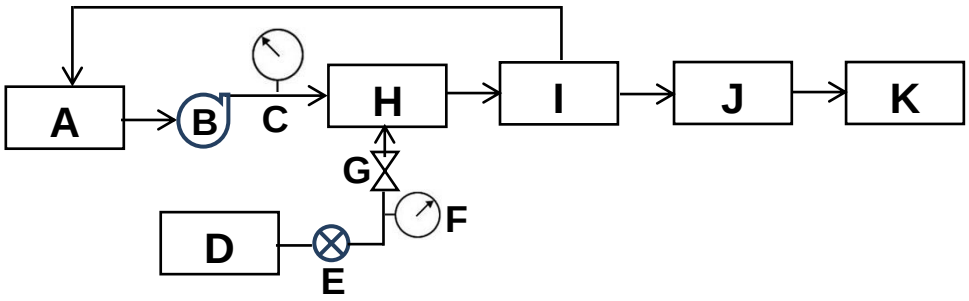

Figure 3. Presentation of the salts reduction process. Where, A: sea water tank, B: pump, C: flowmeter, D: air generator, E: pressure valve, F: pressure manometer, G: valve (general), H: MNBs generator, I: wastewater with air MNBs, J: Filter with graphene, K: treated water tank.

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Step 4: Final analysis of water samples after treatment
The final analysis of salinity and physical and chemical parameters were carried out in the laboratory after treatment with MNBs and Graphene.

The percentage of removal was calculated using the following equation:

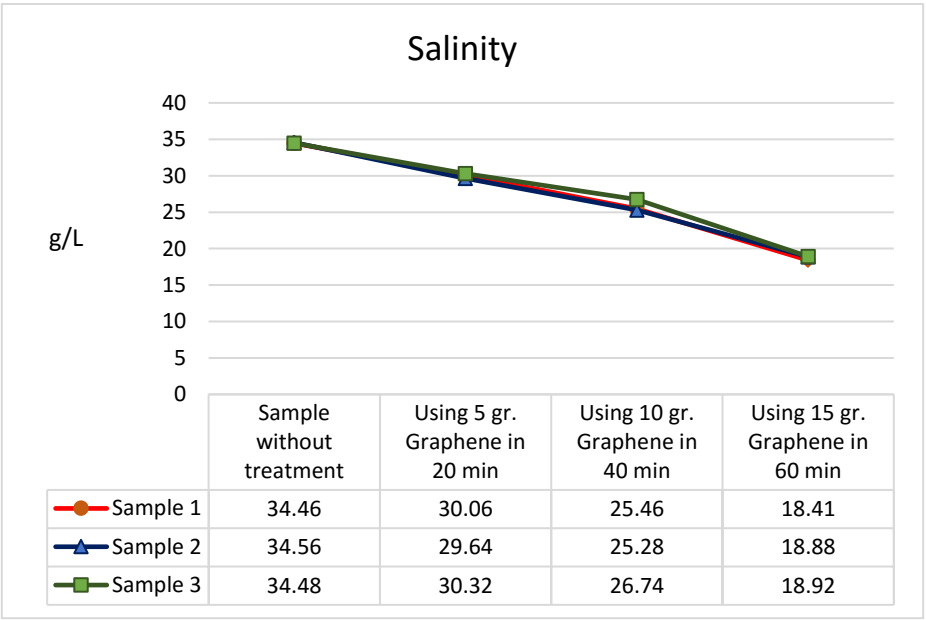
$$\%R = \frac{Ci - Cf}{Ci} * \ 100 \quad \text{..... (1)}$$

Where:
Ci is the initial concentration, Cf is the final concentration.

3. Results

This section details the results obtained from salinity, physical and chemical parameters before and after treatment with MNBs and graphene.

From the data obtained in the laboratory, the following results were obtained, which are detailed below:
The salinity of the seawater for the initial samples M1, M2 and M3 are: 34.46 g/L, 34.56 g/L and 34.48 g/L respectively. After 60 minutes of treatment using 15 grams of graphene, the salinity in the three samples is 18.41 g/L, 18.88 g/L and 18.92 g/L respectively.



	Sample without treatment	Using 5 gr. Graphene in 20 min	Using 10 gr. Graphene in 40 min	Using 15 gr. Graphene in 60 min
Sample 1	34.46	30.06	25.46	18.41
Sample 2	34.56	29.64	25.28	18.88
Sample 3	34.48	30.32	26.74	18.92

Figure 4. Results of Salinity

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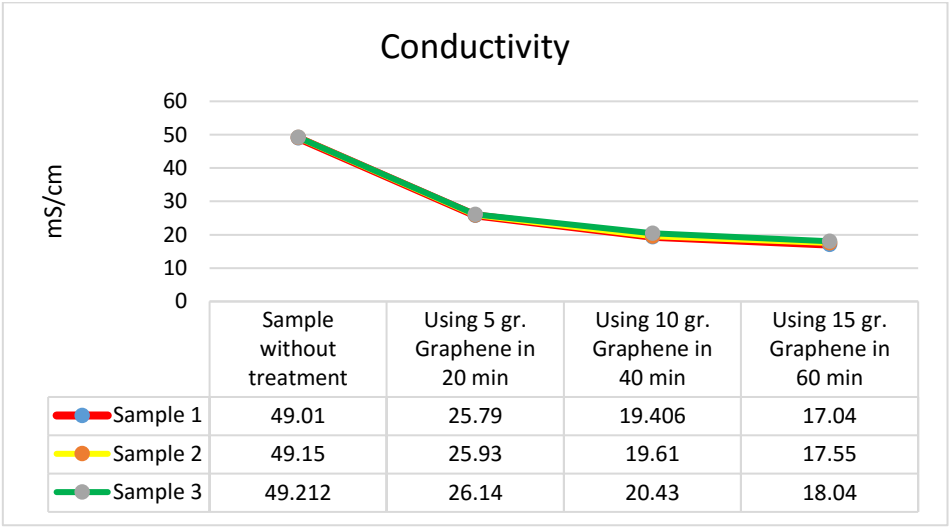
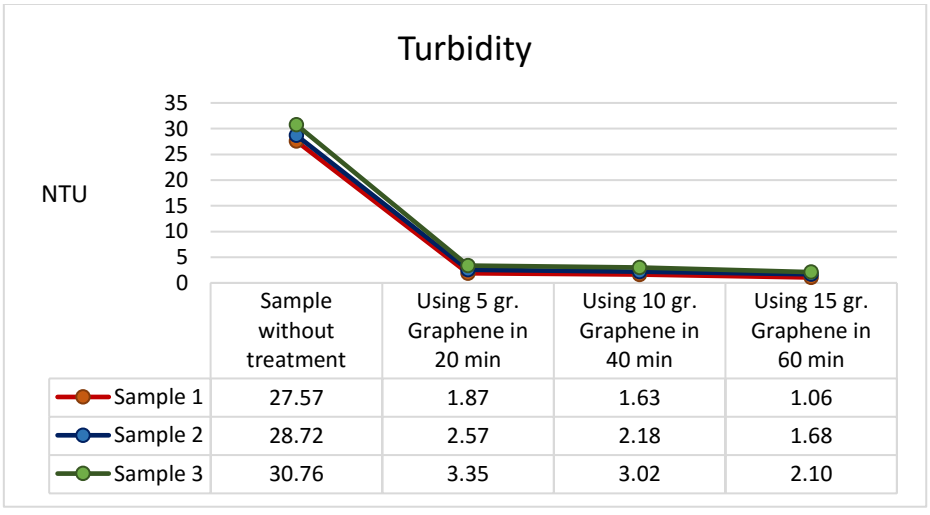
The conductivity for the initial samples of sea water M1, M2 and M3, was: 49.01 mS/cm, 49.15 mS/cm and 49.21 mS/cm respectively. After 60 minutes of treatment using 15 grams of graphene the conductivity was: 17.04 mS/cm 17.55 mS/cm 18.04 mS/cm respectively.



	Sample without treatment	Using 5 gr. Graphene in 20 min	Using 10 gr. Graphene in 40 min	Using 15 gr. Graphene in 60 min
Sample 1	49.01	25.79	19.406	17.04
Sample 2	49.15	25.93	19.61	17.55
Sample 3	49.212	26.14	20.43	18.04

Figure 5. Results of conductivity

The turbidity for the initial samples of sea water 1, 2 and 3, are: 27.57 NTU, 28.72 NTU and 30.76 NTU respectively. After 60 minutes of treatment using 15 grams of graphene, the turbidity was: 1.06 NTU 1.68 NTU 2.10 NTU respectively.



	Sample without treatment	Using 5 gr. Graphene in 20 min	Using 10 gr. Graphene in 40 min	Using 15 gr. Graphene in 60 min
Sample 1	27.57	1.87	1.63	1.06
Sample 2	28.72	2.57	2.18	1.68
Sample 3	30.76	3.35	3.02	2.10

Figure 6. Results of turbidity

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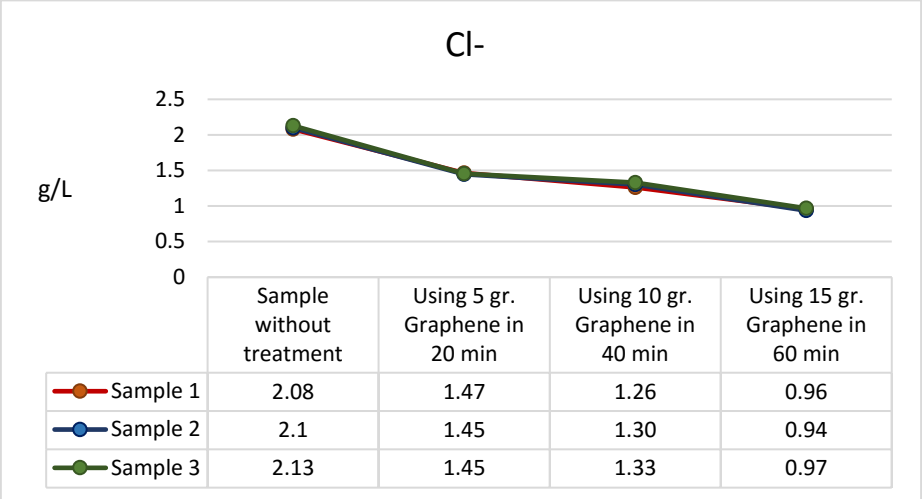
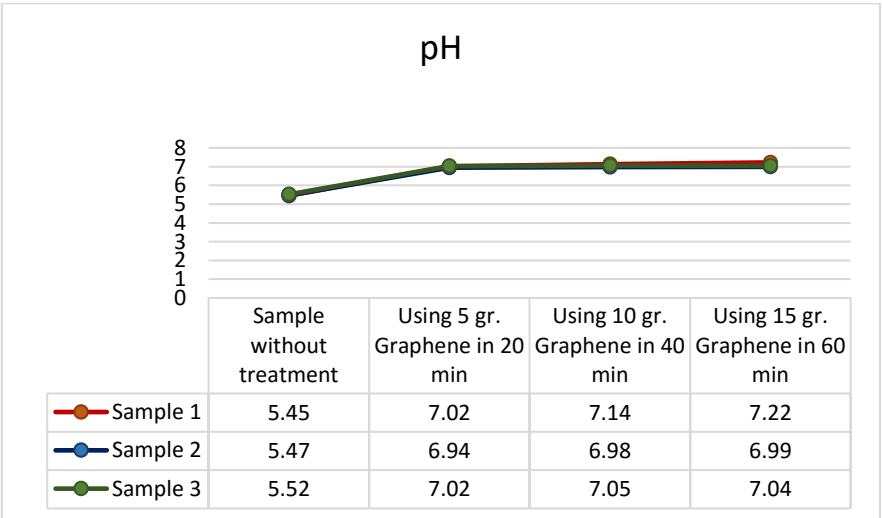
The chloride ions for the initial samples of sea water 1, 2 and 3, were: 0.96 g/L, 0.94 g/L and 0.97 g/L respectively. After 60 minutes of treatment using 15 grams of graphene the chlorides were: 0.96 g/L, 0.94 g/L and 0.97 g/L respectively



	Sample without treatment	Using 5 gr. Graphene in 20 min	Using 10 gr. Graphene in 40 min	Using 15 gr. Graphene in 60 min
Sample 1	2.08	1.47	1.26	0.96
Sample 2	2.1	1.45	1.30	0.94
Sample 3	2.13	1.45	1.33	0.97

Figure 7**.** Results of chlorides ions

The pH for the initial samples of sea water 1, 2 and 3, were: 5.45, 5.47 and 5.52 respectively. After 60 minutes of treatment using 15 grams of graphene the pH values were 7.22, 6.99 and 7.04 respectively.



	Sample without treatment	Using 5 gr. Graphene in 20 min	Using 10 gr. Graphene in 40 min	Using 15 gr. Graphene in 60 min
Sample 1	5.45	7.02	7.14	7.22
Sample 2	5.47	6.94	6.98	6.99
Sample 3	5.52	7.02	7.05	7.04

Figure 8**.** Results of pH

The BOD5 for the initial samples of sea water 1, 2 and 3, was: 1.42 mg/L, 2.42 mg/L and 2.53 mg/L respectively. After 60 minutes of treatment using 15 grams of graphene, the BOD5 values were: 0.45 mg/L, 0.72 mg/L and 0.82 mg/L respectively.

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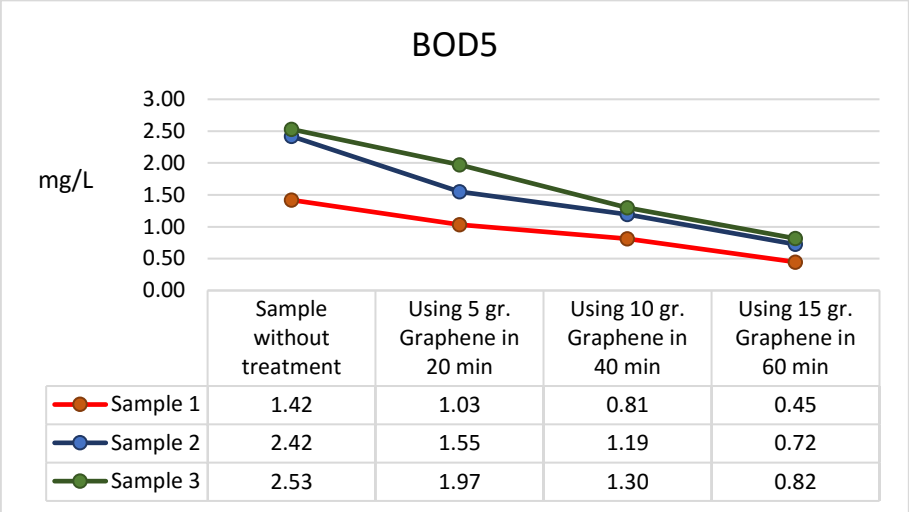
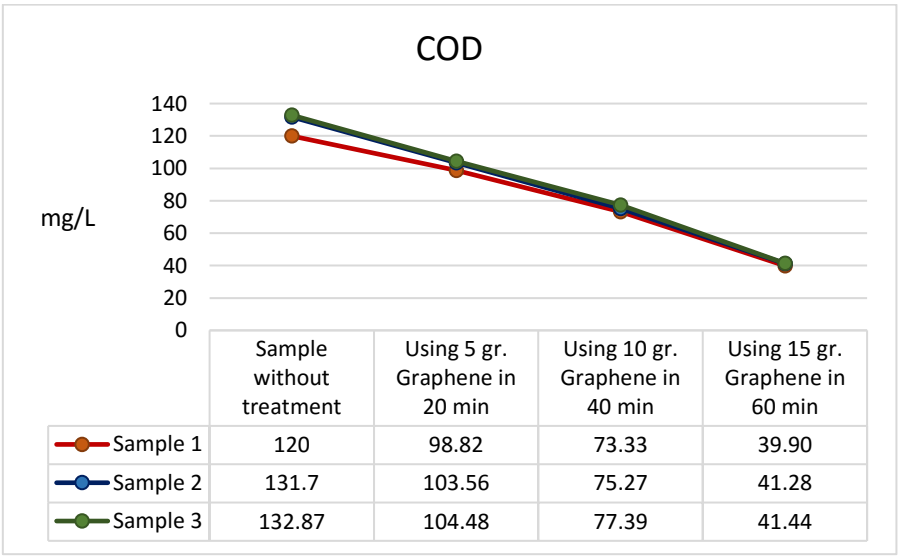


	Sample without treatment	Using 5 gr. Graphene in 20 min	Using 10 gr. Graphene in 40 min	Using 15 gr. Graphene in 60 min
Sample 1	1.42	1.03	0.81	0.45
Sample 2	2.42	1.55	1.19	0.72
Sample 3	2.53	1.97	1.30	0.82

Figure 9. Resultados de BOD5

The COD for the initial samples of sea water 1, 2 and 3 was: 130 mg/L, 131.7 mg/L and 132.9 mg/L respectively. After 60 minutes of treatment using 15 g. of graphene the COD values were: 39.90 mg/L, 41.28 mg/L and 41.44 mg/L respectively.



	Sample without treatment	Using 5 gr. Graphene in 20 min	Using 10 gr. Graphene in 40 min	Using 15 gr. Graphene in 60 min
Sample 1	120	98.82	73.33	39.90
Sample 2	131.7	103.56	75.27	41.28
Sample 3	132.87	104.48	77.39	41.44

Figure 10. Results of COD

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Salinity Removal in the treatment with air MNBs and Graphene:
The removal of salts was determined by each sample, observing that the greatest salt removal occurred in the third time of 60 minutes and with 15 g graphene tending to have a value of 47% (from 34.46 g/L to 18.41 g/L), 45% (from 34.56 g/L to 18.88 g/L) 45% (from 34.58 g/L to 18.92 g/L).

Table 1. Remotion of Salinity

	Salinity (g/L)	Remotion (%)
Initial Sample 1	34.46	
M1T1	30.06	13
M1T2	25.46	26
M1T3	18.41	47
Initial Sample 2	34.56	
M2T1	29.64	14
M2T2	25.28	27
M2T3	18.88	45
Initial Sample 3	34.48	
M3T1	30.32	12
M3T2	26.74	22
M3T3	18.92	45

4. Conclusions

From the results obtained in the present investigation, the following conclusion was reached:

- The system of reduction of salts using Grafenano at laboratory scale improves the quality of beach water, whose efficiency values are: 47%, 45% and 45%, showing that the highest percentage of salinity removal was in the third treatment time with Micronanobubbles and a post-treatment with 15g of graphene.
- It was possible to significantly reduce the concentration of salts to the seawater samples from San Pedro beach, in: 47% (from 34.46 g/L to 18.41 g/L), 45% (from 34.56 g/L to 18.88 g/L) and 45% (from 34.48 g/L to 18.92 g/L) respectively, using Grafenano at laboratory scale. Being the values of greater removal in a treatment time of 60 min with MNBs and a post-treatment at a graphene ratio of 15g.
- The turbidity of seawater samples from San Pedro beach was significantly reduced: turbidity by 96% (from 27.57 NTU to 1.06 NTU), 94% (from 28.72 NTU to 1.68 NTU) and 93% (from 30.76 NTU) to 2.10 NTU). Conductivity was reduced by: 65% (from 49.01 mS/cm to 17.04 mS/cm), 64% (from 49.15 mS/cm to 17.55 mS/cm) and 63% (from 49.21 mS/cm to 18.04 mS/cm) respectively.
- With respect to the pH values increases of 5.45, 5.47 and 5.52 before treatment, to values of 7.22, 6.99 and 7.04 after the treatment respectively. Being these directly proportion to the conductivity.
- It was possible to significantly reduce the chemical parameters to the samples of sea water: from BOD5 in 69% (from 1.42 mg/L to 0.45 mg/L), 70% (from 2.42 mg/L to 0.72 mg/L) and in 68 % (from 1.97 mg/L to 0.82 mg/L).

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References

AQUAFONDO. Agencia Digital. 05 de octubre de 2017. Available in: http://aquafondo.org.pe/

Aylas, Aracely. Obtención de agua potable mediante un tratamiento solar (destilador cascada) del agua de mar en el distrito de la Punta- Callao. 2017. Thesis in environmental engineering. Lima: Universidad Cesar Vallejo.

Chacon, Dianne. Tratamiento de cristalización utilizando el quitosano para la reducción de sal en el agua de mar, en la playa Miramar, Ancón-Lima. 2016. Thesis in environmental engineering. Lima: Universidad Cesar Vallejo.

Rainer Christoph et al. Estudio de materiales grafiticos comunes como aceleradores de evaporación de agua bajo irradiación luminosa por Realidad y Reflexión [online]. Julio-diciembre 2016, n°44. ISSN: 1992-6510. Available in: http://icti.ufg.edu.sv/doc/RyRN44-chmv.pdf

Garcia, Alfonso. Desalinización de aguas salobres mediante el uso de flujos capilares. Master Thesis in advanced technology. México: Centro de investigación en ciencia aplicada y tecnología avanzada, 2013. 73 pp.

INTEGRACIÓN. Peruanos paga hasta diez veces más por agua potable [en línea]. RPP NOTICIAS. 02 de marzo del 2017. Available in: http://rpp.pe/politica/estado/peruanos-pagan-hasta-diez-veces-mas-por-agua-potable-noticia-1034466

Soto, Guido y Soto, Manuel. Proyecto de Desalinización de agua de mar mediante sistema osmosis inversa y energía fotovoltaica para provisión de agua potable en isla damas, Región de Coquimbo. Chile: PHI, 2013. ISBN: 976-92-9089-192-5. Available in: http://unesdoc.unesco.org/images/0023/002309/230987s.pdf

SUNASS. Lima: Superintendencia Nacional de Servicios de Saneamiento. Available in: http://www.sunass.gob.pe/boletin2016/febrero/notacentral1.html

Tsuge, Hideki. Micro-And Nanoburbubles. USA: Pan Stanford publishing, 2014. ISBN: 9789814463102. Available in: https://books.google.com.pe/books?id=KiIbBAAAQBAJ&printsec=frontcover&source=gbs_ge_summary_r&cad=0#v=onepage&q&f=false

Valverde, Jhonny. 2016. Nanotechnology for the Environmental Engineering. In: First International Congress in environmental Engineering oriented to environmental technologies: 6th to 11th October. Lima, pp. 26.

Valverde, Jhonny. 2017. Advances of Micro-Nanobubbles in wastewater. In: First Regional Congress from Students of Environmental Engineering. UNMSM, Lima-Peru: 5th to 10th June 2017.