ASSESSMENT OF BATTERIES INFLUENCE ON LIVING ORGANISMS BY BIOINDICATION METHOD

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ABSTRACT

The investigation of household batteries influence on living organisms was carried out according to the bioindication method based on identification of changes of algae reproduction due to the influence of toxic substances contained in aquatic medium. This makes possible to assess the batteries influence not only by concentration of pollutants, but also by final effect: their toxic action on living organisms. The unicellular algae Chlorella were used as test-object. Batteries (undamaged and damaged) of different types were added to samples of water containing algae.

Similar changes of pH values were observed during 14 days of the research in samples with the same batteries type (both damaged and undamaged). It can be caused by: low content of substances able to change pH value or their instability; neutralization of these substances by bioindicator (algae); insufficient hermeticity of battery casing or its destruction. The greatest change of pH value was noticed at the first day of the research, which indicates on the intensity of batteries influence. Generally, changes of pH value correspond to types of components contained in batteries.

Visual observation using microscope has showed the greatest influence on algae in samples with alkaline batteries, while the minimal effect was observed in samples with zinc-carbon 9V batteries. All the samples with damaged batteries were characterized by higher level of algae destruction in comparison to the undamaged batteries of same type. The results show that all batteries, including undamaged, influence on living organisms when coming to the environment. They change the environment characteristics very quickly. Batteries with undamaged casing cause living organisms destruction as well, possibly due to gradual damage of the casing in aggressive environment.

Keywords: battery, bioindication, environment, living organisms, algae

INTRODUCTION

Waste management problem becomes more acute due to widespread use of materials containing hazardous components. Household batteries very often appear among such materials. They are not collected separately in many countries and freely come to the environment.

It is known that batteries constitute 0.02–0.06% of household waste mass [1–3] and tends to grow (for example, according to [4] batteries sales increased by 29% from 2004 to 2010). Presence of hazardous substances in batteries makes them a significant source of environment pollution. Such substances primarily are as follows: cadmium, lead, mercury, nickel, zinc, dioxins and others [1, 5–9]. Many countries have appropriate legislation.

For example, there is EU Directive [10] obliging the Member States to introduce separate collection system for batteries. But not all these countries have an efficiently operating system [11]. Besides, even despite of legislative and organizational provision [4], as well as public awareness in EU countries, considerable part of batteries is not involved in special collection system. For example, according to [1] 39% of batteries in Denmark are collected together with residual waste. There were only 40% of batteries collected separately in EU countries in 2014 [12]. Moreover, according to [4, 13] heavy metals content in many batteries is over limit value. Therefore, batteries pose a serious danger to the environment. Since the methods of non-hazardous waste utilization are unsuitable for batteries processing, then heavy metals release to air, water and soil is totally uncontrolled [4]. The influence of batteries should be assessed not only by concentration of pollutants, but also by final effect: toxic action on living organisms.

The bioindication method can be used for this purpose. Bioindication is used in environmental research as a method of identification of anthropogenic influence on ecosystem. This method is based on investigation of variable factors influence on different characteristics of biological objects and systems. The biological systems or organisms which are the most sensitive to investigated factors are used as bioindicators [14]. The objective of this study is investigation of batteries influence on living organisms using bioindication method.

MATERIALS AND METHODS

The investigation of batteries influence on living organisms was carried out according to the method based on identification of changes of algae reproduction due to the influence of toxic substances contained in aquatic medium. The unicellular algae Chlorella were used as test-object. 1.5 liters of pond water with some Chlorella was sampled and nutrient medium was provided for Chlorella reproduction (KNO_3 – 0.025 g/l, $MgSO_4 \cdot 7H_2O$ – 0.025 g/l, KH_2PO_4 – 0.025 g/l, K_2CO_3 – 0.0345 g/l, $Ca(NO_3)_2$ – 0.1 g/l). The water was left for 3 days at lighted place for algae reproduction.

Then water volume was divided to 20 samples with adding 10 different types of batteries (2 batteries of each type: damaged and undamaged), and 1 control sample without batteries (see Table 1). The batteries were prepared in a way when one battery had undamaged casing and another one (of the same type) was damaged. This conduced to direct contact of investigated water medium and battery content. The samples were placed at a lighted spot for 14 days. Measuring of the samples pH and visual observation of changes were carried out during 14 days. After that, visual investigation of the samples was carried out at the end of experiment using microscope DCM-300 (400x zoom).

Table 1.
Characteristics of investigated samples and chemical composition of added batteries

Sample	Type of battery added	Content, % [15]								
		Ni	*Cd*	*Hg*	*Fe*	*Zn*	*Co*	*Li*	*MnO_2*	*Electrolyte*
Zinc-carbon batteries										
1	R20			0.001	18	23			28	9
2	R20 (damaged)			0.001	18	23			28	9
3	R6			0.001	18	23			28	9
4	R6 (damaged)			0.001	18	23			28	9
5	R03			0.001	18	23			28	9
6	R03 (damaged)			0.001	18	23			28	9
7	6F22			0.001	18	23			28	9
8	6F22 (damaged)			0.001	18	23			28	9
Alkaline batteries										
9	LR20			0.008	20	17	3		36	9
10	LR20 (damaged)			0.008	20	17	3		36	9
11	LR6			0.008	20	17	3		36	9
12	LR6 (damaged)			0.008	20	17	3		36	9
13	LR03			0.008	20	17	3		36	9
14	LR03 (damaged)			0.008	20	17	3		36	9
Li-Ion batteries										
15	CR 2032				40			3	32	20
16	CR 2032 (damaged)				40			3	32	20
Rechargeable batteries										
17	KR6	20	20						45	20
18	KR6 (damaged)	20	20						45	20
19	Li-Ion phone battery							3	40	32
20	Li-Ion phone battery (damaged)							3	40	32
21	Control sample									

RESULTS AND DISCUSSIONS

pH analysis

The results of pH measuring for samples with undamaged and damaged batteries are shown in Fig. 1 and Fig. 2 respectively. It is clear from Fig. 1 that control sample at the end of the experiment had pH increased by 0.5 in comparison to initial phase, although periodical pH decreasing was observed as well. That can be connected to vital functions of algae ecosystem in the investigated samples.

Comparison of pH dynamics of the samples with undamaged batteries has shown that the dynamics closest to control sample (sample 21) had sample 15 containing Li-Ion battery of CR2032 type. That was probably due to the lowest weight of this type battery among all investigated batteries or due to less aggressive chemical composition. Similar pH dynamics was also noticed for sample 19 (Li-Ion phone rechargeable battery is similar to above mentioned battery of CR2032 type by chemical composition), and samples 13 and 17 as well. The last one should be paid more attention as it contains Ni-Cd rechargeable battery. Therefore, one can assume that the result of this sample was similar to the result of control sample due to absence of contact between sample's water medium and battery content during 14 days of experiment.

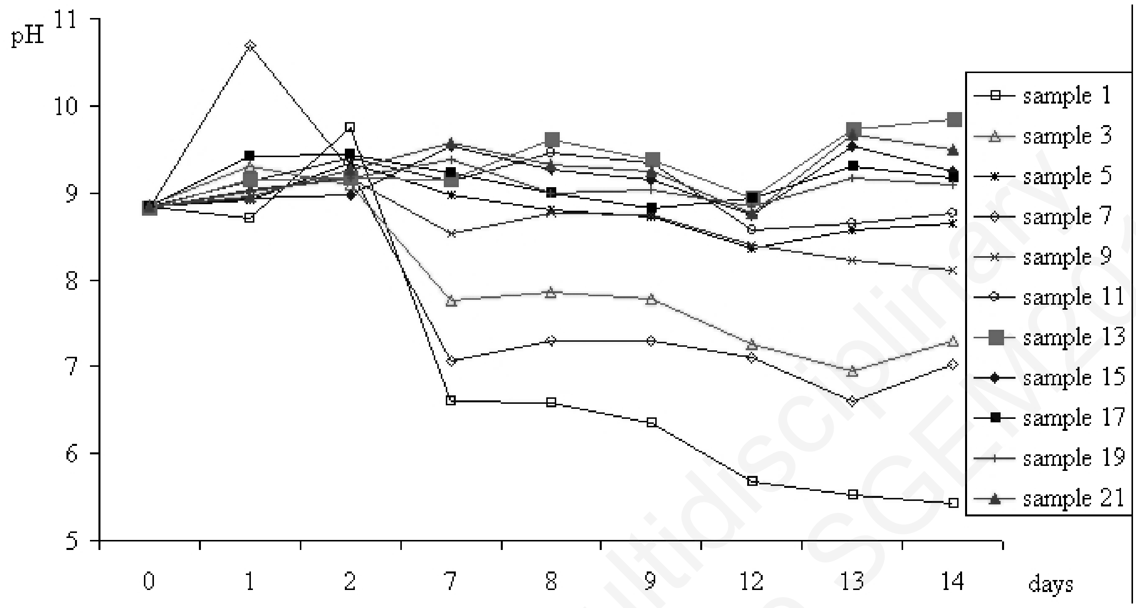


Figure 1. pH of samples with undamaged batteries

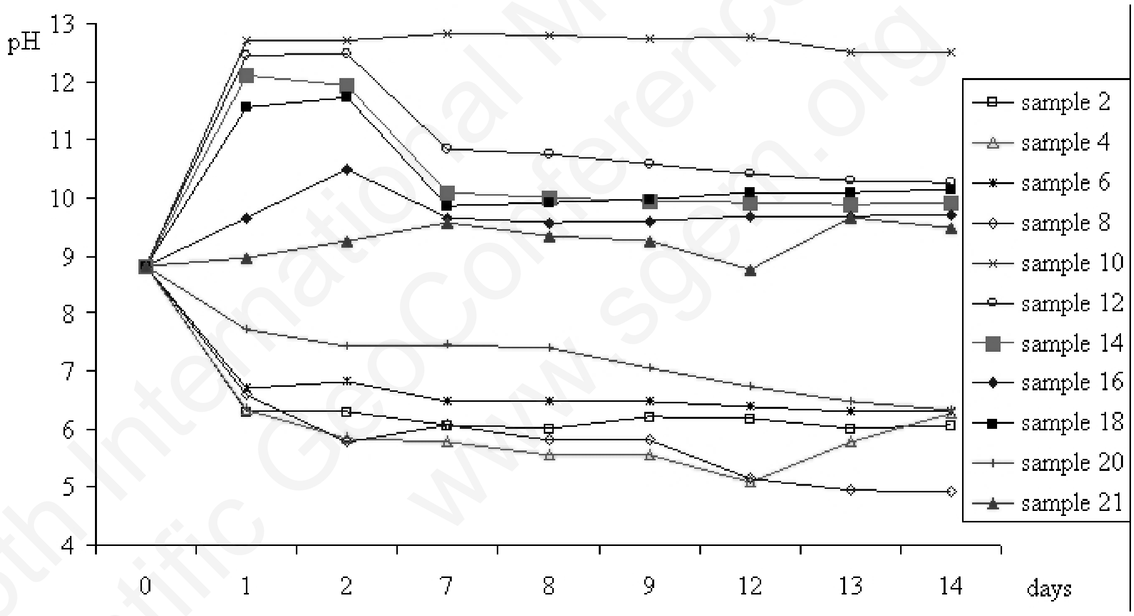


Figure 2. pH of samples with damaged batteries

The most significant pH changes have occurred in the samples 1, 7 and 3 (all contained zinc-carbon batteries). Besides, the sample 1 was the single one where acid environment was noticed at the end of experiment despite of pH increasing due to algae presence. The most likely, such result was caused by much more weight of the battery in the sample 1 (zinc-carbon battery of R20 type) in comparison to majority of other investigated batteries. Therefore, more hazardous substances could potentially come to sample's water medium. The last assumption can indirectly prove the instability of zinc-carbon batteries casing.

It should be also noted that in the sample 7, which was mentioned for considerable pH decreasing, this parameter has dramatically increased at the experiment beginning for a short time. That was the highest pH (11) for the samples with undamaged batteries. This can be the consequence of few factors influence: instability of casing of zinc-carbon battery of 6F22 type that, in turn, could provide the release of electrolyte with ammonium ions into water medium followed by potential their binding by ions of Fe and Zn (for example, to insoluble forms).

The analysis of pH dynamics of the samples with damaged batteries has shown a larger dispersion of pH values in comparison to the samples with undamaged batteries. The samples can be divided into several groups by pH dynamics. The most similar to control sample changes of pH were noticed in the samples 12, 14, 16 and 18. These were the samples containing actually the same batteries (damaged ones) as in the samples with undamaged batteries which have demonstrated pH values similar to those in control sample.

The smallest pH deviation from values in control sample were in the sample with Li-Ion battery of CR2032 type. It should be noted that other above mentioned samples (they correspond to majority of alkaline batteries and to one type of rechargeable batteries) were characterized by dramatic pH increasing (over 12) at the experiment beginning followed by its reducing to control values. It can be explained by alkaline electrolyte release from damaged battery to water medium as was described before. The largest pH deviations from control values were obtained in the samples 8 and 10 which have shown converse dynamics.

The sample 10 with damaged alkaline battery of LR20 type had the highest pH value (almost 13) from the first day of the experiment due to large electrolyte volume (battery of such type has larger dimensions comparing with majority of other batteries). The sample 8 with damaged zinc-carbon battery of 6F22 type had the lowest pH value (below 5 at the end of the experiment) as it was in the case of undamaged batteries. But there was no temporary pH increasing observed in the sample with damaged battery.

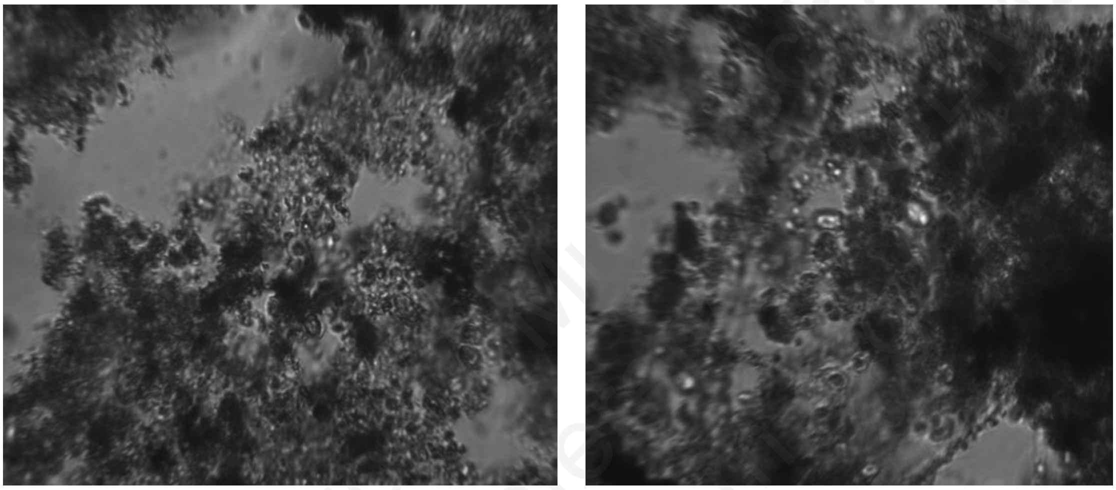
The same dynamics was noticed for other samples where pH gradually reduced to neutral or acid values. These were the samples 2, 4, 6 and 20 (they contained zinc-carbon batteries and rechargeable phone battery). Therefore, potential pH increasing due to electrolyte influence in above mentioned samples could be neutralized by act of other substances of given type batteries. For example, chloride in electrolyte of zinc-carbon batteries can provide pH reducing due to hydrochloric acid formation.

The similar pH values were observed in some samples with the same batteries types, one of which was damaged and other one was undamaged. They include zinc-carbon battery of R20 type, alkaline battery of LR03 type, Li-Ion battery of CR2032 type and rechargeable battery of KR6 type. That could be influenced by few factors: low content of substances able to change pH or their instability, neutralization of such substances by bioindicator (algae), low hermeticity of metal casing of battery or its self-damaging during the experiment.

The most significant pH change took place in the first day that proves the intensity of batteries impact. Generally, pH changes correspond to the type of substances contained in batteries regardless damaged or undamaged they were. Comparing the samples with damaged and undamaged batteries of the same type has shown nearly identical pH dynamics. In the case of zinc-carbon and rechargeable phone batteries, the samples with damaged batteries had constantly lower pH values and alternatively, in the case of other batteries types they had higher pH values. Naturally, it is explained by chemical composition of batteries, including electrolyte type.

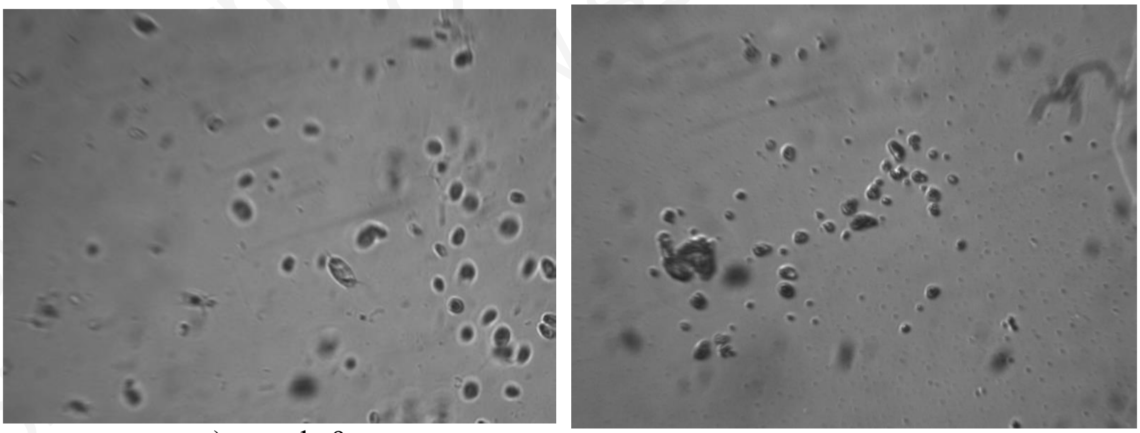
Visual investigation

Visual investigation of the samples by use of microscope at 14th day of the experiment has shown that the largest impact on the bioindicator was found in the samples with alkaline batteries while the lowest influence – in the samples with 9V block batteries of 6F22 type (Fig. 3-5). Moreover, all the samples with damaged batteries were characterized by higher level of living organisms death in comparison with the samples with the same batteries but undamaged.



a) sample 7 b) sample 8

Figure 3. Samples with zinc-carbon batteries of 6F22 type at 400x zoom



a) sample 9 b) sample 10

Figure 4. Samples with alkaline batteries of LR20 type at 400x zoom

The level of bioindicator death was the highest in the samples which had pH values similar to control (almost all alkaline batteries, Li-Ion button and rechargeable batteries), as well as in the sample with highly alkaline environment (alkaline battery of LR20 type). These are the batteries types containing the largest quantity of mercury.

Alternatively, the samples with pH values different from the control sample (all zinc-carbon batteries and damaged Li-Ion rechargeable phone battery) had the lowest level of algae death, except the samples 1 and 2 with zinc-carbon batteries of R20 type.

Therefore, one can assume that pH change during contact between sample medium and battery content is not reliable indicator for defining the degree of batteries impact on the environment.
In turn, the metals contained in batteries affect ecosystems without pH change. For example, the level of algae death is considerable in the samples 17 and 18 with batteries containing nickel and cadmium, especially in the sample with damaged battery, although its pH was similar to values in the control sample.

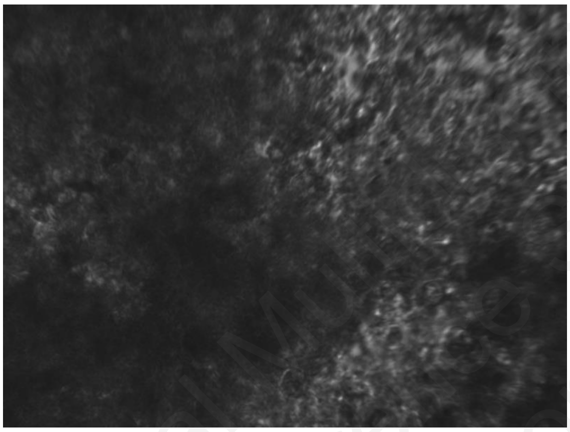


Figure 5. Control sample at 400x zoom

CONCLUSION

The research results have shown that all batteries including undamaged affect living organisms when coming to the environment. They change the environment characteristics very quickly. The most significant pH change took place in the first day that proves the intensity of batteries impact. Batteries with undamaged casing cause living organisms destruction as well, possibly due to gradual damage of the casing in aggressive environment.

Different types of batteries can provide alkaline or acid environment. First of all this depends on electrolyte used. But the research has shown the ambiguity of this parameter influence on living organisms. Much larger impact is caused by hazardous heavy metals (mercury, nickel, cadmium and others) contained in the batteries. When analyzing impact of potentially most hazardous batteries containing mercury, nickel and cadmium, the authors have noticed the most negative reaction of bioindicator in such samples. These batteries include nickel-cadmium rechargeable and all alkaline batteries. Therefore, one can assume that pH change during contact between sample medium and battery content is not reliable indicator for defining the degree of batteries impact on the environment. In turn, the metals contained in batteries affect ecosystems without pH change. Consequently, the additional research of heavy metals impact on living organisms is needed.

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