Studies and Research on the Recovery of Copper from Industrial Waste Solutions by the Cementation Method

Daniela Ionela CIOLEA[1)], Oana Daniela ILCIUC[1)], Marius BERCA[2)]

[1)] University of Petroşani, 332006 Petroşani, Hunedoara, Romania
[2)] Technical University of Cluj Napoca, 400114 Cluj Napoca, Cluj, Romania
*Author for correspondence: cdipentrucdi@yahoo.com

http://doi.org/10.29227/IM-2022-02-08

Submission date: 17-08-2022 | Review date: 18-11-2022

Abstract

*The paper brings original contributions in the particularly complex field of copper recovery from industrial wastewater. The purpose of this experimental research is to recover copper metal powder from wastewater with low copper ion content, by the method of cementation using a scrap iron electrode and to calculate the yield of copper cementation, influenced by the following parameters: initial concentrations of copper ions, pH values and contact time. Recipes were experimentally studied by the cementation method for the recovery of copper from industrially used solutions using iron waste, without consumption of other reagents or energy. Work recipes were designed and one chose three different concentrations: for each solution of prepared concentration: 0.5% $CuSO_4$, 1% $CuSO_4$ and 3% $CuSO_4$, and one performed laboratory experiments at two types of pH (natural pH obtained by dissolving $CuSO_4$*$5H_2O$ in water, pH=2 (adjustment with 0.1 M sulfuric acid solution). The optimal conditions for each recipe have been identified, based on the experimental data obtained from the monitoring of each experiment, to the WTW Multi 350i multiparameter and AAS ZEEnit 700 Analytik Jena spectrometer. The calculation of the yield of obtaining copper powder for each day of the experiment and for each recipe together, the other experimental data led us to the conclusion that the optimal variant for our study is: concentration of 0.5%, at an initial pH of 3.6 after 3 days of experiment and yield of 95.23%.*

Keywords: *recovery of copper; wastewater treatment; copper cementation method*

Introduction

Copper is one of the most valuable and widely used metals in the industry. It is an essential metal for organisms, but in excessive concentrations it can be very toxic for both humans and animals (Peña M.M., Lee J., Thiele D.J., 1999). Copper is a heavy metal found in large quantities in wastewater due to its various applications in industrial sectors, such as the manufacture of printed circuit boards, the metal finishing industry, galvanizing, electrolysis, painting, wood preservation, printing operations, etc. Copper can reach the environment from mines, farms, industrial installations through wastewater discharged into rivers, lakes, but also from natural sources, such as: volcanoes, degraded vegetation, forest fires (Mubarak A., 2006). Copper was the first metal used in undetermined amounts by man. The oldest craftsmen who worked with copper soon found that it is easy to form into sheets with a hammer and sheets in turn worked into other shapes that became more and more complex as their skill increased.

Through the project (https://umfcd.ro/cercetare...SARS-COV-2) PN-III-P2-2.1-SOL-2020-2-0208 Development of innovative solutions for the protection of personnel (exposed professionally) and the population against contamination with the virus SARS-CoV-2, studies of impregnation of cotton or medical equipment made of cotton fabric. Various impregnation recipes were used that allowed to obtain "in situ" the nanoparticles of copper and zinc oxides for the impregnation of cotton fabrics, in different concentrations and ratios. The stability of the impregnation of the nanoparticles was confirmed by chemical analysis and analysis by scanning tissues of the tissues after 1, 3 or 5 washes. It has proved to be a good enough stability and it is expected that even after 10 washes an amount of about 40–50% of the initially impregnated amount will still be fixed on the fabric. The washes involve a pH-neutral detergent for 30–50 minutes at a temperature of 30–40°C ((https://umfcd.ro/cercetare...SARS-COV-2) PN-III-P2-2.1-SOL-2020-2-0208).

Copper is present in normal human serum (the liquid part of the blood) at concentrations of 120 –140 μg/l. Signs of toxicity will be observed if the copper concentration increases significantly above this level. All copper compounds are potentially toxic. Thus, man can be exposed to copper by breathing air, drinking water, food he consumes, by skin contact with copper or its compounds (Solomon F., 2009).

The use of copper to kill algae, fungi and mollusks proves to be very toxic to aquatic organisms. In fact, copper is one of the most toxic metals to aquatic organisms and ecosystems. Copper recovery from wastewater is achieved by various methods, such as bioadsorption, ion exchange, membrane filtration, reverse osmosis, chemical precipitation, electrochemical processes, photocatalysis, cementation (Gunatilake S.K., 2015).

Each of these methods has its own advantages and disadvantages. Unfortunately, some of these methods are difficult to use widely or expensive to apply. The use of the cementation method for the recovery of copper from metallic wastewater can be considered as a relatively simple, inexpensive and environmentally friendly method. Contamination of metal-treated water is a serious problem for many industrial sectors.

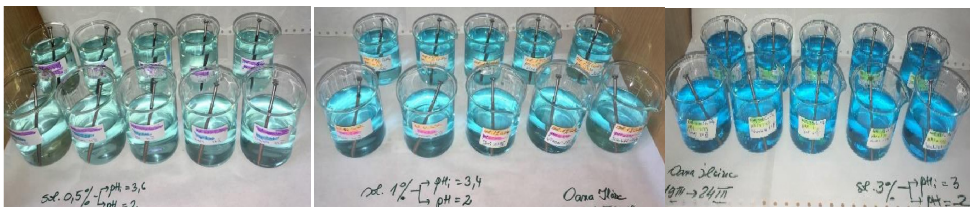

Fig. 1. Samples 3 solutions of different concentrations of $CuSO_4$ prepared for analysis
Rys. 1. Próbki 3 roztworów o różnych stężeniach $CuSO_4$ przygotowany do analizy

Tab. 1. Physico-chemical parameters of synthetic $CuSO_4$ solutions
Tab. 1. Parametry fizykochemiczne roztworu syntetycznego $CuSO_4$

$CuSO_4$ concentration	**pH initial**	**ORP (mV)**	**EC (µS/cm)**	**TDS (mg/l)**	**Salinity (‰)**
0.5%	3.6	+ 178.6	2480	1588	1.3
	2	+ 269	4570	2970.5	2.4
1%	3.4	+ 189.3	4250	2762.5	2.3
	2	+ 267.6	6190	4023.5	3.4
3%	3.0	+ 211.3	10290	6688.5	5.8
	2	+ 267.9	11910	7741.5	6.8

Tab. 2. Cu^{2+} values determined on the AAS ZEEnit 700 spectrometer
Tab. 2. Wartości Cu^{2+} wyznaczone na spektrometrze AAS ZEEnit 700

Time hours	*$CuSO_4$ 0.5% pH=2.0*	*$CuSO_4$ 0.5% pH=3.6*	*$CuSO_4$ 1% pH=2.0*	*$CuSO_4$ 1% pH=3.4*	*$CuSO_4$ 3% pH=2.0*	**$CuSO_4$ 3% pH=3.0**
0	2092.19	2092.19	4184.38	4184.38	12553.14	12553.14
24	628.66	627.33	3187.86	3177.44	4841.17	4601.41
48	488.31	487.35	626.92	623.33	4654.42	1749.41
72	182.26	140.15	483.41	481.71	1841.82	952.12
96	32.81	16.84	91.76	181.65	323.8	904.85
120	10.14	6.51	16.03	19.41	175.5	310.04

There are many different techniques used to treat wastewater to reduce metal content. A common technique involves raising the pH of the wastewater to an alkaline level to induce precipitation of the metal. Although this method reduces the metal content of wastewater, the resulting solid sludge will require additional treatment (Moscatello N., Swayambhu G., Jones G.H., Jiale Xu, Ning Dai, Pfeifer B.A., 2018).

Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many of their ions are known to be toxic or carcinogenic (Fenglian Fu, Qi Wang, 2011). Copper has many practical uses in our society and is often found in coins, electric cables and pipes. However, too much copper can cause adverse health effects.

Materials and Methods

Cementation consists in the precipitation of metals from a solution of its salts by another electropositive metal (sacrificial metal) by spontaneous electrochemical reduction to its metallic state (Peng C., Liu Y., Bi J., Xu H., Ahmed A.S., 2011). The cementation method has several advantages, such as the recovery of metals in relatively pure metallic form, simple control requirements, low energy consumption and is generally a low cost process (Nassef E., El-Taweel Y.A., 2015). Cementation of copper on iron is done by a series of short-circuited electrochemical cells, in which electrons reduce the transfer of Cu2+ from the iron surface through the growing copper deposit. Copper ions are reduced from the surface of the copper deposit. Iron, which supplies electrons, is oxidized in the anodic places on its surface (EL-Ashtoukhy E.S.Z., Abdel A.M.H., 2013). However, it seems that cementing using an iron electrode is the simplest and most reasonable method for recovering copper. Therefore, it produces copper metallic sediments, which are suitable for metallurgical processes.

Eguipment used

Determination of physico-chemical parameters

Using the WTW Multi 350i multiparameter, the following physico-chemical parameters were measured:

- electrical conductivity (EC);
- total dissolved solids (TDS);
- salinity;
- pH;
- redox potential (ORP).

Before the analyzes were performed, the apparatus was calibrated using standard solutions for pH and conductivity.

Determination of heavy metals

Heavy metals were analyzed by flame atomic absorption spectrometry (AAS-F) using the AAS ZEEnit 700 Analytik Jena apparatus. The device allows the analysis of the following heavy metals: Ni, Cd, Cr, Pb, Zn, Cu, Fe, using the lamp specific to each metal. The detection limit of the method is between 0.01–0.08 mg/l, depending on the metal. Prior to analysis, the water samples were acidified to pH 2 (using 65% HNO_3) and filtered.

Cementation method-use of iron electrode

Procedure: studying the scientific information presented in the specialized articles, regarding the cementation method for the recovery of copper from used solutions, one observes the following:

- the mode of work is specific to a laboratory work (small amounts of used copper solutions 0.1–10 l, using continuous mixing and sometimes heating).
- the influence of the pH of the used copper solution on the recovery yield or efficiency (natural pH was

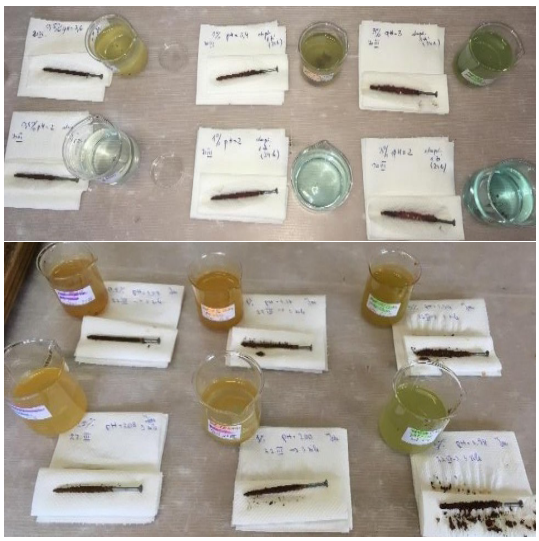

Fig. 2. Samples with the amount of copper deposited on the iron, from different days of the experiment
Rys. 2. Próbki z ilością miedzi osadzonej na żelazie w różnych dniach doświadczeń

Tab. 3. Yield values for the 3 solutions
Tab. 3. Wartości wydajności dla 3 roztworów

Concentration (%)	pH	Optime time (days)	$\eta_{optimal}$
0,5	3.6	3	95.23
	2	3	85.71
1	3.4	3	76.2
	2	4	97.62
3	3	3	86.83
	2	4	96.4

helped with 0.1 M H_2SO_4 solution up to pH 2).

- the working method designed for the experimental part simplifies the laboratory equipment (without agitation, without heating, with initial pH adjustment of $CuSO_4$ solutions prepared in the laboratory at a pH of 2, Fig. 1.) and one sought to identify the optimal conditions for copper deposition in a reasonable time.

One prepared 3 solutions of different concentrations of CuSO4 of 0.5%, 1%, 3% by dissolving the calculated amounts of CuSO4*5H2O for 250 ml volumetric flasks (stock solutions), (Table I) and the parameters were measured with multiparameter WTW Multi 350i.

One monitored day by day, the changes of previously measured parameters, with WTWMulti350i but also the amount of copper deposited (Fig. 2.), along with determining the daily concentration of copper ions remaining in solution at AAS ZEEnit 700 spectrometer, so one could calculate the efficiency and daily efficiency of experiments (Table 2).

Results

One started the experiment by preparing 3 solutions of different concentrations, of 0.5% CuSO4, 1%, 3% by dissolving the calculated amounts of $CuSO_4*5H_2O$ for 250 ml rated flasks. One monitored the changes in previously measured parameters with WTW Multi 350i but also the amount of copper deposited, along with determining the daily concentration of copper ions remaining in solution at the AAS ZEEnit 700 spectrometer, so one could calculate the daily efficiency and effectiveness of our experiments.

For each concentration solution prepared: 0.5% $CuSO_4$, 1% $CuSO_4$ and 3% $CuSO_4$ were performed laboratory experiments at 2 different pH:

a) the natural pH obtained by dissolving $CuSO_4$ in water;
b) pH=2 (adjustment with 0.1 M sulfuric acid solution).

The variation of salinity is observed, for the 3% pH 2 solution, which is fluctuating, reaching 6.8‰. The variation of the concentration of copper ions is observed, for the 3% solution (12553.14 mg / l) at pH 2, which is decreasing, reaching 175.5 mg/l. It is observed that after 4 days from the experiment, the concentration of copper ions reaches 323.8 mg/l, which gives us the possibility to identify an optimal time for the experiment (Fig. 3.).

The synthesis yield is defined as the ratio between the practical mass obtained by copper powder (dry) and the terrorist mass (Călțaru M., Bădicioiu M., 2007).

It is observed that after 4 days the copper recovery efficiency stabilizes at 96.4%. It should be noted that after the first day of the experiment (24h), the yield is almost 89% (Fig. 4). Which demonstrates the effectiveness of the iron waste used in the cementation method.

Table 3 shows yields over 95%, for all 3 optimal variants, but the time to obtain the optimal yield will differentiate the overall optimal variant, which one propose to be: concentration of 0.5%, at an initial pH of 3.6 after 3 days of experiment and yield of 95.23%.

Discussion

The resultated obtained for the variation of pH, EC, salinity, copper ion concentration and yield is the follow:

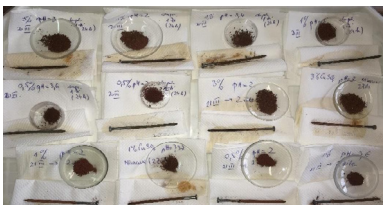

Fig. 3. Samples with the amount of copper deposited on the iron, from different days of the experiment
Rys. 3. Próbki z ilością miedzi osadzonej na żelazie z różnych dni doświadczenia

Fig. 4. The amount of copper powder obtained after one day of experiment
Rys. 4. Ilość proszku miedzi uzyskanego po jednym dniu doświadczenia

0.5 % copper sulphate solution of initial pH=3.6

The pH variation for the 5 days of the experiment is fluctuating, falling between 3.6–4.1 with an average of 3.88 (note that pH=4.1 is obtained after 4 days). The variation of the EC (μS/cm) for the 5 days of the experiment is increasing, ranging between 2480–2860 μS/cm, with an average of 2693.3 μS/cm (note that EC = 2860 μS/cm is obtained after 5 days). The variation of salinity (‰) for the 5 days of the experiment is increasing, ranging between 1.3–1.5‰, with an average of 1.4‰ (note that S=1.5‰ is obtained after 5 days). The variation of the copper ion concentration (mg/l) for the 5 days of the experiment is decreasing from 2092.19 mg/l to 6.51 mg/l (on the 5th day) which demonstrates that in these conditions the method cementation also helps us in solving the problem of the concentration of copper ions in the used industrial solution because after 5 days it reaches ovals below 10 mg/l (a decrease of about 322 times). The calculated synthesis yield is 95.23% after 3 days of experiment.

0.5 % copper sulfate solution at adjusted pH=2

The pH variation for the 5 days of the experiment is increasing, ranging between 2–3.8 with an average of 3.35 (note that pH=3.8 is obtained after 3 days). The variation of the EC (μS/cm) for the 5 days of the experiment is decreasing starting from 4570–2960 μS/cm, with an average of 3370 μS/cm (note that EC = 2960 μS/cm is obtained after 2 days). The variation of salinity (‰) for the 5 days of the experiment is decreasing, starting from 2.4–1.5 ‰, with an average of 1.7‰ (note that S = 1.5 ‰ is obtained after 2 days). The variation of the concentration of copper ions (mg/l) for the 5 days of the experiment is decreasing from 2092.19 mg/l to 10.14 mg/l (on the 5th day), which demonstrates that in these conditions the cementation method also helps us in solving the problem of the concentration of copper ions in the used industrial solution because after 5 days it reaches a value of about 10 mg/l (a decrease of about 209 times). The calculated synthesis yield is 85.71% after 3 days of experiment.

Analyzing the data obtained for the two pH at the 0.5% $CuSO_4$ solution, it is observed that the optimal conditions for cementation would be for the initial pH=3.6, because the yield is 95.23%, after 3 days of experiment.

1% copper sulphate solution at initial pH=3.4

The pH variation for the 5 days of the experiment is fluctuating, falling between 3.4–3.77 with an average of 3.61 (note that pH=3.77 is obtained after 3 days). The variation of the EC (μS/cm) for the 5 days of the experiment is increasing, ranging between 4250–5040 μS/cm, with an average of 4691 μS/cm (note that EC = 5040 μS/cm is obtained after 5 days). The variation of salinity (‰) for the 5 days of the experiment is increasing, falling between 2.3–2.7‰, with an average of 2.51‰ (note that S = 2.7‰ is obtained after 5 days). The variation of the concentration of copper ions (mg/l), for the 5 days of the experiment is decreasing from 4184.38 mg/l to 19.41 mg/l (on the 5th day) which proves that in these conditions the cementation method it also helps us in solving the problem of the concentration of copper ions in the used industrial solution because after 5 days it reaches a value below 20 mg/l (a decrease of about 215 times). The calculated synthesis yield is 76.2% after 3 days of experiment.

1% copper sulphate solution at adjusted pH=2

The pH variation for the 5 days of the experiment is increasing, ranging between 2–3.65 with an average of 3.12 (note that pH=3.65 is obtained after 5 days). The variation of the EC (μS/cm) for the 5 days of the experiment is decreasing starting from 6190–5480 μS/cm, with an average of 5383.3 μS/cm (note that EC = 5480 μS/cm is obtained after 5 days). The variation of salinity (‰) for the 5 days of the experiment is decreasing, starting from 3.5–3‰, with an average of 2.9‰ (note that S=3‰ is obtained after 5 days). The variation of the copper ion concentration (mg/l) for the 5 days of the experiment is decreasing from 4184.38 mg/l to 16.03 mg/l (in the 5th day) which proves that under these conditions the meth-

od cementation also helps us in solving the problem of the concentration of copper ions in the used industrial solution because after 5 days it reaches a value of about 16 mg/l (a decrease of about 261 times). The calculated synthesis yield is 97.62% after 4 days of experiment.

Analyzing the data obtained for the two pH at the 1% $CuSO_4$ solution, it is observed that the optimal conditions for cementation would be for adjusted pH=2, because the yield is 97.62%, after 4 days of experiment.

Solution 3% copper sulfate initial pH=3

The pH variation for the 5 days of the experiment is fluctuating ranging from 3–3.75 with an average of 3.42 (note that pH=3.75 is get after 2 days). The variation of the EC (μS/cm) for the 5 days of the experiment is fluctuating, falling between 10290–11980 μS/cm, with an average of 11418 μS/cm (note EC = 11980 μS/cm is obtained after 5 days). The variation of salinity (‰) for the 5 days of the experiment is increasing, falling between 5.8–6.9‰, with an average of 6.46‰ (note that S=6.9‰ is obtained after 3 days). The variation of the copper ion concentration (mg/l) for the 5 days of the experiment is decreasing from 12553.14 mg/l to 310.04 mg/l (on the 5th day) which demonstrates that under these conditions the method cementation also helps us in solving the problem of copper ion concentration in the industrialized solution because after 5 days it reaches a value of 310 mg/l (a decrease of about 40 times). The calculated synthesis yield is 86.83% after 3 days of experiment.

3% copper sulphate solution at adjusted pH=2

The pH variation for the 5 days of the experiment is increasing, falling between 2–3.43 with an average of 2.96 (note that pH=3.43 is obtained after 4 days). The variation of the EC (μS/cm) for the 5 days of the experiment is fluctuating starting from 11910–11960 μS/cm, with an average of 11421 μS/cm (note that EC = 11960 μS/cm is obtained after 5 days). The variation of salinity (‰) for the 5 days.

Conclusions

The cementation method can recover copper from industrial waste solutions. This study aimed to make a number of original contributions to the particularly complex field of recovery of copper from industrial wastewater by the method of cementation.

The best known reaction for obtaining copper in the laboratory is between iron and copper sulfate. This can be used to obtain copper by depositing it on the piece of metal iron inserted in the industrial water.

95.23% yield of obtaining copper powder indicates the optimal variant at the concentration of 0.5% with an initial pH of 3.6 after 3 days of experiment.

Experimentally it is possible to recover metallic copper powder from wastewater with low copper ion content, by the cementation method using a scrap iron electrode, without consuming other reagents or energy.

Acknowledgments

Faculty of Environmental Science and Engineering, Babes-Bolyai University, Cluj Napoca for the WTW Multi 350i multiparameter and AAS ZEEnit 700 Analytik Jena spectrometer. Faculty of Mining University of Petrosani for research in the Ecopedology Laboratory.

Literatura – References

1. Călțaru M., Bădicioiu M., 2007, Cercetări privind extracția cuprului cu membrane lichide pe support solid de timp fibră tubulară, Revista de Chimie, 58, pp. 1112–1116
2. Fenglian Fu, Qi Wang, 2011, Removal of heavy metal ions from wastewaters. A review, Journal of Environmental Management, 92, pp. 407–418
3. Gunatilake S.K., 2015, Methods of removing heavy metals from industrial wastewaters, Journal of Multidisciplinary Engineering Science Studies, 1, pp. 2912–1309
4. https://umfcd.ro/cercetare-si-dezvoltare/proiecte/proiecte-nationale/dezvoltarea-de-solutii-inovative-pentru-protectia-personalului-expus-profesional-si-a-populatiei-impotriva-contaminarii-cu-virusul-SARS-COV-2Moscatello N., Swayambhu G., Jones G.H., Jiale Xu,
5. Mubarak A., 2006, Removal of copper from dilute solutions by cementation on zinc in baffled batch-agitated vessels, Chem Biochem Eng, 20, pp. 79–83
6. Nassef E., El-Taweel Y.A., 2015., Removal of Copper From Wastewater By Cementation From Simulated Leach Liquors, J Chem Eng Process Technol, 6, pp. 1–6
7. Ning Dai, Pfeifer B.A., 2018, Continuous removal of copper, magnesium, and nickel from industrial wastewater utilizing the natural product yersiniabactin immobilized within a packed-bed column, Chemical Engineering Journal, pp. 173–179
8. Peña M.M., Lee J., Thiele D.J., 1999, A delicate balance: homeo static control of copper uptake and distribution, J. Nutr., 129, pp.1251–1260
9. Peng C., Liu Y., Bi J., Xu H., Ahmed A.S., 2011, Recovery of copper and water from copper-electroplating wastewater by the combination process of electrolysis and electrodialysis, Journal of Hazardous Materials, 189, pp. 814–820
10. Solomon F., 2009, Impacts of Copper on Aquatic Ecosystems and Human Health, Environment & Communities, pp. 25–28
11. EL-Ashtoukhy E.S.Z., Abdel A.M.H., 2013, Removal of copper from aqueous solutions by cementation in a bubble column reactor fitted with horizontal screens, International Journal of Mineral Processing, pp. 65–69

Studia i badania nad odzyskiem miedzi z odpadów przemysłowych metodą cementacji

Artykuł przedstawia oryginalne badania związane z odzyskiwaniem miedzi ze ścieków przemysłowych. Celem badań eksperymentalnych jest odzyskiwanie sproszkowanej miedzi metalicznej ze ścieków o niskiej zawartości jonów miedzi metodą cementacji za pomocą złomowej elektrody żelaznej oraz do obliczenie wydajności cementacji miedzi, na którą wpływają następujące parametry: początkowe stężenia jonów miedzi, wartości pH i czas kontaktu.

Eksperymenty obejmowały odzysk miedzi z przemysłowych roztworów z wykorzystaniem odpadów żelaza metodą cementowania, bez zużycia innych odczynników lub energii.

Plan eksperymentu obejmował trzy różne stężenia $CuSO_4$: dla każdego roztworu o przygotowanym stężeniu: 0,5% $CuSO_4$, 1% $CuSO_4$ oraz 3% $CuSO_4$, przeprowadzono eksperymenty laboratoryjne dla dwu wartości odczynu pH (naturalne pH uzyskane przez rozpuszczenie $CuSO_4 * 5H_2O$ w wodzie, pH=2 (regulacja 0,1 M roztworem kwasu siarkowego).

Optymalne warunki dla każdej receptury zostały określone na podstawie danych eksperymentalnych. W badaniach wykorzystano spektrometry WTW Multi 350i i AAS ZEEnit 700 Spektrometr Analytik Jena. Przeprowadzono obliczenie wydajności pozyskania proszku miedziowego dla każdego dnia doświadczenia i dla każdej receptury. Dane eksperymentalne doprowadziły do wniosku, że optymalnym wariantem dla badania jest: stężenie 0,5%, przy początkowe pH 3,6 po 3 dniach doświadczenia i wydajność 95,23%.

Słowa kluczowe: *odzysk miedzi, oczyszczanie ścieków, metoda cementowania miedzi*

Responses of the Micro-Crustacean, *Daphnia magna*, across Five Generations Continuously Exposed to Di-2-Ethylhexyl Phthalate in Mekong River Water

Vinh-Quang TRAN[1,2], Van-Tai NGUYEN[1,2], Thanh-Son DAO[1,2]

[1)] Ho Chi Minh City University of Technology (HCMUT), Vietnam
[2)] Vietnam National University, Ho Chi Minh City, Vietnam
*Corresponding author; email: dao.son@hcmut.edu.vn

http://doi.org/10.29227/IM-2022-02-09

Submission date: 29-08-2022 | Review date: 20-11-2022

Abstract

Plastic pollution has been considered as an emerging environmental problem, and is among the ecological and human health concerns. Detrimental impacts of plastic pollution on living things are closely related to the plastic additives added onto the polymer during plastic manufacture. Di-2-ethylhexyl phthalate (DEHP) is one of the most common plasticizers and is usually found in water environment worldwide. Plastic additives can cause many negative effects on aquatic organisms such as fish and zooplankton. This study aimed to assess the chronic effects of DEHP on the life history traits of an ecotoxicological model micro-crustacean, Daphnia magna, across five generations (F0–F4). We used the natural water from Mekong River in Vietnam as the medium for the D. magna incubation in laboratory conditions. The concentrations of trace elements (e.g., metals and pesticides) in the natural water were under detection levels of equipment or very low which was sufficient for D. magna to grow well. The results showed that the body length was the main endpoint of the organisms inhibited by DEHP across all generations. DEHP adversely impacted the survival and fecundity of D. magna in the fourth generation (F3) only. The adverse effects of DEHP on body length of D. magna should be the consequence of the energy cost and allocation in the exposed organisms. The survival and reproduction responses of D. magna to DEHP across five generations could be explained by (i) the severe effects of the chemical on many individuals in the organism cohort, and (ii) toxin-tolerant development in the remaining exposed organisms. Although the trace elements in natural water from Mekong River were not toxic to D. magna at very low concentrations, together with DEHP they might enhance impacts on the organism. Besides, a multigenerational exposure to DEHP would reflect clearer impacts on the organism than a single exposure. Our results could be useful for extrapolation on the influence of plasticizers on freshwater zooplankton in nature.

Keywords: *chronic effects, Daphnia magna, energy cost, life traits, plastic additives*

1. Introduction

Plastic emission and pollution are among the most serious threats to aquatic environment and ecosystem globally (Miller et al. 2020; Azevedo-Santos et al. 2021). The di-2-ethylhexyl phthalate (DEHP) is one of the basic and common additives for more than 300 million tons of plastic products annually in the world (Wang et al. 2018; Chen et al. 2020). Globally, the compound DEHP was produced at more than 2 million tons (Rowdhwal and Chen 2018). In natural conditions (e.g., high temperature), DEHP can easily release out of the plastic surface and enter the surrounding environments (Wang et al. 2018). The existence of DEHP in the environment has been reported in many countries such as Finland, Denmark, Germany, Japan, China, Thailand, Poland, Sweden, and Italy (Wowkonowicz and Kijeriska 2017). The highest concentration of DEHP in river water reached 370 μg L-1 in China (Wang et al. 2018). Recently, DEHP has become an emerging pollutant. It is known as an endocrine disrupting chemical and considered as a carcinogenic compound to invertebrates (Wang et al. 2018). However, the impacts of DEHP on aquatic invertebrates are not fully understood.

Micro-crustaceans (e.g., *Daphnia magna*) are among the key animal groups in aquatic ecosystems having important position and function in aquatic food webs (Wetzel, 2001). *Daphnia magna* is the common representative of freshwater micro-crustaceans and is widely used as a model organism for testing the pollutant toxicity (US. EPA 2002; Lampert 2006; APHA 2012). The median lethal concentrations (LC50) of DEHP to *D. magna* were largely varied between 160 and 3,310 μg L-1 (Adams et al. 1995; Brown et al. 1998; Scanlan et al. 2015; Wang et al. 2018). The life history traits of *D. magna* chronically exposed to DEHP have been reported in many studies in which the DEHP concentration up to 500 μg L-1 did not impact survival of the organism (Brown and Thompson 1982; Knowles et al. 1987; Brown et al. 1998; Seyoum and Pradhan 2019; Le et al. 2019). Seyoum and Pradhan (2019) and Le et al. (2019) noted that DEHP enhanced the reproductive capacity of *D. magna*. The authors also found that the DEHP at 390 μg L-1 inhibited the growth of *D. magna*, but the inhibition was not showed at lower concentrations of the chemical.

Generally, all previous studies of the DEHP toxicity to *D. magna* were performed in artificial medium (e.g., ISO). However, the toxicity of DEHP in the artificial environment may not be the same as that in the natural water because of different chemical properties between them. Besides, the responses of *D. magna* to DEHP across multigenerational exposure are not yet fully understood (but see Le et al. 2019). Therefore, to fill the gap, in this study we assessed the effects of DEHP dissolved in natural water from Mekong River at the concentration of 500 μg L-1 on the life history traits of *D. magna* across five generations.

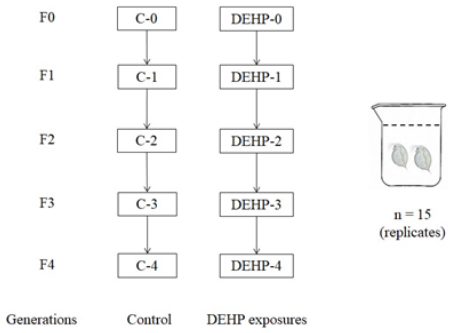

Fig. 1. Experimental setup for *D. magna* across five generations exposed to DEHP dissolved in Mekong River water
Rys. 1. Układ doświadczalny dla *D. magna* w pięciu pokoleniach poddanych działaniu DEHP rozpuszczonego w wodzie Mekongu

2. Materials and methods

2.1. Test organisms

The freshwater micro-crustacean *Daphnia magna* was purchased from Micro BioTest (Belgium) and has been maintained in ISO medium for many years. The organisms were fed with the green alga Scenedesmus sp. and YTC (US. EPA. 2002). The alga Scenedesmus sp. was cultured in a Z8 medium (Kotai 1972). The *D. magna* was raised under the temperature of 25 ± 1°C, the light intensity of less than 1000 Lux, and a photo regime of 14 h light: 10 h dark (APHA 2012).

2.2. Chemicals

The plastic additive Di-2-ethylhexyl phthalate (DEHP, Aldrich Sigma, purification 99.5%) was dissolved in acetone (Merck, Germany) at the concentration of 3292 mg L-1 referred as stock solution. The stock solution was kept at 4°C before the test implementation. The natural water used in this study was collected from Mekong River in Vietnam. The water was settled and then filtered through a GF/A filter (Advantech, Japan) before being used as a medium to culture *D. magna*. The chemical characterization of pesticides (all below 1 µg L-1) and trace metals (mostly below 1 µg L-1, and much far below the 48h-LC50 values to *D. magna*) confirmed that the natural water from Mekong River was suitable for cultivation of *D. magna* (Dao et al. accepted manuscript).

2.3. Experimental design

The chronic experiment was conducted according to APHA (2012) with minor adjustment. At the start of the experiment, nearly 40 mother *D. magna* were randomly selected and transferred into a one-liter glass beaker containing 800 mL of filtered river water. Sixty neonates (<24 hours old) from the second and third broods of the mother *D. magna* were randomly used for the chronic experiment. The experiment was performed over five generations of *D. magna* (Fig. 1). In more detail, at the first generation (called F0) of the experiment, two organisms were cultured together in a 50 mL glass beaker containing 40 mL of filtered river water. We conducted two treatments including the exposure to DEHP and the control. In the exposure, *D. magna* was raised in the natural water containing 500 µg DEHP L-1 while the organisms in the control were just incubated in the natural water without the addition of DEHP. There were 15 replicates in each treatment (n=15). Offspring from the second and third brood of F0 *D. magna* in control and DEHP exposure were used for the next generational experiment (hereafter we called F1) and continuously raised in the same medium as their mothers were (2 neonates per beaker, 15 replicates). This process repeated until the fifth generation (F4). The test concentration of 500 µg DEHP L-1 was chosen for the present study because the highest concentration of phthalates in surface water and landfill leachate could reach up to 370 µg L-1 and 460 µg L-1, respectively (Wowkonowicz and Kijeriska 2017; Wang et al. 2018).

The organisms in each treatment were fed daily with the mixture of green alga Scenedesmus sp. and YTC (US. EPA. 2002). The chronic test was performed in the laboratory conditions (as mentioned above) and lasted for 21 days for each generation (Adema 1978). We conducted this study with data within five generations of exposures because the Covid-19 quarantine was applied in the city before we could complete the experiment on the sixth generation. The test medium (filtered river water and food) in each treatment was totally renewed three times per week. During the time of the experiment, the life history traits including the survival, reproductive performance of *D. magna* were carefully checked and recorded daily. The dead mother *D. magna* and neonates released from each beaker were counted and discarded daily. By the end of the experiment, alive *D. magna* was fixed with Lugol solution (Sournia 1978) and its body length was measured from the head top to the base of tail spine of the *D. magna* on a microscope coupled with a digital camera. The pH and dissolved oxygen (DO) of the test medium were measured and their values ranged from 7.2–7.6 (for pH), and from 7.4–7.9 mg L-1 (for DO) which met the requirements for chronic experiments with *D. magna* according to APHA (2012).

2.3. Data treatment

Sigma Plot version 12.0 was used for data analyses. The Kruskal-Wallis test was utilized to calculate the statistically significant difference ($p < 0.05$) in body length, and accumulative offspring per beaker between control and DEHP exposure.

3. Results and discussion

3.1. The effects of DEHP on the survival of Daphnia magna

In the control, the survival of *D. magna* in all six generations was from 80–93% when the experiments terminated (Fig. 2) which meets the requirement of APHA (2012) for chronic treatments with micro-crustaceans. Similarly, the survival of *D. magna* in DEHP exposures was within the range of 80–100% except the survival of DEHP-exposed *D. magna* in F3 was 53% by the end of experiment.

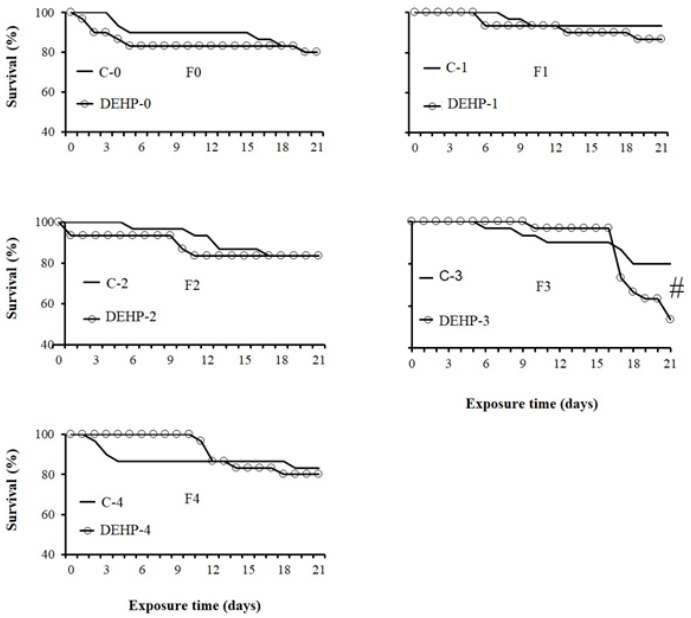

Fig. 2. The survival of *D. magna* in the control and DEHP exposure through five generations. The symbol (#) indicated the significant difference between control and DEHP exposure according to APHA (2012)

Rys. 2. Przeżywalność D. magna w próbce kontrolnej i poddanej ekspozycji na DEHP przez pięć pokoleń. Symbol (#) wskazywał na istotną różnicę między kontrolą a narażeniem na DEHP według APHA (2012)

In the first and second generational exposures (F0 and F1), the Daphnia's survival in present study is consistent with that in previous studies (Seyoum and Pradhan 2019; Le et al. 2019) in which *D. magna* was incubated in DEHP at the concentrations of 390–500 µg L-1. However, a significant decrease of *D. magna* survival (55%) in the third generation (F2) exposed to DEHP (500 µg L-1) was reported by Le et al. (2019). Therefore, the previous studies (Seyoum and Pradhan 2019; Le et al. 2019) and our study have a similar trend of effects reflecting the impact of DEHP on the *D. magna*'s survival was only profound in the later generations of exposure.

Biochemically, DEHP caused a significant reduction in the activities of catalase (CAT) and superoxide dismutase (SOD) enzymes, the antioxidant capacity and detoxifying activities in *D. magna* (Wang et al. 2018). DEHP can interfere the protein synthesis and fatty acid catabolism, consequently influence the normal functions of heart and hepatopancrea in *D. magna* (Scanlan et al. 2015; Ito et al. 2019). Hence, DEHP could indirectly affect the energy storage or cause the glycogen reduction in *D. magna* (Knowles et al. 1987). The compound DEHP could be accumulated and recalcitrant in aquatic organisms. Therefore, the DEHP-exposed *D. magna* would spend energy for biochemical adjustment and damage repair, consequently energy cost (Dao et al. 2018). The exposed organisms could withstand DEHP in the first generations by spending energy and material for survival (F0–F2; Fig. 2) and reproduction maintenance (F1, F2; Fig. 4). However, the *D. magna* could be impaired in a more generational exposure to DEHP (F3) consequently mortality increase (up to 47% of total exposed organisms).

The difference of the affected generations in the previous study (F2; Le et al. 2019) and ours (F3) could be related to the trade-off between survival and development in DEHP-exposed *D. magna*. The DEHP-exposed *D. magna* could face energy cost and material allocation to maintain its normal behaviors and fitness (e.g. survival and growth). Hence the slowdown its growth (see section 3.2) the DEHP-exposed *D. magna* could have a chance to conserve its survival rate similar to the control in F2 (Fig. 2).

Our study presented the initial evidence of *D. magna* continuously exposed to DEHP in natural river water over 5 generations. Interestingly, we found that *D. magna* was more likely to recover or even adapt in its survival to DEHP in the fifth generation (F4). Dao et al. (2018) studied the survival of a micro-crustacean Daphnia lumholtzi by exposed the organism to a cyanobacterial toxin, microcystin, across three generations and observed the tolerance of the organism in the first generation, the significant decrease of the organism in the second generation, and the acclimation of the organism in the third generation. The acclimation or recovery of microcystin-exposed mother *D. magna* was hypothesized with the formation of the genes for synthesis of detoxifying enzymes in its offspring, and thus improve the toxin tolerance in the daughters (Gustafsson et al. 2005). This helps to explain the acclimation of *D. magna* in F4 to the DEHP in present study. Further studies on the gene encoding for antioxidant enzyme and detoxification activities in *D. magna* exposed to DEHP are suggested to clarify.

3.2. The effects of DEHP on the growth of Daphnia magna

The average body length of *D. magna* in the control ranged between 3,000 and 3,610 µm. However, body length of *D. magna* in the DEHP exposure varied from 2,920–3,330 µm which was significant shorter than that in the control ($p < 0.05$; Fig. 3). Our results indicated that DEHP inhibited the growth of the organisms in all five generations.

Body size of *D. magna* is a very important endpoint of fitness because it is highly related to the time of first reproduction and clutch size of the organism (Ebert 1992). However, effects of phthalates on growth or body length of *D. magna*

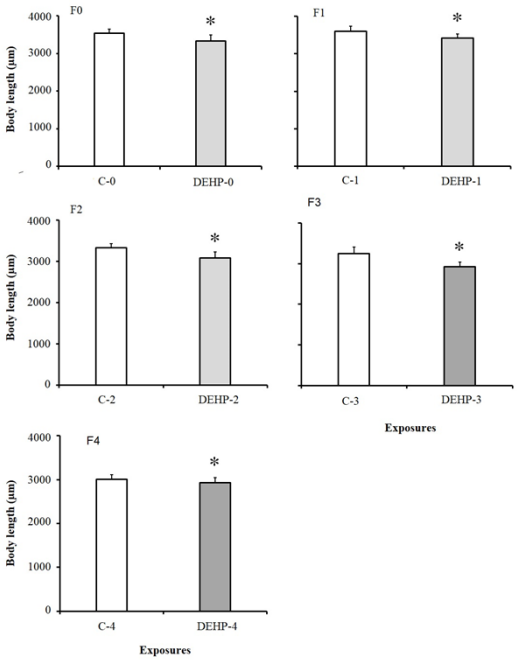

Fig. 3. The body length of *D. magna* in the control and DEHP exposure through five generations. The asterisk (*) indicated the significant difference between control and DEHP exposure by the Kruskal-Wallis test ($p < 0.05$)

Rys. 3. Długość ciała *D. magna* w próbce kontrolnej i w ekspozycji na DEHP przez pięć pokoleń. Gwiazdka (*) wskazuje istotną różnicę między próbką kontrolną a ekspozycją na DEHP w teście Kruskala-Wallisa ($p < 0,05$)

have not been studied (but see Seyoum and Pradhan 2019; Le et al. 2019). Our study firstly revealed the impact of DEHP on the growth of *D. magna* under a multigenerational exposure. The observation in present study was in line with the previous study for the F0 (Le et al. 2019). Seyoum and Pradhan (2019) also recorded a reduction of body length in *D. magna* exposed to DEHP at the concentration of 390 µg L-1 over 14 days. As mentioned above, DEHP could cause the material and energy allocation related to the fitness such as survival, growth, reproduction of *D. magna*. Generally, the DEHP-exposed *D. magna* in our study could maintain its survival at a normal rate during 21 days of incubation from F0 through F4, except F3 (Fig. 2). Therefore, DEHP-exposed organism had to face a trade-off that slowed down its growth consequently a shorter body length than the control *D. magna*.

3.3. The effects of DEHP on the reproduction of Daphnia magna

The reproduction of *D. magna* was calculated as the accumulative neonates released from each beaker in the control and the DEHP exposure during 21 days of treatment. The reproduction of *D. magna* of both control and exposure in F1, F2, and F4 was in a similar range. However, DEHP caused a significant reduction in fecundity of mother *D. magna* in the F0 ($p = 0.024$, Kruskal-Wallis test), and F3 ($p = 0.002$, Kruskal-Wallis test; Fig. 4).

Previous studies revealed that DEHP could enhance the reproduction of *D. magna* at the concentration of 390 µg L-1 (Seyoum and Pradhan 2019) or not inhibited this endpoint of the organism at the concentration of 500 µg L-1 (Le et al., 2019). On the contrary, we found a much lower reproduction in *D. magna* exposed to DEHP in the first generation (F0). Without a doubt – organisms in aquatic environments could be affected by not only a single pollutant but a mixture of pollutants as well. The natural water from Mekong River used in present study had some trace elements at low levels (Dao et al. accepted manuscript) which might have side effects on *D. magna* (Le et al. 2021). The combined effects of DEHP and trace elements in natural water could cause stronger toxic effects on micro-crustacean than the solely impact of DEHP on the organism in standard medium (Dao et al. accepted manuscript). In the second (F1) and third (F2) generations, DEHP-exposed *D. magna* showed signs of reproductive recovery (Fig. 4).

In our study, in the fourth generation (F3) *D. magna* were affected again and the total number of offspring born in DEHP exposure was significantly different from the control ($p < 0.002$). this should be the consequence of the high mortality of DEHP-exposed *D. magna* in F3 (Fig. 2). The much lower number of mother *D. magna* in F3 would lead to a lower number of accumulative neonates. On the other hand, the increase of DEHP-exposed *D. magna* survival in the fifth generation (F4; Fig. 2) resulted in the increase of accumulative neonates (Fig. 4).

The present study showed the effects of DEHP in natural water from Mekong River on *D. magna* across five generations. This could be useful for the extrapolation in situ and the prediction on potential impacts of plastic additives (e.g., DEHP) on freshwater zooplankton in Mekong River, the eleventh highest river loading plastic waste into the seas globally (Lebreton et al. 2017).

Conclusions

This is the first investigation assessing the toxicity of DEHP to *D. magna* incubated in natural water from Mekong River across five generations from the best of our knowledge. High mortality (47%) was found in the DEHP exposure in the fourth generation (F3). DEHP also caused a reduction in fe-

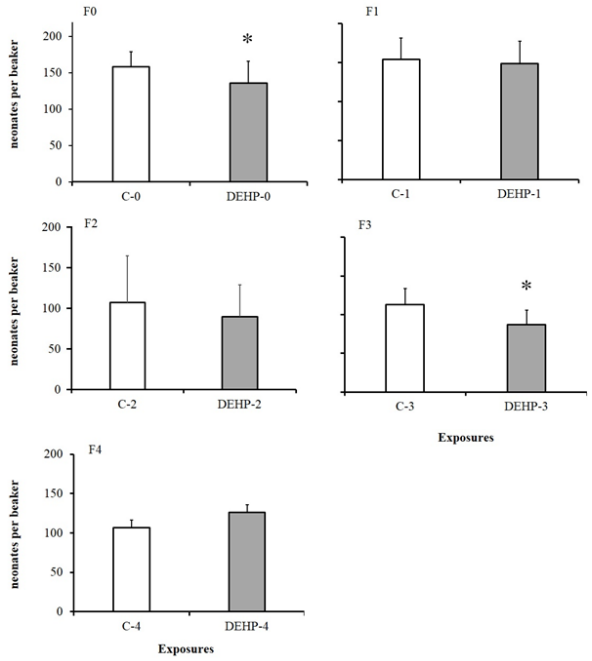

Fig. 4. The accumulative neonates from each culturing beaker in the control and DEHP exposure through five generations. The asterisk (*) indicated the significant difference between control and DEHP exposure by the Kruskal-Wallis test ($p < 0.05$)

Rys. 4. Skumulowana liczba nowych organizamów z każdej próbki hodowlanej w grupie kontrolnej i ekspozycji na DEHP przez pięć pokoleń. Gwiazdka (*) wskazuje istotną różnicę między próbką kontrolną a ekspozycją na DEHP w teście Kruskala-Wallisa ($p < 0,05$)

cundity of mother *D. magna* in F0 and F3. However, the body length of the animal in the DEHP exposure was significantly shorter than that of the control across five generations. The trade-off between the survival, growth and reproduction related to the material and energy allocation would be the root of the responses of *D. magna* to DEHP. The effects of DEHP in natural water from Mekong River are useful to extrapolate the toxicity of this chemical to micro-crustacean in situ, and the effects would become more severe uncomfortable environmental and biological conditions in nature.

Funding

This research is mainly funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 106.99-2019.39, and partly done by the Ho Chi Minh City University of Technology (HCMUT) under the fund for student project to Vinh-Quang Tran. We acknowledge the support of time and facilities from Ho Chi Minh City University of Technology (HCMUT), VNU-HCM for this study.

Literatura – References

1. Adams WJ, Biddinger GR, Robillard KA, Gorsuch J (1995) A summary of the acute toxicity of 14 phthalates esters to representative aquatic organisms. Environmental Toxicology and Chemistry 14(9): 1569-1574. https://doi.org/10.1002/etc.5620140916
2. Adema DMM (1978). *Daphnia magna* as a test animal in acute and chronic toxicity tests. Hydrobiologia 59: 125–134. https://doi.org/10.1007/BF00020773
3. American Public Health Association (APHA) (2012) Standard Methods for the Examination of Water and Wastewater (22nd ed.). American Water Works Association, 1496 pp.
4. Azevedo-Santos VM, Brito MFG, Manoel PS, Perroca JF, Rodrigues-Filho JL, Paschoal LRP, Gonçalves GRL, Wolf MR, Blettler MCM, Andrade MC, Nobile AB, Lima FP, Ruocco AMC, Silva CV, Perbiche-Neves G, Portinho JL, Giarrizzo T, Arcifa MS, Pelicice FM (2021) Plastic pollution: A focus on freshwater biodiversity. Ambio 50(7): 1313-1324. https://doi.org/10.1007/s13280-020-01496-5
5. Brown D, Thompson RS (1982) Phthalates and the aquatic environment: part 1. The effect of di-2-ethylhexyl phthalate (DEHP) and di-isodecyl phthalate (DIDP) on the reproduction of *Daphnia magna* and observations on their bioconcentration. Chemosphere 11: 417–426. https://doi.org/10.1016/0045-6535(82)90045-5
6. Brown D, Croudace CP, Williams NJ, Shearing JM, Johnson PA (1998) The effect of phthalate ester plasticisers tested as surfactant stabilised dispersions on the reproduction of the *Daphnia magna*. Chemosphere 36: 1367–1379. https://doi.org/10.1016/S0045-6535(97)10018-2
7. Chen H, Qin Y, Huang H, Xu W (2020) A regional difference analysis of microplastic pollution in global freshwater bodies based on a regression model. Water 12: 1889. https://doi.org/10.3390/w12071889
8. Dao TS, Vo TMC, Wiegand C, Bui BT, Dinh VK (2018) Transgenerational effects of cyanobacterial toxins on a tropical micro-crustacean Daphnia lumholtzi across three generations. Environmental Pollution 243 (B): 791-799. https://doi.org/10.1016/j.envpol.2018.09.055
9. Dao TS, Nguyen VT, Baduel C, Bui MH, Tran VT, Pham TL, Bui BT, Dinh KV. Toxicity of di-2-ethylhexyl phthalate and tris (2-butoxyethyl) phosphate to a tropical micro-crustacean (Ceriodaphnia cornuta) is higher in Mekong river water than in standard laboratory medium. Accepted manuscript in Environmental Science and Pollution Research.
10. Ebert D (1992). A food-independent maturation threshold and size at maturity in *Daphnia magna*. Limnology and Oceanography 37: 878– 881. https://doi.org/10.4319/lo.1992.37.4.0878
11. Gustafsson S, Rengefors K, Hansson LA (2005) Increased consumer fitness following transfer of toxin tolerance to offspring via maternal effects. Ecology 86(10): 2561-2567. DOI:10.1890/04-1710.
12. Ito Y, Kamijima M, Nakajima T (2019) Di(2-ethylhexyl) phthalate-induced toxicity and peroxisome proliferator-activated receptor alpha: a review. Environmental Health and Prevention Medicine 24(1): 47. https://doi.org/10.1186/s12199-019-0802-z
13. Knowles CO, McKee MJ, Palawski DU (1987) Chronic effects of di-2-ethylhexyl phthalate on biochemical composition, survival and reproduction of *Daphnia magna*. Environmental Toxicology and Chemistry 6: 201-208. https://doi.org/10.1002/etc.5620060305
14. Kotai J (1972). Instructions for preparation of modified nutrient solution Z8 for algae. Norwegian Institute for Water Research, B-11, 5pp.
15. Lampert W (2006) Daphnia: model herbivore, predator and prey. Polish Journal of Ecology 54(4): 607-620.
16. Le TPD, Nguyen VT, Vo TMC, Bui NH, Dao TS (2019) Transgenerational effects of the plasticizer di-2-ethylhexyl phthalate on survival, growth, and reproduction of *Daphnia magna*. Vietnam Journal of Science, Technology and Engineering 61(4): 64-69. https://doi.org/10.31276/VJSTE.61(4).64-69.
17. Le TPD, Nguyen VT, Bui MH, Huynh TN, Huynh AT, Tran VQ, Vo TMC, Tran T, Dao TS, (2021) Single and binary effects of di-2-ethylhexyl phthalate and trace metals (Cd, Pb) on life history traits of *Daphnia magna*. Accepted manuscript in Environmental Quality Management. DOI: 10.1002/tqem.
18. Lebreton LCM, van der Zwet J, Damsteeg JW, Slat B, Andrady A, Reisser J (2017) River plastic emissions to the world's oceans. Nature Communication 8: 15611. https://doi.org/10.1038/ncomms15611
19. Miller ME, Hamann M, Kroon FJ (2020) Bioaccumulation and biomagnification of microplastics in marine organisms: a review and meta-analysis of current data. PloS ONE 15(10): e0240792. https://doi.org/10.1371/journal.pone.0240792
20. Rowdhwal SSS, Chen J (2018) Toxic effects of di-2-ethylhexyl phthalate: an overview. BioMed Research International 2018: 1750368. https://doi.org/10.1155/2018/1750368

21. Scanlan LD, Loguinov AV, Teng Q, Antczak P, Dailey KP, Nowinski DT, Kornbluh J, Lin XX, Lachenauer E, Arai A, Douglas NK, Falciani F, Stapleton HM, Vulpe CD (2015) Gene transcription, metabolite and lipid profiling in eco-indicator *Daphnia magna* indicate diverse mechanisms of toxicity by legacy and emerging flame-retardants. Environmental Science & Technology 49: 7400-7410. https://doi.org/10.1021/acs.est.5b00977

22. Seyoum A, Pradhan A (2019) Effect of phthalates on development, reproduction, fat metabolism and lifespan in *Daphnia magna*. Science of the Total Environment 654: 969-977. https://doi.org/10.1016/j.scitotenv.2018.11.158

23. Sournia A (1978) Phytoplankton Manual UNESCO, UK, 77

24. US Environmental Protection Agency (US EPA), 2002. Methods for measuring the acute toxicity of effluents and receiving waters to freshwater and marine organisms. EPA-821-R02-012, fifth ed. Office of Water, Washington, DC.

25. Wang Y, Wang T, Ban Y, Shen C, Shen Q, Chai X, Zhao W, Wei J (2018) Di-(2-ethylhexyl) phthalate exposure modulates antioxidant enzyme activity and gene expression in juvenile and adult *Daphnia magna*. Archives of Environmental Contamination and Toxicology 75 (1): 145-156. https://doi.org/10.1007/s00244-018-0535-9

26. Wetzel RG (2001) Limnology: Lake and River Ecosystems, 3rd ed. Academic Press, San Diego.

27. Wowkonowicz P, Kijeriska M (2017) Phthalate release in leachate from municipal landfills of central Poland. PloSONE 12(3): e0174986. https://doi.org/10.1371/journal.pone.0174986.

Reakcje mikroskorupiaków, Daphnia magna*, w ciągu pięciu pokoleń stale narażonych na działanie ftalanu di-2-etyloheksylu w wodzie rzeki Mekong*

Zanieczyszczenie tworzywami sztucznymi zostało uznane za narastające zagrożenie środowiskowe i jest jednym z problemów ekologicznych związanych ze zdrowiem człowieka. Szkodliwy wpływ zanieczyszczenia tworzywami sztucznymi na organizmy żywe jest ściśle związany z dodatkami tworzyw sztucznych dodawanymi do polimeru podczas produkcji tworzyw sztucznych. Ftalan di-2-etyloheksylu (DEHP) jest jednym z najpowszechniejszych plastyfikatorów i zwykle występuje w środowisku wodnym na całym świecie. Dodatki do tworzyw sztucznych mogą powodować wiele negatywnych skutków dla organizmów wodnych, takich jak ryby i zooplankton. Badania przedsatwione w artykule miały na celu ocenę ciągłego wpływu DEHP na cechy historii życia modelu ekotoksykologicznego mikroskorupiaka, Daphnia magna*, w ciągu pięciu pokoleń (F0–F4). Jako pożywkę do inkubacji* D. magna *w warunkach laboratoryjnych wykorzystano naturalną wodę z rzeki Mekong w Wietnamie. Stężenia pierwiastków śladowych (np. metali i pestycydów) w naturalnej wodzie były poniżej poziomu wykrywalności sprzętu lub bardzo niskie, co było wystarczające, aby* D. magna *dobrze się rozwijała. Wyniki pokazały, że długość ciała była głównym punktem oceny rozwoju organizmów hamowanego przez DEHP we wszystkich pokoleniach. DEHP negatywnie wpłynął na przeżywalność i płodność* D. magna *jedynie w czwartym pokoleniu (F3). Negatywny wpływ DEHP na długość ciała* D. magna *powinien być konsekwencją zużycia energii i jej alokacji w narażonych organizmach. Reakcje* D. magna *na przetrwanie i reprodukcję pod wpływem DEHP w ciągu pięciu pokoleń można wytłumaczyć (i) poważnym wpływem substancji chemicznej na wiele osobników w populacji organizmów oraz (ii) rozwojem tolerancji na toksyny u pozostałych narażonych organizmów. Chociaż pierwiastki śladowe w naturalnej wodzie z Mekongu nie były toksyczne dla* D. magna *w bardzo niskich stężeniach, to razem z DEHP mogą nasilać oddziaływanie na organizm. Poza tym wielopokoleniowe narażenie na DEHP odzwierciedlałoby wyraźniejszy wpływ na organizm niż jednorazowe narażenie. Przedstawione wyniki mogą być przydatne do ekstrapolacji wpływu plastyfikatorów na zooplankton słodkowodny w przyrodzie.*

Słowa kluczowe: *skutki chroniczne,* Daphnia magna*, zużycie energii, cechy życiowe, dodatki do tworzyw sztucznych*