University of Belgrade, Technical Faculty in Bor

30th International Conference Ecological Truth & Environmental Research 2023

Proceedings

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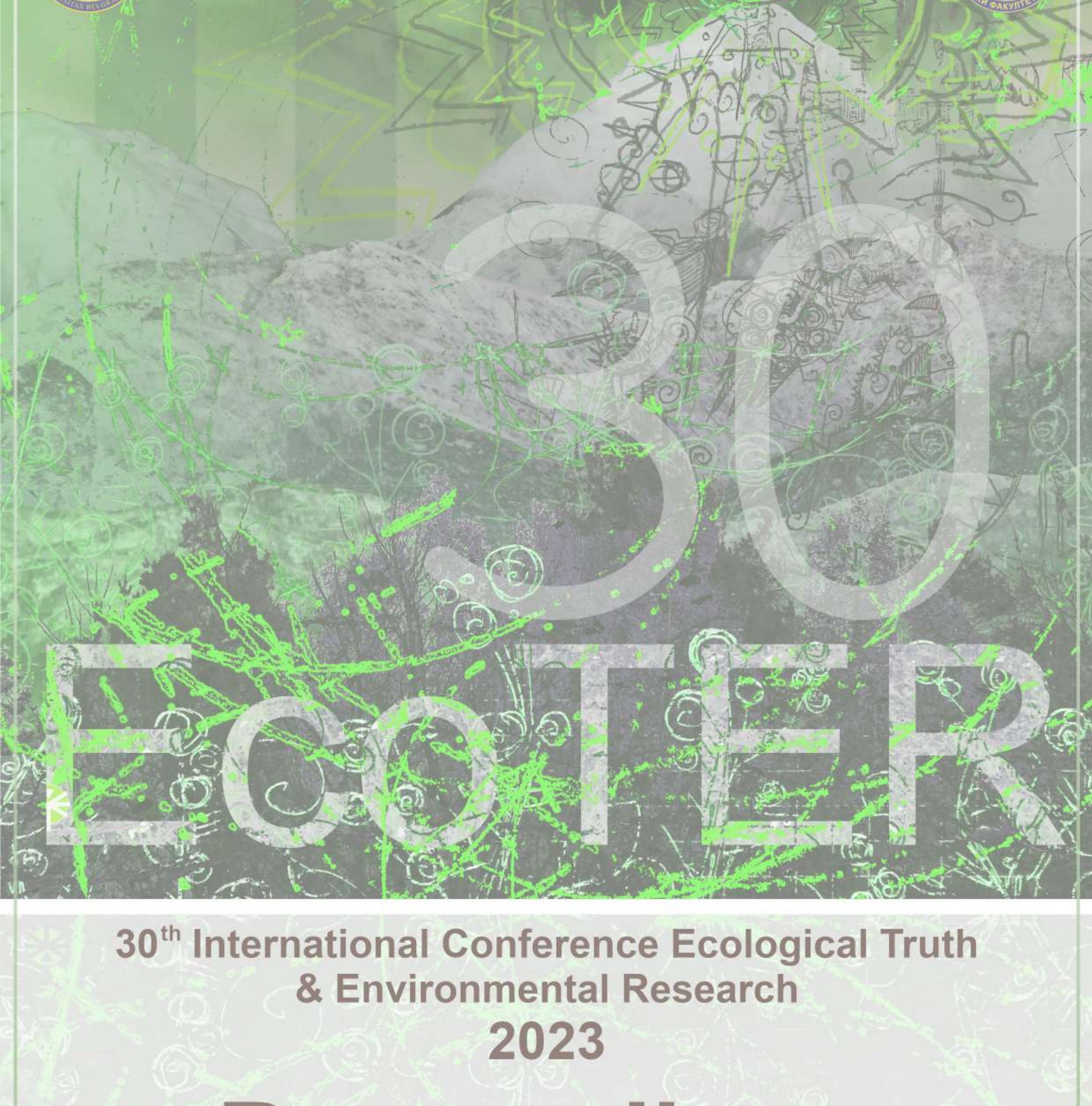

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2023

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30th INTERNATIONAL CONFERENCE

ECOLOGICAL TRUTH AND ENVIRONMENTAL RESEARCH – EcoTER’23

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Publisher: University of Belgrade, Technical Faculty in Bor

For the publisher: Prof. Dr Dejan Tanikić, Dean

Printed: University of Belgrade, Technical Faculty in Bor, 100 copies, electronic edition

Year of publication: 2023

ISBN 978-86-6305-137-9

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

502/504(082)(0.034.2)
574(082)(0.034.2)

INTERNATIONAL Conference Ecological Truth & Environmental Research (30 ; 2023)
Proceedings [Elektronski izvor] / 30th International Conference Ecological Truth & Environmental Research - EcoTER'23, 20-23 June 2023, Serbia ; organized by University of Belgrade, Technical faculty in Bor (Serbia) ; co-organizers University of Banja Luka, Faculty of Technology – Banja Luka (B&H) ... [et al.] ; [editor Snežana Šerbula]. - Bor : University of Belgrade, Technical faculty, 2023 (Bor : University of Belgrade, Technical faculty). - 1 elektronski optički disk (CD-ROM) ; 12 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Preface / Snežana Šerbula. - Tiraž 100. - Bibliografija uz svaki rad.

ISBN 978-86-6305-137-9

а) Животна средина -- Зборници б) Екологија – Зборници

COBISS.SR-ID 118723849

30th International Conference
Ecological Truth and Environmental Research – EcoTER'23

is organized by:

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TECHNICAL FACULTY IN BOR (SERBIA)

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PREFACE

The 30th international conference Ecological Truth & Environmental Research – EcoTER'23 kept three areas in focus: ecology, environmental protection and sustainable development. The conference will be held on Mt Stara Planina in hotel Stara Planina, Serbia, 20–23 June 2023. The monograph is published on the occasion of the 30th anniversary of the conference. On behalf of the scientific and organizing committee, it is a great honor and pleasure to wish all the participants a warm welcome to the conference.

The monograph is published on the occasion of the 30th anniversary of the conference.

We hope to convey the message of the conference, which is that a transformation of attitudes and behavior would bring the necessary changes. This is also an opportunity for the participants who are experts in this field to exchange their experiences, expertise and ideas, and also to consider the possibilities for their collaborative research.

The 30th international conference Ecological Truth & Environmental Research – EcoTER'23 is organized by the University of Belgrade, Technical Faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology, the University of Montenegro, Faculty of Metallurgy and Technology – Podgorica, the University of Zagreb, Faculty of Metallurgy – Sisak, the University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Association of Young Researchers, Bor.

These Proceedings 103 papers from the authors coming from the universities, research institutes and industries in 11 countries: Australia, USA, Brazil, Spain, Portugal, Libya, Italy, Bulgaria, Bosnia and Herzegovina, North Macedonia, and Serbia.

As a part of this year's conference, the 5th Student Session – EcoTERS'23 is being held. We appreciate the contribution of the students and their mentors who have also participated in the conference.

The support of the Gold donor and their willingness and ability to cooperate has been of great importance for the success of the EcoTER'23. The organizing committee would like to extend their appreciation and gratitude to the Gold donor of the conference for their donation and support.

We appreciate the effort of all the authors who have contributed to these Proceedings. We would also like to express our gratitude to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the conference participants for their support to the EcoTER'23. Sincere thanks go to all the people who have contributed to the successful organization of the EcoTER'23.

Prof. Snežana Šerbula,

President of the scientific and organizing committee

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Sustainable development and green economy

Environmental biology

Environmental and material flow management

Student Section

INFLUENCE OF SUBSTITUTES ON THE EFFICIENCY OF ORGANIC CORROSION INHIBITORS

Aleksandar Cvetković[1*], Žaklina Tasić[1], Marija Petrović Mihajlović[1], Ana Simonović[1], Milan Radovanović[1], Maja Nujkić[1], Milan Antonijević[1]

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Abstract

In this paper, a comparison of different organic compounds and their derivatives regarding the effectiveness of corrosion inhibition was made. The following derivatives of organic compounds were taken in consideration: triazole, imidazole, thiophene, hydrazine, thiosemicarbazone and semicarbazone. All of the organic compounds possess one or more heteroatoms in their structure such as oxygen, nitrogen, phosphorus and sulfur. It was found that there is no one given corrosion inhibitor which is the best for all investigated situations. Hence, according to the conditions in which the corrosion takes place, a potential organic corrosion inhibitor should be tested.

Keywords: corrosion, inhibition, organic, inhibition efficiency.

INTRODUCTION

Corrosion is a process of material degradation, most common in aqueous solutions with a large number of potential corrosion agents. Corrosion presents a big risk for human life and leads to large economic losses due to degradation of the infrastructure. Hence corrosion should be prevented or slowed down. One of the many methods used in the corrosion inhibition of metals is the application of organic compounds, known as organic corrosion inhibitors. Prevention and reduction of corrosion is a big area of research in material science. The main benefit is the reduction of economic loss as well the prevention of human casualties as a consequence of structural failure caused by corrosion. The inhibition efficiency of organic molecules is rated by their ability to cover a large percent of a metal surface. These values can be obtained by theoretical methods such as quantum chemical calculations or with experimental procedures and depend on the chemical structure of the investigated compound and medium in which the inhibitor is tested. In order for an organic compound to be classified as a good choice for corrosion inhibition it must contain at least one or more heteroatoms in its structure. In addition to heteroatoms such as nitrogen, oxygen, phosphorus and sulfur, an organic corrosion inhibitor can possesses one or more atomic functional groups and aromatic rings [1–10]. The inhibitive property is correlated with the strength of the bond between the metal surface and the organic compound, consequently the best inhibitors possess some heteroatoms like sulfur, oxygen, nitrogen or phosphorous that introduce a good binding point to the metal surface. In the literature, the most common parameters to be observed, when it comes to corrosion inhibition efficiency, are the highest occupied molecular orbital (E_{HOMO}), the lowest unoccupied molecular orbital (E_{LUMO}) energy as well as the dipole moment and other parameters that are the result of the structure of a given organic compound. The value of corrosion inhibition efficiencies are first looked at through theoretical methods as quantum chemical calculations and later proven with experimental methods such as electrochemical impedance spectroscopy (EIS), electrostatic force microscopy (EFM), mass loss method and other potentiometric methods [1–3,6,10–12].

This paper is a literature review of inhibition efficiencies of following organic compounds: triazoles, imidazole, thiophene, hydrazine, thiosemicarbazone and semicarbazone. Their values of inhibition efficiencies as well as the solution and metal surface were presented in a tabular form [2–10].

RESULTS AND DISCUSSION

Properties of organic compounds as corrosion inhibitors

Triazole and its derivatives as corrosion inhibitors

A triazole is a five-membered organic compound with three nitrogen atoms in the structure [7,13–15].

Mohamed *et al*. [7], Garcia-Ochao *et al*. [13], Sherif *et al*. [14] and Mert *et al*. [15] in their works conclude that triazoles can bind to the metal surface both with physisorption and chemisorption through one or more of their nitrogen atoms. Beside that the main orientation of triazoles is vertical and can make a polymer like chain on the surface of the metal. With different methods, the researchers have obtained different results of corrosion inhibition properties for few triazole derivatives (Table 1).

Table 1 *Inhibition efficiencies of triazole and its derivatives*

Name	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**Metal**	**Solution**	**IE% (min–max)**	**References**
5-amino-1,2,4-triazole	-12.653	-6.068	Copper	/	56^*	[7]
	/	/	Steel	0.5M HCl	77–94	[13]
3-amino-1,2,4-triazole-5-thiol	/	/	Brass	3% NaCl	94.7–98.97	[16]
	/	/	Aluminum	0.5 NaCl	76.2–86.1	[14]
	-5.948	-0.6721	Carbon steel	0.5 HCl	43.1–97.7	[15]
5-amino-1,2,4-triazole-3-thiol	-9.905	-6.504	Copper	/	95^*	[7]

*values from the literature obtained using theoretical methods

Imidazole and its derivatives as corrosion inhibitors

Imidazole is an aromatic organic compound containing two nitrogen atoms in a five-membered ring [9,17].

In the papers by Stupnišek-Lisac *et al*. [17], El-Haddad *et al*. [18], Otmačić *et al*. [19], Larabi *et al*. [20] and Benali *et al*. [21] different findings for imidazole and its derivatives as the corrosion inhibitors are presented. There are various ways for imidazoles to bind to the metal surfaces but the most dominant is physisorption through the nitrogen atoms. The results that the researchers have obtained using different theoretical and experimental metodes are presented in Table 2.

Table 2 *Inhibition efficiencies of imidazole and its derivatives*

Name	E_{HOMO} (eV)	E_{LUMO} (eV)	Metal	Solution	IE% (min–max)	References
Imidazole	-9.497	-0.704	Aluminum	0.5 HCl	20.1–70.7	[18]
	/	/	Copper	0.5M H_2SO_4	22–63	[17]
	/	/	Copper	3% NaCl	49.79–67.14	[19]
2-methyl-imidazole	-9.700	-0.574	Aluminum	0.5 HCl	21.4–76	[18]
4-methyl-imidazole	/	/	Copper	3% NaCl	37.13–63.41	[19]
4-methyl-1-phenyl-imidazole	/	/	Copper	0.5M H_2SO_4	6.8–94.3	[17]
	/	/	Copper	3% NaCl	57.68–94.34	[19]
4-methyl-1-toluene-imidazole	/	/	Copper	0.5M H_2SO_4	2–89	[17]
	/	/	Copper	3% NaCl	27.84–93.03	[19]
2-thiol-1-methyl-imidazole	/	/	Copper	0.5-1M HCl	41.07–87.5	[20]
	/	/	Copper	0.5M H_2SO_4	60.44–80.94	[21]

Thiophene and its derivatives as corrosion inhibitors

Thiophene is a heterocyclic compound that contains a sulfur hetero atom in its structure. The sulfur atom represents the place of the highest charge in the structure of the molecule. Hence, beside the aromatic ring, this hetero atom represents the most likely site of interaction with the metal surface. The authors agreed that most thiophene derivatives bond to the metal surface horizontally which makes them good corrosion inhibitors [10,12,22].

Fauda *et al*. [10], Allal *et al*. [12], Khaled *et al*. [22] and Boulkroune *et al*. [23] used various theoretical and experimental methods to determine the corrosion inhibition efficiencies of thiophene and its derivatives on different metals. The values for inhibition efficiencies are given in the Table 3.

Table 3 *Inhibition efficiencies of thiophene and its derivatives on different metals*

Name	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**Metal**	**Solution**	**IE% (min–max)**	**References**
Thiophene	/	/	Copper	2M HNO_3	32.8–80.6	[10]
	-6.5889	-0.5481	Aluminum	/	73*	[12]
	-8.709	-0.1924	Steel	0.5M H_2SO_4	35.5–43.57*	[22]
2 -thiophene carboxylic acid	/	/	Copper	2M HNO_3	50.6–74.2	[10]
	-9.3557	-1.439	Steel	0.5M H_2SO_4	62.1–78.28*	[22]
2-thiophenyl ethanol	/	/	Copper	2M HNO_3	75.4–83.6	[10]
2-acetylthiophene	-6.8874	-1.9635	Aluminum	/	86*	[12]
thiophene carbo aldehyde	-7.0024	-2.1369	Aluminum	/	92*	[12]
	-9.1906	-1.412	Steel	0.5M H_2SO_4	67.1–69.23*	[22]
	/	/	Steel	1M H_3PO_4	27.22–97.29	[23]

*values from the literature obtained using theoretical methods

Hydrazine derivatives as corrosion inhibitors

Hydrazine contains two nitrogen atoms that are connected with a double bond. In this paper, a few hydrazine derivatives are mentioned, mostly hydrazines with two functional groups such as thiophene, pyrrole, pyridine and furan. The functional groups distribute the electric charge around the molecule which makes their inhibition efficiencies differ. Hydrazines tend to bind to the metal surfaces in the vertical form which is not ideal for corrosion inhibitors [5,11].

Azzouzi *et al*. [5] and Belghiti *et al*. [11] have done both theoretical and experimental investigation of hydrazine with two functional groups of thiophene, pyrrole, pyridine and furan on their inhibition efficiencies on steel. The results are given in Table 4.

Table 4 *Inhibition efficiencies some hydrazine derivatives on steel*

Name	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**Metal**	**Solution**	**IE% (min–max)**	**References**
1,2 - bis(thiophen-2-yl methylene) hydrazine	-5.9529	-2.3333	Steel	2M H_3PO_4	85.75*	[11]
	-7.7033	-4.5146	Steel	1M HCl	50.3–64.2	[5]
1,2 - bis(pyrrol-2-yl methylene) hydrazine	-5.4642	-1.8155	Steel	2M H_3PO_4	84.93*	[11]
	-7.5986	-4.2467	Steel	1M HCl	86.7–95.7	[5]
1,2 - bis(pyridin-2-yl methylene) hydrazine	-6.5020	-2.4688	Steel	2M H_3PO_4	82.04*	[11]
1,2 - bis(furan-2-yl methylene) hydrazine	-5.8718	-2.1695	Steel	2M H_3PO_4	79.5*	[11]

*values from the literature obtained using theoretical methods

Thiosemicarbazone and semicarbazone derivatives as corrosion inhibitors

In semicarbazones and thiosemicarbazones, the main role of binding to the metal surface is performed by the azomethyl group as well as nitrogen atoms. Thiosemicarbazones have better corrosion inhibition efficiency compared to semicarbazones due to the presence of sulfur in place of oxygen atoms in their structure [4,6,24,25].

Goulart *et al.* [4] and Khaled *et al.* [13] performed experimental analysis of thiosemicarbazones and semicarbazones with pyridine as a functional group. The results of their findings are given in Table 5.

Table 5 *Inhibition efficiencies of some tiosemicarbazones and semicarbazones derivatives*

Name	E_{HOMO} (eV)	E_{LUMO} (eV)	Metal	Solution	IE% (min–max)	References
2-pyridine carbaldehyde thiosemicarbazone	-8.525	-0.625	Carbon steel	1M HCl	44–92	[4]
	-8.9898	0.7565	Aluminum	1M HNO_3	20.5–91.2	[24]
2-pyridine carbaldehyde semicarbazone	-9.208	-0.408	Carbon steel	1M HCl	14–38	[4]

CONCLUSION

The various substitutes play a different role in the strength of binding to the metal surface which correlates to the inhibition efficiency of organic compounds. The general trend for good corrosion inhibitors is that they possess one or more atoms of nitrogen, oxygen, sulfur or phosphorus. Beside those atoms, the organic corrosion inhibitor performs better when it has aromatic rings and additional functional groups in its structure.

According to the mentioned facts, the selection of an organic compound as a corrosion inhibitor should be made in relation to the conditions under which corrosion occurs as well as the type of metal.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Science, Technological Development and Innovation of the Republic of Serbia for financial support according to the contract with the registration number (451-03-47/2023-01/200131).

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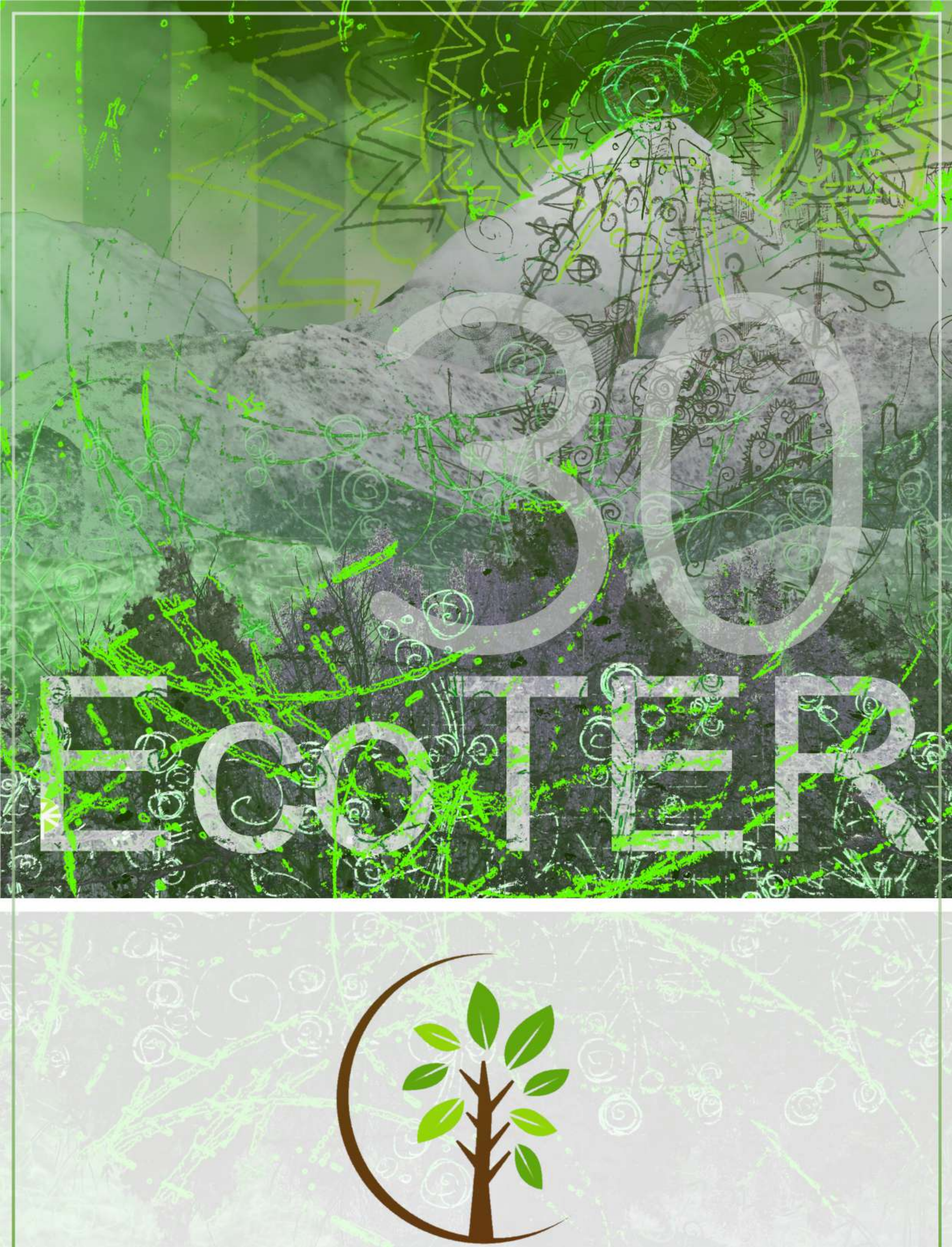

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