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Green Chemical Aspect of Environmental Awareness Development and Antimicrobic Influence Mechanisms of Colloidal Silver, Copper and Gold Compounds: One Possibility of Prevention from COVID-19

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Abstract

Un General Assembly adopted Resolution 57/254 on December 2002 the UN Decade of Education for Sustainable Development 2005-2014. The aim of this strategy is to encourage UNECE members to develop and incorporate education for sustainable development into the formal education system. In B&H 2005-2007, as part of the implementation of the EU CARDS project "Strengthening Environmental Awareness", we have just implemented this UNCE strategy. The printed teacher manual "Living in harmony with the environment" was prepared, printed and promoted through a series of seminars. Unfortunately, today we have testified that environmental awareness is far from developed. This is the case, after all, around the world, which needs to be worked on permanently and more seriously in the future through formal and non-formal education.

In laboratory, we should and have focused on the application of the green chemistry principles, and thus in light of the pandemic we encountered from 2020, it may sometimes be necessary to look for a solution in alternative medicine as the initial arm to solve the problem. Colloidal silver and copper has long been used as antimicrobial, antiviral and antifungal agents. Knowing their effects on bacteria and viruses, perhaps the use of silver colloidal water can do some extent prevent the spread of the virus? This paper aims to remind what the effects of colloidal silver and copper are and to take us back in the history of its use and give ideas for new research.

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Introduction

The environment is a hot topic in the press and classrooms across the world and much has been said about the need for action to protect our planet. If current trends in climate change continue, temperatures could increase between 3 and 6 degrees Celsius by 2050. Such large temperature increases would lead to water shortages for billions of people, reduce agricultural yields, increase malnutrition related deaths by millions and lead to the extinction of a large part of animal species [1].

Education plays a crucial role in raising awareness of environmental challenges and shaping the attitudes and behaviors that can make a difference. A recently released Trends Shaping Education Spotlight looks at the role of education in both preparing and providing our citizens with the skills needed for a sustainable and productive future [2]. The majority of young people is aware of environmental issues and care about them, according to data from the Programed for International Student Assessment (PISA). In 2018, students in the OECD nations as a whole agreed or strongly agreed with the statement that protecting the environment is important to them, and 79 percent indicated they were aware of climate change and global warming [3]. Early environmental awareness and pro-environmental sentiments are greatly influenced by the educational system. They are a significant source of environmental information in the first place: in 2018, almost 9 in 10 school principals said that climate change and global warming were taught in the school curriculum [3]. Importantly, pupils who master science have a greater awareness of environmental problems and a better feeling of responsibility for sustainable development [4-5].

A first step in addressing the issue is raising awareness many classrooms already discuss important issues like recycling or sustainable consumption. However we need to do much more.

So, when UN General Assembly adopted Resolution 57/254 on December 2002 the UN Decade of Education for Sustainable Development 2005-2014 was issued, we started on the issue in B&H 2005-2007, as part of the implementation of the EU CARDS project "Strengthening Environmental Awareness" which means that we have just implemented this UNCE strategy in three steps. The aim of this strategy is to encourage UNECE members to develop and incorporate education for sustainable development into the formal education system [6-7].

Nowadays, we are witnessing unknown diseases that are not only of a local character, but affect the whole world. An example is the latest experience with the Coronavirus Pandemic, which has spread throughout the Globe. Some acquired knowledge has been almost forgotten or ignored due to prejudice, and could prevent the spread of the epidemic and possibly cure them. An example is the ancient knowledge of the bactericidal action of silver, copper and gold. It give the ideas for new Green Chemical research in that field.

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A New Vision of Education for Sustainable Development

Strengthening environmental awareness through formal and non-formal education and actions realized solving some local pollution with NGOs

Through implementation the EU CARDS project "Strengthening Environmental Awareness" in Bosnia and Herzegovina the teacher's manual "Living in Harmony with the Environment" (Figure 1.) was prepared in 2007 in local languages, printed and promoted through the series of seminars across Bosnia and Herzegovina not only for upper grades teachers of primary schools and also for all secondary school classes teachers, but also for journalists and non-governmental organization (NGO's) representatives [8].

Second step was intensive cooperation with media which followed all our activities on the project.

The third one was creating additional 10 subprojects for NGO's to create and implement small projects for solving the local environmental problems.

It is essential to introduce through formal and non-formal education the concept of Green chemistry and the 12 principles. Green chemistry is a continuous effort to solve the issues that chemicals and chemical processes might occasionally result in. It became a notion in the 1990s, and the 12 principles were published to help further direct chemists' efforts in this direction. They are essentially a checklist of methods to lessen the influence of chemicals and chemical synthesis on the environment as well as any possible harm to human health. They were developed by Paul Anastas and John Warner [9,10].

The Green Package education for a sustainable future

In 2000, the *Regional Center for the Environment for Central and Eastern Europe* (REC) in cooperation with Toyota implemented the project of the so-called "*Green Package*" (Figure 2.) of environmental education and education for sustainable development. During 2010, the "Green Package" as a material for educating students in the lower grades of elementary schools, was adapted for students of Bosnia and Herzegovina. It is a multimedia, environmental and educational kit for the education of both teachers and students.

Figure 2: Green Package, a multimedia, environmental and educational kit for the education.

Installing related courses for postgraduate studies at universities

First conceived by the staff of the U.S. Environmental Protection Agency, Green Engineering draws on contributions from many leaders in the field and introduces advanced risk-based techniques including some currently in use at the EPA. The result is creation the Green Engineering Manuel in USA, 1st edition in 2002 and 2nd (Figure 3.) one in 2015 [11-12]. The first one we translated it in Bosnian language and edited in 2009 for universities in Bosnia and Herzegovina [13] .

Figure 1: Teacher's manual "*Living in Harmony with the Environment*"

Figure 3: Green engineering 1st and 2nd edition and translated to Bosnian language – Zeleni inženjering [11-13].

The aim was to provide industry experts with a new approach to engineering chemical processes, products, and systems to reduce environmental impacts approaches for evaluating emissions and hazards of chemicals and processes. Defining effective environmental performance targets requires advanced approaches and tools for evaluating environmental fate. In-depth discussion of unit operation and flow sheet analysis, as well as design and development methods used in the early stages that reduce costs and environmental implications. The economics of environmental improvement projects integrate the chemical processes with other material processing operations. Now it is necessary to include lifecycle assessments: beyond the boundaries of the plant, starting from the raw material to the end of the product's life. Increasingly, chemical engineers are faced with the challenge of integrating environmental objectives into design decisions. Green Engineering gives them the technical tools they need to do so [11-12].

One chapter in the book presents green chemistry, which is defined as the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. A completely new approach to chemical synthesis and the accompanying processes has been presented. It describes qualitative principles to be used in developing alternatives alternative solvents, alternative reactants, and alternative chemistries that may lead to environmental improvements. Furthermore, it describes quantitative optimization-based approaches that have been used to identify environmentally preferable reaction pathways.

Unfortunately, today we have testified that environmental awareness is far from developed. This is the case, after all, around the world, which needs to be worked on in the future on a permanent and more serious basis through formal and non-formal education. And most importantly, is the application of acquired knowledge in practice and everyday life [11-13].

The fact that Sarajevo, as the capital of Bosnia and Herzegovina, faces very poor air quality in the winter period shows why education and government incentives are important. The Sarajevo Canton Winter Field Campaign 2018 (SAFICA) was a study that was carried out in the winter of 2017–2018 with the intention of characterizing the chemical composition of aerosol in the Sarajevo Canton, Bosnia and Herzegovina (BiH), which has one of the poorest air qualities in Europe. This study suggests that a variety of solid (such as wood, pellets, and garbage) and liquid fuels are burned during the production of metals in the Sarajevo Canton. In Sarajevo, this has many homes heated by wood products and a central heating system fueled by gas (a non-polluting source), the study found several fuels that make sense from October through April. Finally, to lessen the detrimental effects of PM on BiH's health, non-polluting energy solutions should be devised and implemented. Clean and low-pollution energy sources, such wind and solar photovoltaic electricity, have the potential to be used in BiH. In particular in the energy sector, low-carbon electricity may offset roughly 99 percent of the excess air pollution linked to morbidity and mortality figures. However, it is essential to make new energy options accessible to everyone through reasonable costs and subsidies (i.e., minimal personal financial investment per individual household). Only in this situation can the populace of BiH be urged to switch to more ecologically friendly heating and energy-usage practices. Electric cars might be utilized in the transportation industry to reduce the harmful effects of combustion, such as PM pollution. Due to the avoidance of using fossil fuels, wood fuels, and trash in several individual houses, there may be additional savings if the transportation and heating sectors were electrified through the use of electric vehicles and electric heat pumps [14-16].

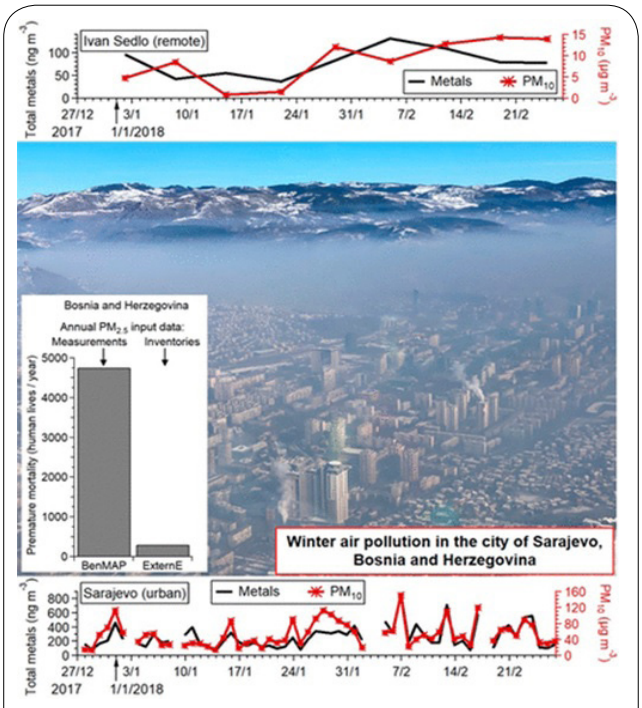

Figure 4: Results of air analysis in Canton Sarajevo [16].

In Bosnia and Herzegovina, due to the lack of legal regulations and education of citizens, we have the appearance of polluted air, improper disposal of waste, discharge of persistent organic pollutants (POPs) into the environment etc.

Fortunately we have The National Cleaner Production Center for Bosnia and Herzegovina (NCPC BH). which is housed at CENER 21. NCPC BH, was founded in 2015, and it pushes Bosnia and Herzegovina's industry toward a low-carbon economy by implementing workable interventions for cleaner, more resource-efficient manufacturing. The Center was established to build on UNIDO's experience supporting National Cleaner Production Programmes (NCPPs) and Centres (NCPCs), in collaboration with UNEP, under the global joint RECP Programme. It aims to foster expertise, service delivery capacity, and implementation of RECP

practices and policies in the nation. One of their ongoing projects is Implementation of Green Chemistry Principles in Industry. By advancing green chemistry (GC) projects in the plastics sector, the project helps to limit the discharge of persistent organic pollutants (POPs) into the environment.The collection of customized exercises aims to create a platform for cooperation between educational institutions and plastic manufacturing businesses, guaranteeing that global experience, real-world examples, and recent advancements in the industry that are available.

By using the suggested technical guidelines and instruments in their technological process, certain businesses will be able to embrace green chemical principles and replace certain contaminants [17,18].

Example of Using Green Chemistry - A Literature-based Perspective Study

Due to rising instances of antibiotic resistance, research into nanoparticles' intrinsic therapeutic potential as antibacterial and antiviral agents has received considerable attention recently. This and other factors make the quest for novel and more potent antibacterial medicines necessary. Numerous studies have shown the potential of nanoparticles in the treatment of different microbial diseases. It is becoming impossible to ignore the therapeutic uses of nanoparticles in viral and microbial research as either delivery agents or broad range inhibitors. In many ways, their high surface area to volume ratio made them an essential chemical for use as delivery agents. Nanoparticles with special features channeled to satisfy certain therapeutic needs have been created using a variety of materials [19,20].

Chemical aspect of antimicrobic influence mechanisms of silver, copper and gold compounds

From history till today - using silver as a medicine

The word "silver" appears in Anglo-Saxon in different spellings such as seolfor and siolfor. A similar form is seen in all Teutonic languages (compare Old High German silabar and silbir). The symbol "Ag" is Latin for "silver"= argentum (compare Greek αργυρος (Argyros) of the Indo-European root means "white" or "shine". The oldest object made of silver was found in Egypt in 4157 BCNE. Hippocrates, the father of modern medicine, wrote that silver has beneficial healing properties against disease as well, and the Phoenicians kept water, wine and vinegar in silver bottles to prevent spoilage. Monks in monasteries used silver containers to store water (Figure 5.) before being placed in a baptism well, and in Orthodox churches all icons are placed in silver frames (Figure 6.) , and in Mecca and the black stone in the wall of the Kaaba (Figure 7.) is studded with silver and no one has ever become infected by touching and kissing. In the middle Ages, royalty used silver pots, plates, knives, spoons, forks, etc, so they did not suffer from the plague [21].

According to Rafique et al., 2016, there are several techniques for synthesis silver nanoparticles (Table 1.). Both "Top-down" and "Bottom-up" strategies can be used to create NPs. Using various size reduction techniques, such as pulse laser ablation, evaporation-condensation, ball milling, and pulse wire discharge method, appropriate bulk material is broken into small particles in the top-down approach. In a bottom-up approach, NPs may be created by self-assembly of atoms into new nuclei, which develop into nanoscale particles, utilizing chemical and biological techniques. Evaporation-condensation is the most widely used process for creating metal NPs in a top-down manner [22].

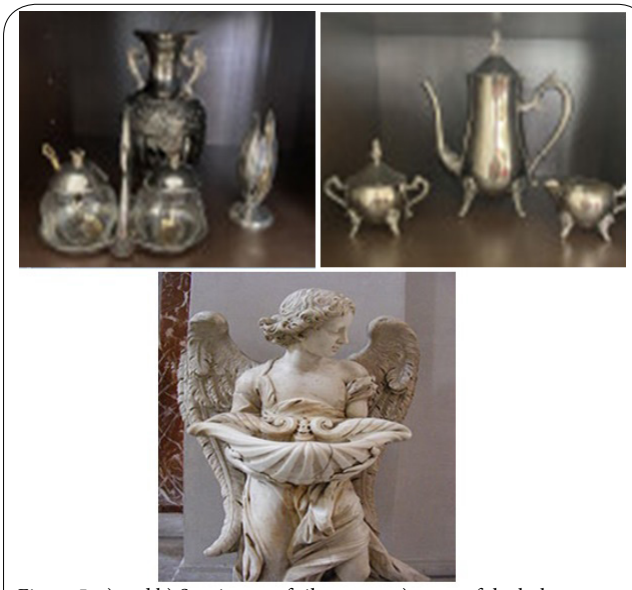

Figure 5: a) and b) Specimens of silverware; c) copy of the holy water tank.

Figure 6: Icon in silver frame.

Figure 7: The black stone embedded in the Kaaba in Mecca is studded with silver.

Synthesis of nanoparticles		
Bottom –up approach		Top-down approach
Green methods	Chemical methods	Physical methods
Using bacteria	Chemical reduction	Pulsed laser ablation
Using fungi	Sonochemical	Evaporation–condensation
Using plant and their extracts	Microemulsion	Arc discharge
Using yeast	Photochemical	Spray Pyrolysis
Using enzymes and biomolecules	Electrochemical	Ball milling
Using microorganism	Microwave	Vapour and gas phase
	Solvothermal	Pulse wire discharge
	Coprecipitation	Lithography
Non-toxic	*Toxic*	

Table 1: Techniques for synthesis of Ag-NPs [22].

Due to a lack of efficient antiviral measures, the COVID-19 pandemic was spreading unchecked. According to research, silver nanoparticles (AgNP) exhibit antiviral qualities and are likely to prevent SARS-CoV-2 [23,24]. Authors Jeremiah et al., 2020, examined the antiviral impact of AgNPs in light of the requirement for a powerful drug against SARS-CoV-2. They tested colloidal silver (cAg), plain elemental Ag nanoparticles of different diameters (AgNPn) and polyvinylpyrrolidone capped 10 nm silver nanoparticles (PVPeAgNP10) against SARS-CoV-2 to find the most effective size and concentration of Ag that could inhibit SARS-CoV2. So several AgNPs of various sizes and concentrations was tested and it was found that particles with a diameter of around 10 nm were effective at inhibiting extracellular SARS-CoV-2 at doses ranging from 1 to 10 ppm, whereas 20 ppm and higher concentrations resulted in cytotoxicity. AgNPs effectively suppressed viral entrance step by compromising viral integrity, as demonstrated by a luciferase-based pseudovirus entry experiment. These findings showed that AgNPs are extremely effective microbicides against SARS-CoV-2, but they should be handled with caution due to their cytotoxic effects and the possibility that, when discarded inappropriately, they might disturb natural ecosystems [25].

In the stdy of Tremiliosi et al., 2020, the pad-dry-cure process is employed to introduce and functionalize an Ag-based compound into polycotton textiles. After a two-minute incubation period, this composite showed promise for suppressing the SARS-CoV-2 virus, with a 99.99 percent reduction in the number of replicates. Additionally, it prevented cross-infections by inhibiting the pathogens *S. aureus, E. coli*, and *Candida albicans* 99.99 percent of the time and does not induce allergies or photoirritation, proving the safety of its use [26]. Other authors who used other strategies to introduce AgNPs into polycotton have observed similar behavior in their research [27].

Noble metals like gold and silver have been prized for millennia for their beauty as well as for their medicinal properties. Due to their distinctive physiochemical and chemical characteristics as well as biological characteristics, such as anti-inflammatory, anti-angiogenesis, antiplatelet, antifungal, anti-cancer, and antibacterial activity, silver nanoparticles (AgNPs) have been used as chemical medicines. More over 20% of deaths worldwide are caused by infectious illnesses, with viruses being mostly to blame for one-third of these fatalities. Middle East respiratory syndrome (MERS), COVID-19, and other highly contagious viral infections are becoming more prevalent, and their spread throughout the world is posing a major danger to both human health and the global economy. Professor Boukef Riadh, at Hôpital Universitaire Sahloul, Tunisia, is conducting a study for a treatment of COVID-19 with colloidal silver. Any patient over the age of 18 who consults the Sahloul emergency room in Sousse with COVID-19 symptoms that have been present for fewer than ten days and who also has a positive COVID-19 result on a PCR test and a standard scanner.Participants of this study are divided in two groups: experimental group which are given oraly colloidal silver solution or by inhalation, nebulization or coloidal silver solution, and placebo group (U.S. National Library of Medicine, ClinicalTrials.gov). These are just a few examples of using colloidal silver in medical purpose [28].

Copper - the killer of bacteria and viruses

A set of traditional anti-infection agents after the latest tests, copper and alloys made of this metal are associated with brass and bronze. More efficient than silver, copper has a strong antiviral and bactericidal effect. In order to reduce the bioburden and restrict environmental transmission of nosocomial infections, touch surfaces consisting of copper-based alloys (Figures 8. and 9.), such as brasses, are employed in hospital settings nowadays [29]. The latest clinical trials of scientists from the US, Britain and Germany have confirmed that copper and alloys made from this metal, primarily brass and bronze, have a strong antiviral function, US media reported [30]. Copper alloy coatings might be useful for health protection in dental practice and can also be used in orthopedic traumatology when paired with effective hygienic/disinfectant methods and cautious surgical technique [31].

Figure 8: Copies of copper dishes in the kitchen.

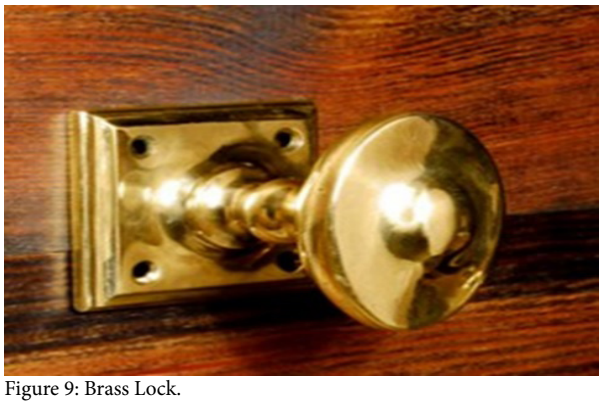

Figure 9: Brass Lock.

Cortes and Zuñiga, 2020 reported that copper oxide or nanocompounds may be used as filters, face masks, clothing, and hospital common surfaces to reduce viruses and bacterial incubation [32].

These results imply that a large portion of the population may have insufficient dietary copper intake and mild copper deficiency. Raha et al. argue that taking a copper supplement may protect against COVID 19 [33].

Hospital outbreaks of numerous Legionnaires' illnesses have lately been linked to cooling towers and potable water distribution systems. However, it has been shown via several studies that the most effective long-term water disinfection system that can be employed in the hospital setting is a copper-silver ionization system [34].

There are several studies regerding green synthesis of copper nanoparticles from different plant material like from leaf extracts of *Ocimum sanctum* [35], leaf extract of *Jatropha curcas* [36], leaf extracts of *Hagenia abyssinica* (Brace) JF. Gmel. [37].

Gold compounds – uses in medicine

Because of their photothermal activity, nontoxicity, polyvalent effects, high capacity to functionalize, and simplicity of detection, AuNPs are anticipated to be crucial in the development of antibacterial action. According to Cui et al., AuNPs' antibacterial effect does not include any ROS-related processes but rather involves adherence to the bacterial membrane, membrane potential alteration, and a decrease in ATP levels. Additionally, it has been discovered that by attaching to the ribosomes, AuNP can block the tRNA [19, 38].

Meléndez-Villanueva et al., 2019., investigated the antiviral efficacy of green chemistry-produced gold nanoparticles (AuNPs-As) against infection with the measles virus. The selectivity index showed that AuNPs-As would be a good viral inactivating agent against MeV infection due to its lack of cytotoxicity at inhibitory doses. Virucidal action can be effective as a therapy after infection as well as a preventative measure before viral infection, preventing the spread of the virus. A possible method to treat and manage MeV and other similar enveloped virus infections may be AuNPs-As [39].

Sccording to the Sani et al., 2021., at this moment, it is difficult to establish and generalize important aspects of AuNPs effects due to the conflicting evidence on their bioactivity in literature, depicting variances in laboratory techniques. These prevent a proper assessment of the cytotoxicity of AuNPs and a judgment from being made. However, the fundamental toxicity and its extent are jointly influenced by the features, preparations, and physicochemical properties of the AuNPs. The results of these reviews revealed little disagreement. Although several other research dispute this claim, certain investigations have indicated that AuNPs are not harmful. More research is needed that will concentrate on characterizing the NPs and changes in physical characteristics both before and after treatment with biological medium in order to draw a comprehensive conclusion.

Conclusion

In summary, it can be concluded that education through formal and non-formal education is a key factor for the application of all principles of Green Chemistry, from students in primary and secondary schools, students at universities, through ordinary people in all aspects of life to people in industry. It is also sometimes necessary to go back to the "roots", i.e. older research, even to what is known as alternative medicine, and try to modify it using the principles of green chemistry.

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