Towards A Sustainable Use of Biocides in Saudi Arabia: Opportunities, Perspectives and Risks

Talal Mouais
Graduate Student,
Renewable Energy Engineering Programme, Effat University,
Jeddah, Saudi Arabia
tamouis@effat.edu.sa

Budoor Salem Alwateedhi
Graduate Student,
Renewable Energy Engineering Programme, Effat University,
Jeddah, Saudi Arabia
bualwated@effat.edu.sa

Tayeb Brahimi
Energy and Technology Research Center,
Effat University,
Jeddah, Saudi Arabia
tbrahimi@effatuniversity.edu.sa

Imtiaz Ahmad
Natural Sciences, Mathematics and Technology Unit
College of Engineering, Effat University
Jeddah, Saudi Arabia
iahmad@effatuniversity.edu.sa

Abstract

The objective of this paper is to investigate the opportunities, perspectives, and risks of employing biocides in Saudi Arabia using qualitative and quantitative parameters of the market. In solving the problem of the impact of biocides on health and environment, prior consideration must be given to the safety of agricultural products, as in excess of 90% of the total amount of biocides that enter the human body from the environment originate from food. The ecological safety of agricultural products can be achieved by compliance with the principles of "greening" of agriculture, developing hydroponic cultivation of crop products, and cleansing the soil of biocides.

Keywords
biocides; sustainability; environment; opportunities; risks, Saudi Arabia

1. Introduction

The twelve green engineering principles form the basis for building safe, effective, and environmentally friendly products. Green Engineering is defined as the design, commercialization, and use of processes and products that minimize pollution, promote sustainability and protect human health and the environmental wellbeing without sacrificing economic viability and efficiency (Anastas et. al., 2003). Using the fundamental principles of chemistry, Green Chemistry is the implementation of a set of twelve principles that reduces or eliminates the use or generation of inherent hazardous substances in the design, manufacture, and application of chemical products. These green principles are essential in optimizing the designs of engineering projects to ensure that they are accepted as a safe and reliable product. A large range of new technologies and changes have been applied to protect the environment and prevent pollution in different industries besides the chemical industry. One of the widely employed chemical substances in everyday life is the biocide, a chemical compound that destroys harmful living organisms but may have toxic, carcinogenic, or disruptive properties in endocrine systems (Rossmoore, 1995). Biocides constitute substances used for water treatment, cooling water systems, wood preservation, paints and coatings, food and beverages, and cosmetics, amongst others. One of the leading uses of biocides is in agriculture, where these substances are used in large areas and aid in the preservation of crops. Many fungicides, herbicides, insecticides, acaroid, nematodes and other groups of agrochemicals form biocides. The intensive use of mineral fertilizers and biocides in agriculture leads to the entry of various poisonous chemicals into the biosphere. Thus, the problem of environmental protection, especially when using biocides, is of utmost importance. In the area of environmental protection and resources, the Kingdom of Saudi Arabia has made enormous strides. The Basic Law of Governance (Article 32) states, "*The State shall work towards the preservation, protection, and improvement of the environment, as well as prevent pollution*" (IBP, 2016). This study focuses on the challenges faced with traditional biocides and offers alternative green solutions.

2. Applications of Biocides

Biocides are chemical agents used to kill all sizes and life stages of organisms, especially microorganisms. There are three main types of biocide: Nonoxidizing biocides, oxidizing biocides, and biodispersants/biopenetrants. Nonoxidizing biocides work via different poisoning methods such as interfering with reproduction, stopping respiration, or lysing the cell wall. Oxidizing biocides kill bacteria through the electrochemical process of oxidation. In this way, the biocide gains an electron from the bacteria, and this electron loss essentially kills the bacteria. Oxidizing biocides are typically made up of chlorine or bromine, and these halogens are the oxidizing agents disrupting the biological cell. Biodispersants/biopenetrants are chemicals that can penetrate and loosen the complex matrix of biofilms, thereby allowing biocides to reach the organisms for more effective annihilation. The table below shows examples of each type of biocide.

Table I. Types of Biocides (Christophersen, 2006)

Biocide Type	Examples
Oxidizing Biocides	Chlorine Bromine Iodine Chlorine dioxide Ozone Hydrogen peroxide
Nonoxidizing Biocides	Isothiazolines 2,2 Dibromo-3-nitrilopropionamide (DBNPA) Carbamates Gluteraldehyde Methylene bisthiocyanate (MBT) Polyquaternary amines Tetrehydro-3,5, dimethyl-2H-1,3,5 thiadiazine-2-thione 2-(tert-butlyamino)-4-chloro-6-(ethylamino)-S-triazine
Biodispersants / Biopenetrants	DTEA II (2-Decylthio ethanamine) DMAD (Fatty acid amide) Dodecylamine acetate Polyquaternary amines

	DOSS (Dioctylsulfosuccinate) Polyoxyalkylenes Enzymes

There are many applications where a biocide is used, as previously mentioned, but by far, the most significant application of biocides is treating the cooling water system.

A cooling water system is one of the most important methods of heat removal from industrial equipment. The cooling water helps to transfer thermal energy from one medium to another. In industrial applications, cooling can be critical to ensure that processes do not cause equipment or products to overheat. Therefore, a cooling water system is considered one of the most important systems in the oil and gas industry, petrochemical industry, and in other applications such as cooling huge buildings and airports

In a typical cooling water system, the cold water is pumped via a pump to different heat exchangers where the thermal energy from the process transfers to the cooling water by heat exchangers. Thereafter, the hot cooling water will become cold again by cooling the source, which is usually plated heat exchangers made cold by seawater. Considering the extent of cooling water losses, process water is used to make up the losses. Also, chemicals are injected into the cooling water to protect the circuit from corrosion.

One of the important chemicals, which is injected into the cooling water system, is a biocide. The presence of bacteria and microorganisms in the cooling water leads to generating biofilm, which results in pitting corrosion and destroys the piping in the cooling water system.

Figure 1 illustrates the stages of biofilm formation adapted from Don Monroe, 2007. The figure illustrates how the bacteria form a biofilm. In the first stage, the bacteria are introduced into the water system through the raw water source, air, makeup water or process contamination. Then, the bacteria become fixed to a surface where they can grow and multiply, creating a biofilm. Finally, in the last stage, the biofilm continues to grow until some of it disperses to colonize new surfaces. The process is then repeated. However, the addition of biocide would prevent such a process from occurring.

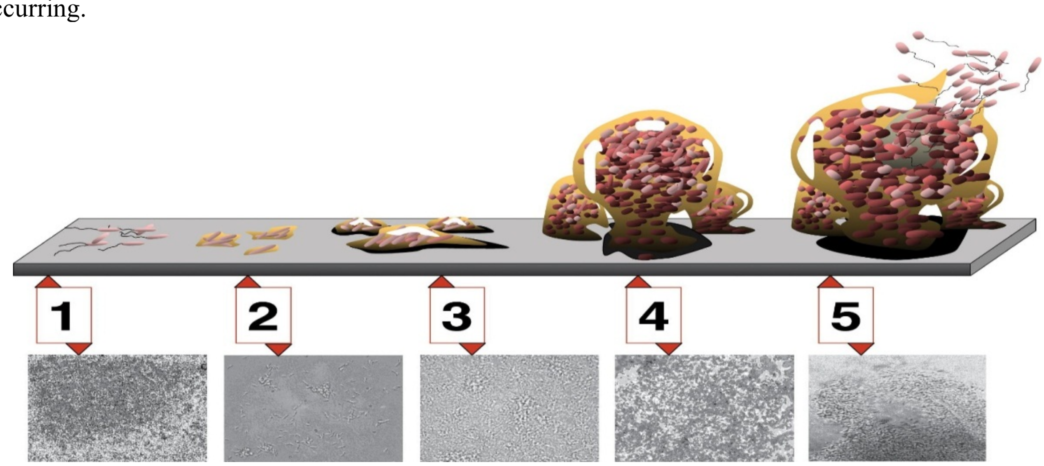

Figure 1. The five stages of biofilm maturation adapted from Don Monroe, 2007

3. The Impact of Biocides on the Environment

The main characteristics of biocides are determined by their behavior in the environment, their effect on harmful organisms, humans, warm-blooded animals, and protected plants. Biocides, falling onto soil during their use, as well as during processing plants with ground and aircraft equipment, destroy soil-borne pests, nematodes, and soil phytopathogens. Moreover, they can be washed off from the surface of plants by rain (Thomas & Brooks, 2010). Whilst in the soil, biocides can adversely affect the life of the organisms that inhabit it, the microbiological processes, as well as the ability of the biosphere to self-clean (Gil & Sinfort, 2005). Depending on the soil conditions and physico-chemical properties, biocides can remain unchanged and maintain their toxicity for a significant time.

The constant use of toxic chemicals can cause the death of not only harmful organisms but is also detrimental to beneficial parasitic and predatory (entomophagous organisms) insects that regulate the number of pest populations. This leads to a violation of the natural connections between organisms in the biocenosis (Møretrø & Langsrud, 2017).

As a result of the destruction of entomophagous organisms, mass reproduction of pests occurs. The initial treatment with biocides was aimed to prevent these species from reproducing. Cases of mass reproduction of spider mites, red fruit mites, beet and cabbage aphids, etc. are known (Thomas & Brooks, 2010). During chemical treatments of cultivated crops, bees, bumblebees, and other plant pollinators die. The use of integrated protection systems can normalize the natural relationships of organisms in biocenosis (Little, 2007). With the intensive cultivation of agricultural land using biocides and violation of instructions of their use, poisoning of birds, especially chicks, has been reported (Møretrø & Langsrud, 2017).
In fields and forests, when using biocides, hares, foxes, and other warm-blooded animals die. The most dangerous substances for them are organochlorine and organophosphorus compounds (Gil & Sinfort, 2005). After being washed out of the soil during rains, biocides infiltrate reservoirs. Massive death of fish can be observed in this case. Also, poisonous chemicals accumulate in fish tissues and aquatic plants. Organophosphorus compounds, synthetic pyrethroids, and most biocides are less toxic to fish compared to dinitrophenol compounds and chlorinated benzenes (Møretrø & Langsrud, 2017). The action of biocides on plants is determined by the anatomical, morphological, biological, and physiological-biochemical characteristics of the individual plant species (Paul, Chakraborty, & Mandal, 2019). The structure of the epidermis, the integrity of the cuticle, the presence of pubescence, and wax coating determine the retention of poisons on the plant, penetration and the degree of their impact.

4. The Impact of Biocides on the Human Organism

Humans come into contact with biocides during fieldwork, and on household plots. Harm can occur to them in the case of direct contact with drugs - through the skin, mucous membranes of the mouth, nose, and respiratory tract. Biocides can also enter the human body in food, which passes through the gastrointestinal tract. Entering the blood, poisonous substances are carried to internal organs. In the body, poisons undergo chemical transformations (oxidation, hydrolytic degradation, and other processes). In some cases, the poison is neutralized; in others, it turns into more toxic compounds. The liver plays an important role in the processes of neutralizing poisons (Gilbert & McBain, 2003). In the human body, poisons largely accumulate in adipose tissue and liver (Paul, Manna & Mandal, 2018). If the amount of poison released from the body (through the kidneys, gastrointestinal tract, skin and lungs) is less than the amount received during the same period, the poison accumulates in the body. Organochlorine and mercury biocides possess material accumulation (Passivirta, et al., 1983). Alternatively, biocides can be accumulated functionally. In this case, products of biocides metabolism are accumulated in the body. Some organophosphorus biocides possess functional accumulation, binding the cholinesterase enzyme in the body (Poole, 2002).
In humans, pesticide poisoning can be acute and chronic. With acute poisoning, a large dose of the poison enters the body immediately, causing a cessation of its functions with specific symptoms. Chronic poisoning occurs with prolonged re-entry of small doses of poison that can accumulate (Garry, Schreinemachers, Harkins, & Griffith, 1996). In addition to the toxic effect of biocides on humans and warm-blooded animals, they have skin-resorptive, blastogenic, and other negative effects (Gil & Sinfort, 2005).
For solving the problem of the impact of biocides on health and environment, priority must be given to the safety of agricultural products, as it is primarily by this route that biocides enter the human body. By employing “green” agriculture, such as cultivating crops hydroponically, or cleaning soil, this will ensure the ecological safety of agricultural products.

5. Green Biocides

Biocides can be classified into four categories, which are preservative, pest control, disinfectant, and other biocidal products (Ashraf et al., 2014). A substance such as a bactericide that causes minimal harm to the environment or destroys the growth of microorganisms is considered a green biocide. The significant requirements of any industrial biocide are to be effective against microorganisms, economical, and compatible with the environment where it is applied. Currently, there is a great need for green biocides that are less toxic, environmentally friendly, safe, and easy to handle and store. For any biocide to be declared a green biocide that is safe for living beings and the environment, it has at first to adhere to the 12 principles of green chemistry.
Further, a green biocide should be prepared from the least toxic renewable raw materials in a manner that avoids waste formation so that it would be cost-effective to produce. It ought to be prepared without solvents, consume minimal energy, and produce no by-products. The production process of green biocides should be safe and hazard-free. The process needs to be accelerated by particular catalysts that are regenerated at the end of the reaction for reuse.

Moreover, the process needs to be monitored using analytical techniques and tools to inhibit contaminants from spreading into the environment.

Ongoing research aims to eliminate the use of traditional biocides or replace them with green, environmentally friendly biocides. Jie et al. (Jie Wen, Zhao, Gu, & Raad, 2009) introduced a green biocide enhancer, ethylenediaminedisuccinate (EDDS), for the treatment of sulfate-reducing bacteria (SRB) biofilms on carbon steel surfaces using glutaraldehyde. Experiments were conducted on 100ml anaerobic vials with carbon steel coupons. They found that EDDS reduced the glutaraldehyde amounts significantly in the inhibition of SRB biofilm establishment and the treatment of established biofilms on carbon steel coupon surfaces. Jie et. al. also (J Wen, Xu, Gu, & Raad, 2012) used a mixture of three green biocides, namely tetrakis-hydroxymethyl phosphonium sulfate (THPS), glutaraldehyde, and ethylenediaminedisuccinate (EDDS) for the treatment of the planktonic sulfate-reducing bacteria (SRB) and to eliminate established SRB biofilms. It was inferred from their experiment that biofilm removal was achieved when 50ppm glutaraldehyde combined with 15% methanol and 1,000ppm EDDS. Omran et. al. (Omran, Fatthalah, El-Gendy, El-Shatoury, & Abouzeid, 2013) developed three green biocides from readily available natural non-edible domestic waste for the treatment of the aforementioned SRB. These three green biocides consisted of the hot water extracts of orange, mandarin peels, and water extract of lupine seeds. Such natural extracts express good biocidal activity against SRB. Silva et. al. (Silva, Rosado, Teixeira, Candeias, & Caldeira, 2015) proposed the formation of green biocides based upon combined methodologies that utilize antifungal tests, chromatographic techniques, FTIR-ATR (Fourier Transform Infrared – Attenuated Total Reflection) spectroscopy, microscopic approaches, and simulation assays that permit the detection of antifungal potential and rapid identification of ground-breaking bioactive compounds. Thus the proposed green biocides indicate great potential for future applications in cultural and built heritage rehabilitation and in being green substitutes to the biocides currently used.

6. Limitations of Using Green Biocides

There is a need for novel green biocides derived from natural products that are easily biodegradable. The desire for safe biocides that are green to the environment is both a primary and policy concern in the USA, Canada, and Europe. The strict US EPA regulations may result in the removal of a large number of biocidal products that are incompatible with the environment. Green biocides may be somewhat less effective than conventional biocides, and regrowth may occur. Moreover, there is concern that bacterial, fungal, and algal species may develop resistance against a commonly used green biocide.

7. Conclusion

Biocides are highly significant in many technical, economic, agricultural, and industrial applications in which they are dosed to avoid any complications associated with microbial, fungal, and algal growth. However, biocides are toxic chemicals that can harm human beings and the environment. Therefore, there is a great need to develop novel types of biocides that are green and environment-friendly. This paper discussed types of traditional biocides, their effects on humans and the natural world, their limitations and how they ought to be replaced by green biocides that are environmentally safe.

Acknowledgments
The authors gratefully acknowledge the support provided by the College of Engineering at Effat University, Jeddah, Saudi Arabia.

Biographies

Dr. Tayeb Brahimi, Assistant Professor at the Department of Electrical and Computer Engineering, at Effat University, Jeddah, KSA. Received his Ph.D. (1992) and Master Degree (1987) from the University of Montreal, Canada. Worked as Research Scientist under Bombardier Chair/Canadair from 1992-1998. In 1998, he joined Jeppesen DataPlan in California, then Peregrine System as Quality Assurance Engineer, and Consultant for Electronic data interchange in Dallas. Dr. Tayeb published more than 100 articles in scientific journals, international conferences, on novel technologies in renewable energy, sustainability, and machine learning. Among other activities, he is a reviewer for many international journals, invited speaker by the Japan Society of Mechanical Engineering, Japan Turbomachinery Association (Ishikawajima-Harima Heavy Industries, Tokyo), The Gulf Educational Conference (http://www.gulfeducation.co.uk/#speakers), the International Conference on Engineering Education & Research (FICEER2015), the Industrial Engineering and Operations Management (IEOM-GCC), and participated in Public Debate on Energy organized by the Government of Quebec, Canada. Current research interest relates to renewable energy (solar, wind, wave, and waste to energy), sustainability, machine learning, and use of technology to support learning. Other areas of interest include the social aspect of renewable energy, testing, and quality assurance for component-based software, and knowledge management.

Dr. Imtiaz Ahmad is an Assistant Professor in the College of Engineering at Effat University in Jeddah, Saudi Arabia. She earned a Master's Degree in Chemical Research (1991) and Ph. D. in Physical Chemistry (1995) from the University of London. Dr. Ahmad has extensive research and academic experience and has been awarded a number of prestigious fellowships that enabled her to undertake cutting-edge research in non-thermal plasma technology, high resolution spectroscopy and astrochemistry in leading academic and research institutions in the UK and Japan, including the Universities of Cambridge, Oxford and Manchester, and Japan's Institute for Molecular Science and the University of Tokyo. She is a Fellow of the Royal Society of Chemistry, a Chartered Chemist, a Chartered Physicist, a Chartered Scientist, a Member of the European Chemist Board and senior Member of the Institute of Physics. Her secondary research interests include disaster relief and faculty training and development.

Talal Mouis is currently pursuing a Master's degree in Energy Engineering at Effat University in Jeddah, KSA. He received his Bachelor's degree from Kansas State University in 2012 in Chemical Engineering. Thereafter, he worked in the petrochemical industry for six years as a production and process engineer. Talal's current research interests relate to renewable energy, sustainability, process engineering, petro-chemistry and product development.

Budoor Salem Alwated is currently studying for a Master's degree in Energy Engineering at Effat University, Jeddah, KSA. She received her Bachelor's degree from Dar Alhekma University in Management Information Systems. She also completed a certificate in Image and Video Processing from Duke University via Coursera, in 2017. She was awarded the best paper entitled "*Solar Irradiation Prediction Using Machine Learning Techniques: The Case of Saudi Arabia*" which was presented in the International Conference on Industrial Engineering and Operations Management, GCC, December 26-28, 2019, in Riyadh, KSA. Budoor is interested in Information Security, Machine Learning, and Renewable Energy.

References

Ansatas, P.T., Zimmerman, J.B. (2003). Design Through the 12 Principles of Green Engineering. Environmental Science & Technology, American Chemical Society, 2003.

Ashraf, Muhammad Aqeel, Ullah, Saleem, Ahmad, Irshad, Qureshi, Ahmad Kaleem, Balkhair, Khaled S, & Abdur Rehman, Muhammad. (2014). Green biocides, a promising technology: current and future applications to industry and industrial processes. Journal of the Science of Food and Agriculture, 94(3), 388-403.

Christophersen, D. (2006). Microbiological control strategy in cooling tower systems. Veolia water solution & technologies, 19, 1-4.

Garry, V. F., Schreinemachers, D., Harkins, M. E., & Griffith, J. (1996). Pesticide appliers, biocides, and birth defects in rural Minnesota. *Environmental Health Perspectives*.

Gil, Y., & Sinfort, C. (2005). Emission of pesticides to the air during sprayer application: A bibliographic review. *Atmospheric Environment*, 5183-5193.

Gilbert, P., & McBain, A. J. (2003). Potential Impact of Increased Use of Biocides in Consumer Products on Prevalence of Antibiotic Resistance. *Clinical Microbiology Reviews*, 189-208.

IBP (2016). *Saudi Arabia Ecology & Nature Protection Laws and Regulation. Handbook Volume 1 Strategic Information*. International Business Publication, Washington, USA.Little, B. (2007). A review of 'green' strategies to prevent or mitigate microbiologically influenced corrosion. *Biofouling*, 87-97.

Møretrø, T., & Langsrud, S. (2017). Residential Bacteria on Surfaces in the Food Industry and Their Implications for Food Safety and Quality. *Comprehensive Reviews in Food Science and Food Safety*, 1022-1041.

Monroe D (2007) Looking for Chinks in the Armor of Bacterial Biofilms. PLoS Biol 5(11): e307. https://doi.org/10.1371/journal.pbio.0050307

Omran, Basma A, Fatthalah, Nesreen A, El-Gendy, Nour Sh, El-Shatoury, Einas H, & Abouzeid, Mohamed A. (2013). Green biocides against sulphate reducing bacteria and macrofouling organisms. *J. Pure Appl. Microbiol, 7*(3), 2219-2232.

Passivirta, J., Särkkä, J., Surma-Aho, K., Humppi, T., Kuokkanen, T., & Marttinen, M. (1983). Food chain enrichment of organochlorine compounds and mercury in clean and polluted lakes of Finland. *Chemosphere*, 239-252.

Paul, D., Chakraborty, R., & Mandal, S. M. (2019). Biocides and health-care agents are more than just antibiotics: Inducing cross to co-resistance in microbes. *Ecotoxicology and Environmental Safety*, 601-610.

Paul, D., Manna, S., & Mandal, S. M. (2018). Antibiotics associated disorders and post-biotics induced rescue in gut health. *Current Pharmaceutical Design*, 821-829.

Poole, K. (2002). Mechanisms of bacterial biocide and antibiotic resistance. *Journal of Applied Microbiology Symposium Supplement*, 55S-64S.

Rossmoore, H. W. (1995). Introduction to biocide use. *Handbook of Biocide and Preservative Use*, 1–18. doi: 10.1007/978-94-011-1354-0_1

Silva, Mara, Rosado, Tania, Teixeira, Dora, Candeias, Antonio, & Caldeira, Ana Teresa. (2015). Production of Green Biocides for Cultural Heritage. Novel Biotechnological Solutions. *International Journal of Conservation Science,* 6 (SI): 519-530.

Thomas, K. V., & Brooks, S. (2010). The environmental fate and effects of antifouling paint biocides. *Biofouling*, 73-88.

Wen, J, Xu, D, Gu, T, & Raad, I. (2012). A green triple biocide cocktail consisting of a biocide, EDDS and methanol for the mitigation of planktonic and sessile sulfate-reducing bacteria. *World Journal of Microbiology and Biotechnology, 28*(2), 431-435.

Wen, Jie, Zhao, Kaili, Gu, Tingyue, & Raad, Issam I. (2009). A green biocide enhancer for the treatment of sulfate-reducing bacteria (SRB) biofilms on carbon steel surfaces using glutaraldehyde. *International Biodeterioration & Biodegradation, 63*(8), 1102-1106.