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ACADEMIA SCIENTIARUM ET ARTIUM KOSOVIENSIS
SEKSIONI I SHKENCAVE TË NATYRËS

# RESEARCH
# 27
# KËRKIME

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KOSOVA ACADEMY OF SCIENCES AND ARTS
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SECTION OF NATURAL SCIENCES

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Amor Abdelkader[*1]

# GRAPHENE AGAINST CORROSION IN CONCRETE. A SHORT REVIEW

Abstract

Graphene represents one of the most interesting nanomaterials due to its unique properties like: mechanical resistance, electrical and thermal conductivity, chemical inertness. It shows barrier properties and impermeability for reactive gases, liquids, acids, and salts. Concrete corrosion is a quite spread phenomenon due to direct contact with seawater, or other aggressive reagents corrosive ions, such as chloride ions, that can easily penetrate the porous cement matrix and diffuse to corrode the steel component. In this short review are shown examples where graphene can be considered as a possible solution especially in the cases when it is a part of a multilayer coating while other materials can act as a barrier form.

*Keywords*: Graphene, concrete, corrosion, inhibitor, anticorrosion coatings

## Introduction

Concrete structures are usually subjected to strain in corrosive environments. It is very common to find concrete structures used for applications that have direct contact with seawater, are exposed to road salts, or react with polluted air. Corrosive ions, such as chloride ions, can easily penetrate the porous cement matrix and diffuse to corrode the reinforcement steel causing a serious reduction of the effective loading cross section and also weaken the bond between the reinforcement and the matrix. [1-3] Polluted air with a high level of carbon gases can react with the reinforcement steel bars in a way that increases their brittleness. [1]  Therefore, expensive repair work is essential to keep the concrete structures functional, and in some cases, this repair could take

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place after a period as short as ten years of the structure becoming operational. The repair work usually uses less durable materials, and it only increases the life of the structure by a few years. Although this repair work can be also delayed by using paint and other kinds of protective coating on the outer surface of the concrete, they are mainly sensitive to frost and more susceptible to crack upon loading. [4]

There is a grown interest in applying the protective coating directly on the reinforcement steel to work as a diffusion barrier and minimise the contact between the steel and the corrosive environment. Several materials have been used as the protective coating, ranging from traditional industrial barriers such as polymer and ceramics to emerging new nanomaterials such as carbon nanotube and nano-particles. [5-7] A perfect protective coating should be thin, provide a diffusion barrier to chemical attack, and preferably transparent.

## Graphene as protective layer

Graphene, the thinnest possible materials with only one atom in its plan, combines both optical transparency and mechanical flexibility that makes it ideal coating material. [8] Graphene also demonstrates an exceptional barrier to reactive gases, liquids, acids, and salts. [9] The outstanding impermeability of graphene is attributed to its very dense crystal structure. Considering the measured C–C bond length is 0.14 nm between the nuclei of carbon atoms in the honeycomb structure, [10] the hexagonal pore diameter of the graphene was estimated to be 0.246 nm (Figure 1a). [11] This pore diameter reduces further to 0.064 nm if the van der Waals radii (0.11 nm) of the carbon atoms are considered. [12] It is, therefore, safe to assume that defect-free graphene is impermeable even for atoms as small as helium. Moreover, the electron cloud of the π-conjugated carbon network is dense and further blocks the gap within its aromatic ring. The electron cloud poses a repelling field to reactive ions, atoms or molecules, which works as an energy barrier that physically isolate the metal substrate from the corrosive environment (Figure 1b). [13]

Despite the clear theoretical benefits of using graphene coating, there are still debates on its practical ability to protect metals from corrosion. Schriver et al., have shown that the graphene grown by CVD techniques forms an efficient protective layer only over short timescale. [14] When considering the corrosion over a long time scale, water, oxygen and some of the ions are able to infiltrate through the defects in the graphene layer to react with the metal substrate. [14] The graphene layer, in this case, promotes the localised types corrosion in a way similar to the crevice corrosion. [15,16] Moreover, the electron transfer is facilitated through the conductive graphene layer, which leads to enhancing the rate of the electrochemical corrosion reaction, unlike the traditional oxide coating where the electron transfer is suppressed by the poor conductivity of the protective layer. [14,15] Also, The chemical nobility of the graphene is a double-edged sword, while it promotes minimum changes of the protective layer, it also means that the coating layer is cathodic to most metals and alloys which facilitated the galvanic coupling on any exposed graphene-metal interface. [17] This kind of graphene-metal coupling promote localized corrosion than uniform corrosion, but it can cause catastrophic failure of the reinforcement steel in the concrete structures, even with minimal mass loss. [18] Similar results were reported for other kinds of carbon nanomaterials when they were applied as anti-corrosion coating. [19] Therefore, defect-free graphene coating in principle can protect from uniform corrosion in a similar mechanism as other cathodic coatings, tin-plating for example, but it enhances the localized corrosion if defects of any kind are present.

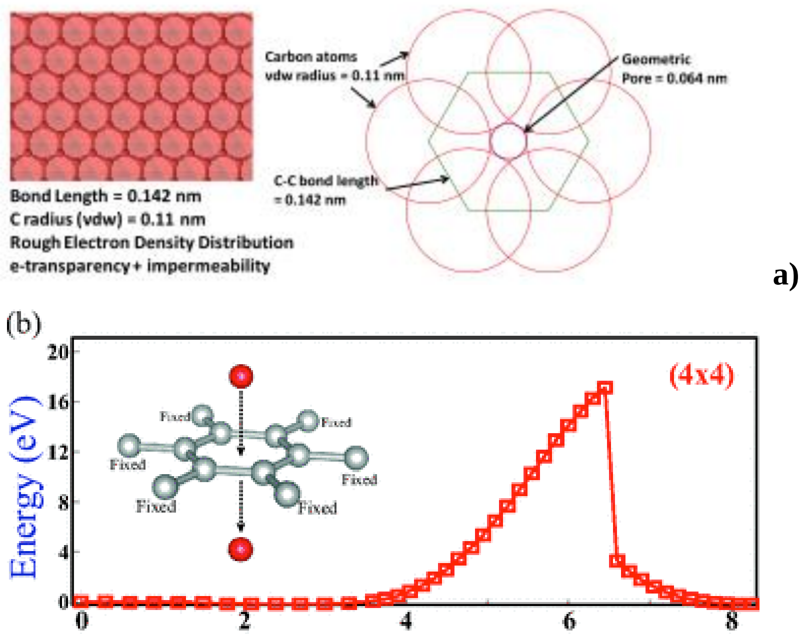


*Figure 1: (a) Close-packed atomic structure of graphene with rough electronic density distribution, [12] (b) Energy barriers for $O_2$ forced to pass from the top to the bottom side of graphene. [13]*

The challenge is therefore to develop a continuous layer of defect-free graphene on the metal substrate. Graphene coatings are usually applied on metals using two major approaches, (i) carbonaceous gas cracking on the surface of the metals using techniques such as CVD, [20] or (ii) depositing graphene flakes from solutions using techniques such as drop casting, dip coating, spin coating or electrophoretic deposation. [21, 22] The first approach is a bottom-up technique that uses high temperature and severe growing conditions, which makes preventing the defects a nontrivial process. Growing multilayer graphene is probably the only solution to minimize the defects, thus providing better protection over a relatively longer time. [23, 24] However, CVD growth of graphene on steel is a challenge, and the graphene sheets usually need to be mechanically transferred from other metal substrates, which raises questions on the coating adhesions. [25] The wet chemical approach, on the other hand, offers more flexibility on the fabrications. It can also be tuned to produce graphene composite and functionalized graphene with different groups that can alert the properties or work as a linker between the coating and the metal substrate. Graphene composites with polymers have shown great resistance to corrosion due to the barrier properties of both components. A key practice to obtain protective graphene-polymer coating is to develop well-dispersed flakes in the polymer matrix, which can be achieved via using a surfactant or chemical modification of the graphene sheets. Examples include using 4-aminobenzoyl group-functionalized graphene to improve the dispersability of graphene in polyaniline, [26] using carboxylated aniline trimer derivative to disperse graphene in waterborne epoxy system, [27] graphene and graphene oxide dispersed in polyurethane using 3-amino- propyltriethoxysilane (APTES) as stabilizer, [28] utilization of poly(2-butylaniline) (P2BA) as a dispersing agent to obtain well-dispersed graphene in epoxy matrix. [29] Another strategy to improve the anticorrosion performance of graphene layers is by breaking the galvanic coupling between graphene and metal using insulating groups introduced on the graphene flakes. In these cases, polymer matrix was not needed to provide an extra barrier and the functional groups, such as APTES, were not used to improve the dispersibility. The chemically bonded groups, usually covalently bonded, played different roles; linking the graphene to the metal substrate, and forming insulating layer to inhibit the galvanic reactions. [30-32]

However, the application of graphene as corrosion protection layer on reinforcements steel in the concrete structure is far more complicated. Under load-bearing conditions, the graphene coating, or even the graphene-polymer composites, may delaminate from the metal substrate due to inhomogeneous stress loading between the coating and the substrate. [33] Moreover, the coating is susceptible to scratching, particularly when considering the abrasion nature of the cement particles that wrap the reinforcement steel. One possible solution is to use graphene as a part of a multilayer coating where other materials can act as a barrier form the abrasion and protect the graphene coating from rubbing. [34] Another possible strategy is to develop coating where graphene can serve as the anodic part of the galvanic cell. Anodic graphene can satisfy good barrier properties, but more importantly, it will corrode before the metal substrate upon exposing the graphene/metal interface to the corrosive environment. Another promising strategy is to develop self-healing coating where the protective coating can recover its barrier properties by healing any crack or scratch. [35]

## Conclusion

Structural integrity and durability of steel that is used for the reinforcement of concrete infrastructure is of great importance because of world-wide use in civil and industrial structures. They don't remain intact over the time as they degrade and become more fragile due to the corrosion of steel rebars especially in the contact with chloride ions in seawater or in the environment and other corrosive agents. Graphene has many distinct properties among nanomaterials and one of them is very high impermeable. It can be used as corrosion inhibitor as a part of a multilayer coating where other materials can act as a barrier form and protect the concrete corrosion.

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Amor Abdelkader

# GRAFENI KUNDËR KORROZIONIT NË BETON. NJË PUNIM REVIAL I SHKURTËR


## Përmbledhje

Strukturat e betonit përdoren në shkallë të gjërë në ndërtimtari, në hapësira të ndryshme dhe janë në kontakt me agjentë oksidues në mjedise të ndryshme korrozive qoftë drejtpërdrejtë me agjentë korroziv në ujë të detit, në kripërat që hidhen për shkrirje të akullit në rrugë ose reagojnë me agjentë korroziv në ajrin e ndotur.

Agjentët korroziv si jonet klorure mund të depërtojnë lehtësisht në matricën poroze të cementit dhe difundojnë deri te struktura e çelikut që përdoret për përforcim të betonit duke e shkaktuar korrozionin dhe njëherit e dobëson lidhjen në mes cementit dhe çelikut.

Ajri i ndotur me përqendrim të lartë të gazeve të karbonit mund të reagojë me shtyllat përforcuese duke e rritur brishtësinë e tyre.

Prandaj për funksionimin afatgjatë të këtyre strukturave të betonit nevojitet një mirëmbajtje e vazhdueshme që është veprimtari e shtrenjtë dhe nganjëhërë duhet bërë në periudha të shkrutëra kohore, më pak se 10 vite pas ndërtimit. Gjatë mirëmbajtjes përdoren materiale më pak të qëndrueshme dhe kjo e zgjat përdorimin e strukturave për disa vite. Përdorimi i ngjyrave ose shtresave të tjera mbrojtëse në shtresën e fundit të betonit mund të zgjasë qëndrueshmërinë e tij, por këto shtresa janë të ndjeshme në ngrirje dhe mund të dëmtohen gjatë kalimit të peshave të rënda.

Prandaj ekziston një rritje e interesimit të përdorimit të shtresave mbrojtëse drejtpërdrejt në çelikun që përdoret për përforcim të betonit. Këto shtresa do të shërbejnë si bafrriera të difuzionit të ajgentëve oksidues dhe do ta minimizojnë kontaktin e drejtpërdrejtë të çelikut me mjedis korroziv. Deri më tani janë përdorur disa lloje të materialeve si shtresa mbrojtëse duke u nisur prej polimerëve dhe keramikës deri te nanomaterialet si nanotubat e karbonit dhe nano grimcat. Një shtresë perfekte mbrojtëse duhet të jetë e hollë, të pengojë difuzionin e agjentëve oksidues dhe mundësisht transparente. Grafeni është materiali më i hollë i mundshëm, me trashësi një atomike, është transparent dhe shumë i qëndrueshëm mekanikisht. Po ashtu është i padepërtueshëm për gazrat e dëmshme, lëngjet, acidet dhe kripërat. Prandaj kohëve të fundit grafeni ka gjetur përdorim si shtresë mbrojtëse e çelikut që dëshmohet me shembuj të shumtë në këtë punim të shkurtër revial.

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Mihone Kerolli Mustafa[*,1,2]

# ASSESSING THE WATER MEGA TRENDS AND IMPLICATIONS IN KOSOVA

## Abstract

Megatrends can be defined as broad, long-term global patterns affecting management practices and processes, ranging from demographic shifts and urbanization to technological advancements, climate change, and geopolitical changes. This paper aims to address the science-policy interface and bring together evidence that develops systemic co-created knowledge while supporting policymaking and decision-making at the Kosovo level to solve environmental issues. A literature review and focus group-based methodology were used first to identify key global megatrends and then reflect on the streamlined process needed to help Kosovo consider the implications of global megatrends (GMTs) and prepare outlook information related to water management. For the case of Kosovo, two global megatrends have been chosen for assessment: GMT 7 (Intensified global competition for resources) and GMT 9 (Increasingly severe consequences of climate change). Our analysis suggests important implications that address the water-related problems in a coordinated manner and the need for societal responses that may be appropriate for the future. Both selected GMTs are participatory in focus and use a systematic approach that needs evidence to prioritize potential impacts on natural resources and climate change in Kosovo. Further, the implications and relevance of the GMT showed the need to strengthen policy measures following national priorities and circumstances.

*Keywords:* global megatrends, environmental foresight, science-policy interface, water management.

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## Introduction

The European Environment Agency (EEA) has been working for years to enhance the science-policy interface and bring together evidence that supports policymaking and decision-making at the European level to solve environmental and water-tackling issues. At this time, it's essential to have an adaptable, sustainable application solution that global megatrends brink to support the change and future of our society. To understand how the identified eleven GMTs will impact the environment in each European country and Europe as a region, the EEA took this initiative to search for the systemic knowledge required and identify the barriers that exist to the creation and use of such knowledge. In this regard, the EEA published a method toolkit, *Mapping Europe's Environmental Future: Understanding the impacts of global megatrends at the national level* [1].

Overall, the term "Mega Trends" encapsulates broad, long-term global patterns affecting or are expected to affect all sectors of society, ranging from demographic shifts and urbanization to technological advancements, climate change, and geopolitical changes. Understanding Mega Trends is pivotal in grasping the future landscape of various sectors, including water management. Water, a critical resource that underpins public health, economic development, and environmental sustainability, is being redefined by these large-scale trends. This paper summarizes key contributions to the discourse on Mega Trends and their implications for assessing the water landscape. Water resource management is a key challenge facing countries globally, especially in changing climate conditions and increasing demands due to population growth and industrialization. Like many other countries, Kosovo has adopted a legal framework for environmental conservation but is facing numerous challenges in effectively implementing water management policies. Kosovo has made efforts to adopt laws that align with European Union (EU) standards, but the lack of enforcement and compliance remains a primary issue. This phenomenon is not unique to Kosovo; the disconnect between policy adoption and implementation is a global problem.

## Global Mega Trends (GMTs)

Understanding Global Mega Trends (GMTs) is crucial for many reasons across different sectors and levels of decision-making of businesses and organizations, as well as comprehension of trends that would allow for informed long-term strategic planning. Policies that reflect the trajectory of these long-term shifts are more likely to be effective and sustainable, addressing the core challenges and opportunities that will come with future transformations. Global Mega Trends (GMTs) (Figure 1) influence worldwide environmental governance. Two Mega Trends are particularly relevant to Kosovo: GMT 7 (Intensified global competition for resources) and GMT 9 (Increasingly severe consequences of climate change) [2].

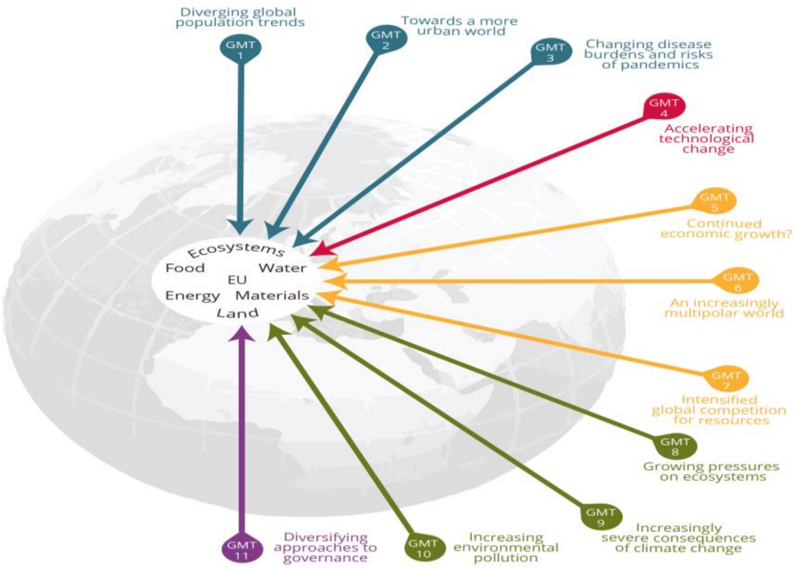



*Figure 1. Global Megatrends (*Source: EEA, 2015a) [2].

## GMT 7: Intensified global competition for resources

The global demand for water resources is increasing exponentially, which exacerbates competition [3]. Kosovar policymakers need to factor in how international demand for water affects domestic supplies [4]. While the literature establishes the global nature of this trend, there is a limited focus on Kosovo's specific circumstances.

The competition is not merely among countries; it also occurs between sectors within a nation (agriculture, industry, etc.) and even among different social and economic groups. For instance, the trend has spawned market mechanisms such as "virtual water trade," where nations with water scarcity import water-intensive goods instead of producing them domestically [5]. While such mechanisms are innovative, they can also lead to vulnerabilities, especially for developing economies dependent on external resources. For Kosovo, this Mega Trend is significant for a variety of reasons. First, Kosovo is a relatively new and small state with a developing infrastructure, making it vulnerable to external market pressures. Its water resources, shared with neighboring countries, become a potential flashpoint for conflict [6]. Kosovo's political scenario, including its relationship with neighboring countries, exacerbates the competition. Regional geopolitics significantly influences water-sharing agreements and management strategies. In such a context, the intensified global competition adds another layer of complexity, potentially inviting external actors who might seek to exploit Kosovo's resources [7]. As global competition intensifies, Kosovo may find its capacity to manage its water resources strained unless preemptive steps are taken. Adaptability failure could result in economic losses, social strife, and potential geopolitical conflicts [8]. While studies are exploring the implications of global resource competition, they often adopt a macro perspective and do not sufficiently delve into how smaller states like Kosovo are uniquely affected [9]. Therefore, there is a need for empirical, Kosovo-specific studies that can offer insights into how this global mega trend is impacting the country's water resources and what strategies can be developed to mitigate adverse effects.

## GMT 9: Increasingly Severe Consequences of Climate Change

The literature shows climate change impacts water resources through increased evaporation rates, altered precipitation patterns, and more frequent extreme weather events. These trends raise questions about Kosovo's adaptive capacities [10] and how these could be bolstered through policy interventions. In the realm of water management, the impact is incredibly profound. Climate variables like temperature and precipitation significantly influence the water cycle. Climate change can exacerbate water scarcity through altered hydrological cycles that result in less predictable and more intense rainfall events [11]. Due to its geographical location, limited water resources, burgeoning industrial and consumer demands, Kosovo faces particular challenges. Changes in precipitation patterns and rising evaporation rates due to higher temperatures, could lead to reduced water availability [12]. In addition, the higher incidence of extreme weather events like floods and droughts further strains Kosovo's already limited adaptive capacities [13].

The ramifications of this Mega Trend will likely have a more pronounced impact on vulnerable populations, including rural communities, the elderly and the economically disadvantaged [14].

Current climate models offer broad-scale projections, but there is an urgent need for localized studies that can provide nuanced insights pertinent to Kosovo [15]. Research should also investigate the social dimensions of climate change to identify the populations most vulnerable to water scarcity and the types of interventions that would be most effective [16]. Understanding this Mega Trend and its localized impacts is crucial for informed policymaking. Kosovo's policymakers need to consider both adaptation and mitigation strategies, which could range from constructing more resilient water infrastructure to initiating community awareness programs focused on water conservation [17].

## Science-Policy Interface (SPI)

The European Environment Agency (EEA) and European Topic Centre (ETC) method toolkit serve as vital resources for defining capacity and expertise in foresight for Kosovo [2]. These toolkits' participatory methods could bridge the gap between scientific research and policy decisions [18]. Given Kosovo's challenges in water management, from weak implementation of laws to susceptibility to global Mega Trends, a strong SPI is essential. Effective SPI practices can help bridge gaps between the complex science of water resources and the practical needs of governance. One major challenge is the 'credibility gap', where policymakers may not fully trust scientific input due to perceived bias, complexity, or irrelevance to immediate concerns [19].

Other challenges may include institutional inertia, lack of resources and capacity constraints that limit the effective utilization of scientific knowledge [20].

## Adaptive and Sustainable Solutions

Evidence-based adaptive management strategies can be translated to the needs of the Kosovo case. The literature suggests a multi-tiered governance approach water resources effectively [21]. Adaptive management involves a structured, iterative process of decision-making in the face of uncertainty, aiming to reduce uncertainty over time via system monitoring [22]. It is particularly crucial for water resource management, given the complex and dynamic nature of hydrological systems [23]. Kosovo could benefit from implementing 'learning-by-doing' strategies [24]. These include monitoring key indicators in real-time, conducting periodic evaluations, and allowing for adjustments in policy and practices based on evidence and performance data. For Kosovo, this involves developing water management practices that are economically viable, socially just, and ecologically sound. Infrastructure investment must consider long-term operating costs, ecological impact, and social acceptability. This could include transitioning from high water usage industries to more sustainable options and investing in water-saving technologies and wastewater treatment plants. Kosovo could invest in technologies for real-time monitoring of water quality and usage, thereby enabling rapid response to emerging issues such as pollution or over-extraction, but also in advanced technologies such as remote sensing, Geographic Information Systems (GIS), and the Internet of Things (IoT).

In general, the paper presents the foresight implication of GMT's and their potential implications on the Kosovo Water thematic aspects, current status, or sustainability of water management.

## Methodology

The methodology used for assessing the implication of the GMTs was in line with the EEA GMTs selection toolkit and "checklist document" developed by the EEA SOER guidelines considering environmental studies and generated from different sectoral and spatial perspectives in Kosovo.

The following steps have been used to analyze the selection of GMTs in the Kosovo case:

1. Exploration of the implications of global megatrends on the environment and environmental policies at the national level;
2. Assessment of sustainability transitions and niche innovations using examples from other countries;
3. Development of methods that enabled countries to reflect on the impacts of the EEA GMTs and their meaning at a national level;

4. Overview of risks and opportunities now and in the future;
5. Considering the implications of GMTs by reviewing studies focused on topics of interest and in line with the level of expertise and capacity within a country.

Considering the data and information from the national level, two global megatrends have been selected to assess their implications in Kosovo: GMT 7: Intensified global competition for resources and GMT 9: Increasingly severe consequences of climate change. Both selected GMTs are analyzed regarding their implications on the national level, their potential effect on the national ecosystems, water quality or resources, human health, and sustainable development. The research is focused on the information gathered from the focus group meetings and data reflected on the assessment of the National Action Programme and other strategies in place related to water use, ecosystem vulnerability, and climate change effects in Kosovo; discussed the prioritizing implications (water & sectors and ecosystem vulnerability) and GMTs 7 and 9; determined initial scoping of implications (likelihood, magnitude and time scales of effects) as well as analyzed opportunities and risks; and provided recommendations for follow-up at the national level. Both proposed methods are participatory in focus and use a systematic approach that needs evidence to prioritize potential impacts on natural resources and climate change in Kosovo based on the knowledge and judgment of the experts and other involved stakeholders.

To develop an improved focus on these implications, five workshops were organized in Kosovo to discuss the selected megatrends, as described by the EEA, and to assess the impact on the Kosovo environment, with a particular focus on water relations to sectors (agriculture, energy, drinking water supply, etc.) and ecosystem vulnerability (wastewater treatment plants, minimum flows, and water levels, etc.). The workshops gathered the main stakeholders to share their knowledge and provide input for the national State of the Environment for Kosovo. In this context of reaching the research objective and investigating the environmental impact of GMTs, the focus group discussions addressed the analyses of effect as well as the potential timescale in which GMTs implications could occur in the Kosovo case. The main discussions were focused on understanding the impacts of global megatrends based on basic resource needs such as food, water, energy, materials, and ecosystems and their services.

# Scoping of GMT implications in the Kosovo case

The national analysis resulted in the selection of GMTs for our national exercise to analyze the potential implications on water. The selected GMT 7 and GMT 9 have been analyzed following the EEA's methodologies.

**Table 1. Summary of GMT implications identified by main stakeholders in Kosovo**

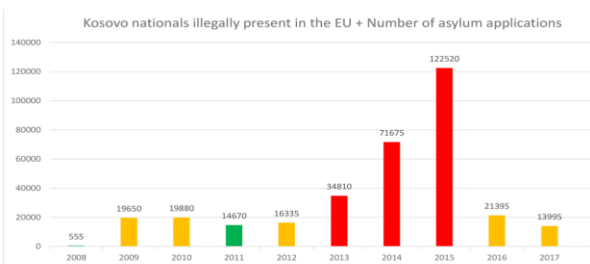
| GMT | Identified GMT implications | National issues considered most likely affected by implications |
|---|---|---|
| GMT 7 Intensified global competition for resources | Effect of the water supply | Structural economic changes and economic risk<br>Overuse of water resources<br>Need for increased renewables and efficiency<br>Not all strategies are developed to implement all the processes<br>Water pollution and flooding<br><br>*The new water reservoirs planned with Kosova's strategic plans in the transboundary rivers shared with North Macedonia, Serbia etc. (e.g. the reservoir planned in Lepenc river which is a tributary of Vardar river).* |
| | Limits on the amount of resources available | |
| | Increased environmental burdens | |
| | Risk for prices & availability of resources | |
| | Insecurity and conflict linked to resource competition | |
| | Need for renewables Biomass and Biogass | |
| | Risk of supply for critical resources | |
| GMT 9 Increasingly severe consequences of climate change | Increased frequency of droughts and fires | River and urban flooding<br>Droughts and erosion<br>Infrastructure damage<br>Risk to food systems<br>Economic risk |
| | Precipitation changes | |
| | Loss of ecosystems/-biodiversity | |
| | Increase in environmental problems – water resources decrease | |
| | Risk to food security | |
| | Allien species | |

**Table 2. Scoping of identified implications**

| **GMT title** | **Prioritized Implications** | **Estimated likelihood (high/low)** | **Magnitude of effect (high/low)** | **Timescale over which implication may occur** |
|---|---|---|---|---|
| | Effect of the water su-pply | High | High | Medium-term |
| GMT7 | Limits on the amount of resources available | High | High | Medium-term |
| | Increased environmental burdens | High | High | Medium-long term |
| | Risk for prices & avail-ability of resources | High | High | Medium-long term |
| | Insecurity and conflict linked to resource competition | Low | Medium | Short-medium term |
| | Need for renewable energy - biomass and biogas | Low to medium | Low to medium | Short-medium-long term |
| | Risk of supply for criti-cal resources | Medium | High | Medium-long term |
| | | | | |
| GMT9 | Increased frequency of droughts and fires | High | High | Short-medium-long term |
| | Precipitation changes | Low to medium | Medium | Short-medium-long term |
| | Loss of ecosystems/biodiversity | Medium | High | Short-medium-long term |
| | Risk to food security and human health | Medium | Medium | Short-medium-long term |
| | Increased damage to (water) infrastructure | Low to medium | Medium to high | Long term |

| | | | | |
|---|---|---|---|---|
| | | Low to medium | Medium | Short term |
| | Effect of the water supply | Medium to high | Medium to high | Short-medium-long term |

**Table 3. Rank of implications –important aspects to be considered further**

<table>
<tr><th colspan="2">GMT7 Intensified global competition for resources</th></tr>
<tr><th colspan="2">Implication: Increase in environmental problems – water resource decrease</th></tr>
<tr><td>Social aspects: effects on human health, loss of jobs due to the decrease in environmental investments, migration (brain drain) internationally, as well as displacement inside the country from rural to urban areas.</td><td>Prioritization of sectors (agriculture has the highest potential) with the highest importance/-potential for development – utilizing/materiallizing resources already available (take advantage of monitoring provided by local communities).<br>


<br>(Source: Garcia, 2020) [25].</td></tr>
<tr><td>Economic aspects: competition for critical resources in the whole region, risk for agriculture and farming regarding resource availability, GDP – export and import of the products.</td><td>The role of donations as a form of investment for development – a small investment could change the situation (according to the priorities, e.g., IPA3 for municipalities now).<br>Improve of the mechanisms in monitoring, implementation and enhancing the capacity building in environmental problems.<br><br>Water Security is closely linked to national security in Kosovo, given its topography and history and its dependence on the Ujman/Iber-Lepenc system.</td></tr>
</table>

| | |
|---|---|
| Governance aspects: lobbying/corruption as competition for resources increases due to environmental problems. | *Lobbying* is considered an important *aspect* of governance; however, environmental issues are often dominated by influential players. It is also followed by governmental changes/reduction in donations/investments because of environmental issues, etc.<br>*Corruption* remains an issue of serious concern. |
| Lifestyle changes – adaptation to the new challenges (e. g., similar to what was seen during the pandemic). | Kosovo needs to make significant progress in climate change mitigation, reducing greenhouse gas emissions, consumption of natural resources and nature protection. The role of financial inclusion and international remittances in Kosovo are important; they led towards the lessons learned after the pandemic effects and provided opportunities to adapt to the new environmental and lifestyle changes [26]. |
| | |
| **Implication: Need for renewable energy - biomass and biogas** | |
| Loss of biodiversity, highly valued eco-systems (e. g. forests) | Holistic and multisector cooperation, programmatic approach.<br><br>Biomass potential is considered forests in Kosovo that represent a good energy source. Researchers confirm that there is potential to increase the capacities of energy from 0 MW in the transmission system to 16 MW for the use of biomass within the next 10 years. Some studies identified an estimated potential of 120 GWh/year for the medium-term to be achieved in recent years [15]. |
| Changes in the amount of air and GHGs emissions, | Taking advantage of EU funding to support the low-income countries' investments. |
| Land use and land cover changes and the issue of land ownership. | Learning from the experiences and knowledge of the other countries. Knowledge transfer. |
| Loss of ecosystem services (e.g. changes in carbon sequestration). | Change in energy mix – switch from fossil fuels to renewable ones. |

| | |
|---|---|
| Insufficient infrastructure to support the increase in renewable energy production (distribution, storage).<br>Cost of the transition for the energy system.<br>Loss of jobs in the energy sector (due to lack of skills). | The need for renewable energy will need to be complemented with energy efficiency measures – nature-based solutions (green roofs, green facades as isolation).<br>Achieve the EU goals concerning renewable energy.<br>Development of the new infrastructure/energy systems that enable distribution and storage of the energy. New job opportunities in the green sector. |
| | Evidence:<br>According to the national energy plan in Kosovo, and about 25,69% of renewable energy was reached in 2019, surpassing its 2020 target by 25%. However, according to the plan, this refers to the sectorial target for heating and cooling being overreached, while contributions of renewable energy to electricity and transport are still very low. |
| **GMT9 Increasingly severe consequences of climate change** | |
| **Implication: Increased frequency of droughts and fires** | |
| Increased loss of biodiversity and forest (loss of habitats and species) | Development of fire management plans and an early warning system for forest fires. |
| Degradation of soil, and agriculture sector impacts (loss of productivity, also as an economic impact). | Development of infrastructure (e.g. artificial lakes) for water accumulation. |
| Forest fires – increased air pollution and GHGs emissions. | Increase people's awareness of the importance of reducing forest fires (especially in the summer season) and changes in their behaviour. |
| Water shortages due to droughts. | Raising awareness for efficient water use and reducing water leaking (increasing artificial resources). |
| Population migration from the affected places (to the more secure places). | Increase the resilience to the impact of droughts and fires. |

| | |
|---|---|
| Loss of the ecosystem services of the forests (loss of the groundwater regulation, increase of the erosion). | Upgrade spatialized management solutions, establish efficient monitoring systems, and invest in technological infrastructure. |
| Increase impact on natural and cultural monuments due to acid rain. | Developing long-lasting infrastructures that can continuously protect the monuments from degradation. |
| Economic impacts due to the loss of people's properties. | Kosovo's unemployment rate (40%) remains very high compared with other European countries [26]. The country relies heavily on remittances from the diaspora due to slow economic progress. Some of the problems burdening Kosovo include high levels of air pollution, a deficient education system, the absence of a visa liberalization agreement with the EU, the impact of the COVID-19 pandemic, which entailed lockdowns and a significant economic contraction as well as property loss. |
| | Evidence: • Warming is becoming higher than average, especially for mountain areas. • Decrease in overall annual precipitation, with most significant decreases in summer. • Increases in winter precipitation, particularly in mountains, resulting in more frequent spring flooding. • In Kosovo, a decline of 50 days per year of snow cover by 2050 |
| **Implication: Risk to food security and human health** | |
| Loss of productivity. | Introduction of crops that are more drought resilient. |
| Internal and external migration due to food security issues. | Development of food control process (improvement of human health and reduced mortality). |
| Lack of food quality control for foods produced in the country and imported. | Development of food control process (improving human health and reducing mortality). |

| | |
|---|---|
| Higher exposure to lower quality products imported to Kosovo (e. g. in the case of meat). | Improvement of incentives (e.g., subsidies) for national food production. |
| Uncontrolled use of pesticides in agriculture (infiltration in the groundwater). | Development of a soil monitoring plan for agricultural land. |
| Lack of local food production and increased imports/increasing food prices lead to lower-income people consuming food of unknown quality. | Increase the agricultural products from the rural areas (local producers) with the support of the government. |
| Lack of *social* and economic determinants of *health* addressed in national policies and programmes that *enhance health* equity. | Increase the government and social capacities to prevent risk and improve human health. |
| | Central-level institutions should intertwine policies to promote agriculture among youth and discourage migration.<br>There should be more quality checks and control of food items, as this is a practice that Kosovo lacks.<br>Proper implementation of legislation in place is needed, and better monitoring mechanisms for the whole food system legislative framework are required.<br>Farmers and producers should be more aware of the importance of professional consulting services and provide training programs to increase their capacities in sustainable production practices. |

The result showed the need to improve the cooperation and interaction between different entities," which is inherent to the concept of sustainable development and knowledge-based system in water management, food security, and nature protection. Another important aspect is the government's stand that must provide financial support for appropriate environmental management planning and work more toward the excellent reformulation of environmental policies. The government investments must be maximized and focused on increasing institutional pluralism in the extension of services, maximizing public welfare, enhancing access to the economic efficiency of the water, energy, infrastructure, and agriculture sectors in the identified GMT's approach.

## Mechanism of collaboration and interaction:

Multi-actor partnerships are proposed as the most effective way of organizing innovations and ensuring sustainability of water management, use of resources, climate change mitigation, food production, community involvement, etc. Enhancement of the partnerships and networking among institutions in charge presents the basis of, solid, effective cooperation, public-private partnerships, institutional pluralism, participation from the producers/organizations, etc. Therefore, the investment in stakeholder capacities through training, environmental knowledge, and exchange is of great interest.

## Policy gaps and needs

This section presents the key environmental legislation developed in Kosovo in line with EU requirements and identifies gaps and needs for improvements. Implementing national legislation in the light of EU legislation is one of the main challenges ahead. Kosovo Environmental Strategy (KES) represents one of the most important steps towards the complete and long-term protection of the environment. The Kosovo Environmental Action Plan (KEAP) is the outcome of the KES operational part, which was an obligation derived from the existing Law on Environment Protection. In the best possible way, obligations deriving from EU laws and international agreements have been taken into account in the development of this document.

Kosovo adopted a wide environmental legal framework where the primary legislation has been complemented and, in some cases, repealed by new environmental laws that continue to envisage incorporation in the EU environmental *acquis*. Therefore, weak implementation is considered to be at the root of weak practices that are openly carried out in most of Kosovo's territory, such as deforestation, illegal building, *poor implementation* of *water* resources management functions, etc. In this regard, Kosovo still suffers from a lack of enforcement and compliance with the laws. On the other hand, the progress related to improving water quality has also been limited in line with Law No. 04/L-147 on the waters of Kosovo. The issue of low administrative capacities, weak water management in terms of organizational structure, number of qualified staff, and the current institutional set-up implements the Law on Water very difficult to coordinate. The planning and preparation of the infrastructure investment are lagging due to the low funding compared to the needs of the water sector. The lack of investments and lack of wastewater treatment facilities continue to hamper the operation of water treatment. In addition, the Kosovo National Water Strategy Document 2017-2036 defines the new actions needed and the measures for water resource conservation and protection [27].

Further, the strategy for climate change is another crucial step in the management policy process of mitigating GHG adopting to climate change for the upcoming years. It is also an opportunity to see the mitigation and adaptation measures that will stimulate sustainable development. This strategy refers to ecological, social, or economic adjustments in response to actual or expected climatic simulations and their effects or impacts. The strategy foresees changes in the processes, practices, and structures to moderate potential damages or benefit from climate change opportunities. Energy Strategy 2017-2026 determines the main factors for the country's economic development, and the increase in social welfare is the security of the energy supply [28]. It also foresees fulfilling targets and obligations in energy efficiency, renewable energy sources, and environmental protection. However, in the Kosovo case, more efforts are needed to strengthen the institutional capacities, enforce legislation, create a safe environment for investments from the business sector, and finance new technologies that will help tackle the environmental challenges and support remediation processes. Another important aspect is strengthening multi-stakeholder cooperation and avoiding overlapping or shared jurisdiction related to water management issues and environmental protection in Kosovo.

# Conclusions

In this paper, we have identified and discussed the implications of two megatrends in relation to water management practice. GMT's practice described in the paper showed that the implication and future development could predict future impacts and then provide solutions on approaches underlining resilience and sustainability assessment. Even though the paper dealt with few specific challenges on water resource availability, water shortages, and increased flood risk, we also recognize that other challenges could form part of further future research, such as the implications of megatrends for effective implementation of environmental assessment and mitigation measures as well as the people's awareness and changes in their behavior.

Another important aspect of the science-policy interface is the need to identify and formulate strategies that require a more extensive research approach and understanding of the implications of GMTs. Further, the relevance of applying GMTs in Kosovo on the water case depends on the economic, social, political, and environmental implications. However, an important focus is how Kosovar society adsorb megatrends' opportunities.

To sum up Kosovo's strategies, there is a need for inter-institutional cooperation that ensures transparent and effective flows of information, knowledge, and financial resources to support sustainable development through effective water resource management, climate change, and environmental protection needs. In this regard, the government will need to identify and select measures that best suit their level of development and governance frameworks in alignment with environmental management, climate change mitigation, and adaptation. Further, the GMT's implications and relevance showed the need to strengthen policy measures following national priorities and circumstances. It is important to undertake policy measures and identify the synergies among economic, environmental, and social objectives and use this information to set policy priorities such as updating the fund schemes, investing in renewables, promoting green technology use in agriculture, encouraging participation of different stakeholders in decision making and promoting green infrastructure, foster the share of adequate information associated with implementing policies.

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Mihone Kerolli Mustafa

# VLERËSIMI I MEGATRENDEVE DHE IMPLIKIMEVE TË TYRE NË UJËRAT NË KOSOVË

## Përmbledhje

Megatrendet globale përdoren gjerësisht sot për të vlerësuar implikimet në praktikat e vlerësimit mjedisor. Kjo metodë përdoret kryesisht për parashikimin dhe planifikimin e hershëm të zgjedhjeve të mundshme që çojnë drejt një zhvillimi të qëndrueshëm mjedisor. Në përgjithësi, megatrendet globale janë forca makroekonomike dhe gjeostrategjike që përdoren për formimin e mundësive të jashtëzakonshme për të parandaluar dhe reduktuar rreziqet mjedisore. Në përgjithësi, termi "Mega Trends" përmbledh modele të gjera, afatgjata globale që prekin ose pritet të prekin të gjithë sektorët e shoqërisë, duke filluar nga zhvendosjet demografike dhe urbanizimi te përparimet teknologjike, ndryshimet klimatike dhe ndryshimet gjeopolitike. Të kuptuarit e Mega Trends është thelbësor për të kuptuar peizazhin e ardhshëm të sektorëve të ndryshëm, duke përfshirë edhe menaxhimin e burimeve ujore. Ky punim synon të përmbledhë kontributet kryesore në diskursin mbi Mega Trendet dhe implikimet e tyre për vlerësimin e peizazhit ujor. Menaxhimi i burimeve ujore është një sfidë kryesore me të cilën përballen vendet në nivel global, veçanërisht përballë ndryshimit të kushteve klimatike dhe kërkesave në rritje për shkak të rritjes së popullsisë dhe industrializimit. Si shumë vende të tjera, Kosova ka miratuar një kornizë ligjore për ruajtjen e mjedisit, por aktualisht po përballet me sfida të shumta në zbatimin efektiv të politikave të menaxhimit të ujit. Kosova ka bërë përpjekje për të miratuar ligje që përputhen me standardet e Bashkimit Evropian (BE), por mungesa e zbatimit dhe pajtueshmërisë mbetet një çështje parësore. Ky fenomen nuk është unik vetëm për Kosovën; shkëputja ndërmjet miratimit dhe zbatimit të politikave është një problem global.

Në këtë punim, ne kemi identifikuar dhe diskutuar implikimet e dy megatrendeve në lidhje me ndërveprimin shkencë-politikë dhe praktikën e monitorimit mjedisor. Rezultatet e nxjerra janë një përmbledhje e punës së angazhuar me Rrjetin Evropian të Informimit dhe Vëzhgimit të Mjedisit për të analizuar rastin e Kosovës. Në rastin e Kosovës dhe rajonit, testimi dhe vlerësimi i aplikimit të GMT-ve është një process i ri, si në kuptim ashtu edhe në zbatim. Megjithatë, analiza e rezultateve dhe informacioneve të gjetura rezultojne interesante në kuptim të trajtimit të lidhjes shkencë-politikë, si në nevojën për identifikimin dhe formulimin e strategjive, që kërkojnë një qasje më të gjerë kërkimore ashtu edhe në kuptim të implikimeve të GMT-ve. Më tej, rëndësia e aplikimit të GMT-ve në Kosovë për rastin e ujit varet nga implikimet ekonomike, sociale, politike dhe mjedisore. Megjithatë, një fokus

i rëndësishëm në të ardhmen është se si shoqëria kosovare i përvetëson mundësitë që ofrojnë megatrendet.

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# ASSESSMENT OF CLINICAL UNCERTAINTY IN BRACHYTHERAPY PROCEDURES: GYNECOLOGICAL APPLICATIONS

## Abstract

Brachytherapy is crucial in modern radiotherapy, offering targeted and effective treatment for various cancers. The success of brachytherapy largely depends on minimizing uncertainties in the treatment process to ensure accurate dose delivery to the tumor while sparing healthy tissues. This paper aims to comprehensively evaluate the sources of uncertainty in brachytherapy procedures, including radioactive source calibration, the position of radioactive source, applicator types, and dose calculation algorithm. According to the findings, the average uncertainty associated with this treatment technique is approximately 10%. Moreover, strategies to reduce these uncertainties and enhance treatment precision and safety will be discussed.

*Keywords*: Brachytherapy, Radioactive source, uncertainty, dose.

## 1. INTRODUCTION

Brachytherapy has emerged as a prominent and effective treatment modality in modern radiotherapy, offering precise and targeted delivery of radiation to cancerous tumors. This technique involves temporary placement of radioactive sources within or close to the

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tumor, enabling high doses of radiation to be administered directly to the malignancy while sparing adjacent healthy tissues. Despite its success, implementing brachytherapy requires a comprehensive understanding of the sources of uncertainty that can impact treatment accuracy and outcomes.

Uncertainty in brachytherapy refers to variations or errors that can occur at different treatment stages, leading to deviation in dose distribution and potential impacts on patient outcomes. These uncertainties may arise from multiple factors, including radioactive source calibration, source positioning accuracy, applicator design, patient-specific anatomical variations, and the accuracy of dose calculation algorithms (1). Properly addressing and quantifying these uncertainties ensures optimal treatment precision, efficacy, and safety.

Before commencing brachytherapy treatments, it is essential to identify and comprehend the sources of uncertainty that can influence the overall treatment plan. Rigorous quality assurance and quality control programs are fundamental in minimizing uncertainties, ensuring accurate and reliable dose calculations, and verifying the proper functioning of treatment equipment. Precise calibration of radioactive sources is critical to achieving the desired dose distribution and accurate dose delivery to the tumor. Moreover, meticulous positioning of the brachytherapy applicator within the target volume is vital for achieving the intended treatment outcome.

Incorporating adaptive treatment strategies to account for patient-specific anatomical variations and uncertainties further enhances the precision and success of brachytherapy (2). By addressing uncertainties proactively and implementing appropriate mitigation measures, clinicians and medical physicists can optimize treatment planning, improve patient care, and reduce the likelihood of potential adverse effects.

The brachytherapy unit has been operational for over two years within the Department of Teletherapy at the Oncology Clinic, University Clinical Center of Kosovo. These experiences have spurred the assessment of uncertainties associated with this technique.

The aim of this research paper is to comprehensively discuss the sources of uncertainty encountered in brachytherapy treatments, offering insights into the practical considerations that need to be taken into account during the treatment planning process. Through a thorough analysis of the various sources of uncertainty and the corresponding strategies to mitigate them, this study provides valuable knowledge to the brachytherapy community, ultimately leading to enhanced treatment accuracy and improved patient outcomes.

## 2. RESEARCH AND DISCUSSION

### 2.1. Uncertainty Definition

The current standardized method for evaluating and expressing measurement uncertainties is founded on the guidelines provided by the Comité International des Poids et Mésures (CIPM) report(3). Over time, this method has undergone further development and refinement by two prominent organizations, namely the International Standards Organization (ISO)(4) and the U.S. National Institute of Standards and Technology (NIST)(5).

This method's primary essence lies in categorizing uncertainties into two main components: Type A and Type B. The Type A uncertainties are statistical and based on the reproducibility of measurements. In other words, they consider the variability in the results that would be obtained if the exact measurement were to be repeated under identical conditions.

On the other hand, the Type B uncertainties encompass all other sources of uncertainty that cannot be adequately described using statistical methods alone. These sources might include systematic errors, instrumental limitations, environmental factors, and other sources of variation that cannot be captured purely through statistical analysis.

When discussing the uncertainty of an observation, two essential terms come into play: precision and accuracy. Precision, which falls under Type A uncertainty, refers to the reproducibility of the observation. In other words, it quantifies the consistency and scatter of repeated measurements. A high precision implies that repeated measures cluster closely around a central value. Accuracy, conversely, is a component of Type B uncertainty and represents the deviation of the observation from the actual value. In other words, accuracy reflects how close the average of the measurements is to the actual or accepted value of the measured quantity. A high accuracy indicates that the measured values are relative to the actual value, regardless of their dispersion.

In dosimetric evaluation for clinical purposes, a crucial aspect is the estimation and expression of uncertainty associated with measurements. To achieve this, a specific approach is adopted, which involves using a parameter denoted as "k" to represent the confidence level in the uncertainty estimation.

When assessing individual uncertainty components, k is set to 1. This means that the uncertainty is estimated conservatively, considering only a standard confidence level. In this case, the individual uncertainty components are not expanded or adjusted beyond their natural variations. However, when estimating an observation's overall uncertainty, the value of k is increased to 2. This expansion to k = 2 signifies a higher confidence level, corresponding to a 95% confidence interval assumption. By setting k = 2 for the overall uncertainty, the dosimetric evaluation accounts for a more comprehensive range of potential uncertainties, providing a more robust estimate of the measurement's reliability and accuracy. This expanded uncertainty range is particularly valuable in clinical applications, where precision and accuracy are critical for ensuring patient safety and effective treatment.

It is important to note that the scope of this report is limited explicitly to dosimetric evaluation for clinical purposes. By adopting this standardized approach to uncertainty estimation and expression, the report aims to enhance the quality and consistency of dosimetric evaluations in clinical practice. This, in turn, contributes to the overall advancement of medical radiation technologies and therapies, with a particular emphasis on patient well-being and safety.

## 2.2. Radioactive Source Calibration

The activity of the radioactive source is a fundamental parameter for dose calculations and treatment planning. However, uncertainties in source calibration due to manufacturing variations or decay corrections can impact the delivered dose. Various dosimetry techniques, such as well-type ionization chambers and TLD (thermoluminescent dosimeters), are used to measure source activity. These methods can introduce uncertainties from 1% to 3% (1).

The source strength for photon emitting sources in terms of Air-KERMA strength Sk or RAKR is recommended by credible international institutions AAPM Report 21, ICRU (6), and IAEA (7). The uncertain source strength calibration of the radioactive source was estimated at 1.5 % (K=1) for high dose rate (8). Upon receipt, the activity of all sources must be measured using a local well-type chamber and then cross-referenced with the manufacturer's certificate of source strength. Should the measured activity surpass the specified tolerance level, an alternative measuring system must be employed until the underlying reason for the deviation is fully understood and explained. This process ensures that accurate measurements are obtained and guarantees the safety and reliability of the sources utilized in various applications. Regular calibration and verification of the measuring systems should also be conducted to ensure their precision and adherence to established standards.

Figure 1 presents the after-loading unit and the well-type ion chamber with the transport wire.

*Figure 1. The after-loading unit and well-type ion chamber*

After measuring the sources ' activity, the results obtained from the well chamber with radioactive source $Ir^{192}$, need to be carefully assessed. The measurements should then be compared against the manufacturer's provided certificate of source strength for IR192. Suppose the measured activity falls within an acceptable tolerance level specified by the manufacturer. In that case, it indicates that the source strength is in line with the expected values, and the sources can be used with confidence.

## 2.3. Position of radioactive source

Robust QA and QC programs are essential to ensure the accuracy and reliability of brachytherapy treatments. However, uncertainties in measurement techniques, instrument calibration, and environmental factors can impact the accuracy of QA and QC measurements.

Comprehensive QA and QC protocols can help minimize uncertainties, with studies reporting uncertainties of around 1% to 3% (2). Accurate placement of the radioactive source within the treatment site is critical for achieving optimal dose distribution. Source position uncertainties arise from imaging modalities, applicator reconstruction, and manual positioning limitations. Studies have shown that uncertainties in source position can range from 1 mm to 3 mm (9).

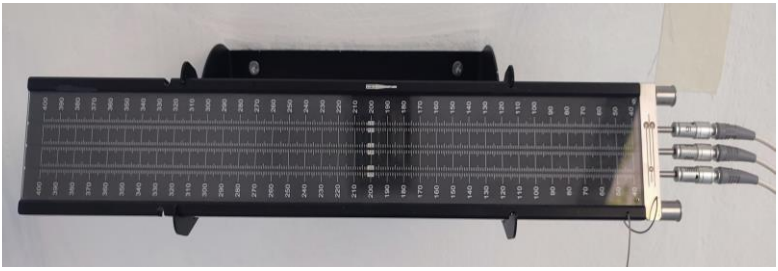

*Figure 2-a. Visual check position of radioactive and dummy Source*

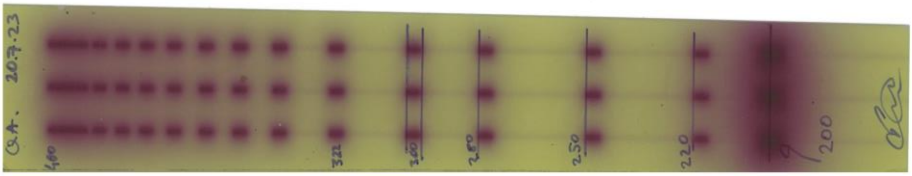

*Figure 2-b. Irradiation of GAFchromic film for specific positions of radioactive source*

Daily quality control is crucial for precisely positioning radioactive sources, especially in medical settings. Image-guided procedures and real-time imaging minimize uncertainties. Figure 2-a shows the use of a ruler to visualize, verify, and calibrate the source, ensuring accuracy. Regular quality control guarantees optimal treatment outcomes by accurately placing the source. Healthcare providers use advanced imaging to monitor the position during treatment, making real-time adjustments if needed. The ruler-based visualization confirms correct placement, allowing calibration if necessary. This approach enhances effectiveness and safety in radiation therapy and other radioactive source procedures.

Regular QA and QC checks, calibration, and intercomparison of measurement devices can contribute to uncertainty reduction. Accurate source positioning of the catheter is crucial before each treatment. A simple device with a dummy source (Figure 2-a) can be used alongside embedded distance markers for precise reference (±0.1 mm). An autoradiograph of the source on film (Figure 2-b) must be performed. During commissioning, this process should be conducted for every channel and transfer tube to ensure reliable and safe radiation therapy. Regular verification is essential to maintain consistency and quality standards.

## 2.4. Applicator types

A crucial aspect in the Image-Guided Adaptive Brachytherapy (IGABT) is the meticulous selection of applicators. Before deciding on a specific applicator for each patient, thorough consideration of all clinical and technical factors is essential. The appropriate choice of an applicator significantly impacts tumor dose coverage, directly influencing rates of local disease control (10). An ideal applicator should conform maximally to the tumor's shape and volume, while also adhering to standardized specifications, ensuring efficient and consistent physical properties for successive implants (10,11).

The process of picking up applicators demands careful attention, as it involves fulfilling specific requirements. By approaching this task diligently, we ensure that the applicators are utilized safely and accurately during medical procedures, adhering to the necessary standards and protocols. This meticulous approach is essential to minimize the risk of errors and to maintain the highest quality of patient care. The dosimetric evaluation is presented on Figure 3.a for ring and 3.b for tandem applicator.

In contrast, the use of an inappropriate applicator or its improper placement can result in inadequate tumor coverage, which cannot be compensated for through optimization. This leads to reduced local disease control and lower disease-free survival rates. Attempts to enhance coverage through optimization might even lead to hazardous hot spots and increased toxicities (11,12). Therefore, the significance of proper applicator selection and positioning cannot be overstated, as they play a crucial role in the success and safety of IGABT treatments. It is imperative to prioritize meticulous planning and evaluation to achieve optimal treatment outcomes and minimize potential risks for the patient.

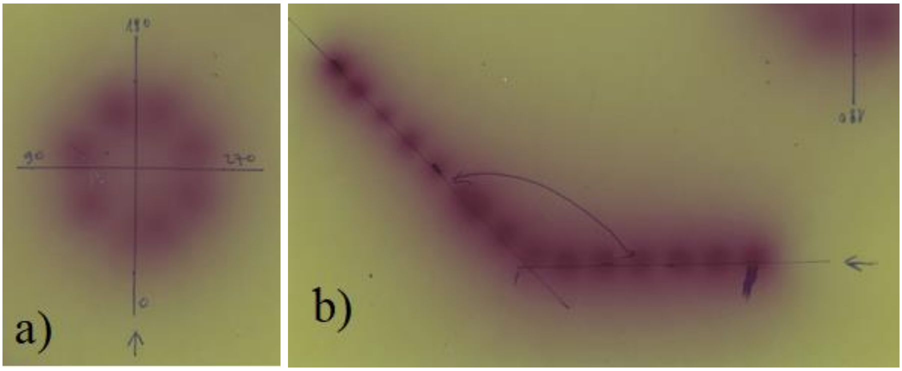


*Figure 3. Radiation dose on GAFchromic film, a) for ring applicator and b) for tandem applicators*

Accurate applicator reconstruction is crucial in IGABT, as even a 1 mm displacement can lead to a 5-6% change in mean DVH parameters (13). Precise placement is essential for effective treatment and minimizing uncertainties. In brachytherapy, applicators can be reconstructed either manually or through library applicators. A comparison of both methods showed that they have a limited impact on the calculated dose. However, using the library method resulted in smaller standard deviations, indicating a lower probability of errors and uncertainties. This suggests that the library applicator approach is more reliable and offers increased accuracy in dose calculations during brachytherapy procedures.

## 2.5. Dose Calculation algorithm

Brachytherapy applicators are available in various shapes and materials, each designed for specific treatment sites. Differences in material density and design can introduce uncertainties in dose distributions. Monte Carlo simulations and dosimetric measurements have shown that these uncertainties can vary from 2% to 5% depending on the applicator type and treatment site (14). Careful selection and commissioning of applicators are essential to minimize uncertainties.

Applicator commissioning is a crucial step that ensures the accurate positioning of source positions relative to the applicator. This verification is achieved through techniques like auto-radiography and imaging. Sectional imaging, especially CT imaging, is commonly utilized during commissioning due to its optimal capabilities (CT slides must be <5mm) . The valuable data obtained from the commissioning process can be stored as library applicators, serving as reliable references for future treatments and enhancing the precision and safety of brachytherapy procedures. Other sources of uncertainty include patient anatomy variations, treatment planning algorithms, and dose calculation models. Patient-specific uncertainties, such as organ motion and density variations, can lead to deviations in dose delivery. Additionally, uncertainties associated with the TPS algorithms and dose calculation models can range from 2% to 5% (15). Addressing these uncertainties requires adaptive treatment strategies and rigorous patient-specific QA processes.

Regular checks of applicators are crucial due to their high frequency of use and exposure to handling, cleaning, and sterilization. Periodic inspection and radiographic evaluation are necessary to ensure their reliability and safety during medical procedures. Otherwise, failing to conduct regular checks of applicators increases the likelihood of enlarging uncertainties. Regular inspections and evaluations help mitigate potential risks, ensuring the reliability and safety of medical procedures and minimizing uncertainty in treatment outcomes.

## 3. CONCLUSIONS

Brachytherapy remains a powerful treatment modality, but its success relies on managing uncertainties in various aspects of the treatment process. The evaluation of uncertainty reveals that each element contributes to the overall uncertainty in brachytherapy procedures like radioactive source calibration (1-3%), source position (1-3%), applicator types (5-6%), and dose calculation algorithm (2-5%) contributes to an estimated total uncertainty of approximately 9 % to 17% in dose delivery.

To reduce these uncertainties and enhance treatment precision and safety, several actions can be taken:

- Regular calibration and quality assurance checks of the radioactive source, dosimetry equipment, and treatment planning systems.
- Implementing image-guided procedures and real-time imaging during treatment to improve source positioning accuracy.

- Commissioning and thorough testing of applicators for specific treatment sites to ensure accurate dose distributions.

By diligently addressing and mitigating uncertainties, the brachytherapy community can provide more reliable and effective treatments, improving patient outcomes and enhanced quality of life.

To enhance the safety level of brachytherapy treatment, medical physicist staff to possess a high level of knowledge and be equipped with adequate instruments. Their expertise and proper tools are crucial in ensuring the safe and effective administration of brachytherapy procedures.

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# VLERËSIMI I GABIMIT KLINIK NË PROCEDURAT E BRAKITERAPISË: APLIKIMET GJINEKOLOGJIKE

## Përmbledhje

Brakiterapia luan një rol kyç në radioterapinë moderne, ofrojnë trajtim të orientuar dhe efektiv për kanceret e ndryshme. Suksesi i brakiterapisë varet shumë nga minimizimi i papërcatueshmërive në procesin e trajtimit për të siguruar dorëzimin e saktë të dozës në tumor dhe ruajtjes së indeve të shëndosha. Kjo punë ka për qëllim të vlerësojë në mënyrë të plotë burimet e papërcatueshmërisë në procedurat e brakiterapisë, duke përfshirë kalibrimin e burimit radioaktiv, pozicionin e burimit radioaktiv, llojet e aplikatorëve dhe algoritmin e llogaritjes së dozës. Nga të gjeturat u vërtetua se papërcaktueshmëria mesatarisht është rreth 10%. Gjithashtu, në këtë hulumtim do të diskutohen strategjitë për reduktimin e këtyre papërcaktësive dhe për të përmirësuar precizionin dhe sigurinë e trajtimit.

Bazuar në përfundimet: Brakiterapia mbetet një modalitet i fuqishëm i trajtimit, por suksesi i saj varet nga menaxhimi i papërcaktueshmërive në aspekte të ndryshme të procesit të trajtimit. Vlerësimi i tyre tregon se çdo element kontribuon në papërcaktueshmërinë e përgjithshme në procedurat e brakiterapisë. Kalibrimi i burimit radioaktiv, pozicioni i burimit, llojet e aplikatorëve, programet e sigurisë dhe kontrollit të cilësisë dhe faktorët tjerë kontribuojnë së bashku në një papërcaktësi totale të shfaqur nga 9 % deri në 17% në dorëzimin e dozës.

Për të reduktuar këto papërcaktushmëri dhe për të përmirësuar precizionin dhe sigurinë e trajtimit mund të ndërmerren disa veprime:

• Kalibrimi i rregullt dhe kontrolli i sigurisë së burimit radioaktiv, pajisjeve të dozimeve dhe sistemeve të planifikimit të trajtimit.

• Zbatimi i procedurave me udhëzime të imazheve dhe imazhim në kohë reale gjatë trajtimit për të përmirësuar saktësinë e pozicionimit të burimit.

• Komisionimi dhe testimi i plotë i aplikatorëve për vende të caktuara të trajtimit për të garantuar shpërndarjen e saktë të dozës.

Duke ngritur kujdesin për uljen e papërcatueshmërive, profesionistët e brakiterapisë mund të ofrojë trajtime më të besueshme dhe efektive, duke çuar në përmirësimin e rezultateve të pacientëve dhe përmirësimin e cilësisë së jetës. Për të rritur nivelin e sigurisë së trajtimit në brakiterapi, është e domosdoshme që stafi i Fizikaneve Mjekësore të kenë nivel të lartë të njohurive dhe të jenë të pajisur me instrumente adekuate. Ekspertiza e tyre dhe mjete të duhura luajnë një rol kyç në sigurinë dhe efektivitetin e administrimit të procedurave të brakiterapisë.

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# THE EFFECT OF SOME INORGANIC AND ORGANIC COMPOUNDS ON THE EFFICIENCY OF FENTON'S PROCESS

## Abstract

Surface water is exposed to chemical pollution that is emitted from a variety of industrial processes. Considering the harms that this brings about, many polluted water treatment methods have emerged. Fenton's process is a method for the destruction of organic pollutants in water media and uses hydrogen peroxide $H_2O_2$ and $Fe^{2+}$ to develop a highly reactive chemical species, which oxidizes organic substances. This research studied the impact of secondary compounds on the Fenton's process during the degradation of a targeted compound. The inhibitory effect on the degradation efficiency of methyl orange (MTO), of five inorganic salts ($NaHCO_3$, $KNO_3$, $Na_2SO_4$, KCl) and four organic compounds (glycine, 2-Azoaminothiazole, ascorbic acid, and, aspartic acid) was studied. It was found that all added compounds slowed the degradation process (although some of them had a minimal effect). Additionally, organic compounds greatly lower the efficiency of MTO degradation compared to the inorganics, and the inhibition of the Fenton process depended on the chemical structure of the interfering compounds.

*Key words*: Fenton, organic compounds, inorganic compounds, efficiency, interference

## Introduction

Water pollution is a very common problem, and it can be of various nature, it is particularly of concern when chemicals cause the pollution. Chemical substances can be introduced into the water environment in many ways, as they are used for the primary purpose in a wide range of human activities such as household products [1], agriculture [2], medicine [3], and the industry in general [4,5]. Some chemicals are

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nutrients for the water plants, resulting in their excessive development, which in turn leads to water body eutrophication [6], while others can be toxic, thereby causing decay and poor growth of living organisms [7,8].

Some organic substances are degradable in the natural environment, whereas some recalcitrant organic substances persist long enough to induce problems in organisms. To prevent the harmful effects of chemical pollutants, the waste materials containing them must be treated before their disposal. Various methods for pollution destruction or separation have been developed in this regard. Separation methods such as adsorption and membrane filtration can only remove the pollutants from the water media or concentrate them so other techniques can further dispose or destroy them [9–11]. The destructive methods for polluted water treatment transform pollutants chemically, thereby removing their toxicity [12,13]. Nowadays, there are several destructive microbiological, chemical, and physicochemical methods for removing organic pollutants from water [14]. A group of destructive methods are advanced oxidation processes that use hydroxyl radicals $^{\bullet}OH$ as an oxidizing reagent [15–18]. Hydroxyl radicals are generated in various ways directly in the solution containing the pollutant where they oxidize it. One of the earliest methods to generate $^{\bullet}OH$ is Fenton's process, during which hydrogen peroxide $H_2O_2$ reacts with $Fe^{2+}$ at pH 3, producing $^{\bullet}OH$ ($E°(^{\bullet}OH/H2O) = 2.8$ V/SHE), which oxidizes organic pollutants [15,19].

$$H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+}$$

The Fenton process for polluted water treatment is restricted by several factors, such as $H_2O_2$ and $Fe^{2+}$ concentration, temperature, and pH [15,17]. But the Fenton's process efficiency towards the oxidation of a targeted pollutant is also expected to be affected by the presence of other substances since there will be competition for $^{\bullet}OH$ between all the substances in the solution. This work was done to evaluate the effect of some organic and inorganic compounds on Fenton's process efficiency. Methyl orange (MTO) solution was treated with Fenton's reagent ($H_2O_2$ and $Fe^{2+}$), and the decrease of the concentration with time was monitored. Then, the compounds to be tested were added in order to observe their effect on the degradation curve of the methyl orange.

## Materials and methods

All reagents were Sigma Aldrich products. The molecules tested as interfering substances, and the methyl orange used in this work were of purity 99% or higher. The sulphuric used for pH adjustment was 98%

purity. Hydrogen peroxide was a 30% solution. The solutions were prepared in distilled water, and the pH was adjusted by adding 1 M sulphuric acid solution drops. The experiments were carried out in a 250 ml beaker under continuous stirring. The batches of methyl orange solution, adjusted to pH 3, were put in the reaction beaker, the interfering substance was added, then hydrogen peroxide of the pre-calculated amount, and the iron sulfate ($FeSO_4$) as a catalyst. Once the $Fe^{2+}$ ions were added in the form of $FeSO_4$, Fenton's reaction started, and samples of the solution were taken regularly at pre-set intervals to be analyzed with a spectrophotometer. The concentrations determined at each sample were plotted against time to construct kinetic curves showing the trend of methyl orange degradation during time.

## Results and discussion

After determining the concentration of MTO at pre-set intervals, it was graphed against time to reveal the decreasing trend. First, the MTO solution alone was treated with Fenton's reagent, which produced a base curve where no interfering compounds were present. Then, the following experiments were performed, adding the given interfering compound, in several trials in increasing concentrations.

Figure 1 shows the degradation graphs of MTO in the presence of three inorganic salts, namely $NaHCO_3$, $KNO_3$, and $Na_2SO_4$. The initial concentration of MTO (0.01 mM) starts to decrease immediately after the addition of Fenton's reagent due to the oxidation reaction of MTO with $^{\bullet}OH$. In the beginning, the decrease is very fast, represented by the steep part of the curve, as the reagents are consumed, the curve becomes flatter until there is no change in concentration any further. When the interfering compounds are added, the degradation reaction of MTO decelerates, resulting in an upward shift of the curves. However, as the bar graphs show, this only occurs at high concentrations of added salts. A significant deceleration of the degradation is observed when $NaHCO_3$ is added at 500 mM, $KNO_3$ at 1000 mM, and $Na_2SO_4$ at 300 mM. At lower concentrations, these compounds had almost no effect on the oxidation of MTO by $^{\bullet}OH$. The observed effect of these compounds on MTO degradation can be explained mostly by the fact that they also react with $^{\bullet}OH$ according to the following reactions [20]:

$$HCO_3^- + {}^{\bullet}OH \rightarrow CO_3^{-\bullet} + H_2O$$

$$NO_3^- + {}^{\bullet}OH \rightarrow NO_3^{\bullet} + OH^-$$

$$SO_4^{2-} + {}^{\bullet}OH \rightarrow SO_4^{-\bullet} + OH^-$$

Thus, the amount of hydroxyl radicals $^{\bullet}OH$ in the solution will be smaller, resulting in a smaller rate of MTO degradation.

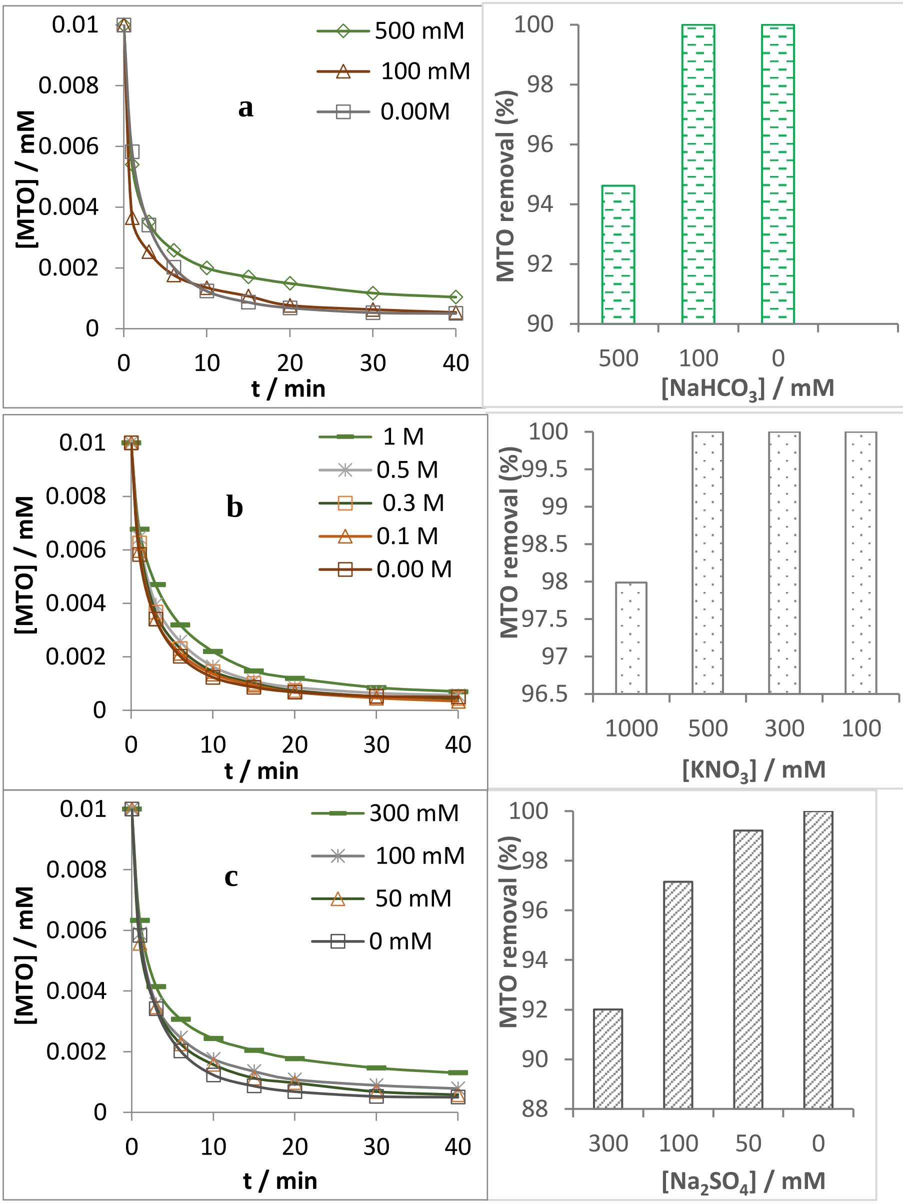


*Figure 1. Degradation curves of MTO at various concentrations of interfering substance: a) $NaHCO_3$, b) $KNO_3$, c) $Na_2SO_4$. $[MTO]_0$ = 0.01 mM, $[H_2O_2]$ = $[Fe^{2+}]$ = 0.08 mM, pH = 3, $V_s$ = 250 ml.*

Unlike the above salts, $Na_3PO_4$ and KCl behave very differently. When they are added to the solution being treated by Fenton's reagent, the MTO degradation rate is lowered significantly, even when they are added at very low amounts. The decrease of the degradation rate is manifested with a significant upward shift of the reaction curves, meaning that the reaction of the $Cl^-$ with $^{\bullet}OH$ is faster than the previous ones.

$$Cl^- + {}^{\bullet}OH + H^+ \rightarrow ClO^{\bullet} + H_2O$$

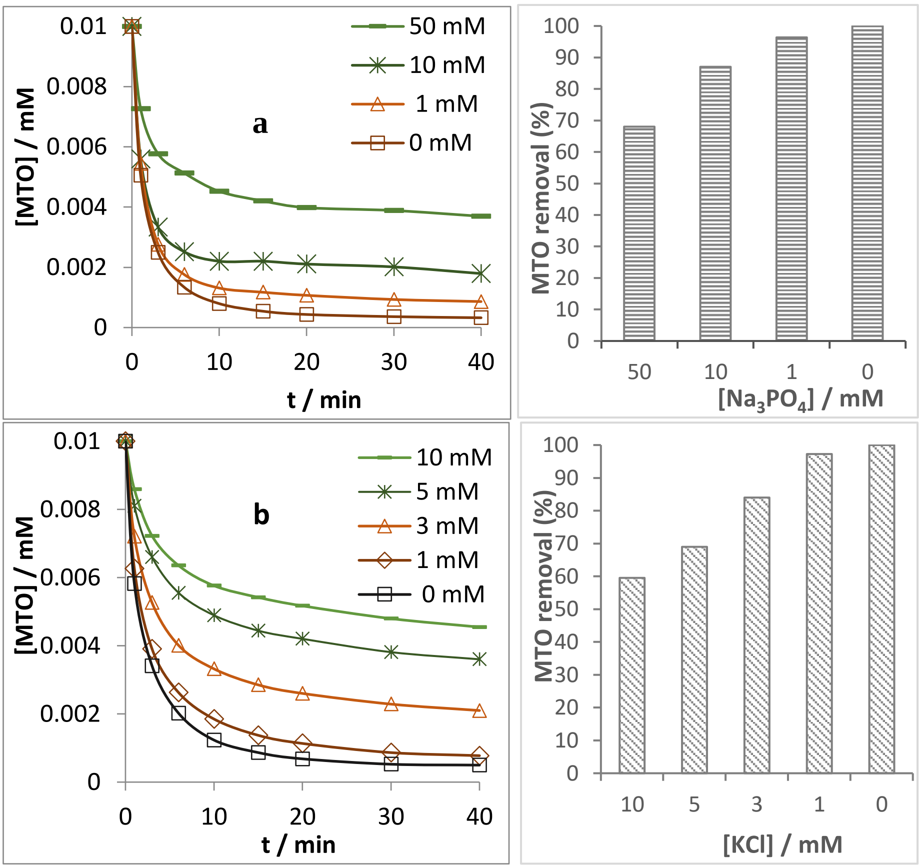


*Figure 2. Degradation curves of MTO at various concentrations of interfering substance: a) $Na_3PO_4$ and b) KCl. $[MTO]_0 = 0.01$ mM, $[H_2O_2] = [Fe^{2+}] = 0.08$ mM, pH = 3, $V_s = 250$ ml.*

In the case of $PO_4^{3-}$, the decrease in the degradation efficiency is a consequence of the increase of the pH of the solution when $PO_4^{3-}$ is added. At pH higher than 3, the precipitation of $Fe^{2+}$ and $Fe^{3+}$ is highly accelerated, which results in a lower quantity of •OH produced, which yet again is manifested with a lower MTO degradation rate.

Figure 3 presents the degradation plot of MTO in the presence of glycine. Adding glycine did not influence the degradation kinetics up to 3 mM. At 5 mM, the degradation line has a smaller gradient, whereas at 10 mM, the complete degradation could not be reached.

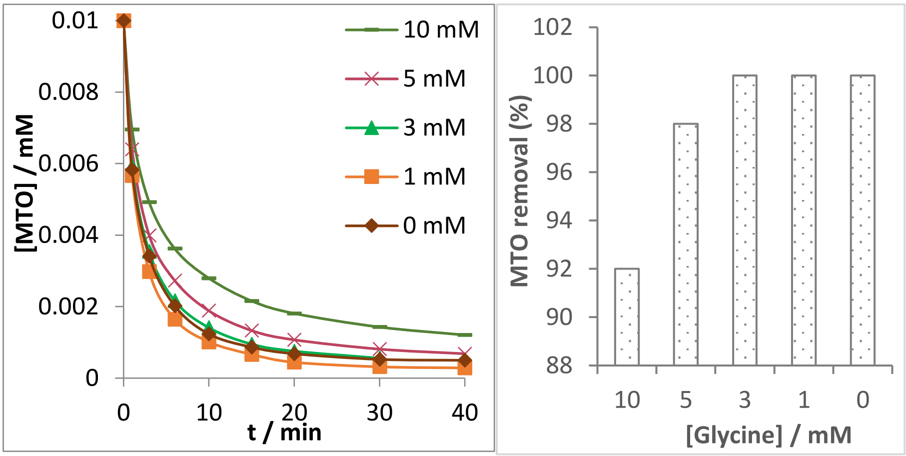


*Figure 3. Degradation curves of MTO at various concentrations of glycine. $[MTO]_0 = 0.01$ mM, $[H_2O_2] = [Fe^{2+}] = 0.08$ mM, pH = 3, $V_s = 250$ ml.*

A very different situation arises when other organic substances are added, namely 2-Azoaminothiazole, ascorbic acid, and aspartic acid. The interfering effect of these compounds is detectable even at very small concentrations, as low as 0.01 mM. In the case of 2-Azoaminothiazole and ascorbic acid, at a concentration of 10 mM, the degradation of MTO is almost stopped at 80%. The bar graphs indicate a progressive lowering of degradation efficiency with the amount of interfering compound added. The first two compounds, shown in figure 3, hamper the degradation of MTO the most. This can be explained by their more complex structure and the types of reactions •OH reacts with organic compounds [15,21]. Hydroxyl radicals react with organic substances in three modes: abstraction of hydrogen, which results in water molecule formation and the organic fragment, the electrophilic addition to a non-saturated bond, and redox reaction. 2-Azoaminothiazole and ascorbic acida heterocyclic five-membered ring with non-saturated bonds. This provides many ways by which hydroxyl radicals can react with them, resulting in a greater consumption of oxidant, hence less MTO oxidation. Aspartic acid on the other hand, has no ring in its structure, it is a smaller molecule, and it only has two unsaturated bonds, thus a smaller number of ways it can react with •OH. Similarly, it can be argued that glycine has an even simpler chemical structure than the three other compounds studied.

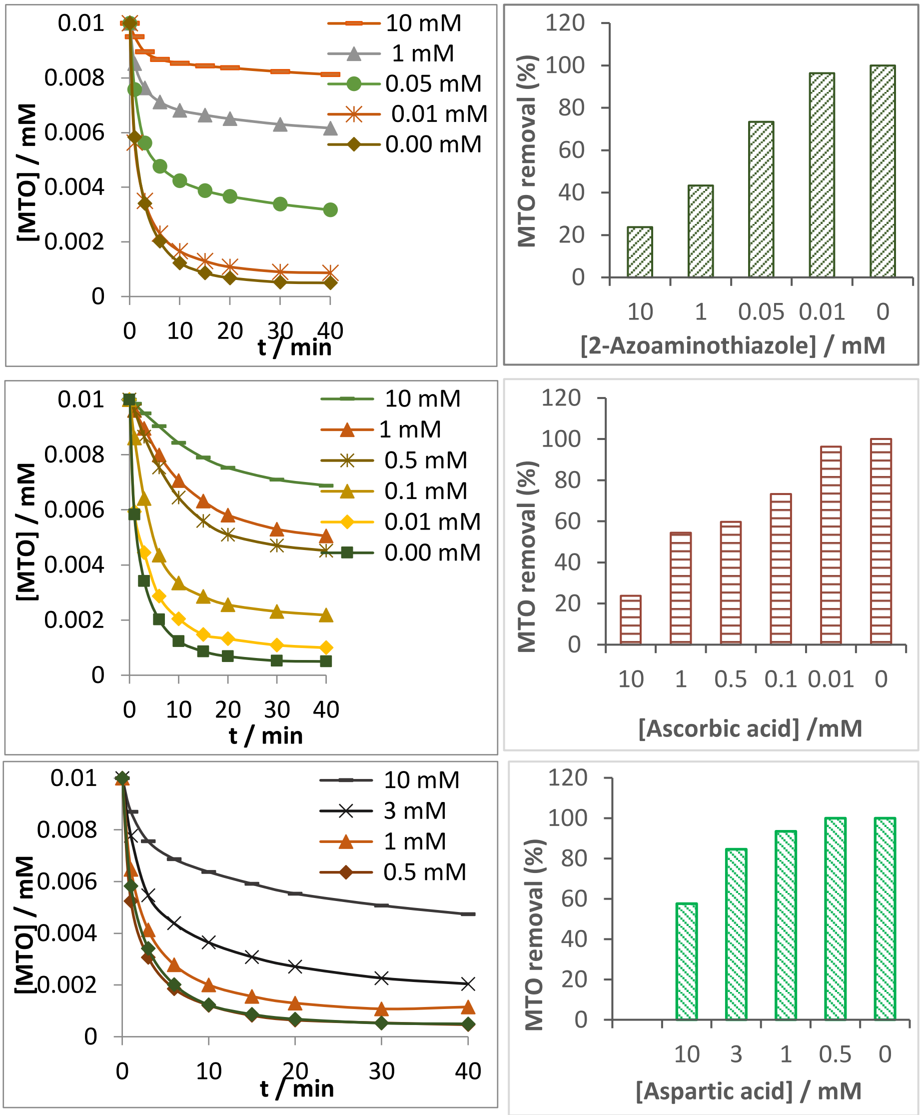


*Figure 4. Degradation curves of MTO at various concentrations of organic compounds. a) 2-Aminothiazole, b) Ascorbic acid, c) Aspartic acid. $[MTO]_0$ = 0.01 mM, $[H_2O_2]$ = $[Fe^{2+}]$ = 0.08 mM, pH = 3, $V_s$ = 250 ml.*

# Conclusion

During the Fenton process, methyl orange could be degraded entirely in about 20 minutes at the given $H_2O_2$ and $Fe^{2+}$ concentration. However, the addition of other compounds hampered the complete degradation. The $NHCO_3$, $KNO_3$, and $Na_2SO_4$ had a minimal effect, they could barely slow the MTO degradation, even at very high concentrations. The two remaining salts significantly reduced the degradation efficiency. On the other hand, organic compounds had a strong effect even at low concentrations. The more significant inhibitory effect of organic compounds is a result of their complex reactivity with hydroxyl radicals. One organic molecule consumes a lot of $^{\bullet}OH$, compared to the inorganic compounds studied in this research, which consume only one. From the results of this research,, organic compounds have a stronger interfering effect in the degradation reaction of chemical pollutants with Fenton's reagent compared to inorganic compounds. The effect will depend strongly on the chemistry of the particular substance.

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# EFEKTI I DISA KOMPONIMEVE INORGANIKE DHE ORGANIKE NË EFIKASITETIN E PROCESIT FENTON

## Përmbledhje

Ndotja e ujit tashmë është një problem shumë i zakonshëm dhe serioz. Është sidoms problematike ndotja e ujit me kimikate, sepse shumë prej tyre nuk shkatërrohen në kushtet e ambientit dhe si pasojë qëndrojnë aty për një kohë të gjatë, duke dëmtuar dhe shkatërruar organizmat dhe proceset bioligjike. Ndotësit kimik futen në ambient në mënyra të ndyshme nga proceset industriale. Për të pengur ndotjen e ujërave me substanca kimike, janë bërë shumë hulutime për të gjetur metoda për pastrimin e ujërave hedhurinë. Ndër metodat që përdoren për pastrimin e ujërave janë: adsorbimi, filtrimi membranor, zbërdhimi mikrobiologjik i ndotësve dhe metoda të tjera kimike, fotokimike dhe elektrokimike.

Ndër metodat kimike për degradimin e ndotësve kimik në mjedis ujorë, është procesi Fenton, i cili bën pjesë në grupin e metodave që quhen "Metodat e avancuara të oksidimit". Procesi Fenton bazohet në reaksionin e peroksidit të hidrogjenit me jonet e hekurit II, i cili jep radikale hidroksile, të cilat kanë potencial redoks shumë të lartë ($E°(^{\bullet}OH/H_2O)$ = 2.8 V/SHE) dhe i oksidojnë substancat organike duke i shkatërruar ato. Në procesin Fenton ndikojnë shumë faktorë; përqëndrimi i reagjentit Fenton ($H_2O_2 + Fe^{2+}$), temperatura dhe vlera e pH. Por kur bëhet fjalë për degradimin e një substance specifike, ndikim pritet të kenë edhe substancat dytësore prezente në tretësirën që trajtohet.

Në këtë hulumtim është studiuar ndikimi i disa substancave inorganike dhe organike në efikasitetin e degradimit të një komponimi model, përkatësisht metil oranzhit, me anë të procesit Fenton. Eksperimentet janë realizuar në një reaktor cilindrik në të cilin është vendosur tretësira e metil oranzhit nën përzierje të vazhdueshme dhe pH 3 (vlera optimale për zhvillimin e procesit Fenton). Së pari metil oranzhi është degraduar me anë të procesit Fenton si i vetëm, dhe është ndërtuar lakorja e degradimit, pra zvogëlimi i përqëndrimit të metil oranzhit gjatë kohës C = f(t). Pastaj janë shtuar komponimet e studiuara dhe lakoret e fituara C = f(t) të metiloranzhit janë krahasuar me lakoren, kur ai është degraduar pa prezencën e komponimeve të përmendura.

Nga rezultatet e fituara është vërejtur që komponimet inorganike të studiuara, $NaHCO_3$, $KNO_3$, $Na_2SO_4$, $Na_3PO_4$, and KCl, e pengojnë më pak procesin Fenton në krahasim me ato organike; glicinë, 2-Azoaminotiazol, acid askorbik, dhe acid aspartik. Ngadalësimi i degradimit të metil ornazhit është pothuajse i papërfillshëm në prezencën e $NaHCO_3$, $KNO_3$ dhe $Na_2SO_4$, ndërsa

KCl dhe $Na_3PO_4$ zvogëlojnë efikasitetin e degradimit të MTO në sasi 60 deri në 68% respektivisht kur shtohen në përqëndrime 10 mM KCl dhe 50 mM $Na_3PO_4$. Ndryshe nga këto, me përjashtim të glicinës, komponimet organike kanë ndikim shumë më të madh. Në përqëndrime 10 mM zvogëlojnë degradimin e metil ornazhit në rreth 20%. Në të gjitha rastet zvogëlimi i efikasitetit të degradimit të metiloranzhit është pasojë e konsumimit të radikaleve hidroksile nga komponimet konkurente.

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Arlinda Bresa[1], Bedri Dragusha[*,1]

# ADDRESSING THE IMPACT OF OCCUPANT BEHAVIOUR ON BUILDING ENERGY CONSUMPTION IN KOSOVO

## Abstract

The current energy crisis has urged governments worldwide to take swift action to mitigate overall energy consumption. Considering that buildings account for around 40% of the total energy consumption, it is highly important to focus on improving the building energy performance, which has been among the main established strategies for sustainable development and energy savings. Although the implementation of energy efficiency measures in buildings is of crucial and undeniable importance, due to the time-consuming retrofit procedures, it is important to address other easy-to-access possibilities to reduce energy consumption in buildings. Hence, one of the main factors influencing the energy consumption of buildings is occupant behavior and energy efficiency awareness. Due to the lack of research regarding occupant behavior in Kosovo, it is highly important to elicit the common behavior tendencies of building users regarding energy usage, discuss energy efficiency awareness, and identify possible measures to increase such awareness nationally. This research presents a review of interdisciplinary research studies and it provides insights into the impact of occupant behavior on the energy consumption of buildings and the strategies used by other countries to motivate energy behavior change. Furthermore, it discusses the possible discourse of introducing behavioral science approaches on the national level, such as eco-feedback, social interaction, and gamification as motivators for the energy-efficient behavior of occupants in Kosovo. The findings and insights from the existing literature can be used as a ground base to draft new energy policies for energy occupant behavior in Kosovo.

*Keywords*: Occupant behavior, energy efficiency in buildings, behavioral science, energy policy

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# 1. Introduction

The building sector, including residential and commercial buildings, accounts for around 40% of the overall energy consumption [1]. Hence, buildings have a high potential for energy savings. Although various measures can be applied to mitigate the energy consumption in buildings, and their effect is imperative, other indicators can be , such as the utilization of new energy-efficient technologies. However, the investment in technologies does not suffice to guarantee low energy consumption in buildings. Therefore, further actions are needed, such as accounting for the impact of occupant behavior on the building's energy use. According to research [2], to reach the 2050 energy target worldwide as set by the Paris agreement, behavioral-based regulations and policies must be fostered alongside the conventional building energy performance measures in the building sector. It is said that the most sustainable energy is the energy not used, therefore, the most cost-effective and swift actions toward sustainable energy could be the energy-conscious and pro-environmental behavior change of the building users.

Recently, the crucial role of human behavior in building energy performance has gained increasing attention in research regarding buildings [2]. The research trend regarding human behavior and their role in building energy efficiency was presented in Figure 1, where related published studies were analyzed using the VOSviewer software [3]. The role of lifestyle and behavioral change on one side and science-based policy on the other has been further illuminated during the pandemic [4]. Hence, it is important to include occupant behavior as a crucial indicator in building energy consumption and to promote energy-aware behavioral change in occupants. However, considering that occupants spend around 90% of their time indoors according to [5], it is important to facilitate an optimal trade-off between the energy consumption curtailment actions and indoor comfort conditions.

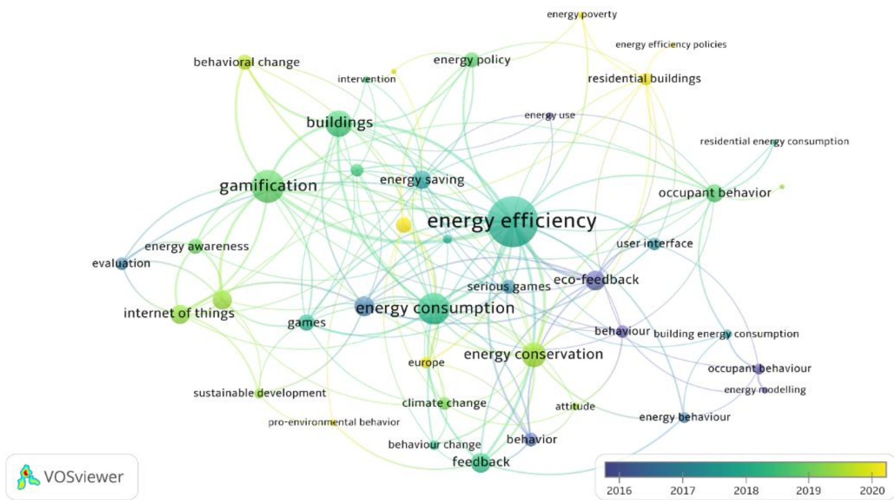


*Figure 1. The research trend regarding human behavior and its impact on energy efficiency in buildings.*

This review elaborates on the role of occupant behavior in energy consumption in buildings by presenting research studies conducted in this regard. Furthermore, it elicits possible interventions to mitigate energy waste from occupants and increase energy awareness.

## 2. The role of occupant behavior in energy efficiency in buildings

The impact of human behavior alteration was especially noticed during the pandemic [6]. Several studies have shown the significant effects behavior and lifestyle change have on energy savings in buildings. For instance, research [7] showed that the electricity demand decreased by 15-23% during the first lockdown in Poland due to the closure of commercial buildings. Furthermore, a maximum of 63.5% of energy consumption reduction in China was reported during lockdown measures [8]. But, although the energy use in commercial buildings was reduced during the pandemic, a shift was noticed after the ease of the pandemic measures. Thus, as reported in [9], an increase in energy demand between 10.18%-69.48% was reported in Europe's top five economies, such as Rome and Paris. This resulted from different HVAC systems being used in office buildings to ensure higher indoor air quality. Other studies that revealed significant energy savings in buildings from behavior change were elaborated on in [10], and some are presented in Table 1.

Table 1. Studies including the energy-saving potential of behavioral change in buildings

| | Building type | The type of energy considered | | | | Energy savings from occupant behavior |
|---|---|---|---|---|---|---|
| | | Heating | Cooling | Electricity | Lighting | |
| **[11]** | Residential | X | X | X | | 10-30% |
| **[12]** | | X | | | | 17-41% |
| **[13]** | | X | | | | 27% |
| **[14]** | | X | | X | X | 62-86% |
| **[15]** | | | | X | | 50% |
| **[16]** | | | | X | | 10% |
| **[17]** | Offices | X | X | X | X | 23.60% |
| **[18]** | | X | X | X | X | 9-60% |
| **[19]** | | | X | X | X | 50% |
| **[20]** | University | | | X | | 15-18% |

From Table 1, it can be seen that the energy savings differ significantly depending on the study, building type, and the type of energy considered. Energy behavior highly influences heating, cooling, lighting, and overall electricity consumption. More energy-aware choices lead to lower energy consumption, such as turning off lights when not using the room or avoiding hidden energy waste by unplugging devices.

Despite the role of human behavior in terms of occupant-building interaction, the role of the human dimension in building energy consumption is pertinent throughout the whole life cycle of buildings. Starting from the design phase up to the operation of the buildings, different stakeholders' roles can significantly impact buildings' energy performance as reported in research [2]. Figure 2 shows the different stakeholders during the life cycle of a building, namely the role of building designers, operators and managers, policymakers, etc.

Human behavior regarding building energy consumption is divided into adaptive and non-adaptive behavior [21]. The adaptive behaviors represent the occupant’s efforts to adapt or adjust their indoor environment according to their needs and preferences. This includes adjusting the thermostat setpoints, window and blinds operation, and using different appliances such as personal heaters, fans, etc. On the other hand, non-adaptive behavior presents the action that occupants exhibit regardless of the indoor conditions, e.g., occupancy, standard use of home or office appliances, etc.

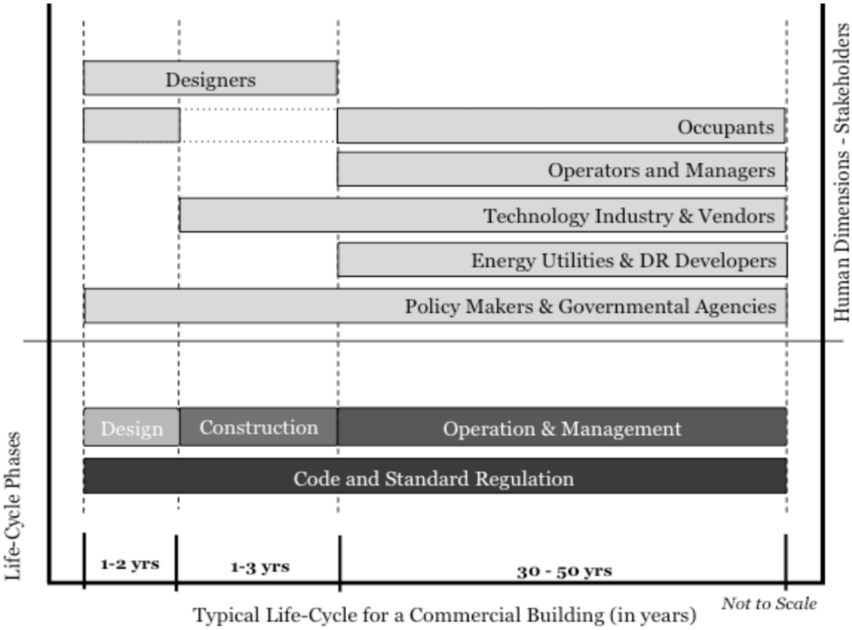


*Figure 2. The different stakeholders during the life cycle of typical buildings [2].*

This shows that the impacts of human actions affect the energy-related outcomes of buildings in different phases. On the other hand, research has reported on how people can influence energy consumption in buildings in particular and sustainable energy transitions in general [4]. Figure 3 shows the aggregated people-centered energy solutions.


*Figure 3. Presenting the aspects of how people can affect energy solutions [22]*

Many studies focus on behavioral change initiatives and their impact on energy savings. For instance, research [23] evaluated the European behavioral change programs for 11 countries, and research [24] presented a thorough literature review on the use of behavioral science theories to analyze the energy behavior of occupants. They introduced the DNA (drivers, needs, and actions) framework to categorize the drivers of occupant behavior, the needs, and the actions that were taken by the occupants in 130 published studies. Research [25] elaborates on the impact of energy behavior by using micro-economic theories to identify the indicators and implications of energy behavior change.

## 3. Occupant behavior-related energy policies

The energy-related impact of buildings generally is directed through policies, standards, regulations, and incentives from policy-makers and governmental agencies. Furthermore, more cause-specific programs and initiatives, such as behavioral-related energy efficiency programs and initiatives, are introduced as well in the policy domain [25]. These are considered among the most cost-effective energy efficiency strategies [16]. Such regulations can be applied for individual and collective behavioral changes to achieve energy efficiency goals in buildings and the sustainable energy transition.

In recent years, due to the pandemic and global political developments, these significant events resulted in increased energy demand and a surge in energy prices. This influenced policymaking worldwide to primarily focus on short-term and swift solutions and leave the sustainable energy transition plans secondary. To ease the economic implications, especially for low-income consumers, some EU Member states introduced support mechanisms such as tax exemptions [26]. However, the development of occupant behavior policies needs special consideration from the policymakers and a detailed understanding of human-dependent energy efficiency measures and their corresponding limits. Hence, when introducing such policies and regulations, it is essential to estimate their acceptability by occupants [27].

The actions from policymakers and government agencies are exhibited through awareness and informational campaigns, promotion of technology investments to increase the energy-consciousness at a building and urban level, and translating actions into regulatory norms and standards to reduce energy consumption from occupant behavior. Furthermore, policymakers need to structure initiatives and design interventions by leveraging multidisciplinary knowledge from the technical viewpoint and the social science aspect. For instance, extracting knowledge from building science, behavioral science, social science, psychology, data science, building automation, and design and intertwining these aspects can lead to better-informed decisions.

Drawing from social sciences, the interventions that can influence occupant behavior individually or collectively are eco-feedback, social interaction, and gamification [10]. Eco-feedback is important as it informs informinginforms informed occupants of the consequences of their actions in real real-time so that they canmake more informed choices. Social interactions enable comparison among peers or communities so that the social norm influences them to lower energy consumption. Lastly, gamification is used to reduce energy consumption by engaging occupants in actions such as playful competitions. However, the long-lasting effect of such measures still needs further exploration.

## 3.1. Energy behavior-related strategies in Kosovo

Occupant behavior accounts for a significant share of the performance gap between actual and planned energy consumption in buildings [28]. Hence, including this factor in the computation of building energy consumption is important. Considering that energy performance in Kosovo's buildings is mainly conducted with traditional physics-based approaches and rarely uses advanced modeling and simulation tools that can incorporate the human dimension as well, the actual energy consumption of buildings in Kosovo is much higher than the planned consumption.

Depending on the approach, policy strategies can be established as persuasive instruments through education or communication initiatives, incentives through price reduction or tax policies, or more coercive interventions by setting limits or bans [29]. Although there have been several attempts to promote energy awareness through governmental actions, they have not resulted in long-lasting behavioral changes. For instance, Kosovo institutions introduced an initiative to subsidize households' energy consumption if their energy consumption is lower in September 2022 compared to September of the previous year, 2021. Although it presents a positive incentive, the results showed that the energy consumption was 5% higher than the previous year [30]. However these results could have been influenced by many factors, and no research was conducted on individual households to estimate the impact of this initiative. Furthermore, other initiatives presented by the government were subsidizing households for energy-efficient appliances such as heat pumps [31]. Additionally, the government introduced many energy-saving regulations in September 2022 [32], including switching lights off, lowering indoor temperature setpoints, etc.

The lack of energy-related research in Kosovo in general, and regarding occupant behavior presents explicitly a gap that needs to be addressed. For instance, there is no evidence of the drivers or motivators that would influence positive energy behavior for Kosovo citizens. Similar studies were conducted in Romania [33] and Turkey [34], which resulted in identifying drivers that motivate people towards energy-saving actions and help policymakers make informed decisions. Furthermore, there is a shortage of occupant-related studies such as on their intentions to adopt energy efficiency measures, use new technologies, and engage in pro-environmental and energy-aware actions.

Although currently, the driving force towards altered energy behavior is the increase in energy prices in the energy market, other indicators could have an impact as well. For instance, the increase of energy awareness in Kosovo would lead to energy-conscious choices by occupants, consequently resulting in lower energy use and less environmental impact [2]. This would enable the energy demand to gravitate towards more responsible and sustainable transformations to meet the user's needs [35]. For example, informing occupants on the importance of peak shaving by offsetting their daily chores to periods with less energy demand would enable less energy overload and lower costs for them as consumers. This can be tackled by emphasizing the importance of energy saving, conscious energy use, and the role of occupants in the school curricula, starting from elementary schools in science courses up to high schools [36]. Youth are known to be change agents, and considering that Kosovo is among the countries with the youngest population, the energy behavior change should start from the youth. Furthermore, the awareness campaigns should be expanded at the local and national levels. However, it is always important to convey the information comprehensively to occupants of different backgrounds.

Another solution would present the application of interventions on a community, local, or broader level. By using eco-feedback either on an individual level or by comparing energy usage among consumers, healthy competition would lead to reducing energy consumption. This can also be expanded into a gamification approach among communities [37], [38]. This can be enabled by stakeholders such as energy providers or policymakers.

## 4. Discussion

Despite the crucial importance of technical energy efficiency interventions in buildings, it is highly important to focus on the changes in human behavior simultaneously. According to [39], merging occupant behavior changes and building improvements can reach up to 75-95% of building energy consumption reduction. In times of need, when swift actions are necessary, immediate and low-cost responses can only be sought from occupant energy behavior. The energy saving in buildings can result from individual or collective behavior change. The impact of collective behavior during the pandemic [4] was reported as an excellent example of collective change toward a sustainable energy transition.

The inner dynamic nature of occupant energy behavior can only be tackled and elucidated by a multidisciplinary approach. Hence, when introducing new policies, regulations, or initiatives, it is important to informed decisions, thoroughly examined actions, not just popular ones, and test the acceptability rates of proposed actions as mentioned in [40].

Hence the findings and recommendations regarding energy behavior and related energy policies are:

- Increasing energy awareness and energy literacy by emphasizing the importance of energy savings actions in schools and through growing awareness programs,
- Introducing interventions that have been proven to be efficient solutions toward action change, such as eco-feedback, social interaction, and gamification,
- More energy behavior-related research studies will help make more informed decisions.
- Energy behavior-related policies should be carefully structured, well-informed, and properly conveyed,
- Different stakeholders in the building sector should be addressed in introduced policies through the building life cycle.

- Synergies between different fields should be sought when structuring energy behavior policies and actions for a well-rounded approach,
- Transfer learning of existing policies successfully implemented in other countries should be adopted.

Future studies need to focus on comprehensive qualitative and quantitative research on occupant behavior in Kosovo by including a diverse set of buildings, from different regions within the country including diverse demographics.

## 5. Conclusion

This review paper discusses the impact of occupant behavior on the building’s energy performance and possible actions to mitigate energy consumption. The impact was reported to vary significantly among studies and depending on the building type, considered energy type, and location. Furthermore, existing strategies and regulations were presented, and recommendations were given to increase general awareness of the crucial role of occupants in buildings in Kosovo. Among Kosovo's most used energy policies include incentives and regulations communicated as directives. Further interventions to initiate energy behavior change should be explored, such as eco-feedback, social interventions, and gamification, which could be viable short-term or long-term solutions.

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# ADRESIMI I NDIKIMIT TË SJELLJES SË NJERËZVE NË KONSUMIN ENERGJETIK TË NDËRTESAVE NË KOSOVË

## Përmbledhje

Kriza energjike ka nxitur reagime të shpejta nga qeveritë për të zvogëluar konsumin e përgjithshëm të energjisë. Meqë sektori i ndërtesave është ndër konsumuesit më të mëdhenj të energjisë, me një pjesëmarrje në përqindje prej 40%, është shumë e rëndësishme që të përmirësohet performanca energjetike e ndërtesave. Edhe pse rritja e performancës energjetike në objekte është pa diskutim ndër mënyrat më efikase për ruajtjen energjisë dhe është ndër strategjitë më të përdorura për zhvillim të qëndrueshëm, aplikimi i masave energji efiçiente kërkon shumë kohë, prandaj, kërkohen zgjidhje më të shpejta për uljen e konsumit të energjisë. Përveç shkallës së efiçiencës së objektit, dihet që një ndër ndikuesit për të mëdhenj të konsumit të energjisë në objekte është edhe sjellja apo zakonet e konsumit të energjisë të banorëve. Për shkak të mungesës së hulumtimeve lidhur me sjelljen e banorëve në Kosovë sa i përket konsumit të energjisë dhe vetëdijesimit energjetik, është shumë e rëndësishme që të analizohen tendencat e përgjithshme të njerëzve për konsum të energjisë, të diskutohet vetëdijesimi i përgjithshëm sa i përket konsumit të energjisë dhe të identifikohen masat e mundshme për rritjen e nivelit nacional të këtij vetëdijesimi. Ky punim revial paraqet një përmbledhje të literaturës ndërdisiplinore ekzistuese, duke theksuar ndikimin e sjelljes së njerëzve në konsumin energjetik të objekteve dhe strategjitë ekzistuese të shteteve tjera dhe të Kosovës për motivimin e banorëve për ndryshim të sjelljeve në sjellje pro-energji efiçiente. Po ashtu, ky punime shtjellon mundësinë e aplikimit të metodave të shkencave shoqërore e bihevioriste siç janë “eco-feedback”, ndërveprimi social, gamifikimi etj. Gjetjet nga ky punim janë të rëndësishme për shpalosjen e mënyrave për hartimin e politikave të reja energjetike në nivel të vendit për zvogëlim të konsumit energjetik nga banorët. Disa nga gjetjet dhe rekomandime nga literatura e shqyrtuar në këtë punim janë:

– Rritja e vetëdijes dhe njohurive të përgjithshme mbi konsumin energjetik duke theksuar rëndësinë energjetike dhe mjedisore të veprimeve të njerëzve në objekte, duke filluar që në vitet e hershme të shkollës përmes fushatave vetëdijesuese.
– Aplikimi i intervenimeve që kanë rezultuar të suksesshme në shtetet tjera siç është “eco-feedback” (njoftimi i banorëve se si sjellja e tyre ndikon pozitivisht apo negativisht në mjedis), si dhe intervenime të tjera si ndërveprimi social apo gamifikimi.

- Në Kosovë mungojnë hulumtime lidhur me ndikimin e sjelljeve njerëzore në energjetikë, prandaj është e rëndësishme të rritet fokusi në hulumtime të tilla.
- Politikat apo strategjitë energjetike që lidhen drejtpërdrejtë me sjelljet e njerëzve, duhet të hartohen me kujdes të shtuar, të jenë të mirë-informuara dhe të bëhet shpërndarja adekuate e informatave.
- Të krijohet sinergji në mes të fushave të ndryshme për koordinim kur bëhet hartimi i politikave energjetike që lidhen me sjelljen e njerëzve që të konsiderohen aspekte të ndryshme gjithëpërfshirëse.

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# NANOSCOPIC GUARDIANS: SILVER NANOPARTICLES IN PROTECTION OF METALS AND ALLOYS AGAINST CORROSION. A REVIEW

Abstract

Corrosion, a global economic burden, has an influence on various industries, including automotive, construction, aerospace, and oil and gas, resulting in production delays and additional costs. This study focuses on the role of nanomaterials, namely silver nanoparticles, in corrosion prevention. Nano-materials have different physicochemical properties and are useful in a variety of fields, including manufacturing, environmental preservation, healthcare, agriculture, and food sector improvements. Because of their well-known anti-bacterial and adsorption properties, silver nanoparticles are being studied for their potential in corrosion prevention. Biological methods, such as the use of plant extracts, are being investigated as a sustainable and environmentally benign option for synthesis processes. Silver nanoparticles are employed as corrosion inhibitors in various applications, highlighting their versatility and effectiveness in corrosion protection.

*Keywords:* corrosion protection, silver nanoparticles, nanomaterials, corrosion inhibitor.

## Introduction

Corrosion can be described as the gradual deterioration of a material due to chemical interactions with its immediate environment. The impact of corrosion on metallic structures carries substantial implications for the global economy. As per projections by the World Corrosion Organization (WCO), the present global economic burden attributable to corrosion, often referred to as the Cost of Corrosion (COC), exceeds a staggering $2.5

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trillion, which is approximately equivalent to 3.4% of the total worldwide Gross Domestic Product (GDP)[1].

Corrosion exerts a substantial influence on the cost implications of maintaining and executing restoration efforts across various domains, including automobiles, consumer electronics, aircraft, infrastructure like bridges and overpasses, and industrial facilities engaged in energy generation, pharmaceutical production, water desalination, petrochemical processing, and more. The consequences of indirect corrosion encompass specific setbacks such as production delays, interruptions, and the imposition of additional costs, including taxation and overhead expenses. NACE's[2] comprehensive survey highlights significant shifts in the strategic approach to corrosion management and the adoption of cutting-edge innovations, particularly within the automotive sector, which serves as a notable success story in corrosion prevention. This transformation highlights the industry's ability to adapt and employ advanced techniques and technologies to effectively combat the detrimental effects of corrosion.

Corrosion causes significant damage in many major industries (automotive, construction, aerospace, oil and gas, etc.). Researchers have made many attempts to reduce the corrosion rate of materials by utilizing protective coatings, metal plating, and corrosion inhibitors. Depending the nature of the metal, the environment, and the presence of other reducing agents, corrosion inhibitors are used to prevent metals from corroding. Among the frequently used inhibitors are molecules and compounds such as benzotriazole, imidazole's derivatives, Schiff bases, green corrosion inhibitor ionic liquids, smart coatings, drugs, nanomaterials, etc. It's not clear to us what the use of carbon nanotubes with aryl radicals of the same diazonium salt is [2], and it's also not clear how carbon nanotubes can be fermented with aryl resins from diazonium salts. However, such layers have been shown to reduce the corrosion of metals [3–7] and are very easy to apply/surface treat [8].

Corrosion also substantially threatens numerous critical industries, including automotive, construction, aerospace, and the oil and gas sector, among others [9–17]. This broad spectrum of industries affected by corrosion encompasses a range of molecules and compounds used for corrosion inhibition, such as benzotriazole [18, 19], derivatives of imidazole [20–22], Schiff bases [23,24], environmentally

[2] NACE - National Association of Corrosion Engineers (https://webstore.ansi.org/sdo/nace)

friendly corrosion inhibitors [25–27], ionic liquids [28,29], smart coatings [30], pharmaceutical compounds [31–33], nanomaterials [34–36] and more. Notably, there is a noticeable lack of research on the use of carbon nanotubes that contain aryl radicals that come from the same diazonium salt [30]. Nevertheless, these novel approaches have demonstrated their effectiveness in mitigating metal corrosion [31–35], and they offer the additional advantage of ease of application and surface treatment [36]. In the contemporary landscape, nanotechnology has emerged as a dynamic and rapidly evolving field, boasting substantial implications across many academic domains. This flourishing domain owes its momentum to the extraordinary and unparalleled physicochemical attributes demonstrated by nanomaterials within the specific dimensions of 1 to 100 nanometers. Nanomaterials have emërged as a remarkable class of materials, encompassing a wide array of examples wherein at least one dimension falls within the remarkably precise nanometric range [37].

Through considered design, nanomaterials (fullerenes, carbon nanotubes, graphene, carbon quantum dots, nanodiamonds, carbon nanohorns, nanoporous materials,core–shell nanoparticles, silicene, antimonene, MXenes, 2D MOF nanosheets, boron nitride nanosheets, layered double hydroxides, and various metal-based nanosized materials) offer the possibility of achieving exceptionally expansive surface areas. What sets nanomaterials apart is their capacity to exhibit extraordinary magnetic, electrical, optical, mechanical, and catalytic properties that diverge significantly from their bulk counterparts. Nanomaterials possess the intriguing ability to finely tune their properties to specific requirements by meticulously controlling factors such as size, shape, synthesis conditions, and suitable functionalization. These attributes encompass a strikingly augmented surface area, remarkable mechanical properties, unique optical behaviors, and heightened reactivity on a chemical level [1] [38]. As a result of these exceptional qualities, nanomaterials within this size range have found extensive and diverse utility across a broad spectrum of industries and sectors. These applications span manufacturing, environmental conservation, healthcare, agriculture, and even food-related innovations [39,40].

## Nanoparticles

The application of nanoparticles has a significant historical background, dating back to ancient civilizations approximately 4500 years ago. During this time, humanity unintentionally utilized nanoscale materials for various purposes [37,41]. In recent years, there has been considerable interest in silver nanoparticles (AgNPs), which have been extensively explored using nanotechnology-based approaches [42]. The fundamental impetus behind the investigation of nanoparticles arises from the phenomenon referred to as the quantum size effect. When investigating metal and semiconductor nanoparticles, which possess diameters on the order of a few nanometers, they exhibit significantly improved electronic and optical characteristics strongly influenced by their size and, in some cases, their shape. These nanoparticles occupy a unique position between individual atoms or molecules and bulk materials [41–45].

## Synthesis of Silver Nanoparticles

The emergence of silver nanoparticles (Ag NPs) represents a significant breakthrough in nanotechnology [46,47]. The nanoparticles hold remarkable physicochemical characteristics and demonstrate strong antibacterial activities, making them highly versatile for various applications [41,42,48]. During an era characterized by the emergence of antimicrobial resistance (AMR)[49], a problem that has been identified as a significant global health hazard by the World Health Organization (WHO, 2020), silver nanoparticles have emerged as a potential avenue for addressing this resistance [50]. The prevailing consensus among numerous studies suggests that nanoparticles possess the ability to circumvent microbial resistance mechanisms, with minimal contradictory evidence available. Furthermore, silver nanoparticles demonstrate superior antibacterial activity compared to specific antibiotics. The methods employed in the production of silver nanoparticles (AgNPs) show significant diversity, spanning a wide range of synthesis routes that range from physical [48,51] and chemical ones to biological approaches [41,48,52].

Although chemical approaches are widely used, they have certain limitations [41,42,45]. One notable restriction of these methods is their limited compliance with environmentally sustainable practices, but recent research suggests that efforts have been made to address this concern [51,52]. In contrast, physical methods demonstrate promise in terms of sustainability; nonetheless, biological methods fully exemplify the concepts of green chemistry [37,53,54], as they fit almost flawlessly with these environmentally responsible activities.

The biological synthesis of nanoparticles entails the creation of these nanomaterials by harnessing the capabilities of natural sources, which may include plant extracts, and  microorganisms like bacteria and fungi [42, 53, 54]. Numerous botanical species can be utilized for the dual purpose of reducing and stabilizing nanoparticles [51,54]. Many researchers have chosen the biological methodology to fabricate metal or metal oxide nanoparticles, employing various components of plants such as leaves, stems, roots, and fruits, as illustrated in Figure 1.


*Figure 1. A broad approach for the synthesis of silver nanoparticles utilizing plant-based materials.*

**The use of silver nanoparticles for corrosion mitigation.** Silver nanoparticles can operate as an anti-corrosion agent through the induction of protective layer formation on metal surfaces. When silver nanoparticles (AgNPs) were added and mixed with polymeric materials, for example, they greatly slowed down the corrosion of aluminum and mild steel substrates [55–64].In a study, Solomon et al. produced a poly(methacrylic acid)/silver nanoparticle composite (PMAA/AgNPs) through the in situ mixing of aqueous solutions of PMAA and silver nitrate, utilizing natural honey as a reducing and stabilizing agent [56]. The electrochemical findings indicate that the composite has shown significant efficacy as a corrosion inhibitor for aluminum in an acid-induced, corrosive environment. The efficiency of inhibition had an upward trend as the concentration of the composite grew, while it exhibited a downward trend as the temperature ascended. The potentiodynamic polarization analysis findings determine that the PMAA/AgNPs composite exhibits the characteristics of a mixed-type corrosion inhibitor.  When corrosion tests are done on an aluminum electrode in a 0.5 M $H_2SO_4$ solution, the composite stops corrosion about 85.6% of the time when 1000 ppm of PMAA/AgNPs are present.

Researchers conducted a separate documented investigation using a comparable yet environmentally responsible methodology to examine the effects of a chitosan/silver composite on the inhibition of St37 steel corrosion in a corrosive medium consisting of a 15% HCl solution [59]. Through the application of various electrochemical and advanced surface characterization techniques, including energy dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), and scanning electron microscopy (SEM), the researchers successfully verified the presence of a Chitosan/Silver film adsorbed onto the St37 surface. The isotherm studies revealed that temperature significantly influences the adsorption of the nanocomposite. Physisorption dominated the adsorption process at lower temperatures, while chemisorption prevailed at higher temperaturesEmploying a concentration of 1000 ppm of the AgNP-composite successfully attained a significant level of corrosion inhibition, amounting to 97.09%.The corrosion inhibition tests of St37 steel in 15% $H_2SO_4$ aqueous media were conducted using a comparable method, employing a composite of carboxymethyl cellulose and silver nanoparticles [57]. At a temperature of 60 °C, the weight loss technique resulted in an inhibition efficiency of 96.37%. Researchers have observed that the combination of carboxymethyl cellulose (CMC) and silver nanoparticles (AgNPs) inhibits both the anodic and cathodic reactions.inhibitedEmploying the Langmuir adsorption isotherm can elucidate the adsorption phenomenon. Basik et al. successfully developed a nano-composite, denoted as Cys/Ag-Au NCz, using Cysteine-based silver-gold [58]. They effectively employed this material to mitigate the corrosion of mild steel in a 1 M HCl environment.Before conducting the corrosion investigations, the synthesized material underwent comprehensive characterization using modern techniques. The researchers utilized X-ray diffraction (XRD) analysis, employing Debye-Scherer calculations, to determine the average crystalline size of Ag-Au nanoparticles. The results revealed a relatively uniform size dispersion, with an observed average size of 22 nm. Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX) confirmed the presence of the anticipated elemental peaks (carbon, oxygen, nitrogen, sulfur, silver, and gold) within the nanocomposite, while also revealing the nanoparticles' spherical morphologyThe system's corrosion performance achieved a corrosion inhibition rate of 95% at a concentration of 300 ppm.Asafa et al. [62] conducted a thorough examination of the impact of biosynthesized silver nanoparticles (AgNPs) on the corrosion inhibition of mild steel, stainless steel, and aluminum in a corrosive environment of 1.0 M HCl.

The results of this study showed that the surface interaction between AgNPs and these materials is very important. This was clear because the materials had high inhibition efficiencies of 52% for mild steel, 70% for stainless steel, and 62% for aluminum. Narenkumar et al. [63] studied the utilization of bioengineered silver nanoparticles synthesized using the leaf extract of Azadirachta indica.Researchers found that the extract had dual functionality, acting as reducing and stabilizing agents. These nanoparticles were investigated as an anti-corrosive inhibitor for mild steel in cooling towers, specifically in the presence of microbial-induced corrosion caused by Bacillus thuringiensis EN2, a bacterium isolated from cooling towers. The researchers' investigation revealed that the silver nanoparticles (AgNPs) showed a notable ability to effectively hinder biofilm development on the mild steel (MS1010) surface, resulting in a significant decrease in corrosion rates. The corrosion rate dropped to 0.5 mm per year, and the effectiveness of the inhibition was very high, at 77%. This is in contrast to using only plant extract, which caused a rate of corrosion of 2.2 mm per year and an effectiveness of 52% inhibition.

## Conclusions

The incorporation of silver nanoparticles as corrosion inhibitors represents a significant progress in enhancing corrosion inhibition methodologies. These nanoparticles have showcased exceptional efficacy in protection metals and alloys from corrosion across diverse and challenging corrosive environments. The adoption of green synthesis methods, incorporating plant extracts in the synthesis process, significantly amplifies the sustainability of their production. The ongoing exploration of silver nanoparticles as a corrosion prevention method is poised to usher in innovative approaches to tackle the prevalent challenge of material degradation. Continuous research and development in this field are expected to extend the spectrum of potential applications for silver nanoparticles in corrosion control. The advancement in utilizing silver nanoparticles holds promise for the development of novel solutions and treatments, effectively addressing the widespread issue of material deterioration.

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Avni Berisha

# MBROJTËSIT NANOSKOPIK: NANOGRIMCAT E ARGJENDIT NË MBROJTJEN E METALEVE DHE ALIAZHEVE KUNDËR KORROZIONIT

## Përmbledhje

Korrozioni është një fenomen që është shumë i përhapur dhe e paraqet degradimin gradual të materialeve, në radhë të parë të metaleve, si pasojë e ndërveprimeve të tyre me mjedisin. Duke ditur shkallën e gjërë të përdorimit të metaleve në degë të ndryshme të industrisë si dhe në infrastrukturë, mbrojtja e tyre nga procesi i korrozionit si rezultat i ekspozimit të vazhdueshëm në mjedise të ndryshme agresive është domosdoshmëri. Sipas Organizatës Botërore të Korrozionit vlerësohet se dëmi i korrozionit, i njohur si Kostoja e Korrozionit, tejkalon 2 500 miliardë dollarë, që është ekuivalente me 3.4% të Produktit të Brendshëm Bruto të botës. Dëmet e përmasave të tilla shkaktojnë pasoja të mëdha për sektorë të ndryshëm si: industrinë e automjeteve, pajisjeve elektronike të konsumit, industrinë e transportit, atë të infrastrukturës, të prodhimit dhe bartjës së energjisë, të çkripëzimit të ujit, atë të petrokimisë etj. Ndikimi i korrozionit shtrihet përtej dëmtimit të drejtpërdrejtë të materialeve, duke shkaktuar vonesa në prodhim, ndërprerje dhe kosto tjera shtesë.

Korrozioni i metaleve ndodh në radhë të parë për shkak të pranisë së agjentëve të ndryshëm oksidues në mjedisin që i rrethon ato prandaj për të mbrojtur ato nga korrozioni në mënyrë sa më efikase duhet përdorur shtresat mbrojtëse që mund të jenë të natyrës së ndryshme. Një ndër substancat më efikase që e bëjnë atë janë një sërë komponimesh të njohura si inhibitorë korrozioni të tilla si: benzotriazolët, derivatet e imidazolëve, aminat e ndryshme, bazat e Schiff-it, lëngjet jonike dhe së fundmi nanomaterialet. Nanomaterialet, të cilat karakterizohen nga dimensionet në rangun 1 deri në 100 nanometra, shfaqin veti të veçanta fiziko-kimike. Këto materiale, përfshirë: fullerenët, nanotubat e karbonit, grafenin, oksidin e grafenit, pikat kuantike, nanogrimcat etj. ofrojnë veti të jashtëzakonshme të ndryshme nga ato që shfaqin materialet e njëjta në shkallë makroskopike. Nanogrimcat e ndryshme, me efektin e tyre të "madhësisë kuantike", përfaqësojnë potencialin e nanomaterialeve në adresimin e çështjeve të lidhura me korrozionin dhe përtej tij. Nanogrimcat e argjendit kanë aftësi që të veprojnë si agjentë anti-korroziv duke indukuar formimin e një "shtrese mbrojtëse" në sipërfaqet e metaleve e të aliazheve. Në të shumtën e rasteve këto nanogrimca sintetizohen duke përdorur ekstraktet e bimëve si "reduktues e stabilizues sipërfaqësor" përmes "kimisë së gjelbërt" dhe si të tilla ato në shumë hulumtime shkencore janë treguar si efektive në zvogëlimin e shpejtësisë së korrozionit të metaleve e të aliazheve të ndryshme.

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