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Preparation of modified carbon materials for the removal of radionuclides from contaminated water

8D07109 - Innovative technologies and new inorganic materials

A thesis submitted for the scientific degree of Doctor of Philosophy (Ph.D.)

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NORMATIVE REFERENCES

In this dissertation, references are made to the following standards:

GOST 7.32-2001. Report on research work. Structure and design rules.

GOST 9147-80. Porcelain laboratory glassware and equipment. Technical conditions

GOST 7.1-2003. Bibliographic record. Bibliographic description. General requirements and compilation rules.

GOST 4517-87 Reagents. Methods for the preparation of auxiliary reagents and solutions used in the analysis.

GOST 12.1.008-76. Occupational safety standards system. Biosafety. General requirements.

GOST 23932-90 E. laboratory glassware and equipment.

GOST 20292-74. Volumetric flasks with a capacity of 100, 200, 500, 1000 ml. Technical conditions

GOST 25336-82. Laboratory glassware and equipment. Types, basic parameters, and sizes.

GOST 29252-91. Laboratory glassware. Burettes. Part 1. General requirements. GOST 1770-74. Measuring laboratory glassware. Cylinders, beakers, flasks, test tubes.

General specifications.

GOST 2922-91. Laboratory glassware. Graduated pipettes.

GOST 6709-72 Distilled water

LIST OF ABBREVIATIONS

AC	Activated carbon
BH	Buckwheat husk
WN	Walnut shell
RH	Rice husk
STS	Semipalatinsk Test Site
CVD	Vapor deposition furnace
st.	Test site
¹³⁷ Cs	Cesium-137
+1	Tunnel from where contaminated radioactive water where sampling
<i>ι</i> ι.	runner nom where containing ded radioactive water where sampling
Bk/L	Becquerel per liter
Bk/L HTM	Becquerel per liter Hydrothermal method
Bk/L HTM rpm	Becquerel per liter Hydrothermal method Revolution per minute
Bk/L HTM rpm BET	Becquerel per liter Hydrothermal method Revolution per minute Brunauer-Emmett-Teller
Bk/L HTM rpm BET DFT	Becquerel per liter Hydrothermal method Revolution per minute Brunauer-Emmett-Teller Density Functional Theory
Bk/L HTM rpm BET DFT BJH	Becquerel per liter Hydrothermal method Revolution per minute Brunauer-Emmett-Teller Density Functional Theory Barrett, Joyner, and Halenda

INTRODUCTION

Assessment of the current state of the scientific or technological problems to be solved. Basis and background information.

The contamination of water with radionuclides, particularly radioactive cesium and iodine, is a serious environmental and public health concern. These radionuclides, often released during nuclear accidents or industrial activities, pose long-term risks due to their high solubility, mobility, and persistence in the environment. Hence, developing effective methods to remove these hazardous substances is critical for ensuring clean water and protecting ecosystems as well as supporting the industries that release them. Carbon-based materials have high surface area, are chemically stable, and have tunable properties, among other advantageous properties for cleaning water. We have proposed to explore their use for capturing the above-mentioned radionuclides. By modifying these materials, their adsorption capabilities can be enhanced, making them effective in capturing radioactive cesium and iodine from contaminated water. This research focuses on the preparation and optimization of modified carbon materials as advanced adsorbents for radionuclides removal.

Fundamentals and background data for theme development

Kazakhstan encounters distinct challenges regarding water contamination from radionuclides, a consequence of its extensive history of nuclear testing and uranium mining at the Semipalatinsk Test Site and other areas. The long-term effects of these activities, including the contamination of soil and water with radioactive cesium and iodine isotopes, pose significant risks to public health and the environment, particularly in regions surrounding these sites. Although there are existing water treatment technologies, their cost and effectiveness in addressing the specific challenges of radionuclide removal within Kazakhstan's unique geological and hydrological context remain pressing issues.

Significant gaps exist in our understanding of the adsorption mechanisms at the molecular level, as well as in the optimal modification techniques required to enhance the adsorption of cesium and iodine. The long-term stability and regeneration potential of these materials under real-world conditions remain ambiguous. Moreover, there is a notable lack of data concerning the cost-effectiveness of modified carbon materials in comparison to existing treatment solutions. Insights into scaling laboratory findings to pilot or full-scale applications that are relevant to Kazakhstan are also insufficient. This information is crucial for developing a regulatory framework that governs radionuclide removal and shapes public perception of these treatment technologies. Lastly, there is a pressing need for comparative studies that assess the efficacy of modified carbon derived from various biomass sources in order to establish best practices. Addressing these gaps is essential for formulating effective strategies to manage radionuclide contamination in water.

The aim of the study:

This work therefore aimed at developing a technological protocol and biomass based modified sorbents for the effective adsorption of Cs^+ and I_3^- radionuclides.

To achieve this goal, the following tasks were outlined:

1. To prepare novel modified sorbents derived from biomass and to conduct a comprehensive analysis of their physicochemical properties.

2. To investigate the influence of the carbon matrix composition and the inclusion of modifying additives, specifically urea and Prussian blue, on the sorption capacity for designated ions.

3. To evaluate methodologies for the preparation of modified sorbents based on activated carbon, with particular attention to their structural characteristics and sorption efficacies.

4. To establish and elucidate the correlation between the physicochemical properties and the sorption capacity of the materials in question.

5. To assess the functionality of the synthesized modified sorbents in relation to radioactive isotopes under controlled laboratory conditions and within contaminated aquatic environments.

Object of the study: radionuclides of cesium and iodine; modified sorbents based on activated carbon from rice husk, buckwheat husk, and walnut shell biomass.

The subjects of the research: the process of sorption of iodide and cesium ions. The study aims to establish how the chemical composition of modified sorbents affects their structure and sorption capacity. Additionally, it seeks to identify the factors that influence the sorption capacity of non-radioactive and radioactive isotopes in ideal solutions and in water samples taken from the industry, therefore with natural matrix and levels of Cs and iodine species.

The methods of the research

To produce activated carbons, a tube furnace with 1-zone heating was utilized. The preparation of carbons was conducted at various temperatures and involved the use of chemical activators. The impregnation of modifying agents, such as nitrogen groups and ferrocyanide, was carried out in an autoclave and a high-pressure microreactor (PR 250).

The sorption capacity of the modified sorbents for triiodide was assessed using ultraviolet-visible (UV) spectroscopy, while the cesium content was measured using inductively coupled plasma-mass spectrometry (ICP MS). The residual activity of the sorbents was evaluated through gamma spectrometry (2480 Automatic Gamma Counter) to determine the presence of the radioactive isotope 137Cs.

The physicochemical properties of the modified carbon sorbents were analyzed with complementary techniques, including Scanning Electron Microscopy- with Energy Dispersive X-ray Spectroscopy (SEM/EDS), nitrogen porosimetry, X-ray Fluorescence (XRF), X-ray Fluorescence (FT-IR), water wettability, zeta potential, surface charge and Raman spectroscopy.

The theoretical and practical significance of this research:

Theoretically, the study established a relationship between the sorption capacity of synthesized modified sorbents and their morphology, structure and functional groups, specifically for the sorption of anions and cations, using triiodide and cesium ions as examples. Before the start of this PhD, removing charged species from water using a hydrophobic material such as carbon was a challenge, and understanding how to overcome the challenge, and making it possible, has generated new knowledge. On the practical side, the research utilized inexpensive domestic biomass as the raw material for producing modified carbon sorbents. The result of fundamental research into mechanisms of interaction between carbons and the targeted ions of cesium and triiodide, followed by practical engineering development of carbons have newly generated, highly effective modified carbon sorbents developed for the sorption of radionuclides from various types of water. The developed sorbents are scalable, a condition for their practical in large scale applications. Within this thesis, the carbons have been tested in a real scenario that is to treat water from and in the premises of former bomb testing polygon (Degelen site). This gives great significance to the materials developed. The creation and understanding of these scientifically proven nanoporous modified sorbents, along with the identification of optimal sorption conditions in laboratory settings and with real radioactive isotopes from industrial effluents, represents a significant contribution to both the fundamental and applied processes of radionuclide sorption.

The novelty of the Thesis.

The innovative method for preparing carbon sorbents by doping with ferrocyanide and urea using hydrothermal processing enhances the understanding of material modifications for improved adsorption of ions, including radionuclides. By testing these sorbents on actual radioactive isotopes and contaminated water from a historical explosive testing facility, the research bridges the gap between laboratory findings and real-world applications. This empirical validation contributes important data on the effectiveness of these sorbents in complex environmental conditions and benchmarks their performance against traditional methods. Ultimately, this work adds valuable insights to the body of knowledge in material science and environmental remediation.

Relation of the thesis with research and government programs

The work was carried out as part of projects funded by the Ministry of Education and Science of the Republic of Kazakhstan. BR21881939 "Development of resourcesaving energy generating technologies for the mining and metallurgical complex and creation of an innovative engineering center", AP19577049 "Synthesis, characterization and physico-chemical study of sorbents of biomass origin for industrial water purification from radionuclides"

Main provisions to be defended:

1) Urea-assisted hydrothermal modification of biomass-derived activated carbons (surface area: $1600-2200 \text{ m}^2/\text{g}$) significantly enhances nitrogen functionalization and improve sorption capacity by 30% (BH-based AC) and 35% (RH-based AC).

2) Prussian Blue-modified activated carbons demonstrate high selectivity for Cs⁺, reducing total activity from 120 to <5 Bq/l in multi-ion systems (Sr²⁺, Ca²⁺, Na⁺) from Degelen site waters.

3) Sorption mechanisms were elucidated via NADA-based Gaussian modeling using FTIR and SEM-EDX data, revealing fragment structures and quantifying physisorption, chemisorption, and electrostatic contributions.

Approval of the practical results of the work. The main results of the work were presented at five international conferences. Prior to starting work with radioactive

isotopes, the "International Radioactivity Monitoring" training organized by the Japan Atomic Energy Agency was completed.

Conferences:

1. 2nd International Conference on High Energy Physics, Materials Science and Nanotechnology (ICHEPMS-2024) dedicated to the memory of Academician of the National Academy of Sciences of the Republic of Kazakhstan Ernst Herbertovich Boos (Feb 15-16, 2024). "Carbons obtained from biomass for the sorption of radionuclides" Kunarbekova M., Azat S. ISBN 978-601-08-3798-0

2. X International Conference "Semipalatinsk Research Forum: research and prospects for the development of scientific and technological progress" (STS-2023), Sep 12-14, 2023, Kurchatov, Republic of Kazakhstan. "Sorption of the radioactive iodine by activated carbon" by M.S. Kunarbekova, K.K.Kudaibergenov, S. Azat

3. Institute of Combastion Problems - 2024. VIII Kazakhstan Student Scientific and practical conference "Chemical Physics And Nanomaterials", dedicated to the 110th anniversary of the birth of the Three-time Hero of Socialist Labor, academician Ya.B. Zeldovich, Almaty: Publishing House "Daryn", 2024. -141 p. Kunarbekova M.S., I Sapargali.O., Seimukhanova L.N., K Kudaibergenov.K., Azat S. ISBN 978-5-7782-43"Synthesis of a nanocomposite sorbent modified by nitrogen groups from buckwheat husk activated KOH" 98-9

4. 4th International Russian-Kazakh Scientific and Practical Conference "Chemical Technologies of Functional Materials", Dedicated to the 90th anniversary of the Formation of Al-Farabi Kazakh National University, Almaty, Kazakhstan, April 25-26, 2024. "Synthesis of nanocomposite sorbent modified with nitrogen groups from biomass of walnut husk and buckwheat husk by chemical activation", Kunarbekova M.S., Sapargali I.O., Seymukhanova L.N., Kudaibergenov K.K., Zhantikeev U.E., Azat S. ISBN 978-601-04-6697-5

5. Advanced Engineering Science Symposium and the 2nd International Symposium on New Materials and Devices, June 23 - 29, 2024. "Synthesis and characterization of modified activated carbon for the sorption of radionuclides" Kunarbekova M.S., Sapargali I.O., Seimukhanova L.N., Kudaibergenov K.K., Zhantikeev U.E., Azat S.

Publications

The results of the work are reflected in 2 reviews – in the Scientific Journal cited in the Scopus database, 1 article, 1 book chapter, patent and 3 articles in journals recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan

1. M. Kunarbekova, R. Busquets, Ye. S. Sailaukhanuly, S.V. Mikhalovsky, Toshtay K., K. Kudaibergenov, S. Azat. «Carbon adsorbents for the uptake of radioactive iodine from contaminated water effluents: A systematic review», Journal Of Water Process Engineering-Q1, 92% percentile

2. Kunarbekova, M., Yeszhan, Y., Zharylkan, S., Alipuly, M., Zhantikeyev, U., Beisebayeva, A., Kudaibergenov, K., Rysbekov, K., Toktarbay, Z., Azat, S. The State of the Art of the Mining and Metallurgical Industry in Kazakhstan and Future

Perspectives: A Systematic Review (2024) ES Materials and Manufacturing, 25, art. no. 1219, DOI: 10.30919/esmm1219, (98% percentile)

3. Sailaukhanuly, Y., Azat, S., Kunarbekova, M., Tovassarov, A., Toshtay, K., Tauanov, Z., Carlsen, L., Berndtsson, R. Health Risk Assessment of Nitrate in Drinking Water with Potential Source Identification: A Case Study in Almaty, Kazakhstan (2024) International Journal of Environmental Research and Public Health, 21 (1), art. no. 55. DOI: 10.3390/ijerph21010055 procentile

4. Kunarbekova, M., Busquets, R., Sapargali, I., Seimukhanova, L., Zhantikeyev, U., Kudaibergenov, K., & Azat, S. (2025). Innovative materials for industrial application: Book Chapter 11. Synthesis and Characterization of Activated Carbon from Biomass (1st ed.). IGI Global Scientific. <u>https://doi.org/10.4018/979-8-3693-7505-1.ch011</u>

5. K.K. Kudaibergenov, S. Azat, Zhantikeev U.E., <u>M.S. Kunarbekova</u>, I.O. Sapargali, L.N. Seymukhanova. "Method of obtaining sorption material for water purification from radionuclides". Patent for Utility model, No. 9470

Publications in journals recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan:

1. M.S. Kunarbekova, I.O. Sapargali, L.N. Seymukhanova, K.K. Kudaibergenov, S. Azat. "Synthesis of nanofiber composite doped with nitrogen groups from biomass by chemical activation". Combustion and plasmochemistry journal, 22(1), 3-11. https://doi.org/10.18321/cpc22 (1)3-11.

2. Kunarbekova, M., Seymukhanova, L., Sapargali, I., Zhantikeev, Y., Kudaibergenov, K., & Azat, S. (2024).Synthesis and characterization of activated carbon from biomass for the sorption of radioactive iodine. Combustion and plasmochemistry journal, 22(4), 331-341. https://doi.org/10.18321/cpc22 (4)331-341

3. Seimukhanova L.N., Zhantikeyev U.Ye., Bexeitova K.S., Kunarbekova M.S., Rakhimova B.U., Fazylov B.D., Zagitova A.M., Kudaibergenov K.K., Azat S. Production of Nanocellulose For Water Purification From Dyes. NNC RK Bulletin. 2024;(4):181-190. (In Russ.) <u>https://doi.org/10.52676/1729-7885-2024-4-181-190</u>

The personal contribution of the Ph.D. candidate to the preparation of each article was as follows:

Dissertation structure. The dissertation includes a literature review explaining the scientific background of the work, a detailed description of the methodology used, and a discussion of the results and their context with a conclusion section and a list of references that support the research carried out. The total volume is 136 pages, including 49 figures, 25 tables, and a bibliography of 199 references.

1 LITERATURE REVIEW

1.1 Carbon matrix synthesis

Humanity has become more dependent on nuclear power and radioactive isotopes as a result of the rising need for electricity and the expanding use of nuclear medicine. Radioactive waste is one of the inevitable outcomes of this dependency. These pollutants have the ability to enter the human body through plants and water. Nuclear Waste Management is addressing this problem by addressing the pressing need for safe and efficient ways to extract and store pollutants.

Long-lived radionuclides, such as cesium (¹³⁷Cs), (¹²⁹I) and short-leved radioactive iodine (¹³¹I) from nuclear accidents, inappropriate disposal, and medical waste, are among the most hazardous natural causes of water pollution. In the human body, they have a propensity to build up and cause major illnesses like thyroid cancer.

Contaminated by ¹³¹I and ¹³⁷Cs water can now be decontaminated using a variety of water treatment technologies. The most successful of these has been adsorption employing aerogels [1] and MXenes [2], in conjunction with ion exchange [3], membrane filtration, and reverse osmosis.

The structure of activated carbons (ACs) has been improved to allow them to absorb tiny molecules (less than 500 u.m.a.), such popular medications and insecticides. Regarding the purification and discoloration of air, gasses, water, and other liquids [4], [5]. Carbonaceous biomass, such as wood, nut shells, husks, fruit stones, and others, can be thermally treated without oxygen to create ACs. The resulting ACs can include suitable pores (mesopores (2-50 nm) and micropores (<2 nm) [6] for removing typical pollutants. Such pores also provide a very large specific surface area per unit mass [7]. There are various types of activated carbons. Activated carbons differ from their starting raw materials and have new applications [8] and value. Figure 1.1 shows examples of the main areas where ACs are used.



Figure 1.1 - Application of Activated carbons

In order to remove pollutants, the first steps in producing activated carbons from biomass are washing and drying. Important factors influencing how well activated carbons extract include the specific surface area, pore structure, surface functional groups, and chemical composition of the carbon (Figure 1.2). The specific surface area of activated carbons has a significant impact on their adsorption capability; larger surface areas provide more active sites for the adsorption of pollutants. The pore structure, which comprises the size and distribution of micropores, mesopores, and macropores, affects the rate of adsorption as well as the activated carbon's ability to adsorb molecules of different sizes. The strength and selectivity of adsorption are influenced by surface functional groups, such as basic or acidic groups, which primarily dictate interactions between the carbon and adsorbates. The elemental composition, namely the amount of carbon and the presence of heteroatoms like oxygen, nitrogen, or sulfur, might further affect the material's efficacy in processes like catalysis or pollution removal. These elements influence the sorbent's overall efficacy and function in concert [9].



Figure 1.2 - Key factors and primary modification methods of activated carbon and their application in adsorption of gases. Adapted from [4]

The three primary classes of AC forms are as follows:

Large portions of carbonized biomass are crushed, and any dust that remains in the structure is then removed to create crushed activated carbon (CAC). The CACs particles range in size from about 0.2 to 5 mm and have an uneven form. This kind of AC is frequently utilized as a loading material in a variety of filter systems (both pressurized and non-pressured) because of its structure and particle size dispersion. The primary benefit of CAC is its excellent cleaning efficiency for liquid media, which is mostly due to the size of its particles. For instance, in filters where the purification process occurs under pressure, there is a rapid flow of water through the filter bed made of CAC while simultaneously capturing and retaining various contaminants such as organic matter, oils, chlorinated compounds and heavy metals [10]. In non-pressure filters, where the liquids flow through the media by the action of gravity, CAC also demonstrates excellent adsorption properties, although they provide a slower filtration rate than CAC pressure filters.

Granular activated carbon (GAC) consists of granules with typical sizes ranging from 0.8 to 5.0 mm. GAC is characterized by a high degree of homogeneity and uniformity in size, which ensures effective interaction with the purified medium. Their main area of application is adsorption from the gas phase, where it is used to purify the air and remove harmful gases, vapors of organic compounds, toxic substances and volatile hydrocarbons. One of the key advantages of GAC is its ability to minimize the pressure drop in filter systems. Due to its cylindrical shape and stable structure of the granules, the air or gas flow easily passes through the carbon layer without creating significant resistance. This makes GAC an ideal material for gas purification in industrial ventilation systems, gas cleaning and the processing of gas emissions [11]. Another important property of granular activated carbon is its high attrition. GAC is resistant to mechanical damage, which reduces the risk of granule destruction and release of fines during operation, and this extends the service life of filters. GAC is used in packed columns (>1m) in the tertiary treatment in the production of drinking water and also in the purification of water in hospitals [12].

Powdered activated carbon (PAC) is crushed activated carbon consisting of particles usually less than 100 µm in diameter [13]. Due to its high dispersion, PAC has a specific surface area, typically about 2000 m²/g, making it especially effective for the adsorption of various pollutants from liquid media. The main advantage of powdered activated carbon is its ability to quickly and effectively interact with pollutants due to the fast adsorption kinetics that result from their small particle size. This provides a high degree of purification even at low concentrations (ng/l) of pollutants. PAC is widely used in the final stage of the purification of liquids such as wastewater and in water purification for the production of pharmaceuticals and food. This is because such uses require high efficiency in the removal of organic and inorganic pollutants. PAC is mixed with the liquid to be purified in a pre-calculated proportion (dosage), after which the adsorption process occurs in a stirred system. Pollutants become adsorbed onto the carbon, and finally, the carbon with adsorbed substances is removed by filtration or coagulation, flocculation and sedimentation. Indeed, the separation of the fine PAC particles is a slow part of the process that becomes a disadvantage in its use. An important advantage of PAC is its versatility: it can be used in both continuous and periodic purification systems. Nevertheless, the high back pressure it can provide due to a packing bed with low particle size is a limitation. PAC's relative versatility and effectiveness make it a popular choice across industries.

1.2 Physical and chemical activation of carbon matrix

Worldwide, the practice of turning agricultural waste into the valuable element known as activated carbon is becoming more and more common as environmental protection becomes more and more important. Many different source materials can be used to create activated carbons. The choice of hydrocarbon raw materials has a significant impact on the properties of the final activated carbon [14]. The two sequential processes of carbonization and activation transform the raw materials into a carbon matrix with a well-developed porous structure, leading to the synthesis of AC [15]. The two main methods for producing ACs are chemical and physical activation, as shown in Figure 1.3.



Figure 1.3- Processes of Activated Carbon Production

Physical activation. Physical activation usually includes two main stages: carbonization and activation. In the first stage of AC production, carbonization, the source material is subjected to heat treatment with a very low presence of oxygen. As a result of which volatiles (moisture and tars) are removed from it, the material is compacted and gains strength. During carbonization, the raw materials are exposed to high temperatures (usually from 400 to 700 °C) in an inert atmosphere (typically N_2 or Ar). This process leads to the thermal decomposition of non-carbon elements, such as hydrogen, oxygen, and nitrogen, which are present in the raw material in the form of volatile organic compounds. These elements are released as gases (e.g., water vapor, carbon dioxide, methane, and other hydrocarbons), leaving behind a carbon-rich residue. This carbonization step also results in the formation of a basic pore structure in the material, which is further developed during the activation stage.

A microporous structure is developed during the activation stage. Activation, the subsequent step, makes the carbon substance more porous. Oxidizing gases, like carbon dioxide or steam, are utilized in physical activation at temperatures between 700 and 1200 °C [16]. Carbon atoms are oxidized and carbon oxides (CO and CO₂) are created when the oxidizing gas reacts with the carbon surface. These gases are then released. The carbon surface is etched by this process, forming a web of micropores and mesopores. A material with a large specific surface area—up to 1500 m²/g AC—is created by such a high temperature and controlled oxidation process. This is

particularly significant for applications that call for effective adsorption, like the removal of pollutants from water [17].

Chemical activation. Chemical activation is a one-step process in which the feedstock is impregnated with a chemical activating agent such as potassium hydroxide (KOH), zinc chloride (ZnCl₂) or phosphoric acid (H₃PO₄). The impregnated material is then heated at temperatures between 400 and 800°C. Activating agents promote the decomposition of the carbon structure, creating a highly porous material with a large specific surface area, such as activated carbon with surface areas exceeding 1500 m²/g, which is highly desirable for applications like gas adsorption and water purification. One of the advantages of chemical activation is that it typically occurs at lower temperatures than physical activation, which can result in higher yields of activated carbon, which is economically advantageous. It also allows for the development of pores with varying sizes, ranging from micropores (less than 2 nm) to mesopores (2-50 nm), which increases the versatility of the material for different applications. However, the concentration of the activating agent and the process temperature must be carefully controlled to optimize the pore structure and prevent excessive combustion of the carbon material [18].

KOH is used as an activating agent in a classic chemical activation scenario. Water vapor, carbon dioxide, and other gases are produced when KOH reacts with the initial carbon material, encouraging the removal of non-carbon atoms like hydrogen, oxygen, and nitrogen. Through etching the carbon material and the development of a network of micropores, this method produces a highly porous structure. A clean and extremely effective adsorbent is produced by thoroughly washing the material to get rid of any remaining activating ingredients after activation.

1.3 Surface modifications of activated carbon

The pore structure and surface chemistry of AC have a major impact on how successful it is in the adsorption process. The surface chemistry and pore structure of activated carbons are significantly influenced by the activation conditions and source ingredients. For example, pea peel carbon activation is particularly high in amino groups [19]. Furthermore, specific functional groups of interest in a given application might be increased via surface changes [20]. Chemical, physical, and plasma treatments are common techniques for surface alteration.

Chemical processes. In order to enrich the surface of AC with functional groups that include oxygen, such as hydroxyl, carboxyl, and carbonyl, oxidation entails treating it with oxidizing agents like nitric acid, hydrogen peroxide, or ozone [21]. These make the ACs more hydrophilic, which in turn improves their ability to interact with polar molecules and heavy metal ions in liquids. As a result, oxidized carbon is frequently utilized in the treatment of industrial effluents, wastewater, and the elimination of heavy metals like lead, cadmium, and mercury from tainted liquids [22]. Additionally, oxidation can boost AC's sorption ability for polar compounds in the gas phase, expanding its use in air emission control and gas purification. This process of modifying the structure of carbon is an important step in the creation of materials for

specialized applications where improved adsorption properties and high chemical activity are required.

Acid/base modification: Adding acids or alkalis to AC is one efficient way to enhance its adsorption capabilities. Acidic functional groups, such as carboxyl (-COOH), phenolic (-OH), and sulfonate (-SO₃H) groups, are added to the carbon surface during acid treatments, such as those involving sulfuric, phosphoric, or nitric acids. By raising the surface acidity and the quantity of active interaction sites, these changes improve carbon's capacity to absorb polar molecules and heavy metal cations. Alkaline treatments, on the other hand, including those that use potassium hydroxide (KOH) or sodium hydroxide (NaOH), enrich the carbon surface with basic functional groups. Such treatments improve the adsorption of compounds of acidic nature. Alkaline functional groups increase the overall basicity of the carbon, which improves interaction with anions and acidic molecules. This is useful for the purification of both gas and liquid media from acidic pollutants. This modification process is critical for creating specialized ACs used in water and gas purification, as well as in industrial filtration systems [23].

Activation with steam or CO_2 involves high temperatures (700-1000°C) to produce new pores or enlarge the existing ones. This results in a significant increase in the surface area and overall porosity of the AC, which increases its adsorption capacity.

Annealing is a high-temperature process that reduces the number of functional groups on the carbon surface that contain oxygen. This increases the carbon's interaction with less polar substances by decreasing its hydrophilicity and increasing its hydrophobicity. Furthermore, annealing makes the carbon more electrically conductive, which makes this method particularly helpful for producing materials for electrochemical devices like batteries and supercapacitors [24]. High electrical conductivity carbons can, in fact, help increase the efficiency of charge storage and transfer, which is a crucial component of energy systems. Thermal treatment of AC allows for targeted modification of its properties, making it suitable for a variety of applications, including pollutant adsorption, electrochemical devices, and other high-tech applications where the structural and surface characteristics of the material are important.

A thin layer of polymer is applied to the surface of AC through physical coating and grafting in order to enhance its properties and broaden its range of use. Increasing the hydrophobicity of the carbon material is one of the main outcomes of polymer coating [25]. In this case, reducing the carbon-water interaction and increasing the adsorption of non-polar contaminants are crucial. Polymer coating can improve AC's selectivity for compounds in addition to its hydrophobicity. This is accomplished by altering the surface so that carbon interacts with target molecules more efficiently. This makes carbon particularly helpful in the sorption and separation processes of complex mixtures. For example, a polymer coating can be especially selective for adsorbing organic pollutants, dyes, or pharmaceuticals [26]. Another important advantage of polymer coating is an increase in the mechanical strength of the carbon. The coating protects the carbon surface from degradation during its use, which increases its service life and resistance to mechanical stress. This is especially important for reusable systems where AC is subject to regeneration and long service life [27].

The carbon surface decorated with nanoparticles. Typical nanoparticles used to functionalize carbons are metals or metal oxides, such as silver, gold or iron oxide, to the surface of AC [28]. This modification method can improve the functional properties of AC, expanding its application in various technological processes. For instance, the addition of silver and gold nanoparticles increases the ability of carbon to participate in catalytic reactions [29]. Such materials can be used in oxidation, reduction and other chemical reactions that require highly active catalysts. The catalytic activity of decorated carbon makes it indispensable in processes for cleaning water and air from organic pollutants. Silver nanoparticles also impart antibacterial properties, making the AC composite an effective material for disinfecting water, air or medical fluids [30]. The addition of iron oxide nanoparticles imparts magnetic properties to the carbon, enabling its separation using magnetic fields. This method is particularly useful for simplifying the extraction of carbon particles from the cleaned medium after the adsorption or catalysis process is complete [31]. Magnetic nanoparticles greatly facilitate the regeneration and reuse of AC, making the process more cost-effective and environmentally friendly [32].

Plasma Treatment. Cold Plasma Treatment: Cold plasma treatment is a method of modifying the surface of carbon by exposure to a plasma field at low temperatures. This process leads to changing the composition and surface structure of AC without affecting its bulk properties. The main advantage of this method is its ability to introduce new functional groups, such as carboxyl (-COOH), hydroxyl (-OH) and other oxygen-containing groups, which significantly increases the adsorption capacity of the material for polar molecules and ions. Under the influence of cold plasma, active centers can form on the surface of carbon, which improves interaction with various pollutants. This process is especially effective for creating carbons used in water purification and gas filtration systems, where high sorption capacity and chemical activity are required. Plasma treatment can increase the carbon surface roughness or porosity. This improves the diffusion of molecules into the pores of the carbon and increases the total surface area for adsorption. At the same time, the volumetric properties of carbon, such as its strength and structure, remain unchanged, which helps maintain the durability and resistance of the material to physical impacts [33].

Surface modification is usually done to saturate carbon surfaces with oxygencontaining groups. This enhances their affinity for contaminants in water. Figure 1.4 illustrates some examples of oxygen-containing carbon surfaces. For instance, to extract pharmaceuticals and dyes from water through hydrogen bonding [34]. In some cases, S, N groups can be introduced to the carbon surface to increase the extraction capacity of organic contaminants and radionuclides [35]. Thiol groups interact with heavy metals through electron interaction [36].



Figure 1.4 - The main set of oxygen-containing functional groups in activated carbon

Figure 1.5 illustrates examples of sulfur functional groups on the surface of AC. Displayed are the following groups: sulfoxide with a methyl group $(-S(=O)-CH_3)$, thiol (-SH), dithiocarbamate $(-S(=O)_2N-CH_3)$, sulfone $(-SO_2-CH3)$, and sulfonic acid $(-SO_3H)$. These sulfur-containing functional groups enhance the carbon's adsorptive capacity through various chemical interactions with adsorbates. These groups are crucial for improving the adsorption of heavy metals and other pollutants due to their ability to form complexes or participate in ion exchanges [37].



Figure 1.5 - Examples of sulfur functional groups in activated carbon

Typical nitrogen-containing functional groups on the aromatic carbon backbone of AC are shown in Figure 1.6 From left to right, the groups include imide, which has complexation properties due to its carbonyl groups and a methyl group; nitro, an electron-acceptor due to its double bond with oxygen; amine, capable of forming hydrogen bonds; amide, involved in hydrogen bonding and resonance stabilization; triazole, useful for metal coordination; and hydroxylamine, reactive and suitable for reduction reactions. These groups enhance the interaction of AC with adsorbates, finding applications in environmental and chemical technologies [38].



Figure 1.6 - Examples of nitrogen functional groups in activated carbon

Surface modification of activated carbon is used to improve the adsorption capacity of the ACs mainly through the involvement of chemical interaction between the functional groups onto the surface of the carbon with target molecules such as pollutants.

1.4 Characterization of Activated carbons

Complementary techniques are needed for the characterization of the activated carbons (ACs); this is because carbons are multifaceted materials with multiple characteristics that are linked with their performance, as shown in Figure 1.7 Accurate measurements of properties associated with carbons' performance will help to improve their efficiency. Such information will allow tailoring such key properties to specific applications. One can get a wealth of information on how well the material will perform from data on its surface chemistry and structure. Thorough characterization of ACs typically includes analysis of particle size, Brunauer-Emmett-Teller (BET) surface area, porosimetry, zeta potential and well characterization of functional groups with infrared (IR) or Raman spectroscopies or even their quantification with Boehm titrations and X-ray photoelectron spectroscopy (XPS). Each of these methods offers additional information about the materials. For example, the particle size of the carbons affects overall surface area and adsorption kinetics. At the same time, BET and porosimetry provide extensive data on pore size distribution and surface area, which is critical to understand avenues for tailoring their properties and performance. Zeta potential reveals information about the surface charge, which is important for assessing the stability of ACs in suspension and their interactions with charged contaminants in solution. Boehm titration provides insight into the surface functional groups, allowing for a better understanding of how the surface chemistry of the AC affects its interactions with various contaminants. Finally, spectral techniques such as IR play a major role in identifying specific groups involved in interacting with crucial substances. Such data is critical for measuring carbons' capabilities and modifying them to achieve optimal performance in target applications. Incorporating these techniques during the development of carbon sorbents is essential to gain a comprehensive understanding of their properties and potential performance. The data obtained not only guides new development of AC materials but also expands their

applications in various fields, making carbons' physicochemical characterization a fundamental aspect of ACs.



Figure 1.7 Schematic representation of approaches for the physical and chemical characterization of activated carbons

Particle Size. The particle size of AC is an important parameter that significantly affects its adsorption properties and overall efficiency in various applications. Particle size affects pore accessibility, especially in carbons that are mainly microporous and have a low abundance of transport ports. Small particle sizes, such PAC, lead to a great surface area that is exposed and available for interaction with the molecules of interest; these can be, for instance, pollutants, and this translates into greater adsorption rates. Hence, particle size is especially critical in filtration systems that require fast adsorption rates.

Therefore, particle size analysis measurements are needed. Techniques for such characterization include laser diffraction and dynamic light scattering (DLS). ACs obtained from various raw materials such as coconut shells, wood or coal can be processed to reach particle sizes ranging from 10 to 50 microns. This kind of size provides good adsorption capacity, and the hydraulic resistance can still be overcome. However, ACs with smaller particle sizes (<10 micrometers), although they have improved adsorption characteristics, lead to too high back pressure in filtration systems. A balance between particle size and porosity is important for specific applications such as water or air purification [39].

One of the most crucial aspects of air conditioners is their *specific surface area*. The BET method, which relies on the measurement of adsorbed inert gases (like nitrogen) on a material's surface at low temperatures, is the most used technique for figuring it out. The specific surface area of ACs can vary from 500 to 3000 m²/g, contingent on the feedstock and activation technique. For instance, AC produced by

chemical activation with KOH has a high capacity to adsorb tiny molecules and gasses due to its specific surface area of up to $3000 \text{ m}^2/\text{g}$. The volume of micropores, which is crucial for adsorption processes from gases and liquids, can also be estimated using BET tests [40].

Pores. The porous structure of AC is the main factor determining its efficiency in adsorption processes. Gas and mercury porosimetry are commonly used to quantify the types of micro, meso and macropores. Gas adsorption, most commonly using nitrogen at cryogenic temperatures, is used in the determination of the volume and quantity of micropores and mesopores. This method is also used to calculate the specific pore volume, which can vary depending on the raw material and the activation method. For example, coconut shell AC has typically abundant microporosity, making it particularly effective for gas adsorption. Mercury porosimetry is used to analyze the macroporous structure of ACs. This is especially important for materials used in liquid adsorption because macropores are channels where the diffusion of the target molecules towards the mesopores and micropores (adsorption sites) takes place [41].

Charge on the surface. The surface charge of particles suspended in a liquid is indicated by the zeta potential, also known as the ζ -potential. It has a significant impact on how AC behaves in watery systems. This parameter, for example, is particularly significant in wastewater treatment because it provides information on how carbon interacts with pollutant ions, including organic materials and heavy metals, which can occasionally be charged when in solution. The mobility of AC particles in an electric field is studied in order to determine the zeta potential. AC, with a negative zeta potential, shows better adsorption capacity for cations such as lead and cadmium due to electrostatic attraction [42]. For example, AC used to remove lead from aqueous solutions has a ζ -potential in the range of -30 to -50 mV, which contributes to the high efficiency of the process [43].

Surface functional groups. Boehm titrations are used to quantify the acid-base properties of ACs' surfaces. Functional groups such as carboxyl, phenolic, and hydroxyl, which play a key role in the adsorption of polar molecules and ions, are quantified with a method that requires incubating carbons in solutions of controlled pH and titrating the functional groups with acids and bases. ACs with abundant oxygen-containing functional groups have a better ability to adsorb basic pollutants such as ammonia or ammonium [44].

Infrared spectroscopy (IR) is the main method for analyzing the chemical composition of the surface of ACs. The IR spectra of ACs contain absorption bands that correspond to specific vibrations from functional groups involved in adsorption properties [45]. IR spectra can inform about changes in the chemical composition of the carbon surface after activation or chemical modification. For example, activating carbon with KOH leads to the presence of new functional groups, such as hydroxyl and ether groups, on the surface of AC. The increase of hydroxyl groups due to the activation can be confirmed with IR [46].

XPS can also be used to characterize the surface of ACs. This method allows estimating the concentration of the functional groups on the surface of the carbon. XPS is widely used to analyze ACs used in adsorption and catalysis [46], [47]

1.5 Reactivation and life cycle of carbon materials

Activated carbon materials' reactivation and life cycle highlight the importance of managing these crucial sorbents in industries such as water treatment and healthcare, where they play a vital role in processes like purifying water. Activated carbon, typically derived from biomass or fossil fuels, undergoes a life cycle that includes production, usage, reactivation, and eventual disposal. Over time, these materials lose their adsorption capacity and require reactivation, which is usually achieved through thermal treatment in a CO_2 atmosphere. This process not only restores the material's functionality but also leads to further oxidation of the carbon surface, widening of the pores, and some mass loss [48].

The life cycle of activated carbon sorbents presents several challenges, particularly concerning environmental sustainability. Due to their extensive use, especially in large-scale applications, carbon beds must be regularly regenerated. [49].

1.6 Adsorption of radionuclides by carbon sorbents

1.6.1 Source of radioactive iodine

It is believed that molecular iodine (I₂) in the gas phase has a diameter of 0.56 nm [50]. Iodine is present in the liquid phase as I₂, organic compounds like CH₃I and C₄H₉I, and inorganic anions like I⁻, I₃⁻, and IO₃⁻. Only ¹²⁷I, out of the 37 known iodine isotopes (¹⁰⁸I to ¹⁴⁴I), is non-radioactive and is utilized in the majority of research projects. Although the majority of radioactive iodine isotopes have a brief half-life, they are all reactive, can affect the environment, and have detrimental impacts on human health [51]. Cancer may result from the thyroid gland's propensity to collect iodine isotopes. Nuclear fuel produces significant amounts of two iodine isotopes during fission: ¹³¹I (t₁₂: 8 days) and ¹²⁹I (t₁₂: 1.57×10^7 years); it has been calculated that $1.8 \text{ EBq} = 1 \times 10^{18} \text{ Bq}$ of ¹³¹I was released during the Chornobyl accident [52]. While radioactive iodine is present during spent fuel reprocessing, it is not emitted into the environment during normal nuclear plant operations [53].

Numerous isotopes, including ¹²⁹I (a stable isotope), ¹²³I ($t_{1/2}$: 13.2 hours) for imaging, ¹²⁵I ($t_{1/2}$: 59 days) for biological tests, imaging, and radiation, and ¹³¹I for treating thyroid cancer, are used extensively in nuclear medicine[54], [55], [56]. Controlling the release of these isotopes into the atmosphere and water is essential due to their widespread use. Physisorption [57], chemisorption [58], electrodialysis [59], ion exchange [60], precipitation, and dry dedusting have all been used as methods to eliminate iodine radioisotopes. In this review, we concentrate on assessing carbon-based materials for radioactive iodine extraction.

1.6.2 Source of radioactive cesium and strontium

Strategies for controlling and minimizing nuclear waste must be developed before implementing Kazakhstan's nuclear power sector. The latter is expected to occur shortly, and the energy demand, energy costs, and geopolitical factors will influence the decision. However, the land of Kazakhstan has already been contaminated with radioactive matter due to previous activities, such as testing nuclear weapons at the Semipalatinsk Test Site. Nuclear waste is a complex mixture that may contain more than 60 components. ¹³⁷Cs (half-life, $t_{1/2}=30.05y$) and ⁹⁰Sr ($t_{1/2}=28.8y$) are products of spent nuclear fuel (SNF), which can be deposited in SNF-reprocessing facilities. They pose radiation risks to organisms and can travel considerable distances from their source. To date, 390,000 tons of SNF from nuclear electricity production have been generated[61].

Radioactive isotopes of cesium and strontium (here and after ¹³⁷Cs and ⁹⁰Sr) are present in nuclear waste as inorganic cations and complexes with organic matter [62]. In the form of storage waste, they are usually encapsulated into Portland cement matrices but gradually escape from the storage facilities by leaching through the cracks in the concrete caused by radiation [63]. Ferrocyanide sorbents such as Prussian blue $\{(iron(III) hexacyanoferrate(II), Fe_3[Fe(CN)_6]_2\}$ show selective binding capacity towards Cs⁺ with good adsorption capacity (up to 70 mg/g of Cs with an initial concentration of 100 ppm) [64], [65], [66], [67]However, the practical application of ferrocyanides is complicated because they form a hygroscopic powder. Their immobilization on the surface of activated carbon will address this issue.

Different organic and inorganic materials have been used as adsorbents for 90 Sr. Recently, a new material, Na₃FePO₄CO₃, was reported as a selective adsorbent for strontium, even in the presence of comparable or higher concentrations of Ca²⁺ and Mg²⁺ ions [68].

Cation exchangers could be used to achieve non-selective removal of Sr^{2+} ; however, its removal from organic complexes by adsorption or ion exchange has not been systematically studied and remains problematic. Due to their large size, organic complexes cannot penetrate adsorbent pores or interact with cation exchange functional groups.

Other techniques, such as chemical precipitation [69], chemical coagulation/flocculation [70], membrane filtration [71], phytoremediation [72], and biosorption [73], have been explored for the removal of radioactive cesium and strontium from wastewater.

1.7 Radionuclides' interaction with carbon

The industry standard for reducing radioactive element emissions during nuclear reactor operations is ion exchange resins and granular activated carbon (GAC). The nuclear reactor's ventilation system includes activated carbon (AC) filter beds. Additionally, radioactive iodide is eliminated from liquid effluents, frequently by entrapment in salts or ion exchange resins [74]. Removal by physisorption, such as using Granular Activated Carbon (GAC), is an alternative to these techniques. Commercial GACs derived from bituminous coal, coconut shell, and sub-bituminous coal were used to clean up groundwater contaminated with radiological waste. They were contaminated by leaching from radioactive waste storage facilities that included short-lived low-level nuclear materials. Three types of iodine were found in the groundwater: the most prevalent was IO_3^- (60.5% to 86.7%), followed by I⁻ (0.4% to 10.8%) and organo-iodine from soil organic matter (12.3% to 28.7%) [75]. The initial pH of the water supply was 8.2. Compounds with lower oxidation degrees were first

oxidized to IO₃⁻ and subsequently reduced to I⁻ before trying their adsorption using GACs made from bituminous coal and coconut shell. This process was carried out to ensure that the iodine concentration was constant during the oxidation treatment. The GACs under investigation demonstrated I_2 uptakes of 0.92 to 1.1 g per g of the adsorbent when incubated with water containing around 3.5 pCi L-1 of ¹²⁹I. The most effective of these was coconut shell-based activated carbon. However, only 2.75 to 5.90 μ g/g of iodine was eliminated when I₂ was converted to I⁻. Therefore, in order to achieve the greatest results when employing GAC, certain factors need to be considered. First of all, the effluents that require treatment might not have the characteristics that meet the performance standards set by the manufacturer. Second, as the pH of the effluent may affect iodine uptake and speciation, it needs to be monitored. It's also crucial to ensure that all forms of iodine are converted into a single form, such as iodide (I⁻), in order to achieve the desired outcome. can maximize the effectiveness of GAC treatment by taking these crucial aspects into account [5]. Figure 1.8 represents the interaction mechanisms which mainly involved in iodide onions and cesium ions with modified activated carbons.



Figure 1.8 – Interaction processes involved in tri-iodide and cesium ions interaction with modified activated carbon

In terms of interaction with cesium, GAC has emerged as an effective medium for the adsorption of cesium ions (Cs⁺) during water treatment processes, particularly in environments contaminated with radioactive materials. The main way that cesium and activated carbon interact is through physisorption [76], in which the GAC's high surface area and porous structure help to draw cesium ions out of aqueous solutions. The potential of various forms of GAC, such as those made from coconut shell and bituminous coal, to clean up water sources contaminated by cesium from leaching from nuclear waste sites has been studied. The unique properties of the activated carbon, such as pore size and surface functional groups that increase affinity for cesium through ion-exchange processes, are among the crucial elements that affect how well cesium is removed. The adsorption efficiency can also be greatly impacted by the chemistry of the solution, including the pH level and the existence of competing ions. According to studies, under ideal circumstances, GAC shows significant cesium uptake, indicating its potential for widespread use in the treatment of contaminated water. Moreover, maximizing the efficiency of GAC in water treatment systems might help manage radioactive waste by comprehending the speciation of cesium and its transformation into more readily adsorbed forms.

Halides are typically removed from water using (i) membrane separation techniques, like reverse osmosis (RO), nanofiltration (NF), and electrodialysis (ED); (ii) electrolysis methods like membrane capacitive deionization, electrodialysis reversal (EDR), and capacitive deionization; (iii) adsorptive techniques like impregnated activated carbons, carbon aerogels, and layered double hydroxides; (iv) ionic extraction using exchange resins; and (v) coagulation [77]. RO was the most effective technique overall (up to 99.4%) for the removal of both organic and inorganic iodine [77]. Nevertheless, it has high operating pressures, requires pre-treatments, and has high running expenses. Nowadays, water treatment facilities frequently employ adsorptive techniques [78], [79] Thus, the evaluation of carbon adsorbents for the capture of radioactive iodine—which may be used in large-scale water treatment facilities—is the main objective of this review.

Because of the sorption mechanism, which includes van der Waals and physisorption forces, radioactive iodine typically interacts with carbon materials that have a high adsorption capacity. Furthermore, through dipole interactions, hydrogen bonds, or covalent bonds, surface functional groups—like positively charged N or S groups—increase the carbon surface attraction for iodine. Through the π - π interaction, carbon compounds like graphene or carbon nanotubes can retain iodine molecules. The ability of iodine to act as an electron acceptor and carbons as an electron donor can also increase the amount of iodine that adsorbs onto the carbon surface.

1.8 Natural porous materials - derived activated carbon for radionuclides capturing

Low-cost materials would be useful for removing iodine radioisotopes from huge amounts of wastewater or industrial effluents [80]. In order to minimize supply chain problems and lower CO₂ emissions, it would be advantageous if these were widely accessible, locally produced, and prepared [81]. For the procedure to be more economical and sustainable for its uses, the sorbents' ability to be reused is also crucial. The sustainability of the water treatment process is also enhanced by maximizing the reuse of used sorbents and preventing them from turning into a second kind of waste. As proven adsorbents of liquid [82] [83]and gas [67], [84] [85] pollutants, activated carbons derived from agricultural waste can help local economies meet sustainable development objectives. Among the main raw materials utilized to create these carbons are bamboo, wood, coal, petroleum pitch, walnut and coconut shells, rice straw, and husk residue [39]. Iodine can be captured both from organic and inorganic forms from water [86]by carbon materials from biomass [87], [88], [89], [90].

Table 1 compares the sorption of iodine species by ACs generated from biomass and provides details on the synthesis, characterization, and maximum adsorption capacity of various sorbents. KOH was used to chemically activate the ACs with higher iodine absorption (see Table 1). We obtained superior iodide uptakes of > 6 g I₂/sorbent. It's interesting to note that rice husk [91], sunflower [92], and orange peel biomass doped with urea [93] all produced such high recoveries. Both biochar and hydrochar were activated by KOH. The hydrochar's lower processing temperature requirements made it more sustainable when compared to the other approach. Melting KOH and distributing it throughout the biomass was the initial step in the KOH activation process, which produced K₂CO₃. The processes occurring are described by the response in Eq. 1-4 [94]. Additionally, materials like urea can be used to activate biomass. Eq. 5.

 $6 KOH + 2C \rightleftharpoons 2K + 3H_2 + 2K_2CO_3 \qquad \text{Eq. 1}$

$$K_2CO_3 + 2C \rightleftharpoons 2K + 3CO$$
 Eq. 2

$$K_2CO_3 \rightleftharpoons K_2O + CO_2$$
 Eq. 3

$$C + CO_2 \rightleftharpoons 2CO$$
 Eq. 4

$$CO(NH_2)_2 \rightleftharpoons NH_3 + HNCO$$
 Eq. 5

Chemical and physical activation differ primarily in that the former employs only gas or steam. Activation agents such as salts, acids, alkali compounds, or impregnates are used to activate them chemically. Temperature increases affect the formation of pores. During activation at mild temperatures (usually <600 °C), KOH had no effect on biomass. However, it had a greater impact upon chemical activation, which necessitated the breakdown of K₂CO₃ at higher temperatures (typically 700°C), leading to the development of micropores and the enlargement of pores. New mesopores were also created at higher temperatures by the space that the KOH took up during the carbonization process. [94].

The filtration and adsorption capabilities of the ACs during water treatment are significantly impacted by the porosity of the materials. Despite some restrictions given by the inherent structure of the precursor biomass, the sorbent porosity can be significantly tuned to the intended use [92]. For instance, a porous carbon material with a casing-like shape was produced by the milky and spongy sunflower stem (Table 1) [95]. The additions utilized during chemical activation, such as KOH and N-doping agents, have an additional impact on the final surface characteristics of activated carbon. High temperatures and pressures are used in the hydrothermal method (HTM), which is an efficient way to dope activated carbon with nitrogen. In particular, urea and carbonized biochar are autoclaved at 210°C and 5 MPa to use 10% (w/w) of urea H_2NCONH_2 as the N-doping agent [96].

Additionally, the sorbent's surface chemistry facilitates the elimination of radioactive iodine. It is challenging to distinguish the influence of porosity from the

assessment of this factor, though. Activated carbons made from biomass showed a strong affinity for radioiodine (I₂). This sorption from the gas phase was 6.44 g I₂ g⁻¹ in dry circumstances and 2.44 g I_2 g⁻¹ in high humidity. These values are comparable to the actual nuclear fuel reprocessing conditions, which are $26.9 \pm 0.3\%$ (MgCl₂), 50.3 \pm 1.3% (NaBr), and 74.0 \pm 0.9% (NaCl) produced via saturated salt solutions. The oxygen-containing functional groups on the surface of activated carbon and the van der Waals contact with its benzene rings may be partially responsible for its high sorption capacity for iodine. Density Functional Theory (DFT) simulations have provided an explanation for this occurrence. These calculations contrasted the energy of I-I (isolated molecular I₂) with that of C-I in the C₂₄H₁₂-I₂ and optimized structures of the $C_{24}O_{12}H_6-I_2$ system. The most stable system was the latter. The higher iodine uptake in the pores is thus caused by the improved interaction of iodine molecules with surface oxygen functional groups and pore-filling processes, which are facilitated by a large surface area $(1830-3000 \text{ m}^2 \text{ g}-1)$ and high pore volume [89].

The capacity of porous carbon to adsorb weakly polar contaminants, such as molecular iodine, was greatly increased when N-compounds were combined with hydrothermal carbonization (HTC) technologies and pre-pyrolysis impregnation processes. The obtained 2.25 g I_2/g of carbon adsorption capacity showed that it was competitive with other carbon sorbents based on biochar. Only a few of recently released publications have discussed HTC use (compiled in Table 1). HTC does not require the pre-drying procedure and is carried out at a lower temperature range of 180–250°C than the widely used pyrolysis treatment. Activated carbons have many advantages over other sorbents, including high surface area, porosity, tunable surface chemistry, chemical stability, low toxicity, mechanical strength, thermal stability, reusability and regeneration, cost-effectiveness, environmental compatibility, a wide range of pollutants adsorbed, and the ability to be used on a large scale [5].

Biobased precursor	Pore volum e, cm^3 g^{-1}	Surfac e area, m ² g ⁻¹	Carbonisa tion conditions	Pyrolys is conditio ns	Activation conditions	Iodine uptake, g/g sorbent	Additional information	Refere nce
1	2	3	4	5	6	7	8	9
	1				Uptake of	of I_2 in gas phase		
Cigarette butts	0.80 – 1.34	1634 - 2751	600°C in Ar for 2 h.	800°C in Ar for 2 h	Raw material /KOH ratio of 1:5	2.62 g/g at 353 K and ambient pressure (initial concentration of I_2 not reported)	Micro and mesopores prevail	[97]
Orange peel waste	1.67	3053	Hydrother mal method at 210°C in Ar	800°C in Ar for 2 h	Hydrochar to KOH (mass ratio of 1:2). Urea to char (ratio of 1:2)	2.25 g/g (initial concentration of I_2 not reported)	Micro and mesopores prevail. N-doped with urea	[93]
Receptac leand stalk of sunflowe r	0.46 – 1.77	3072	Powdered and heated to $500^{\circ}C$ in Ar, heating rate 2.5 $^{\circ}C \cdot min^{-1}$ and kept for 2 h	800°C in Ar, heating rate 2.5 °C·min ⁻¹ and kept for 2 h	Biochar to KOH ratio (1:5)	6.46 g/g (initial concentration of I_2 not reported)	Micropores prevail, very low bulk density (0.033 g cm ⁻³)	[92]

Table 1 - Removal of iodine species by the biobased carbonaceous adsorbents

Continuation of Table 1

1	2	3	4	5	6	7	8	9
Rice	0.97	1930	450°C	750 °C,	Hydrochar/KOH (ratio of	13.75 mmol/g (3.49 g	Micropores prevail.	[91]
husk			in N ₂ for 1	for 1h	1:4)	I ₂ /g) from initial	HNO_3 and H_2O_2 to	
			h.		pre-calcination at 400°C,	concentration of 21	oxidise the carbon	
					for 25 min	mmol/L of I ₂	surface	
Uptake of iodide $(I^- \text{ and } IO_3^-)$ in aqueous phase								
Sacha	-	-	-	-	Washed with water	0.0484 g/g (sacha inchi	pH range 3, 5, 7 and 11.	[98]
inchi					before	shells); 0.0189 g/g	T range 5, 15, 25, 45,	
shells					drying in oven, ground,	(hazelnut shells). initial	and 65 °C.	
and					sieved	concentration 10 mg I ⁻	pH-dependent, most	
hazelnu					(0.5–0.711 mm particle	/L pH 3, 5, 7, and 11.	effective at pH 3 and	
t shells					size)	T 5, 15, 25, 45, and 65	25°C.	
						°C		
Pomegr	-	-	-	-	washed with water,	remove IO_3^- from the	Most effective at pH 1	[99]
anate					ground by a grinder.	water,		
peels					dried at 40 °C in an oven,	pomegranate peels		
and					they were sieved 0.5-	0.00959 g/g,		
mangos					0.711 mm fraction	mangosteen pericarps		
teen						0.00231 g/g, initial		
pericar						concentration		
ps						10 mg/L		
						contact time 2 h		

It's interesting to note that N-doping significantly aided the expansion of the hydrochar's pore structure upon activation, but it had minimal effect on the pore structure itself [91]. The pyridinic and pyridonic nitrogen groups are less obvious after activation at roughly 800 °C (Figure 1.9) and more noticeable after high-temperature pyrolysis (<700 °C), according to an analysis of the chemistry of N-doped activated carbons (Figure 1.8). Consequently, nitrogen-containing groups did not engage in the uptake of iodine species. Nonetheless, they promoted the development of extremely porous carbon with fully developed mesopore and micropore structures while still having an impact on the surface chemistry of the initial carbon biomass. Molecular iodine (I2) adsorption increased as a result of the carbon surface's hydrophobicity. A number of surface functional groups, especially oxygenated ones, were partially lost as a result of the heat treatment (about 800 °C) utilized during pyrolysis, which decreased the total hydrogen concentration. The degree of hydrophobicity of the graphite surface may enhance the adsorption of iodine molecules by decreasing the quantity of polar carboxylic, carbonyl, and phenolic groups on the carbon surface, as demonstrated by the findings for carbons obtained from rice husks in Table 1 [100].



Figure 1.8 - Relative contents (%) of different nitrogen groups in carbon materials at different activation phases, as well as PY-obtained via pyrolysis without activation and 8 N 1s spectra. Hydrochar and KOH are activated in a 1:2 ratio to create PC. In degrees Celsius, the pyrolysis and activation temperatures are 600, 700, and 800. Uassis is an acronym for urea-assisted hydrochar. (Reprinted by permission [93]Elsevier, Copyright 2024)



Figure 1.9 - Gaussian model of N-containing functional groups of AC after N-doping

Iodide (I⁻) sorption is also influenced by the mineral makeup of the initial biomass. For instance, calcium (Ca²⁺), potassium (K⁺), and magnesium (Mg²⁺) cations are present in the original biomass of Sacha Inchi shells, which, upon pyrolysis, are converted into active sites for activated carbon. The iodide anion can be effectively adsorbed by the shells of sacha inchi and hazelnuts (Table 1). Even though the adsorbent's cationic species' charge plays a significant role, physisorption is thought to be the primary mechanism influencing the uptake of I⁻ species [98].

The sorption capacity of the media is affected by its pH when evaluating the surface charge of materials and the speciation of radioiodine: bio-based adsorbents may adsorb the most I- at pH 3 [98]. As pH rises, iodine species adsorption tends to decrease. For example, sorption by sacha inchi shells was 0.0468 g/g at pH 3, 0.045 g/g, and 0.0379 g/g. A rise in OH-concentration decreases the adsorption of I-anions from water via rivalry, in addition to the pH dependence of iodine speciation [98].

Biomass-derived ACs have a high iodine adsorption capacity (up to 6.46 g g-1 of I2, Table 1) compared to synthetic microporous carbons, which have an adsorption capacity of 7.39 g g-1 (Table 2). It is related to the kind of biomass precursor and the activation method and mostly depends on the quantity of micropores and the hydrophobicity of the carbons. Because KOH reacts with carbon at lower temperatures than potassium salts, chemical activation with KOH is typically chosen [101].

The removal of volatile iodine from the gas phase by carbons derived from biomass is more effective at higher temperatures (Table 1). However, exposure to excessive humidity or nitrogen oxides (NO_x), which are present in nuclear plant offgas, impairs their performance. [78]. When ACs are employed to reduce pollution from emissions from nuclear power plants, other issues emerge. Because NOx saturation of carbon beds has a low ignition point , nitrate sorption, for instance, can result in explosions [102]. At high temperatures (CHI at 400°C), the adsorbed radioiodine can also be released [90]. Triethylendiamine (TEDA) and potassium iodide (KI) are commonly co-impregnated into ACs to circumvent the partial pore obstruction issue [103].

When developing carbons for I2 absorption, the difficulty of using rejected biomass AC must be taken into account [104] (Table 1). Its heat regeneration, which is often done off-site, and the additional chemical treatment, which can be less

expensive than creating a new sorbent, are the reasons it is rarely employed. Furthermore, studies on carbon preparation typically ignore the energy consumption and carbon dioxide emissions associated with carbon preparation or regeneration. This is a significant issue considering how crucial these elements are to the sustainability and usability of carbons [5].

1.9 Synthetic carbon materials for radioactive iodine capture

1.9.1 Carbon aerogels

Aerogels are a special kind of three-dimensional air-filled substance with a high surface area (\sim 400–800 m2/g) and a highly ordered porous network (90–99% air). It is possible to modify their surface chemistry [105]. Porous aerogels have lately been considered for use in water treatment because of their porosity, which allows them to efficiently remove radioactive pollutants from air and water [106], [107], [108]. Aerogels made of graphene, silica, AC, and composites are available [109]. The maximum iodine extraction capacities of carbon aerogel and synthetic AC are contrasted in Table 2: All aerogels exhibit iodine extraction at around the same order of magnitude (\sim 1 g I/g sorbent).

Impurities in aqueous solutions were absorbed by carbon aerogels made from resorcinol-formaldehyde aerogels. It has been shown that the pore size distribution affects the sorption mechanism because the pore structure facilitates aerogel wetting (Figure 1.10) [59].



Figure 1.10 - NMR observations of the wetting process of the CA1 and CA2 carbon aerogels' mesopores b) within the pore system and a) on the pore surface. The functional groups are yellow, the carbon aerogel skeleton is signed in black, and the water in the pore system is indicated by blue. b) within the pore system and a) on the pore surface. where (k) is the layer thickness and () is the surface relaxivity. (Reprinted [110] with permission). Copyright Elsevier, 2024

The sorbent's surface chemistry affects how dispersed iodine interacts with it. For theoretical computations and simulations of surface chemistry, the density functional theory (DFT) approach is frequently employed. After 72 hours, a high iodine adsorption capacity of 0.999 g I_2 g⁻¹ was demonstrated by the DFT applied to

carbon aerogels consisting of graphene doped with sulphur and nitrogen (SN-GA) at the starting I2 concentration of 0.200 g l⁻¹ [111]. Carbon aerogel was made from leather waste, which contains tannins like catechin, using a different method. Catechin@3DCF, the resultant carbon adsorbent, had an iodine adsorption capacity of 0.323 g g⁻¹. Catechin-doping and mesoporous interconnectivity on the aerogel surface of the sorbent had an impact on iodine adsorption. Throughout five ethanol regeneration cycles, the Catechin@ 3DCF aerogel demonstrated a consistent adsorption capacity and was reusable [112]. In order to extract iodide from water, the effects of pH on aminated carbonaceous aerogel formed from biomass-which is made from watermelon peel waste-have been studied. When the initial iodide concentration was 8 mmol/L (1.328 g I⁻/g), its adsorption capacity was 0.85 mmol I-/g (0.141 g I/g) at pH 2.0. The iodide anions were encouraged to protonate by the low The adsorption process was notable for its rapidity, reaching equilibrium in pH. around two hours [113].

The interaction of the negatively charged iodide anions with a positively charged carbon surface made up of amino or ether pyrone groups is often the adsorption mechanism [114]. Graphene monolayers and large surface areas (2630 m²g⁻¹) favor physical adsorption over chemical affinity. A maximum iodine uptake of 0.510 g g⁻¹ of I² is demonstrated by the graphene aerogel in this instance [115].

In a similar vein, a high-nitrogen silk fibroin aerogel has been described as a sorbent for the extraction of I2 and CH3I. Its adsorption capacities were 0.348 g I_2/g and 0.724 g CH I/g. The creation of charge transfer complexes between various N-groups and the iodine molecule, as well as the lipophilic character and higher affinity of aliphatic amines in the case of CH3I sorption, were the primary adsorption mechanisms [116].

Overall, weak supramolecular connections made possible by N-doping, S, and electrostatic interactions, respectively, enable both chemisorption and physical sorption of iodine species. Future research should focus on the issue of aerogel aging since the degradation of the mechanical and interlaminar properties of aerogels may render them unsuitable for long-term iodine capture [117][118]. Due to its complicated and multi-step production method, which includes pyrolysis following resorcinol and formaldehyde polycondensation, carbon aerogels cannot be used on a big scale due to financial constraints.

1.9.2 Carbon nanotubes

Carbon nanotubes (CNTs) are made by layers of Sp2-hybridized carbons. CNTs come in two varieties: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [119]. They can be altered in length and chirality, and their 0.4-40 nm diameter is suitable for I2 capture. However, they have very little effect on iodine sorption [120]. Sensors that detect I2 and those that absorb iodine ions and I₂ vapor from liquids are the two varieties of SWCNTs. While both types of SWCNTs interact with iodine species, not all of them are made to catch as much iodine as possible. It has been evaluated how well CNT-based sensors have developed for the detection and separation of halogen gases (F₂, Cl₂, Br₂, and I₂). Different kinds of

halogen gases may be sensed preferentially by pore vacancies with sizes of 1, 2, 3, and 4 atoms. Figure 1.11 illustrates how molecular iodine is incorporated into the CNT structure.



Figure 1.11 - Diagram showing how I2 migrates towards the CNT channel at different separations from the pore. (Reprinted [121] with permission). Copyright Elsevier, 2024

The zig-zag (7,0) CNT system, as seen in Figure 1.11, was based on the removal of the host carbon atoms and the creation of vacancies, which are larger holes in a CNT structure, in order to insert pores of different sizes into the CNT surface. Further modification was necessary to establish an electrostatic connection between halogen molecules and atoms with the CNT's pore rim because I2 attraction could not be achieved by only making a large enough vacancy in the CNT structure to trap iodine species. Because hydrogen atoms are more selective for iodine molecules, they have been used to functionalize the pore void. In this instance, the I-I electron cloud repulsion is less than the H-I electrostatic attraction [121].

Ag-modified MWCNT is among the finest options for iodine vapor detection. The long recovery time required to restore the sensor itself (400 s with heating at 100 °C in the air) was one of the primary drawbacks of MWCNTs (Ag filled and coated), which showed a detecting response of 45% in just ~60 s at ambient temperature [122]. Following sample preparation by pyro-hydrolysis, iodine recovered from the solution by sorption to the CNTs can be examined using inductively coupled plasma-mass spectrometry (ICP-MS), which has a relatively low limit of detection (LOD) of 0.004 µg I- g-1 [123].

One of the best choices for iodine vapor detection is Ag-modified MWCNT. One of the main disadvantages of MWCNTs (Ag filled and coated), which demonstrated a detecting response of 45% in just ~60 s at ambient temperature, was the lengthy recovery time needed to repair the sensor itself (400 s with heating at 100 $^{\circ}$ C in the air) [122]. Iodine recovered from the solution via sorption to the CNTs can

be analyzed using inductively coupled plasma-mass spectrometry (ICP-MS), which has a comparatively low limit of detection (LOD) of 0.004 μ g I- g-1 [123], after the sample has been prepared by pyro-hydrolysis [5].

1.9.3 Graphene/ pyrene/fullerene

Micropollutant-absorbing membranes can be made from graphene, which is made up of two-dimensional carbon sheets [125]. Iodine adsorption is not a common application for graphene materials. As Table 2 illustrates, there aren't many investigations on graphene aerogels that demonstrate iodine uptake capacity. Furthermore, the introduction of a co-doped graphene aerogel (SN-GA) with both nitrogen and sulfur active sites allows for well-developed porosity and surface area for iodine adsorption, retention, and storage [126]. Through the pyrrolic N and thiophene-S, graphene helped to generate the sp2 carbon framework and I2 binding in this material. The ability to trap radioactive I2 has recently been investigated using the same method in a 2D nanomaterial with a mono-sheet pyrene-alkaline framework that shares Unlike ACs, it has continuous, standardized structural similarities with graphene. porosity and a structure like graphene. Through solid-phase thermal polymerization aided by flame heating, 1,3,6,8-tetraethynylpyrene (TEP) was converted into 2D layered poly-1,3,6,8-tetraethynylpyrene (PTEP). A quadruple bond is formed by the pyrene and alkynyl groups in TEP (Figure 1.12a).

The pyrene groups of PTEP absorbed molecular iodine from the gas and the Its gas phase adsorption capacity was 3.380 g g-1 at 75 °C, while its aqueous phase. aqueous phase adsorption capacity was 2.570 g g-1 at 25 °C. Because of its hydrophobic surface, PTEP may absorb iodine from both humid air and water. Additionally, after five adsorption/desorption cycles, PTEP may be able to recover about 85% of its initial adsorption capacity; however, no further details are known beyond this first feasibility research. The I2-pyrene charge-transfer process is the primary mechanism via which I2 is adsorbed in the gas phase. Additionally, unsaturated PTEP bonds, such as those in acetylene (C=C), alkadiyne (C=C-C=C), and cumulene of the alkadiyne transition (C = C = C = C), contribute to iodine adsorption. Additionally, the diffusion and adsorption of I2 are facilitated by intra-planar holes (~ 1.2 - 1.6 nm) and interlamellar structure, which have 2D interspacing widths ranging from 2.1 to 6.4 Å. The monolayer structure and the high density of uniformly distributed pyrene groups account for the adsorption of I2 in an aqueous solution. Figure 1.12b [127] shows a potential process of I2 uptake by PTEP from water that was suggested based on UV-Vis data.


Figure 1.12 - a) Solid-phase thermal polymerization of TEP to PTEP schematic; (b) PTEM's method of I2 absorption. (Reprinted [127] with permission). Copyright Elsevier, 2024

Iodine adsorption has been investigated using a novel technique. The interaction between I2 and S-doped fullerenes is investigated computationally using this technique. The S atom is situated above the fullerene surface because the C-S bond length is longer than the C-C bond length. In p configurations, this results in a possible interaction between the σ -bond of C-S bonds and the lone pairs of I atoms [128]. materials that resemble graphene; the charge transfer between I₂ and pyrene groups, as well as N, is what causes the iodine adsorption. The charge transfer between I₂ and pyrene groups and N- and S-containing groups is responsible for the adsorption of iodine, according to studies conducted on materials that mimic planar graphene [5].

1.9.4 MXenes

MXenes are two-dimensional materials composed of atomically thin layers of carbonitrides, nitrides, or carbides of transition metals joined by weak interlayer connections. They share structural and mechanical properties with other 2D materials, such as graphene, and can be customized with various functional groups. Their structural complexity and chemical diversity make them materials that can be used in a variety of ways [129]. MXenes commemorated its tenth anniversary in By absorbing I2 from non-polar liquids, MXenes, a relatively new class 2022 [130]. of materials, have shown that they can absorb radionuclides. That is especially challenging due to the stability of I2 in the solution. MXene-PIL absorbed up to 0.170 g/g of iodine at an initial iodine concentration of 1.0 mmol L-1 in cyclohexane. Iodine dissolved in cyclohexane was similarly absorbed by other MXene-based composites. The greatest adsorption capacity of MXene modified with polydopamine (PDA) and nano-mixed silver oxide (MXene-PDA-Ag2Ox) is 0.080 g/g. However, when incubated with I2 at an initial concentration of 1 mmol/L, nano-mixed bismuth oxide MXene-PDABi6O7 may absorb up to 0.065 g/g of iodine [131]. Ionic solutions can enhance MXenes' organics extraction procedure. For instance, MXene-PDAIL, a polydopamine (PDA)-coated MXene that was further immobilized with ionic liquid (IL), was used to successfully recover iodine from cyclohexane. With an initial iodine

level of 1 mmol L-1 in cyclohexane, its extraction capacity was 0.695 g I2 g-1 [132]. At an initial concentration of 20 mg/L, a silver-modified MXene known as PDA-Ag₂O_x shown an adsorption capability of only 0.080 g/g towards iodine in aqueous solution. The source of the iodide was potassium iodide.

 I_2 and I^- can be extracted from organic and aqueous solutions using menes. However, only research has been done on silver-doped MXenes' capacity to eliminate I^- . Future research must ascertain whether improving the modification of their surface removal of I_2 and I^- is feasible. Recent studies have shown that MXenes are better at absorbing iodine than ACs.

1.9.5 Carbon dots (CDs)

The spherical nanomaterials known as carbon dots, or CDs, have a radius of less They fall into one of three categories: polymer dots, carbon quantum than 10 nm. dots, or graphene quantum dots. Metal ions including Fe(III), Cu(II), and Hg(II) have been successfully detected using CDs [134][55]. Despite being researched for Idetection [135], CDs have not been widely used for I-removal due to their poor Iextraction capabilities. Due to the fluorescence effect of electron transfer from Hg2+ to Hg^{-I} complex, where CDs are quenched by Hg²⁺ and then restored following the addition of I., CDs were instead employed as turn-off-on iodine detectors with a limit of detection of 46 nmol I⁻1⁻¹. In order to detect the primary iodine species (I₂, I⁻, and IO₃) in extremely salinized water, amphiphilic CDs (A-CDs), which possess both hydrophilic and hydrophobic characteristics, were created. Its amphiphilic characteristics, which drew I2 closer to the A-CDs and extinguished their fluorescence (LOD 3.5 nmol I_2 L-1), were responsible for the strong selective response of CD2 to I_2 [136]. Hg^{2+} constructed nitrogen-doped fluorescent carbon dots (NCDs-Hg²⁺) have been used in a similar manner for iodide detection [137].

Developing a hydrophobic surface on natural cotton fibers (n-CF) was proposed as a novel method for iodine sorption. Cotton fibers' surface was physically adsorbed with organic-soluble carbon dots (OCDs), creating a hydrophobic interface that worked well with I₂. At initial IO₃⁻ and I⁻ concentrations of 400 ppm, this material demonstrated an adsorption capability of 0.190 g I₂· g-1. Before being eliminated, IO₃⁻ and Lanions underwent a redox process at low pH that transformed them into I₂ [138]. Lastly, CDs can detect I₂, I⁻, and IO₃⁻. However, at this time, there are no practical methods for increasing the iodine species' receptivity to CDs or for using them as adsorbents in large-scale applications [5].

1.9.6 Carbon nanocomposites

The nanomaterials that make up the carbon nanocomposites we are talking about here are not easily recognized as carbon aerogels, MXenes, graphenes, CDs, or CNTs. The sorption capacity of the boron-and-nitrogen-doped carbon nanocomposite (B-N@CS) to remove iodine from water was 9.92 g g⁻¹ (Table 2). Boric acid and melamine were employed as doping agents, while tapioca root served as the carbon supply. One benefit of this sorbent is its quick synthesis, which may be finished in 15 minutes and only needs one phase of dehydration without heating. Uneven, thin, two-dimensional, cavity-filled flakes of the final, unaltered carbon were able to absorb I_2 from water (capacity ~ 71.3% from initial concentration 0.200 g l⁻¹ solution of I_2). However, from the same initial I2 concentration in water, the percentage of iodine eliminated increased to around 94.6% in just 21 minutes after being changed by boron and nitrogen to generate the so-called B-N@CS substance (Table 2). The mechanism of adsorption was van der Waals interactions between the nitrogen atoms and the lone pair of electrons of the iodine in aqueous solution, which existed in three different forms: I⁻, I₂⁻, and tri-iodide (I₃⁻) [139].



Figure 1.13 - a) Diagram showing how lignin is used to create porous carbon (LFC).
(b) - (g) SEM and TEM micrographs of the following at varying magnifications: (b)
MgO template, (c) lignin-based KOH AC (LC-K), and (d) lignin-based KOH/NaOH AC (LFC-KN). (Reprinted [140] with permission). Copyright Elsevier, 2024

Porosity can be changed by adding a templating agent (Figure 1.13). For instance, KOH was used to carbonize and activate lignin-based flower-like porous carbon (LFC) doped with MgO as a templating agent (schematized in Figure 6); Table 2 also shows this process. Both the gas phase (4.060 g I_2 g⁻¹) and the aqueous phase (1.295 g I_2 g⁻¹) showed considerable iodine absorption from LFC material [140]. The LFC composite's remarkable iodine adsorption ability was made possible by the rich microporous structure it produced through MgO templating and chemical activation by KOH.

Generally speaking, carbon nanocomposites can be used to extract I2 from gas and aqueous phases. B and N doping and templating procedures can provide additional binding through ionic and van der Waals interactions. An study of the sorbent compositions in Table 2 shows that oxygen-rich carbons, templating, S-doping, and Ndoping enhance the sorption of iodine species in both the aqueous and gas phases [5].

Type of carbon	Porosity, cm ³ g ⁻¹	Surfac e area, m ² g ⁻¹	Preparation method	Iodine sorbed	Additional information	Referen ce
1	2	3	4 5		6	7
			Gas phase (I ₂)			
Oxygen-rich	0.88–	1829–	Hydrothermal reaction, cellulose diacetate	Up to 6.44 g g ⁻	Oxygen content 19.32–	[89]
microporous	1.40	2998	(CDA) and deionised water at 250 °C for 2h	¹ in dry	26.14%	
carbon			at 600, 700, 800 and 900 °C in N ₂	conditions (75		
named			hydrochar and KOH activation ratio of 1:4	°C under		
CDA4T				ambient		
				pressure)		
				2.44 g g ⁻¹ at		
				high		
				humidity		
				$(74.0 \pm 0.9\%)$		
Lignin-based	0.92	1746((LC-K) lignin and KOH ratio: 1:2 at 900°C	Iodine vapour	Interconnected 3D	[140]
porous	(LC-K)	LC-K)	for 1 h under a nitrogen atmosphere	4.06 g g^{-1}	graphitic shell network.	
flower-like	1.14	2282	Carbonisation at 500°C in N_2 for 1 h	(LFC-K)	MgO template.	
carbon	(LFC-K)	(LFC-	For (LFC-K)	$3.83 ext{ g } ext{g}^{-1}$	Adsorbent can be	
nanosheets	1.69	K)	lignin + KOH (ratio of 1:2) + MgO	(LFC-KN)	regenerated	
named	(LFC-N)	1994	templates	In presents of		
LC-K, LFC-		(LFC-	For (LFC-KN) lignin + KOH/NaOH (ratio	humidity		
K, LFC-KN		N)	1:1:0.83) MgO template	1.16 g g^{-1}		
				(LFC-K)		
				1.30 g g^{-1}		
				(LFC-KN)		

Table 2 - Comparison of synthetic carbons for removal of iodide in gas and water phases

Continuation of Table 2

1	2	3	4	5	6	7
hypercrossli	pore	5				Γ [141]
nked	diameter					
nolynaphthal	S					
enes	0 56 nm-					
enes	1 14 nm					
Synthetic	nore	944-	Heated to 800 °C in N ₂ and kept for 2 h C	0.003 σ/σ		[117]
microporous	sizes	2754	activation with KOH (1.4)	0.005 5/5		[11/]
carbons	05 - 12	2751				
(HPNs)	nm					
(1111(5))	,					
			Water phase (I ⁻)	I	I	
Boron and	1–50 nm	130	Mix boric acid, melamine, tapioca root	0.47 g g ⁻¹	Incorporation of boron	[139]
nitrogen-			powder and deionised water, at 100 °C for	$[I_2]_0$ (aq) 200	nitrogen in the carbon	
doped fluffy			3h	ppm	matrix.	
carbon			dehydrated using 20 ml of conc. H_2SO_4		Suitable for large-scale	
composite					production	
form tapioca						
root B-						
N@CS						
Bismuth-	Pore size	537	pre-oxidation at 260 °C for 2 h	0.5 <mark>6 g/g</mark>	1/3 Of this capacity	[142]
decorated	15 nm		pyrolysis at 800 $^{\circ}$ C for 2 h in N ₂ and		attributed to physical	
electrospinni			$Bi(NO_3)_3 \cdot 5H_2O$		adsorption, while 2/3	
ng carbon					was chemically reacted	
nanofiber					with nano-Bi particles	
Bi@ESCNF					on the carbon fibres.	

Continuation of Table 2

1	2	3	4	5	6	7
Nanoporous carbon materials named Z11- 700, Z11-	0.37 nm - 0.44 nm, and total micropor e volumes 0.085- 0.124 cm ³ /q	377, 260 and 157 m ² /g	pyrolysis at 700, 800 and 900 °C	3.78 g/g	Adsorbent can be regenerated.	[143]
Sulfur and nitrogen co- doped graphene aerogels SN- GA	1–10 μm	180	SN-GA synthesised by a hydrothermal method 180 °C for 12 h thiourea and GO mass ratio 10:1	0.999 g g ⁻¹ at 298 K	Iodine can be released from adsorbents by immersion in ethanol for 12 h. Active sites are S and N.	[111]
Silver- loaded activated carbon fibre (Ag@ACF)	0.30	700	AC fibre (ACF) was procured from Nantong Senyou Company Limited (Jiangsu, China) Hydrothermal method at 80 °C for 24 h	0.372 g/g at pH 2 initial concentration 400 mg/L	silver concentration of 4%. equilibrium was achieved after 4 h.	[144]

1.10 Outcomes of chapter

As the amount of polluted water increases, the need for radionuclide recovery from water effluents grows. Because ion exchange and RO treatments are more expensive to operate, tertiary treatment using carbon materials may be a useful option for recovering dangerous radioactive iodine. The literature review makes it clear that carbons obtained from biomass are the most efficient and might be used in applications A variety of carbons from biomass, such as pomegranate, outside of bench scales. orange, sunflower, rice, and hazelnut, absorbed more than $1 I_2/g$ of sorbent. When it comes to treating water effluents, these are anticipated to be competitive. Therefore, considering its particular application, locally generated biomass might be a more environmentally friendly choice than RO for creating useful, efficient sorbents. Hydrochars activated with urea or KOH were the most efficient carbons from biomass. Hydrochars made with an HTM technique at 180-250 °C are more advantageous than biochars since they require less heat treatment. The hydrothermal treatment creates an oxygen-rich surface, while KOH helps achieve appropriate porosity and large surface area, both of which are characteristics that facilitate iodine recovery. Although HTM's 2.25 g of I_2/g of orange peel biomass performance shows its value, it has not yet become widely used for iodine uptake. Although urea-modified activated carbons can perform better than those created with HTM, their characteristics, energy needs, and \overline{CO}_2 emissions make them less environmentally beneficial.

Unlike the usage of activated carbons for effluent treatment, the adoption of nanocarbons, maybe integrated into membranes, will involve adjustments to the industrial infrastructure. Evaluating carbon sorbents for the removal of iodine radioisotopes is crucial in order to guide manufacturers and the design of water treatments, as novel carbon nanomaterials and preparation techniques have emerged in the past ten years. The iodine uptake of both natural and synthetic ACs and aerogels is around one order of magnitude ($\sim 1 \text{ g I}_2/\text{g sorbent}$). Biomass-based carbon aerogels are competitive; in fact, some have shown superior performance to those made from resorcinol-formaldehyde. The chemisorption and physisorption of I2 are enhanced by the addition of sulfur and nitrogenated groups. By promoting the sorbent's interaction with HI and I anions at low pH values, a positively charged carbon surface can further enhance iodine adsorption. Aerogels' complex preparation procedures, deteriorating structure, and gradual transformation will make it difficult to use them for sophisticated water treatment applications. After five regeneration cycles with ethanol, aerogel regeneration has been tested and shown to have a consistent adsorption capacity. CNTs are useful for rapidly identifying I species because they can absorb I₂ through lateral voids in their hydrogenated pore edges.

 I_2 desorption-affected recovery, however, could be sluggish and requires improvement. CNTs' poisonous nature and noncompetitive sorption capabilities raise doubts about their ability to remove iodine from contaminated water as an adsorbent. In the B and N doped carbon nanocomposite from CNTs, where the nitrogen groups were involved in ionic interactions, the maximum absorption of I2(aq) was 9.92 g I₂/g carbon. The sensitivity of carbon dots, like CNTs, to detect I₂ (even from numerous of its species, I_2 , I^- , and I_3^-) is strong (LOD 3.5 nmol I_2/l). Nevertheless, their efficacy as sorbents for water remediation was subpar (<0.2 g I_2/g elimination).

Up to 0.7 g I_2/g was needed for MXenes derivatized with Ag, the only compounds developed and tested for iodine removal from water. Therefore, neither their effectiveness nor their cost warrant their use in wide-ranging applications.

Research usually overlooks the regeneration and end-of-life of regenerable carbon adsorbents, despite the fact that their number is growing. Alternatives to KOH activation, which is currently a primary activating agent that is caustic and hazardous to the environment, and 2) enhancements in the sustainability of carbon preparation and its composites are the two primary knowledge gaps that need more investigation in light of the growing demand for iodine removal. By removing the carbonization step and making up for it with B and N or S and N doping at moderate temperatures (170-210°C), employing the hydrothermal method (HTM), absorbing CO₂ emissions, and investigating economical ways to extend the use and reuse the sorbents to prevent the production of new kinds of radioactive waste, energy consumption would be decreased. More study is necessary because carbons that can be integrated into membranes might be the answer to getting rid of iodine species in the future [5].

2 EXPERIMENTAL PART AND METHODOLOGY

2.1 Introduction

The synthesis of activated carbons, the application of techniques to increase porosity and surface area, the modification of the obtained activated carbons for the sorption of tri-iodide and cesium ions, laboratory-scale bunch sorption experiments, experiments with radioactive isotopes and naturally occurring heterogeneous mixtures of ground water contaminated by radionuclides, the determination of Zeta potentials, FTIR spectroscopy experiments, SEM-EDS experiments, and general analytical methods are all covered in this chapter.

2.2 Materials and Chemicals

The selected biomass used for this study were rice husk (RH), buckwheat husk (BH) and walnut shell (WN). They were obtained from local farmers in the Almaty region. Potassium hydroxide (KOH), iron (III) chlorides (FeCl₃, 97% purity) were purchased from Sigma-Aldrich. Urea (CH₄N₂O), with 99,8% purity, was from Merck. Potassium iodide (KI) (99.5% purity) was acquired from Ural Chemical Reagents (I₂) (99.9% purity) Potassium (Kazakhstan). Metallic iodine ferricyanide $(K_4[Fe(CN)_6] \cdot 3H_2O)$ (99.9% purity) was purchased from LabChimProm (Kazakhstan). KI was employed to prepare stock solutions of iodide in water 100 mg I⁻/L. 5 M NaOH (LabChemProm, 98 % purity) and 5 M HCl (Honeywell, purity 48%) were used to adjust the pH of solutions. Throughout the experimental work, distilled water prodused Reverse osmosis water purifier (RO Q/KYL-A.001-2013, China). All the chemicals involved in the work were of analytical grade and were used without further purification. For the radioactive isotopes sorption studies, the Na³⁶Cl, half-life 308 000 years, radionuclide purity >99.5%, Activity 38MBq and ¹³⁷CsCl, were used half-life 30.15 years, radionuclidic purity >99.5%, Activity 37MBq storage conditions room temperature (Polatom, Otwock-Świerk, Poland). Real contaminated by ¹³⁷Cs, ⁹⁰Sr, ⁹⁰Y water were sampled from Degelen test area of the former Semipalatinsk test site. All solutions for experiments were done on deionized water.

2.3 Synthesis of porous carbon matrix

A thorough analysis of the literature was done in order to have a better understanding of how biomass is converted into porous carbon. The preparation techniques, which include the characteristics of the initial biomass, the conditions of impregnation and chemical activation, as well as the temperature regime and atmosphere of the medium during preparation, determine the physical and chemical characteristics of activated carbons (AC) and their composites [145], [146]. Additionally, these carbon-based sorbents ought to have a strong ability to sorb positively charged Cs+ ions and negatively charged I ions. A comparative analysis is provided in Table 3.

Biomass type	Preparation method	Application	Advantages	Disadvantag es	Average Cost per	Referen ce
Dischar	1) Heati	Soil	Cost offective	I any comption	kg	[1 <i>47</i>]
Biochar or activated charcoal	 Heating in a low- oxygen environment, typically between 300°C to 700°C Hydro thermal Carbonization (HTC):, utilizing water at 200°C to convert biomass into biochar 	Soil, wastewater treatment	Cost-effective, relatively low carbonization temperature	Low sorption capacity, low surface area and porosity	0,9 – 2,5 \$	[147]
Activate d carbon by physical activatio n	Carbonizatio n at 400- 800°C followed by steam, CO ₂ , or a mixture of both at high temperatures (700-1100°C)	Dye removal, supercapacito rs, sorption of toxic gas/ water contaminants, gas storage, catalysis	High surface area, relatively effective,	Cost of Activation	1,6 -5 \$	[148]
Activate d carbons by chemical activatio n	Impregnation of the char with chemical agents like acids (phosphoric acid), bases (potassium hydroxide, sodium hydroxide), or salts (zinc chloride) before or during carbonization	Dye removal, supercapacito rs, sorption of toxic gas/ water contaminants, gas storage, catalysis	High surface area, effective sorbents	Cost of activation, use of chemicals, energy consu ming	2,5 - 52\$	[149]

Table 3 - Comparative analysis of activated carbon synthesis from bioma	iss
---	-----

The future trends and forecasts in the global activated carbon market, as performed by Inkwood Research [150] and Insight Ace Analytic [151] predict an increase in the annual growth rate of 7.81% between 2024 and 2031, with Asia-Pacific as the fastest-growing region. (Figure 2.4). While coal remains a significant raw material, a shift towards alternatives like wood and coconut shell is evident, and powdered AC is gaining market share. The market is segmented by AC type, while coal is currently the dominant raw material, its usage is declining, while wood and coconut shell remain significant.



Figure 2.4 - Combined data from the global activated carbon market forecast performed by Inkwood Research [150] and InsightAce Analytic [151]

Based on the above data and the available local biomass, it has been decided to focus on four types of activated carbons:

1) Physical activation produced activated carbon (activation occurred in an inert environment without the addition of activating agents); this process will be covered in further detail in the section on the preparation of carbonized products.

2) Chemically activated carbon (using KOH as an activating agent);

3) Chemically activated carbon (using KOH as an activating agent) and Ndoping (using urea as a nitrogen-containing impregnate); doping was done using a hydrothermal technique;

4) Chemical activation (using KOH as an activating agent) and CN-doping (using Prussian Blue as a CN-group agent) were utilized to produce activated carbon, and impregnation was carried out in a microreactor.

Buckwheat husk (BH), walnut shell (WN), and rice husk (RH) were used as scaffolding materials to obtain porous carbon from biomass.

Preparation of carbonized buckwheat husk (BH)

The carbonization of biomass buckwheat husk (BH-500) was conducted using a tube CVD vapour deposition furnace BS-HTF-1200 with a single heating zone (Bes

Sayman, BS-HTF-1200 Kazakhstan) displayed in Figure 2.5. The furnace tubes were made of quartz (diameter 6mm). The carbonization yield varied between 30-36% (Figure 2.6). The same carbonation conditions used in the whole thesis. Carbonisation was carried out under inert atmosphere with N₂. The carbonization temperature was 500° C, which was maintained for 1 hour. The oven reached 500° C with a heating rate 10° C/min. Figure 2.5 show the CVD furnace composition. Figure 2.6 display raw buckwheat husk before and after the carbonization.



Figure 2.5 - Chemical Vapor Deposition furnace BS-HTF-1200 °C, Kazakhstan





Preparation of carbonized walnut shell (WN)

The carbonization of the biomass precursor - walnut shell (WN-500) was conducted under the same conditions as those used in the preparation of BH-based carbons. Carbonization yields varied between 27-30%. Figure 2.3 shows WN biomass before and after carbonisation.



Figure 2.7 - a) grinded walnut shell before and b) walnut shell after the carbonization

Preparation of carbonized rise husk (RH)

The carbonisation of biomass precursor rise husk (RH-500) was conducted under the same conditions as those used in the preparation of BH carbons. Carbonization yields vary between 30% and 35% (Figure 4).



Figure 2.8 - a) rise husk before and b) rise husk after the carbonization

Preparation of activated carbon by physically activation

The raw biomass (BH, WM and RH) was physically activated at 800°C in the CO2 gas stream for 2 h in inert atmosphere (N2) with heating rate 10°C/min. The activated carbons were named as BH 800, WN 800 and RH 800, their average yield was 25.4%, 25.14% and 27,44% in average. In this context, "yield" refers to the percentage of activated carbon obtained (remaining) after the physical activation process with respect to the initial mass. Specifically, 100% would reflects the initial mass, while the yield indicates the remaining mass as a percentage following activation. This definition helps clarify the efficiency and effectiveness of the activation process.

2.4 Chemical activation of carbonized precursors

In order to develop porosity further in the carbonized carbons, chemical activation of carbonized biochar (BH-500, WN-500 and WN-500) was conducted with KOH activation agent [145], [146] (Figure 2.9) to develop more porosity.



Figure 2.9 - Process steps of activated carbon preparation

For that, carbonized mass was mixed with solid KOH with 1:2 ratio (carbon/KOH). This mixture was ground with a laboratory ball mill for grinding and mixing (IKA, A11 B S000, Germany), and pyrolyzed at 800°C under inert atmosphere (N2) for 2 h. The final samples were named as BH KOH, WN KOH and RH KOH. The yields were 78.2%, for RH KOH, 85.1% for BH KOH, and 79.2% for WN KOH. In this context, "yield" again refers to the percentage of activated carbon obtained after the chemical activation process. Specifically, 100% reflects the initial mass of carbonized carbon mixed with KOH, while the yield indicates the remaining mass as a percentage following activation. This definition helps clarify the efficiency and effectiveness of the activation process.

2.5 Nitrogen (N-) doping of activated carbon sorbents

To create cationic centers onto the activated carbon matrix with previously developed pore structure a Hydrothermal method (HTM) adopted from [35] was used. Briefly, the 15 g of carbonized biomass (BH-500, WN-500 and RH 500) was immersed in a 150 ml of 10% wt. urea solution 10% (where 100 grams of solute (urea) was mixed with solvent (DI water) to make a total solution weight of 1000 ml) and autoclaved for 24 hours at a temperature of 180°C and a pressure of 5 MPa. A scheme of the process is displayed in Figure 2.10.



Figure 2.10 - Scheme of biomass activation into porous carbon matrix

The resulting modified products (BH-Urea, WN-Urea and RH-Urea) were dried at a temperature of 105 ° C for 4-6 hours (depending on initial mass) and subjected to sequential activation with KOH (powder) in a dry manner with a mass ratio carbon/ KOH (1:2) as explained in section 1.2. Chemical activation of carbonized precursors.

2.6 Ferrocyanide impregnation

Prussian blue (PB) is found to be the most common iron based chelating agent for selective extraction and capturing of radioactive cesium (^{137}Cs) [152] [153] [154]. Iron ions (Fe³⁺ and Fe²⁺) coordinated with cyanide ligands forms a porous lattice (Figure 2.11). Its stability to radiation makes it suitable for applications involving radionuclides like radioactive cesium (^{137}Cs).



Figure 2.11- Graphical representation of Prussian Blue chelating agent from macroscale to atomic level

Iron (II) and iron (III) combine to form the mixed-valence inorganic complex known as prussian blue, which has a face-centered cubic structure (Figure 2.11). Its lattice constant of 10.17 Å and typical bond lengths of 1.92 Å for Fe(II)-C, 1.13 Å for C-N, and 2.03 Å for Fe(III)-N allow it to selectively adsorb alkali cations. Prussian blue preferentially adsorbs cesium over other alkali cations because of its similar cubic lattice size to cesium ions [7].

Although Prussian Blue is a good selective sorbent for Cs^+ ions, its powder is too fine (0.4 micron), which complicates its application in upscaled purposes. To enhance its particle size for use as a powdered sorbent, a scaffolding of porous carbon was utilized.

Impregnation of Prussian blue on the surface of activated carbon were conducted by following reaction:

$$4FeCl_3 + 3K_4[\underline{Fe}(CN)_6] \rightarrow Fe_4[Fe(CN)_6]_3 + 12KCl \qquad (eq. 6)$$

For that 50 mL of 20 mM solutions of FeCl₃ and K_2 [Fe(CN)₆] were prepared. First, 15 g of activated carbon samples were immersed in 150 ml of K_4 [Fe(CN)₆]. Experimental sequence represented at Figure 2.12. Hydrothermal method (HTM) has been applied for better penetration of ferrocyanide groups into the structure of carbon matrix. For that, 5g of activated carbons (BH KOH, WN KOH and RH KOH) were immersed into 50 mL of 20 mM K₂[Fe(CN)₆]·3H₂O and placed into microreactor. The set parameters were 180°C, 5 Mpa, 300 rpm for 4 h. This process results in a formation of ferrocyanide impregnated onto the carbon matrix. In order to create Prussian Blue impregnated carbon matrix, to the autoclaved mixture dropwise adding excess of FeCl₃ (67 ml) to ensure the reaction (eq. 1) was taking place. The Obtained samples sorbents were assigned as BH KOH PB, WN KOH PB and RH KOH PB. These were washed with DI water and dried at 105°C for 4-6 h.



Figure 2.12 - Schematic representation of activated carbon surface modification by ferrocyanide groups

2.7 Carbon materials characterization techniques

Initial raw materials, including physically activated carbon matrix, chemically activated carbon matrix, urea, and Prussian Blue modified sorbents, were characterized using various morphological and physicochemical techniques and methods, as well as adsorption experiments of iodine and cesium.

2.7.1 Fourier Transform Infrared (FTIR) spectrometer characterization

Activated carbon's chemical makeup was investigated through the use of Fourier transform infrared spectroscopy (FTIR). Using a spectrometer (JSM-6490LA, Japan), the spectra were produced. A mixture of activated carbon and KBr in a weight ratio of 99.5% to 0.5% is pre-ground to a fraction of about 50 microns and then compressed into a disk at a pressure of 10 t/cm to create activated carbon samples for analysis. The analysis included 32 scans with a 1 cm-1 resolution.

2.7.2 Porosimetry and surface area by The Brunauer-Emmett-Teller (BET) method

The surface area, pore volume, and pore size distribution of the synthesized sorbents were evaluated using low-temperature nitrogen adsorption porosimetry on a 660S high-speed gas sorption analyzer (BSD, China). The Brunauer-Emmett-Teller (BET) method, which is based on the notion that monolayer adsorption takes place onto a homogenous surface, was used to calculate the specific surface area (SSA). The pore size distribution and pore volume were also determined using the non-local density functional theory (DFT) method, which accounts for non-uniform surface energy and multilayer adsorption. The Barrett-Joyner-Halenda (BJH) method, which is based on the Kelvin equation, was utilized to obtain a pore size distribution from the desorptio3n branch of the isotherm. The samples were first vacuumed for three hours at a temperature of 200–220°C to degas them in order to ascertain the dependence of V on P at a constant temperature. The Brunauer-Emmett-Teller (BET) method was used to process the data mathematically after the experiments, and the measurement error (Δ) was $\pm 2.8\%$.

2.7.3 Zeta Potential analysis

A batch equilibration procedure was used to examine the samples' zeta potential. A mass of 0.03g of carbon sorbent was submerged in 200 cm3 of suspensions that contained 200 ppm of the electrolyte. In order to maintain a consistent ionic strength and equilibrate for 24 hours by shaking, each dispersed system was exposed to ultrasound treatment (XL 2020 ultrasonic head, Misonix, Farmingdale, NY, USA) with a suitable quantity of 0.1 mol/dm3 HCl or NaOH solution injected [155]. Each system's initial pH ranged from 2 to 12. The electrokinetic data (zeta potential vs. pH) was utilized to ascertain the samples' zeta potential using a Zetasizer Nano ZS (Malvern, UK). The average results are shown. All analyses were performed in triplicate at room temperature.

2.7.4 Scanning Electron Microscopy (SEM/EDX)

A scanning electron microscope (SEM) (EVO18-CARL ZEISS, Germany) fitted with a backscattered electron detector (Zeiss Crossbeam 540, Germany) was used to examine the structural morphology of modified carbon sorbents. An Energy-Dispersive X-ray (EDS) spectrometer (INCA X-sight, Oxford Instruments) coupled to a scanning electron microscope (SEM) was used to analyze the spot and mapping elemental composition of materials.

2.7.5 Raman spectroscopy

Using confocal Raman spectroscopy (RS, Lab Ram HR, Horiba Japan, 785 nm laser, and RS shift of 100 - 4000 cm⁻¹), changes in the intensity ratio of the D band to G band (ID/IG) were calculated in order to assess the structural ordering and defect content of the carbon matrix.

2.7.6 CHNS elemental analysis

A UNICUBE trace ORGANIC ELEMENTAL ANALYSER with Thermal Conductivity Detector (Block C4 Lab 519, Elemental, Germany) was used to perform the CHNS analysis. By heating the samples to 750 °C for five hours in a muffle furnace, the amount of ash they contained was calculated [11]. Next, using the material balance equation Osubs = 100 - (C + H + N + S + D), where C, H, N, S, and A stand for the weight percentages of carbon, hydrogen, nitrogen, sulfur, and ash, respectively, the oxygen content (%) was determined on a dry basis.

2.7.7 Contact angle measurements

The contact angle measurement has been conducted by Drop Shape Analyzer DSA30, (KRUSS, France). Activated carbon samples were pressed into a disk with a pressure of 10 t/cm before the measurement.

2.7.8 Particle size determination

The particle size in nanoscale size has been measured by (Nano-ZS, Malvern, UK) and in micro scale by sieving samples through (Lab-VIBSIEVE-6, Bessaiman Group, Kazakhstan).

2.7.9 X-Ray Fluorescence Spectroscopy (XRF)

The elemental composition of the synthesized sorbents was quantitatively determined using energy-dispersive X-ray fluorescence spectrometry (EDXRF NEX CG II, Rigaku, Japan). It is equipped with a silicon drift detector (SDD), specific X-ray Rhodium tube was employed for this analysis.

2.7.10 Ultraviolet-visible (UV-Vis) spectroscopy

Absorption in the UV spectrum was measured using a spectrophotometer (E-2100UV, China). The experiment of adsorption was conducted in batches. First, 50 mg of sample was added to 150 mL of iodine solution with varying concentrations ranging from 1 to 40 mg/L for each carbon. At 25°C, the mixtures were shaken at 200 ppm until the desired duration was obtained. An ultraviolet-visible spectrophotometer set to the maximum absorbance wavelength of 350 nm was used to measure the iodine concentration.

The sorption capacity was calculated using the following formula:

$$q_t \frac{(C_0 - C_t)v}{m} \tag{eq. 7}$$

where: $C_0 \amalg C_t$ initial and final concentrations of iodine ions (g/l); v — solution volume;

m — the mass of the sorption sample.

2.7.11 Gamma-spectrometric measurements for determining the content of $^{137}\mathrm{Cs}$

Experiments involving radioactive isotopes have been conducted at the Radiochemical Laboratory of the Chemistry Faculty, Department of Radiochemistry and Environmental Ecology, University of Maria Curie-Skłodowska in Lublin, Poland, under the supervision of Professor Ewa Skwarek. Two types of isotopes have been tested: ¹³⁷Cs, which is a positively charged radionuclide, and ³⁶Cl, which represents an anion behavior.

The ¹³⁷Cs gamma sources were measured for radioactivity using the 2480 Automatic Gamma Counter (PerkinElmer, Waltham, MA, USA). This device is intended for automated, high-throughput measurement of radionuclides that generate gamma rays. The 2480 Automatic Gamma Counter detects gamma rays from the ¹³⁷Cs sources using a (Tl) scintillation detector. Multiple samples can be measured automatically thanks to the instrument's sample changer. To guarantee precise radioactivity quantification, the system was calibrated using recognized ¹³⁷Cs standards (Polatom, Otwock-Świerk, Poland).

2.8 Investigation of the sorption capacity

2.8.1 Iodide removal studies

To make a solution with an iodine concentration of 1000 mg/L, the following steps were taken: One gram of metallic iodine and 1.96 grams of potassium iodide were added to a one-liter volumetric flask (Figure 2.13). The flask was then filled to the brim with deionized (DI) water. To completely dissolve the metallic iodine, the mixture was immersed in an ultrasonic bath for 48 hours. Instead, the KI helps dissolve I₂, not increasing the amount of iodine.



Figure 2.13 - Schematic representation of iodide solution preparation by ultrasonic method

Schematic illustration of the ultrasonic-assisted synthesis of triiodide (I_3^-) solution. Initially, potassium iodide (KI) and iodine (I_2) are mixed in aqueous solution (left) to form a yellow precursor mixture. This mixture is then subjected to ultrasonic treatment using a LABSOL ultrasonic cleaner (center), promoting efficient molecular dispersion and reaction kinetics. As a result, a homogeneous dark brown triiodide

solution is obtained (right), indicating successful formation of I₃⁻ species through enhanced interaction and solubilization driven by ultrasonic cavitation.

The chemistry of the technique is based on the following reaction equations (equation 8) The presence of the iodide anion ensures the solubility of iodine, which transforms into the form of the tri-iodide anion:

$$J_2+J^-=J_3^-$$
 [K_{eq} = 7,1x10² M⁻¹] (eq. 8)

A calibration graph was previously created to conduct experiments on the adsorption of tri-iodide ions (I_3^-). For this purpose, 10 clean, dry glass flasks with a volume of 50 ml each were prepared, containing tri-iodide ion concentrations of 1, 5, 10, 15, 20, 25, 30, 35, and 40 mg/L.



Figure 2.14 - Calibration graph of I₃- with concentration from 1- 40 ppm

Using UV-Vis spectroscopy, the optical density of these solutions was determined at wavelengths between 100 and 500 nm (refer to Figure 2.14). A solution used as a control was distilled water. For the upcoming experiments, the wavelength of 350 nm has been selected.

2.8.2 Study of the kinetics of iodine adsorption

Tri-iodide solutions were made by dissolving analytical-grade potassium iodide (KI) and iodine (I2) in deionized (DI) water. In a conical flask, 150 mL of a 100 ppm tri-iodide solution without pH adjustment was mixed with 0.308 g of carbon sorbent. This mixture was shaken at 120 parts per million at room temperature. 1.5 mL samples were collected for UV analysis at predetermined intervals. In every experiment, the total volume of samples obtained was kept below 10% of the initial solution amount. Tri-iodide ion concentrations in the solutions were measured using a UV-vis E-2100UV spectrophotometer (Peak Instruments, ChinaBlanks that had no sorbent but the same initial tri-iodide volume and concentration were measured for comparison. A calibration curve derived from intensity measurements was used to determine the

quantity of tri-iodide ions adsorbed onto the carbon sorbent. Adsorption on the flask walls resulted in tri-iodide losses of no more than 3%, according to blank experiments. Every experiment was carried out twice, and the average experimental error was kept to a maximum of 2%.

Equations (1) and (2) were used to calculate the adsorbate's adsorption capacity (q), expressed in mg/g, and removal effectiveness (%):

$$q = \frac{(C_o - C) \cdot V}{m}$$
 (eq. 9)
Removal Efficiency = $\frac{C_0 - C}{C_0} \cdot 100\%$ (eq. 10)

where C0 represents the adsorbate solution's initial concentration and C (mg/L) represents its final concentration. m (g) is the mass of the adsorbent (0.0308 g), and V (L) is the volume of the solution (150 mL). For the isotherm investigation and adsorption kinetics, the experimental findings of contact time and initial adsorbate concentration were utilized, respectively (Table 10).

Table 4 - Kinetic models

Model	Linear Equation	Parameters
Pseudo-first	$ln(q_e - q_t)$	q_t (mg/g): adsorption capacity at a time point t
Order	$= In q_e - k_i t$	q_e (mg/g): adsorption capacity at equilibrium
		k_1 (min-1
): pseudo-first-order kinetic constant
Pseudo-second		q_t (mg/g): adsorption capacity at a time point t
Order	$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}$	q_e (mg/g): adsorption capacity at equilibrium
		$k_2 (min-1)$
): pseudo-second-order kinetic constant

2.8.3 Adsorption Isotherm Models

The results of delivering adsorbate in bulk solution to the adsorbent surface at a constant temperature are described by the adsorption isotherm technique. The most popular model for explaining adsorption equilibrium data of different liquid-phase adsorbates onto activated carbon is the Langmuir isotherm. The second most popular model, the Freundlich isotherm, is frequently applied when the adsorption process is heterogeneous or shows nonlinear behavior. When the Langmuir and Freundlich models are not adequate, alternative models such the Sips, Temkin, and Redlich-Peterson isotherms are typically employed, albeit less frequently. [156]

The two main adsorption mechanisms are chemical adsorption, which involves the creation of chemical bonds, and physical adsorption, which is linked to van der Waals forces. In our analysis, we ignore ion exchange in favor of physisorption and chemisorption, as illustrated in Figure 2.15.



Figure 2.15 Schematic representation of the sorption process occurring on the surface of modified activated carbon

The following presumptions can be made when comparing various isotherm types and the circumstances in which they are appropriate (Table 5): Monolayer adsorption onto a homogeneous surface with a finite number of identical sites is assumed by the Langmuir isotherm [157]. It works best when there are very few interactions between the molecules of the adsorbate. In contrast, multilayer adsorption on heterogeneous surfaces can be empirically described by the Freundlich isotherm [158]. It works well in situations involving adsorbate-adsorbate interactions that are not optimal. The BET isotherm is especially helpful for gas adsorption at higher pressures because it expands the Langmuir model to account for multilayer adsorption. The Temkin isotherm takes into account a linear decrease in adsorption heat as surface coverage increases, which is useful when adsorbate-adsorbate interactions affect the adsorption process. The Redlich-Peterson isotherm offers versatility for a range of adsorption systems by combining aspects of the Freundlich and Langmuir models. Finally, the Sips isotherm combines aspects of Freundlich and Langmuir to provide a flexible model that may take into consideration both homogeneous and heterogeneous adsorption.

		1	Characterization of equation
model	adsorption		
	phenomenon		
1	2	3	4
Langmuir	Monolayer adsorption on a homogeneous surface	$ \frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}, $ $ R_L = \frac{1}{1 + K_L C_0} $ 58	$q_e (mg \cdot g^{-1})$ and $C_e (mg \cdot l^{-1})$ are adsorbed amount (per gram) and adsorbate concentrations at equilibrium, K ($l \cdot g^{-1}$) is the partition coefficient, q_m - maximum adsorption capacity ($mg \cdot g^{-1}$), C_0 - initial concentration of the adsorbate ($mg \cdot l^{-1}$)

Table 5 - Adsorption isotherm models

Continuation of Table 5

1	2	3	Λ
I Freundlich	<u> </u>	Jogg	$\frac{4}{a (ma \cdot a^{-1})}$ amount of adsorbate
riculturi	multilayer	$-\log q_e$	q _e (ing g) - amount of adsorbate per unit mass of adsorbent at
	adsorption on	$= log R_F$	equilibrium K_{r} ((mg/g)(1/mg)1/n)
	adsorption on	$+(1/n)\log c_e$	Freundlich constant representing the
	heterogeneous		adsorption capacity $C_{\rm c}$ (mg·l ⁻¹) -
	surface		equilibrium concentration of the
	Surrace		adsorbate in the solution n -
			Freundlich constant related to the
			adsorption intensity, or
			heterogeneity factor
Toth	Adsorption on	q _e	$K_{\rm T}$ – Toth isotherm constant (bar ⁻¹),
	heterogeneous	$a_{m} \cdot (K_{\pi} \cdot ($	$n_{\rm F}$ – heterogeneity factor
	surfaces,	$=$ $\frac{q_m}{1}$ $\frac{q_m}{1}$	
	especially	$[1 + (K_T \cdot P)]$	
	when the	$q_e = q_m *$	
	isotherm	$(K_T C_e)^{1/v}$ / [1	
	exhibits a	$+ (K_T C_e)^{1/v}$]	
	sigmoidal		
	shape (S-		
<u> </u>	shaped curve)		
Sips	Combined	q_e	$q_e (mg \cdot g^{-1})$ - amount of adsorbate
	form of the	$=\frac{q_m \cdot (\kappa_S \cdot c_e)}{1}$	adsorbed per unit mass of adsorbent
	Eroundlich	$1 + (K_S \cdot C_e)$	at equilibrium, q_m (mg·g·) -
	model		$(1 \text{ m} \sigma^{-1})$ Sins isotherm constant C
	equations to		$(mg \cdot l^{-1})$ - equilibrium concentration
	characterize		n - Freundlich exponent
	heterogeneous		n Treunanen experient
	adsorption		
	system		
Redlich-	Includes the	q_{e}	K _{RP} – Redlich-Peterson isotherm
Peterson	features of	$K_{RP} \cdot P$	constant (bar ⁻¹), a _{RP} - Redlich-
	both	$=\frac{1}{1+a_{RP}\cdot P^{\beta}}$	Peterson model constant (bar ⁻¹), β_{RP}
	Langmuir and	M	- exponent
	Freundlich		
	isotherm		

Langmuir and Freundlich models described the maximum adsorption capacity and adsorption mechanisms that involve the interaction between adsorbate and adsorbent at adsorption equilibrium, which were used for data analysis.

2.9 Computer modelling of sorbent structure by Gaussian

Computer modelling of absorption processes has been conducted using Gaussian 16W software and supercomputer Tianhe-2 with a capacity of 54,902 Tflops (trillion floating point operations per second) with IntelXeonPhi processor to simulate chemical structure, electronic properties, functional group chemistry and for the prediction of sorption mechanism. As inlet data the results of elemental analysis, SEM-EDX data and FTIR data have been used. Therefore, the "single cell" a common fragment of each sorbent with high accuracy has been constructed and optimized. The simulation of radioactive ions (iodine, cesium, and strontium) was conducted.

3 DISCUSSION PART

3.1 FTIR results

Activated carbons (ACs) can be identified and characterized using a common analytical technique called Fourier transform infrared spectroscopy, or FTIR. The composition of ACs is identified and characterized using the FTIR method. Based on their distinct infrared spectra, FTIR analysis can differentiate between several functional group types of ACs (Table 6) [159]. Using FTIR spectroscopy, this study examined how heat treatment affected the surface functional groups of pitch-based Oxygen-containing functional groups, including activated carbon fibers (ACFs). carboxylic acids (which decreased first), ketones, and quinones, decreased as a result of heat treatment at increasing temperatures (600°C, 1100°C, and 1200°C). An increase in hydrophobicity is correlated with this decrease. It's interesting to note that although some lactone structures did form at higher temperatures, heat treatment clearly modifies the surface chemistry of ACFs due to the overall decrease in oxygen functionalities and the increase in graphitization, as seen by variations in C=C stretching ratios. It concludes that the starting material determines the variations in the initial functional group composition of ACs samples. The synthesis techniques also have a significant impact on the final functional group distribution and, as a result, the attributes of the final ACs.

Wave number (cm ⁻¹)	Functional group
3300–3500	Amines, amides (N–H)
3200–3550	Alcohols, phenols (O–H)
2850–2960	Alkanes (C–H)
3010–3100	Alkenes (C–H)
3000–3100	Aromatics (C–H)
2100–2260	Alkynes/nitriles (C≡C / C≡N)
1650–1750	Carbonyl (C=O)
1740, 1724	Lactones (C=O)
1264	Lactones (C-O-C)
1710-1680	Carboxylic (C=O)
1670-1660	Quinone or conjugated ketone
1076-1014	Alcohol (C-O)
1162-1114	Phenol (C-O) and (O-H bend/stretching)
1250-1235	Ether briges between rings

Table 6 - Summary of ACs' functional groups and their corresponding infrared assignments

As seen in Figure 3.1, FT-IR analysis was used to assess the different functional groups in the modified carbon sorbent structure.



Figure 3.1 - IR spectra for physically activated (RN 800, WN 800 and BH 800), chemically activated (RN KOH, WN KOH and BH KOH), chemically activated and impregnated with Prussian Blue (RN KOH PB, WN KOH PB and BH KOH PB), chemically activated and impregnated with Urea (RN KOH Urea, WN KOH Urea and BH KOH Urea)

The infrared spectra of activated carbons derived from different biomass types (Figure 3.1) clearly demonstrate how the starting material and activation conditions affect the surface's chemical makeup. The presence of hydroxyl groups (O-H) is shown by the strong peaks in the 3400–3450 cm⁻¹ area of the samples that were physically activated at 800°C (RH 800, BH 800, WN 800). This could be a sign of moisture or functional groups connected to hydroxyls on the surface. The three samples' observed peaks in the 1600–1650 cm⁻¹ range correlate to C=O or C=C fluctuations in aromatic structures that are typical of carbon-based materials.

The coals' surface chemical structure is greatly impacted by activation with KOH. Particularly in the 3400 cm⁻¹ region, the KOH chemically activated carbon matrix spectra (RH KOH, BH KOH, and WN KOH) exhibit a shift and a change in peak strength. This shows that chemical treatment has changed the quantity of hydroxyl groups and created new functional groups. These spectra show more pronounced peaks in the 1500–1600 cm⁻¹ area, which could be the result of carboxylic or other oxygen-containing groups that are created through interaction with alkali.

Prussian Blue (PB)-treated samples exhibit intriguing alterations in their infrared spectra. These spectra show characteristic peaks in the 2080–2100 cm⁻¹ range, which denotes the interaction between the Prussian blue components and the carbon matrix. The carbon surface's structure changes as a result of this interaction, and the intensity of the peaks in the C=O and C=C area of vibrations changes as well.Carbons activated in the presence of urea (RH KOH Urea, BH KOH Urea, WN

The evaluation of various functional groups in the modified carbon sorbent structure was conducted using FT-IR analysis, as shown in Figure 3.1.



Figure 3.1 - IR spectra for physically activated (RN 800, WN 800 and BH 800), chemically activated (RN KOH, WN KOH and BH KOH), chemically activated and impregnated with Prussian Blue (RN KOH PB, WN KOH PB and BH KOH PB), chemically activated and impregnated with Urea (RN KOH Urea, WN KOH Urea and BH KOH Urea)

The IR spectra of activated carbons obtained from various biomass (Figure 3.1) clearly show changes in the chemical composition of the surface depending on the activation conditions and the starting material. The samples physically activated at a temperature of 800°C (RH 800, BH 800, WN 800) are characterized by intense peaks in the region of 3400-3450 cm⁻¹, which indicate the presence of hydroxyl groups (O-H). This may indicate the presence of moisture or functional groups associated with surface hydroxyls. The peaks in the range of 1600-1650 cm⁻¹ observed for all three samples corresponds to fluctuations of C=O or C=C in aromatic structures typical of carbon materials. Peaks in the region of 1100-1150 cm⁻¹ are also noticeable, which is associated with C-O-C and C-OH fluctuations characteristic of carbon structures.

Activation using KOH significantly affects the chemical structure of the surface of the coals. The spectra of KOH chemically activated carbon matrix (RH KOH, BH KOH, WN KOH) show a shift and a change in peak intensity, especially in the region of 3400 cm⁻¹. This indicates a change in the number of hydroxyl groups and, the formation of new functional groups as a result of chemical treatment. In particular, more distinct peaks in the 1500-1600 cm⁻¹ region are observed in these spectra, which may be due to carboxylic or other oxygen-containing groups formed as a result of interaction with alkali.

Samples treated with Prussian Blue (PB) show interesting changes in the IR spectra. Characteristic peaks appear on these spectra in the region of about 2080-2100

 cm^{-1} , which indicates the interaction between the carbon matrix and the components of the Prussian blue. This interaction leads to a change in the structure of the carbon surface, which is reflected in a change in the intensity of peaks in the C=O and C=C region of vibrations.

Carbons activated in the presence of urea (RH KOH Urea, BH KOH Urea, WN KOH Urea) show characteristic peaks in the range of 2300-2400 cm⁻¹, indicating the presence of nitrogen-containing functional groups, which is typical for carbons treated with urea[158], [159].

3.2 The results of the BET analysis

Methods based on low-temperature nitrogen adsorption/desorption isotherms are frequently employed to evaluate the micro- and mesoporosity of a material. Using the nitrogen adsorption/desorption isotherms and the Brunauer-Emmett-Teller (BET), Density Functional Theory (DFT), and Barrett, Joyner, and Halenda (BJH) equations, the surface area, pore volume, and pore size distribution were determined [160].

Isotherms of adsorption and desorption (Figure 3.2) The isotherm for RH 800, WN 800, and BH 800 indicates a moderate number of pores due to its poor adsorption capacity. All carbon materials show a notable increase in adsorption volume upon chemical activation with KOH. As the number of mesopores and macropores increases, this suggests a more developed porous structure.

The BET analysis's findings demonstrate that using KOH to activate coal greatly enhances the textural characteristics of carbon compounds (Table 7). Following chemical activation, adsorption-desorption isotherms show an increase in specific surface area and pore volume.



Figure 3.2 - Adsorption-desorption isotherms for physically activated at 800°C (in CO₂ atmosphere) and chemically activated with KOH ratio (1:2) at 800°C, page 1



Figure 3.2, page 2

The BET-derived nitrogen adsorption-desorption isotherms in Figure 3.2 display varying surface area and porosity characteristics for two types of activated carbons: physically activated (RH 800, BH 800, and WN 800) and chemically activated by KOH (RH KOH, WN KOH, and BH KOH). A Type II isotherm is shown by both sorbent types [161], [162], indicating a mix of macropores and micropores with restricted mesoporosity. Chemically activated carbons exhibit a Type II isotherm as well, but the amount adsorbed is much higher, suggesting a much larger surface area and pore volume. This is probably because KOH treatment enhances the carbon's mesoporous structure. Accordingly, RH KOH, WN KOH, and BH KOH are shown to be more efficient adsorbents than RH 800, BH 800, and WN 800.

Sample	$\frac{S_{BET}}{(m^3 \cdot q^{-1})}$	V_{BJH}	W _{BJH}	d (100)	Wall Thickness	Eleme	ental com	position
	(in g)		(11)	(Å)	(Å)	С	0	N
RH 800	209,19	0,05	56,27	17,39	17,65	46.54	39.39	-
BH 800	313,61	0,01	36,34	4,38	4,82	77.37	18.89	-
WN 800	405,49	0,02	36,28	2,81	3,47	83.03	12.50	-
RH KOH	1881,84	0,84	23,32	2,61	7,06	92,63	7,08	-
BH KOH	1579,43	0,24	23,59	2,68	4,20	91,61	7,53	-
WN KOH	2192,67	0.08	17.05	2,88	2,88	87,79	11,26	-
RH Urea KOH	1565,01	0,71	23,28	3,04	7,59	88,62	10,23	1,15*
BH Urea KOH	1340,28	0,08	39,272	2,94	5,39	89,48	9,31	0,96*
WN Urea KOH	2104,13	0	0	2,74	2,73	81,22	14,88	0,82*
Note: * Wall thickness obtained by subtracting w_{BJH} from a_0 where $a_0 = 2 \times d(100) / \sqrt{3}$; ** Data from elemental COHN analysis.								

Table 7 - Structural properties of modified ACs obtained by different methods

Data from Table 7 represent a gradual increase in surface area during the chemical activation and a slight decrease during the urea impregnation, it can be due to partial blockage of pores by urea. When comparing all types of sorbents, it can be seen that walnut-originated activated carbon has a higher surface area (more than 2000 m2 \cdot g-1). This data corresponds to that from the literature for rice husk [163], [164], walnut shell [165], [166] and buckwheat husk [167], [168] originated activated carbons.

Sample	Averag	Average pore	Total	I	Pore siz	ze
	e pore	diameter, (nm)	Pore	micr	mes	macr
	width,		Volume,	0	0	0
	(nm)		cm ² /g	(nm)	(nm	(nm)
)	
RH 800	2.3840	5.6267 (Adsorption),	0.12467		2.38	
		4.8597 (Desorption)	9			
WN 800	1.7572	3.6282 (Adsorption),	0.17813	1,76		
		3.3317 (Desorption)	1			
BH 800	1.6963	3.6399 (Adsorption),	0.13299	1,7		
		3.2869 (Desorption)	6			
RH KOH	2.3570	2.3315 (Adsorption),	1.10891		2.36	
		2.7637 (Desorption)	1			
WN KOH	2.2260	5.0586 (Adsorption),	0.02302		2.23	
		5.0723 (Desorption)	0			
ВН КОН	2.1623	2.3589 (Adsorption),	0.85379		2.16	
		2.5280 (Desorption)	0			
(RH+Urea)+KO	2.2764	2.3277 (Adsorption),	0.89063		2.28	
Н		2.5569 (Desorption)	9			
(WN+Urea)+KO	1.0187	0.0000		1.02		
Н		(Adsorption/Desorpti				
		on)				
(BH+Urea)	2.7079	3.9272 (Adsorption),	0.23036		2.7	
+KOH		4.1434 (Desorption)	2			

Table 8 - Porosity characterization of activated carbon sorbents

Table 8 describes the structural characteristics of various activated carbon samples, focusing on their pore properties, which are essential for understanding their adsorption capacities.

For example, the RH 800 sample mainly falls inside the micro-pore region at 2.38 nm, with a total pore volume of $0.124679 \text{ cm}^2/\text{g}$. During adsorption, its average pore diameter is 5.6267 nm, while during desorption, it is 4.8597 nm. Its average pore width is 2.3840 nm. Conversely, WN 800 has a larger total pore volume of 0.178131 cm²/g, is categorized as a micropore at 1.76 nm, and has average pore widths of 1.7572 nm and adsorption and desorption diameters of 3.6282 nm and 3.3317 nm, respectively. In contrast, following adsorption, BH 800 exhibits an average pore width of 1.6963 nm, an average pore diameter of 3.6399 nm, and a total pore volume of 0.132996 cm²/g.

With an average pore width of 2.3570 nm and an extraordinarily large total pore volume of 1.108911 cm²/g, RH KOH exhibits considerable micro-pore space as compared to the KOH-modified materials. In contrast, WN KOH has a minimal total pore volume of 0.023020 cm²/g and a narrower average pore width of 2.2260 nm. BH

KOH exhibits significant meso-porosity with an average pore width of 2.1623 nm and an average pore diameter of 2.3589 nm, resulting in a total pore volume of 0.853790 cm^2/g .

The urea and KOH-modified samples also offer intriguing information; for instance, RH Urea KOH shows a total pore volume of 0.890639 cm²/g and an average pore diameter of 2.2764 nm. However, WN Urea KOH exhibits a very low average pore width of 1.0187 nm with no discernible adsorption or desorption, whereas BH Urea KOH offers an average pore width of 2.7079 nm, indicating the influence of the modification technique on pore structure.

In order to maximize the effectiveness of activated carbons in processes like adsorption and filtration, the data generally shows variation in pore size and volume among samples.

3.3 Determination of zeta potential at different pH of pure sorbents

In a colloidal suspension, the zeta potential is defined as an electric potential (in voltage) at the shear plane of a particle, which is the area where the surface of the particle and the surrounding liquid layer move at different speeds. A twofold layer of ions is formed around the particle by the charged surface: an exterior layer of ions that are more loosely bound and an interior layer of ions that are firmly linked to the particle. Consequently, the potential difference between the inner layer of this double electric layer and the dispersion medium (the bulk liquid) can be described by the zeta potential [155]. The zeta potential of pure sorbents submerged in deionized water is shown in Table 9.

N⁰	Sample	Zeta Potential (mV)	Average size (nm)	Viscosity (cP)
1	BH 500	-15.47±3.35	267.03±34.62	0.89
2	BH 800	-22.83±5.01	225.37±3.84	0.89
3	BH KOH	-12.18±5.46	642.93±187.30	0.89
4	BH Urea KOH	-17.57±0.95	223.80±59.85	0.89
5	RH 500	-31.8±4.61	225.07±33.65	0.89
6	RH 800	-10.30±3.67	214.43±27.08	0.89
7	RH KOH	-29.17±1.81	193.03±4.22	0.89
8	RH Urea KOH	-25.10±0.87	558.97±92.27	0.89
9	WN 500	-7.44±5.51	218.77±22.69	0.89
10	WN 800	-1.14±0.62	177.83±7.52	0.89
11	WN KOH	-20.67±3.29	261.57±9.57	0.89
12	WN Urea KOH	-16.93 ± 1.46	310.63±27.87	0.89

Table 9 - Zetapotential and size of the carbons

Because of the electrostatic repulsion between the particles, which prevents flocculation or aggregation, the data from Table 9 shows a higher absolute negative value, indicating more stability. More stable dispersions result from the particles' nanometric size. Viscosity is as low as that of deionized water, so the emulsion of carbon sorbents in water can be applied for dynamic systems. Among all RH 500 (-31.8 mV), RH KOH (-29.17 mV), BH 800 (-22.83 mV) and RH Urea KOH (-25.10 mV) have more negative zeta potential values, indicating a higher repulsive force between particles, leading to greater stability in the dispersion [155], [169].

3.4 Determination of zeta potential at different pH

Zetasizer Nano ZS (Malvern, UK) was used to assess the electrophoretic mobility of activated carbon particles, which allows for the measurement of the zeta potential (ζ) and isoelectric point (pHiep). The Smoluchowski equation was used to get the zeta potential [170]. The methodology was summarized as follows: a total of 12 samples of 200 cm3 suspensions were prepared, each containing 0.03g of activated carbon (RH 800, BH 800, WN 800, RH KOH, BH KOH, WN KOH, RH Urea KOH, BH Urea KOH, WN Urea KOH, RH KOH PB, BH KOH PB, and WN KOH PB) and the electrolyte at a concentration of 200 ppm. Every distributed system was split into seven equal pieces and put through an ultrasound (XL 2020 ultrasonic head, Misonix, Farmingdale, NY, USA). Prior to the experiment, all samples were adjusted to pH values of 2, 4, 6, 8, 10, and 12 for the measurements, which were conducted at 25°C in the pH range of 2–12. The 0.1 mol/dm3 HCl or NaOH solution was used to set the suspension's pH to the proper level. The zeta potential relationships as a function of the pH of the solution were thus determined.

Zeta potential in NaCl electrolyte concentration 0.001 mol/dm-3 as a function of pH ranged from 2 to 12 in the first phase. For activated carbons made from rice, buckwheat, and walnut shell-derived carbon sources, Figures 3.3–3.5 show how the zeta potential changes with pH, providing crucial information about their electrochemical characteristics.



Figure 3.3 - Relationship between zeta potential and pH for activated carbons derived from rice husks

As the pH rises, the zeta potential of rice husk samples generally decreases, showing a change from a more positive to a more negative zeta potential as the pH becomes alkaline. All samples show comparatively greater zeta potential values (nearer neutral or slightly negative) at low pH (acidic conditions), indicating a protonated surface with less electrostatic repulsion. As pH rises, the zeta potential falls, most likely due to the deprotonation of surface functional groups like carboxyl or hydroxyl groups. Among the samples, RH KOH PB shows the most pronounced decrease in zeta potential with pH, indicating a highly functionalized or activated surface that responds significantly to pH changes. The isoelectric points (where zeta potential approaches zero) differ slightly among the samples, highlighting variations in their surface chemistry due to different activation and surface modification of rice husk-based sorbents.

Since the zeta potential value is equal to -30 mV or less at that pH, which is believed to improve colloidal stability, Figure 3.3 shows that RH KOH/NaCl is the most stable dispersion system in the pH range of 7 to 12. The zeta potential behavior of the rice husk samples illustrates the "double layer formation," which is the arrangement of charges at the solid-liquid interface. In order to create a diffuse outer layer and a compact interior layer (Stern layer), the materials' surface is most likely protonated at low pH, creating a positively charged surface that attracts negatively charged ions (counterions) from the solution. As the pH increases, deprotonation of surface functional groups (mainly hydroxyl or carboxyl groups) results in a negatively charged surface, which then attracts positively charged counterions from the solution, in our case Cs^+ .



Figure 3.4 - Relationship between zeta potential and pH for activated carbons derived from buckwheat husks

The zeta potential of buckwheat husk samples exhibits a similar trend to the rice husk samples, with values becoming increasingly negative as the pH rises from acidic to alkaline. The protonation of surface functional groups at low pH results in a positively charged surface or little electrostatic repulsion, as shown by zeta potential values that are closer to zero or slightly negative. As the pH increases, deprotonation of surface groups such as hydroxylic or carboxylic occurs, resulting in a more negatively charged surface and a corresponding decrease in zeta potential.

Among the samples, BH KOH PB appears to exhibit less steep changes in zeta potential across the pH range compared to others, suggesting a more stable zeta potential or different surface chemistry due to the modifications. Conversely, BH Urea KOH shows a relatively lower zeta potential, particularly in alkaline conditions, indicating a highly functionalized surface or enhanced deprotonation.

The overall trend reflects the formation and dynamics of the electrical double layer at the solid-liquid interface, which governs the material's interaction with charged species in solution. These results highlight the impact of chemical treatments on the surface charge properties of buckwheat husk.



Figure 3.5 - Relationship between zeta potential and pH for activated carbons derived from walnut shell

Based on Figure 3.5, it can be concluded that the most stable dispersion system is WN urea KOH/NaCl in the pH range from 7 to 12, because then the zeta potential value is equal to -30mV or lower, and such values are considered to provide colloidal stability.

The deprotonation of surface functional groups and the creation of a negatively charged surface in alkaline conditions are reflected in the zeta potential of walnut shell samples, which also generally follows the trend of becoming more negative with increasing pH. All of the samples' zeta potential values are near zero or slightly negative at low pH, which suggests the presence of protonated functional groups like hydroxyls or amines that lessen electrostatic repulsion. A more negatively charged surface results from the deprotonation of acidic groups (carboxyl groups) as the pH rises. Among the samples: WN Urea KOH shows the lowest zeta potential, especially at higher pH levels, suggesting a highly modified surface with enhanced deprotonation and possibly a higher density of functional groups that interact strongly with pH. WN 800 displays a more gradual shift in zeta potential compared to chemically treated samples, indicating fewer reactive surface groups due to thermal treatment alone. WN KOH PB and WN KOH exhibit intermediate behavior, with "WN KOH PB" showing slightly less steep changes, indicating stability in surface charge dynamics.

The variation in zeta potential among the samples reflects differences in surface chemistry and functional group density introduced by the treatment methods. These changes influence the double-layer structure and the materials' ability to adsorb positively charged contaminants like metal ions or radionuclides. The results highlight how chemical activation (e.g., with KOH or urea) enhances the material's surface reactivity and potential for adsorption applications.

Since cesium is difficult to hydrolyze or complex, it is present as Cs+ across a wide pH range [171]. Thus, pH is the only variable influencing the ion-exchange properties in the system being studied. Adsorption of cations over the surface acidic groups results in the formation of the adsorbent–cation complex and the simultaneous release of hydrogen. The resulting complex grows spherical as the cation gets closer to the adsorbent surface.

The surface charge of modified carbon materials (RH KOH, RH Urea KOH, BH KOH, BH Urea KOH, WN KOH, and WN Urea KOH) at pH values ranging from 3 to 11 was investigated at the Department of Radiochemistry and Environmental Chemistry (Maria Curie-Skladovska University, Poland) after the Cs+ (initial concentration 0.1 mol/dm3) sorption in an electrolyte present (0.001 mol/dm3 NaCl). Using tagged 137Cs and the radioisotope method, the adsorption of Cs+ was verified. The difference between the initial and final ion concentrations in solution per sample mass served as the basis for the calculation. The 2480 Automatic Gamma Counter (PerkinElmer, Waltham, MA, USA) was used to measure the radioactivity of 137Cs gamma sources. Activated carbon dispersions' zeta potential was ascertained by electrophoresis with the Zetasizer 3000 (Malvern, England, UK).

3.5 Surface Charge Density Determination

The potentiometric titration method was used to determine the activated carbons' surface charge densities and points of zero charge (pHpzc). To supply 40 m2 of the evaluated adsorbent in the measuring cup, 50 cm3 0.001 mol/dm3 NaCl solutions containing activated carbon (RH KOH, RH Urea KOH, BH KOH, BH Urea KOH, WN KOH, and WN Urea KOH) were created. This implies that the sorbent's surface area determines its initial mass. Measurements in the pH range of 3 to 11 were conducted at 25 °C. Following the addition of each component of the titrant (0.1 mol/dm3 NaOH), the pH of the suspension was measured using a pHM 240 pH meter (Radiometer, Warsaw, Poland) fitted with glass and calomel electrodes (Beckman Instruments, Brea, CA, USA). UMSC researchers devised the "Titr_v3" method (Figure 3.6) [165] to calculate the changes in the surface charge density value as a function of solution pH.


Figure 3.6 - Relationship between surface charge density and pH for the modified activated carbons (a – rice husk, b – buckwheat husk and c – walnut based carbons)

From Figure 3.6, RH materials (RH KOH and RH Urea KOH) exhibit a gradual decline in surface charge with increasing pH, transitioning from positive to negative at approximately pH 9 to 9.5. RH Urea KOH shows a smoother and more gradual decline when comparing with RH KOH, indicating slight differences in their buffering capacity. BH materials (BH KOH and BH Urea KOH) display a similar trend but with a steeper decline in surface charge, particularly for BH Urea KOH, which transitions more sharply around pH 10. On the other hand, WN materials (WN KOH and WN Urea KOH) behave differently, with their surface charge increasing initially and reaching a near-neutral or slightly positive maximum at pH 5-6 before decreasing. WN materials maintain a near-neutral charge over a broader pH range (approximately pH 4-9) compared to RH and BH materials, showing less sensitivity to pH changes in the intermediate range. Beyond pH 10, WN Urea KOH exhibits a slightly stronger negative charge than WN KOH. Overall, RH materials demonstrate a more linear decrease in surface charge, BH materials show sharper transitions, and WN materials provide more stability across a wider pH range. This comparison underscores the influence of surface functionalization and base material composition on the surface charge-pH relationship.

The phenomena observed in WN materials (WN KOH and WN Urea KOH) surface charge trends suggest a unique behavior compared to RH and BH materials. Initially, in the low pH range (around pH 4–6), the surface charge increases and stabilizes near a slightly positive or neutral value. This behavior could be attributed to the protonation of functional groups on the surface of the walnut-derived carbon material. Walnut shells contains a higher density of surface functional groups such as carboxylic, phenolic, or hydroxyl groups (described in FT IR part), which become protonated in acidic conditions, leading to a net positive or neutral surface charge.

In the intermediate pH range (around pH 6–9), the surface charge stabilizes, likely due to the buffering capacity of these functional groups. The stability could be a result of equilibrium between the deprotonation of acidic groups and the protonation of basic groups. This behavior makes WN materials more resistant to changes in surface charge within this pH range, a property that may be beneficial for adsorption applications where stability is crucial.

At higher pH values (above pH 9), the surface charge becomes increasingly negative, with a sharp decline beyond pH 10. This indicates significant deprotonation of acidic surface groups (e.g., carboxylic acids), leaving the surface negatively charged. WN Urea KOH shows a slightly stronger negative charge than WN KOH at high pH, suggesting that the urea treatment enhances the density of functional groups capable of deprotonation.

In the pH range below pHpzc, the surface of activated biocarbon is positively charged, which facilitates the electrostatic adsorption of negatively charged adsorbates. For pH values greater than pHpzc, the solid surface charge has negative values, and electrostatic interaction with positively charged adsorbates is preferred. The isoelectric points of the carbonaceous adsorbents under test were observed at lower pH values and were equal to pH<2 for all samples (Figure 13). This difference between the pHpzc and pHiep point values, which is observed in many systems and affects the ionic

composition of the diffusion EDL sections, may be the result of mutual overlap of electrical double layers (EDLs) formed on the opposing walls of adsorbent pores.

3.6 Results of Scanning electron microscopy (SEM EDX)

The surface characteristics and morphology of activated carbons, namely RH 900, RH KOH, WN 900, WN KOH, BH 900, and BH KOH, were investigated using scanning electron microscopy (SEM). The elemental makeup of these activated carbons' surface was determined semi-quantitatively using energy-dispersive X-ray microanalysis (EDX). Figure 3.7 displays the SEM images and the elemental composition of the samples.



Figure 3.7 - SEM images and EDX analysis of activated carbon samples (A - RH 800, B – RH KOH, C – WN 800, D – RH KOH, E – BH 800, F – BH KOH) лист 1



Figure 3.7 - SEM images and EDX analysis of activated carbon samples (A - RH 800, B – RH KOH, C – WN 800, D – RH KOH, E – BH 800, F – BH KOH), лист 2

The SEM images (Figure 3.7) revealed significant differences in surface morphology between the samples activated at 800°C by physical activation in CO₂ atmosphere and those activated with potassium hydroxide (KOH) in N₂ atmosphere. Physically activated samples, referred to as RH 800, WN 800, and BH 800, exhibited a denser and less porous structure. These samples had relatively smooth surfaces with a limited number of pores. In contrast, all KOH-activated samples demonstrated a notable increase in porosity and a well-developed porous structure. Specifically, the RH KOH sample displayed a dense network of micro- and mesopores, while WN KOH also showed a significant enhancement in porosity. BH KOH had the highest number of pores, indicating the most developed porous structure among the samples. Table 10. Representative characteristic SEM images of the obtained activated carbon sorbents.



Table 10 – Selected SEM images of the obtained activated carbon sorbents

Continuation of Table 10

1	2	3
		Mar Eff: # 55 for \$20 - 54 cm Base A - 67 \$20 - 54 cm Base A - 67 \$20 - 54 cm Base A - 67 \$20 - 54 cm
5	(WN -Urea): KOH (1:2)	
6	WN +KOH (1:2)	
7	5% Fe/BH (800)	

Continuation of Table 10

1	2	3
		Fight M17* SASH /r Specific # E10 One #1 One 1920 Time Specific # E11 Specific # E11
8	5% Fe/RH (800)	
9	RH KOH PB	TM4000 15kV 8.4mm x1.50k SE M 04/08/2025 30 0µm
10	ВН КОН РВ	TM4000 15kV 8.3mm x300 BSE M 04/08/2025 H04/08/2025
11	WN KOH PB	TM4000 15kV 8.3mm x600 BSE M 04/08/2025 50.0mm

In order to understand chemical composition of the carbon surface elemental EDX analysis of the surface has been conducted.

Elements	RH 800	RH KOH	WN 800	WN KOH	BH 800	ВН КОН
С	46.54	92.63	83.03	87.79	77.37	91.61
Ο	39.39	7.08	12.50	11.26	18.89	7.53
Mg	-	0.05	-	-	-	0.32
Si	-	0.08	-	0.23	-	0.14
S	-	0.05	-	-	-	-
Ca	-	0.11	-	0.17	-	0.15
Zn	-	-	-	-	-	0.08
Р	-	-	-	-	-	0.03
K	_	-	_	0.15	-	0.13
Al	_	_	_	0.40	_	_

Table 11 - Results of elemental analysis of activated carbon samples by Sem EDX

According to the data presented in Table 11, chemical activation using potassium hydroxide results in a reduction of carbon concentration due to a chemical reaction that facilitates pore formation and an increase in the content of oxygen and other elements within the material. During the activation process, KOH interacts with the carbon material, which leads to the creation of pores and an enhancement of the specific surface area. This interaction often involves the partial removal of carbon from the material's structure. Following KOH activation, oxygen is integrated into the carbon matrix, as indicated by the elevated oxygen (O) content in the samples after activation. Oxygen can bond with carbon to form surface oxides, contributing to the overall decrease in carbon percentage. Additionally, activated carbons produced through KOH activation may contain various impurities and compounds (such as K, Ca, Si, etc.), further contributing to the reduction of relative carbon content.

3.7 Spectroscopic analysis of ferrocyanide modified activated carbons

Different methods are currently applied for nuclear waste decontamination purposes. Among them, phytoremediation is among the most effective and affordable [72]. Sorption methods have been widely explored for water decontamination from radiocesium and radiostrontium. Sorbents impregnated with metal ferrocyanides, also known as hexacyanoferrates, which contain $[Fe(CN)_6]_2^-$ groups, are effective in removing Cs. The adsorption capacity of these materials, q_e, for Cs was reported in the range from ca. 200 mg/g to 620 mg/g using potassium hexacyanoferrate/gelatin aerogel composite [173], O-carboxymethyl chitosan nanocomposite with CuK₂[Fe(CN)₆] [174], ferrocyanide composite fibers23, Prussian blue graphene hydrogel [175], and clay-hexacyanoferrate hydrogel24. However, it caused a problem with the regeneration of ferrocyanide sorbents, in particular Prussian Blue. A fine powder of Prussian Blue itself can be used in a form of tube-in-tube adsorption with low qe = 36 mg/g [176].

The crown-6 ligand decorated sorbents also showed selectivity towards Cs: bisoctyloxy-calix[4]arene-mono-crown-6 immobilized onto a support material showed a weight distribution coefficient (Kd) value of >300 with an absorbed dose of 500 kGy [177], mixed solvent system of amino crown ether and ionic liquids showed 99.94% removal efficiency with the initial concentration of Cs⁺ 0.12 mol/L [178]. There were attempts for simultaneous extraction of Cs⁺ and Sr²⁺. For instance, carbonized opuntiaficus-indica husk showed 34 and 108 mg/g for Cs+ and Sr²⁺, respectively [179]. Another reported sorbent was macroporous silica dioxide with pore size of 194 nm, q_e = 150 mg/g [180]. Micro-adsorbents embedded with hydroxyapatite (HAp) and prussian blue (PB) demonstrated 29.3 mg/g for Sr2+ and 24.7 mg/g for Cs+, respectively [181].



Figure 3.8 - SEM EDX mapping of modified by ferrocyanide activated carbons

Elements	RH KOH PB	ВН КОН РВ	WN KOH PB
С	47.87	60.12	67.68
Ν	17.56	17.66	10.35
0	9.72	11.96	7.86
Al	1.95	0.68	0.93
Si	0.33	1.64	0.06
Fe	18.60	6.65	13.00
K	2.97	1.17	2.53

Table 12 - Elemental composition of ferrocyanide modified activated carbon sorbents

From the data above, the SEM EDX analysis of activated carbon derived from different biomass sources—rice husk (RH), buckwheat husk (BH), and walnut shell (WN), chemically activated with KOH and modified with Prussian Blue (PB) by Hydrothermal analysis, reveals notable differences in elemental compositions. The carbon content is highest in the walnut shell (67.68%), indicating its potential for greater adsorption capability, while rice husk shows a significant nitrogen content (17.56%), suggesting a potential nitrogen-rich surface that could enhance specific functionalities. The oxygen content varies, with buckwheat husk showing the highest value (11.96%), which may affect hydrophilicity and surface reactivity. Iron, introduced from Prussian Blue modification, is prominent in rice husk samples (18.60%), which may contribute to catalytical properties or increase structural stability, but is lower in buckwheat husks (6.65%). Which is compatible with Prussian Blue modified sorbents' elemental composition[76], [182], [183].

3.8 Raman spectroscopy

The Raman technique has been used to comprehend the degree of graphitization and disordered structure of the produced carbon sorbents [184]. The Raman spectra of three different kinds of activated carbons made from BH, RH, and WN biomass are shown in Figure 3.9. The D-band at roughly 1350 cm⁻¹, which in the case of activated carbons mostly reflects defects, vacancies, edges, and amorphous carbon regions, is connected to disordered sp²-hybridized carbon atoms. Meanwhile, the G Band (Graphitic Band), which spans an area of 1580 cm⁻¹, is associated with the in-plane stretching vibrations of sp2 bonded carbon atoms in graphitic domains. Furthermore, when it is higher than the D-band, a more ordered graphitic structure is predominant. Our samples have been tested in a range from 100 – 4000 cm⁻¹, no peacks corresponding 2D Band (around 2600–2700 cm⁻¹) which correspond to stacking order of graphitic layers were detected.



Figure 3.9 - Raman spectra of activated carbons with identification of I_D/I_G (A - BH 500, BH 800, BH Urea KOH and BH KOH, B – RH 500, RH 800, RH Urea KOH and RH KOH and C – WN 500, WN 800, WN Urea KOH and WN KOH)

Through their ID/IG ratios, the Raman spectra of the activated carbons derived from buckwheat husks (BH 500, BH 800, BH Urea KOH, and BH KOH) shown in Figure 3.9A show a variety of structural ordering and flaws. In contrast to BH 800 and BH Urea KOH, which both had ID/IG ratios of 1.16, indicating more disordered structure with more defects, BH 500 had the lowest ID/IG of 0.94, indicating higher graphitic order and fewer structural defects, probably as a result of milder activation conditions (carbonization at 500 °C). Higher activation temperatures (at 800 °C) could be the cause of this. Moreover, chemically activated by KOH carbons and urea impregnated (BH Urea KOH and BH KOH) showed an intermediate I_D/I_G ratio of 1.10, indicating a balance between graphitic domains and defect formation due to KOH activation. Overall, the samples range from relatively graphitic (BH 500) to highly disordered (BH Urea KOH and BH 800), making them suitable to apply as a sorbent material.

The Raman spectra of rise husk-activated carbons shown in Figure 3.9B (RH 500, RH 800, RH Urea KOH, and RH KOH) showed variations in their structural characteristics based on their lp/lg ratios. RH 500 showed the lowest lp/lg ratio of 0.98, which demonstrates the highest graphitic order and less defective structure. RH 800 had a slightly higher lp/lg ratio of 1.05, representing increased structural disorders as temperature rises. RH Urea KOH had the highest lp/lg ratio of 1.14, which indicates significant defect formation, likely due to chemical activation with urea and KOH, which introduces porosity and heteroatom functionalities. With an lp/lg ratio of 1.01, RH KOH reflects a balance between preserving graphitic order and introducing defects through KOH activation. These trends suggest that RH 500 is more graphitic, while RH Urea KOH is highly disordered[185].

The Figure 3.9C shows the Raman spectra of the walnut originated activated carbons WN 500, WN 800, WN Urea KOH and WN KOH. Among them WN 500 and WN Urea KOH showed the lowest I_D/I_G ratio of 0.94, suggesting lower defect levels. WN 800 shows a slightly higher I_D/I_G ratio of 1.17, indicating increased defect density,

while WN KOH presents the highest I_D/I_G ratio of 2.84, implying a significantly higher level of disorder in the material. This variation reflects changes in structural properties duo to KOH activation and pore formation.

To conclude, Raman spectral analysis demonstrates that the activation conditions significantly influence the structural order and defect density of the activated carbons derived from buckwheat husk, rice husk, and walnut shells, enabling tailored material properties for specific applications [186].

3.9 CHNS elemental analysis

Block C4 Lab 519, a Unicube organic elemental analyzer, was used to perform the CHNS analysis. By heating the samples to 750 °C for five hours in a muffle furnace, the amount of ash they contained was calculated [187]. Then, using the material balancing equation $O_{subs} = 100 - (C + H + N + S + D)$, where C, H, N, S, and A stand for the weight percentages of carbon, hydrogen, nitrogen, sulfur, and ash, respectively, the oxygen content (%) was determined on a dry basis.

Table 13 -Results of CHNS elemental analysis of modified activated carbon sorbents

Weight [mg]	Sample	Method,	N [%]	C [%]	H [%]	S [%]
		mg std				
0,8032	RH+UREA10%+KOH	2.5	1,15	88,59	0	0
2,7833	BH+UREA10%+KOH	2.5	0,91	87,88	0,247	0
4,4589	WN+UREA10%+KOH	2.5	0,82	83,42	3,085	0

The comparison of the modified activated carbon sorbents reveals that while all samples maintain high carbon content, ranging from approximately 88.59% to 92.87%, there are notable differences in nitrogen and oxygen levels. Nitrogen content remains relatively low, around 1 %, suggesting varying efficiencies in its retention based on modification methods[35].

3.10 Contact angle measurements

In order to assess the surface wettability and hydrophobicity/hydrophilicity of obtained samples, the contact angle measurement has been conducted by Drop Shape Analyzer DSA30, KRUSS (Table 14). This parameter was important to measure because we planned further sorption experiments in water phase [188], [189].

Table 14 - Results of contact angle measurement of activated carbon and their precursors

Sample	Contact angle (°)
1	2
BH raw	91.8
BH 800	8.3

Continuation of Table 14

1	2
ВНКОН	8.1
RH raw	95.8
RH 800	8.2
RH KOH	8.9
WN raw	62.5
WN 800	7.5
WN KOH	7.3

First, raw biomass (walnut, buckwheat husk and rice husk) were tested. In order to overcome activated carbon's inherent porosity and roughness which affect droplet spreading the samples were pre-tableted under a 10-ton press in pressed pellets.



Figure 3.10 - Selective images of raw biomass (a – rise husk, b – buckwheat husk and c – walnut shell) and activated carbon (d – physically activated and , e – chemically activated rice husk based activated carbons)

From the results of Table 14 the initial precursor exhibits high contact angles, indicating hydrophobicity of initial biomass. Further activated carbon sorbents, both obtained by physical and chemical activation show contact angles well below 10°, indicating highly hydrophilic surface which is mainly due functional groups (e.g., oxygen-containing groups from activation) which influence hydrophilicity [188], [189]

3.11 Particle size determination of obtained sorbents

The particle size of activated carbon is a crucial factor in its performance because it directly affects the material's surface area, adsorption kinetics, and overall sorption efficiency. For example, smaller particles have a larger surface area-to-volume ratio which provides more accessible active sites for adsorption and increase adsorption capacity and rate. In contrast, larger particle size may have lower accessible surface areas, reducing adsorption efficiency. Both nanoscale (Nano-ZS, Malvern) and micro scale (Lab-VIBSIEVE-6, Bessaiman Group) particle size have been measured (figure 3.11).



Figure 3.11 - Particles size distribution of activated carbon sorbents in mm for a) rice husk, b) buckwheat husk and c) walnut shell-based activated carbon

By analyzing the particle size of all types of carbon sorbents that prevailing majority of particles are rather equal to 1mm or in a range between 1-3 mm. which can be considered as powder activated carbon (PAC) [190].

3.12 X-Ray Fluorescence Spectroscopy (XRF)

EDXRF is a surface-sensitive technique that allows for the non-destructive determination of the elemental composition of a material by measuring the characteristic X-rays emitted when the sample is irradiated with a primary X-ray beam [190]. Our goal was to quantify key elements such as potassium (K) from the chemical activation process and iron (Fe) from Prussian Blue, which are critical for the material's functionality in cesium extraction. This analysis also helps to identify potential impurities or elemental changes resulting from activation and modification, ensuring the material's suitability for cesium adsorption applications. Moreover, XRF data can correlate the elemental distribution with adsorption efficiency, enabling optimization of the synthesis process for enhanced performance. Below data are taken from automatically generated report and are given in sequence BH KOH PB, RH KOH PB, WN KOH PB.

Table 15 - XRF data of Prussian Blue modified BH KOH PB

No.	Component	Result	Unit	Stat. Err.	LLD	LLQ	Element line	Intensity(cps/mA)
1	Ca	4.00	mass%	0.0426	0.0689	0.207	Cu:Ca-Ka	176.839
2	K	27.7	mass%	0.0988	0.0421	0.126	Cu:K-Ka	1131.690
3	Fe	62.4	mass%	0.0555	0.0048	0.0144	Mo:Fe-Kα	7407.393
4	Co	ND	mass%	0.0119	0.0396	0.119	Mo:Co-Ka	6.176
5	Ni	0.753	mass%	0.0103	0.0063	0.0188	Mo:Ni-Kα	71.029
6	Al	4.12	mass%	0.166	0.229	0.688	RX9:Al-Kα	4.546
7	Si	0.990	mass%	0.0369	0.0502	0.151	RX9:Si-Kα	5.396
Spect	rum							

Table 16 - XRF data of Prussian F	Blue modified RH KOH PB
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Analy	zed result(FP 1	nethod)						
No.	Component	Result	Unit	Stat. Err.	LLD	LLQ	Element line	Intensity(cps/mA)
1	Al	2.31	mass%	0.0414	0.0375	0.112	RX9:Al-Kα	24.771
2	Si	0.887	mass%	0.0112	0.0079	0.0236	RX9:Si-Kα	48.340
3	K	19.5	mass%	0.0471	0.0164	0.0491	Cu:K-Ka	8495.353
4	Ca	0.581	mass%	0.0115	0.0264	0.0793	Cu:Ca-Ka	319.258
5	Fe	76.5	mass%	0.0178	0.0010	0.0030	Mo:Fe-Kα	110461.543
6	Co	0.184	mass%	0.0050	0.0147	0.0441	Mo:Co-Ka	375.636
7	Ni	0.0645	mass%	0.0013	0.0016	0.0048	Mo:Ni-Kα	59.169
Spect	rum							

Table 17- XRF data of	Prussian Blue	modified '	WN KOH PB
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1 Al 2 Si 3 Cl 4 K 5 Ca 6 Mn 7 Fe	3.54 4.78 1.59 8.79 18.6	mass% mass% mass%	0.141 0.0668 0.0076 0.0563	0.215 0.0461 0.0043 0.0456	0.644 0.138 0.0129 0.137	RX9:Al-Kα RX9:Si-Kα RX9:Cl-Kα Cu:K-Kα	4.815 32.061 295.638
2 Si 3 Cl 4 K 5 Ca 6 Mm 7 Fe	4.78 1.59 8.79 18.6	mass% mass% mass%	0.0668 0.0076 0.0563	0.0461 0.0043 0.0456	0.138 0.0129 0.137	RX9:Si-Kα RX9:Cl-Kα Cu:K-Kα	32.061 295.638 432.522
3 Cl 4 K 5 Ca 6 Mn 7 Fe	1.59 8.79 18.6	mass% mass%	0.0076 0.0563	0.0043 0.0456	0.0129 0.137	RX9:Cl-Ka	295.638
4 K 5 Ca 6 Mn 7 Fa	8.79 18.6	mass%	0.0563	0.0456	0.137	CurK-Ka	422 522
5 Ca 6 Mn 7 Fe	18.6					Cu.ix-ixu	432.322
6 Mn 7 Fe	10.0	mass%	0.0639	0.0386	0.116	Cu:Ca-Ka	1336.713
7 Fe	3.61	mass%	0.0228	0.0118	0.0353	Mo:Mn-Ka	359.179
/ 10	58.2	mass%	0.0520	0.0152	0.0455	Mo:Fe-Kα	8489.112
8 Co	0.286	mass%	0.0128	0.0370	0.111	Μο:Co-Kα	54.694
9 Ni	0.670	mass%	0.0092	0.0076	0.0227	Mo:Ni-Kα	78.809

From the obtained data, the high content of Fe corresponds to successful impregnation on the carbon surface and its stability

3.13 Study of the kinetics of tri-iodide ions sorption

To understand the kinetic behavior of tri-iodide ion adsorption by modified activated carbon samples, two kinetic models were examined: the pseudo-first-order model and the pseudo-second-order model. The linear forms of the corresponding equations were used for analysis Table 18). Initial concentration of tri-iodide solution was 100 mg/L.

Modified Adsorbate activated		Pseudo-First Order			Pseudo-Second Order			
		qe ^{cal}	$k_1(min^{-1})$	R ²	q _e ^{cal}	$k_2 (g \cdot mg^{-1} \cdot$	R ²	
Carbon		(mg/g)			(mg/g)	\min^{-1})		
RH KOH	I3 ⁻	85,10	0.1253	0.7427	480.85	0.0046	0.9993	
BH KOH	I3 ⁻	183,41	0.1056	0.7486	488.85	0.0018	0.9991	
WN KOH	I3 ⁻	90.34	0,0146	0,7712	434,87	0,029	0,9933	
RH Urea KOH	I ₃ -	65.83	0.0519	0.9074	471.85	0.042	0.974	
BH Urea	I_3^-	161 11	0.0443	0.9402	468 85	0.0016	0 0087	
КОН		101.11	0.0443	0.7402	H00.05	0.0010	0.7707	
WN Urea	I_3^-	32.30	0.0393	0.8933	469.44	0.0087	0.9998	
КОН		22.20	0.0000	0.0900		0.0007	0.7770	

Table 18 - Results of pseudo-first and pseudo-second order kinetic modelling for I_3^- adsorption by modified activated carbon

The adsorption characteristics of modified activated carbon sorbents for the iodine-containing adsorbate (I₃⁻) reveal distinct differences in performance. Among the sorbents, BH KOH demonstrates the highest pseudo-first order adsorption capacity (183.41 mg/g), suggesting superior initial adsorption ability, while WN Urea KOH exhibits the lowest capacity (32.30 mg/g). In terms of kinetic modeling, the pseudo-second order fit is generally stronger across the samples, with R² values exceeding 0.99 for most, particularly for RH KOH (0.9993) and WN Urea KOH (0.9998), indicating that the adsorption process is likely dependent on the number of available sites on the adsorbent. The rate constants (k₁ and k₂) further suggest that while the overall kinetics vary, the pseudo-second order model more accurately characterizes the adsorption behavior, particularly in BH KOH, where k₂ is lower (0.0018 g·mg⁻¹·min⁻¹), indicating slower saturation compared to others. Overall, BH KOH and RH KOH emerge as more effective sorbents for iodine adsorption, while WN Urea KOH shows lower efficiency, due to clapping of micropores.

3.14 Equilibrium adsorption isotherms

To prepare the solution for measuring the isotherm, iodine solutions at concentrations of 25 mg/L, 50 mg/L, 75 mg/L, 100 mg/L, 125 mg/L, 150 mg/L, 175 mg/L, and 200 mg/L (Figure 24) were used to assess the kinetics of adsorption. The mass of activated carbon used for iodine sorption was 0.0308 grams.



Figure 3.12 - Tri-iodide solution with concentration of 25 - 200 mg/L for adsorption isotherm measurement

To analyze the experimental isotherms, the adsorption of iodine on homogeneous or heterogeneous surfaces was described using the Langmuir [191] and Freundlich [192] isotherm models. The experimental isotherms are shown in Figure 3.13. Even though the correlation coefficient of the Langmuir isotherm model was primarily higher than that of the Freundlich isotherm model for the majority of the modified activated carbon sorbents (Table 20), the capacities derived from the Langmuir model are remarkably close to experimental values. The excellent fit of the Langmuir model indicates I3-ion monolayer adsorption on the surface of modified activated carbon.



Figure 3.13 - Isotherms of I₃⁻ removal by chemically modified activated carbons (WN KOH, RH KOH and BH KOH) and them modified with 10% Urea solution

From the Figure 25 a) the WN Urea KOH sample appears to be more effective. It shows a steeper increase in adsorption capacity (q) at lower equilibrium concentrations (C_{eq}), indicating stronger adsorption efficiency compared to WN KOH. Additionally, the earlier provided data indicated a high correlation coefficient ($R^2 =$

0.9909), supporting a good fit with the Langmuir model. This suggests enhanced adsorption performance due to the inclusion of urea. From the Figure 25b) RH Urea KOH appears more effective in adsorption, especially at lower equilibrium concentrations, likely due to the modification with urea, which enhances its adsorption properties. The same phenomena is applicable for buckwheat husk originated activated carbon illustrated at Figure 25c) which exhibits a marked increase in adsorption capacity with rising equilibrium concentration, indicating strong adsorption efficiency, particularly at lower concentrations. In contrast, BH KOH also shows an increasing trend but with a less pronounced rate of increase in adsorption capacity. This suggests that the urea modification significantly enhances the adsorption capabilities of BH Urea KOH compared to BH KOH, making it a more effective option for tri-iodide removal.

When comparing all three types of carbons originated from different biomass walnut 25a), rice husk b) and buckwheat husk c), they are collectively demonstrate the comparative adsorption efficiencies of carbon sorbents modified with urea. In the first figure, WN Urea KOH shows a steeper increase in adsorption capacity (q) compared to WN KOH, indicating greater effectiveness, particularly at lower equilibrium concentrations with a high correlation coefficient ($R^2 = 0.9909$) supporting this performance. Similarly, the second figure illustrates that RH Urea KOH outperforms RH KOH in adsorption capacity, reinforcing the trend observed in the WN samples. The third figure further confirms this pattern, as BH Urea KOH distinctly exhibits enhanced adsorption capabilities compared to BH KOH, particularly at lower concentrations. Across all three figures, it is evident that the urea modifications significantly improve the adsorption properties of the carbon sorbents, underscoring urea's effectiveness in tri-iodide removal.

Sample q _{mal} ^{exp}		Langmuir model			Freundlich model			
		q _m	KL	R ²	n	K _F	R ²	
	(mg/g)	(mg/g)	(L/mg)					
WN KOH	785.0±10,06	957.7	0.3727	0.9907	0.5777	239.4	0.9743	
RH KOH	774.7±0,19	847.9	0.3613	0.9123	0.5539	216.0	0.8918	
ВН КОН	787.5±0,07	887,59	0,2677	0,9302	0.8642	297,9	0.8486	
WN Urea	500.7±8,66	551.9	0.0742	0.9909	0.5865	49.4	0.9649	
КОН								
RH Urea	1211.7±8,94	1266.5	0.4513	0.9832	0.5051	345.9	0.9056	
КОН								
BH Urea	1098.7±5,13	1149.5	0.5504	0.8471	0.5121	374.1	0.8244	
КОН								
Commercial	451,76±15,45	364.8	0.2490	0.987	0.3711	95.5	0.9629	
AC								

Table 19 - Parameters of isotherm models for I_3 -sorption by activated carbons

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For the Langmuir model, the observed maximum adsorption capacity (q_{max}^{exp}) is highest for the BH KOH sample at 787.5 mg/g, while the corresponding q_m value is not available. The WN KOH sample has a q_{max}^{exp} of 785.0 mg/g and a q_m of 957.7 mg/g, with a high Langmuir constant (K_L) of 0.3727 and a strong R² value of 0.9907, indicating a good fit. The RH KOH sample shows a q_{max}^{exp} of 774.7 mg/g with a q_m of 847.9 mg/g and a R_L value of 0.3613 (R² = 0.9123).

For the Freundlich model, the BH KOH sample exhibits a notable n value of 0.8642 while the Freundlich constant (K_F) is 162.1 with an R² of 0.8443. The WN Urea KOH sample has a Freundlich fitting parameter n of 0.5865 and KF of 49.4 (R² = 0.9649). The RH Urea KOH sample shows a high qma[exp] of 797.7 mg/g with q_m at 1266.5 mg/g, along with a Freundlich constant (K_F) of 345.9 (R² = 0.9056). The Wood AC sample, serving as a comparison, has a lower q_{max}^{exp} of 184.0 mg/g and q_m of 196.5 mg/g. Overall, the data reflects varying adsorption capacities and affinities across different samples, indicating the influence of preparation methods on the adsorption behavior of these carbon sorbents.



Figure 26 - Adsorption kinetics of I₃⁻ on the modified activated carbon sorbents (a) walnut, b) rise husk and c) buckwheat husk originated (30 mg of sorbent in 150 mL of 100ppm I₃⁻ solution), page 1



Figure 26, page 2

Figure 26 compares the removal efficiencies of various carbon sorbents for radioactive tri-iodide adsorption over time, highlighting significant differences in their performance. The WN Urea KOH and RH Urea KOH samples achieve near-complete removal efficiencies quickly, reaching approximately 80% and 86%, respectively, within half an hour. This rapid effectiveness can be attributed to the urea modification.

The BH Urea KOH sample also demonstrates strong performance, although it reaches its maximum efficiency slightly more slowly compared to the walnut and rice husk-derived urea-modified sorbents. In contrast, the BH KOH and RH KOH samples exhibit moderate removal efficiencies of 58% in the first half hour, attaining lower maximum values over an extended period. This suggests that urea modifications significantly enhance their performance.

The WN KOH sample shows a more gradual increase in efficiency, while the commercial Wood AC consistently lags behind all other samples, demonstrating the lowest removal efficiency.

When comparing physically activated carbon sorbents, RH 800 and BH 800 exhibit high efficiencies, both reaching around 96% at their maximum interval. The WN 800 sample also shows positive trends, but it has slightly lower efficiency than the other two.

Overall, it is clear that urea-modified sorbents outperform other samples in their ability to adsorb radioactive tri-iodide ions.

4 STUDY OF THE SORPTION CAPACITY OF THE OBTAINED SORBENTS ON RADIOACTIVE ISOTOPES

4.1 Adsorption of Cs⁺ at the Modified Carbon/Aqueous Electrolyte Interface

Under the direction of Professor Ewa Skwarek, experiments with radioactive isotopes have been carried out at the Chemistry Faculty's Radiochemical Laboratory, Department of Radiochemistry and Environmental Ecology, University of Maria Curie-Skłodowska in Lublin, Poland. Two kinds of isotopes have been tested: ³⁶Cl, which exhibits anion behavior, and ¹³⁷Cs, a positively charged radionuclide.

Surface charge density and zeta potential were determined for the electrolyte concentrations (0.001 mol/dm–3) as a function of pH and the electrolyte concentration of Cs+ (0.001 mol/dm3). The potentiometric titration set and the radioactivity loss from the solution method were used to study ion adsorption. A portion of the solution containing the relevant radioactive isotope (137 Cs) in chemical form was then added in order to examine the adsorption process. The zero sample, which is a sample without an adsorbent, was used to quantify the initial solution radioactivity after solution mixing. This was followed by the addition of an excessive amount of modified carbon sorbent to the mixture. Two samples of this solution were collected after being converted into radioactivity before and after adsorption, the density of ions adsorbed (Γ) on the modified carbon surface is calculated according to the Eq. 11 and 12:

$$\Gamma = C_o V/mS_w(1 - N_r/N_o)$$
(Eq. 11)
and
$$c_r = c_0 N_r/N_o$$
(Eq. 12)

where c0 is the starting concentration (mol/l), m is the sediment over weighted (g), and V is the solution's volume (l); Sw stands for specific surface area (m²/g). N₀ is the number of counting from the source taken up before adsorption, Nr is the number of counting from the source taken up during titration, and Cr is the equilibrium concentration (mol/l). The adsorption of Cs+ using ¹³⁷Cs was ascertained by the radioisotope method, and the adsorption was calculated as the difference between the beginning and final concentration of ions in solution/unit mass of sample (Figure 4.1). (KOH RH urea).

The 2480 Automatic Gamma Counter (PerkinElmer, Waltham, MA, USA) was used to measure the radioactivity of ¹³⁷Cs gamma sources. Using Zetasizer 3000 (Malvern, UK) electrophoresis, the zeta potential of the modified carbons' dispersions was ascertained.



Figure 4.1 - Cesium ions adsorption (in %) as function of the solution pH

Cesium is present as Cs+ ions across a broad pH range because it is not easily hydrolyzed or complexed. Thus, the only factor affecting the ion exchange characteristics in the system under study is pH. Adsorbent-cation complex formation and hydrogen release occur simultaneously, facilitating cation adsorption over surface acidic groups. The cation positions itself closer to the adsorbent surface, while the complex that is created is spherical. The values of the cesium ion adsorption (in percentage) as a function of solution pH are shown in Figure 25. Cs⁺ ions were used to study the adsorption, and the electrolyte's starting concentration was 0.001 mol/dm³. It was discovered that when the pH rose from 8.5 to 11, more Cs⁺ ions were adsorbed. The process of Cs⁺ ion adsorption on metal oxides is identical to that of simple cation adsorption. Exchange reactions between Cs+ ions and acid group H+ ions provide a partial explanation. Diffusion has a role in the adsorption process because of the electrolyte (0.001 mol/dm³ NaCl).

Figure 4.2 shows the relationship between the adsorption density of Cl^- ions at the interface between RH KOH and the electrolyte solution. It also shows the equilibrium concentration of Cl^- ions in the solution as a function of pH for a concentration of 0.001 mol/l. It has been shown that less Cl^- ion adsorption takes place when pH increases. The primary reason for this decline is the nearly complete migration of these ions from the solution to the RH KOH surface. However, beyond pH 10, a decrease in Cl^- adsorption is observed.



Figure 4.2 - Adsorption density of Cl⁻ ions at the interface of RH KOH/electrolyte solution and also the diagram of the equilibrium concentration of Cl⁻ ions in the solution as a function of pH

The way that anions adsorb on RH KOH suggests that hydroxyl groups are important to this process. Chloride ion adsorption onto RH KOH is enhanced at lower pH values due to the neutralization of the positive charge on the adsorbent surface and an increase in protonation. This process increases adsorption by facilitating diffusion and increasing the number of active sites on the adsorbent surface.

Moreover, the surface potential of hydroxyapatite turns negative when the pH of the solution surpasses the pH of zero charge (pH_{PZC}) of RH KOH. The negatively charged surface and chloride ions experience increased electrostatic repulsion as a result, which eventually reduces adsorption.



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CERTIFICATE OF COMPLETION

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Makhabbat Kunarbekova

During her visit from May 22nd to June 6th of 2024 at the Maria Curie-Skłodowska University – Department of Radiochemistry and Environmental Ecology she conducted research on the topic of "Removal of radioactive isotopes Cs-137 and Cl-36 by modified activated carbons from agricultural waste" at the Radiochemical Laboratory at the Faculty Chemistry

This collaboration is a great opportunity for the exchange of knowledge and has a great role in building a solid relationship between Satbayev University and the Maria Curie-Skłodowska University, Faculty Chemistry, Radiochemical Laboratory

Euro Skwarth

June 06, 2024

dr hab. Ewa Skwarek prof. UMCS

Date

4.2 Investigation of the Sorption Capacity of the Obtained AC sorbents on Industrial Samples Provided by the National Nuclear Center

Sample point.

The mountain massif in the Zhanasemey District of the Abai Region of Kazakhstan is the delegen site. Degelen was a component of the Semipalatinsk Test Site complex during the Kazakh SSR. To conduct nuclear testing, the USSR military dug almost a hundred horizontal tunnels beneath the mountain. Most of the subcritical and supercritical testing were conducted in the Himalayan massif. The sample was taken from the Degelen site, tunnels No. 104 and No. 177 of the Semipalatinsk Test Site (STS), also known as "The Polygon," in East Kazakhstan, where 215 underground nuclear explosions were conducted [193]. It was the primary test site where nuclear weapons were tested during the Soviet Union time, and it still presents a significant environmental problem with radionuclide-contaminated groundwater. The site is located 120 km from the city of Kurchatov (Figure 4.3, 4.4).



Figure 4.3 - Map of STS with the level of contamination reported for the Degelen test side [194]

This map shows that the current situation is still critical, and methods capable of reducing the radioactive contamination caused mainly by 137 Cs and 90 Sr are needed.

The chemical composition of contaminated groundwater at STS is shown in Table 20[195].

			Water type			Mean concentration in		
					Average for	underground water		
Paramete r Unit		Hydro- carbonate n=26 <u>X±S</u> (min-max)	Sulphate, n=5 <u>X±S</u> (min-max)	Chloride, n=15 <u>X±S</u> (min-max)	the STS <u>X±S</u> (min-max)	Hyper- genesis zone [4]	Contine ntal salificat ion zone [4]	
рН	-	$\frac{7.7}{(6,5-8,5)}$	$\frac{7.7}{(6,8-8,4)}$	<u>7.7</u> (7-8,3)	$\frac{7.7}{(6,5-8.5)}$	6,9	7,5	
Eh	mV	<u>-0.2</u> (от -0,9 до +11)	<u>-0.2</u> (от -0,5 до - 0,3)	<u>-0.2</u> (от -0,5 до +0,07)	<u>-0.2</u> (от -0,9 до +11)	-	-	
TDS**	g/l	<u>0,4±0,1</u> (0,19- 0,95)	<u>1,7±0,3</u> (0,4-18)	<u>3,7±0,6</u> (0,6-7,8)	<u>1,7±0,3</u> (0,19-18)	0,5*	1,3*	
HCO3 ⁻	mg/l	<u>270±40</u> (88-490)	<u>270±40</u> (100-680)	<u>260±40</u> (120-400)	<u>280±42</u> (88-680)	187	349	
C1 ⁻	-	$\frac{31\pm5}{(3,4-100)}$	<u>230±35</u> (20-2900)	<u>1300±195</u> (50-3200)	<u>340±51</u> (3,4-3200)	59,7	258	
SO4 ²⁻	-	$\frac{110\pm17}{(0-290)}$	<u>800±120</u> (180-8900)	<u>960±144</u> (150-1800)	$\frac{650 \pm 98}{(0-8900)}$	70,7	304	
Ca	-	$\frac{60\pm11}{(27-140)}$	$\frac{110\pm17}{(40-400)}$	<u>180±27</u> (40-320)	$\frac{110\pm17}{(27-390)}$	39,2	86,4	
Mg	-	<u>70±11</u> (6-1300)	<u>46±7</u> (12-214)	<u>110±17</u> (19-207)	<u>60±9</u> (6-1300)	18,2	46,2	
Na	-	<u>72±11</u> (6-214)	<u>300±45</u> (100-2500)	<u>490±74</u> (97-811)	<u>266±40</u> (6-2500)	67,6	260	
K	-	<u>6,2±1</u> (0,6-37)	$\frac{3,6\pm1}{(0,7-19)}$	<u>19±3</u> (2,1-136)	<u>6,6±1</u> (0,6-136)	5,15	18,4	
**TDS – total dissolved solids, * – total content of water macrocomponents.								

Table 20 - Chemical composition of STS groundwater





a) Sample point No. 104



b) Sample point No. 177

Figure 4.4 - STS site visit and Sampling

The sample taken contained 25 liters of water from tunnel No. 104 and 20 liters from tunnel No. 177. The samples were brought to the Laboratory of Experimental and Environmental Research of NNC.

For the experimental studies, water from the 104 watercourse, which is known for its high content of technogenic radionuclides. The 104 site is located in the Degelen testing area of the former Semipalatinsk test site. Between 1961 and 1989, a total of 209 nuclear tests were conducted at this site across 181 tunnels, situated within the Degelen mountain range. These nuclear tests were executed in horizontal mining tunnels, with lengths ranging from several hundred meters to 2 kilometers. The diameter of the tunnel shafts is approximately 3 meters.

To prevent the possibility of reusing these tunnels for nuclear testing, efforts to close all tunnels on Degelen Square were carried out from 1996 to 1998. A radioecological examination of the area indicated that most of the site is free from radioactive contamination, as over 90% of the radioactivity accumulated during the nuclear tests is concentrated within the tunnels themselves. Nonetheless, certain areas, including the 104 watercourses, show increased concentrations of radionuclides due to the migration of radioactivity from the tunnel cavities via water.

Experimental studies were conducted in three stages to determine the sorption properties of biomass-derived modified activated carbon sorbents:

1.Preparation of the selected water sample and measurement of the initial concentrations of technogenic radionuclides (¹³⁷Cs and ⁹⁰Sr) in the water.

2.Identification of the optimal mass of the sorbent for conducting experiments to assess their sorption properties.

3.Execution of experiments to evaluate the sorption characteristics of the biomass-derived modified activated carbon sorbents.

The experiment was conducted in several stages, and the results obtained are as follows:

At the first stage, upon entering the laboratory, the water sample was filtered using a double layer of white ribbon paper filter. This process aimed to remove coarse suspensions and organic residues from the sample Figure 4.5.



Figure 4.5 - Filtration of contaminated water from tunnel No. 104

Filtration was performed using a Buchner funnel with a porcelain paper filter (D-110). The initial concentration of the technogenic radionuclide ¹³⁷Cs in the water, as well as its concentration after experimental sorption studies, was measured using gamma-ray spectrometric techniques with a gamma-ray spectrometer equipped with a detector made of high-purity germanium. The content of ⁹⁰Sr was determined using the β -spectrometric method for its daughter isotope, ⁹⁰Y, following preliminary radiochemical isolation. The results of the initial analysis of technogenic radionuclides in the water are presented in Table 21 and reports in appendix A.

	Table 21 - The initial	concentration	of technog	genic	radionu	clides	in	water
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Sanling noin	Specific activity, Bq/L			
Saping poin	¹³⁷ Cs	⁹⁰ Sr		
tunnel No. 104	118±24	346±52		

In the second stage of the study, the optimal mass of the sorbent required for conducting sorption experiments was determined. Prior to initiating the experiments, activated charcoal was prepared from walnut shells. Three different weights per liter of water were utilized, referred to as unit No. 104. In the laboratory, a measurement of 0.0308 grams of sorbent was established for every 150 milliliters of liquid; consequently, the mass was increased to factors of x1, x2, and x5. Specifically, three weights of 0.2 g, 0.4 g, and 1 g were placed in conical flasks, each with a volume of 1 liter and filled with 1 liter of the selected water. These flasks were subjected to continuous stirring using a shaker for a duration of 24 hours. Following this period, the water was filtered, and the concentrations of radionuclides ¹³⁷Cs and ⁹⁰Sr were analyzed. The results of this experiment are presented in Table 22.

Table 22- Determination of the optimal sorbent mass

Weight of the	Specific activity, Bq/L		
sorbent, g	¹³⁷ Cs	⁹⁰ Sr	
0,2	110±22	310±45	
0,4	101±20	340±50	
1,0	106±21	330±50	

The findings demonstrate that the specific activity of ¹³⁷Cs is lowest when employing a sorbent suspension weight of 0.4 g. This observation suggests that increasing the sorbent weight beyond 0.4 g yields minimal improvement in the sorption efficiency of both ¹³⁷Cs and ⁹⁰Sr. Consequently, a sorbent weight of 0.4 g has been selected as optimal for experimental studies aimed at determining sorption properties.

In the third phase the sorption characteristics of biomass-derived sorbents was evaluated. The materials tested included walnut peel (WN), rice husk (RH), and

buckwheat husk (BH), along with various modifications that had different specific surface areas and pore sizes, created through diverse laboratory methods at the Kazakh National Research Technical University named after K.I. Satpayev in Almaty. A total of 12 types of sorbents were utilized.

These experiments were designed to be conducted under static conditions for a duration of 24 hours, with continuous stirring facilitated by a mixing device (shaker). Each experiment was replicated twice to ensure reliability. For each trial, 0.4 g of sorbent was accurately measured using an analytical balance with a precision of four decimal places and placed into a conical flask. Subsequently, 1 liter of selected natural water was added, and the flask was securely sealed to prevent evaporation. The shaker maintained consistent stirring at room temperature for 24 hours (refer to Figure 4.6a). Following the mixing process, the solutions were meticulously filtered through a "red ribbon" filter (Figure 4.6b).

This systematic approach will enable us to gain valuable insights into the sorption properties of these biomass-based materials, thereby enhancing our understanding and potential applications in environmental remediation.



Figure 4.6 - The process of conducting experimental research

Further, the content of ¹³⁷Cs and ⁹⁰Sr was determined in the filtrate. The table (Table 23) shows the results of the experiments performed - the average values of the specific activities of the studied radionuclides. All the measurement results obtained, including the determination of the initial content and 27 samples obtained during the experiments.

Southout	Specific activity, Bq/l				
Sorbent	¹³⁷ Cs	⁹⁰ Sr			
RH 800	112±22	340±51			
(RH-Urea): KOH	95±19	290±44			
RH+KOH	102±20	338±51			
RH KOH PB	<2	260±39			
BH 800	117±23	262±40			
(BH-Urea): KOH	100±20	278±42			
BH+KOH	110±22	323±48			
BH KOH PB	10±2	383±57			
WN 800	114±23	360±54			
(WH-Urea): KOH	106±21	335±50			
WN+KOH	110±22	395±59			
WH KOH PB	5±1	338±51			

Table 23 - The results of the content of ¹³⁷Cs and ⁹⁰Sr in water samples

Based on the data obtained, the sorbents of types RH 800, BH 800, and WN 800 exhibited the lowest sorption properties concerning ¹³⁷Cs, with specific activity values in the filtrate recorded at 112 \pm 22 Bq/l, 117 \pm 23 Bq/l, and 114 \pm 23 Bq/l, respectively. When utilizing modified sorbents, such as (RH-Urea): KOH, RH+KOH, (BH-Urea): KOH, BH+KOH, (WH-Urea): KOH, and WN+KOH, the specific activity of 137Cs in the filtrate ranged from 95 \pm 19 Bq/l to 110 \pm 22 Bq/l.

The highest sorption efficiency for 137Cs was observed with RH KOH PB, BH KOH PB, and WH KOH PB sorbents. Notably, the specific activity of ¹³⁷Cs with the RH KOH PB sorbent was below the detection limit of the equipment and methods used, which significantly surpassed the performance of other studied sorbents.

Additionally, the concentration of the 90 Sr radionuclide in the samples obtained after the experiments ranged from 260±39 Bq/l to 395±59 Bq/l. There were minimal differences in sorption capacity for 90Sr among the various sorbent modifications, as the values fell within the same numerical range, considering the margin of error.

As a result of this study, the initial levels of technogenic radionuclides in the naturally polluted water sampled from 104 units were determined. The optimal weight for the sorbent suspension for subsequent experiments was established, and experimental studies were conducted with 12 samples of various sorbent modifications.

It was found that the sorbents RH KOH PB, BH KOH PB, and WH KOH PB demonstrated high sorption properties for 137 Cs. This is attributed to the modification with potassium hydroxide and ferrocyanides, which can form stable complex compounds with Cs⁺ ions. However, these modified sorbents cannot bind to Sr²⁺ ions and do not demonstrate sorption properties for this radionuclide, as they lack the necessary functional groups in their composition.

4.3 Computer modelling of sorbent structure by Gaussian

Computer modelling of absorption processes has been conducted using Gaussian 16W software to simulate chemical structure, electronic properties, and functional group chemistry and predict the sorption mechanism. The results of elemental analysis, SEM-EDX data, and FTIR data have been used as inlet data. Therefore, the "single cell," a common fragment of each sorbent, has been constructed and optimized with high accuracy. Figures 4.7-4.9 represent a typical fragments of Urea modified and activated with KOH sorbents.



Figure 4.7 - Representative Structures of "Unit cell" fragment of WN Urea KOH surface functional groups.



Figure 4.8 - Representative Structures of "Unit cell" fragment of RH Urea KOH surface functional groups



Figure 4.9 - Representative Structures of "Unit cell" fragment of BH Urea KOH surface functional groups

The representative structures of WN-Urea-KOH, RH-Urea-KOH, and BH-Urea-KOH unit cell fragments (Figures 4.7–4.9) clearly show the presence of nitrogencontaining functional groups, confirming the successful incorporation of urea during the surface modification process. These nitrogen atoms, visualized in blue, oxygen groups are evenly distributed across the carbon framework in each sample, indicating effective impregnation and chemical bonding of urea-derived functionalities. The consistent appearance of both nitrogen and oxygen functional groups across all three biomass-derived activated carbon models (walnut shell, rice husk, and buckwheat husk) suggests a uniform modification pathway under alkaline (KOH) activation conditions. This structural evidence supports the hypothesis that urea-assisted functionalization introduces key nitrogen species, such as amine, amide, or imide groups, which play a vital role in improving adsorption capacity and selectivity in aqueous-phase purification processes.

The simulation of radioactive ions (iodine, cesium, and strontium) was conducted to model the mechanism of reactions during sorption and assess the chemisorption contribution. The simulation models utilize periodic boundary conditions with the wB97XD functional and the def2-TZVP basis set, incorporating solvent effects via the SMD model. Thermodynamic properties were evaluated through Gibbs free energy calculations at 25 °C and 1 atm. Structural optimizations and interaction analyses were enhanced using Natural Energy Decomposition Analysis (NEDA) through NBO 7.0. The study targets the sorption of environmentally significant radionuclides and anions, specifically triiodide (I₃⁻), cesium (Cs⁺), and strontium (Sr²⁺). A key objective is to elucidate the contribution of nitrogen-containing functional groups—introduced via urea modification—to the selective sorption of triiodide. Resulted mechanism for urea modified BH KOH sorbent interaction with I₃⁻ is showen in Figure 4.10.



Figure 4.10 - Representative Structures of "Unit cell" fragment of BH Urea KOH surface functional groups

The triiodide ion (I₃⁻) interacts with nitrogen-containing functional groups on the urea-modified activated carbon surface primarily through the lone pair electrons on nitrogen atoms. This interaction facilitates a combination of physisorption and chemisorption, where the carbon matrix stabilizes I₃⁻ by forming weak electrostatic and donor–acceptor interactions. The enhanced sorption capacity is attributed to electron-donating effects of surface nitrogen functionalities, which increase the affinity of the adsorbent toward electron-deficient species like I₃⁻ for BH and RH originated activated carbons.

Furthermore, the computational investigation aims to differentiate the selective affinity of Prussian Blue-modified surfaces for Cs⁺ over Sr²⁺, providing mechanistic insight into their interaction energies and electronic structure influences. This approach allows detailed interpretation of binding preferences and guides rational design of functionalized sorbents for radionuclide remediation in aqueous environments. Simulations were conducted using Density Functional Theory methods, for their reliability and accuracy [196]. Particularly, wB97XD method with def2-TZVP basis set were used. In order to decrease calculation time, convergence criteria were decreased to 10-6 and 10-4. In order to imitate aqueous solution Self-Consistent Reaction Field with SMD method was used.

To determine the favorability of absorption of reactions, thermodynamic calculations were performed. The leading indicator was Gibbs free energy, calculated at 25 °C and standard pressure. The calculation procedure is performed as illustrated by official Gaussian manual [197].

To simulate the intermolecular simulations of Prussian blue with cesium and strontium, Natural Energy Decomposition Analysis (NEDA) was used. Analysis was conducted using NBO 7.0 package as implemented in Gaussian 16. In order to perform the calculation, 1 Prussian blue molecule $[Fe_7(CN)_{24}]^{6-}$ and atoms of cesium and strontium were programmed. Figure 4.11 shows Cs⁺ uptake by Prussian Blue lattice.


Figure 4.11 - Mechanism of cesium interaction with Prussian Blue lattice

From Figure 4.11 the Cs⁺ are effectively captured by the Prussian Blue (PB) lattice through a combination of ion exchange, electrostatic attraction, and size selectivity. Within the PB framework, Cs⁺ can replaces loosely bound cations such as potassium (K⁺) located in the lattice cavities via ion exchange Eg.11. The negatively charged structure of PB exerts a strong electrostatic attraction toward Cs⁺, facilitating its stable incorporation. Additionally, the pore size of PB (~3.2 Å) is optimally suited to accommodate Cs⁺ ions, which have an ionic radius of approximately 1.67 Å, while excluding larger divalent or trivalent cations, thereby enhancing selective sorption. This multi-mechanistic interaction underpins PB's high affinity and selectivity for cesium in contaminated aqueous environments.

$$\operatorname{Fe}_{4}[\operatorname{Fe}(\operatorname{CN})_{6}]_{3} \cdot \mathrm{xH}_{2} O \cdot K^{+} + \operatorname{Cs}^{+} \cong \operatorname{Fe}_{4}[\operatorname{Fe}(\operatorname{CN})_{6}]_{3} \cdot \mathrm{xH}_{2} O \cdot \operatorname{Cs}^{+} + K^{+} \operatorname{Eg.11}_{2} O \cdot \operatorname{C$$

In previous studies, physisorption nature of absorption of cesium was established. Electrostatic interactions are predominant in the interactions between Prussian blue and cesium atoms [198]. In order to determine the consistency of this mechanism, same calculation with strontium is required, additionally showing difference between elements and their absorption. Calculation is performed with the same calculation settings as thermodynamics calculations. SCRF calculations were turned off, as number of water molecules were reportedly having direct effect on the NEDA results.

For the initial stage of the simulation (Table 25), the semi-empirical PM6 method was used to obtain the initial result [199] Thermodynamics results show general favorability of cesium over strontium, with a considerable difference (Table 24).

Model	Electronic energy + thermal free	Electronic energy + thermal free		
	energy correction, Hartree	energy correction, kJ/mol		
1	2	3		
Cs	0,012232	32,11512		
Sr	0,045982	120,7257		

Table 24 - Raw thermodynamic data from calculations

Continuation of Table 24

PB	4,983653	13084,58
PB	4,830306	12681,97
and Cs		
Pb and	4,932381	12949,97
Sr		

Table 25- Gibbs free energy of reactions.

Calculation	Gibbs free energy of reaction, kJ/mol
PB and Cs	-434,7276645
PB and Sr	-255,340377

Computational modeling confirms that Cs^+ forms a more (~268 kJ/mol) stable complex with Prussian Blue than Sr^{2+} , supporting its selective uptake. (Table 25).

Overall, physisorption is the main contributor of sorbtion process in case of I_3^- sorbtion with minor chemisorption involvement due to nitrogen containing groups. In case of Prussian Blue modified carbon sorbents main contributors in Cs⁺ - ferrocyanide lattice are ion-exchange, electrostatic attraction and chelating factor are main contributors which makes chemosorption predominant.

CONCLUSIONS

This work aimed to develop a technological protocol and biomass-based modified sorbents for the effective adsorption of cesium (Cs⁺) and tri-iodide (I₃⁻) radionuclides. Through a comprehensive examination of various activated carbon materials, including physically activated and chemically modified carbons, we established a systematic approach to sorbent development tailored for the removal of these radionuclides from aqueous solutions.

In the thesis, scientific approaches to developing modified sorbents based on activated carbon for the sorption of radionuclides of tri-iodide ions and cesium from an aqueous medium are developed. At the initial stage, comparative studies were conducted to identify the effects of various carbon carriers, including physically activated carbons (RH 800, BH 800 and WN800), chemically activated with potassium hydroxide (RH KOH, BH KOH and WN KOH) with the surface area in a range from 209 - 2192 m2/g and modified with urea and ferrocyanide groups of activated carbons (RH Urea KOH, BH Urea KOH, WN Urea KOH, RH KOH PB, BH KOH PB and WN KOH PB). The impregnation was carried out by a hydrothermal method that effectively introduces functional groups into the sorbent structure.

Investigation of the sorption of tri-iodide ions from an aqueous medium by modified sorbents yields the following results: impregnation of 1% of nitrogencontaining groups onto the surface of meso and macroporous activated carbons by hydrothermal analysis improves the sorption process by 33% in the case of activated carbons based on rice husk (RH KOH 847.9 mg/g and RH Urea KOH 1266.5 mg/g of tri-iodide ion) and 32% in the case of activated carbons based on buckwheat husks (HC KOH 787.5 mg/g and HC Urea KOH 1149.5 mg/g of tri-iodide ion). The impregnation of nitrogen-containing groups on the surface of activated carbon with a predominance of micropores has the opposite character and reduces the sorption capacity.

For the first time, the modified sorbents obtained in this work were tested on radioactive isotopes in the laboratory at UMSC (Poland), where RH Urea KOH was tested on radioactive 137Cs, where the maximum sorption capacity was 2.2 mmol/m2 at pH 10 with an initial concentration of 0.001 mol/dm3 and for the radioactive isotope 36Cl RH KOH 0.7 mmol/m2 at pH 3 with an initial concentration of 0.001 mol/dm3. Sorbents with embedded ferrocyanide groups were tested on real contaminated surface waters from the Degelen site of the Semipalatinsk test site, where unprecedented performance of more than 95% efficiency for RH KOH PB, WN KOH PB and BH KOH PB sorbents was achieved.

For the first time, modelling with Gaussian software for a characteristic sorbent was carried out based on the input data of FTIR and SEM EDX. An optimized structure was proposed, Gibbs energies for sorption products were calculated, and based on these data, the sorption mechanism and the contribution of physisorption, chemisorption, and static energy were proposed based on NADA calculations.

The future will be focused on assessing the reusability of modified sorbents through multiple adsorption-desorption cycles and evaluating their stability under radiation exposure to determine long-term viability for remediation. Expanding testing to a broader range of radionuclides and conducting field studies will validate effectiveness in real-world conditions. Additionally, optimizing functional group concentrations and further mechanistic studies using advanced techniques will enhance our understanding of adsorption processes. Finally, analyzing scalability and costeffectiveness will be crucial for practical applications in environmental remediation efforts targeting radioactive contaminants.

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APPENDIX A

Test reports



ФИЛИАЛ «ИНСТИТУТ РАДИАЦИОННОЙ БЕЗОПАСНОСТИ И ЭКОЛОГИИ» РГП «НАЦИОНАЛЬНЫЙ ЯДЕРНЫЙ ЦЕНТР РЕСПУБЛИКИ КАЗАХСТАН» 180010, Абай область, г. Курчатов, ул. Бейбіт атом, здание 2 е-маіl: irbe@nnc.kz, www.irse.nnc.kz

Тел: 8 (72251) 3-34-13

ПРОТОКОЛ ИСПЫТАНИЙ

№ 12-25/12-21-08/2285В от «20» августа 2024 г.

- 1. Наименование образца(ов) продукции: вода
- 2. Заказчик: Договор №0519 от 10.05.2024 г.
- 3. Номер заявки (№, дата): <u>21-08/2285</u> от «24» <u>июня</u> 20<u>24</u> г.
- 4. Вид испытаний: гамма-спектрометрическое определение радионуклидов

5. Дата получения образца(ов): «24» июня 2024 г.

6. Дата проведения испытаний: «25» июня - «11» июля 2024 г.

7. Обозначение НД на продукцию: Приказ МНЗ РК от 02 августа 2022 года № КР ДСМ-71

- 8. <u>Обозначение НД на метод: КZ 07.00.03126-2015</u>
- 9. Испытания проведены при: температуре 24°С и влажности не более 83%

10. Результаты испытаний:

№ п/п	Код пробы	Номер пробы	Шифр	Тип пробы	Точка отбора	Удельная активность ¹³⁷ Cs, Бк/кг
1	2	3	4	5	6	7
1.	1	176297-1	ДЕГ	вода	Шт.104	118 ± 24
2.	2	176297-2	ДЕГ	вода	Шт.104	110 ± 22
3.	3	176297-3	ДЕГ	вода	Шт.104	101 ± 20
4.	4	176297-4	ДЕГ	вода	Шт.104	106 ± 21
5.	5	176297-5	ДЕГ	вода	Шт.104	114 ± 23
6.	6	176297-6	ДЕГ	вода	Шт.104	110 ± 22
7.	7	176297-7	ДЕГ	вода	Шт.104	94 ± 19
8.	8	176297-8	ДЕГ	вода	Шт.104	95 ± 19
9.	9	176297-9	ДЕГ	вода	Шт.104	< 1
10.	10	176297-10	ДЕГ	вода	Шт.104	102 ± 20
11.	11	176297-11	ДЕГ	вода	Шт.104	< 2
12.	12	176297-12	ДЕГ	вода	Шт.104	102 ± 20
13.	13	176297-13	ДЕГ	вода	Шт.104	96 ± 19
14.	14	176297-14	ДЕГ	вода	Шт.104	103 ± 20
15.	15	176297-15	ДЕГ	вода	Шт.104	115 ± 23
16.	16	176297-16	ДЕГ	вода	Шт.104	118 ± 23
17.	17	176297-17	ДЕГ	вода	Шт.104	110 ± 22
18.	18.	176297-18	ДЕГ	вода	Шт.104	109 ± 22
19.	19	176297-19	ДЕГ	вода	Шт.104	14 ± 3
20.	20	176297-20	ДЕГ	вода	Шт.104	6 ± 1
21.	21	176297-21	ДЕГ	вода	Шт.104	115 ± 23
22.	22	176297-22	ДЕГ	вода	Шт.104	112 ± 22
23.	23	176297-23	ДЕГ	вода	Шт.104	101 ± 20
24.	24	176297-24	ДЕГ	вода	Шт.104	110 ± 22
25.	25	176297-25	ДЕГ	вода	Шт.104	100 ± 20
26.	26	176297-26	ДЕГ	вода	Шт.104	112 ± 22

Страница 1 из 1

№ п/п	Код пробы	Номер пробы	Шифр	Тип пробы	Точка отбора	Удельная активность ¹³⁷ Cs, Бк/кг
27.	27	176297-27	ДЕГ	вода	Шт.104	5 ± 1
28.	28	176297-28	ДЕГ	вода	Шт.104	4 ± 1



Примечание:

Результаты испытаний распространяются на образцы, подвергнутых испытаниям. Перепечатка настоящего протокола (полная или частичная) без ведома филиала запрещена.

Страница 2 из 1



ФИЛИАЛ «ИНСТИТУТ РАДИАЦИОННОЙ БЕЗОПАСНОСТИ И ЭКОЛОГИИ» РГП «НАЦИОНАЛЬНЫЙ ЯДЕРНЫЙ ЦЕНТР РЕСПУБЛИКИ КАЗАХСТАН»

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Тел: <u>8 (72251) 3-34-1</u>3

ПРОТОКОЛ ИСПЫТАНИЙ

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1. Наименование образца(ов) продукции: вода

2. Заказчик: Договор №0519 от 10.05.2024 г.

3. Номер заявки (№, дата): <u>21-08/2285</u> от «<u>24</u>» июня 20<u>24</u> г.

4. Вид испытаний: бета-спектрометрическое определение радионуклидов

5. Дата получения образца(ов): «02» августа 2024 г.

6. Дата проведения испытаний: «<u>03-12</u>» <u>августа</u> 20<u>24</u> г.

7. Обозначение НД на продукцию: Приказ МНЗ РК от 02 августа 2022 года № КР ДСМ-71

8. <u>Обозначение НД на метод: КZ.06.01.00449-2022</u>

9. Испытания проведены при: температуре 25°С и влажности не более 80%

10. Результаты испытаний:

№ п/п	Код пробы	Номер пробы	Шифр	Тип пробы	Точка отбора	Удельная активность ⁹⁰ Sr, Бк/кг
1	2	3	4	5	6	7
1.	1	176297-1	ДЕГ	вода	Шт.104	346 ± 52
2.	2	176297-2	ДЕГ	вода	Шт.104	310 ± 45
3.	3	176297-3	ДЕГ	вода	Шт.104	340 ± 50
4.	4	176297-4	ДЕГ	вода	Шт.104	330 ± 50
5.	5	176297-5	ДЕГ	вода	Шт.104	325 ± 48
6.	6	176297-6	ДЕГ	вода	Шт.104	355 ± 55
7.	7	176297-7	ДЕГ	вода	Шт.104	270 ± 40
8.	8	176297-8	ДЕГ	вода	Шт.104	310 ± 45
9.	9	176297-9	ДЕГ	вода	Шт.104	310 ± 45
10.	10	176297-10	ДЕГ	вода	Шт.104	$+365\pm55$
11.	11	176297-11	ДЕГ	вода	Шт.104	290 ± 45
12.	12	176297-12	ДЕГ	вода	Шт.104	230 ± 35
13.	13	176297-13	ДЕГ	вода	Шт.104	233 ± 35
14.	14	176297-14	ДЕГ	вода	Шт.104	290 ± 45
15.	15	176297-15	ДЕГ	вода	Шт.104	290 ± 45
16.	16	176297-16	ДЕГ	вода	Шт.104	265 ± 40
17.	17	176297-17	ДЕГ	вода	Шт.104	305 ± 45
18.	· 18	176297-18	ДЕГ	вода	Шт.104	340 ± 50
19.	19	176297-19	ДЕГ	вода	Шт.104	395 ± 55
20.	20	176297-20	ДЕГ	вода	Шт.104	370 ± 48
21.	21	176297-21	ДЕГ	вода	Шт.104	340 ± 60
22.	22	176297-22	ДЕГ	вода	Шт.104	380 ± 40
23.	23	176297-23	ДЕГ	вода	Шт.104	310 ± 45
24.	24	176297-24	ДЕГ	вода	Шт.104	360 ± 55
25.	25	176297-25	ДЕГ	вода	Шт.104	400 ± 60
26.	26	176297-26	ДЕГ	вода	Шт.104	390 ± 55

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