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NEW MATERIALS BASED ON MAGNETIC POLYMERIC COMPOSITES WITH ENVIRONMENTAL APPLICATIONS

DOCTORAL THESIS
SUMMARY

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Keywords: nitrites, nitrates, amperometric sensors, magnetic nanoparticles, magnetic polymeric composites, recyclable adsorbent systems, anions, cations, heavy metals.

Introduction

Environmental pollution is a constant problem that leads to many diseases that affect human health and early death, thus leading to poor sustainable development and affecting society and the economy. The presence of toxic elements in the environment (organic and inorganic pollutants) caused by anthropogenic or natural causes is a severe environmental problem that has generated considerable interest in science and the public (Busetti et al., 2005; Landrigan et al. al., 2019).

The effects of environmental pollution (soil, water, and air) through chemicals/fertilizers are due to intensive industrialization/agriculture and rising living standards worldwide, thus becoming a challenge for human health. (Xu et al., 2018). Furthermore, the use of natural resources in an intensive and inappropriate use leads to the soil, water, and air pollution. As a result, nature no longer manages to keep up to regenerate itself (Muralikrishna et al., 2017).

The conventional methods of detection or depollution, respectively, have certain limitations on efficiency, selectivity, and sensitivity to detection or de-pollution, presenting characteristics that are not cost-effective from a financial or environmental point of view.

Nanotechnology, especially iron oxide magnetic nanoparticles with a high surface-to-volume ratio and magnetic properties, can be one of the potential tools for nanomaterials handling in wastewater treatment.

Hence the necessity to develop new composite materials used in environmental pollutants detection and to develop systems for their adsorption and magnetic separation from contaminated waters.

Thus, the idea of the doctoral thesis entitled "**NEW MAGNETIC POLYMER COMPOSITES MATERIALS WITH APPLICATIONS IN ENVIRONMENTAL PROTECTION**" was born.

Objectives of the study

The doctoral thesis entitled “**NEW MAGNETIC POLYMER COMPOSITES MATERIALS WITH APPLICATIONS IN ENVIRONMENTAL PROTECTION**” presents three main objectives:

(i) The development of a new hybrid magnetic polymers composite electrode materials used in the production of an amperometric sensor for nitrite detection;
(ii) Development of recyclable systems for nitrate depollution from wastewater, using an innovative magnetic separation technique;
(iii) Monitoring the content of major ions and heavy metals in irrigation water, soil, and vegetables in an agricultural area of Botoșani County;

The thesis is composed of six chapters, the first two chapters representing the study of literature and introducing the importance of monitoring environmental factors in the field of environmental pollution, highlighting the standard methods used in this regard. Also, the theoretical part is presented an ample "state of the art" in terms of electrochemical sensors and types of modified electrode materials developed, as well as their use in the detection of various compounds or elements with a polluting character emphasizing the environmental pollution with nitrites.

The following four chapters of the thesis represented by the experimental part contain personal contributions, presented as follows: "***Electrode materials based on magnetic nanoparticles coated with inorganic silica polymer (SiO2)***" where a new magnetic nanocomposite material was obtained, with application into the development of modified electrode materials.

Magnetic nanocomposites are a combination of magnetic nanoparticles with superparamagnetic behavior embedded in an inorganic silica polymer matrix, with excellent adsorption properties, and particularly Toluidin Blue dye, used as an organic molecule that acts as a mediator for nitrite detection.

In addition, the development of a new hybrid nanocomposite material, "***Hybrid magnetic polymeric composite electrode materials for amperometric nitrite sensor***," was described based on a combination of hybrid nanocomposites such as magnetic nanoparticles, inorganic polymer (SiO_2), and different types of organic polymers.

All the chosen polymers have an affinity in terms of dye adsorption, so implicitly for the Toluidine Blue dye, an organic molecule with a mediating role in the detection of nitrites.

Subsequently, "***Magnetic hydrogel composites based on cross-linked poly (acrylic acid) used as a recyclable adsorbent system for nitrates***" was presented regarding the use of magnetic hybrid nanocomposites based on cross-linked polyacrylic acid as recyclable magnetic systems used in the adsorption of pollutants, especially nitrates, using an innovative magnetic separation technique of nitrate-laden material from wastewater.

Finally, is presented "***Monitoring the content of major ions and heavy metals in irrigation water, agricultural soil, and vegetables grown in investigated greenhouses***," which illustrates an extensive study of monitoring of soil and vegetables in terms of ions content (anions, cations, and heavy metals), respectively nutrients, from an agricultural area in Botoșani County.

CH. I. DETECTION, MONITORING, AND DEPOLUTION OF SUBSTANCES WITH AN ENVIRONMENTAL TOXIC EFFECT

I.1. Environmental pollution with toxic substances

Environmental pollution can be defined as a physical, chemical, and biological degradation of environmental factors so that environmental changes falling within the term pollution directly or indirectly affect human health (Moschella et al., 2005).

Pollution is a term that can be defined as any substance of the broad category of xenobiotic compounds, which are released into the environment by anthropogenic actions and occur in a higher concentration than "natural levels" (Richards & Shieh, 1986). Urban development a fast way, as well as industrialization, has led to the release of huge amounts of xenobiotic compounds into the environment (Tabrez & Ahmad, 2011).

Environmental pollutants are divided into organic and inorganic pollutants. Some of the organic pollutants are biodegradable contaminants, while the class of inorganic pollutants represents the contaminants such as toxic heavy metals (arsenic, lead, chromium, etc.), but also a number of other air pollutants from toxic gas emissions.

In recent years, in addition to contamination with heavy metals and other substances, pollution with nitrates and nitrites has become one of the main problems in groundwater management. Nitrates and nitrites are compounds that result from the oxidation of nitrogen. They can be present both in synthetic forms and as natural products with very severe negative effects on living organisms, but also on the environment. (Menció et al., 2016). Nitrates and nitrites are commonly found in fertilizers, manure, some soils, and meat preservation and can also be released through certain industrial processes.

I.2. Environmental pollution with nitrites

Soil is one of the most important ecological factors, and the population depends on this factor for food (Mamidwar & Bhandarkar 2015). It is known that plant nutrition is one of the most important factors for controlling the productivity of agricultural products, therefore, soil fertilization, pest control, irrigation and agricultural activities increase the efficiency of the soil.

Nowadays, the soil has become quite poor in nutrients, poor quality or inefficient, this effect being due to the uncontrolled use of chemical fertilizers that have a negative effect on land and environmental health (Mamidwar & Bhandarkar 2015).

Like soil, water contamination is a result of agricultural and industrial activities. Water pollution by nitrites can lead to an imbalance in the biogeochemical cycle by interfering with denitrification/nitrification processes. The consequences on the ecological status, due to the high level of nitrites concentration, are given by the contamination of groundwater by the percolation of these highly soluble ions by natural aquifers (Almeida et al., 2010).

I.3. Specific methods used for nitrites determination in the environment

Taking into account the adverse effects that may occur due to the ingestion of a higher amount of nitrites than the recommended daily intake, it is indispensable to monitor nitrites due to the high toxic effect on the human body. In most cases, nitrite monitoring is a substantial challenge due to the presence in the environment of other similar contaminants such as nitrates, ammonium, phosphates, and sulfates, which function as interference in nitrite detection.

Numerous methods used in the detection and quantitative determination of nitrites and/or nitrates are reported in the literature, such as spectrophotometry (Tsikas, 2007) (Griess method), chemiluminescence (Nagababu & Rifkind, 2007), electrochemistry (Cao et al., 2019) or chromatography (Zhao et al., 2015); each method having advantages and disadvantages in use.

Due to the laborious and expensive methods used in the detection of nitrites, there is a special interest in the construction of simple sensors for their detection, because nitrites play an important role in many areas (Yang, 2014).

Electrochemical sensors are thus of great interest, converting the electrical signal into a chemical signal (Naveen et al., 2017).

Depending on the method of measurement, the electrochemical sensors can be divided into three broad categories as follows: conductometric, potentiometric, and amperometric. (Vetelino & Reghu 2011).

CH. II. ELECTRODE MATERIALS WITH APPLICATIONS IN THE DEVELOPMENT OF AMPEROMETRIC SENSORS FOR NITRITE DETECTION

II.1. Classification of electrode materials with applications in electrochemistry

Historically, electrochemical sensors began in the 1950s by monitoring oxygen emitted from industrial areas.

Various sensors have been developed and applied in recent years for contaminants detection using electrochemical sensors, attracting attention due to their easy detection system and relatively low processing costs.

The essential specific requirements of the electrode materials are the catalytic ones, the conductivity, the corrosion resistance, the hardness, the current load, respectively the shape, and the size. In addition, many of the basic requirements of electrode materials are directly influenced by the material's inherent characteristics. Thus, a sensory layer for detecting target analytes is placed on the surface of a conductive substrate (Kumaravel et al., 2015).

The materials used to obtain the electrochemical sensors are divided into two categories, namely conventional and unconventional materials. From the class of conventional materials, the electrodes are found as metals such as Au, Ni, Hg Pd, and Pt, or As (Terzi et al., 2019), carbon nanotubes (Lawal, 2016), graphite and metal oxides, carbon nanomaterials, graphene (Bollella et al., 2017).

The present studies in the literature performed on unmodified electrodes have various limitations in detection. However, the limitations are limited to the contamination of the electrode surface due to unwanted adsorption/precipitation and unspecific redox behavior; these electrodes serve to transfer heterogeneous electrons (Adarakatti & Kempahanumakkagari, 2018).

These limitations required the development of sensors based on new electrode materials, whose intrinsic properties exceeded the boundaries of conventional materials.

II.2. Modified electrode materials used in the construction of amperometric sensors

The new electrochemical sensors are being developed to improve electrochemical properties over previous-generation sensors. The improvements are related to properties related to mechanical, chemical, and electrochemical stability, the possibility of incorporating a relatively high concentration of active electrocatalyst, respectively preventing its diffusion into the environment, and much lower response times.

The electrochemical properties can thus be improved by selecting advanced electrode materials with outstanding properties and finding innovative constructive solutions that go beyond the limits of classical electrodes (Tajik et al., 2021).

In the particular case of using the amperometric method, the current is measured as a result of an electron transfer reaction, while the potential is controlled with a potentiostat (Hryniewicz et al., 2021).

In concrete terms, the modification of the working electrode surface brought several advantages, such as the transfer of the physicochemical characteristics of the modifying agent in the operation of the working electrode, significantly improved electrocatalytic activity, and high selectivity of the analyte (Tajik et al., 2021).

The studies show various amperometric sensors based on electrodes modified with new nanocomposite materials, composed of Mg_2Al-NO_3 nanoparticles (Hdiouech et al., 2019), platinum nanoparticles decorated with nanocomposite of reduced graphene oxide (Pt/rGO) (Dhara et al., 2018), glassy carbon modified with functionalized cerium oxide nanocomposites of Pd @ CeO_2-NH_2 (Guler et al., 2018), TiO_2 nanocomposites/reduced graphene oxide (Harraz et al., 2019), ZnO @ SiO_2 nanospheres (Khan et al., 2016), multilayer modified carbon glass, based on multi-walled carbon nanotubes, functionalized with chitosan and ionic liquids (Gr / MWCNTs / Ch-IL) (Jalalvand, 2018).

Thus, to obtain amperometric sensors, another method of modifying the surface of conventional electrodes is the adsorption of various organic or inorganic materials, acting as a mediator in the oxidation of the analyte of interest on the surface of the electrode. Immobilizing a suitable mediator at the electrode surface allows the migration of electrons between the modified electrode and the species in the solution. The oxidation process occurs at a relatively lower overpotential (Ispas et al., 2021).

II.3. New electrode materials modified with magnetic nanoparticles for the development of amperometric sensors for nitrite detection

The use of suitable electrode material, modified with a suitable catalyst, can increase the catalytic current in pollutants detection, particularly nitrites and nitrates.

Magnetite (Fe_3O_4) is a material that is easy to use as a modifier element due to its unique structural, chemical, and magnetic properties and low production cost through affordable and environmentally friendly preparation methods (Koterwa et al., 2021).

The recent studies presented in the literature report the use of magnetic nanoparticles in preparing electrode materials for the construction of electrochemical sensors. For example, Fe_3O_4 magnetic nanoparticles were used to obtain modified electrode material of Fe_3O_4@PDA@MnO_2 type, for lead detection in water (Wang et al., 2020), to obtain modified electrode material based on $Fe_3O_4/Bi_2O_3/C_3N_4$, for the construction of a sensor used in the detection of Cd^{2+} and Pb^{2+} ions (Pu et al., 2021).

Studies showing the use of Fe_3O_4 magnetic nanoparticles in the preparation of modified electrode materials to construct amperometric sensors for nitrite detection are very few.

Due to the many benefits of improving the electrochemical properties of amperometric sensors using magnetic nanoparticles, the opportunity arose to develop new electrode materials used in nitrite detection.

Recent studies conducted in the doctoral studies present the preparation of new composite materials based on magnetic nanoparticles of magnetite Fe_3O_4, incorporated in an inorganic matrix of silica SiO_2, a material that has been successfully used in the construction of an amperometric sensor for the nitrites detection from various environmental samples (Ispas et al., 2018).

II.4. New electrode materials modified with polymers or polymeric composites for the development of amperometric sensors

The macromolecules of conductive polymers and composites formed with other elements can conduct electricity, which is the fundamental property for electrochemical applications (Kondratiev et al., 2016).

Conductive polymers have been used successfully in developing new sensors, the most used polymers being polyacetylene, polythiophene, polyaniline, and polypyrrole (Ran et al., 2017).

When the polymers are used in electrochemical applications, the polymer matrix must offer several advantages, such as easy modification of the electrode surface and a chemical structure that allows the attachment of chemical and biological molecules to the electrode structure, selectively detects specific analytes, provides mechanical and chemical resistance to the electrode thus modified, allows easy and homogeneous diffusion of the analyte to the electrode, but at the same time prevents leakage of possible mediators on the electrode surface into the analysis medium (Alzari et al., 2009).

Taking into account the characteristics required of a polymeric material used as a surface modifying material, it was concluded that the class of cross-linked polymers, which form hydrogel structures, has major advantages for meeting these requirements, hydrogels being networks of three-dimensional cross-linked hydrophilic polymers (Groll et al., 2004).

The most commonly polymeric materials used as hydrogels in detection are poly(N isopropylacrylamide), poly(acrylamide), poly(vinyl alcohol), poly(vinyl imidazole), poly(vinyl pyrrolidone) or poly(ethylene glycol) (Onay et al., 2018).

Specifically for nitrites detection from environmental samples, there are only a few references in the literature about such systems. Cîmpean et al. (2017) present the construction of an electrode material based on cross-linked hydrogel of the poly (2-hydroxyethyl methacrylate), modified with a mediator of Toluidine Blue, for the detection of nitrites in the water. Also, personal work presents the preparation of new modified electrode material based on a combination of magnetic nanoparticles coated with a layer of silica and encapsulated in a polyacrylic acid hydrogel cross-linked polymer matrix (Ispas et al., 2021).

PERSONAL CONTRIBUTIONS

CH. III. ELECTRODE MATERIALS BASED ON MAGNETIC NANOPARTICLES COATED WITH INORGANIC POLYMER SILICA (SiO_2) LAYER

The first chapter of the experimental part describes the preparation of a magnetic nanocomposite with applicability in developing new modified electrode materials. The magnetic nanocomposite material is MNPs-SiO_2, an association between Fe_3O_4 iron oxide nanoparticles with superparamagnetic behavior and excellent magnetic properties, incorporated in a silica (SiO_2) matrix, with an excellent adsorption capacity in general and particularly of the Toluidine Blue dye, an organic molecule with a mediating role in the detection of nitrites.

III.1. Synthesis of magnetic nanocomposites (MNPs-SiO_2)

Magnetic nanocomposites (MNPS-SiO_2) based on magnetic nanoparticles (Fe_3O_4) coated with inorganic silica (SiO_2) polymer were obtained from two reaction steps (Ispass et al., 2018), namely, the synthesis of magnetic nanoparticles (MNP_S) of iron oxide, magnetite (Fe_3O_4), using the co-precipitation method of (Ispas et al., 2020), followed by encapsulation of magnetic nanoparticles in a matrix of SiO_2 using Stoeber method (Stober et al., 1968).

III.2. Physico-chemical and electrochemical characterization of magnetic nanocomposites embedded in silica (SiO_2)

The morphology study of magnetic nanoparticles (MNP_S) and SiO_2 coated magnetic nanocomposites was conducted by transmission (TEM) and/or scan (SEM) electron microscopy measurements (**Figure 1**).

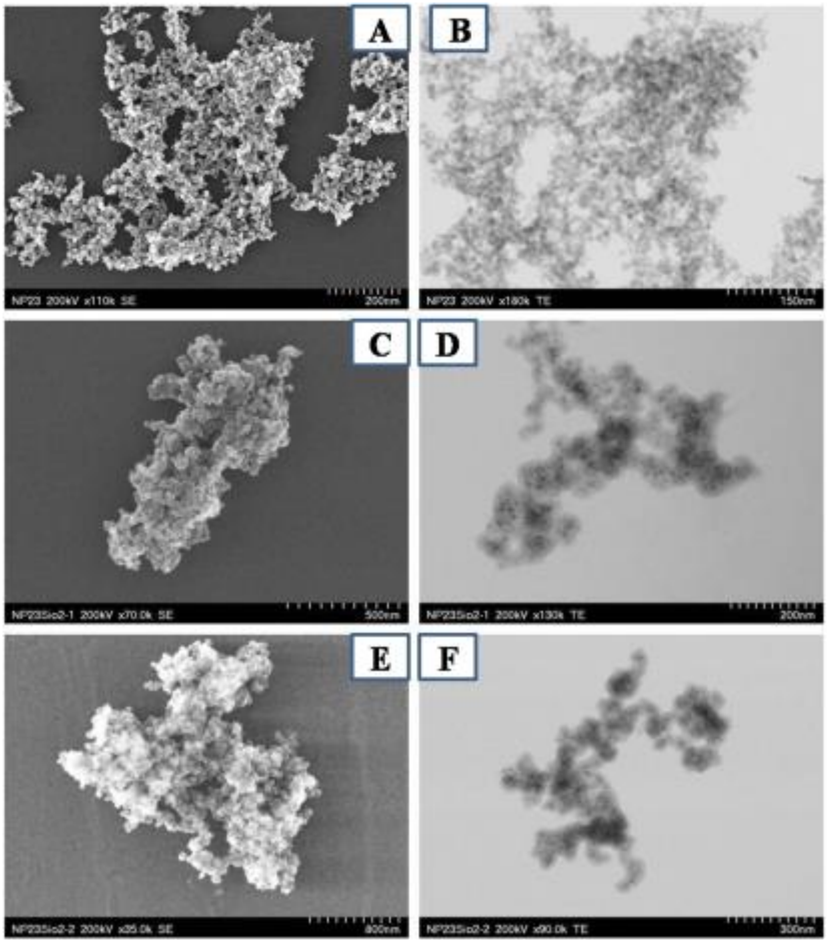

Figure 1. SEM and TEM images of magnetic nanoparticles (MNPs) and SiO_2-coated magnetic nanocomposites (MNPs): **A** (SEM), **B** (TEM) uncovered magnetic nanoparticles; **C** (SEM), **D** (TEM) for magnetic nanocomposites MNPs- SiO_2-1; **E** (SEM), **F** (TEM) for the magnetic nanocomposite MNPs- SiO_2-2.

The TEM image in **Figure 1** (**B**) shows the non-covered magnetic nanoparticles, showing a well-dispersed uniform polyhedral structure with an average diameter of 10 nm. For magnetic composites, MNPS-SiO_2-1, **Figure 1** (**D**) and MNPS-SiO_2-2, **Figure 1** (**F**), the SiO_2 matrix incorporating nanoparticles can be easily observed.

The materials were structurally characterized using FTIR spectroscopy, and the analysis of the recorded spectra identified the following characteristic bands: the band located at 3420 cm^{-1}, for the SiO_2 matrix; in addition to the characteristic bands of the SiO_2 matrix, the magnetite-specific band (Fe_3O_4) is located around 500 cm^{-1}, a band that confirms the successful formation of MNPS-SiO_2 magnetic nanocomposites by the encapsulating of magnetic nanoparticles (MNPS) in the SiO_2 matrix.

Magnetic properties of magnetic nanocomposites (MNPS-SiO_2) have also been highlighted by magnetic moment measurements (Ispas et al., 2018), obtaining a high saturation of magnetization value, MS, (81.3 emu/g) of magnetic nanoparticles, followed by a decreasing of magnetization with the increase of the non-magnetic component, (SiO_2 matrix) reaching 43,6 emu/g for MNPS-SiO_2-1 and 33.5 emu/g for MNPS-SiO_2-2.

An extensive adsorption study of Toluidin Blue dye (TBO) using MNPS-SiO_2 magnetic nanocomposites was conducted in which the behavior of the adsorption efficiency of MNPS-SiO_2 (50 mg) with the initial concentration of TBO was initially investigated at concentrations between 2 and 20 mg/ml. Adsorption efficiency is in accordance with the Langmuir model, in which the adsorption capacity of the material is directly proportional to the concentration of the initial solution at low concentrations, entering a plateau at higher concentrations when surface saturation occurs. Thus, it has been estimated that the optimal initial concentration of TBO is 15 mg/ml, where the maximum adsorption efficiency is about to 86% saturation value.

The adsorption efficiency of TBO dye was studied with an increasing dose of MNPs-SiO_2 and it was observed that the adsorption efficiency decreases with an increasing dose of adsorbent material, so the maximum adsorption rate was about 87%. Thus, an antagonistic behavior was observed in the classical adsorption model, due to the appearance of a nonlinear decrease with increasing dose of adsorbent material, this phenomenon being due to the possible aggregation processes and sedimentation of MNPs-SiO_2 at higher doses.

Adsorption efficiency behavior of TBO as a function of the pH of the initial solution was also studied and it was observed that the maximum adsorption efficiency is about 90% at a neutral pH, a result which is correlated with the value of the point of zero charge (pzc), where the maximum stability of MNPs-SiO2 was obtained, around pH 7.

The obtained magnetic nanocomposites (MNPs, MNPs-TBO, MNPs-SiO_2-1, MNPs-SiO_2-2, MNPs-SiO_2-1-TBO-1, MNPs- SiO_2-1-TBO-2, MNPs- SiO_2-2-TBO -1 and MNPs- SiO_2-2-TBO-2) were subsequently electrochemically characterized in the presence and absence of nitrite (**Figure 2**), to highlight its oxidation at the surface of the modified electrodes, in phosphate buffer solution, pH 7, at a low scan rate (10 mV s^{-1}) (Ispas et al., 2018).

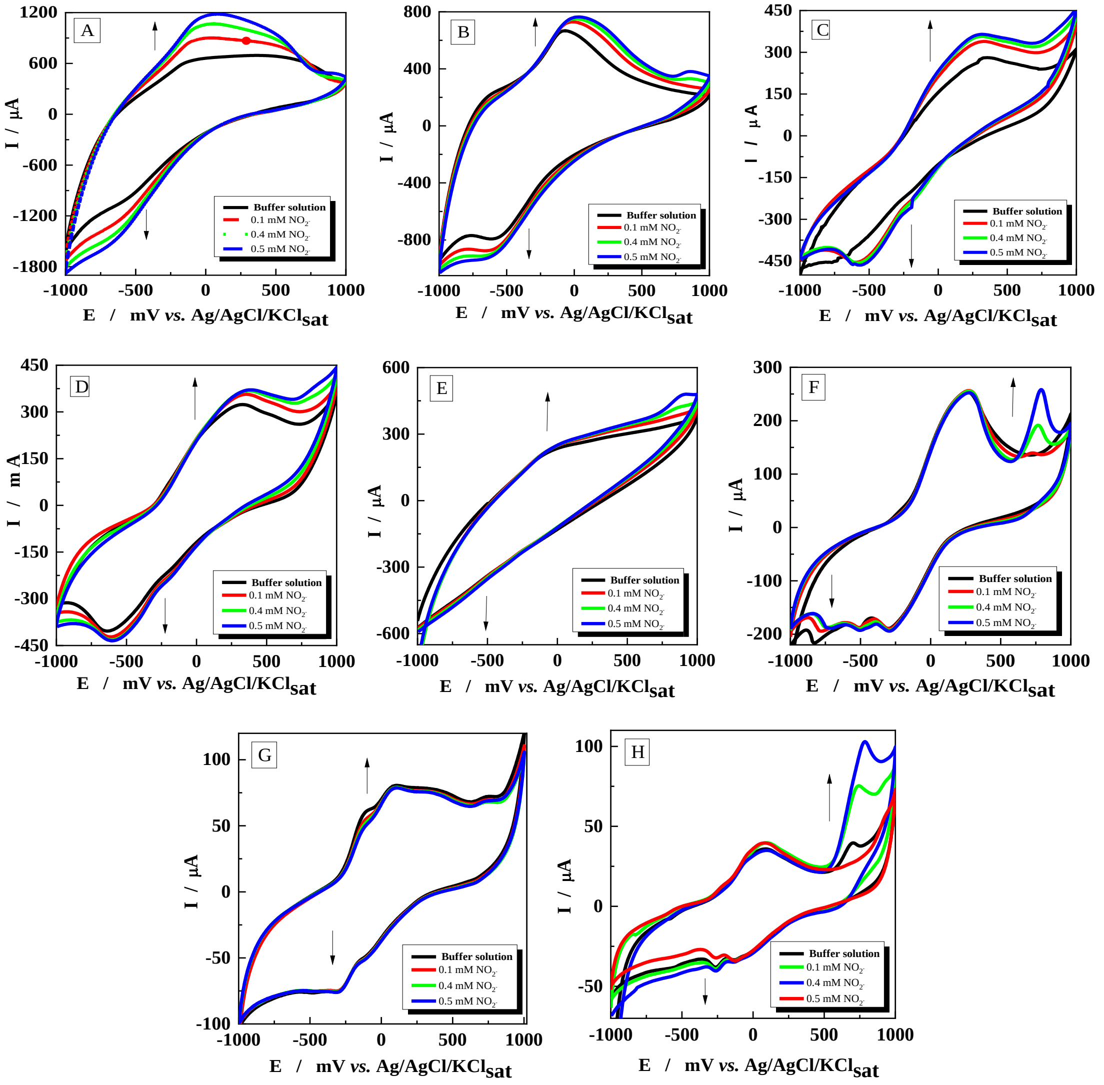

Figure 2. Study of the electrocatalytic effect of the prepared electrode materials:
(A) MNPs; **(B)** MNPs- TBO; **(C)** MNPs-SiO$_2$-1; (**D)** MNPs-SiO$_2$-2;
(E) MNPs-SiO$_2$- 1- TBO – 1; (**F)** MNPs SiO$_2$- 1- TBO -2;
(G) MNPs-SiO$_2$-2- TBO -1; (**H)** MNPs-SiO$_2$-2- TBO -2.
Experimental conditions: supporting electrolyte, 0.1 M phosphate buffer, pH 7;
scan rate, 10 mV s^{-1}.

Comparing the electrocatalytic effect of the analyzed electrode materials (**Figure 2**), it was observed that the best electrocatalytic effect was obtained for the electrodes modified with the nanocomposites MNPs-SiO$_2$-1-TBO-2 (**Figure 2F**) and MNPs-SiO$_2$-2-TBO-2 (**Figure 2H**).

Following the study of the electrocatalytic effect, the calibration curves were elevated (**Figure 3**) (Ispas et al., 2018) for NO$_2^-$, determining the main analytical parameters as follows:

the sensitivity was 31.2 mA / M (R / N = 0.995 / 9) for MNPs-SiO_2-1-TBO-2 and 37.5 mA / M (R / N = 0.998 / 12) for MNPs-SiO_2-2-TBO -2; the linear range is 0.008-0.8 mM for MNPs-SiO_2-1-TBO -2 and 0.02-1.6 mM for MNPs-SiO_2-2-TBO-2, and the detection limit (calculated as the ratio between signal and noise of 3) was 1 μM, for both modified electrodes MNPs-SiO_2-1-TBO-2 and MNPs -SiO_2-2-TBO-2. The value of the detection limit is relatively good compared to other values from literature (Arvand & Hassannezhad 2014).

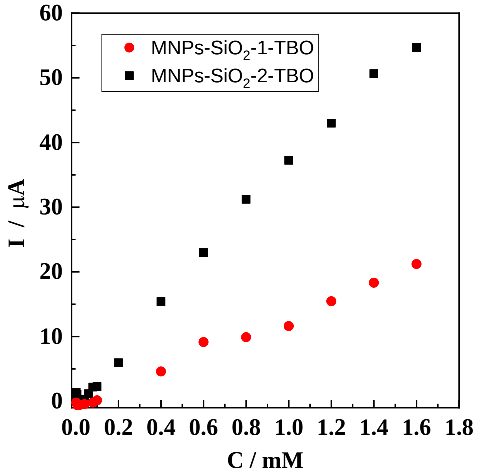

Figure 3. Calibration curves for nitrite, as measured using NP-SiO_2-1-TBO and NP-SiO_2-2-TBO electrodes
Experimental conditions: applied potential, +800 mV *vs.* Ag/AgCl/KCl_{sat}, supporting electrolyte, 0.1 M phosphate buffer solution, pH 7

Subsequently, the obtained modified electrodes (**MNPs-SiO_2-1-TBO -2 and MNPs-SiO_2-2-TBO -2**) were applied in the detection of nitrites in groundwater samples, using the standard addition method.

III.3. Conclusions

- The preparation of a magnetic nanocomposite used in the development of new modified electrode materials has been described. Magnetic nanocomposite material (MNPs-SiO_2) hosting an association between iron oxide nanoparticles (Fe_3O_4) with superparamagnetic behavior and excellent magnetic properties, embedded in a silica (SiO_2) matrix, with excellent adsorption capacity of Toluidine Blue dye, an organic molecule that acts as a mediator in the detection of nitrites.
- Correlating the data of the adsorption study, the adsorption efficiency of MNPs-SiO_2 with the initial concentration of TBO, the adsorption efficiency of TBO with increasing the dose of MNPs-SiO_2, and the effect of pH on the adsorption efficiency of TBO dye using MNPs-SiO_2, thus the optimal conditions for adsorption of TBO using MNPs-SiO_2 magnetic nanocomposites were established.
- Electrochemical characterization of new electrode materials based on magnetic nanocomposites (MNPs-SiO_2) was performed, using cyclic voltammetry as an electrochemical investigation technique.
- The two obtained modified electrodes (MNPs-SiO_2-1- TBO -2 and MNPs-SiO_2-2- TBO -2) were tested to detect nitrites in groundwater samples, using the standard addition method. It has thus proved possible to use the prepared sensors for the determination of nitrites in real water samples.
- The effect of several chemical species on possible interferences in the amperometric determination of nitrites has also been studied. The results showed that the following ions SO_4^{2-}, CO_3^{2-}, Cl^-, NO_3^-, Na^+, K^+, Ca^{2+}, and Mg^{2+} in concentrations 100 times higher than nitrite, had no visible effect on the current responses to a concentration of 0.1 mM nitrite.

CH. IV. MAGNETIC HYBRID POLYMERIC COMPOSITE ELECTRODE MATERIALS USED TO OBTAIN AN AMPEROMETRIC SENSOR FOR NITRITES DETECTION

This chapter presents the development of a new hybrid material, obtained by associating an magnetic inorganic component represented by magnetic nanocomposites of MNPs-SiO_2 and a non-magnetic organic component, represented by polymeric materials with different functions. Thus, three types of organic polymers were used: a hydrogel-type polymer, poly acrylic acid (pAAc), a cation exchanger-type polymer, poly(2-acrylamido-2-methylpropane sulphonic acid sodium salt) (pAMPS), and a natural bioactive polymer, chitosan (CHIT).

IV.1. Synthesis of magnetic hybrid polymer composites (NPs-SiO_2-Poly)

In the combination of magnetic hybrid polymeric composites (NPs-SiO_2-Poly), magnetic nanoparticles act as a specific nanoadsorbent for certain molecular species, as well as a material that gives composites the special property of being able to be magnetically manipulated by an external magnetic field, an important property involved in magnetic separation processes. The intermediate layer of silica (SiO_2) provides chemical and mechanical stability, which a simple polymeric layer cannot provide to the final material. Coating each magnetic nanoparticle with a thin layer of SiO_2 prevents the magnetic interaction between the nanoparticles, but significant improvements in surface aggregation and biocompatibility are made. The outer polymeric layer has excellent adsorption properties of highly structured molecules, such as Toluidine Blue Dye (TBO), a mediator used in the nitrite detection.

The first two synthesis steps were described in the previous chapter. Subsequently, the encapsulation of magnetic nanocomposites (MNPs-SiO_2) in various polymeric matrices were performed: (i) polymer hydrogel for obtaining a magnetic hybrid polymeric composites (NPs-SiO_2-pAAC), by free radical polymerization method (Elliot et al. 2004), using acrylic acid (AAc) as the reaction monomer, N, N'-methylene bisacrylamide (BIS) as the crosslinking agent and ammonium persulfate (APS) as the initiator of the polymerization reaction, (ii) polymer with typical exchanger structure of cations, such as poly (2-acrylamido-2-methylpropane sulfonic acid) (pAMPS by the free radical polymerization method, using the sodium salt of 2-acrylamide-2-methylpropane sulfonic acid (AMPS) as the reaction monomer, N, N'-methylene bisacrylamide

(BIS) as a crosslinking agent, tetramethylethylenediamine (TEMED) as a reaction accelerator and aqueous ammonium persulfate solution (APS) as a polymerization reaction initiator (Ispas et al., 2021), or (iii) polymer with structure of bioactive polymer, such as chitosan (CHIT) (López et al. 2013).

The magnetic polymeric hybrid compounds thus: SiO_2-pAAc, MNPs-SiO_2-pAMPS, MNPs-SiO_2-CHIT were subjected to an extensive adsorption study, for the immobilization in their structures of the TBO dye, acting as a mediator, in the electrochemical nitrite detection (Ispas et al., 2021).

IV.2. Physico-chemical and electrochemical characterization of magnetic polymeric hybrids (NPs-SiO_2-Poly)

The morphology of magnetic polymeric hybrid composites (NPs-SiO_2-Poly) was performed by transmission (TEM) and/or scanning (SEM) electron microscopy measurements (Ispas et al., 2021). In the TEM microscopy image of the non-covered magnetic nanoparticles (MNPs) in **Figure 4a**, a uniform structure of well-dispersed magnetic nanoparticles with an average diameter of about 10 nm can be observed. From the TEM image, **Figure 4b**, the SiO_2 layer can be seen on the surface of the nanoparticles.

Also, TEM microscopy images show the morphology of polymer-coated magnetic hybrid composites, MNPs-SiO_2-pAAc (**Figure 4c**), MNPs-SiO_2-pAMPS (**Figure 4d**), MNPs-SiO_2-CHIT (**Figure 4e**). The structure of these polymer-coated magnetic hybrid composites was confirmed by FTIR measurements (Ispas et al., 2021).

The magnetization curves of MNPs, MNPs coated with SiO_2 shell, MNPs-SiO_2 and polymer-coated magnetic clusters MNPs-SiO_2-pAAc, MNPs-SiO_2-pAMPS and MNPs-SiO2-CHIT, show superparamagnetic behavior for all samples at room temperature. The saturation magnetization value was 71.2 emu/g for the initial necked MNPs, a very good magnetization value for MNPs.

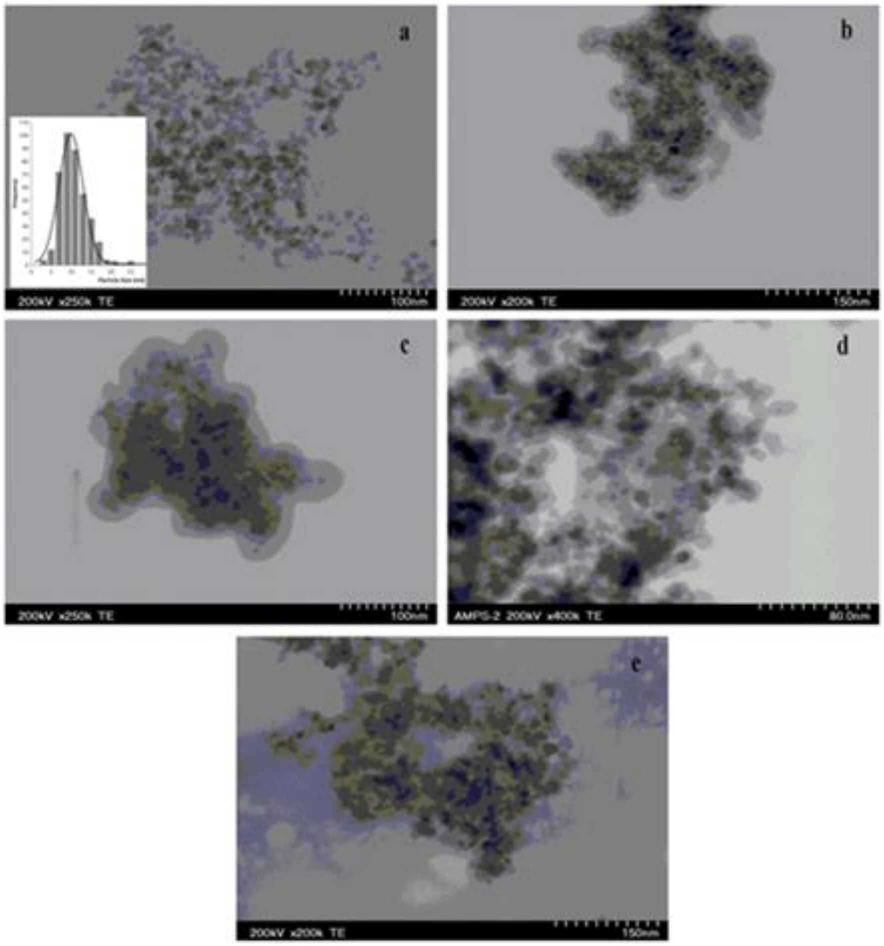

Figure 4. The morphology of the MNPs (a) and MNPs coated with SiO_2 shell, MNPs-SiO_2 (b) and polymer-coated MNPs MNPs-SiO_2-pAAc (c), MNPs-SiO_2-pAMPS (d) and MNPs-SiO_2-CHIT (e).

The electrochemical characterization (**Figure 5**) (Ispas et al., 2021) of the electrode materials was performed using cyclic voltammetry. The electrocatalytic response of modified electrodes with nanoparticles or magnetic nanocomposites prepared under different conditions to nitrite oxidation has been studied comparatively.

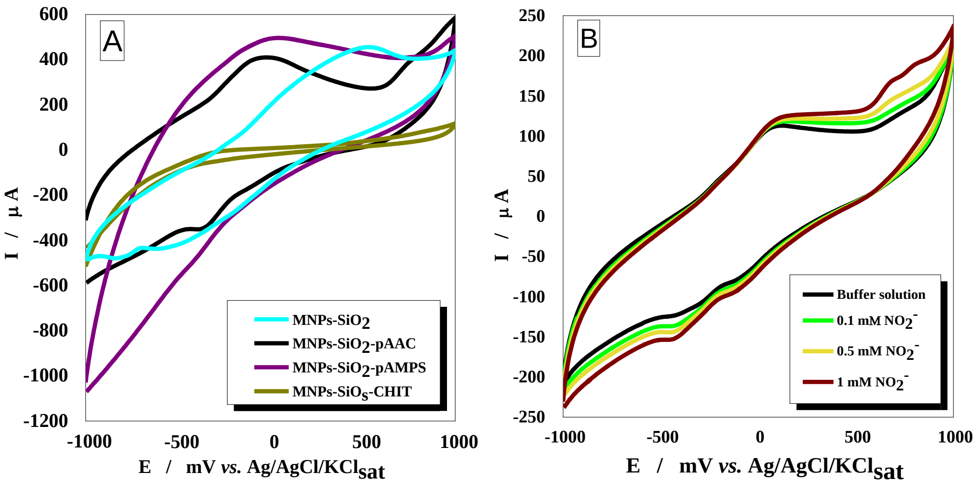

Figure 5. (a) Electrochemical response of carbon paste electrodes modified with MNPs-SiO$_2$, MNPs- SiO$_2$-pAAc, MNPs-SiO$_2$-pAMPS, MNPs-SiO$_2$-CHIT;
and (b) electrocatalytic effect of carbon paste electrodes modified with MNPs-SiO$_2$-pAAc.
Experimental conditions: supporting electrolyte, phosphate buffer solution, pH 7;
scan rate, 50 mV s^{-1} (A) and 10 mV s^{-1} (B)

Figure 5B shows an increase in the intensity of the oxidation peak with an increase in nitrite concentration in the solution. Thus, the modified electrode (MNPs-SiO$_2$-pAAc) has a good electrocatalytic effect on nitrite oxidation and can be used in the nitrite detection processes.

The amperometric measurements for MNPs-SiO$_2$-pAAc-modified carbon paste electrodes were performed in a stationary regime, at an applied potential of + 0.01 V *vs.* Ag/AgCl/ KCl$_{sat}$, in phosphate buffer of pH 7, in magnetically stirred solutions, and the calibration curve is presented in **Figure 6**.

The detection limit was 20 µM for MNPs-SiO$_2$-pAAc. The detection limit presents a good value and is closed to values obtained in a previous study (Ispas et al. 2018), 1 µM. The main analytical parameters are *sensitivity*: 10.79 mA/M (R/N = 0.999/5); *linear domain*: 0.08–1 mM. These parameters are smaller than those obtained in (Ispas et. 2018) but are normally not too high, due to the high difference in applied potential values.

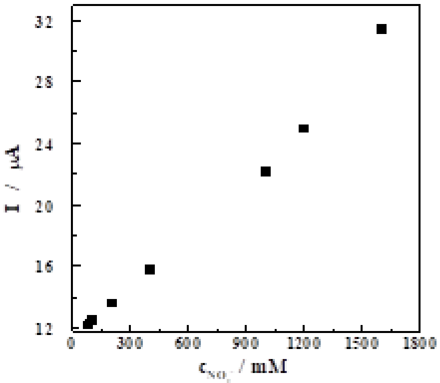

Figure 6. Calibration curves for nitrite, as measured using MNPs-SiO_2-pAAc electrode.
Experimental conditions: applied potential, +100 mV *vs.* Ag/AgCl/KClsat;
supporting electrolyte, 0.1 M phosphate buffer solution, pH 7.

In conclusion, this material presents the most important advantage, decreasing the applied potential to + 0.01 V *vs.* Ag/AgCl/KCl_{sat} and also, it presents good analytical parameters for nitrite detection.

The as-prepared electrochemical sensors using the new magnetic polymeric nanocomposite electrode materials, MNPs-SiO_2-pAAc, have been used in quantitative measurements of nitrite by different kinds of real samples, such as soil water and vegetables **(Table 1)** coming from an agricultural area of Romania.

Table 1. Nitrite concentration in real samples (soil, water, vegetables/leaves)

Sample	**Sample features**	**Concentration of NO_2^-**
Soil	deep 0-20 (cm)	1.93
		1.37
		2.1
	deep 20-40 (cm)	1.83
		1,97
		1.73
Irrigation water	1	0,68
	2	0,7
Vegetables	Cucumber	0,48
	Tomatoes	0,32
	Peppers	0,29
	Eggplants	0,32
Leaves	Cucumber	0,303
	Tomatoes	0,212
	Peppers	0,07
	Eggplants	0,216

IV.3. Conclusions

- Modified electrode materials, based on a combination of hybrid nanocomposites such as MNPs, magnetite (Fe_3O_4), inorganic polymer (SiO_2), and different types of organic polymers were prepared and studied. Three types of organic polymers were used, a hydrogel-type polymer, poly acrylic acid (pAAc), a cation exchanger-type polymer, poly(2-acrylamido-2-methylpropane sulphonic acid sodium salt) pAMPS, and a natural bioactive-type polymer, CHIT.
- The best electrochemical response was obtained for the electrode modified with MNPs-SiO_2-pAAc, compared to the other three tested materials.
- The electrochemical measurements proved that the electrode modified with MNPs-SiO_2-pAAc has a good electrocatalytic effect on nitrate oxidation and can be successfully used in detection.
- The main analytical parameters determined are: sensitivity, 10.79 mA / M (R / N = 0.999 / 5), linear range between 0.08 and 1 mM and detection limit of 20 µM.
- The as-prepared electrochemical sensors using the new magnetic polymeric nanocomposite electrode materials, MNPs-SiO_2-pAAc, have been used in quantitative measurements of nitrite by different kinds of real samples, such as soil and water coming from an agricultural area of Romania.

CH. V. MAGNETIC HYDROGEL COMPOSITES BASED ON CROSS-LINKED POLY (ACRYLIC ACID) USED AS A RECYCLABLE ADSORBENT SYSTEM FOR NITRATES

The aim of this study was to use magnetic hybrid nanocomposites based on cross-linked polyacrylic acid as recyclable magnetic systems for pollutants adsorption, especially nitrates, using an innovative technique of magnetic separation of nitrate from wastewater. The main objective was to test the material obtained in successive cycles of adsorption-desorption of NO_3^-.

V.1. Synthesis of magnetic hydrogel nanocomposites (MNP-pAAc) based on cross-linked polyacrylic acid

Polyacrylic acid cross-linked magnetic polymeric nanocomposites were prepared by two reaction steps. Firstly, the magnetic nanoparticles (MNPs) of iron oxide, magnetite (Fe_3O_4), using the coprecipitation method were prepared and secondly, the encapsulation of magnetic nanoparticles in a cross-linked polyacrylic acid polymer matrix (Ispas et al., 2018, Ispas et al., 2020).

V.2. Physico-chemical characterization of magnetic hydrogel nanocomposites (MNP-pAAc) based on cross-linked polyacrylic acid

Magnetic nanocomposites were morphologically characterized using transmission/scanning microscopy (STEM). The morphology images are represented in **Figures 7a**, **and b** (Ispas et al., 2020). As shown in **Figure 7a**, the magnetic nanoparticles are coated with a thin layer of cross-linked polyacrylic hydrogel.

To confirm the structure of magnetic hydrogel nanocomposites (MNP-pAAc) based on cross-linked polyacrylic acid, the materials were characterized using FTIR spectroscopy. From the association of the specific bands of the two components, namely, the magnetic component, and some characteristic bands of polyacrylic acid, was demonstrated the successful formation of magnetic hydrogel nanocomposites based on cross-linked polyacrylic acid.

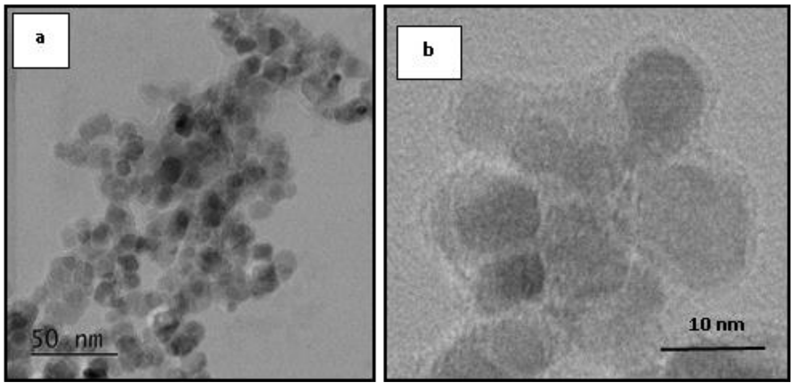

Figure 7. TEM microscopy images for magnetic hydrogel nanocomposites (MNP-pAAc) based on cross-linked polyacrylic acid (various magnifications)

The structural characterization using the X-ray diffraction showed that the identified structure is in perfect agreement with the cubic structure of the reverse spinel of the magnetite (Fe_3O_4, JCPDS card no. 85-1436) and is also similar to the results reported in the literature (Gong et al., 2003; Liao et al., 2001).

The magnetic polymeric nanocomposites were analyzed from a magnetic point of view, showing a superparamagnetic behavior at room temperature, with high saturation magnetization values. Magnetic nanoparticles (MNPs) showed a saturation magnetization value of 70 emu/g, with a slight decrease to 58 emu/g due to the coating of magnetic nanoparticles with a layer of polyacrylic acid. A decreased magnetization is considered normal, considering that the polymer coating is nonmagnetic and provides significant information on the presence and thickness of this coating.

V.3. Adsorption/desorption study of nitrate using magnetic hydrogel nanocomposites (MNP-pAAc) based on cross-linked polyacrylic acid

The adsorption efficiency of NO_3^- using magnetic hydrogel nanocomposites (MNP-pAAc) based on cross-linked polyacrylic acid was investigated in correlation with various parameters, such as the initial concentration of nitrate, the amount of adsorbent material, and the pH of the adsorption medium, using UV-VIS spectroscopy technique and a specific protocol used in previous studies (Crăciunescu et al., 2017; Ispas et al., 2018).

For the adsorption efficiency of nanocomposites with the initial NO_3^- concentration, standard solutions of NO_3^- of different concentrations between 1 and 20 mg/ml were prepared, at pH = 7, adding the same dose of adsorbent material (50 mg), and the samples thus prepared were incubated for 30 min in a thermostatic stirring bath at a constant temperature. Thus, the optimal initial NO_3^- concentration was determined to be about 2 mg/ml, where the adsorption efficiency is almost maximum, around 90%.

The investigation of efficiency adsorption of NO_3^- according to increasing the dose of MNP-pAAc was performed by adding standard NO_3^- solutions of the same concentration (10 mg/ml), at different doses of adsorbent material, ranging between 10-1000 mg. The samples thus prepared were incubated for 30 minutes in a thermostatic stirring bath at a constant temperature. It was found that the optimal dose of composite (MNPs-pAAc) is 100 mg, where the adsorption efficiency (calculated as the mass percentage of NO_3^- adsorbed by MNP-pAAc from the initial solution) is almost maximum, at around 90%.

To study the effect of pH on adsorption efficiency of NO_3^- using MNP-pAAc magnetic hydrogel composite, NO_3^- solutions of the same concentration (10 mg/ml) were prepared with pH values from 2 to 10, and the same dose of MNP-pAAc magnetic hydrogel (100 mg). The samples thus prepared were incubated for 30 min in a thermostatic stirring bath, at a constant temperature. It was observed that there is almost no difference in the adsorption efficiency of NO_3^- with the pH, obtaining an adsorption efficiency of about 90% for all pH values.

Magnetic hydrogel composites (MNP-pAAc) were used to test their recyclability capacity of NO_3^- adsorption in five successive adsorption-desorption cycles, using the initial NO_3^- concentration of 10 mg/ml and 100 mg of MNP magnetic hydrogel composite. Maximum adsorption efficiency was observed in the first cycle at around 90%, followed by a slight decrease in the adsorption efficiency in the next four adsorption cycles, but still considered relatively high. Maintaining the adsorption capacity throughout the 5 cycles of adsorption/desorption at a high level, 80 - 90%, is an important advantage of MNP-pAAc magnetic hydrogel composites over disposable materials.

To determine the model which describes the NO_3^- adsorption using the magnetic hydrogel composite (MNP-pAAc), the adsorption experiments were performed under isothermal conditions, using an initial NO_3^- concentration of 2 to 500 g/L, at three different temperatures (30, 40, and 50 °C) (Ispas et al., 2020). In the present study, the equilibrium adsorption of NO_3^- using the magnetic hydrogel composite (MNPs-pAAc) was analyzed, according to the linear shape of the Freundlich model. According to the Freundlich model, the study shows predictable values of NO_3^- adsorption. In addition, it shows a very good overlap with experimental NO_3^-

adsorption data at equilibrium, using the magnetic hydrogel composite (MNPs-pAAc), at all three temperatures. According to the Freundlich model, the adsorption mechanism confirms that the adsorption process has a heterogeneous base, which is in agreement with the chemical structure of the adsorbent material.

V.4. Conclusions

- A magnetic separation technique has been proposed to retain a significant toxic inorganic pollutant (nitrate) from wastewater, using a polymeric magnetic composite adsorbent system with recyclability potential.
- The maximum separation efficiency was relatively high, between 80-90%, while the magnetization value was around 60 emu/g, which corresponds to a relatively high value for this type of magnetic hydrogel polymer composite. This feature makes the synthesized material a potential material in water purification applications. However, the most important aspect related to the properties of this material is that it can be recycled, washed, and reused, which is a degree of novelty in the literature for similar materials.
- The recycling properties of the material have been demonstrated by five successive cycles of adsorption-desorption. The adsorption capacity of the material has been maintained at a high level, this aspect being a particularly important advantage for materials used only once. An additional solution is obtained to avoid secondary pollution by applying the material for the effective depollution of nitrate from the wastewater.

CH. VI. MONITORING THE CONTENT OF MAJOR IONS AND HEAVY METALS IN IRRIGATION WATER, AGRICULTURAL SOIL, AND VEGETABLES GROWN IN INVESTIGATED GREENHOUSES

In order to assess the impact on human health associated with vegetable consumption, it is essential to monitor the quality of agricultural soil and vegetables, because the contamination of the food chain is one of the main routes of human exposure to heavy metals, various anions, and cations, leading to potential health risks.

The main purpose of the presented study was to monitor the soil and vegetables in terms of ions content (anions, cations, and heavy metals) and nutrients from an agricultural area in Botosani County.

VI.1. Description of the study area

The study area is located in the village of Hudum, Curtești commune, in the rural area of Botoşani county (located in the northeastern part of Romania). For the study presented in this chapter, the analyzed vegetables (onions, cucumbers, tomatoes, lettuce, eggplant and peppers) and soil were taken from a complex of greenhouses (17 greenhouses, of which four (S1 - S4) were taken as a sampling bridge) (**Figure 8**).

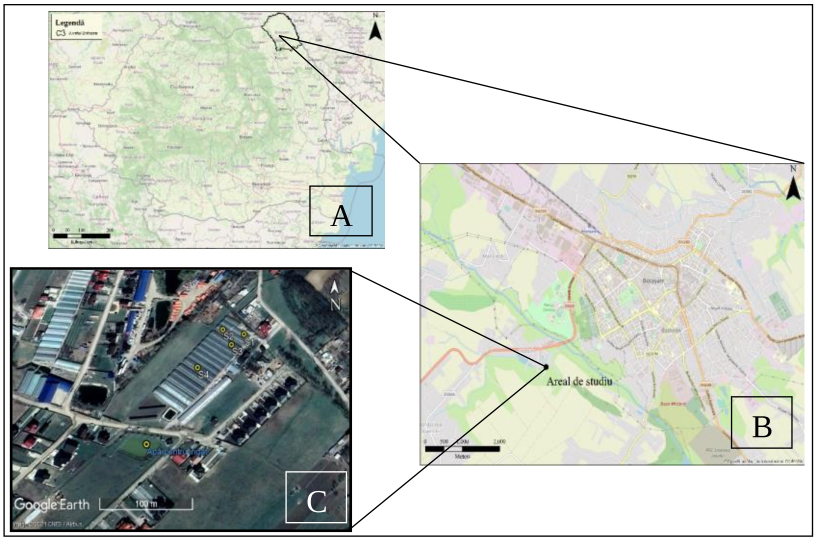

Figure 8. Location of the sampling area in north-eastern Romania (A), Botoșani county (B), the investigated greenhouses S1 - S4 (C); (Google Earth)

VI.2. Methods used in the sampling, processing and analysis of soil, irrigation water and vegetable samples

This study was performed between June 2016 and April 2017, being collected a total of 200 soil samples, on profiles from 0 to 160 cm. At the same time, 34 samples of vegetables were taken. The samples were analyzed using Ion Chromatography (Dionex 1500 IC, USA).

As in the case of the determination of dissolved ions, in order to determine the concentration of heavy metals, the soil, vegetables, and water samples selected for analysis (July - 2016, October - 2016, January - 2017; March and April - 2017) were processed according to national/international standard protocols, before performing analyzes by the atomic absorption spectrometry (AAS) method, a method also used by Nassif & Saade (2010).

After sampling, the physical parameters of the soil were determined according to the national protocols as follows: humidity (SR ISO 11465: 1998), granulometry - method of sedimentation and sieving (SR EN 14688-2: 2005; SR ISO 11465: 1998), organic matter (STAS 7107 / 1-76), soil density - fluid immersion method (ISO 17892-2: 2014) and free swelling index/adsorption capacity (IS-2720-PART-40 -1970).

Physico-chemical parameters such as pH, redox potential (Eh), electrical conductivity (EC), and soil salinity were determined from the supernatant suspension of soil (1: 3 v: v) according to SR ISO 10390: 2015, using a portable multiparameter (WTW Multi 350i). Determination of the physico-chemical parameters of vegetables was limited to the determination of pH and redox potential.

The determination of the chemical parameters identifying the dissolved ions from the soil was performed by analyzing the aqueous soil extract using a method adjusted according to Stanisic et al., (2011), by assisted extraction using a rotary mixer with deionized water (18.2 MΩ cm at 25°C) in the ratio 3: 1.

For the analysis of dissolved ions in irrigation water, the samples were previously filtered through filter paper (0.45 µm). The determination of ions in vegetables was also performed according to the protocol used in the study performed by Liu et al. (2016).

The analysis of heavy metals (Pb, Fe, Zn, Ni, Cd, Cu, Cr) from the soil, irrigation water, and vegetables was performed according to the atomic absorption spectrometry (AAS) method, using a ZEEnit 700 system (Analytik Jena) equipped with air burner - acetylene, a graphite furnace and special system of lamps with cavity cathode for each metal.

VI.3. Results and discussions

Analyzing the humidity and density of soil, the results are 19.72 and 30.32% g/kg for humidity, generally decreasing with depth. In contrast, the soil density (1.55 - 2.01 g/cm^3) increased with the depth of the soil profile. The adsorption capacity of soil showed high values (80 - 110%), due to the abundance of clay fraction that retains large volumes of water and has extremely small pore size, which leads to slow migration of water.

From the point of view of the general chemical parameters of the soil, it was observed that the pH varied between 7.3 and 7.7, and without significant fluctuations in the depth of the soil profile, the electrical conductivity (EC) fluctuated between 233.50 and 869.67 μS/cm, while the salinity showed values between 0.0 and 0.36 ‰.

In terms of pH values identified in irrigation water, this parameter was identified with slightly basic pH values (7.4 and 8.0), registering higher values during July 2016 and a relatively low level in terms of conductivity (1,171 - 1,310 μS/cm).

From the point of view of anions and cations concentrations identified in the soil (**Figure 9**) (Ispas et al., 2020), was observed a slight decrease in concentrations from June to October 2016, and after that was identified a slow increase in concentrations especially for Na^+ and K^+, with maximum mean values of 127.4 mg/kg for Na^+ in July 2016 and 69.9 mg/kg for K^+ in January 2017.

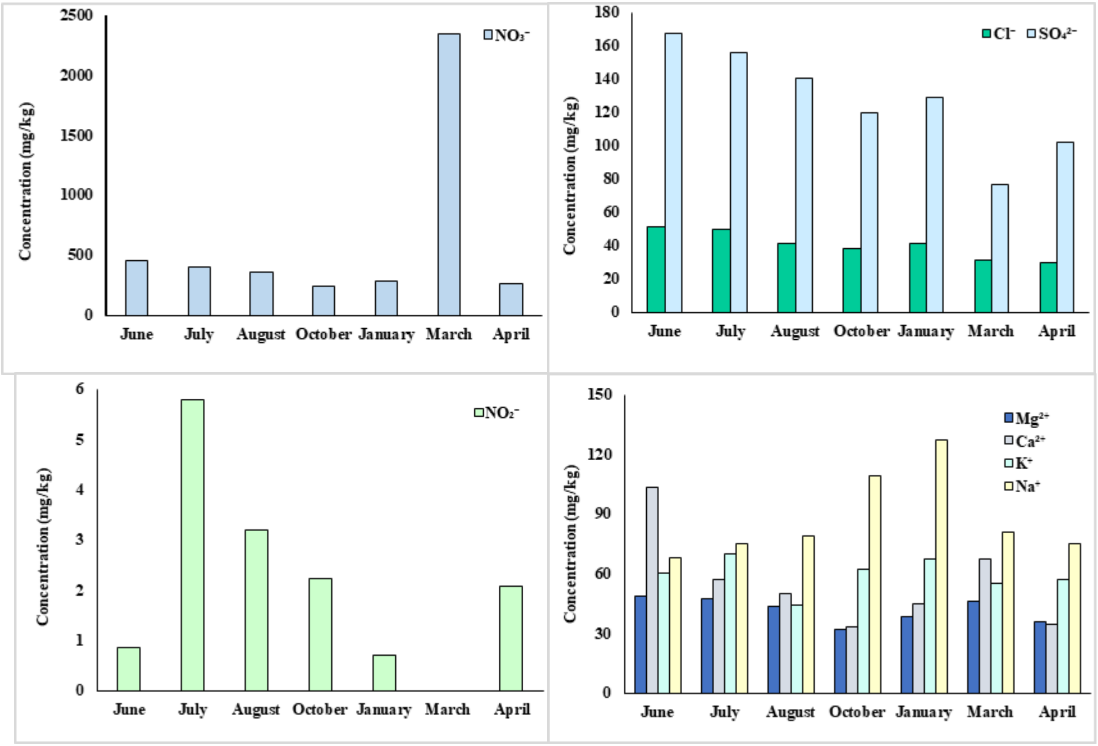

Figure 9. Monthly variation of ions and anions in the soil, represented as average values

The ions concentrations of the whole soil profile (0-160 cm) were also represented graphically as average values. The results showed a decreasing trend with the depth of soil profile, the highest values being for NO$_3^-$, especially between 0 and 60 cm (**Figure 10**) (Ispas et al., 2020). This indicates the impact on the natural composition of the surface soil in terms of the distribution of humus and natural nutrients in the soil horizons, because of the fertilizer application.

The anions concentration (**Figure 10**) was dominated by the presence of NO$_3^-$, with values between 32.76 and 5619.3 mg/kg, SO$_4^{2-}$ (27.21 and 390.9 mg/kg), while the dominant cations had been Na$^+$ (0.02 - 437.9 mg/kg) and K$^+$ (0.02 - 337.05 mg/kg).

Given that the agricultural soil was irrigated relatively constant during the summer (June, July, and August 2016), irrigation water samples were also taken to analyze the concentration of dissolved ions, and the results are shown graphically in **Figure 11**.

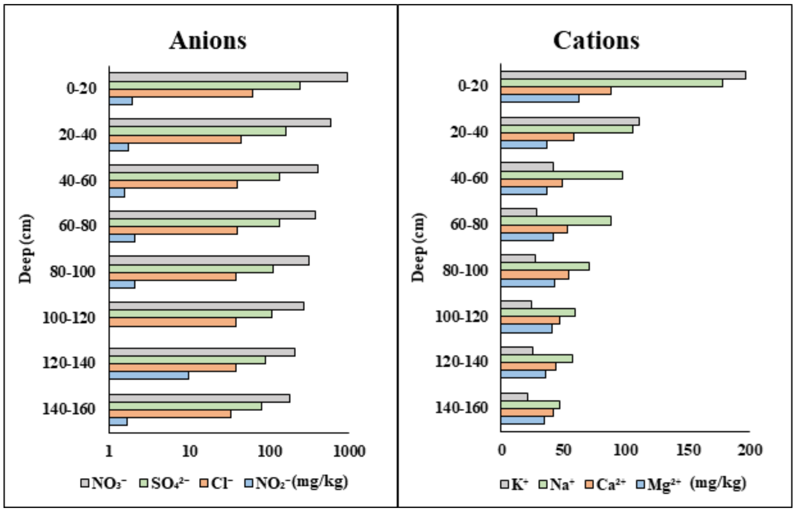

Figure 10. Fluctuation of dissolved ions on the depth of the soil profile in the form of average values for all sampling periods

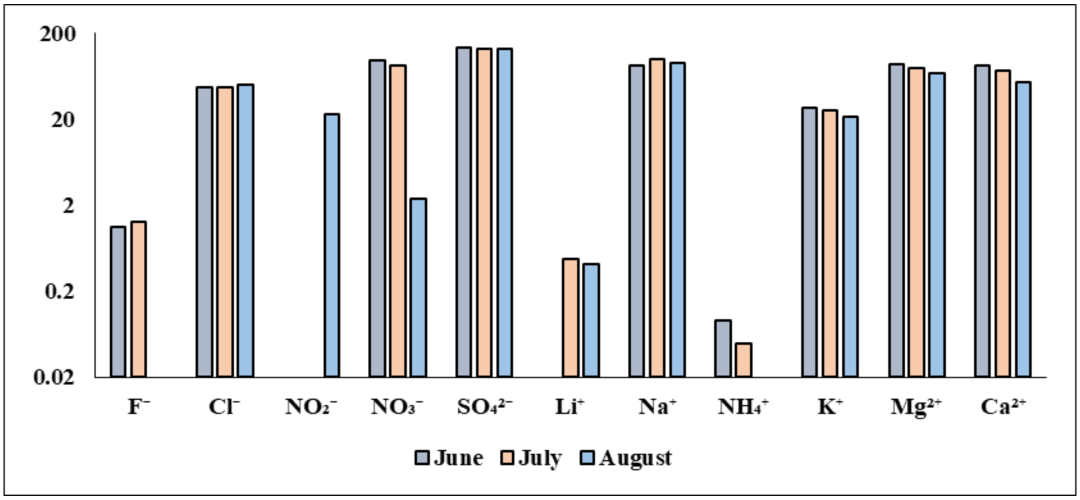

Figure 11. Fluctuation of dissolved ions in irrigation water

Regarding the monthly fluctuation of dissolved ions in irrigation water, there was a slight decrease in June and July 2016 (except for Cl^-, NO_2^-, and Na^+ ions). Except F^-, NO_2^-, and NO_3^- ions, the ion content (**Figure 11**) falls within limits imposed by national legislation (Law No. 458 of 8 July 2002).

For the analyzed vegetables, it was observed that the ion identified in the highest concentration was K^+, the hierarchy in relation to the other ions in the following: $K^+ > Cl^- > SO_4^{2-} > Na^+ > PO_4^{3-} > Ca^{2+} > NH_4^+ > Mg^{2+} > NO_3^- > NO_2^-$. Following the classification of the ions identified in vegetables according to their maximum concentration, it was observed that the vegetable in which the accumulation of potassium ion was in the highest concentration (3705.5 mg / kg) is lettuce (collected in April 2017 from the greenhouse 2).

In the case of the leaves from the analyzed vegetables, the classification according to the maximum value of the concentration of each ion was established as follows: K^+ > SO_4^{2-} > Na^+ > NH_4^+ > Mg^{2+} > PO_4^{3-} > NO_3^- > Ca^{2+} > Cl^- > NO_2^-; as in the case of vegetables, the highest concentration was identified for potassium (6013.3 mg/kg) in eggplant leaves taken in June 2016 from the greenhouse 3.

After analyzing the concentration of dissolved ions in soil and vegetables, the transfer factor for NO_2^- and NO_3^- was applied. The result of NO_3^- transfer was low, being below 1 for most samples, indicating that the vegetables did not accumulate a significant amount of nitrates from the soil.

Given the toxicity of nitrites and nitrates, was calculated the daily intake of vegetables and it was found that tomatoes, cucumbers, onions, and lettuce contribute more to the intake of nitrates than peppers or eggplant.

The daily intake of nitrates and nitrites brought by ingesting these vegetables represents up to 2.15% of the accepted daily dose (AZA), AZA- NO_3^- (222 mg of NO_3^-/day), and 0.95 - 9.05% of AZA - NO_2^- (4.2 mg NO_2^-/day) for an adult with a bodyweight of 60 kg, according to international law (FAO / WHO, 2003; EFSA, 2008), which indicated that the consumption of these vegetables does not represent a risk factor for human health.

The content of heavy metals in the soil was calculated as the total mean values for all greenhouses and months of sampling, following descending order of concentration as follows: Fe> Zn> Ni> Pb> Cu> Cr and Cd.

The levels of all metals identified were below the alert/intervention level for sensitive soils (Order no. 756/1997), indicating that their presence should not pose any risk to human health or other environmental factors (Ispas et al., 2022).

Also, analyzing the presence of heavy metals in the water used for irrigation of crops, it was found that Ni (0.002-0.01 mg/l), Cu (0.04-0.05 mg/l), and Zn (0.10-0.27 mg/l) were in very low concentrations, being below the national limits allowed by the specific legislation (Law 458/2002), for Cr and Cd, the concentrations were very low, below the detection limit of the device, for all water samples analyzed (Ispas et al., 2022).

The concentrations of heavy metals were analyzed for vegetables grown in March and April 2017. The content of heavy metals varies significantly due to the different absorption capacities of vegetables. Thus, a higher absorption affinity was observed for Cu, Zn, and Fe, than for Ni, Pb, Cr, and Cd (Ispas et al., 2022).

The transfer factor (TF) of heavy metals from soil to vegetables was also calculated. The results indicated that the transfer factor values vary greatly, depending on the type of vegetable. Generally, the values of TF were very low, with concentrations ranging from 0.003 (TF-Fe) to 0.94 (TF-Cu) following the next sequence: TF – Cu > TF – Zn > TF – Pb > TF – Ni > TF - Cr > TF – Fe (Ispas et al., 2022).

The contamination factor for soil was also calculated, and the mean values were 2.3 (Cd), 1.30 (Ni), 1.1 (Pb), 0.99 (Zn), 0.86 (Cu), 0,56 (Fe), and 0.52 (Cr). So that the analyzed soil was classified at the level of low contamination with metals Cu, Fe, and Cr and moderately contaminated with Pb, Ni, and Cd (Ispas et al., 2022).

Following the calculations made to determine the level of soil enrichment with heavy metals by calculating the enrichment factor (EF) the values fluctuated between: 1,9 - 7,4 (Cd), 2,2 - 2,5 (Ni), 1,4 - 2,5 (Pb), 0,8 - 2,1 (Zn), 1,0 - 1,6 (Cu) and 0,6 - 1,2 (Cr) (Ispas et al., 2022).

The results thus obtained showed a moderate enrichment with Ni, Pb, and Cd, and for the other elements, their presence was quite deficient (Ispas et al., 2022).

Following the application of the geoaccumulation Index (Igeo) formula, it was observed that there was no significant fluctuation in the geoaccumulation of heavy metals. Index values ranged from -0.4 to 1,5 (Cd), -1.6 to -0.4 (Zn), -2.1 to -1.2 (Cr), -1.5 to -0.7 (Cu), -0.3 and -0.1 (Ni), -0.9 and -0.1 (Pb), resulting that the studied area is classified as uncontaminated (Ispass et al, 2022).

The pollution load index (LI) was calculated to determine the pollution degree of different metals in the same location, compared to different greenhouses and seasons. Thus, it was observed that the LI of the upper soil analyzed varies between 0,7 and 1,01, with an average of 0,85 below 1 in all the greenhouses studied, indicating that the respective agricultural area is not polluted (Ispas et al., 2022).

Assessing the ecological risk factor and the potential ecological risk, the average values obtained from the calculation of the ecological risk factor (ERF) for Cd (17,3), Ni (6,5), Pb (5,2), Cu (3,4), and Cr (1,0) were below the limit of 40 (quantifiable value of the ecological risk factor), suggesting a low ecological risk. The potential ecological risk factor (PER) is ranged from 11,9 to 141,3, with an average value of 34.4. PER below 150, indicating a low ecological risk (150) (Ispas et al., 2022).

Assessment of exposure to heavy metals from food consumption is very important, the oral intake is considered the main source of contamination through the food chain (Garg et al., 2014; Rehman et al., 2018).

Calculating this index, it was observed that onion consumption leads to a higher intake of Fe, Zn, and Cu, while salad consumption brings a higher intake of Fe, Zn, and Pb. The estimated daily intake of heavy metals by consumption of onions and lettuce does not exceed the maximum tolerated daily allowance required by international authorities. So if these vegetables are consumed in reasonable quantities (0.022 - 0.028 kg/day), their intake does not pose a health risk consumers (Ispas et al., 2022).

VI.4. Conclusions

- By the quantitative analysis of the majority of ions in the sampled soil, it was observed that the most abundant ions present in the soil solution were NO_3^-, Na^+, SO_4^{2-} and K^+.
- Depending on the average values identified for anions and cations in vegetables, the descending order is as follows $K^+ > Cl^- > SO_4^{2-} > Na^+ > PO_4^{3-} > Ca^{2+} > NH_4^+ > Mg^{2+} > NO_3^- > NO_2^-$.
- In the case of irrigation water, the concentration of the majority of ions was relatively low except for the NO_2^- ion, where the maximum permissible concentration (0.5 mg/L) was exceeded 45.28 times in August 2016, and for NO_3^- exceeded the maximum allowed limit (50 mg/L) was only 1.9 times in June 2016.
- The intake of nitrites and nitrates brought by the consumption of the analyzed vegetables was 2.15% to 9.05% of the accepted daily concentration.
- By calculating specific indices for determining the degree of heavy metal loading of soil and vegetables in the studied agricultural area, it was observed that there is no significant loading with heavy metals that exceeds the limits imposed by the legislation in force and does not endanger human health through the consumption of vegetables.

GENERAL CONCLUSIONS

Two new modified electrode materials have been developed MNPs-SiO_2 represented by an association between Fe_3O_4 iron oxide nanoparticles incorporated in a silica (SiO_2) matrix, used in the development of electrochemical sensors for the detection of NO_2^-;

Both of these electrodes were tested in experiments for nitrites detection in groundwater samples, using the standard addition method;

Three magnetic polymeric nanocomposites based on magnetic nanoparticles (Fe_3O_4) and polymers were synthesized and characterized: a hydrogel-type polymer, polyacrylic acid; a cation exchanger-type polymer, poly(2-acrylamido-2-methylpropane sulphonic acid sodium salt) (pAMPS) and a natural bioactive polymer, chitosan (CHIT), which were later used in the development of modified electrodes;

An electrochemical sensor based on polyacrylic acid polymeric nanocomposites has been developed (MNPs-SiO_2-pAAc), which was successfully applied in quantitative measurements of NO_2^- on actual samples (soil, irrigation water, vegetables, leaves) from an agricultural area of Romania;

Polyacrylic acid cross-linked hydrogel-type magnetic polymeric nanocomposites (MNP-pAAc) with applicability in NO_3^- adsorption from contaminated waters were synthesized;

Hybrid magnetic nanocomposites based on cross-linked polyacrylic acid (pAAC) were used as recyclable magnetic nitrate adsorption systems, using an innovative technique for magnetic separation of nitrate from wastewater;

Monitoring of soil and vegetables in an agricultural area was performed by analyzing the anion content (Cl^-, Br^-, F^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}), cation (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}), and heavy metals (Zn, Cu, Ni, Cr, Pb, Cd, and Fe) in various vegetables and water used for irrigation;

The distribution of anions and cations on the depth of the soil profile of the seasonal fluctuations of the content of ions and heavy metals in vegetables, soil, and irrigation water, was evaluated;

The transfer factor of NO_2^- and NO_3^- ions, respectively, metal ions from the soil to vegetables and leaves, was calculated, and the results indicated that the vegetables did not accumulate significant amounts of the two ions and heavy metals;

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