BABEȘ-BOLYAI UNIVERSITY
FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING

DOCTORAL THESIS

-ABSTRACT-

Scientific coordinator
Prof.dr. Liana Maria Mureșan

PhD student
Ana-Maria Săcară

Cluj-Napoca

2018

FACULTY OF CHEMISTRY AND
CHEMICAL ENGINEERING

Chemistry Doctoral School

Adsorption and electrochemical detection of certain pollutants from aqueous solutions

Scientific coordinator
Prof.dr. Liana Maria Mureșan

PhD Student
Ana-Maria Săcară

Cluj-Napoca

2018

THESIS TABLE OF CONTENTS

INTRODUCTION

Concern for the environment has become more and more stringent in the last decade due to climate change and lower availability of drinking water. These are everyday problems in parts of the world that affect local populations directly and immediately, but the effects are felt globally over time. Pollution has reached almost everywhere, and its effects are increasingly visible. Water pollution is a major problem that has become increasingly apparent with industrial progress, plus the creation of more and more waste that invades the seas and oceans.

Industrial waste waters can contain dyes or heavy metals or even various endocrine disruptors (such as phthalates, organochlorinated compounds such as dichlorodiphenylyl-trichloroethane (DDT) and dichlorodiphenylyl dichloroethylene (DDE) - its metabolite, polychlorinated biphenyls (PCB), bisphenol (BPA) and dioxins). Maintaining these substances within limits is a challenge that can only be dealt with by appropriate legal regulations. Unfortunately, many dangerous pollutants do not have clear limits in the law, so that their emission into the environment can occur accidentally or willfully without any consequences.

As a negative example, Malachite Green dye can be considered. This industrial dye, considered as a hazardous substance, is not regulated by the European Commission, although it has very similar properties to that of Violet Crystal (which is limited to 30 mg / kg or 0.003% by weight, according to section 43 of Annex XVII of REACH) and proven toxic effects.

The main objectives of this work are precisely the retention of Malachite Green (MG) and its detection from synthetic aqueous samples in order to develop new methods of depollution.

In the first part, MG retention is presented with natural, unconventional materials by adsorption.

In order to find new, efficient and economically cost-effective ways to remove dyestuffs, we have used adsorbents that are accessible and environmentally friendly (eg biomass from fir cones, activated charcoal, etc.). This paper addressed the removal of MG by adsorption with biomass from fir cones, fir trees (Abies nordmanniana), grape stalk and live terrestrial moss. Detection was performed by UV-Vis spectrophotometry, but due to the complexity of the matrix of real samples, detection of MG in aqueous solutions is often laborious, difficult or even impossible with established techniques, so it was decided to try a new selective method, using electrochemical methods.

In the second part, MG detection is developed with the help of new modified electrodes, proposed as sensitive and selective dye sensors. Various materials, such as cerium nanoparticles, silica powders, organic molecules, or carbonaceous materials, have been used for sensor development. Electrochemical methods have advantages in detecting analysts of interest due to their speed, simplicity, low cost, and the possibility of prompt miniaturization of the apparatus (compared to other applicable analytical methods).

I. THEORETICAL ASPECTS

Water pollution with various organic coloring compounds has its origin, most often, in the textile industry. This branch of light industry is the most frowned upon by green chemistry because it does not respect many of its principles and it is not in agreement with the ideology of sustainable development either. Depollution of industrial effluents should be done until concentrations of pollutants are reached which fall within the limits imposed by the applicable environmental legislation so as not to affect the aquatic ecosystems in which they are discharged.

In order to find new, efficient and cost-effective ways to remove dyestuffs, we have used adsorbents that are as accessible and environmentally friendly as possible (eg biomass from fir cones, activated charcoal, etc.)

On the other hand, the detection of colorants by conventional methods involves sophisticated and expensive equipment, as well as staff with specialized training. The same can be said for heavy metals such as Pb, Cd, Hg or As ions. Electrochemical methods offer a quick, cheaper, easier to use but also more environmentally friendly alternative. The use of electrodes modified as specialized electrochemical sensors allows reaching detection limits comparable to standard methods but requires optimization for each analyte.

In the present paper, the removal of Malachite Green dye by adsorption on biomass from fir cones, fir tree needles, grape stalks and live bryophytes, as well as its detection and heavy metal detection using electrochemical methods, using modified electrodes, has been addressed.

1. Malachite Green

Malachite Green (MG) is an organic compound used as a coloring agent in the textile industry and more recently as a veterinary antifungal product in aquariums.

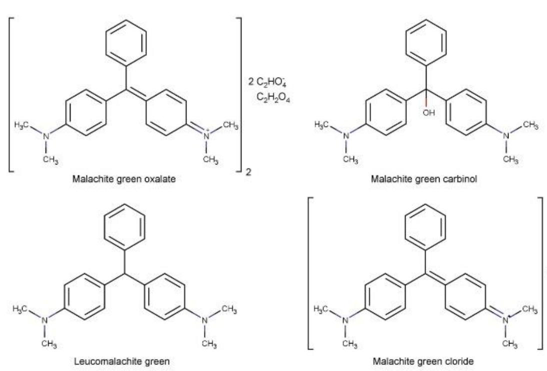

Fig. 1 Chemical structures of MG in diferent formes [1]

The property of inhibiting the proliferation of different mushroom species is known, but the use of this dye in treatments is strongly disputed due to increased toxicity to fish. Industrially, MG is used to give color to textiles, leather and paper.

1.1. Structure and properties

MG is part of the class of triarylmethane dyes. The different structures do not affect the color of the solution except the reduced color, which is colorless. The molecular weight of the ionic dye is 329.461 g/mol and has the following molecular formula: $C_{23}H_{25}N_2$.

1.2. Applications

MG is primarily used as a coloring agent, so thousands of tons of this compound are produced annually for this application [2]. Due to the intense color it has, MG is also used as a coloring agent for some biological samples to be analyzed under microscope [3]. MG has been used as an antifungal and ectoparasiticidal agent since 1936 [4]. Its antifungal activity is proven for the oapons of the genus *Saprolegnia* and for other types of fungi that infest the eggs of cultured fish. The colorless (leuco) form of MG is used in forensic chemistry to highlight blood traces [5]. MG has been used frequently in the 1950s to expose thieves. When handling the marked goods, they may notice an intense skin coloring that lasts a few days without washing with an alcohol or acetone type solvent [6]. Finally, it can be said that MG may also be used as a pH indicator due to the two electronic transitions that change its color [7].

MG first transition	
pH under 0.2	pH over 1.8
MG second transition	
pH under 11.5	pH over 13.2 (colorless)

Fig. 2 MG color shifts acoortding to pH [7]

1.3. Dye synthesis

MG was first obtained in 1877 by Fischer by condensation of a two-molecule dimethylaniline benzaldehyde molecule.

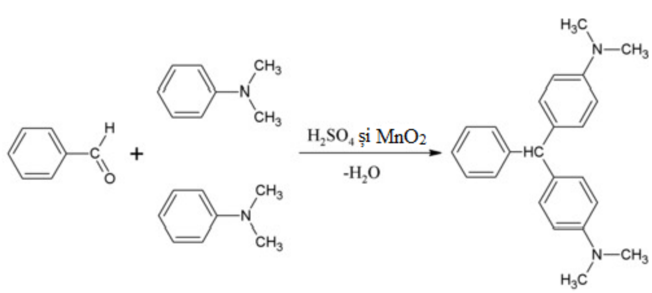

Fig. 3 MG synthesis reaction

In the first step of the condensation the basic form results in leuco malachite [8]. In the second step, the colorless compound is oxidized in the presence of oxidizing agents with high electrochemical potential (PbO_2 or MnO_2) in the ionic form, that of MG, which is colored [9].

2. Biosorption

Biosorption is a complex process by which the polysaccharide matrix of a biological material traps ions from an aqueous solution in its structure. The process may involve several mechanisms: physical adsorption, chemisorption, ion exchange, complexation, coordination, chelation, or micro-precipitation. Due to the polyvalent nature of this process, its full understanding is difficult to achieve but absolutely necessary in order to use and find new and more efficient materials than those known so far [10].

2.1. Adsorbents

Natural adsorbents are materials of biological origin capable of containing pollutants of interest from aqueous solutions through well-studied mechanisms. A priority in this respect is agricultural waste due to its abundance and economic and logistic accessibility.

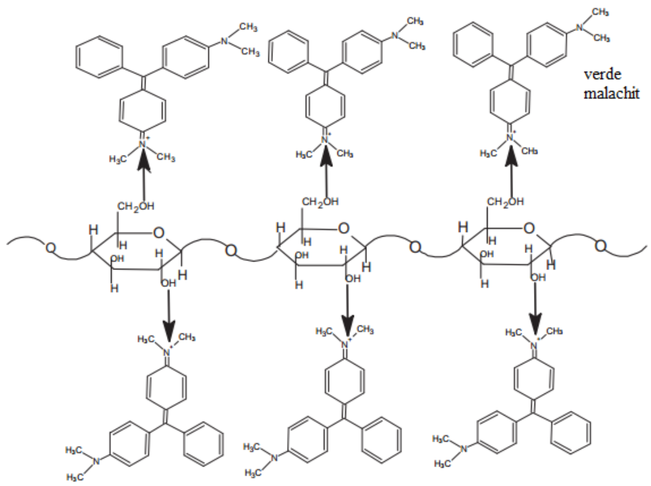

Fig. 2.1.1 MG binding to celulose

Another category of potential materials is represented by those based on chitine [11] or chitosan [12] matixes. A last category includes zeolites, diatomites and clays, as well as different mixtures of these silicious materials [13].

Synthetic adsorbents includ organic polymeric adsorbents, ion change resins, synthetic zeolites, silicagel, activated carbon etc.

3. MG adsorption investigation by mathematical modelling

3.1. Adsorption isotherms

Typically, adsorption is described by isotherms, namely equations that mathematically specify the amount of adsorbent retained as a function of pressure (for a gas) or concentration (for a liquid) at constant temperature. Most often, the linearized forms of these equations are used to facilitate mathematical operations.

The *Langmuir isotherm* is based on the premise of a single molecular layer adsorption that takes place on a finite number of sites with the same adsorption energy without side interactions between molecules adsorbed on neighboring centers [14].

The *Freundlich isotherm* considers that adsorption takes place on heterogeneous surfaces, and the adsorption centers are both different in nature and energy. This model assumes that there is a direct link between adsorption capacity and the concentration of the pollutant at equilibrium.

The *Temkin isotherm* takes into account indirect adsorbate-adsorbate interactions, assuming that the adsorption energy, expressed as thermal energy, decreases linearly with the degree of coverage [15].

The *Dubinin-Radushkevich isotherm* is generally applied to characterize an adsorption process with a Gaussian distribution of energy on a heterogeneous surface [16,17].

3.2.Mathematical models

3.2.1. Kinetic model

A single model will best correlate with the data involved, so the choice is clear based on the value of R^2. By means of these models, the slowest stage of the process can be identified. It is well known that the reaction rate is directly proportional to the adsorbate concentration when adsorption is the only process occurring on the surface of the adsorbent. In this case, we have a *pseudo I order kinetic model* [18,19]. The *pseudo II order kinetic model* is based on the assumption that there is a proportionality between the sorption capacity and the number of active sites occupied by the sorbent.

3.2.2. Modelul difuzional

To characterize a biosorbtion process, it is necessary to understand the diffusion mechanism in the two characteristic stages, external and internal. This step is particularly important because diffusion is always present in an aqueous medium, and adsorption processes can often be the determining rate step, which is why this aspect should be treated from a kinetic point of view. In the case of diffusion, the coefficient that shows correlation between the process and model is the value of the intercept and not the linear regression coefficient, as in other cases. The value of R^2 can still confirm whether the model is indeed the right one for the studied process.

3.2.3. Thermodinamic study of adsorption

A thermodynamic study at equilibrium based on isothermal processes was also performed in the last part of the analysis on adsorption results using mathematical models. Thermodynamic parameters, including free enthalpy (ΔG °), entropy (ΔS °) and enthalpy variance (ΔH °), were determined and analyzed.

3.2.4. ANFIS modelling

ANFIS modelling has become a powerful and efficient instrument for extracting tricky information from experimental data [21,22]. Models built by using ANFIS are destined to find a mathematical correlation between a given set of experimental input-output data that are linked by a causality relationship [23].

4. MG detection in aqueous solutions

4.1.NON-electrochemical methods (HPLC, MS, FIA, UV-Vis, SERS)

Malachite Green is a triaryl methane organic compound with specific properties that can be found in both aqueous and biological (tissues) media. Considering this, it is normal that the usual methods of determination are part of the type used for organic compounds with similar properties. This category includes HPLC, MS, FIA, UV-VIS, SERS as stand-alone or coupled techniques for determination og MG in different real samples.

4.2.Spectroelectrochemistry

Spectroelectrochemistry is a method that combines reaction-oriented electrochemistry and spectroscopy focused on speciation, a combination that allows a more complete analysis of electron transfer processes and redox reactions in general. This technique is a convenient method for obtaining redox spectra and potentials and to observe the chemical reactions of some electrogenerated species [24].

4.3. Electrochemical methods

4.3.1. Modified electrodes

Electrochemical sensors transform the interaction between the electrode and the species to be determined in a useful signal either spontaneously or as a result of an external electrical stimulus. The development of electrochemical sensors continues to be a growing area of electrochemistry. Improvements in the stability, selectivity, and characteristics of these sensors are highly desirable to meet the new challenges generated by complex samples such as clinical and environmental samples. One area that offers significant potential for improving the characteristics listed above is chemically modified electrodes (CME). The ability to control and manipulate their surface properties can lead to a variety of attractive possibilities.

5. Heavy metal water pollution

Heavy metal pollution has become one of the most serious environmental problems today. Depollution of heavy metal effluents is particularly important due to their persistence in the environment. In recent years, various methods of removing heavy metals from wastewaters have been extensively studied. These technologies include precipitation, ion exchange, adsorption, membrane filtration, coagulation and flocculation, flotation, and electrochemical methods. It is apparent from the literature that ion exchange, adsorption and membrane filtration are the most frequently studied methods for treating wastewater loaded with heavy metals [25].

5.1. Detection methods for heavy metal ions

Heavy metals can be detected by various methods such as spectrometry (AAS, MS), spectrophotometry - colorimetry (by complexing with organic reagents that change color once they bind the metal), but also electrochemical. Atomic Absorption Spectroscopy (AAS) is an analytical technique used to quantify metals and metalloids by converting a sample to vapor and measuring absorbance at a wavelength specific to the element of interest.

II. ORIGINAL CONTRIBUTIONS

In the first part of this paper the results which represent the original contributions of the doctoral student regarding the removal and detection of Malachite Green (MG) from aqueous solutions are presented. Pollutant removal was achieved by biosorption, a process presented and explained in the theoretical aspects, on biomass derived from fir (*Abies nordmanniana*) cones and needles, grape stalk, but also on two species of live terrestrial moss.

On the other hand, in the context of the need to verify the residual concentration of MG in biosorption treated waters, detection of this colorant is a matter of great interest. Initially, MG detection was performed by UV-Vis spectrophotometry. As an alternative to this method, several sensitive and selective sensors for MG detection have been developed in the thesis, starting from a chemically modified glassy carbon electrode using several materials with electrocatalytic properties.

A second objective of the research was the development of electrochemical sensors based on glassy carbon electrodes modified with silica nanoparticles and Nafion for the selective detection of Cd (II) ions. Several types of mesoporous silica have been used, characterized by large specific areas and good adsorption properties for improving the performance of electrochemical sensors.

Some attempts have also been made to produce new modified electrodes for the detection of MG and Cd (II) that did not have the expected performance, but which gave rise to further investigations that led to a deeper understanding of the processes involved in electrochemical detection of these species.

6. MG adsorption using fir (*Abies nordmanniana*) cone biomass

Following the biosorption study, we can say that this depollution process is a simple, inexpensive and viable alternative to classic methods of removing dyestuffs. Working parameters have an important contribution to the overall process efficiency, so optimal values have been determined for each. From the results we noticed the following: the biomass adsorption capacity is directly proportional to the initial concentration of the pollutant, it varies inversely with the size of the particles and is directly related to the amount of adsorbent used and the contact time (until installation of equilibrium).

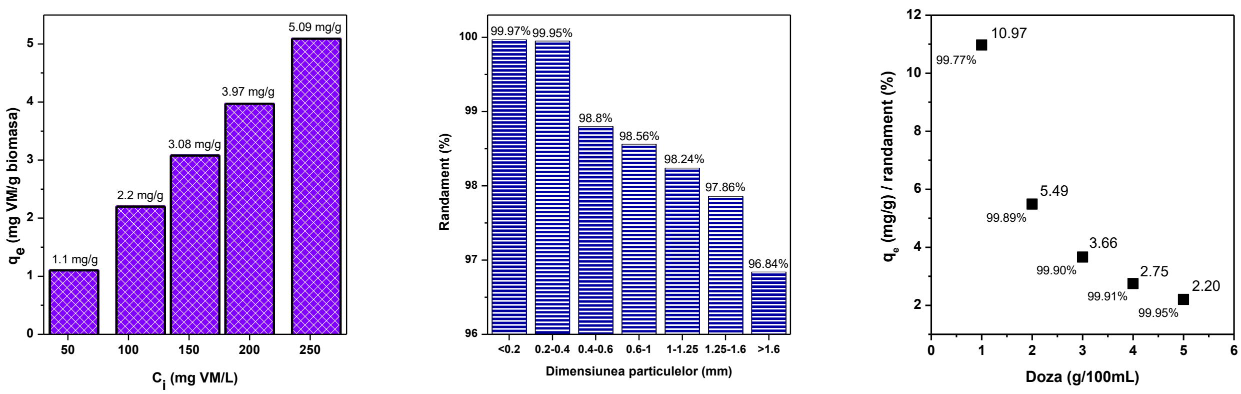

Fig. 4 The influence of various working parameters

All these aspects are well known and explained in the literature, respecting the same behavior regardless of material. Particularly, however, in the case of MG biosorption, an acidic pH of 3.3 was determined to be most desirable for the adsorption process and a system temperature of 60 ° C.

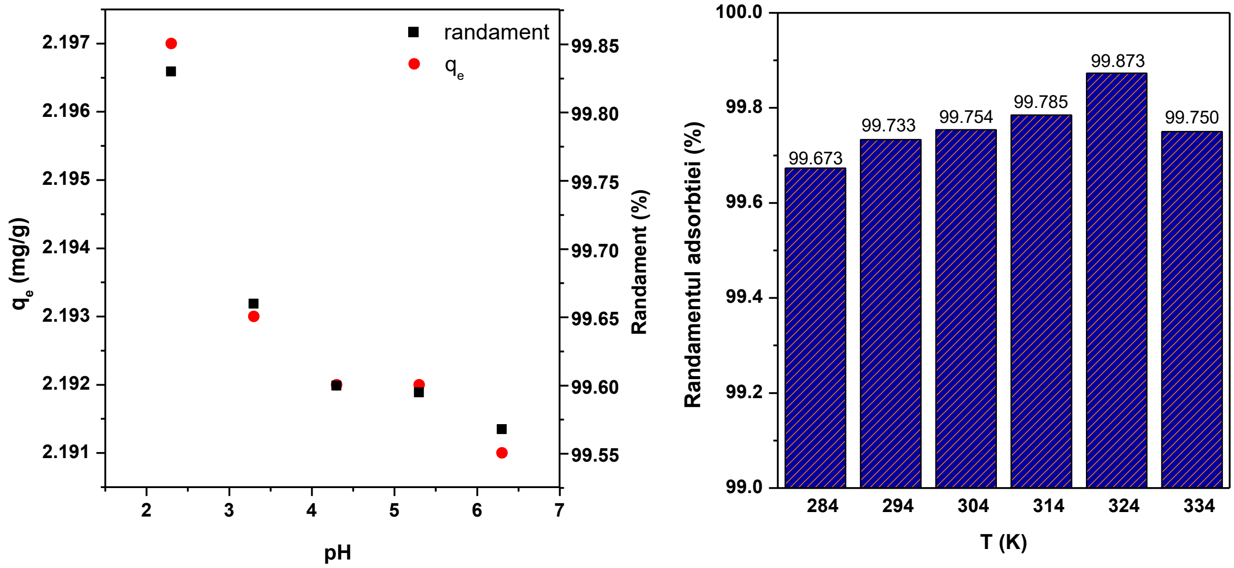

Fig. 5 The influence of solution pH and temperature

The process evolves after a second order kinetics, involving diffusion in the process mechanism, adsorption taking place according to the Freundlich isotherm. These results were confirmed and supplemented by ANFIS predictions.

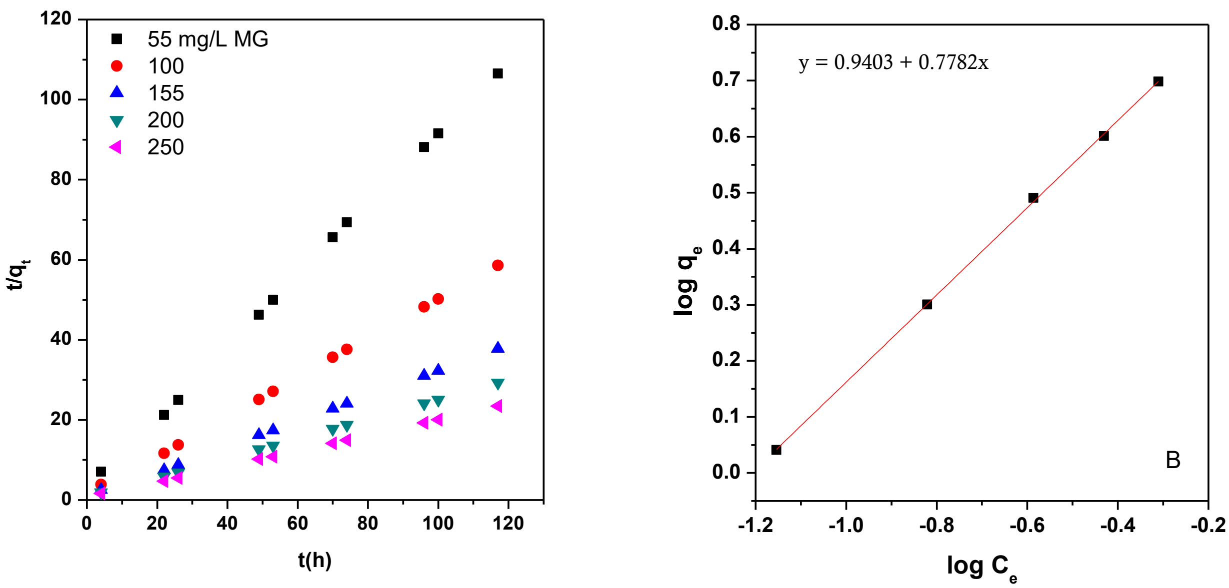

Fig. 6 Pseudo-second order kinetics Freundlich liniarisation models

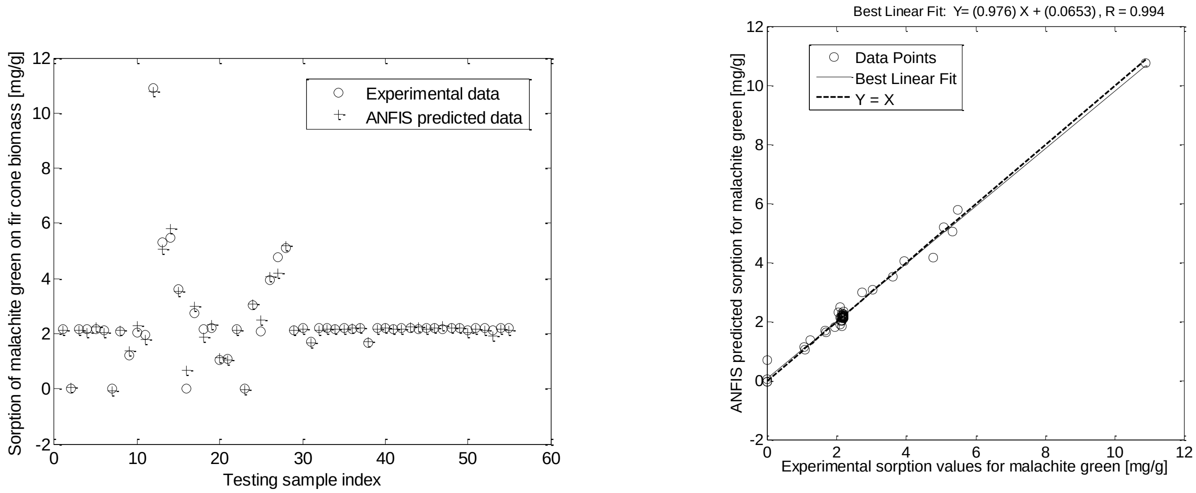

Fig. 7 ANFIS prediction results

7. MG adsorption using other biomaterials

Biomass made from fir needles had good performance in removing MG, but the natural wax layer is an obvious impediment that has to be removed. Immobilization in the alginate matrix was very favorable in terms of adsorption capacity yield.

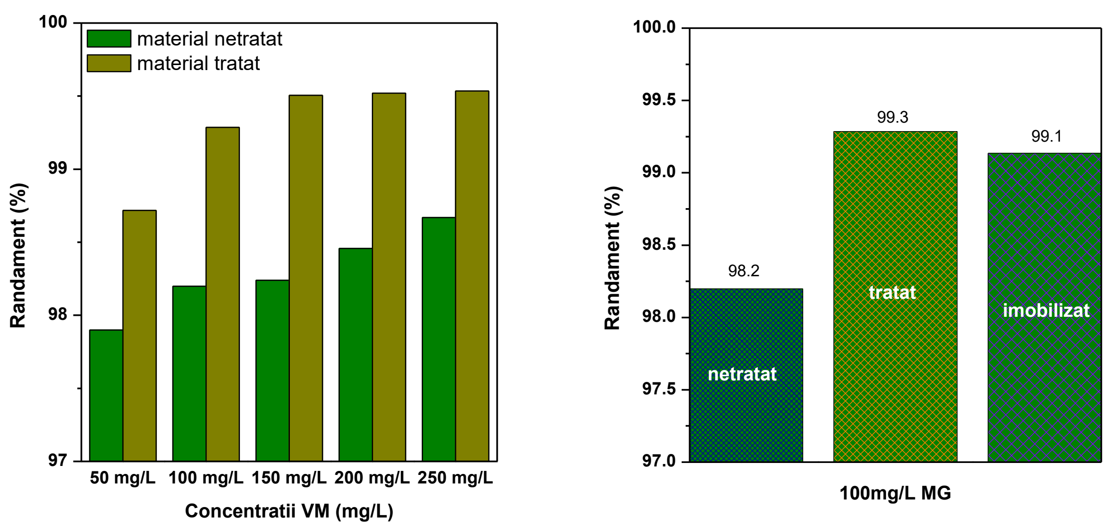

Fig. 8 Adsorption yelds for different biomass types obtained from fir needles

Grape stalk also has a good depollution potential, naturally having many functional groups that play an important role in this respect. The logistics and economic availability of grape stalk are the main advantages of using it as a biosorbent.

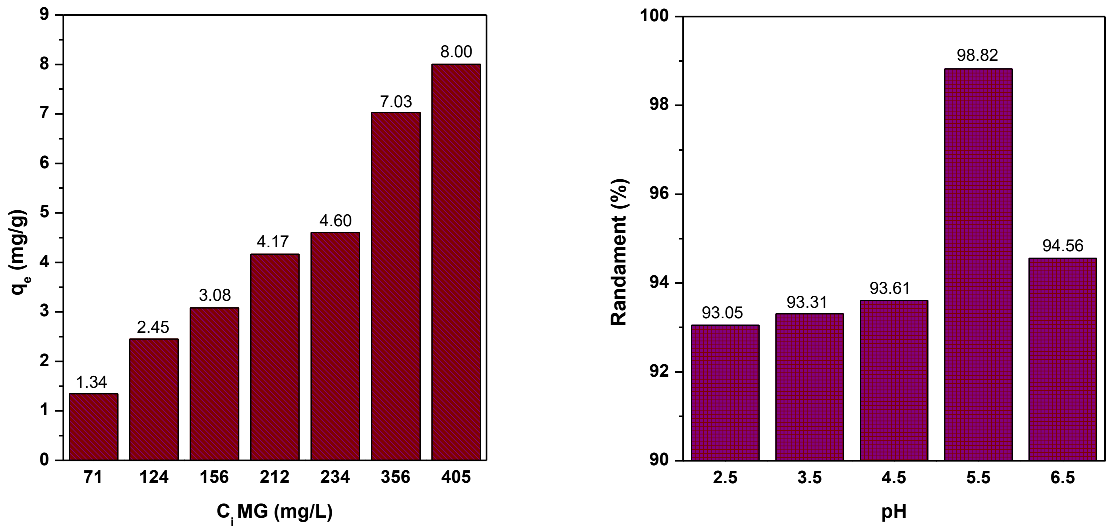

Fig. 9 Adsorption yelds of grape stalk depending on intial dye concentration and solution pH

In terms of yield, all materials were very effective, but in order to make a comparison between the biomasses presented, q_e (adsorption capacity) can be considered as a common factor. This parameter is much more descriptive than the particular yield of the material, so we can safely say that under the given conditions biomass obtained from fir cones was the best material tested with q_e = 10.97 mg/g, followed by grape stalk with q_e = 8.00 mg/g and finally fir needles with q_e = 4.92 mg/g. Live moss were the most effective biomaterial tried for removing MG, but the study of adsorption should be continued and optimized both in terms of working parameters and ethical considerations.

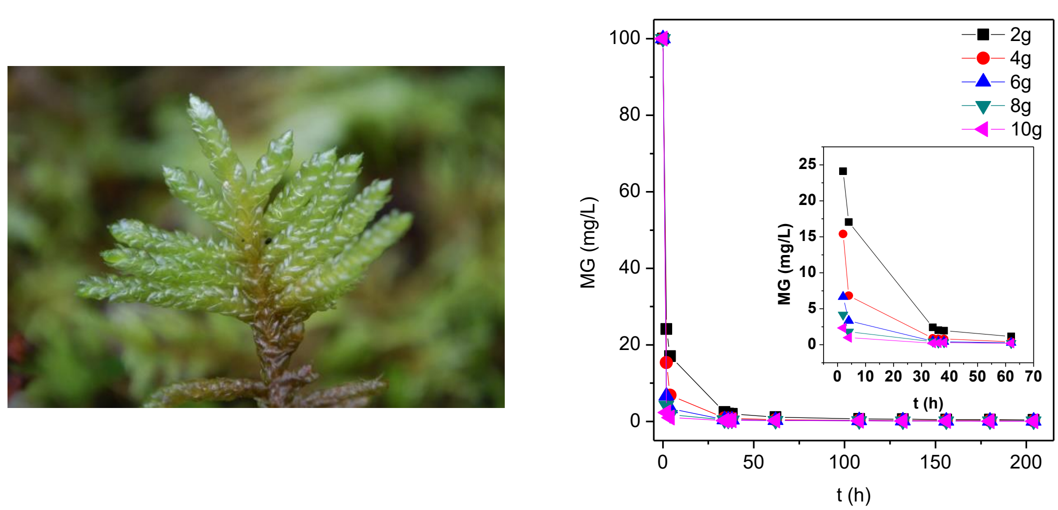

Fig. 10 *Pseudoscleropodium purum* (image) and the adsorption rate of MG from a solution with C_i = 100 mg/L

8. Electrochemical sensor based on glassy carbon modified with carbonaceous nanomaterials (GC/carbon/Nafion)

In an attempt to develop a MG-sensitive electrode by using simple and accessible materials, several carbon-modified electrodes have been prepared and characterized in this study. The peak current of MG oxidation by SWASV was proportional to the dye concentration over a wide range across all the electrodes tested.

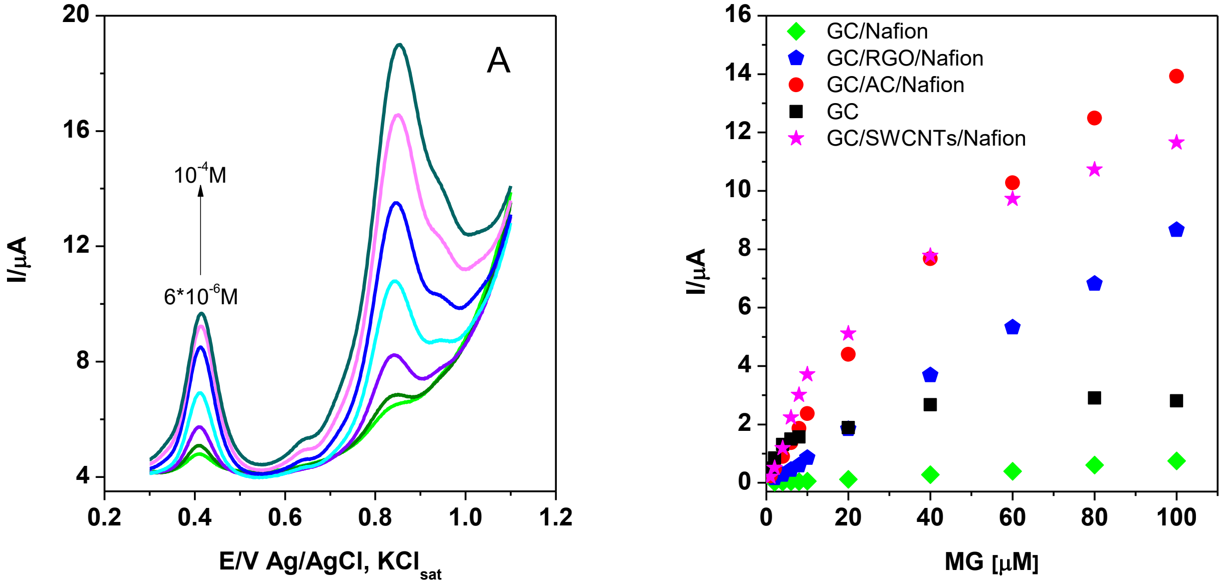

Fig. 11 SWASV curves at GC/SWCNT/Nafion and calibrartion curves

All the carbon based materials tested demonstrated a beneficial effect in the MG detection process due to the higher active surface and improved conductivity, which led to a more sensitive sensor with a lower detection limit than the unmodified glassy carbon electrode.

Table 1. Electroanalitical parameters

	GC/Nafion	**GC/SWCNT/ Nafion**	**GC/RGO/Nafion**	**GC/AC/Nafion**
Sensitivity (A/M)	0.008±0.001	0.236±0.003	0.087±0.011	0.403±0.013
Liniar domain (μM)	2 – 100	1 – 10	1 – 90	1 – 10
DL (μM)	7.880	0.3308	3.9372	0.7763
R^2/N	0.9945/10	0.9990/6	0.9986/10	0.9945/6

Carbon Nanotubes (SWCNT) have proven to be an excellent material for the development of sensible sensors, providing the best results in SWASV and amperometry with low detection limits. The new artisanal, AC-based material has not achieved SWCNT performance, but is comparable to commercial RGO, while being much cheaper and more affordable.

9. Electrochemical sensor based on glassy carbon modified with cerium nanoparticles ($GC/CeO_2/Nafion$)

In this study, a new electrochemical sensor for determining MG dye was made by modifying the surface of a GC electrode using a suspension of CeO2 nanoparticles (NP) and Nafion solution. The obtained GC/CeO2/Nafion electrode demonstrated good stability, sensitivity and selectivity to MG and a low detection limit.

Table 2. Electroanalitical parameters

Electrod	Method	Sensitivity (A/M)	DL* (μM)	Liniar domain	R^2/N
GC		0.29± 0.02	3.260	1 - 4	0.995/3
GC/Nafion	SWASV	0.0080±0.0002	7.880	2 - 100	0.9945/10
$GC/CeO_2/Nafion$		0.28 ±0.01	1.025	1- 10	0.9942/6

The electrocatalytic effect exerted by CeO_2 was mainly attributed to the easy change in the oxidation state between Ce^{4+} and Ce^{3+}, as well as the presence of oxygen vacancies/defects in the NP lattice structure, alternating between CeO_2 and CeO_2-x during redox reactions.

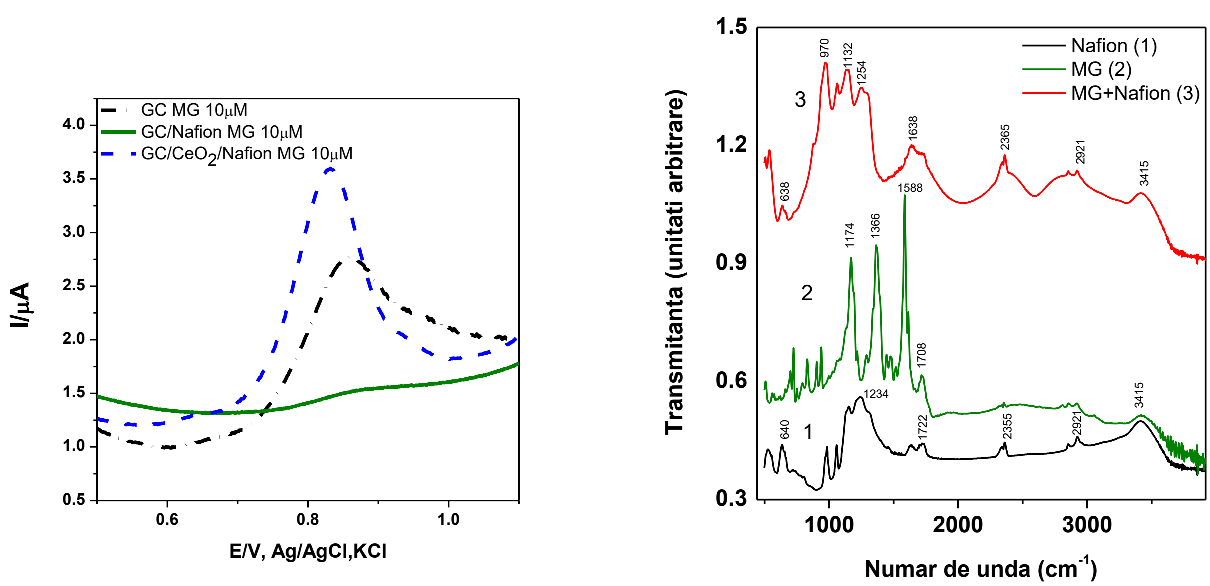

Fig. 12 Electrocatalytic effect of Ce on the electrochemical response of the electrode; FT-IR spectra

A favorable ionic association of the cationic dye with the sulfonate group of the Nafion ionomer was highlighted by FT-IR measurements, justifying the choice of Nafion as an immobilizing matrix for CeO_2 NP.

Table 3. UV-Vis and electrochemical detection results in a real sample

No. sample	**Detected (μM)**		**Retrieval interval (%)**
	UV-Vis Spectroscopy	**GC/CeO₂/Nafion Electrod**	
1	11.812 ± 0.115	11.457 ± 0.159	94.39 – 101.12
2	12.138 ± 0.116	11.943 ± 0.184	

Comparison of the results obtained for real samples with the standard method for detecting shows the comparable performances of the new electrode with UV-Vis spectroscopy results, without having the limitions of the spectroscopic analysis in terms of interference from different colored natural matrices that may compromise such determinations.

10. Electrochemical sensor based on glassy carbon modified with silica nanoparticles (GC/silica/Nafion) for MG detection

Three different mesoporous silica powders were used to prepare modified glassy carbon electrodes coated with a ion exchange polymer - Nafion for use in the electrochemical detection of MG.

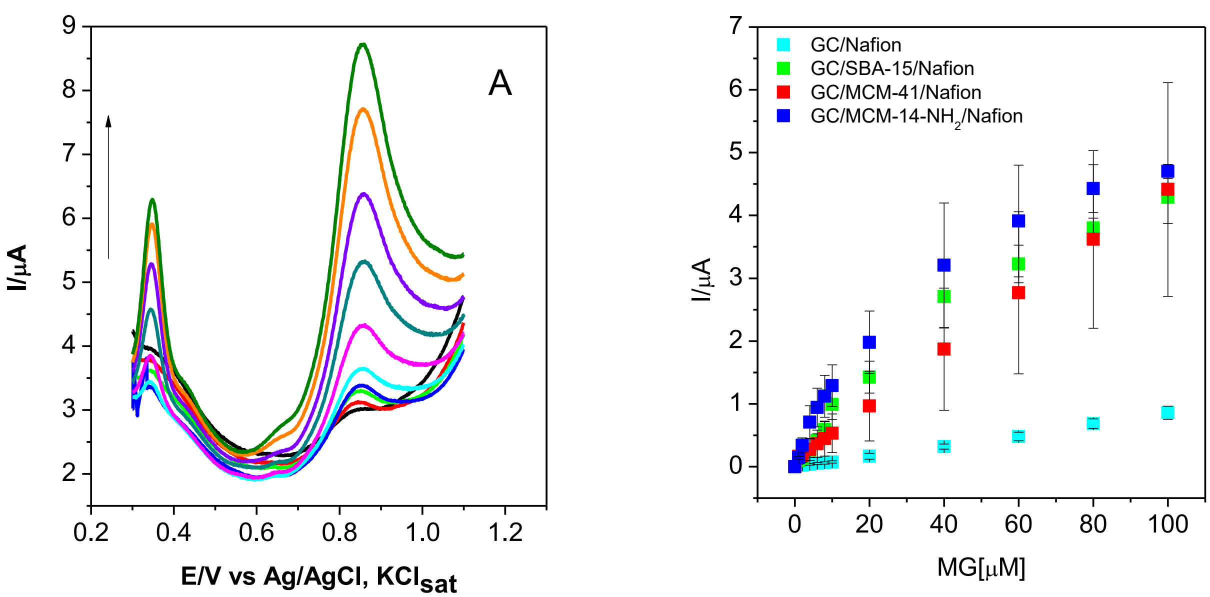

Fig. 13 SWASV curves at GC/MCM-41-NH_2/Nafion and calibration curves

Sensor preparation is simple, fast and cost-effective. The adsorbent properties of silica powders and their ordered structure were exploited in a preconcentration step, and the accumulated species were detected by square wave voltammetry. The presence of any type of silica at the surface of the electrode improved the electrochemical response compared to the unmodified GC electrode. On the other hand, the presence of MCM-41-NH_2 in the composite matrix on the surface of the electrode led to the best results in MG detection compared to the other modified electrodes. The GC/MCM-41-NH_2/Nafion electrode showed good stability, sensitivity and selectivity for MG, with a low detection limit.

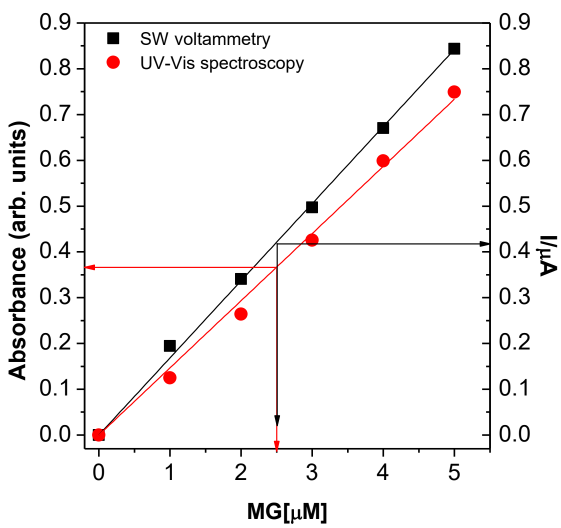

Fig. 14 Interpolation of the real sample value on the calibration curve

Table 4. MG retrieval values for GC/MCM-41-NH_2/Nafion and UV-Vis spectroscopy

Detected (μM)		**Retrieval (%)**
UV-Vis Spectroscopy	**GC/CeO_2/Nafion Electrod**	
10.00 ± 0.01	10.3 ± 0.1	103

Real sample analysis presents the comparable performances of the new electrode with UV-Vis spectroscopy results, but does not have the limitation of spectroscopic analysis in terms of interference from a colored natural matrix that may compromise such determinations.

11. Electrochemical sensor based on glassy carbon modified with PTZ (GC/PTZ)

The attempt to develop a mediator system for easier oxidation of MG only succeeded in the possibility of attaching MCM-41-NH_2 functionalized silica to PTZ (1-mono-10H-phenothiazine), but detection using this sensor did not give the expected results. The oxidation capacity of PTZ appeared to be reduced due to intramolecular association through hydrogen bonds. The first monoelectronic oxidation step, which took place around 0.25 V, generated the cation radical, this value being slightly modified by the nature of the solvent. There are no favorable interactions between MG and PTZ, therefore the GC/PTZ based electrochemical system is not suitable for MG detection.

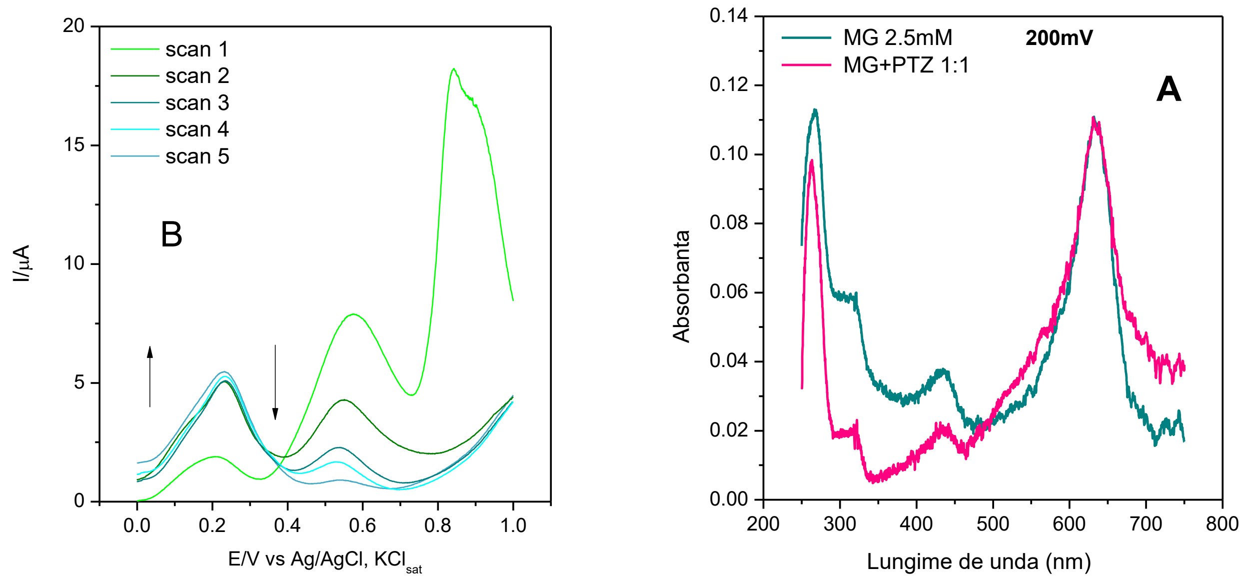

Fig. 15 SWASV consecutive curves at GC/PTZ; SEC spectra for MG, MG+PTZ at 200 mV

The SEC measurements have revealed changes in the absorption spectrum of PTZ in the presence of MG, previously explained by weakening the intramolecular hydrogen bonding of the compound due to steric interactions between PTZ and MG, thus confirming the already assumed and reinforcing the conclusion that the PTZ-based system is suitable for the detection of MG in both aqueous media and organic media.

12. Electrochemical glassy carbon based sensor modified with silica NP for Cd^{2+} ion detection

Four different OMS (ordered mesoporous silica) powders were used in the study to prepare modified GC electrodes coated with Nafion to be used for the electrochemical detection of Cd^{2+} in water samples. Silica powders had a positive effect on the detection of metal ions due to their good adsorption properties. The high specific area of the OMS was certainly a significant aspect in their performance. In some cases, the most important role is played by amino groups, which have a beneficial effect, most likely due to the possibility of complexation of cadmium ions. Even if the detection limit values determined for the new silica-modified electrodes are slightly higher than those reported in the literature, they are still lower than those stipulated in European legislation and therefore GC/silica/Nafion electrodes could be successfully used for the detection of Cd^{2+} from aqueous solutions.

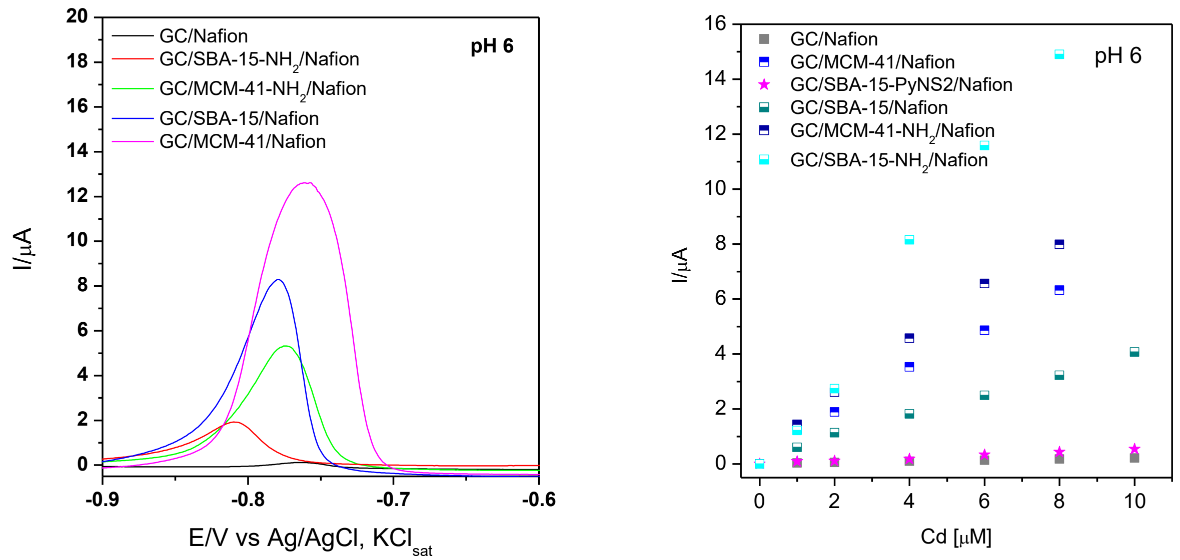

Fig. 16 GC/silice/Nafion electrodes' response at pH 4.4 and 6, SWASV curves and calibrartion curves

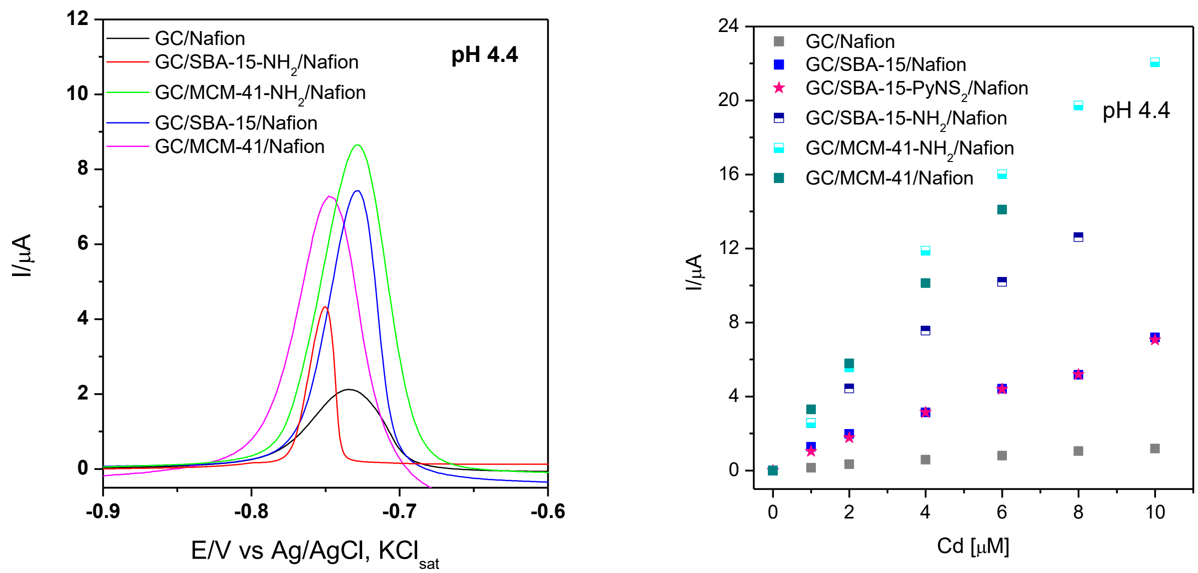

Table 5. Electroanalitical parameters

Electrod	Sensitivity (A/M)		DL (µM)		Liniar domain		R^2/N	
	pH 6	pH 4.4	pH 6	pH 4.4	pH 6	pH 4.4	pH 6	pH 4.4
GC/Nafion	0.013 ± 0.001	0.165 ± 0.049	4.79	4.14	0 - 100	0 - 10	0.9987/12	0.9914/7
GC/SBA-15/Nafion	0.389 ± 0.013	0.564 ± 0.023	1.10	0.94	0 -10	0 -10	0.9942/7	0.9920/7
GC/SBA-15-NH_2/Nafion	1.483 ± 0.047	1.462 ± 0.052	0.66	0.73	0 - 8	0 - 8	0.9960/6	0.9950/6
GC/MCM-41/Nafion	0.633± 0.040	2.553 ± 0.098	1.32	0.51	0 - 6	0 - 8	0.9963/5	0.9942/6
GC/MCM-41-NH_2/Nafion	0.703 ± 0.030	2.716 ± 0.099	1.18	0.49	0 -10	0 - 6	0.9909/7	0.9901/5

GENERAL CONCLUSIONS

Finally, the conclusions of all the studies described in the paper are presented and, based on them, the general conclusions that will conclude the paper are formulated.

- Following the biosorption study of MG on fir cones, we can say that this depollution method is simple, inexpensive and viable, with the potential to be used as an alternative to the classic methods of removing dyestuffs. The investigated work parameters contribute to the efficiency of the global process, delimiting optimal values for each. The results were confirmed and supplemented by ANFIS predictions. In conclusion, it can be said that the removal of MG from waste water by biosorption is a viable process, at least at a laboratory level, which has obvious advantages over the classical processes in terms of costs and environmental impact, and fir cones are an appropriate material in this sense.
- As a general conclusion on adsorption by other natural materials, we can say that they have great potential in terms of efficiency, but they are not a viable solution at an industrial level in powder form, so their immobilization into a composite material could be a successful solution to this.
- Live moss were by far the most effective biomaterial employed to remove MG, but the study of adsorption should be further studied and optimized both in terms of working parameters and ethical considerations.
- Spectrophotometric detection of the residual concentration of MG in the solution may suffer significantly from the interference resulting from the spontaneous extraction of the natural pigments contained in the adsorbent materials, so this aspect should be taken into account for determinations.
- One of the possible solutions to this problem is changing the analytical method and the electrochemical detection of the active redox species is a first candidate due to the efficiency and low cost. Various materials can be used to make chemically modified electrodes with various characteristics and performance.
- All tested carbon materials have demonstrated a favorable effect on the GC electrode due to increased active surface and improved conductivity, which has led to a more sensitive sensor with a lower detection limit. Carbon nanotubes (SWCNT) have proven to be an excellent material for the development of sensible sensors, providing the best results in SWASV and amperometry with low detection limits. The new artisanal, AC-based material has not achieved SWCNT performance, but is comparable to commercial RGO, while being much cheaper and more affordable.
- The obtained GC/CeO_2/Nafion electrode demonstrated good stability, sensitivity and selectivity to MG and a low detection limit. The electrocatalytic effect exerted by CeO_2 nanoparticles certainly

contributed to electrode performances, along with the favorable ionic association of MG with the sulphonate group of the Nafion ionomer.

- Different ordered mesoporous silica (OMS) powders have been used to prepare electrodes for MG detection. Sensor preparation is simple, fast and cost-effective. Silica adsorbing properties and ordered structure have improved electrochemical response compared to unmodified GC electrode. Particularly, the GC/MCM-41-NH_2/Nafion electrode showed good stability, sensitivity and selectivity to MG, with a low detection limit.

- The attempt to develop a mediator system for easier oxidation of MG did not give the hoped-for results. The oxidation potential of 10H-phenothiazine-carboxylic acid appeared to be reduced due to the intramolecular association through hydrogen bonds. There are no favorable interactions between MG and 10H-phenothiazine-carboxylic acid and therefore the GC/PTZ-based electrochemical system is not suitable for MG detection. The SEC measurements have revealed changes in the absorption spectrum of PTZ in the presence of MG, previously explained interactions, thus confirming what has already been assumed and reinforcing the conclusion that the PTZ-based system is not suitable for MG detection.

- Finally, OMS were used to prepare modified GC electrodes for Cd^{2+} detection in water samples. This time, all silica powders had a positive effect on the detection of metal ions due to their adsorption properties. The high specific area of the OMS was certainly a significant aspect in their performance. In some cases, the most important role is played by amino groups, which have a beneficial effect, most likely due to the possibility of complexation of cadmium ions.

As an overview of the whole work, it can be said that depollution with natural materials is possible and even capable of impressive performance, being a potential alternative to established methods, provided that the optimum conditions are met.

Electrochemical detection of MG has yielded promising results with all tested materials in terms of detection limit. Of all the electrodes developed, GC/CeO_2/Nafion was noted through performance due to the special nature of the electrode material.

Bibliography:

1. Culp, S. J. & Beland, F. A. Malachite Green: A Toxicological Review. *J. Am. Coll. Toxicol.* 15, 219–238 (1996).

2. Kurnick, N. B. Methyl Green-Pyronin I. Basis of selective staining of nucleic acids. *J. Gen. Physiol.* **3,** 243–265 (1949).
3. Foster, F. J. & Woodbury, L. The use of malachite green as a fish fungicide and antiseptic. *Progress. Fish-Cult.* **18,** 7–9 (1936).
4. Srivastava, S., Sinha, R. & Roy, D. Toxicological effects of malachite green. *Aquat. Toxicol.* **66,** 319–29 (2004).
5. Shutler, G. G. & Tompkins, D. C. Bloodstain characterization in the EAP, Hp, Hb, AK and GLO I typing systems using minigels and the PhastsystemTM. *Forensic Sci. Intenational* **39,** 97–104 (1988).
6. Clogger, T. J. The Use of Aniline Dyes and Anthracene in the Detection of Petty Theft. *Police J.* **27,** 51–56 (1954).
7. Ross, E. *et al.* Indicator reagents. *Ullmann's Encyclopedia of Industrial Chemistry* (2002).
8. Răducan, A., Olteanu, A., Puiu, M. & Oancea, D. Influence of surfactants on the fading of malachite green. *Cent. Eur. J. Chem.* **6,** 1624–44 (2008).
9. Ayyangar, N. R. & Tilak, B. D. Chapter III – Basic Dyes. *Chemistry of Synthetic Dyes* (1971).

10. Qaiser, S. Mechanism of Heavy Metal Removal by Agro Fibers - Chapter 7. Mechanism of Biosorption. (Universitatea de Inginerie și Tehnologie, 2009).

11. Tang, H., Zhou, W. & Zhang, L. Adsorption isotherms and kinetics studies of malachite green on chitin hydrogels. *J. Hazard. Mater.* **209–210,** 218–225 (2012).
12. Bekçi, Z., Özveri, C., Seki, Y. & Yurdakoç, K. Sorption of malachite green on chitosan bead. *J. Hazard. Mater.* **154,** 254–261 (2008).
13. Crini, G. Non-conventional low-cost adsorbents for dye removal: A review. *Bioresour. Technol.* **97,** 1061–1085 (2006).

14. Ghoul, M., Bacquet, M. & Morcellet, M. Uptake of heavy metals from synthetic aqueous solutions using modified PEI – silica gels. *Water Res.* **37,** 729–734 (2003).
15. Sabnis, R. W. *Handbook of Acid-Base Indicators*. (CRC Press, 2007).

16. Dubinin, M. M. The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface. *Chem. Rev.* **60,** 235–266 (1960).

17. Dada, A. O., Olalekan, A. P., Olatunya, A. M. & Dada, O. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn2+ Unto Phosphoric Acid Modified Rice Husk. *J. Appl. Chem.* **3,** 38–45 (2012).
18. Bhagavathi, T., Vijayaraghavan, J., Sardhar, S. & Sekaran, V. Investigation on removal of malachite green using EM based compost as adsorbent. *Ecotoxicol. Environ. Saf.* **118,** 177–182 (2015).
19. Hema, M. & Arivoli, S. Adsorption kinetics and thermodynamics of malachite green dye unto acid activated low cost carbon. *J. Appl. Sci. Environ. Manag.* **12,** 43–46 (2008).
20. Nguyen, H. T., Prasad, N. R., Walker, C. L. & Walker, E. A. *A First Course in Fuzzy and Neural Control*. (Chapman & Hall/CRC, 2003).
21. Jang, J. S. R. ANFIS: adaptive-network-based fuzzy inference systems. *IEEE Trans. Syst. Man Cybern.* **23,** 665–685 (1993).
22. Mitra, S. & Hayashi, Y. Neuro-fuzzy rule generation: survey in soft computing framework. *IEEE Trans. Neural Netw.* **11,** 748–768 (2000).
23. Heineman, W. R. Spectroelectrochemistry: The combination of optical and electrochemical techniques. *J. Chem. Educ.* **60,** 305 (1983).
24. Fenglian, F. & Qi, W. Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manage.* **92,** 407–418 (2011).

Scientific activity

Published work:

1. Săcară, A.-M., Indolean, C., Mureşan, L.M. (**2016**). Adsorption, equilibrium and kinetic study of malachite green removal from aqueous solutions using fir (*Abies nordmanniana*) cones biomass, *Studia UBB Chem.*, LXI(3), 183-194.
2. Săcară, A.-M.,C. Cristea, Mureşan, L.M. (**2017**) Electrochemical detection of Malachite Green using glassy carbon electrodes modified with CeO_2 nanoparticles and Nafion , *J. Electroanal. Chem.*, 792 (2017), 23-30.
3. Săcară, A.-M., Nairi V., Salis A., Turdean G.L., Mureşan, L.M. (**2017**) Silica-modified Electrodes for Electrochemical Detection of Malachite Green, *Electroanalysis,* 29(11), 2602-2609.
4. Săcară, A.-M., Mureşan, L.M. (**2017**) Electrochemical Sensors for Malachite Green Based on Carbonaceous Nanomaterials, *Studia UBB Chem*., LXII(3), 145-156.
5. Săcară, A.-M., Cristea C., Lovasz T., Porumb D., Molnar E., Mureşan, L.M. (**2017**) Electrochemical oxidation of 10H-phenothiazine-1-carboxylic acid, *Studia UBB Chem*., LXII(4), 121-128.
6. Săcară, A.-M., Indolean C., Cristea V.M., Mureşan, L.M. (**2017**) Modeling biosorption for removal of malachite green with *Abies nordmanniana* cones using adaptive neurofuzzy interference system methodology, *Chem. Eng. Commun,* - trimis spre publicare.
7. Săcară, A.-M., Pitzalis F., Salis A., Turdean G.L., Mureşan, L.M. (**2018**) Glassy carbon electrodes modified with ordered mesoporous silica for cadmium ions electrochemical detection, *Microporous & Mesoporous Materials,* – trimis spre publicare

Conferences attended

- International U.A.B. – B.EN.A. Conference on Environmental Engineering and Sustainable Development, Alba Iulia, Romania, 28-30 May 2015, poster – "Removal of triarylmethane dye Malachite Green from aqueous solutions using fir (*Abies alba*) needles biomass. Equilibrium, thermodynamic and kinetic studies".
- Applied Nanotechnology and Nanoscience International Conference, Paris, France, 5-7 November 2015, poster – "Electrochemical detection of Malachite Green using carbonaceous nanomaterials".

- Conferința Studenților din cadrul Programului POSDRU, Băile Felix, 19-21 Decembrie 2015, prezentare – “Eliminarea Verdelui Malachit din soluţii apoase sintetice utilizând biomasă obţinută din tescovină”.
- Electrochemistry in Nanoscience International Conference, Lille, France, 23-25 May 2016, poster – “Modified glassy carbon electrodes for electrochemical detection of Malachite Green using activated carbon from fir (*Abies alba*) cones”.
- International U.A.B. – B.EN.A. Conference on Environmental Engineering and Sustainable Development, Alba Iulia, Romania, 25-27 May, 2017, poster – “Silica modified electrodes for Malachite Green detection in polluted water“.
- 6th Regional Symposium on Electrochemistry of South-East Europe, Balatonkenese, Hungary, 11-15 June, 2017, prezentare – “Glassy carbon electrode modified with nano-CeO_2 and Nafion for Malachite Green detection in aqueous solutions”.
- A XXXV-a Conferinta Nationala de Chimie, Caciulata, 2-5 octombrie 2018, poster – “Detection of cadmium ions at glassy carbon electrodes modified with ordered mesoporous silica”.