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Action of activated waters on plants after adverse chemical effects, imitating acid rain

Teodora P. Popova*, Toshka E. Petrova, Metodi Petrichev, Miglena Valyova

University of Forestry, 1756 Sofia, Bulgaria
**Corresponding author:* dr_tpopova@abv.bg

Abstract

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Studies have been carried out to test the effect of catholytes for protection of plants from the species coriander (*Coriandrum sativum),* oregano *(Origanum vulgare),* lemon balm *(Melissa officinalis),* mint *(Mentha piperita)* and mint (*Mentha spicata)* after treatment with sulfuric acid solutions with pH 4.87, 5.76 and 5.91, resembling acid rains. The results show that acid rains have an adverse effect on plants, even at relatively low acidity. They damage the plants and cause a loss of freshness, etiolation and some of them die after their effects. The most vulnerable to acid rain effects are the coriander, *M. spicata* and oregano, and the most resistant is the lemon balm. The present studies show for the first time that catholytes prepared with 0.05% NaCl, also with a combination of 0.05% NaCl and 0.05% Na_2CO_3 as well as 0.4% NaCl and 0.4% Na_2CO_3, and applied 1.5 hours after treatment with acidic solutions, have a beneficial effect on the plants. Two-fold treatment with catholyte is more effective than one-off, although the differences are not significant. It has been established for the first time that catholyte can be a reliable and effective remedy for plant protection in order to prevent significant damage to plants and ensure their rapid recovery after acid rains.

Keywords: catholyte; acid rain; plant protection; coriander; oregano; lemon balm; mint

Introduction

One of the world's biggest environmental problems today is acid rain. It is a side effect of combustion of solid and liquid fuels and residual emissions from other pollutants. In the process of combustion of solid fuels, toxic gases such as sulfur dioxide (SO_2) and nitrogen oxides (NO_x) are released. Although there are natural sources of sulfur and nitrogen oxides, more than 90% of sulfur and more than 95% of nitrogen emissions in North America and Europe are of human origin. Once released into the atmosphere, they can be chemically converted into secondary contaminants such as nitric acid and sulfuric acid – both dissolving easily in water. As a result, any rain falling off in areas with higher emissions of these gases is slightly acidic. The effect on nature and in particular on plants is negative. Many trees lose their leaves and their tops become thinner. The acid rain is absorbed by the soil, threatening the survival of these trees, also makes them more susceptible to pests such as viruses, molds and insects (Tennesen, 2010; Dimitrova, 2019).

It has already been proven that acid rain is a serious environmental problem. The chemical composition of precipitation affects the composition of soils, surface waters, coastal areas, different ecosystems, state of vegetation, man-made buildings and infrastructures, as well as cultural and historical monuments. Contaminated air accelerates the corrosion of metals, causes considerable damage to cultural monuments, and significantly reduces the quality of agricultural production. Acid rainfall has a negative effect on natural ponds, forests, soils and all organisms living in these ecosystems (Valcheva & Hristova, 2016).

Air pollution is a global problem and has a negative impact on human health and on the environment. Industry and transport vehicles pollute the air with sulfur dioxide, nitrogen oxides, lead aerosols, ammonia, phenol, hydrogen sulphide and other harmful substances. One of the main problems is the exceeding of the permissible air concentrations of fine particulate matter, sulfur dioxide and nitrogen oxides, which, falling into the atmosphere, react with water vapor and are converted into nitric and sulfuric acid. The acid compounds fall on the ground as rain, snow, mist, or as a dry deposition. Rainwater is often more acidic due to natural emissions of SO_2, NOx and organic acids. In contact with carbon dioxide in the air and in the absence of pollutants, it has a pH value of 5.6, while the neutral water has a pH of 7.0. The pH values of acid rainfall influenced by anthropogenic emissions are in the range of 3.5 – 5.0 (Dimitrova, 2019).

Statistics show that annually in the atmosphere enter between 70 and 100 million t of sulfur dioxide. It attacks the plants and reduces their fertility, but also corrodes the metals, destroys rocks and various monuments, affects the animals. Acid rains also affect freshwater ecosystems by altering the chemical composition and pH of the water. This also affects the health of the human being, mainly by provoking the development of respiratory diseases, dry and persistent cough, dizziness, headache, burning of the eyes, skin irritations, allergies, weakening of immune defense of the body, etc. (Hristova et al., 2016; Valcheva & Hristova, 2016).

The Geneva Convention of 1979 is the first international legally binding instrument to address long-range transboundary air pollution on a broad regional basis and the European Monitoring, and Evaluation Program (EMEP) is a science-based program created for this purpose by international cooperation. Rainfalling is a major natural process for self-purification of the atmosphere. The type and quantity of pollutants in precipitations depends on the processes of gripping the pollutants from the water drops during and at the place of formation of the clouds, as well as the under cloud washing of the local pollutants in the atmosphere during the rainfalling process (Dimitrova, 2019).

Acid rains today are very common and are one of the serious problems that have a negative impact on plants. They are the result of the increasing environmental pollution, and especially of the atmosphere with toxic gases from industry, energy and transport. By damaging plants, these rains cause losses in the various branches of agriculture. For these reasons, the search for funds and opportunities to reduce and prevent the negative effects of these rains is a current task today. As environmentally friendly and affordable agents, ionized aqueous solutions could be a means of combating these adverse effects. Therefore, the purpose of this study is to test the action of catholytes on plants after treatment with acidic solutions similar to acid rain.

Materials and Methods

Catholytes:

• Catholyte 1, prepared with 0.05% NaCl;

• Catholyte 2, prepared with combination of 0.05% NaCl and 0.05% Na_2CO_3, pH;

• Catholyte 3, prepared with combination of 0.4% NaCl and 0.4% Na_2CO_3.

Activation time in ionizer "Ashbakh" (Germany): 12 min.

Structured alkaline water Adva® („Suppletec Ltd.", London, England), No L2202183, best before 22.02.2019, purchased from the market, pH 9.0 on the lable and 6.88 before the experiments, ORP: -1 (before the experiments).

Acid solutions

Three different aqueous solutions of sulfuric acid have been tested. Simulated acid rain (SAR) was prepared by using of 20% H_2SO_4 as a stock solution. It was diluted with distilled water in order to obtain three different concentrations: 0.001% with pH 5.91, 0.0015% with pH 5.76.and 0.002% with pH 4.87, respectively. The control plants were sprayed only with tap water (pH 8.92, ORP 218 mV, 22.1^{0}C) in the same quantity. Each solution was measured three times at pH meter "Manual multi-parameter analyzer" model Consort C1010 (Consort bvba, Belgium) for pH, mV and temperature.

Plants

Commercially purchased plants planted in individual pots of the following species were used:

• Coriander (*Coriandrum sativum*) class 1, producer "Melissa Fruct Ltd.", Sandanski, Bulgaria;

• Oregano (*Origanum vulgare*) in pots, class 1, L46/5. Manufacturer "Bloom Fetish", Bulgaria;

• Lemon balm (*Melissa officinalis*) in pots, class 1, L46/5. Manufacturer "Bloom Fetish", Bulgaria;

• Mint (*Mentha piperita*) standard 12, L47/04. Producer "Razcvet", Stara Zagora, Bulgaria;

• Mint (*Mentha spicata*) garden house planted in separate pots (groups of three stalks in a pot) grown under room conditions.

Experimental setting

The experimental plants in individual pots were divided into groups of 20 plants per group. Each of these was sprayed with an acidic solution, as each was treated with a certain solution (one of the three used in the experiment). Group No. 1 was treated with acidic solution 1 (pH 4.87), group 2 with acidic solution 2 (pH 5.76) and group 3 with acidic solution 3 (pH 5.91). The plants were divided into subgroups and after 90 min they were sprayed with various catholytes as follow:

- Treated with catholyte 1 (pH 11.64);
- Treated with catholyte 2 (pH 11.59);
- Treated with catholyte 3 (pH 11.02);
- Treated with water Adva (pH 6.88).

24 hours later half of the plants from each experimental group were treated again with the same catholytes or structured water.

Controls:

- Acid untreated plants of the test species sprayed with an equivalent amount of tap water;
- Plants of the studied species treated with acidic solutions but not treated with catholyte.

The test and control groups were grown under the same conditions in a light room at room temperature. They were observed for one week.

Results and Discussion

Results

The physical indicators pH, ORP, and temperature of the catholytes tested are presented in Table 1.

The composition and physical indices of the acidic aqueous solutions used can be seen in Table 2.

One hour after the treatment with acidic solutions, all plants were saddened and their freshness decreased by about 20% (Fig. 1). The negative effect of acidic influences was even more pronounced the next day (a decrease in freshness to 50-70% of the baseline), which can be seen from Table 3, Table 4, Table 5 and Table 6. The freshness of the untreated with acids and catholytes plants was good (100%) throughout all the study period and served as a comparison when considering the effect of the solutions (Fig. 2).

From Fig. 1 it can be seen that the oregano and mint (*M. spicata*) are more vulnerable to the effects of the acidic solutions than the lemon balm.

The results of the follow-up of the effects of the test catholytes on the treated with acidic solutions test plants and the catholyte untreated controls observed in the following days are presented in Table 3, Table 4, Table 5, Table 6 and Fig. 2, Fig. 3, Fig. 4.

From Fig. 2 and from the data presented in Table 6, it can be seen that structured commercial water has no regenerating effect on the test plants exposed to acidic influences.

The results show that after acid rain the plants do not recover 100%. At higher acidity (pH 4.87), 80% of the plants survive, and at pH 5.76 and 5.91 – 90%, the rest perish. However, all catholyte-treated plants survive and recover 100% after acid rain like impact, regardless of its acidity.

It can be seen from the data in the tables and figures that treatment with acidic solutions imitating acid rain has a negative effect on the test plants. The results are in dependence of the concentration of the acid in the applied solutions.

The strongest adverse effect on the treated plants showed acid solution No. 1, followed by No. 2 and solution No. 3. Treatment with alkaline solutions of catholytes had a positive effect and reduced the harmful effect of the acid on the plants. The result was dependent on the concentration of the acid in the applied solution prior to the catholyte treatment as well as on the catholyte type. After treatment with catholytes, Group 3 plants treated with the acidic solution of the highest pH (5.91) recovered most speedily and in the highest degree. Still at 24 and 48 hours, their freshness was 90% compared to that before treatment with catholyte (80%). In group 2 the effect at 24 and 48 hours was slightly lower than that of group 3 but better than the non-treated with catholytes controls. Group No. 1 treated with the acidic solution with the lowest pH (4.87) recovered most slowly under the influence of the catholytes.

Table 1. Physical indicators of the catholytes used

Starting composition	pH	ORP, mV	t°C
C 1. Aqueous sodium chloride solution 0.05%	11.64	-273	18.6
C 2. Aqueous sodium chloride (0.05%) and sodium carbonate (0.05%) solution	11.59	-275	18.4
C 3. Aqueous sodium chloride (0.04%) and sodium carbonate (0.04%) solution	11.02	-238	19.2

ORP – oxidation-reduction potential

Table 2. Physical indicators of the acidic aqueous solutions used

Solution	Composition	pH	ORP mV
1	100 µl of 20% H_2SO_4 in 1000 ml distilled H_2O	4.87	124.33
2	75 µl of 20% H_2SO_4 in 1000 ml distilled H_2O	5.76	83.00
3	50 µl of 20% H_2SO_4 in 1000 ml distilled H_2O	5.91	70.18

Fig. 1. Part of plants 1 hour after treatment with acidic solution 1 with pH 4.87: Top left – oregano; top right – lemon balm; bottom left – part of the plants (mint *M. spicata*) after treatment with acidic solution 2 with pH. 5.76; bottom right – part of the plants (coriander) after treatment with acidic solution 3 with pH 5.91

Table 3. Results of the effect of catholyte 1 (pH 11.64) on acid treated test plants and untreated with catholytes controls, presented as a percentage of freshness in comparison non-treated with acid and catholytes plants

Group №	24 h		48 h		7 day	
	Test plants	Controls	Test plants	Controls	Test plants	Controls
1 A 1 B	70% 80%	50%	80% 90%	70%	100% 100%	80%
2 A 2 B	80% 90%	60%	80% 90%	70%	100% 100%	90%
3 A 3 B	80% 90%	70%	90% 100%	80%	100% 100%	90%

A – once treated with catholyte 1; B – twice treated with catholyte 1; Controls – without catholyte

Table 4. Results of the effect of catholyte 2 (pH 11.59) on acid treated test plants and untreated with catholytes controls, presented as a percentage of freshness in comparison non-treated with acid and catholytes plants

Group №	24 h		48 h		7 day	
	Test plants	Controls	Test plants	Controls	Test plants	Controls
1 A 1 B	60% 70%	50%	70% 80%	70%	100% 100%	80%
2 A 2 B	70% 80%	60%	80% 90%	70%	100% 100%	90%
3 A 3 B	70% 80%	70%	80% 90%	80%	100% 100%	90%

A – once treated with catholyte 2; B – twice treated with catholyte 2; Controls – without catholyte

Table 5. Results of the effect of catholyte 3 (pH 11.02) on acid treated test plants and untreated with catholytes controls, presented as a percentage of freshness in comparison non-treated with acid and catholytes plants

Group №	24 h		48 h		7 day	
	Test plants	Controls	Test plants	Controls	Test plants	Controls
1 A 1 B	60% 70%	50%	70% 80%	70%	100% 100%	80%
2 A 2 B	70% 80%	60%	80% 90%	70%	100% 100%	90%
3 A 3 B	70% 80%	70%	80% 90%	80%	100% 100%	90%

A – once treated with catholyte 3; B – twice treated with catholyte 3; Controls – without catholyte

Table 6. Results of the effect of structured water (pH 6.88) on acid treated test plants and untreated with catholytes controls, presented as a percentage of freshness in comparison non-treated with acid and catholytes plants

Group	24 h		48 h		7 day	
	Test plants	Controls	Test plants	Controls	Test plants	Controls
1 A 1 B	50% 50%	50%	70% 70%	70%	80% 80%	80%
2 A 2 B	60% 60%	60%	70% 70%	70%	90% 90%	90%
3 A 3 B	70% 70%	70%	80% 80%	80%	90% 90%	90%

A – once treated with structured water; B – twice treated with structured water; Controls – without catholyte or structured water

Fig. 2. At 24 hours after treatment with acid solutions: top left - part of the control plants treated with acidic solutions but not treated with catholytes; top right – part of control plants not treated with acidic solutions and catholytes; bottom left – part of the plants treated with acid solutions and 1.5 h later with catholyte 2; bottom right – part of the plants treated with acid solutions and 1.5 h later with structured water

Fig. 3. Plants of groups 1, 2 and 3: on the left – 48 h after treatment with acidic solutions and catholyte 3; on the right – untreated plants

Fig. 4. On the 4th day after treatment with acidic solutions: top left – part of the control plants treated with acidic solutions but not treated with catholytes; top right – part of control plants not treated with acidic solutions and catholytes; in the middle left – part of the plants treated with acidic solutions and treated twice with catholyte 1; in the middle right – part of the plants treated with acidic solutions and treated twice with catholyte 1; bottom left – part of the plants treated with acidic solutions and treated once with catholyte 1; bottom right – part of the plants treated with acidic solutions and treated twice with structured water

The best regenerating effect showed catholyte 1. The other two catholytes also had good effect and were similar in efficacy. Two-fold treatment with catholyte promoted the faster recovery of acid-stricken plants. Structured commercial water did not have a restorative effect on acid-treated plants even after twice application.

Discussion

The most common substances that pollute the soil are sulfur and nitrogen oxides coming from the atmosphere. They fall into the soil along with precipitation, increase its acidity and significantly reduce the fertility and quality of agricultural produce harvested from these areas. Acidic soils are very often barren, as microbiological processes, leading to an increase in soil fertility, have been disturbed. Land acidification is also caused by the penetration into the soil of various sulfur and nitrogen compounds together with organic waste from cities, livestock farms and poultry farms. As a result of complex chemical transformations under the influence of various microorganisms of these wastes are released sulfur and nitrogen oxides, forming sulfuric and nitric acid, which increase the acidity of the soil and the aquatic environment (Hristova et al., 2016; Valcheva & Hristova, 2016; Dimitrova, 2019).

That is why in our experiments with reproduction of the effect of acid rain on plants we used aqueous solutions of sulfuric acid with which maximum to resemble the composition and pH of these rains under natural conditions.

Catholyte is a solution with alkaline properties obtained from water in the electrolysis process. Its taste, smell and color are not different from these of the water, but it differs of water by the indicators redox potential, acidity/ alkalinity – pH and the presence of active micro- and macro-elements. The catholyte has antioxidant and immune stimulating properties and accelerates regeneration of tissues in animals and humans, and in the introduction of certain minerals during its preparation, it helps in diabetes, hypertension, osteoporosis and other diseases. It is a simple, affordable and inexpensive means of maintaining the balance between acid-forming and alkali-forming products in the live organism, since it has a pH of 7 to 12, depending on activation (Ashbakh, 2008; Gluhchev et al., 2015, 2018; Ignatov et al. 2015).

So far, however, no studies have been carried out to establish the regeneration properties of catholytes on plants and possibilities for their use for plant protection. The results of the current studies show that catholyte given 1.5 hours after treatment with acidic solutions resembling acid rain has a beneficial effect on the plants. Particularly quick and efficient is its restorative effect on plants treated with the least acidic solution. However, after exposure of the plants to high acidity solutions, the effect of catholyte is slower, especially after application of the solution with highest acidity.

On the one hand, the results obtained by us show that acid rain has an adverse effect on plants, even with relatively low acidity. They damage the plants and cause a loss of their freshness and vitality, and some of them die after their effects. On the other hand, the data we have obtained show that the catholyte can be a reliable and effective means of preventing damage to plants and their rapid recovery. Therefore, for valuable and frail agricultural or ornamental plants, catholyte treatment after acid rain would be important for reducing plant losses and their quickly recovery from the adverse effects. Especially recommended is the method of plant regeneration we offer for plants that are highly vulnerable to acid rain, as shown by our experiments, such as coriander, mint, oregano, and others. The structured commercial water, however, does not have a regenerating effect on acid-affected plants probably due to the weakening of its properties after staying on the market. The catholytes we used were stored for only 2 weeks at room temperature, whereby obviously their activity is preserved to a considerable extent.

It is also important to mean that the plants we have used are not only herbs and spices, but also honey plants in the flowering phase. According to Gurgulova et al. (2010, 2011) electrochemically activated aqueous solutions, to which the catholytes belong, are harmless to bees, and they do not disturb the chemical and organoleptic properties of honey and bee products. These facts give us additional reasons to believe that using our proposed method of counteracting the negative effects of acid rain by treatment with catholytes would also be useful for beekeepers.

Conclusions

Experimentally, the adverse effects of acid rain on plants have been established, even in relatively weak acidity. The damaging effect of the acidic solutions was more pronounced at higher acidity.

From the plants we tested, the most vulnerable to acid rain were the coriander (*Coriandrum sativum)*, the mint (*Mentha spicata)* and the oregano *(Origanum vulgare)*, and the most resistant was the lemon balm *(Melissa officinalis)*.

It was established for the first time that catholyte can be a reliable and effective means of preventing damage to plants and their associated losses after acid rain. Even with a single treatment with catholytes after imitation of acid rain, plants recovered more speedily and more efficiently than the untreated with catholyte. Two-fold treatment with catholyte was more effective than one-off, but the differences were not significant. All tested catholytes had a good regenerative effect on the damaged plants, but the highest one was that of the catholyte 1.

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