Removal of heavy metals and suspended solids from shrimp culture wastewater in Bushehr Province, using cold plasma technology

Aeinjamshid Kh. [1]*; Dashti M.A. [2]

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Abstract

The present work has been carried out to investigate the removal efficiency of active oxygen, produced by using APGP cold plasma sterilizer, on the heavy metals of Hg, Pb and Total Suspended Solids in discharge wastewater of Shif shrimp culture complex and Persian Gulf SPF shrimp research center in Bushehr province.

The maximum of removal efficiency for Hg and Pb were 66% and 74%, respectively, in 10 ppm samples. The removal efficiency for Hg and Pb in pilot phase in all studied samples were 100%. The maximum of removal efficiency for TSS was 76.3% in Persian Gulf SPF shrimp research center wastewater. The removal optimum time for all studied parameters was one hour. The results of variance analysis showed a negative and significant relationships between active oxygen and the concentrations of Hg, Pb and TSS (p-values <0.05).

The concentrations of Hg, Pb and TSS in the treated wastewaters with active oxygen were less than the Iranian Environmental Protection Organization (IEPO) regulations for discharge limit into surface water.

Keywords: Removal of heavy metals, Suspended solids, Cold plasma, Shrimp complex, Bushehr

1-Shrimp Research Center, Iranian Fisheries Science Research Institute, Agricultural Research, Education and Extension Organization, Bushehr, Iran.

2-Aray Plasma Gostar Pars, Persian Gulf Science and Technology Park, Bushehr, Iran.

*Corresponding author's Email: kh.aeinjamshid@areeo.ac.ir

Introduction

The growth of human population and the subsequent development in urban and industrial activities has endangered the coastal and marine habitats to various pollution. Heavy metals such as Mercury and lead, form toxic complexes in marine ecosystems and are very dangerous for the vital functions of living organisms. These metals are one of the stable and non-biodegradable pollutants which can enter the environment with effluent or wastewater of various industries (Babel and Kurniawan, 2004).

Choosing the best technology for treatment of urban and industrial wastewater is one of the important issues for environmental protection. New technologies make it possible to convert industrial effluents into reusable water sources. In the near future, these resources may be used in agriculture, industrial applications and beyond (Chen, 2017).

Advanced oxidation processes are a wide range of chemical treatment methods for remove of organic matter (and sometimes minerals) in water and wastewater (Antonopoulou *et al.*, 2014).

Plasma is one of the sources of advanced oxidizing species which can generate strong electric fields, energetic charged particles, ultrasound, ultraviolet rays and even shock waves, in addition to producing positive and negative ions, free radicals (• H, • OH, etc.), also produce UV rays and active molecules (nitrogen oxide, ozone and hydrogen peroxide) (Bruggeman, 2016).

Cold plasma technology is a method that is effective at normal ambient temperatures. Although cold plasma technology has not yet been used commercially on a large scale, its equipment can be easily produced on any scale. However, it is necessary to evaluate the effects of this technology for water purification on an industrial scale as well as its impact on water quality (Agostino, 2005).

The purpose of this study was to evaluate the feasibility of using cold plasma technology to remove or reduce heavy metals and suspended solids in effluent of Shif shrimp farm complex and Persian Gulf SPF shrimp research station.

Materials and methods

Water sampling for study of heavy metals (Hg and Pb) and Total Suspended Solids (TSS), with three replicate, has been carried out in all studied stations in Summer 2017.

The studied station were Shif shrimp farm complex (Shif) and Persian Gulf SPF shrimp research station (Persian Gulf station), belonged to Iran Shrimp Research Center, which are located along the coastal waters of Bushehr province (Fig. 1 and Table 1).

Temperature, salinity and pH were recorded at each station. The samples immediately transported to the Iran Shrimp Research Center (ISRC) laboratories, to exposed with active oxygen, produced by using Arya

Plasma Gostar Pars (APGP) cold plasma sterilizer.

Water temperature and pH were recorded by using Hach multiparameters model HQ40d and salinity was recorded with an Atago S/Mill refractometer. Water samples for analysis of heavy metals have been collected by using 2-L Hydro-Bios Ruttner sampler and fixed with concentrated Nitric acid. Heavy metals (Hg and Pb) concentrations were measured by Voltammetric method, using Metrohm 797 VA computrace polarograph according to Metrohm Application Bulletin (2005). TSS sampling and analysis has been done based on AHPA (2005) Method.

Figure 1: The studied area in Bushehr province, Persian Gulf.

To investigate the removal efficiency of active oxygen on the concentration of heavy metal and TSS value, 10 litters of collected waters of each station transferred to three aquariums. Then produced active oxygen by using APGP cold plasma sterilizer were injected to water samples (Fig. 2).

Also the effect of active oxygen were studied on standard solution of 1, 5 and 10 ppm of Hg and Pb.

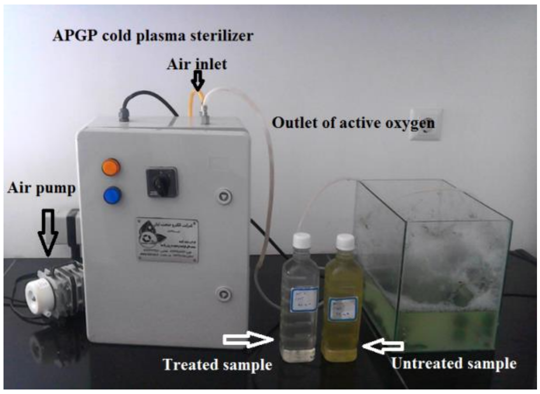

Figure 2: Injection of active oxygen to studied samples.

The removal efficiency and optimum removal time calculation

The removal efficiency for studied parameters was calculated based on equation 1.

1) Removal efficiency (%) = (X-Y)/X×100.

where as X = concentration of each parameters in untreated sample and Y = concentration of each parameters in treated sample.

The optimum removal time for studied parameters was calculated based on equation 2.

2) Optimum removal time = $(C_2-C_1)/(t_2-t_1)$

Table 1: Geographical Position of studied station, Bushehr province waters, 2011.

Row	Station	Geographical Position	
		Lat (N)	Long (E)
1	Shif shrimp farm complex	29° 01' 01"	50° 55' 40"
2	Persian Gulf SPF shrimp research station	28° 54' 49"	50° 49' 01"

where as t_1= Initial reaction time, t_2= Secondary reaction time, C_1= concentration of each parameters in t_1 and C_2=concentration of each parameters in t_2.

Data processing and statistical analysis have been done by using Excel 2010 software.

Results

Effect of active oxygen on Hg.

The averages of Hg concentration in Shif shrimp farm complex (Shif) and Persian Gulf SPF shrimp research station (Persian Gulf station) effluent were 1.00 and 0.00 (nd) ppb, respectively.

Summary results of Hg concentration in standard solutions after reaction with active oxygen are collected in Tables 2.

The average of Hg concentration in 1, 5 and 10 ppm solutions declined to 490±12, 2020±7 and 3380±7 (ppb) after 5 hours treatment with cold plasma sterilizer.

The correlation coefficient between Hg and active oxygen in 1, 5 and 10 ppm solutions were -0.94, -0.94 and -0.76, respectively. Strong negative correlation between Hg concentration and active oxygen revealed that concentration of Hg in studied solutions are decreases with increasing of active oxygen concentration.

The maximum of removal efficiency of Hg in 1, 5 and 10 ppm solutions were 50%, 60% and 66%, respectively. The optimum removal time for all studied solutions was 1 hour.

The removal efficiency of Hg in Shif and Persian Gulf station effluent were 100%. Their optimum removal time was 1 hour.

Effect of active oxygen on Pb.

The averages of Pb concentration in Shif shrimp farm complex (Shif) and Persian Gulf SPF shrimp research station (Persian Gulf station) effluent were 1.03±0.01 and 1.02±0.01 ppb, respectively. Summary results of Pb concentration in standard solutions after reaction with active oxygen are collected in Tables 3.

The average of Pb concentration in 1, 5 and 10 ppm solutions declined to 720±7, 2400±7 and 2620±0 (ppb) after 5 hours treatment with cold plasma sterilizer.

The correlation coefficient between Pb and active oxygen in 1, 5 and 10 ppm solutions were -0.71, -0.97 and -0.84, respectively. Strong negative correlation between Pb concentration and active oxygen revealed that concentration of Pb in studied solutions are decreases with increasing of active oxygen concentration.

The maximum of removal efficiency of Pb in 1, 5 and 10 ppm solutions were 28%, 52% and 74%, respectively. The optimum removal time for all studied solutions was 1 hour.

The removal efficiency of Pb in Shif and Persian Gulf station effluent were 100%. Their optimum removal time was 1 hour.

Table 2: The variation of Hg concentration (ppb) in standard solutions before and after of exposure to active oxygen.

Conc. of standard solutions (ppb)	Exposure time (hr)				
	0.5	**1**	**2**	**4**	**5**
1000	820±12	770±12	650±7	520±7	490±12
5000	3860±7	3700±7	3140±0	2670±0	2020±7
10000	5460±0	5260±7	4850±7	4270±7	3380±7

Table 3: The variation of Pb concentration (ppb) in standard solutions before and after of exposure to active oxygen.

Conc. of standard solutions (ppb)	Exposure time (hr)				
	0.5	**1**	**2**	**4**	**5**
1000	790±7	780±7	740±12	730±0	720±7
5000	4650±7	4470±7	4320±7	3440±7	2400±7
10000	5760±7	5520±12	5070±12	4050±12	2620±0

Table 4: The variation of TSS (ppm) in effluent of studied stations before and after of exposure to active oxygen.

TSS (ppm)	Exposure time (hr)				
	0	**0.5**	**1**	**2**	**4**
Shif shrimp farm	206.0±0.01	192.0±0.01	135.0±0.01	103.0±0.01	96.0±0.01
Persian Gulf station	209.0±0.01	146.0±0.01	83.5±0.01	71.5±0.01	49.5±0.01

Effect of active oxygen on Total Suspended Solids (TSS).

The average of TSS value in Shif and Persian Gulf station effluent were declined from 206.0±0.01 and 209.0±0.01 to 96.0±0.01 and 49.5±0.01 (ppm) after 4 hours treatment with cold plasma sterilizer. Summary results of TSS value in standard solutions after reaction with active oxygen are collected in Table 4.

The correlation coefficient between TSS and active oxygen in Shif and Persian Gulf station were -0.85 and -0.81, respectively. Strong negative correlation between TSS concentration and active oxygen revealed that value of TSS in studied stations are decreases with increasing of active oxygen concentration.

The maximum of removal efficiency of TSS in Shif and Persian Gulf station were 53% and 76%, respectively. The optimum removal time for all studied solutions was 1 hour.

Discussion

Cold plasma is a unique technology that enables the production of oxygen allotropes, known as reactive oxygen species or active oxygen, from pure oxygen gas or oxygen of the fresh air.

The maximum of removal efficiency of Hg in standard solution was 66% in 10 ppm samples and its minimum value was 51% in 1 ppm solution. The removal efficiency of Hg in pilot station was 100%.

The highest removal efficiency of Hg in standard solution in present work was lower than the results of Khodabakhshi (2015) which investigated the use of nanotubes coated with iron oxide to remove of mercury (93%), but this value in pilot station is higher than Khodabakhshi results.

The concentration of mercury in treated samples with cold plasma sterilizer is equal to the guideline of Iran Environmental Protection Organization for discharge of mercury into surface waters (0 ppb) (Shaeri and Rahmati, 2012).

The maximum of removal efficiency of Pb in standard solution was 74% in 10 ppm samples and its minimum value was 28% in 1 ppm solution. The removal efficiency of Pb in pilot station was 100%.

The highest removal efficiency of Pb in standard solution and pilot station of present work was higher than the results of Badmus (2007) which investigated the use of hydrogen peroxide to remove lead (72%).

The concentration of Pb in treated samples with cold plasma sterilizer is lower than the guideline of Iran Environmental Protection Organization for discharge of lead into surface waters (1 ppm) (Shaeri and Rahmati, 2012).

The maximum of removal efficiency of TSS was 76% in Persian Gulf station effluent. The removal efficiency of TSS in present work was higher than the results of Azarian (2007) study which examined the application of electrolysis process to remove TSS using steel electrodes (41%) and Bani Saeed (2007) (72%), but this value is lower than results of Sugiarto (2014) (99.8%) and Azarian (2007) which study the application of electrolysis process to remove TSS using polished aluminum electrodes (94%).

The lowest value of TSS in studied samples after treatment with cold plasma sterilizer was 49.5±0.01 which is higher than the guideline of Iran Environmental Protection Organization for discharge of Total Suspended Solids into surface waters (40 ppm) (Shaeri and Rahmati, 2012).

References

Agostino, R.P.D., Favia, P., Oehr, C. and Wertheimerv, M.R., 2005. Plasma Process. *Polym*., 2, 7.

Antonopoulou M., Evgenidou E., Lambropoulou D. and Konstantinou I., 2014. A review on advanced oxidation processes for the removal of taste and odor compounds from aqueous media, *Water Res*, 53, 215-234.

APHA, 2005. Standard Methods for the Examination of Water and Wastewater. 21st Edition, TSS 2-58, Washington DC.

Azarian, Q., Kimiaei Talab, A., Mesdaghi Nia, A. and Vaezi, F., 2007. Investigation of suspended solids and COD from effluent by electrolysis process. 10th National Conference on Environmental Health, Hamadan, Iran.

Babel, S. and Kurniawan, T.A., 2004. Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Hemosphere*, 54(7), 951–967.

Bani Saeed, N., Jafarzadeh, N., Turkian, F. And Eidan, Gh., 2007. Investigation of the possibility of using dissolved air flotation (DAF) in the removal of organic and suspended matter from the water of Karun River, 3rd National Congress of Civil Engineering, Tabriz, University of Tabriz, Faculty of Civil Engineering, https://www.civilica.com/Paper-NCCE03-NCCE03_468.html

Bruggeman, P.J. et als., 2016. Plasma liquid interactions: A review and roadmap. *Plasma Sources Science and Technology*, 25, 1.

Chen, D.H., 2017. Sustainable water management and technologies, Vol II, CRC Press Taylor & Francis Group, pp.146-168.

Khodabakhshi, A., Asgharian, H., Fadaei, A. and Sedehi, M., 2015. Investigation of Mercury (Hg+2) removal from aqueous media by multi-walled carbon nanotubes coated with iron oxide, *Journal of Shahrekord University of Medical Sciences*, 17(6), 33-44.

Metrohm Application Bulletin, 2005. Application Bulletin No. 230/2e. Voltammetric determination of zinc, cadmium, lead, copper, thallium, nickel and cobalt in water samples according to DIN 38406 Part 16.

Shaeri, A. and Rahmati, A., 2012. Laws, regulations, rules and standards of the human environment. Haq Publications.

Scholtz, V., Pazlarova, J., Souskova, H., Khun, J. and Julak, J., 2015. Nonthermal plasma--A tool for decontamination and disinfection. *Biotechnol Adv*., 1 (33), 1108-19.

Sugiarto, A.T., Permanawati, R. and Prakoso, T., 2014. Bleed water treatment using non-thermal plasma methods. International Seminar Chemical Engineering in Minerals and Materials Processing, Bandung, Indonesia, October 30th-31st.Aydoğdu, A. and Selver, M., 2005. An investigation of helminth fauna of the bleak (*Alburnus alburnus* L.) from the Mustafakemalpasa Stream, Bursa, Turkey. *Turkish Journal of Parasitology*, 301, 68-71.