Short communication

A note on a design protocol for deoxygenation of water

I. Zekos*, M.M. Stack

Department of Mechanical and Aerospace Engineering, University of Strathclyde, 75 Montrose Street, Glasgow G1 1XJ, UK

ABSTRACT

Selection of a water deoxygenation method presents some challenges due to the broad range of options including physical, chemical, electrochemical and biological techniques. This communication presents the design of an apparatus developed for efficient and simple deoxygenation of water for the purpose of electrochemical corrosion studies in a lab environment. The design is modular and can be scaled to meet processing needs. The operation of the apparatus is based on the combination of nitrogen bubbling and surface absorption to achieve complete and uncontaminated deoxygenation of water. Tests conducted on this apparatus revealed that pressurisation of the apparatus enhances economy and performance while increasing nitrogen injection rate accelerates deoxygenation. However, a point was identified, at which a balance between economy and performance is achieved and further injection rate increase suffers from diminishing returns.

1. Introduction

Removal of dissolved oxygen from water is an important process used in a number of industries in order to mitigate issues such as corrosion, poor heat transfer, oxidation of food and pharmaceuticals or even gas bubble disease in fish [1]. There are a number of physical, chemical, electrochemical [2] and biological methods for deoxygenation of water available. Physical methods include thermal degassing, vacuum degassing, nitrogen purging, desorption and degassing through a membrane [3–8]. Chemical methods include the use of reagents such as sodium sulphite [9], Wood's metal alloy [10], or hydrazine [11] and biological methods include the use of glucose oxidase [12] and yeast [13]. All the aforementioned methods come with shortcomings such as low efficiency, water contamination, high capital and operating cost, low production rate, production volume limitations, and complicated protocols. Quite often a combination of methods is selected to work around the shortcomings of individual methods. The selection of the appropriate method or combination of methods that fit the intended purpose is essential to achieve economical, rapid and simple deoxygenation of water. According to ASTM G119-09 (2016) Standard Guide for Determining Synergism between Wear and Corrosion [14] and Stack et al. [15–17] an essential part of determining wear and corrosion synergism is achieved by conducting tests under cathodic protection to quantify the corrosion-free mechanical degradation contribution. However cathodic protection alone does not fully eradicate the effect of corrosion, but in conjunction with deoxygenation of water it allows for a truly corrosion-free test to be conducted without the need

to reduce the potential to values at which hydrogen redox reaction occurs and affects the mechanical properties of the specimen. This communication aims to present the design of an apparatus that is capable of complete deoxygenation of water for the purpose of corrosion studies in a lab environment.

2. Design methodology

The deoxygenation setup was fabricated using a 105 l water tank that sits inside a steel cage designed to prevent deformation of the tank (Fig. 1). The tank is fitted at the top with a pressure gauge to monitor pressure, a ball valve to regulate pressure and a pressure relief valve to maintain a gauge pressure of 3.5 PSI. At the lower part of the tank there is a ball valve that acts as the water inlet and outlet and at the bottom of the tank sits a ceramic fine bubble diffuser connected to a regulated nitrogen supply. All components are widely available and allow for quick and easy assembly of the apparatus.

2.1. The protocol

The apparatus is sealed and purged with oxygen-free nitrogen of 99.98% purity (BOC) to ensure maximum efficiency [4]. Nitrogen purging is conducted at a rate of 1 l/min for 20 min. By displacing the atmospheric air with the injected nitrogen the interfacial area between nitrogen and the water is increased, leading to an increased rate of gas absorption [3]. Deionised water, at room temperature (20 °C) with an average DO concentration of 6.5 ppm, is then introduced in the rig at a
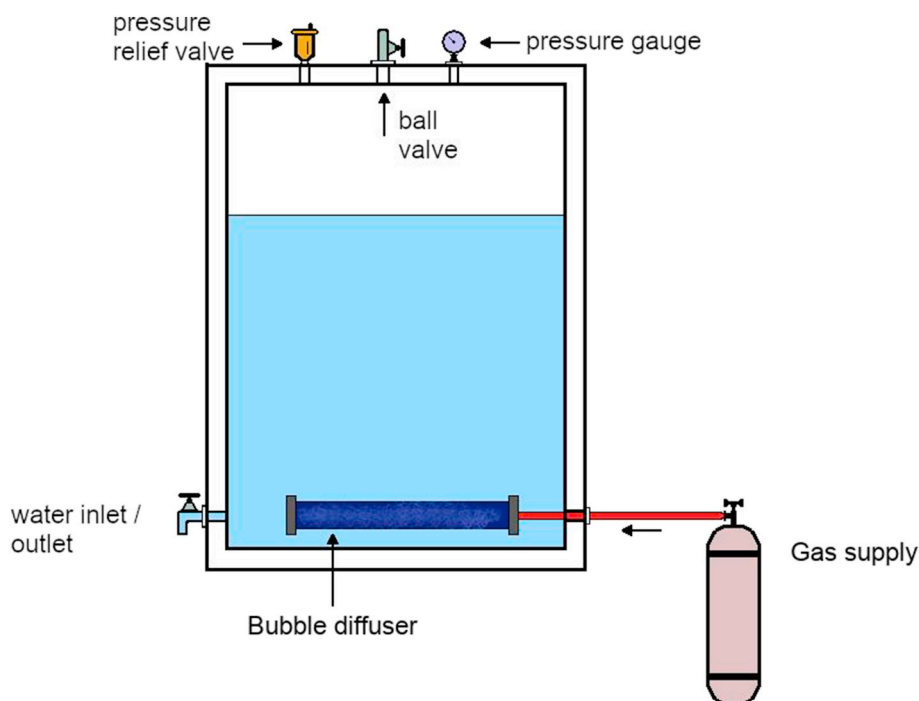

Fig. 1. Schematic of experimental apparatus for the deoxygenation of water.

rate of ~5 l/min while nitrogen injection continues at a rate of 1 l/min, amounting to a total use of 29, 34 or 39 l of nitrogen for the preparation of 45, 70 or 95 l of water respectively. At the completion of the process water DO concentration has been reduced to an average of 5.6 ppm. The injected nitrogen is broken down into micro-bubbles by the submerged sintered ceramic bubble diffuser with a mean pore diameter of 37 μm. Although for a fixed number of bubbles, big bubbles offer greater area for bubble-liquid gas exchange and are more effective than their smaller counterparts, for a fixed gas supply the bubble number and residence time increases with decreasing size leading to smaller bubbles being more effective deoxygenators [1,3]. The pressure relief valve keeps the system at a constant gauge pressure of 3.5 PSI. The pressure build-up accelerates the absorption of nitrogen through the water surface. The absorption through the surface is further enhanced by the surface agitation caused by the breaching bubbles. After a predetermined amount of time dependant on injection rate the solution is fully saturated with nitrogen and the DO levels have been reduced to 0.00 ppm as measured using a HI-2400 (Hanna Instruments) dissolved oxygen meter and Rhodazine-D reagent ampules (CHEMetrics).

3. Results and discussion

In order to determine the most efficient, and economical way of deoxygenation, and further expand the understanding of the process, nitrogen purging was conducted for 45, 70 and 95 l of water, using injection rates of 1, 2, 3, 4 and 5 l/min, under pressure and in an open environment.

Fig. 2 displays a trend of rapid deoxygenation at the initial stages of processing. However, the rate of deoxygenation steadily declines with decreasing dissolved oxygen (DO) concentration. The reduced DO concentration leads to less N_2 bubbles – DO interaction which slows down the rate of deoxygenation. This trend is present for all injection rates and environments.

In Fig. 3 the processing time required to achieve complete deoxygenation of 70 l of water in an open and a pressurised environment was plotted for a range of injection rates. It is evident that the pressurisation of the environment (3.5 PSI gauge pressure) accelerates the deoxygenation of water. At 1 l/min injection rate, pressurisation

reduced the processing time by 30%, however at the higher injection rates of 2, 3, 4 and 5 l/min the effect was reduced down to 7%, 4.5%, 5.5% and 12% respectively. In both the open and pressurised environment an increase in injection rate led to a decrease in the processing time. In both environments the degree of reduction in processing time is diminished at injection rates beyond 3 l/min.

Fig. 4 displays the deoxygenating performance of 45, 70 and 90 l of water in a pressurised environment (3.5 PSI gauge pressure). It can be seen that although the volume increase from 45 to 70 l is substantial (~60%) it is not accompanied by an analogous increase in the deoxygenation duration. In fact, the largest increase in the deoxygenation time was that of 1 min for the 1, 4 and 5 l/min injection rates while the duration for the 2 and 3 l/min injection rates remained constant. Minor duration increases are also noticed when comparing the processing time of 45 and 90 l. The 100% increase in volume leads to a 3, 2, 2, 4, and 8 min increase for the 1, 2, 3, 4 and 5 l/min injection rates respectively. Looking at the processing duration increase in terms of percentage, a trend is revealed. There is a 2.7%, 3%, 4.6%, 11.7% and 28.5% increase for the 1, 2, 3, 4 and 5 l/min injection rates respectively. It is clear that the effect of volume increase becomes more noticeable with greater injection rate values. The overall insignificant gains in the processing time with volume increase, can be interpreted by examining the geometry of the apparatus. Water volume increase only led to an increase in the height of the water column while the cross sectional area was left unaffected. The N_2 bubbles will travel the full height of the column regardless and it appears that their DO-removal properties are barely affected by traveling distance.

Looking at the consumption data in Fig. 5, it is clear that even the minor pressurisation of 3.5 PSI (gauge pressure) greatly affects consumption. Pressurisation reduces the nitrogen consumption by an average of 12.5%. Consumption in the pressurised environment follows an almost linear relationship with injection rate whereas in the open environment nitrogen consumption decreases with increasing injection rate until it reaches a low point at 3 l/min and further increase causes an increase in consumption.

The N_2 consumption data for the deoxygenation of 45, 70 and 95 l (Fig. 6) reveal an overall higher N_2 consumption for greater water volumes. However, the N_2 consumption per litre of water data portray
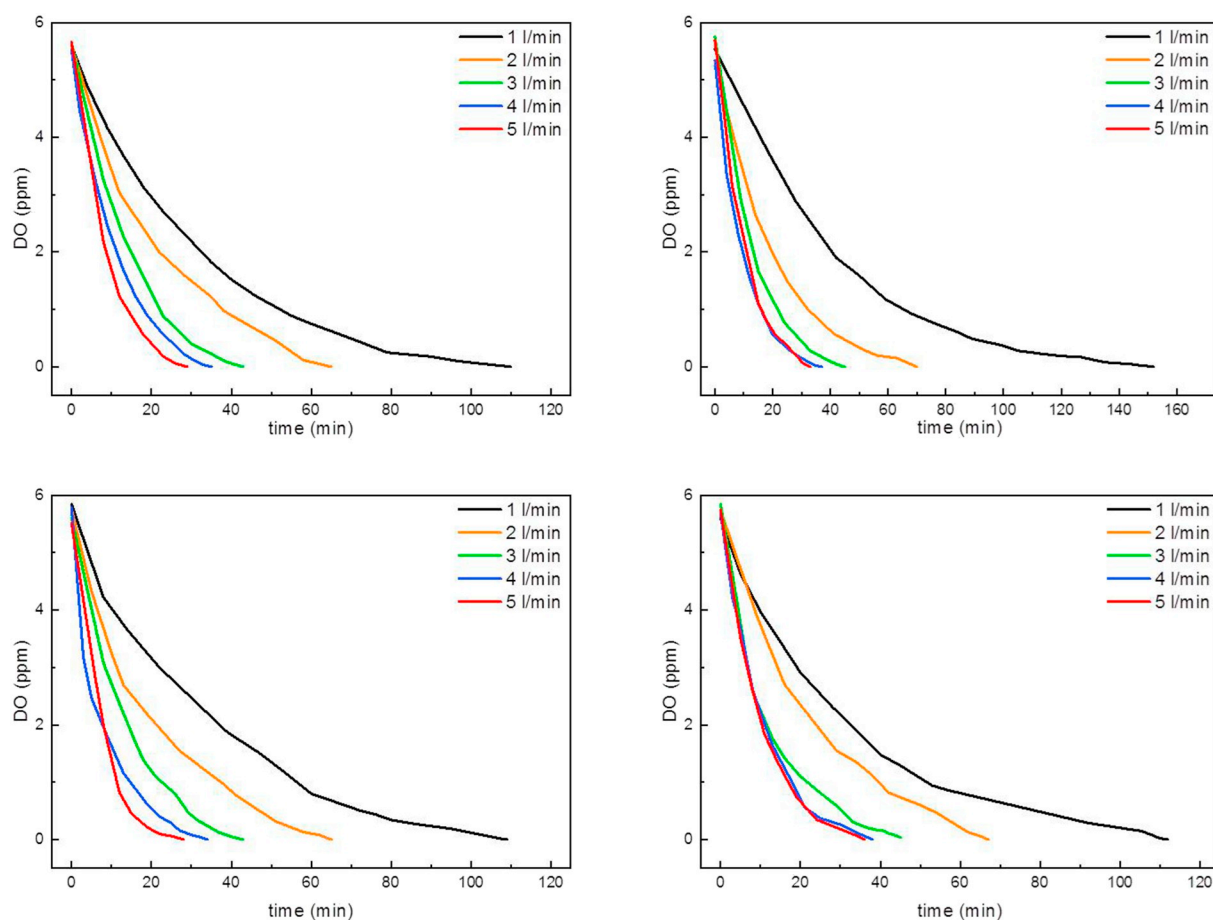
Fig. 2. Deoxygenation performance of 70 l under 3.5 PSI gauge pressure (top left), 70 l in an open environment (top right), 45 l under 3.5 PSI gauge pressure (bottom left) and 95 l under 3.5 PSI gauge pressure (bottom right).
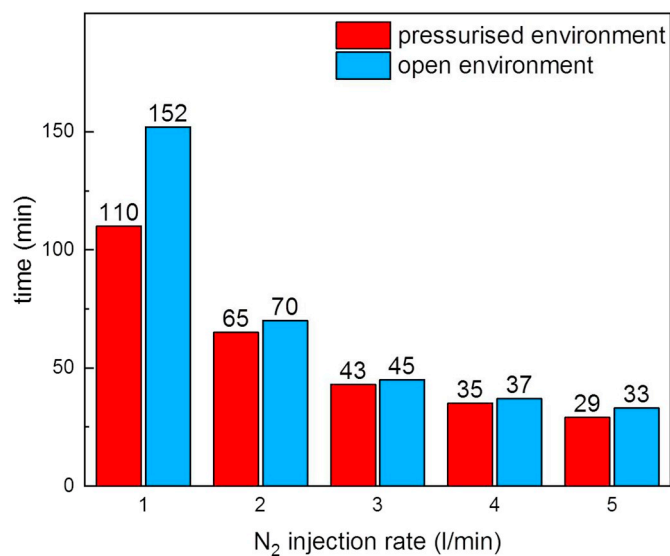

Fig. 3. Deoxygenation performance of 70 l of water in both open and pressurised environments.

Fig. 4. Deoxygenating performance of 45, 70 and 95 l of water under 3.5 PSI gauge pressure.

staggering differences (Fig. 7). The deoxygenation of 45 l displays the highest consumption of N_2 per litre of water ranging from 3.07 to 3.76 l/l, while deoxygenation of 95 l is the most economic option with consumption values ranging from 1.59 to 2.31 l/l. Furthermore, consumption increases with increasing injection rate, although for both the deoxygenation of 45 and 70 l, the consumption value for 3 l/min
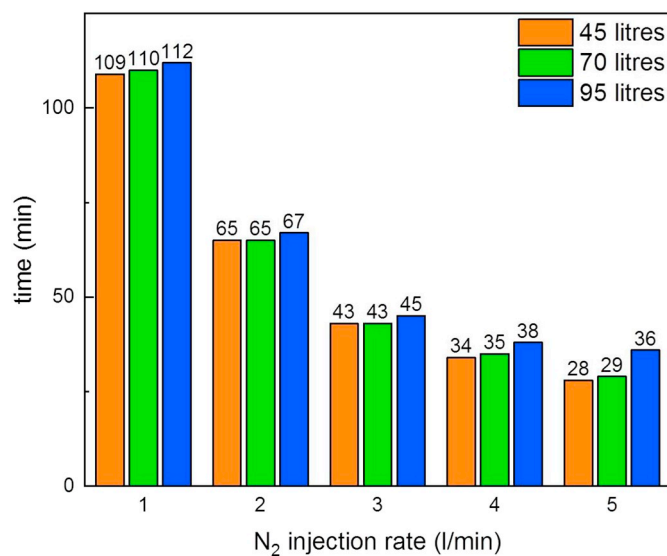
injection rate is slightly lower than that for the 2 l/min injection rate.

It is clear that increasing the volume leads to a greater overall economy while lower injection rates also offer greater economy at the expense of processing time.

Deoxygenation in this apparatus is achieved by two physical mechanisms; nitrogen bubbling and surface absorption. By pressurising the
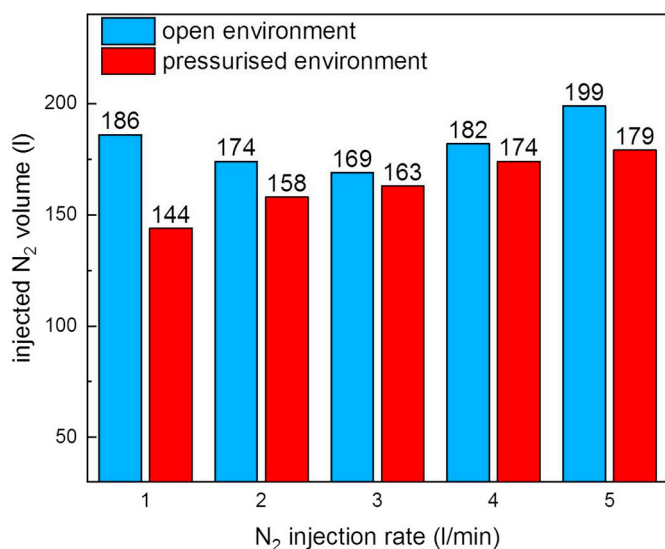
Fig. 5. Nitrogen consumption for the deoxygenation (including apparatus purging) of 70 l of water in an open and pressurised environment.
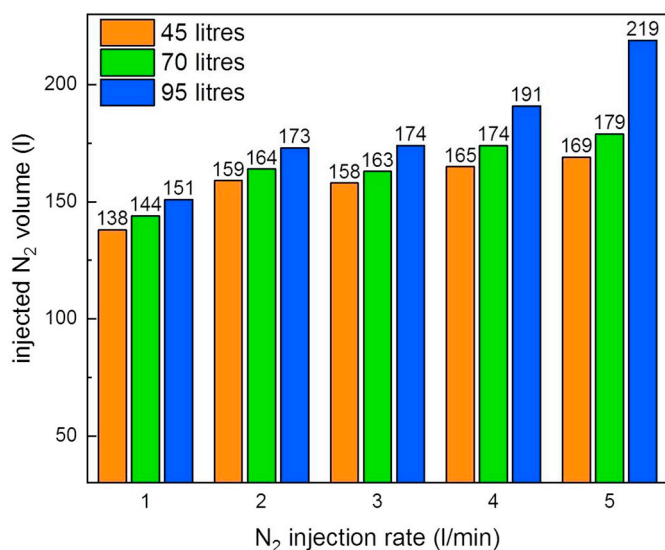

Fig. 7. Nitrogen consumption per litre of water under 3.5 PSI gauge pressure.

Fig. 6. Nitrogen consumption for the deoxygenation (including apparatus purging) of 45, 70 and 95 l of water under 3.5 PSI gauge pressure.
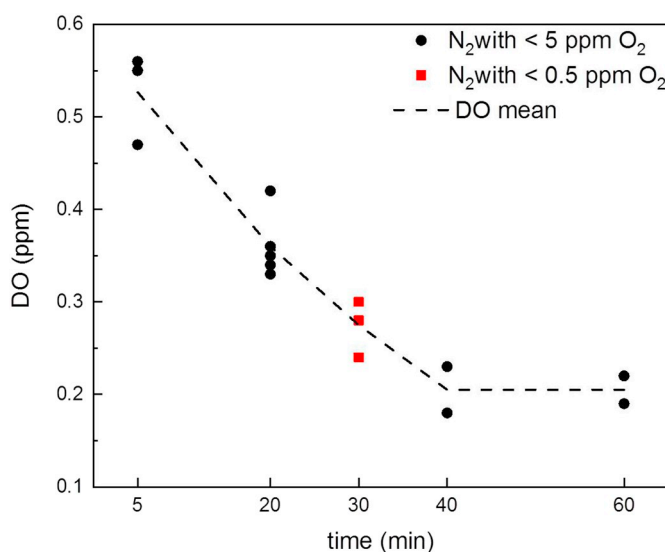
Fig. 8. Performance of N_2 purging plotted from data presented by Butler et al. [3].

environment, the mechanism of surface absorption is enhanced. The enhancement of surface absorption accelerates processing time and enhances economy by making the process less dependent on continuous nitrogen injection. In the open environment, nitrogen bubbling is the main mechanism of deoxygenation. Based on the consumption (Figs. 5, 6 and 7) and performance (Figs. 3 and 4) data, the system appears to reach a critical point at the 3 l/min injection rate. At 3 l/min, a critical number of bubbles is generated that fully engulfs the volume of water achieving optimum deoxygenation; further increase in injection rate marginally shortens the processing time and mostly increases consumption. However, it must be noted that this critical point is dependent on a number of parameters unique to this apparatus.

There are several alternative deoxygenation techniques that offer comparable results such as that by Lausier et al. [5] who by using a nitrogen powered permeator achieved a reduction in DO from 8.37 to 0.7 ppm with one pass and down to 0.12 ppm with an additional pass, or that presented by Polyanskii et al. [7] who by using a sorption membrane achieved DO concentration of less than 0.01 ppm.

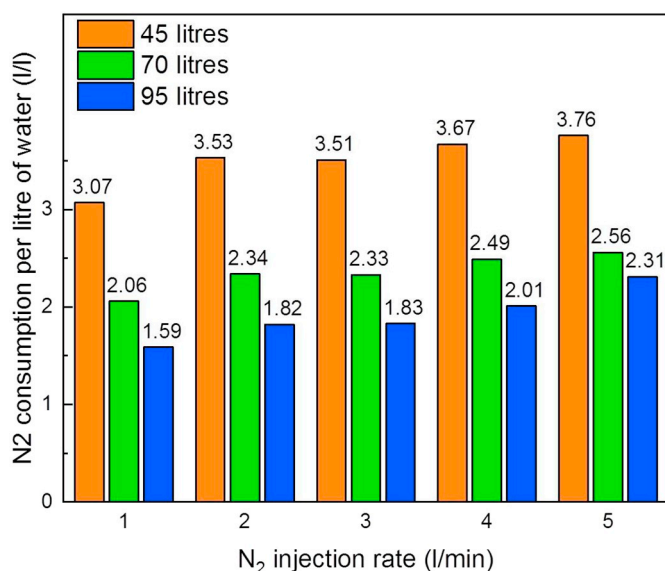However, nitrogen purging was selected as it is a very efficient and

simple technique which can also be seen in the comparison of water deaeration techniques by Butler et al. [3]. By plotting the DO measurements (Fig. 8), it can be seen that the system achieves rapid deoxygenation even after only 5 min. Its high efficiency can be attributed to the extremely high injection rate for a small volume of water (1.5 l/min for 1 l of water). The use of higher purity nitrogen, based on a very small sample size, appears to have no effect and follows the same trend of deoxygenation. The process appears to slow down at around the 0.2 ppm mark, behaviour also observed in the author's apparatus, which in this case could be due to oxygen reabsorption from the surface or due to the oxygen present in the nitrogen gas. A larger sample size is required to attain a conclusive image of the system's performance.

4. Conclusions

This communication presents the design of an apparatus that is capable of rapid, complete, simple and economical deoxygenation of small batches of water for the purpose of corrosion studies in a lab environment. It employs the combined effect of two physical methods

without the use of energy or chemical reagents that contaminate the water. The design is modular and can be scaled to adjust production batch size. It also allows for the user to optimise its performance and economy by adjusting nitrogen injection rate and pressure. However, as every other deoxygenation process examined, this apparatus has two minor limitations. The production of deoxygenated water is non-continuous and the produced water is saturated with dissolved nitrogen. Although nitrogen is inert and in temperatures below 150 °C its effect is limited to nitrogen-fixing bacteria but in temperatures above 150 °C it may be involved in abiotic redox reductions.

Tests conducted on the apparatus revealed that:

1. The rate of deoxygenation by N_2 purging is proportional to the DO concentration.
2. Efficiency and economy can be enhanced by designing a tall processing column with a small cross sectional area.
3. Maximising batch size and maintaining low injection rates can also enhance economy at the expense of processing time.
4. Applying pressure enhances surface absorption which in turn enhances economy and accelerates deoxygenation.
5. Increasing the N_2 injection rate accelerates the deoxygenation process, however after a certain point, 3 l/min for this specific apparatus, there are diminishing returns.

Acknowledgements

References

[1] Y. Zhang, G. Zhou, A. Prosperetti, Bubbles as a means for the deaeration of water bodies, J. Environ. Eng. 143 (2017) 04017034 (1–10). doi:10.1061/(ASCE)EE. 1943-7870.0001205.

[2] V.S. Gurskii, D.A. Kirpikov, E.Y. Kharitonova, Y.V. Tsapko, I.M. Yasnev, Catalytic deoxygenation of high-purity water using membrane electrode units, Russ. J. Appl. Chem. 88 (2015) 1656–1660, https://doi.org/10.1134/S107042721510016X.

[3] I.B. Butler, M.A.A. Schoonen, D.T. Rickard, Removal of dissolved oxygen from water: a comparison of four common techniques, Talanta 41 (1994) 211–215, https://doi.org/10.1016/0039-9140(94)80110-X.

[4] I. Martić, A. Maslarević, S. Mladenović, U. Lukić, S. Budimir, Water deoxygenation using hollow fiber membrane module with nitrogen as inert gas, Desalin. Water Treat. 54 (2015) 1563–1567, https://doi.org/10.1080/19443994.2014.888677.

[5] J.M. Lausier, R.J. Gerraughty, A.N. Paruta, Efficient deoxygenation of water by gas permeation, J. Pharm. Sci. 60 (1971) 1906–1907, https://doi.org/10.1002/jps. 2600601240.

[6] A. Ito, K. Yamagiwa, M. Tamura, M. Furusawa, Removal of dissolved oxygen using non-porous hollow-fiber membranes, J. Memb. Sci. 145 (1998) 111–117.

[7] L.N. Polyanskii, V.S. Gorshkov, D.D. Vakhnin, T.A. Kravchenko, Sorption-membrane system for deep deoxygenation of water, Nanotechnologies Russ 10 (2015) 558–564, https://doi.org/10.1134/S1995078015040151.

[8] P.A. Akol'zin, Corrosion prevention by the deoxygenation of water by the desorption method, Corrosion 16 (1960) 178t–180t, https://doi.org/10.5006/0010-9312-16.4.114.

[9] K.D. Efird, V.M. Putnam, A sea water deaeration procedure for conducting electrochemical experiments, Corrosion 34 (1978) 250–251, https://doi.org/10.5006/0010-9312-34.7.250.

[10] W.A. Patrick, H.B. Wagner, Method for complete deoxygenation of water, Anal. Chem. 21 (1949) 752–753, https://doi.org/10.1021/ac60030a036.

[11] J.-S. Moon, K.-K. Park, J.-H. Kim, G. Seo, The reduction reaction of dissolved oxygen in water by hydrazine over platinum catalyst supported on activated carbon fiber, Appl. Catal. A Gen. 184 (1999) 41–48, https://doi.org/10.1016/S0926-860X (99)00086-1.

[12] A. Karimi, F. Mahdizadeh, D. Salari, A. Niaei, Bio-deoxygenation of water using glucose oxidase immobilized in mesoporous MnO2, Desalination 275 (2011) 148–153, https://doi.org/10.1016/j.desal.2011.02.053.

[13] Y. de Lafontaine, S.-P. Despatie, Performance of a biological deoxygenation process for ships' ballast water treatment under very cold water conditions, Sci. Total Environ. 472 (2014) 1036–1043, https://doi.org/10.1016/j.scitotenv.2013.11.116.

[14] ASTM International, ASTM G119-09(2016) Standard Guide for Determining Synergism Between Wear and Corrosion, (2016), pp. 1–6.

[15] M.M. Stack, M.T. Mathew, C. Hodge, Micro-abrasion–corrosion interactions of Ni–Cr/WC based coatings: approaches to construction of tribo-corrosion maps for the abrasion–corrosion synergism, Electrochim. Acta 56 (2011) 8249–8259, https://doi.org/10.1016/j.electacta.2011.06.064.

[16] M.M. Stack, T.M. Abd El Badia, On the construction of erosion–corrosion maps for WC/Co–Cr-based coatings in aqueous conditions, Wear 261 (2006) 1181–1190, https://doi.org/10.1016/j.wear.2006.03.038.

[17] M.M. Stack, N. Pungwiwat, Erosion–corrosion mapping of Fe in aqueous slurries: some views on a new rationale for defining the erosion–corrosion interaction, Wear 256 (2004) 565–576, https://doi.org/10.1016/S0043-1648(03)00566-0.