ADVANCED TECHNOLOGIES FOR WATER QUALITY MONITORING AND PURIFICATION FROM HEAVY METAL IONS

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Providing the population with clean drinking water has become a priority task around the world according to the World Health Organization. However, this issue is complicated by the growing population, higher water quality standards and, at the same time, increasing of water and wastewater pollutions, which poses a serious threat to human health and environment.

This problem is most acute today during the hostilities in Ukraine. Missile strikes are not only accompanied by consequences for people and infrastructure, but also the environment suffers from this. The level of heavy metals in natural resources is increasing significantly. Therefore, during martial law and post-war recovering in Ukraine, water quality control and purification are critical parts of environmental protection.

It is known that most of the current detection techniques for water analysis are based on optical and mass spectroscopy measurements and require long detection cycles, as well as specific chemicals which may cause secondary pollution.

Water purification methods that allow the removal of heavy metal ions from water without changing the degree of oxidation are based on sorption, ion exchange, and membrane technologies. The use of sorption methods is associated with the cost of sorbents.

In this work, for water quality control and purification, our research group used advanced technologies, such as laser-induced breakdown spectroscopy and biosorption treatment.

Laser-induced breakdown spectroscopy (LIBS) is a novel atomic emission spectroscopic nanotechnology used to determine the elemental composition of a sample. LIBS has several advantages, including easy sample pre-treatment, fast operation, chemicals free during the process, and identification of multi-state substances simultaneously, rapidly, and remotely [1].

Biosorbents are biological materials used to remove pollutants from water, such as heavy metals, dyes, and pharmaceuticals. They are derived from natural sources like bacteria, fungi, algae, and agricultural waste such as fruit shells, and are valued as being a cost-effective and environmentally friendly method for water purification [2].

Experimental LIBS system includes five main components. These are the sample holder, the laser source, the optical path, the spectrometer, and the data analysis unit. For the first series of experiments, we built setup for the Single-pulse LIBS consists of Nd:YAG laser Continuum Minilite with a pulse duration of 10-15 ns, a repetition rate of 10 Hz, a maximum pulse energy of 850 mJ, and wavelength of 1064 nm with the USB 4000 Ocean Optics Spectrometer.

Firstly, our research team focused on the application of chemical replacement combined with surface-enhanced LIBS (CR-SENLIBS) for the detection of heavy metal ions, such as Fe^{3+} and Cu^{2+} in aqueous solutions and natural waters [3].

The main aqueous solutions 500 mg/L of $FeCl_3$ and $CuCl_2$ were dropped into Al alloy plates and dried on aluminium foils. LIBS experiments of Al plates also were conducted. LIBS

spectra containing information about these metals were collected immediately after microplasma generation in visible optical spectrum region.

LIBS spectra were compared with theoretical database NIST LIBS of American National Institute of Standard and Technology. From the main solutions of 500 mg/L of $FeCl_3$ and $CuCl_2$, working solutions with concentrations 2.5–50 mg/L of $FeCl_3$ and $CuCl_2$, were prepared by dilution with distilled water. After microplasma generation, our research team found 14 LIBS spectra for 2.5–50 mg/L $FeCl_3$ and $CuCl_2$. In agreement to the NIST LIBS database, in the LIBS spectra obtained from 50 mg/L $FeCl_3$ and $CuCl_2$, we received three standard peaks for Fe (λ_8=358.23 nm, λ_9=374.90 nm, and λ_{10}=384.12 nm), one standard peak for Cu (λ_7=521.87 nm), and built the calibration curves. The Limits of detection for Fe and Cu were found.

After conducting LIBS experiments with the natural waters of Ukraine and based on calibration curves, the Fe^{3+} and Cu^{2+} content of the Dnipro River, Blue Lake (Kyiv) and natural source of Obukhiv, were calculated and compared with MPC from World Health Organization. It was found that for Dnipro River: Fe^{3+} 0.23 mg/L, Cu^{2+} 0.15 mg/L, for Blue Lake: Fe^{3+} 0.2 mg/L, Cu^{2+} 0.12 mg/L, as well as for natural source of Obukhiv: Fe^{3+} 0.17 mg/L, Cu^{2+} 0.1 mg/L. According to the WHO for Ukrainian natural sources, MPC for $Fe^{3+}$and Cu^{2+}equal of 0.2 mg/L and 0.1 mg/L, respectively [4].

The purification of industrial and municipal wastewater is a non-negotiable requirement for both environmental protection and public health. Proper wastewater purification is the key to preserving natural waters from pollution. Among the most hazardous contaminants, heavy metals pose a unique and severe threat because of their fundamental nature. Unlike organic pollutants, heavy metals are non-degradable; they cannot be broken down chemically or biologically and persist indefinitely in environment. The global transition toward a circular economy requires converting industrial waste streams into valuable resources. Biosorbents derived from agro-industrial waste provide a compelling, sustainable solution to heavy metal contamination [5].

The purpose of this part of investigation was to create novel sorption materials from walnut shells using two distinct modification processes and subsequently assess their capacity for removing inorganic ecotoxicants. The raw material consisted of walnut shells crushed to a particle size of 1–2 mm. The sorbents were prepared by treating the shells with either pure acetic acid (AA) or a mixture of acetic acid and 9 % hydrogen peroxide (AAHP). Both reactions were performed at 90 ºC with a solid-to-liquid ratio of 5:1.

Sorption of inorganic heavy metal ions was studied using iron Fe^{3+} and copper Cu^{2+} model solutions, with concentrations ranging from 10–50 mg/L and 50–250 mg/L, respectively, over a 120-minute period using 0.50 g of sorbent and 50 mL of solution. Concentrations were monitored spectrophotometrically.

The chemical modifications induced significant and beneficial structural changes in the walnut shell matrix (Table). During treatment in the hot AA medium, the primary mechanism was acid hydrolysis. This promoted the selective removal of both low- and high-molecular-weight polysaccharide components and facilitated the dissolution of mineral components. This structural cleaning had a profound positive impact on the pore volume of the sorbent 1, making the binding sites more accessible. The addition of the strong oxidizing agent (AAHP) resulted in a much more significant decrease in the yield of the lignocellulosic material. This yield loss was directly attributed to the efficient removal of a substantial portion of aromatic substances, primarily lignin. Consequently, the content of remaining polysaccharides (cellulose and hemicellulose) significantly increased in the modified sorbent 2, simultaneously reducing the mineral content by more than half compared to the initial raw material.

Table. Characteristics of walnut shells and obtained biosorbents

Material / sorbent	Sorbent yield, %	Component content, %			
		cellulose	lignin	minerals	others
Walnut shells	–	41.2	37.5	2.3	19.0
Sorbent 1	86.0	27.3	48.3	0.3	24.1
Sorbent 2	40.2	76.8	0.8	1.2	21.2

It is known that due to the presence of various functional groups (methoxyl, hydroxyl, carbonyl), plant materials are characterized by certain sorption properties for metal cations. In addition, heavy metal ions can bind tannins contained in unmodified walnut shells to form insoluble compounds. An important role in ion-exchange properties is also played by the mineral component that can participate in ion exchange reactions.

Since the initial sample is characterized by the maximum content of mineral substances and a high content of lignin, organic substances with various functional groups, it has the maximum sorption capacity for Fe^{3+} and Cu^{2+}. Modification of the walnut shell in an AA environment leads to a significant decrease in the content of mineral components, but the relative content of lignin increases slightly. Perhaps this is why the sorption capacity of sorbent 1 for heavy metal cations is slightly reduced. The lowest sorption capacity for the studied ions corresponds to the sample with the maximum content of the polysaccharide component. Overall, the obtained plant sorbents demonstrated a high sorption capacity toward heavy metal ions: Fe^{3+} were removed with a capacity ranging from 18–29 mg/g, and Cu^{2+} removal capacity ranged from 33–44 mg/g. These figures position the modified walnut shells as competitive alternatives to commercial heavy metal adsorbents.

Therefore, by investing in water quality monitoring and purification, using advanced technologies, such as laser-induced breakdown spectroscopy and biosorption treatment, it is possible better manage and protect the water resources, which are essential for public health, agriculture, and economic development. Our main goal is to help in creation of environmental sensors to assess and improve the availability and quality of water, which are essential for health and wellbeing in general around the world and for Ukraine in difficult period of war.

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UTILIZING LEATHER PRODUCTION RESIDUES TO DEVELOP FUNCTIONAL COLLAGEN GELS FOR BIOMEDICAL APPLICATIONS

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The leather industry generates huge volumes of waste, which constitute a significant environmental burden. It is estimated that up to 60–70% of raw hide is converted into waste, a significant portion of which consists of trimmings from mechanical processing and semi-finished products. Most of these residues, such as fleshings, limed pelt, and delimed pelt, are rich in protein – collagen, a valuable natural polymer. Collagen, as the main component of the extracellular matrix, is widely used in biomedicine for creating implants, tissue engineering scaffolds, drug delivery systems, and wound healing materials. Therefore, the development of effective and environmentally friendly methods for extracting high-quality collagen from leather production waste is an extremely relevant task, aligning with the principles of the circular economy and contributing to reduced environmental pollution. The aim of this work was to investigate the feasibility of obtaining biomedically suitable collagen from various types of leather industry waste and to evaluate the characteristics of the resulting gels.

Materials and Methods. Three main types of waste were used for the experimental studies: limed pelt, delimed pelt, and fleshings. Each type of waste underwent pre-treatment to remove undesirable impurities (e.g., fat and mineral salts). Specifically, limed pelt samples were subjected to a delining stage using 3% ammonium sulfate at a temperature of 38-40ºC for 1 hour. After grinding to a size of 3×3 cm, protein components were extracted using a sequential extraction method. A combination of alkaline and acidic treatment methods was applied to optimize the yield and purity of the collagen. A total of three sequential extractions were performed for each waste type to maximize protein yield. The isolated collagen solution was subjected to dialysis and lyophilization. The quantitative protein content in the extracts was determined by two independent methods: Biuret and Bradford. Furthermore, the mass fraction of moisture, minerals, and total nitrogen in the starting materials was determined. To assess the suitability of the obtained collagen for biomedical application, its physicochemical properties were investigated, including thermal stability, rheological characteristics, and the ability to form gels under physiological conditions. A crucial step involved evaluating the purity and molecular structure of the collagen using SDS-PAGE electrophoresis to confirm the presence of characteristic α- and β-chains.

Results. Analysis of the initial raw materials showed that delimed pelt has the highest mass fraction of total nitrogen (an indicator of protein content), approximately 15.0%, while limed pelt contains a high percentage of mineral substances (up to 10.7%), mainly due to lime residues. Fleshings, although containing the most minerals (up to 31.7%), have a relatively low total