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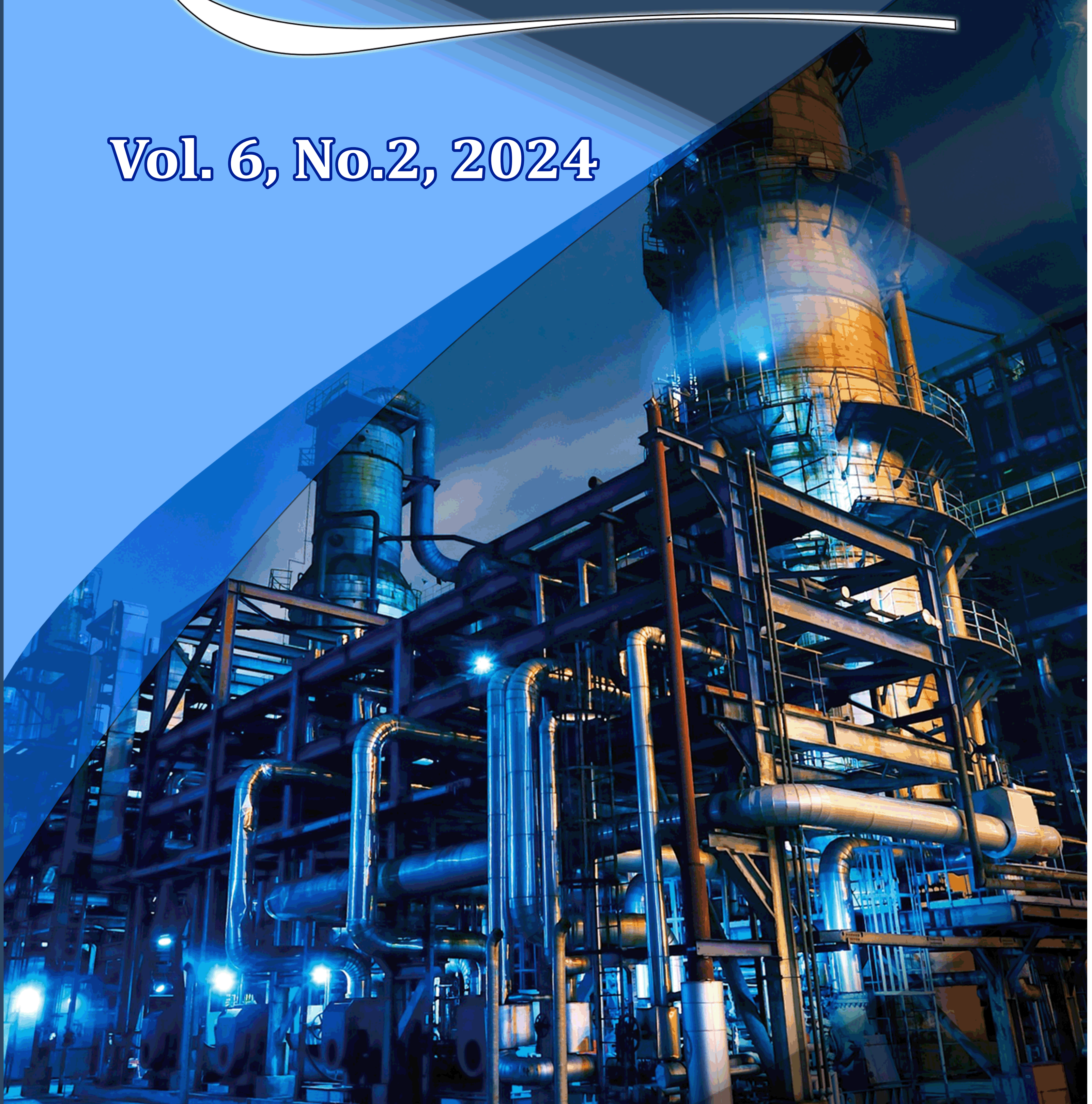

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CONTENT

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GAMMA RADIATION EFFECTS ON THE pH OF 1,2,4-TRICHLOROBENZENE IN DIVERSE SOLVENT SYSTEMS

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The radiolytic degradation of 1,2,4-trichlorobenzene (TCB) in various organic solventsmethanol (MeOH), ethanol (EtOH), isopropanol (iPrOH), hexane, benzene, and toluene was investigated by monitoring pH changes at different absorbed radiation doses (0 to 288.6 kGy). A consistent decrease in pH across all solvent systems was observed, indicating the formation of acidic by-products such as hydrochloric acid (HCl) as a result of TCB dechlorination. The extent of pH change was more pronounced in polar solvents (MeOH, EtOH, iPrOH) compared to non-polar (hexane) and aromatic solvents (benzene, toluene), suggesting that solvent polarity plays a crucial role in influencing radiolytic degradation pathways. Oxygenated by-products, including phenols and chlorinated biphenyl's, were identified in aromatic solvents, while alcohol-based solvents promoted more acidic by-products. These findings enhance the understanding of solvent effects on the radiolytic degradation of persistent organic pollutants (POPs) and support the potential of gamma irradiation for environmental remediation applications.

***Keywords**:trichlorobenzene, gamma irradiation, nuclear chemistry, pH, dechlorination, environmental remediation.*

INTRODUCTION

POPs, such as hexachlorobenzene, hexachlorocyclohexane, DDT, and DDE, pose significant environmental and health risks due to their stability and resistance to degradation [1]. POPs are known for their persistence in the environment, bioaccumulative potential, and toxicity to humans and wildlife [2]. Due to their carcinogenic properties, these pesticides have been listed in the POPs list of the Stockholm Convention, to which Azerbaijan is a member [3]. The degradation of POPs in different environmental contexts has been of great interest to scientists aiming to purify water, protect food chains, and safeguard ecosystems [4]. Various purification methods have been explored to find optimal approaches in terms of cost-effectiveness and environmental sustainability, but each method presents its own limitations [5].

Traditional methods for degrading POPs, such as chemical degradation and bioremediation, often struggle with the recalcitrant nature of these compounds [6, 7]. Chemical degradation, which uses strong oxidizing or reductive agents, can be effective but typically requires harsh conditions and may produce harmful secondary pollutants [8]. Bioremediation, though more environmentally friendly and cost-effective, relies on microorganisms to break down pollutants. This method is often limited by the bioavailability of POPs and the adaptability of microbes to the polluted environment. Additionally, certain POPs are highly resistant to microbial degradation [9].

To overcome these limitations, alternative methods, such as advanced oxidation processes (AOPs) and gamma irradiation, have been explored [10, 11, 12]. AOPs, which involve the generation of highly reactive species like hydroxyl radicals (•OH), can non-selectively oxidize and degrade organic pollutants [13]. Fenton's reagent, photocatalysis, ozonation, and sonolysis are examples of AOPs, each offering unique advantages but requiring specific conditions such as light, catalysts, or ultrasonic waves [14, 15, 16, 17]. While AOPs have been widely applied to the degradation of POPs, they are typically water-based processes and their efficiency may be hindered by the solubility of pollutants in water.

Gamma irradiation, on the other hand, has emerged as a highly promising technique for the degradation of POPs [11, 12, 18, 19, 20]. It generates reactive species, including hydroxyl radicals, solvated electrons, and hydrogen atoms, which trigger a series of radiolytic reactions leading to the breakdown of complex organic molecules [21, 22]. The efficiency of gamma irradiation depends on several factors, such as the absorbed radiation dose, the type of solvent, and the nature of the pollutant [23]. Previous studies have shown that gamma irradiation can effectively degrade chlorinated organic compounds, but little attention has been paid to the impact of irradiation on the pH of pollutant-solvent systems. Understanding these pH changes can shed light on the formation of radiolytic by-products, such as acidic or basic species, which may play a role in the degradation pathways.

This study aims to investigate the effect of absorbed radiation dose on the pH of TCB (Fig.1) in various organic solvents. TCB was chosen for this study due to its structural similarity to chlorinated POPs, providing insights into the radiolytic degradation pathways relevant to POP remediation. By examining how the pH changes with increasing doses of gamma radiation, we seek to better understand the radiolytic degradation mechanisms of TCB in different solvent environments. These insights are critical for optimizing gamma irradiation as a remediation technique for POPs, particularly in designing efficient processes that minimize toxic by-products and ensure the complete breakdown of hazardous compounds.

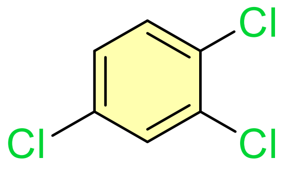


Fig.1. Chemical structure of 1,2,4-TCB

Six organic solvents (MeOH, EtOH, iPrOH, hexane, benzene, and toluene) were selected to investigate their role in the radiolytic degradation of TCB. These solvents differ in their polarity and dielectric constants, as detailed in table 1.The differences in these properties allow for a comprehensive understanding of how solvent environments influence the radiolytic degradation process. Polar solvents are expected to promote faster pH changes due to their ability to stabilize reactive intermediates, while non-polar and aromatic solvents may exhibit different degradation behaviors.

The radiolytic degradation of TCB in different solvent environments provides an opportunity to explore the relationship between solvent properties and degradation efficiency, offering insights into the optimization of gamma irradiation for environmental remediation.

EXPERIMENTAL PART

The methods applied in this study are consistent with those reported in previous research [11].

Standard solutions of TCB were prepared in MeOH, EtOH, iPr-OH, hexane, benzene, and toluene, with concentrations ranging from 1.4 g/L to 2.0 g/L. Each solution was subjected to gamma irradiation using a cobalt-60 source, with radiation doses ranging from 0 to 288.6 kGy. To monitor changes in the pH of these solutions throughout the irradiation process, pH measurements were conducted at specific dose intervals.

To ensure that dissolvable compounds, such as chloride ions (Cl^-) or other compounds that could affect the pH of the system, were properly transferred into the aqueous phase, 1 µL from each irradiated sample was mixed with 9999.9 µL of distilled water. This step was necessary because pH measurements are only valid in aqueous solutions. The mixture allowed the radiolytic by-products that could influence the pH to dissolve into the water phase for accurate measurement.

After obtaining the pH of the diluted solution (d.), the original pH (or.) of the non-dissolved solution was calculated using the following approach. The pH represents the concentration of hydrogen ions [H^+], which is related to pH by the equation (I):

$$pH = -log\,[H^+] \qquad \text{(I)}$$

For a diluted solution, the [H^+] concentration changes according to the dilution factor (DF). Since the sample was diluted by a factor of 10,000, the hydrogen ion concentration in the original solution was calculated as (II):

$$[H^+]or. = [H^+]d. \times DF \qquad \text{(II)}$$
$$[H^+]or. = [H^+]d. \times 10^4$$

Where [H^+]diluted was derived from the measured pH (m.) (III):

$$[H^+]d. = 10^{-pH}\,(m.) \qquad \text{(III)}$$

Finally, the pH of the original solution was obtained using the formula (IV):

$$pH\,(or.) = -log\,[H^+]or. \qquad \text{(IV)}$$

This process allowed for the accurate determination of the original pH of the non-dissolved organic solution, reflecting the influence of radiolytic by-products after irradiation.

A Hanna Instruments EDGE pH/ORP meter (HI2002-02) equipped with a glass-body, refillable combination pH electrode (HI11310) was used for all pH measurements during the study. This electrode is specifically designed for general laboratory use and features a broad pH measurement range from 0 to 14, with a temperature range of -5°C to 100°C, making it suitable for accurately monitoring pH in a variety of organic solvents. The electrode's double-junction system prevents contamination of the reference cell, ensuring stable and precise readings even in chemically aggressive or non-aqueous solutions.

In addition, the HI11310 electrode is equipped with an integrated temperature sensor, allowing for automatic temperature compensation, which improves measurement accuracy under varying temperature conditions. Calibration was performed using up to five points with standard buffer solutions (pH 4.01, 7.01, and 10.01) to ensure precision throughout the experiments. The electrode also features data storage capabilities, reducing the need for recalibration between uses. This setup was crucial in ensuring reliable pH monitoring under the various conditions tested in this experiment.

To validate the accuracy of the pH measurements, a calibration curve (fiq.2) was generated using standard buffer solutions with known pH values. The actual pH values (4.01, 7.01, and 10.01) were compared to the pH values measured by the electrode. Minimal deviations were observed, with differences of approximately ±0.01, ensuring the pH measurements during the experiments were within acceptable accuracy limits. The calibration curve helped to confirm the reliability of the pH meter for the duration of the study.

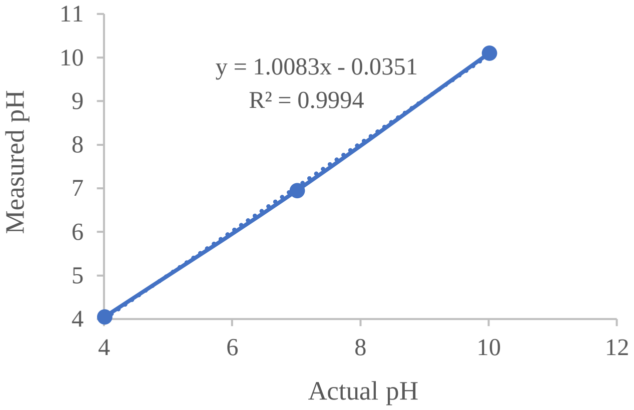


Fig.2. Calibration curve showing the relationship between actual pH values and measured pH values using standard buffer solutions

RESULTS AND DISCUSSION

The effect of gamma irradiation on the pH of TCB solutions in various organic solvents was evaluated at specific dose intervals. The pH changes over these doses are illustrated in fiqure3.

pH change in polar solvents

A rapid decrease in pH was observed for TCB in MeOH, EtOH, and iPr-OH as the irradiation dose increased, as shown in the first graph in figure 3. In MeOH, the pH dropped sharply from an initial value of 3.51 to 1.67 by 48.1 kGy and continued decreasing slightly, stabilizing at 1.08 at 288.6 kGy. Similarly, in EtOH, the pH decreased from 3.3 to 1.31 by 48.1 kGy, reaching its lowest value of -0.05 at the highest dose of 288.6 kGy. In iPr-OH, the pH also exhibited a marked decrease, dropping from 3.31 to 1.62 by 48.1 kGy and stabilizing around 0.17 at 288.6 kGy.

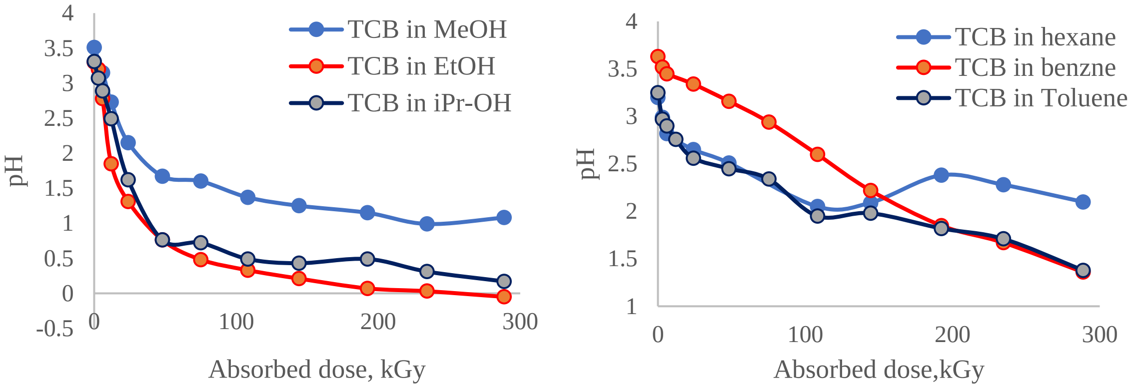


Fig.3. pH changes of TCB solutions in different solvents as a function of absorbed dose.

The decrease in pH in these polar solvents suggests the formation of acidic by-products, likely due to the dechlorination of TCB, as well as the production of other radiolytic products. The sharp pH decline indicates that these solvents facilitate the formation of reactive intermediates, such as solvated electrons and hydrogen radicals, which accelerate the breakdown of TCB and enhance the production of acidic compounds like HCl.

pH change in low polar solvents

In low polar and aromatic solvents, as shown in the second graph, the pH changes were more moderate compared to polar solvents. In hexane, the pH dropped from an initial value of 3.2 to 2.51 by 48.1 kGy, stabilizing around 2.1 at 288.6 kGy. In benzene, the pH decreased from 3.63 to 3.16 by 48.1 kGy, with a more significant decrease to 1.36 at 288.6 kGy. Toluene followed a similar pattern, with the pH decreasing from 3.25 to 1.38 at the highest dose.

In hexane, benzene, and toluene, the formation of less reactive by-products leads to a more gradual pH decline. The lower ability of these solvents to stabilize reactive intermediates, compared to polar solvents, results in slower dechlorination of TCB and the formation of fewer acidic products. This moderate pH change is reflective of the solvent's lower polarity and limited capacity to stabilize radiolytic intermediates, which affects the overall extent of TCB degradation and the formation of by-products like HCl.

Significant pH decreases were observed in polar solvents. This can be attributed to their ability to stabilize reactive species, including solvated electrons and hydrogen radicals, generated during gamma irradiation. These reactive intermediates are more efficiently stabilized in polar solvents, leading to enhanced dechlorination and more rapid degradation of TCB. In contrast, non-polar exhibited more moderate pH changes, likely due to their lower capacity to stabilize these reactive intermediates. The solvent properties, as outlined in table 1, play a crucial role in determining the extent of radiolytic degradation and the formation of acidic by-products.

Influence of Solvent Properties on Radiolytic Degradation

The variation in pH changes observed across the different solvents can be attributed to their inherent physical properties (table1**).** These properties, including polarity index and dielectric constant, directly influence the stabilization of reactive species during gamma irradiation, ultimately impacting the efficiency of the radiolytic degradation process.

Table 1

Properties of the selected solvents

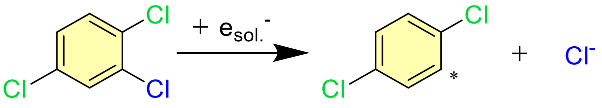
Solvent	Polarity Index [24]	Dielectric Constant [25]
MeOH	5.1	32.7
EtOH	4.3	24.3
iPrOH	3.9	18.3
Hexane	0.1	1.89
Benzene	2.3	2.28
Toluene	2.4	2.38

The solvents MeOH, EtOH, iPrOH, hexane, benzene, and toluene vary in polarity and dielectric constant. These properties directly influence TCB degradation and pH changes during gamma irradiation. MeOH and EtOH, which have higher polarity indices and dielectric constants, are more efficient in stabilizing reactive species, such as solvated electrons and hydrogen radicals. This leads to more extensive dechlorination and larger decreases in pH. iPrOH, while still polar, exhibits a slightly lower dielectric constant and polarity index compared to MeOH and EtOH, resulting in less efficient stabilization of reactive species and a more moderate decrease in pH. In contrast, non-polar solvents like hexane and aromatic solvents like benzene show less pronounced pH changes, likely due to their lower ability to stabilize reactive intermediates. These differences underscore the importance of solvent properties in influencing radiolytic degradation and optimizing gamma irradiation processes for effective POP remediation.

Mechanism of the Process

The degradation of TCB under gamma irradiation is driven by the formation of reactive species such as solvated electrons ($e^-_{sol.}$) and hydrogen radicals (H*), which attack the chlorinated carbons in TCB [11]. The following mechanism explains the formation of Cl^- ions, HCl, and various by-products:

1. Dechlorination of TCB:



This reaction produces a chlorinated radical and Cl^-, which, in the presence of hydrogen radicals (H^*) or proton (H^+), forms HCl, contributing to the pH decrease.

1.Formation of HCl:

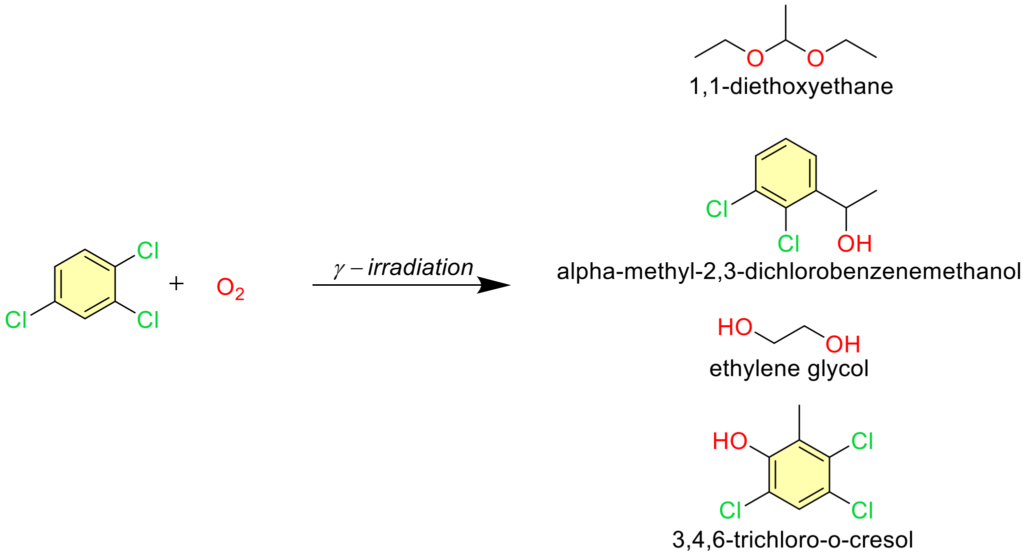
$$Cl^- + H^* \longrightarrow HCl + e^-$$

$$Cl^- + H^+ \longrightarrow HCl$$

The formation of HCl is a key factor in the sharp pH declines observed in polar solvents.

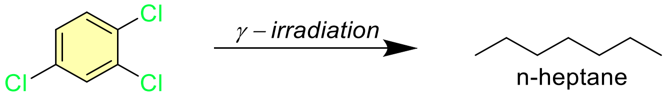
2. Formation of Oxygenated By-products:

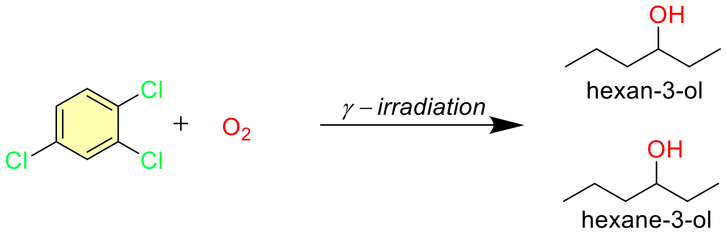
Oxygenated radicals in polar solvents lead to various by-products. 1,1-diethoxyethane and alpha-methyl-2,3-dichlorobenzenemethanol were identified in EtOH, while ethylene glycol and 3,4,6-trichloro-o-cresol were observed in MeOH, contributing to further pH decreases. The possible conversion pathway, combined for both systems, is shown below:



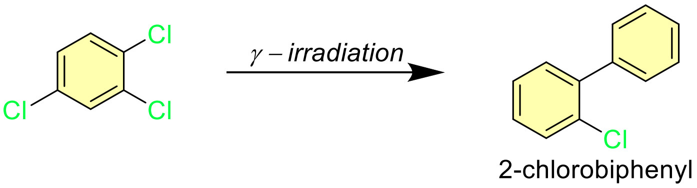
3. By-products in Hexane and aromatic solvents:

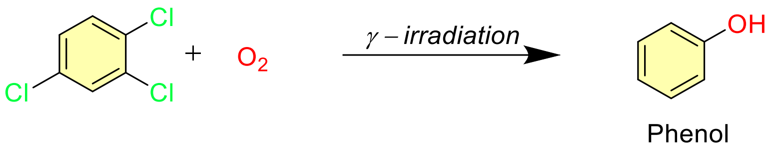
In hexane, the slower production of HCl and oxygenated by-products like hexan-2-one, hexan-3-ol, and n-heptane contribute to the moderate pH changes observed.





In aromatic solvents like benzene and toluene, oxygenated compounds such as phenol and 2-chlorobiphenyl are formed, impacting the pH throughout irradiation.





RESULTS AND DISCUSSION

The data indicate a consistent trend of decreasing pH with increasing radiation dose across all TCB-solvent systems, reflecting the formation of acidic by-products during radiolytic degradation. The variation in pH changes across solvents demonstrates the influence of the solvent's chemical environment on degradation pathways and by-product stability.

The observed pH decreases are primarily attributed to the formation of HCl and other acidic organic compounds. In polar solvents, the hydroxyl groups enhance the generation of reactive species, leading to a more pronounced formation of acidic by-products:

- **MeOH**: The pH drops significantly, indicating a robust formation of acidic by-products, with the sharpest decrease in pH observed early in the irradiation process, stabilizing around lower values at higher doses.
- **EtOH**: Similar to MeOH, EtOH shows rapid pH decreases, reaching low values at the highest radiation doses, indicating substantial degradation and acid formation.
- **iPrOH**: The pH decline is less severe than in MeOH and EtOH, indicating slightly lower efficiency in generating acidic by-products, although a clear downward trend is present.
- **Hexane**: The moderate pH change is likely due to its non-polar nature, which limits the formation of reactive species and acidic products, with stabilization observed at higher doses.
- **Benzene and Toluene**: Both solvents exhibit similar pH trends, influenced by their aromatic nature, which leads to the formation of oxygenated by-products rather than significant production of acidic species like in alcohols. The pH decrease is more gradual, reflecting less efficient degradation and acid formation compared to polar solvents.

In polar solvents significant pH decreases are linked to their ability to stabilize reactive species generated during gamma irradiation. Their high polarity and dielectric constants enhance the stabilization of reactive intermediates, such as solvated electrons and hydrogen radicals, promoting more efficient dechlorination and degradation of TCB. As a result, these solvents exhibit larger pH reductions compared to non-polar solvents.

Non-polar solvents exhibited more moderate pH changes. Their lower polarity and dielectric constants reduce the formation and stabilization of reactive intermediates, leading to slower degradation processes and smaller pH changes. These findings highlight the importance of solvent selection in optimizing gamma irradiation for the degradation of POPs.

These results underscore the importance of solvent polarity and structure in determining the radiolytic degradation pathways and the formation of by-products.

CONCLUSION

The gamma irradiation of TCB in various organic solvents, including MeOH, EtOH, iPrOH, hexane, benzene, and toluene, demonstrated a consistent decrease in pH with increasing absorbed doses. This pH reduction is indicative of the formation of acidic by-products, particularly HCl, due to the dechlorination of TCB. The rate and extent of pH change varied significantly between solvents, with polar solvents showing sharper pH drops compared to non-polar solvents.

The results suggest that solvent polarity and molecular structure play crucial roles in influencing the radiolytic degradation pathways and the stability of the resulting by-products. Polar solvents, which stabilize reactive radiolytic species more effectively, facilitated more efficient formation of acidic by-products, leading to greater pH reductions. In contrast, aromatic solvents like benzene and toluene, while showing pH decreases, primarily led to the formation of oxygenated by-products such as phenols and methylated benzenes, rather than a significant buildup of acidic species.

This study provides valuable insights into the radiolytic degradation of POPs in organic solvent systems, highlighting the importance of solvent selection in optimizing gamma irradiation processes for environmental remediation. The findings contribute to the development of more effective gamma irradiation-based technologies for the degradation of hazardous organic compounds.

REFERENCES

1. Guo, W., Pan, B., Sakkiah, S., Yavas, G., Ge, W., Zou, W., Tong, W., & Hong, H. (2019). Persistent organic pollutants in food: contamination sources, health effects and detection methods. International Journal of Environmental Research and Public Health, 16(22), pp. 4361. https://doi.org/10.3390/ijerph16224361
2. Sharma, B. M., Bharat, G. K., Tayal, S., Nizzetto, L., Cupr, P., & Larssen, T. (2014). Environment and human exposure to persistent organic pollutants (POPs) in India: A systematic review of recent and historical data. Environment International, 66, pp. 48–64. https://doi.org/10.1016/j.envint.2014.01.022
3. Sheriff, I., Debela, S. A., & Mans-Davies, A. (2022). The listing of new persistent organic pollutants in the stockholm convention: Its burden on developing countries. Environmental Science & Policy, 130, pp. 9 https://doi.org/10.1016/j.envsci.2022.01.005
4. Zacharia, J. T. (2019). Degradation pathways of persistent organic pollutants (POPs) in the environment. In IntechOpen eBooks. pp. 79645 https://doi.org/10.5772/intechopen
5. Devendrapandi, G., Liu, X., Balu, R., Ayyamperumal, R., Arasu, M. V., Lavanya, M., Reddy, V. R. M., Kim, W. K., & Karthika, P. (2024). Innovative remediation strategies for persistent organic pollutants in soil and water: A comprehensive review. Environmental Research. pp. 118404.https://doi.org/10.1016/j.envres.2024.118404
6. Ruomeng, B., Meihao, O., Siru, Z., Shichen, G., Yixian, Z., Junhong, C., Ruijie, M., Yuan, L., Gezhi, X., Xingyu, C., Shiyi, Z., Aihui, Z., & Baishan, F. (2023b). Degradation strategies of pesticide residue: From chemicals to synthetic biology. Synthetic and Systems Biotechnology, 8(2), pp. 302313 https://doi.org/10.1016/j.synbio.2023.03.005

7. Swathy, K., Vivekanandhan, P., Yuvaraj, A., Sarayut, P., Kim, J. S., & Krutmuang, P. (2024). Biodegradation of pesticide in agricultural soil employing entomopathogenic fungi: Current state of the art and future perspectives. Heliyon, 10(1), e23406. https://doi.org/10.1016/j.heliyon.2023.e23406
8. Kumari, P., & Kumar, A. (2023). ADVANCED OXIDATION PROCESS: A remediation technique for organic and non-biodegradable pollutant. Results in Surfaces and Interfaces, 11, 100122. https://doi.org/10.1016/j.rsurfi.2023.100122
9. Ayilara, M. S., & Babalola, O. O. (2023). Bioremediation of environmental wastes: the role of microorganisms. Frontiers in Agronomy, 5. https://doi.org/10.3389/fagro.2023.1183691
10. Deng, Y., & Zhao, R. (2015). Advanced Oxidation Processes (AOPs) in wastewater treatment. Current Pollution Reports, 1(3), pp. 167–176. https://doi.org/10.1007/s40726-015-0015-z
11. Karimov, S., Abdullayev, E., Millet, M., & Gurbanov, M. (2024). Radiolytic degradation of 1,2,4-trichlorobenzene (TCB) in some organic solvents by gamma rays: The kinetic properties of complete dechlorination of TCB and its pathway. *Heliyon*, *10*(10), e31547. https://doi.org/10.1016/j.heliyon.2024.e31547
12. Iskenderova, Z. I., & Gurbanov, M. A. (2018). Radiation chemical degradation of 1,2,4-trichlorobenzene in aqueous media. Chemical Safety, *2(*2(4)), pp. 112–118. https://doi.org/10.25514/chs.2018.2.14108
13. Khan, Z. U. H., Gul, N. S., Sabahat, S., Sun, J., Tahir, K., Shah, N. S., Muhammad, N., Rahim, A., Imran, M., Iqbal, J., Khan, T. M., Khasim, S., Farooq, U., & Wu, J. (2023). Removal of organic pollutants through hydroxyl radical-based advanced oxidation processes. Ecotoxicology and Environmental Safety, 267, 115564. https://doi.org/10.1016/j.ecoenv.2023.115564
14. Tagg, A. S., Harrison, J. P., Ju-Nam, Y., Sapp, M., Bradley, E. L., Sinclair, C. J., & Ojeda, J. J. (2016). Fenton's reagent for the rapid and efficient isolation of microplastics from wastewater. Chemical Communications, 53(2), pp. 372–375. https://doi.org/10.1039/c6cc08798a
15. Ahmad, K., Ghatak, H. R., & Ahuja, S. (2020). A review on photocatalytic remediation of environmental pollutants and H2 production through water splitting: A sustainable approach. Environmental Technology & Innovation, 19, 100893. https://doi.org/10.1016/j.eti.2020.100893
16. Aidoo, O. F., Osei-Owusu, J., Chia, S. Y., Dofuor, A. K., Antwi-Agyakwa, A. K., Okyere, H., Gyan, M., Edusei, G., Ninsin, K. D., Duker, R. Q., Siddiqui, S. A., & Borgemeister, C. (2023). Remediation of pesticide residues using ozone: A comprehensive overview. The Science of the Total Environment, 894, 164933. https://doi.org/10.1016/j.scitotenv.2023.164933
17. Divine, C., March, L., Kalra, S. S., & Hurst, J. (2023). Sonolysis and Super critical water oxidation (SCWO): development maturity and potential for destroying PFAS. Groundwater Monitoring & Remediation, 43(4), pp. 18–33. https://doi.org/10.1111/gwmr.12619
18. Aidoo, O. F., Osei-Owusu, J., Chia, S. Y., Dofuor, A. K., Antwi-Agyakwa, A. K., Okyere, H., Gyan, M., Edusei, G., Ninsin, K. D., Duker, R. Q., Siddiqui, S. A., & Borgemeister, C. (2023). Remediation of pesticide residues using ozone: A comprehensive overview. The Science of the Total Environment, 894, 164933. https://doi.org/10.1016/j.scitotenv.2023.164933

19. Egerić, M., Matović, L., Savić, M., Stanković, S., Wu, Y., Li, F., & Vujasin, R. (2024). Gamma irradiation induced degradation of organic pollutants: Recent advances and future perspective. Chemosphere, 352, 141437. https://doi.org/10.1016/j.chemosphere.2024.141437
20. Trojanowicz, M. (2020). Removal of persistent organic pollutants (POPs) from waters and wastewaters by the use of ionizing radiation. The Science of the Total Environment, 718, 134425. https://doi.org/10.1016/j.scitotenv.2019.134425
21. González-López, L., Kearney, L., Janke, C. J., Wishart, J., Kanbargi, N., & Al-Sheikhly, M. (2022). On the Mechanism of the Steady-State Gamma Radiolysis-Induced Scissions of the Phenyl-Vinyl Polyester-Based Resins. Frontiers in Chemistry, 9. https://doi.org/10.3389/fchem.2021.803347
22. LaVerne, J. A. (2000). OH radicals and oxidizing products in the gamma radiolysis of water. Radiation Research, 153(2), pp. 196–200 https://doi.org/10.1667/0033-7587(2000)153
23. Getoff, N. (2002). Factors influencing the efficiency of radiation-induced degradation of water pollutants. Radiation Physics and Chemistry, 65(4–5), pp. 437–446. https://doi.org/10.1016/s0969-806x(02)00342-0
24. Polarity Index. (n.d.). https://macro.lsu.edu/howto/solvents/Polarity%20index.htm
25. Dielectric Constant. (n.d.). UW Hompage.https://depts.washington.edu/eooptic/linkfiles/dielectric_chart%5B1%5D.pdf

ВЛИЯНИЕ ПОГЛОЩЁННОЙ ДОЗЫ РАДИАЦИИ НА pH ТХБ В РАЗЛИЧНЫХ ОРГАНИЧЕСКИХ РАСТВОРИТЕЛЯХ

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Радиолитическое разложение 1,2,4-трихлорбензола (ТХБ) в различных органических растворителях — метанол (MeOH), этанол (EtOH), изопропанол (iPrOH), гексан, бензол и толуол — изучалось путем мониторинга изменений pH при различных поглощённых дозах до 288,6 кГр. Во всех системах растворителей наблюдалось последовательное снижение pH, указывающее на образование кислых побочных продуктов, таких как соляная кислота (HCl), в результате дехлорирования ТХБ. Степень изменения pH была более выраженной в полярных растворителях (MeOH, EtOH, iPrOH) по сравнению с неполярными (гексан) и ароматическими растворителями (бензол, толуол), что указывает на ключевую роль полярности растворителя в радиолитических путях разложения. В ароматических растворителях были идентифицированы кислородсодержащие побочные продукты, включая фенолы и хлорированные бензолы, в то время как спиртовые растворители способствовали образованию более кислых побочных продуктов. Эти выводы способствуют лучшему пониманию влияния растворителей на радиолитическое разложение стойких органических загрязнителей и подтверждают потенциал применения гамма-облучения для целей экологической ремедиации.

Ключевые слова: *трихлорбензол, гамма-облучение, ядерная химия, pH, дехлорирование, экологическая ремедиация.*

1,2,4-TRXİLORBENZOL + HƏLLEDİCİ SİSTEMLƏRİN pH GÖSTƏRİCİSNƏ QAMMA ŞÜALANMANIN TƏSİRİ

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1,2,4-trixlorobenzolun (TXB) müxtəlif üzvi həlledicilərdə – metanol (MeOH), etanol (EtOH), izopropanol (iPrOH), heksan, benzol və toluol – radiolitik parçalanması müxtəlif udulma dozalarında (0-288,6 kGy) pH dəyişikliyini müşahidə etməklə tədqiq edilmişdir. Bütün həlledici sistemlərdə pH-ın ardıcıl olaraq azalması müşahidə olunmuşdur, bu isə TXB-nin dexlorlaşması nəticəsində xlorid turşusu (HCl) və digər turşu xarakterli məhsulların əmələ gəldiyini göstərir. pH-ın dəyişmə intensivliyi polyar həlledicilərdə (MeOH, EtOH, iPrOH) qeyri-polyar (heksan) və aromatik həlledicilərə (benzol, toluol) nisbətən daha çox olmuşdur, bu isə həlledicinin polyarlığının radiolitik parçalanma mexanizminə əhəmiyyətli təsir etdiyini göstərir. Aromatik həlledicilərdə fenollar kimi oksigenli məhsullar identifikasiya edilmiş və spirt əsaslı həlledicilərlə müqayisədə daha az turşu məhsullarının əmələ gəldiyi müəyyən edilmişdir. Bu nəticələr üzvi həlledicilərin radiolitik parçalanmaya təsirini daha yaxşı anlamağa kömək edir və qamma şüalanma metodunun ətraf mühitin təmizlənməsi proseslərində potensial tətbiqini stimullaşdırır.

Açar sözlər: *trixlorbenzol, qamma şüalanma, nüvə kimyası, pH, dexlorlaşma, ətraf mühit.*

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COMPOSITION, STRUCTURE AND APPLICATION OF OIL METALLOPORPHYRINS (Review)

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This review covers an analysis of published scientific papers in the field of metalporphyrins contained in natural raw material-oil. Existing methods of identification and methods for determining the content of metalporphyrins in oils are considered. Methods for the extraction of porphrins from residual oils were analyzed. The most interesting directions of using oil metalporphyrins in the synthesis of new chemical systems have been presented.

Much attention is paid to the consideration of possibilities of using of metalporphyrins as ingridients in catalysis, preparation of medical preparations for the diagnosis and treatment of various diseases and the creation of new composite materials based on polymers, the production of inorganic-organic hybrid materials wirh valuable properties.

Keywords: *oil porphyrins, identification methods, content of porphyrin compounds in oil fractions, application, metalporphyrin catalysts, new composite materials.*

1. Composition and properties of heavy and high-viscosity oil

The majority reserves of heavy and highly viscous oil make up for about 80% of the world's oil resources. At the same time, due to the development of fields of light and medium oils and the growing consumption of oil and petroleum products, the share of high-viscosity heavy oils involved in processing will inevitably increase [1, 2].

The operation of these oil wells is complicated by the deposition of asphalt, resin, and paraffin components on the walls of pipelines. In oil field practice, the term “asphalt, resin, paraffin deposits” is understood [3] as part of the mass of asphalt, resin, and paraffin oils(APRO) that is released from them under the influence of external factors and is sorbed (deposited) on the surface of pipes, equipment, and oil-saturated rocks.

ARPO is not a simple mixture of asphaltenes, resins and paraffins, but is a complex structured system with a pronounced core of asphaltenes and a sorption-solvation layer of petroleum resins [4].

It has been revealed [5] that asphalt-resin substances (ARS) are heterocyclic compounds of a complex hybrid structure, which include nitrogen, sulfur, oxygen and metals. Up to 98% of DIAs are aromatic and naphthenic structures [5, 6]. According to the author [4], the framework of the structure of resin and asphaltenes molecules forms a hydrocarbon skeleton, constituting 70-90% of the total weight of the molecules. It was revealed that in the series hydrocarbons-resins-asphaltenes there is a gradual tendency towards depletion in hydrogen and enrichment in carbon; the proportion of aromatic elements of the structure increases, and the degree of their condensation increases; the proportion of carbon atoms in the peripheral part decreases; the specific gravity of atoms in the central core of molecules increases - a polynuclear structure with a strong predominance of aromatic rings.

The term “paraffins” includes the entire hydrocarbon part of the deposits, but n-paraffins predominate [7], and in smaller quantities it contains naphthenic (cycloalkane) and aromatic hydrocarbons with long alkyl chains [8, 9].

The resins that make up ARPO are semi-liquid, sometimes semi-solid, dark brown or black substances. The relative density of resins is from 0.99 to 1.08 g/cm^3 their molecular weight can reach 1200 [10]. It has been established [4], that on average resins contain up to 15-17% oxygen, sulfur, and nitrogen. As the molecular weight of resins increases, the content of oxygen, sulfur and nitrogen decreases. The basis of the structure of resin molecules is flat a condensed polycarbocyclic network consisting predominantly of benzene rings. This structural network may contain naphthenic and heterocyclic rings (five and six-membered). The peripheral part of the condensed paraffin resin system is replaced by hydrocarbon radicals (aliphatic, cyclic and mixed). The nature and amount of these substituents strongly depends on the properties of the oil. Substituents may include functional groups (-OH, -SH, -NH$_2$, =CO, etc.). When heated to 260-350°C, the resins begin to compact and turn into asphaltenes [6].

Asphaltenes are polycyclic aromatic highly condensed structures with short aliphatic chains in the form of dark brown amorphous powders. The density of asphaltenes is slightly greater than unity. Asphaltenes contain 80-86% carbon, 7-9% hydrogen, up to 9% sulfur and oxygen, and up to 1.5% nitrogen. Asphaltenes do not crystallize and cannot be separated into individual components or narrow fractions. When heated above 300-400 ºC, they do not melt, but decompose, forming carbon and volatile products. Asphaltenes are the heaviest and polar components of oil and are prone to association [11], their particles are polydisperse and therefore the molecular weight can range from 2000 to 4000 amu. [10]. Asphaltenes are considered as resin compaction products. An asphaltene particle is a “micelle”, the core of which consists of high-molecular polycyclic condensed compounds of a predominantly aromatic nature, and the adsorption layer is formed by low-molecular surface-active compounds, including resins and naphthenic acids, which, together with the aliphatic components of oil, form the solvation shell of the micelle [5].

The amount of metal in crude oil typically varies from a few ppm to 1000 ppm. The metals found are sodium, potassium, lithium, calcium, strontium, copper, silver, vanadium, manganese, tin, lead, cobalt, titanium, gold, chromium, nickel, they are usually found in combination with naphthenic acid in the form of soap in the form of complex organometallic compounds such as metalloporphyrins or petroporphyrins [12].

Research results have shown that almost all metals and metalloporphyrins of oil are concentrated in asphaltene-resin components [13]. Among all petroleum components, the maximum concentration of vanadium is found in asphaltenes than in crude oil [14].

The presence of metal complexes in oils, in particular vanadium and nickel, significantly reduces the performance properties of petroleum products and aggravates the environmental situation [15]. It is known [16] that a high content of metals, in particular vanadium and nickel, is also a serious problem when processing heavy petroleum feedstocks, as it leads to irreversible deactivation of catalysts as a result of metal deposition on the active surface, blocking the pore space and destruction of the catalyst structure. Moreover, it was revealed [17] that these metalloporphyrins can play an important role in the aggregation of asphaltenes, being captured by these high molecular weight fractions of oil [18].

2. Composition and structure of metal porphyrins in heavy oils

Porphyrins were first discovered in oil fields in 1879. Author[19] showed that the complex compounds found in oils are mainly vanadium and iron porphyrins.Based on numerous studies [20, 21], it was shown that porphyrin compounds of oil are a very complex mixture of homologues belonging to five series. Within each series, individual homologues differ in the number of methylene groups (CH_2) in the alkyl side chains.

The presence of metalloporphyrins in crude oil has been known for many years, but their role in the physicochemical properties of petroleum fluids, such as the aggregation of high molecular weight phases, remains unknown. In [22], these properties are studied using various molecular models characterizing the nature of these interactions. It has been shown that the phenomena of aggregation of asphaltenes - porphyrins are less dependent on pp-type interactions and are more dependent on the formation of an H-bond between the side chains of both compounds.

Porphyrins are non-trivial molecules. The unique properties of MP are due to the unusual geometric and electronic structure of porphyrin ligands, the presence in them of a developed aromatic conjugated system, a macrocyclic ring built from carbon and nitrogen atoms, and a number of other features [15] Their composition, complex and variable geometric and electronic structures, combining a wide variety of influences with the environment, provide them with wide biological functions and application in a wide variety of fields of technology. This circumstance causes great interest in porphyrins.

It is known [15], that porphyrins are compounds in which four pyrrole rings are connected by methine bridges into a single cyclic conjugated system, which is based on a 16-membered macrocycle containing 4 nitrogen atoms. The founder of porphyrins is porphine (fig.1); radicals of saturated and unsaturated hydrocarbons, acids, esters, aldehydes, aromatic compounds, etc. can act as a substituent.

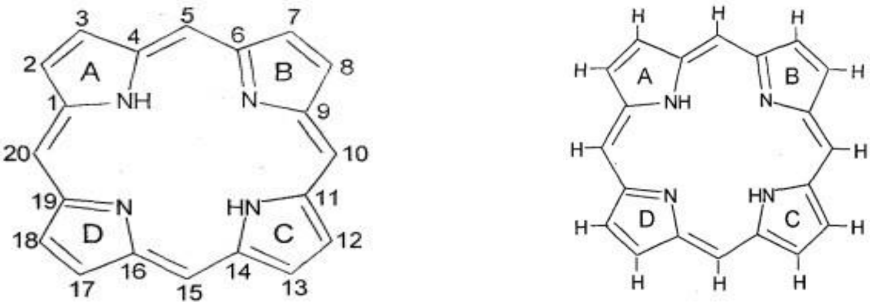


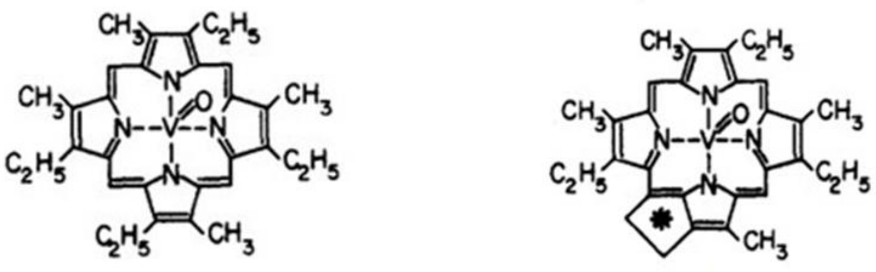
Fig.1. The founder of porphyrins is porphin

These porphyrins are called free porphyrin bases and are quite rare in nature. Porphyrins are usually found in the form of metal complexes formed when imine hydrogens are replaced by a metal. In chlorophylls it is magnesium, in prosthetic groups of hemoglobins, cytochromes, etc. – iron [23].

The authors of the work [14] the structures of metalloporphyrins in the composition of asphaltenes were established. It was revealed that the main part of MPs consists of vanadyl porphyrins of etio- and deoxyphylloerythroetio-types (fig.2).

It is necessary to take into account that metals (metalloporphyrins) are valuable associated components, the content of which in oils and their residues can be comparable and even exceed their content in ore sources [15].

Thus, the isolation of metalloporphyrins will make it possible not only to optimize oil refining processes, but also to obtain porphyrin concentrates that have a number of valuable properties, as well as to determine the most promising ways of using these compounds.



a) b)

Fig.2. Structures of vanadyl porphyrins: deoxophylloerythro-thioporphyrin (DPEP) (a), $C_{32}H_{34}N_4V$-(IV)-O; etioporphyrin III (ETIO) (b), $C_{32}H_{36}N_4V$(IV)O [24]

3. Identification and methods for determining the content of metalloporphyrins in oils

For the analysis of porphyrins, the authors of [20, 25-31] the most widely used are electron spectroscopy (ESP), mass spectrometry and NMR.

To identify MP structures and calculate their concentration in oils, ESP is more often used. In addition, from the 60-70s, mass spectrometry methods began to be used [20, 25, 26], liquid chromatography [27, 28], NMR spectroscopy [29; 30]. In general, spectroscopic methods (UV, IR, NMR spectroscopy, mass spectrometry) provide the necessary information about individual details of the structure, about the state of the d-electrons of the macroring and associated fragments, about the nature of molecular orbitals, about the mutual influence of atoms, about the nature of electronic influences of the metal atom on the state of heteroatoms and functional groups of porphyrins.

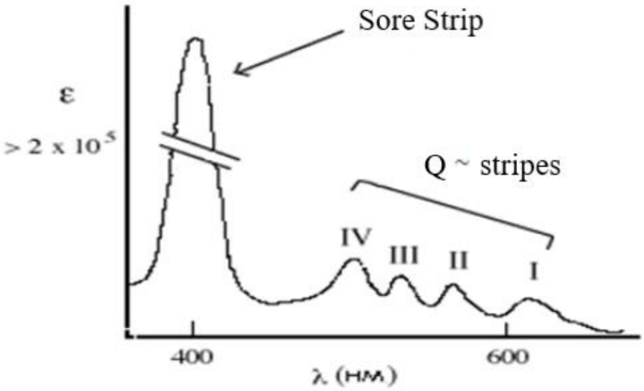
NMR spectroscopy is the most informative method for studying structure. Scientists have found that to take NMR spectra it is necessary to isolate spectrally pure porphyrins, which is very labor-intensive and not always possible in the case of residual oils, when the oil itself is rarely possible isolating more than 3-5 grams, and isolating porphyrins in quantities sufficient to take NMR spectra (30-50 mg) is almost impossible. In mass spectrometric analysis, researchers face a similar problem.

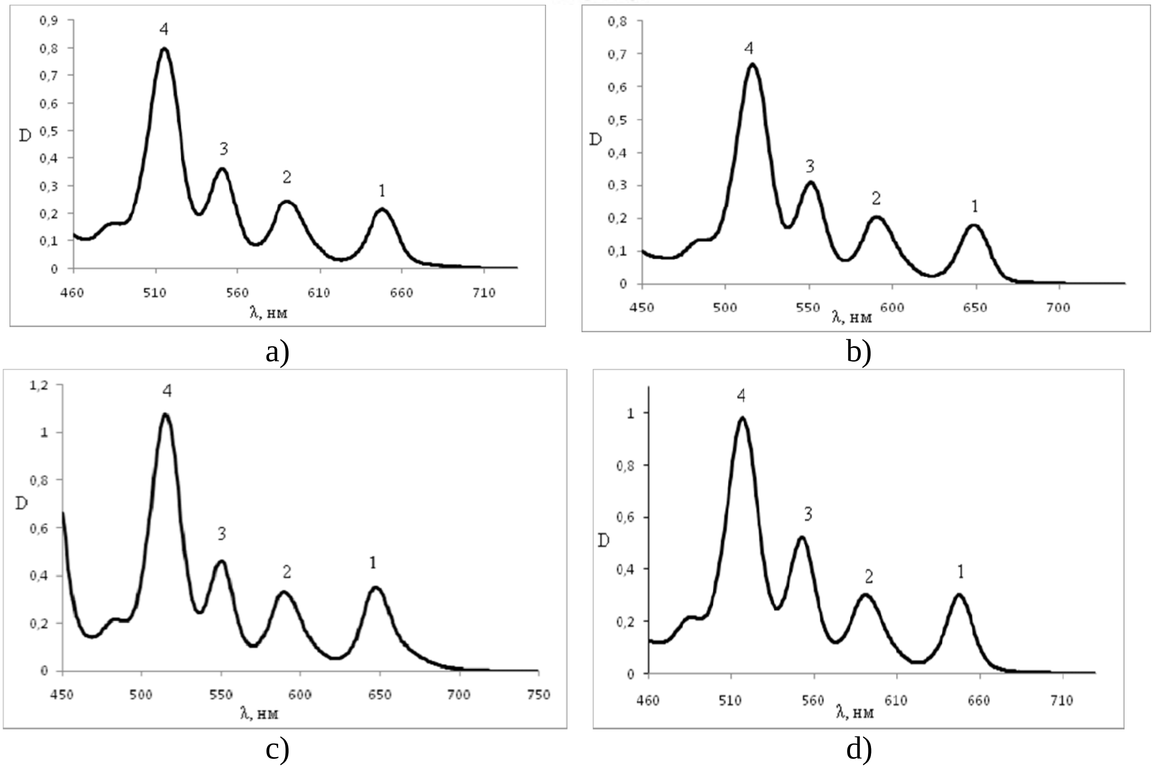
Studying the IR spectra of organic compounds allows one to obtain important information about the structure and optical properties of molecules [31]. However, the application of Fourier infrared spectroscopy methods to very complex molecules often brings very limited information. It was revealed that porphyrins from this point of view are very difficult compounds. The absorption band of porphin, corresponding to NH stretching vibrations, is located at 3305 cm^{-1}, tetraphenylporphin - 3315 cm^{-1}, mesoporphin - 3305 cm^{-1}.

It has been established that porphyrins have a bright color and a unique structure of bands in the ESP. They are identified by their electronic spectra and their purity is judged. The visible region of the spectrum is more often used, since it is more sensitive to structural features. In this spectral region, metalloporphyrin complexes contain two absorption bands, designated α and β. The position of the bands, as well as the ratio of their intensities, depends on the metal included in the porphyrin core. For nickel porphyrin complexes, the α and β absorption bands are located at 515 and 550 nm, and for vanadyl porphyrins these bands are shifted to longer wavelengths at 530 and 570 nm, respectively [32].

Compared to metalloporphyrins, the electronic absorption spectra of free bases carry more structural information. In the EAS of free porphyrin, in addition to the Soret band (in the near violet region of the spectrum 400-410 nm), there are four maxima of relatively low intensity in the visible region of the spectrum (620, 565, 535 and 500 nm, designated I, II, III and IV, respectively, fig.3) [33]. Based on the ratio of the intensities of these bands, one can judge the structure and composition of porphyrins. The most characteristic spectra of porphyrins, designated as phyllo-, etio-orodo-, and DFEP-types, are shown in figure 1.4 [34, 35].

Based on the intensity of the Soret band, the concentration of free porphyrin bases in the studied objects is determined, using, depending on the type of porphyrin, an extinction coefficient in the range of 1.60 - 2.17 105 l/ (mol cm) [35].





a) b)

c) d)

Fig.3. UV spectra of porphyrin bases: a) etio- b) phyllo- c) rhodo- d) deoxyphylloerythroetio types

Determination of the quantitative content of porphyrin compounds in petroleum fractions, such as resins, asphaltenes, and oils, showed that the separation of fractions is accompanied by partial fractionation of vanadyl and nickel porphyrins [36]. In this regard, there is no need for chromatographic separation of porphyrins; it is sufficient to extract MP from resins and asphaltenes. Oils, due to their rather light color, can be spectrophotometered without additional processing; they only need to be dissolved in a small amount of benzene [36, 38].

The concentration of porphyrins in oils depends on a large number of factors. It has now been shown that with an increase in the metamorphic transformation of oil, the concentration of porphyrins decreases [36, 39].

4.Methods for isolating porphyrins from residual oils

Oil can be considered as a potential source of porphyrin compounds for technical and other purposes, since heavy oils are characterized by increased density and viscosity due to the high content of resinous-asphaltene substances and metal-containing components, including cobalt- and nickel-containing ones. In present time enough studied in detail There are petroleum porphyrins, which belong to nitrogen-containing compounds [40].

This part discusses the most common and promising methods for isolating metalloporphyrins from heavy oils and oil residues.

Methods for isolating metal-containing compounds from oils and petroleum components can be divided into three groups [41]:

- chemical interaction of various compounds with oil components with the formation of new chemically stable compounds;
- extraction isolation and precipitation with solvents, based on the different solubility of individual compounds in different solvents;
- complexation, chemical adsorption and ion exchange chromatography, in which rather weak chemical bonds of various compounds with petroleum porphyrins are formed.

Isolation of metal-containing compounds from oils and oil components by chemical interaction of various compounds with oil components with the formation of new chemically stable compounds. The technique is based on the treatment of oil and oil components with strong acids, when used, demetallation of metalloporphyrins occurs with their further transition to the acid phase. Acetic and formic acids saturated with hydrogen bromide [42, 43], sulfuric [44] and phosphoric acids [45] are used as demetallating agents. However, technical difficulties do not allow large-scale experiments. Treatment with hydrochloric acid does not lead to the formation of free porphyrin bases. Demetallization with phosphoric acid requires a fairly high temperature (180°C) [45].

In work [45] revealed that a high yield is achieved by demetallization of a concentrate of petroleum metalloporphyrins using concentrated sulfuric acid. Demetalation occurs at a low temperature (13-15°C) in 3-5 minutes, while a small part of metalloporphyrins remains in the form of metal complexes, and the bulk (80-90%) is converted to free bases. The destruction of free porphyrin bases during a short time of contact with acid is negligible. Based on the reaction of sulfuric acid with synthetic vanadyl, nickel and copper etioporphyrins, the authors of [46] came to the conclusion that sulfuric acid is the mildest known demetalating reagent. However, this is not entirely true for petroleum porphyrins, since prolonged contact with acid leads to their destruction.

The most convenient method for better separating petroleum products into groups with their subsequent analysis, as well as quantitative determination of the chemical composition of petroleum products, is the liquid adsorption chromatography method [47]. In this method, the separation of free porphyrins of different structures isolated from metal complexes is carried out on a chromatographic column.

The method of extracting metalloporphyrins with oil-immiscible solvents (ethyl alcohol [48], acetonitrile [49], and N, N-dimethylformamide (DMF) [50]) with further purification of the extract has found wide application in laboratory conditions. When comparing the selectivity and degree of extraction of metalloporphyrins with these solvents, it was found that DMF extracts metalloporphyrins most completely, and when used, all metalloporphyrins are extracted, while acetone and alcohols extract mainly their most polar part [50]. Several patents describe the extraction of vanadyl porphyrins with 2-pyrrolidone [51] and butyrolactone [52]. However, the data described in these patents were obtained for oils with low levels of vanadyl porphyrins and asphaltenes. For light oils with a relatively low content of asphaltene-resin substances, the third group of isolation methods is most suitable for the extraction of petroleum porphyrins - complexation with Lewis acids, which are most often used as anhydrous metal halides. The essence of the method is the formation of molecular complexes of petroleum metalloporphyrins with titanium or iron halides, insoluble in hydrocarbon systems, followed by the isolation of these complexes, destruction and regeneration of metalloporphyrins. The advantage of extraction methods is the mild process conditions, which completely eliminates the possibility of any chemical transformations [53].

Currently, the possibility of extraction of metalloporphyrin concentrates from asphaltenes has been little studied. There are only a few publications in the literature that study the efficiency of extraction of metalloporphyrins from asphaltenes with various solvents. For example, in [54], a comparative study was carried out on the possibility of extracting vanadyl porphyrins from asphaltenes of oil from the Romashkinskoye field with various solvents. Acetonitrile, acetone, n-butanol, ethanol, as well as a mixture of benzene and methanol were used as extractants. It has been shown that acetone and acetonitrile exhibit the highest efficiency. However, complete extraction of metal-containing compounds from asphaltenes has not been achieved.

A significant portion of metalloporphyrins and metal-containing compounds of vanadyl and nickel of non-porphyrin nature remains in asphaltenes. Extraction was carried out at the boiling point of the solvent. It has been shown that no solvent is capable of extracting more than 65% of the total content of vanadyl porphyrins.

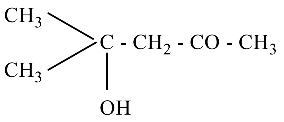
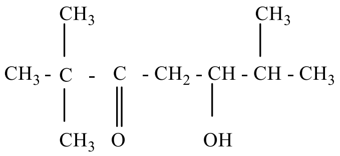
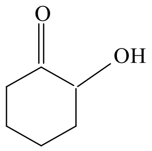
The work [55] proposed a method for obtaining vanadyl porphyrins from asphaltite using three-stage extraction with acetone. Extraction was carried out in a Soxhlet apparatus to prevent loss of asphaltite and evaporation of acetone within an hour. The authors showed that extraction with acetone in a Soxhlett apparatus, compared with traditional alcohol-acetone or alcohol extraction, allows one to increase the degree of extraction of vanadyl porphyrins from asphaltite. Temperature drop from 56 up to 25°C has virtually no effect on the yield of vanadyl porphyrins. When the temperature decreases to 0°C, the degree of extraction of vanadyl porphyrins decreases to 14%.

Literature data indicate the promise of isolating metalloporphyrins from oils and heavy oil residues using solvents and their mixtures.

The results of a study of a number of new bifunctional organic reagents as extractants for the selective extraction of petroleum porphyrins from asphaltenes are presented, their spectral characteristics are studied, and the dependence of the recovery rate on the mass ratio of the extractant and petroleum feedstock is revealed. The best results are obtained with a weight ratio of 1:30.

Table 1

Some characteristics of synthesized by extractants I-III used for the selective extraction of oil metalloporphyrins

№	The structure and name of ketone alcohols	Molecular mass	Characteristic absorption bands in the IR spectrum, ν cm^{-1}
I	 2-methylpentanon-4-ol-2	116	3520 (-OH), 1708 (C=O)
II	 $CH_3-C(CH_3)_2-C(=O)-CH_2-CH(OH)-CH(CH_3)-CH_3$ 2,2,6-trimethylheptanon-3-ol-5	172	3595 (-OH), 1711 (C=O)
III	 2- hydroxycyclohexanone	114	3340 (-OH), 1715 (C=O)

The isolated mixture of metalloporphyrins is first subjected to demetallization with hydrochloric acid (pH = 1-2), turning into a mixture of porphyrins, then, to obtain individual metal porphyrin complexes, the required transition metal ions are introduced into the porphyrin ring by treating the mixture with salts of these metals. It is shown that the yield of synthesized petroleum porphyrins is 42-85%, depending on the nature of the metal.

1. Synthesis of new chemical systems based on petroleum metalloporphyrins

Petroleum porphyrins can be used as catalysts, semiconductor compositions, sensitizers, dyes, and also in medicine for the production of antitumor drugs [56].

A characteristic feature of metalloporphyrins is their diversity, which, in combination with a unique molecular structure, determines their ability to act as drugs, catalysts, photosensitizers, various dyes, organic semiconductors, etc.

As petroleum feedstocks become heavier, attention to the challenges of processing heavy petroleum feedstocks and their deposits increases, both to increase efficiency and reduce oil refining costs, and to produce new chemical systems based on them.

In this regard, the development and research of new modified chemical systems based on metalloporphyrins isolated from heavy, highly viscous oil or oil residues are of great interest.

Demetallization of petroleum metalloporphyrins

As a consequence, it seems necessary to optimize traditional processes for the preparation and processing of oils and heavy oil residues in order to obtain concentrates with the standard content of certain rare metals (depending on their content in the original oil) without deteriorating the economic indicators of the production of target oil products [57].

It has been revealed that during oil preparation processes, salts of alkali and alkaline earth metals, some acidic compounds (fatty and naphthenic acids, acidic resins), as well as vanadium, arsenic and nickel compounds, which are partially concentrated on the surface of water globules, pass into wastewater.

Oil prepared in the fields is then subjected to a secondary, deeper purification at the oil refinery to a salt content of less than 5 mg/l and water content of less than 0.1 wt. %. When the chloride content is reduced to 5 mg/l, iron, calcium, magnesium, sodium and arsenic compounds are almost completely removed from the oil, and the vanadium content is reduced by more than 2 times, which is extremely important from the point of view of the quality of jet and gas turbine fuels, petroleum cokes and other petroleum products.

However, deep demetallization of oils in traditional electric desalting plants is impossible, since transition metals form fairly strong organometallic compounds with hydrocarbon and heteroatomic components of oil. This determines the relevance of research devoted to the development of various modifications of desalting processes in order to increase the degree of metal recovery [58].

Scientists [59] propose a technology for the selective isolation of metals, sulfur and other elements by conducting high-frequency electrolysis of oil under thin film conditions in flow-through electrolyzer reactors. The implementation of the technology comes down to passing the purified oil through electrolysis cells. By changing the electrolysis modes and current density, it is possible to consistently isolate impurities contained in oil and petroleum products, including metals and non-metals. The peculiarity of the electrolyzer is the design of the cells, which provide minimal hydrodynamic resistance with a high ratio of the electrode surface to the processed volume, which intensifies the process and increases its energy efficiency. Impurities, which include metals, accumulate in the receiving fluid, which is not consumed. Removal of impurities from the receiving process fluid is achieved by mechanical filtration. The degree of extraction of impurities (compounds of vanadium, nickel, cobalt, molybdenum, as well as sulfur, etc.) can reach 99%.

The authors have proposed a number of methods for oil demetallization using electrolytic systems [60, 61]. There is an effective way to demetallize and desulfurize crude oil in a stream [59], which ensures the implementation of reagent-free electrochemical technology taking into account environmental requirements: the processing of crude oil in a stream is carried out electrochemically using an alternating asymmetric current. The products obtained as a result of demetallization, desulfurization and extraction of the necessary valuable components can be used as raw materials for the needs of industrial production.

The patent [62] describes a method for transferring metals and/or amines from the hydrocarbon phase to the aqueous phase in the process of oil desalting by adding a composition of a certain composition to an emulsion of hydrocarbon and water. The use of this method makes it possible to transfer most metals from crude oil into the aqueous phase during the desalting process.

A method for demetallization of oil using electrical desalting equipment was proposed in a patent [63]. In the processes of oil dehydration and desalting, a demetallizing agent is supplied along with a demulsifier and fresh water. The crude oil is further processed in an electric field using special electric desalting cylinders, after which the next stage of a similar demetallization procedure is carried out. The efficiency of extracting metals (calcium, iron, manganese) from high-viscosity oil can approach 100% under certain process conditions.

The main factors influencing the efficiency of demetallization are the viscosity of the feed oil, the type and concentration of the demetallizing agent, and the acidity of its aqueous solution. A decrease in the viscosity of an oil sample has a beneficial effect on its mixing with demetallizing agents and their interaction with metal ions formed during the dissociation of salts such as carboxylates and phenolates [63, p. 1345].

2. Porphyrins as photosensitizers for hydrogen production

In article [64], the authors concluded that porphyrin molecules are a very promising class of photosensitizers for photocatalytic hydrogen production. It is known that the photosensitizer must have good long-term stability storage in aqueous solution, without side photoreaction and efficient production of separated ionic products upon irradiation in the presence of an electron donor or acceptor. In many cases where electron transfer processes in the excited state are bimolecular, an important requirement for the photosensitizer is the presence of a high triplet yield. Porphyrins are found to have most of the above desirable properties to be used as a photosensitizer for photoinduced H_2 generation.

Among the various metalated porphyrins, those containing a metal center Mg (II), Zn (II), Pd (II), Cd (II), Pt (II), Al (III) or Sn (IV) have the corresponding excited state, properties and stability required for H_2 production systems. In addition, substitution at the periphery of the porphyrin ring can be used to fine-tune the redox potential of porphyrins.

Harriman studied various metalloporphyrins as photosensitizers. Hydrogen is formed by irradiation of porphyrin in an aqueous solution containing a number of electron donors (ethanol, glucose, lactate, H_2S, hydrogenated nicotinamide adenine dinucleotide (NADH), carboxylic acids or hydroxylamine) and colloidal platinum [65]. The process is subject to reductive quenching at the porphyrin triplet.

In various studies, colloidal platinum has been used as a catalyst for the production of hydrogen from glucose [66-68]. In addition, the production of hydrogen from glucose with a combination of glucose dehydrogenase and hydrogenase has also been studied by scientists [69, 70]. Saiki and Amao studied a biohydrogen production system that is associated with the degradation of a polysaccharide (sucrose or maltose) with invertase and glucose dehydrogenase [71].

Hydrogen produced by colloidal platinum using photosensitization water-soluble meso-tetrakis-zinc (p-sulfonatophenyl) porphyrin in the presence of methyl viologen (MV2+) as an electron relay reagent (1). Continuous production of hydrogen gas was observed when a sample solution containing polysaccharide, invertase, glucose dehydrogenase, nicotine denine dinucleotide amide (NAD+), MV2+ and colloidal platinum was irradiated with visible light. After 240 min of irradiation, the amount of hydrogen produced in the system using sucrose or maltose was estimated to be 3.1 or 0.35 μmol, respectively.

Harada used a complex between a free base monoclonal antibody and zinc porphyrin to construct an energy conversion system [72]. Monoclonal antibody 2B6 was bound to meso-tetrakis-zinc (4-carboxyphenyl) porphyrin (2) and after binding, the lifetime of the excited triplet state increased from 0.5 to 1.2 ms. The stable cationic radical of viologen was obtained by irradiating the solution, containing a complex of 2B6, with 2, MV2+ and ethylene diamine tetraacetic acid (EDTA). When colloidal platinum was used as a catalyst, the formation of photoinduced hydrogen was observed under continuous irradiation with visible light.

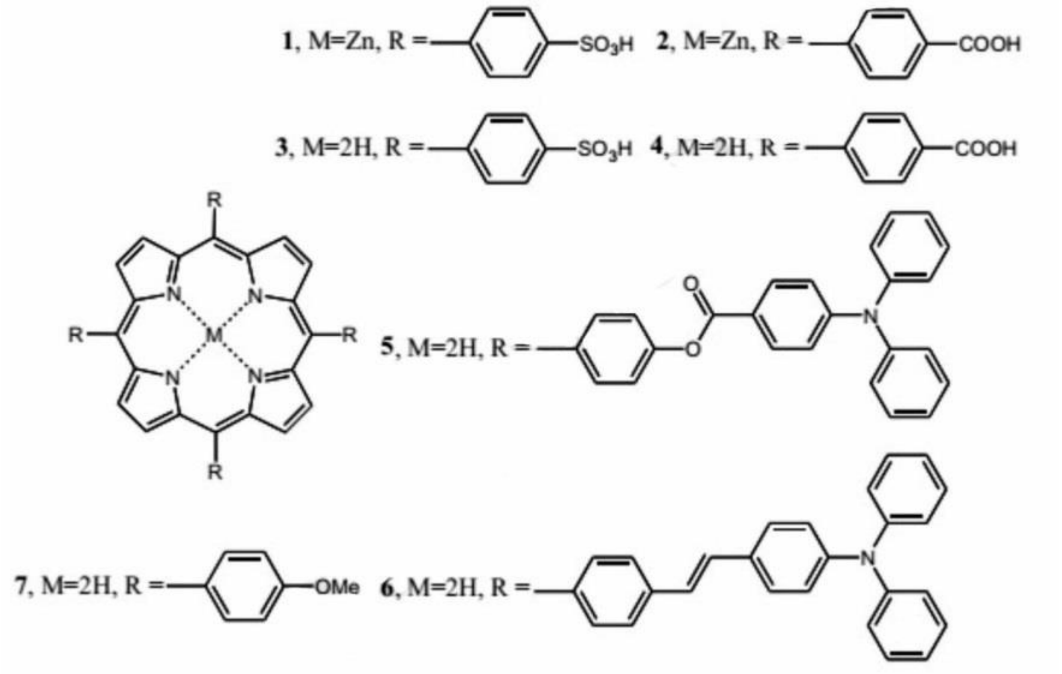


Fig.4. Molecular structure of porphyrins 1-7

In the third case, nanocomposites were used as photocatalysts for hydrogen. These nanocomposites were composed of meso-tetrakis (p-sulfonatophenyl) porphyrin (3) as a photosensitizer and platinum (Pt) nanoparticles as a catalyst [73]. Porphyrin was also useful in preventing agglomeration of Pt nanoparticles. Fluorescence and photoelectrochemistry studies have shown that effective electron transfer occurs from the donor to the metal acceptor of the nanonucleus. In addition, the nanocomposites were photocatalytically active and produced hydrogen.

Rosseinsky [74] about a stable water-resistant porous metal-organic porphyrin framework that can generate hydrogen from water photocatalytically. Microcrystalline porous material is formed based on the reaction of $AlCl_3$ $6H_2O$ with the free base of mesotetra (4-carboxylphenyl) porphyrin (4). The release of a small amount of H_2 was observed after illumination with visible light in an aqueous EDTA/MV2+/Pt colloidal solution for 15 h.

Researchers have studied nanocomposites formed by functionalizing Pt nanoparticles with highly branched porphyrin photosensitizers [75]. Conjugates (5) and (6) of donor-bridge-acceptor synthesis were synthesized; triphenylamine branches are used as energy donors in these compounds.

The sensitizers are in direct contact with the metal core in nanocomposites, and electron transfer between the organic moiety and the platinum particles must be efficient. Hydrogen is detected when nanocomposite systems are irradiated with ultraviolet radiation, the hydrogen evolution of Pt-6 is higher than for Pt-5, given that the ethylene bond between tetraphenylporphyrin and triphenylamine is superior to the ether bond.

In order to simulate the process of photoinduced electron transfer of the photosynthetic reaction center, scientists have developed donor-acceptor covalently bonded systems [14]. Yang created a photocatalytic system that uses a nanocomposite made of Pt functionalized with self-assembled conjugates of 5,10,15,20-tetrakis(hydroxyl)phenyl) porphyrin (TPPH) (7) and pyrene sulfonic acid (PSA) and as a reducing agent EDTA in the absence electronic mediator [76]. A system without an electron mediator is not only simpler in nature, but also eliminates the reverse reactions associated with the transfer of an electron to the mediator [77]. It turned out that photoinduced energy transfer occurs from the photoexcited state of pyrene to the porphyrin, followed by electron transfer from the excited porphyrin fragment to the platinum catalyst.

Photocatalytic hydrogen evolution from the system demonstrates the feasibility of constructing a photocatalytic system that uses a Pt nanocomposite functionalized with self-assembled donor/acceptor conjugates. It is worth noting that the generation of photochemical hydrogen only occurs when PSA absorbs UV rays, while visible light from absorbed TPPH is nonproductive.

Revealed [64] that porphyrins and metalloporphyrins act as a good photosensitizer for photocatalytic hydrogen production, comparable to more popular classes of sensitizers such as ruthenium polypyridine dyes.

Playing primarily the role of photosensitizers, some porphyrin systems have also found use as hydrogen-evolving catalysts. These are systems containing transition metal centers such as Co, Fe, Ru, Os, in which the catalytic activity is associated with their variety of readily available oxidation states. From this point of view, metalloporphyrin and related species, with the additional stability provided by the macrocyclic ligand, are similar to other complexes of the same metals, both with respect to catalytic mechanism and performance. A possible disadvantage of these porphyrin-based systems is their strong chromophore nature, which can cause competition for light absorption by the photosensitizer at the relative concentrations used in photocatalytic experiments, however this effect is usually negligible.

3. The use of metalloporphyrins as a catalyst

Porphyrins and metalloporphyrins are compounds that have a number of unique properties. Analysis of literature data showed that porphyrins are mainly used as catalysts in a variety of chemical, electrochemical and photochemical processes. The high catalytic activity of porphyrins is due to the aromatic nature of the conjugated π-system of the macrocycle, the conjugation of a coordinated metal atom with this π-system and a slight change in the oxidation state of some central metal atoms [76].

Among the chemical processes occurring with the participation of porphyrins, a special place belongs to electrocatalytic ones. A large number of works in this area relate to the study of catalyzed electroreduction of molecular oxygen [79]. One of the new areas of application of porphyrins is the catalysis of the anodic oxidation of sulfur dioxide. Research in this area has begun to develop in the last 10 years in connection with the search for new environmentally friendly fuels [80]. A very important area in which porphyrins have found practical application is the catalytic oxidation of hydrogen sulfide, mercaptans and other RHS-type compounds with atmospheric oxygen. This process is used to treat wastewater from oil refineries, non-ferrous metallurgy enterprises, desulfurization of petroleum products and natural gas [81]. Metalloporphyrins catalyze the autoxidation of alcohols and phenols, aldehydes and carboxylic acids [82].

Research has found that cobalt is a compatible metalloporphyrin used for this purpose [86].

Other advantages of metalloporphyrin immobilization include (I) localization of the metal center, which minimizes self-destruction of the catalyst and dimerization of metalloporphyrin; (II) easy isolation of the heterogeneous catalyst from the reaction field; (III) the possibility of using catalysts in flow reactors; (IV) easy reuse/recycling of the catalyst, which minimizes environmental impact.

Selective catalytic materials can result from controlling the formation of either a porous support structure or a three-dimensional matrix network [87]. In fact, controlling particle morphology is one of the major challenges in the industrial use of silica. Based on their “unusual” structure and properties, layered materials, fibers and exposed nanotubes/nanoscrolls are potential materials for immobilization/encapsulation of active metal complexes. After immobilization, homogeneous active particles are converted into a heterogeneous catalyst, and its selectivity and high activity are maintained. In this regard, halloysite, a tubular mineral clay belonging to the same class as kaolinite [87], is a promising carrier for metalloporphyrin immobilization.

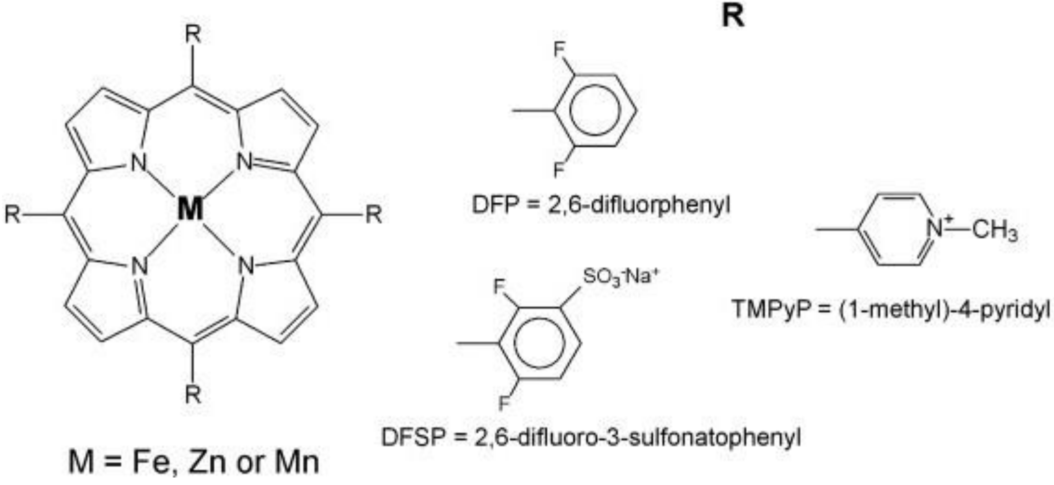


Fig.5. Structure of metalloporphyrins for the production of catalysts

It was revealed that the immobilization of metalloporphyrin occurs on the edges/surfaces of halloysite nanotubes, and the structure of the catalyst is preserved. A study of the catalytic activity of the catalyst obtained by immobilization on halloysite for the oxidation of alkanes showed that this catalyst is highly efficient and highly selective for the production of alcohol .

4. Use of metalloporphyrins for the production of medicines

Currently, numerous studies are devoted to searching for the possibilities of using porphyrins in medicine as medicines. The development of drugs and other biologically active agents based on porphyrins is, apparently, one of the promising applied areas in the problem of using porphyrins [79-86].

The most effective sensitizer is photoditazine (a chlorine derivative), however, it does not always accumulate in tumor cells with sufficient contrast to normal ones. An important and urgent task is to increase the contrast of sensitizer accumulation.

The photodynamic effect of porphyrins served as the basis for the use of compounds in photochemotherapy of tumors of other diseases. It has been discovered that some natural and synthetic porphyrins have significant catalytic and enzymatic activity, due to which they can act as activators or sensitizers of processes.

The main areas of practical use of porphyrins are blood substitutes, carriers and accelerators of drug transfer, immunofluorescent analysis methods, cancer therapy, diagnosis and therapy of malignant neoplasms [86].

Porphyrins and iron porphyrin complexes capable of adsorbing, transferring and desorbing oxygen are used as blood substitutes (complexes of tetraamidophenylporphyrinimidazole and tetrapivalamidophenylporphyrin with iron (II), as well as tetracarboxyphenyl porphyrin with carbohydrates and fatty acids).

A number of authors recommend hematoporphyrin derivatives, the molecules of which are attached to the surface of liposomes containing active substances, as carriers and accelerators of drug transfer.

One of the promising areas for the practical use of porphyrins is immunofluorescent analysis. Porphyrin compounds have been proposed as marker molecules (tetracarboxyphenyl porphyrin derivatives), especially for highly sensitive accelerated immunofluorescence analysis.

Particular attention is paid to aspects of the use of porphyrins in oncological practice. Experimental studies of the distribution of porphyrins in tissues, their fluorescence and photodynamic action served as the basis for the clinical use of natural and synthetic porphyrins. Porphyrins are a valuable marker of latent tumors, identifying and delineating the boundaries of cancerous tissue. Most often, the procedure is carried out as follows: porphyrin is administered intravenously in a total dose of 20-50 mg, after a certain time (usually 24 hours), de visu red fluorescence is recorded after illumination with UV light. According to the authors of this technique allows you to diagnose cancer of the lungs, stomach, rectum and other organs [87].

The second direction of clinical use of porphyrins is the combination of chemotherapy and the action of light. The photosensitizing effect of porphyrin was observed on a variety of biological objects: protozoa, mammals, cell cultures, bacteriophages, viruses, as well as nucleic acids, proteins and amino acids. Thus, the clinical use of porphyrins is developing in two directions:

a) local administration of porphyrin and irradiation of malignant tissues; b) activation of the body’s defense system by porphyrin.

The effectiveness of photochemotherapy using porphyrins and their metal complexes has been proven to directly inhibit the growth of cancer cells.

In recent years, much attention has been paid to the creation of pharmaceuticals for the treatment of diseases caused by the human immunodeficiency virus. Drugs that do not cause side effects have been proposed for the treatment of lymphadenitis, lymphadereopathies, AIDS and other diseases, containing porphyrin compounds and their derivatives as active ingredients.

The use of the unique properties of porphyrins opens up new prospects for researchers and practical medicine in the treatment of various diseases.

5. Immobilization of metalloporphyrins on natural and synthetic polymer carriers

Porphyrins are included in many medications, but, as is known, all drugs have a limited duration of action, after which they are eliminated from the body. Moreover, the smaller the molecular weight of the drug, the faster it is excreted. For prolonged action of medicinal drugs, it is proposed that a physiologically active substance with pharmacological properties be grafted onto a carrier polymer due to the formation of ester bonds, salt and others, which are easily hydrolyzed in the body.

One of the areas that has been intensively developing recently is the fixation of active metalloporphyrins on a polymer matrix.

An analysis of the literature data showed that the nature of the attachment of porphyrins to the polymer matrix can be different. In a number of studies, the immobilization of porphyrins and their complexes was carried out through coordination bonds. The attachment of porphyrins is carried out due to the interaction of functional groups of polymers and porphyrins with the formation of secondary amine, ester and other functional groups. The fact of immobilization of porphyrins and metal complexes in the above works is confirmed by the authors using electron and IR spectroscopy, elemental analysis for nitrogen, as well as a spectrophotometric method for determining the mass fractions of metal in the case of polymer metalloporphyrins.

Polymer-bound porphyrins are of significant interest from the point of view of their therapeutic effects. However, studies on the synthesis of polymer derivatives of porphyrins and their metal complexes are scarce, so the development of new methods for immobilizing porphyrins and their metal derivatives on a polymer matrix and expanding the scope of their applications is of undoubted interest.

The possibility of modifying metalloporphyrins from heavy petroleum residues may stimulate the further development of more efficient and economical technologies for the production of effective drugs.

CONCLUSION

We reviewed 109 experimental results on metallopotphyrins published in 88 articles the following conclusions can be drawn from this data:

- Refering to the existing methods of isolation of metalloporphyrins, the method of extraction is of less importance than the type and nature of the substances used as extractants that ensure the maximum degree of extractions of metalloporphyrins from oil residues.
- It is very important to select physicochemical methods and calculation methods for identifying isolated metalloporphyrins, indicating their purity and individuality.
- The replacement of one metal with another in order to obtain metalloporphyrin complexes of individual metals (usually transition metals) requires the selection of special conditions and methods for the demetallization of oil porphyrins.
- The wide possibilities of application as catalysts for various reactions medical drugs and other industries are very large and require further research.

REFERENCES

1. Mohammad A., Ali V., Mohsen E. Heavy Oil Upgrading via Hydrodynamic Cavitation in the Presence of an Appropriate Hydrogen Donor. Journal of Petroleum Science and Engineering. 2017, № 15, pp. 55-61
2. Yashchenko I.G. Heavy oils of Russia enriched with toxic metals. Mining Vedomosti. 2011, № 7, pp. 26
3. Elemanov B.D., Gershtansky O.C. Complications during oil production. Nauka, 2007, 420 p
4. Ivanova L.V., Burov E.A., Koshelev V.N. Asphalt, resin and paraffin deposits in the processes of production, transport and storage. Electronic scientific journal "Oil and Gas Business."2011, № 1, pp. 268-284
5. Sharifullin A.V., Baybekova L.R., Suleymanov A.T. Features of the composition and structure of oil deposits. Oil and Gas Technologies. 2006, № 6, pp. 19-24

6. Sharifullin A.V., Baybekova L.R., Khamidullin R.F. Composition and structure of asphaltene-resin-paraffin deposits in Tatarstan. Oil and Gas Technologies. 2006, № 4, pp. 34-41
7. Petrova L.M., Force T.R., Yusupova T.N., Mukhametshin R.Z., Romanov G.V. The influence of deposition of solid paraffins in the formation on the phase state of oils during field development. Neftekhimiya. 2005, T.45, № 3, pp. 189-195
8. Agaev S.G., Zemlyanskaya E.O., Gultyaev S.V. Paraffin deposits of the Verkhnesalat oil field in the Tomsk region. Oil refining and petrochemistry. 2006, № 3, pp. 8-12
9. Achugasim O., Ojinnaka Ch., Osuji L. Management of petroporphyrins in a crude oil polluted environment . Eur.Chem.Bull. 2013, 2(10), pp. 794-796
10. Serebryakov A. O. Features of the composition, properties and processing of oils of the Azerbaijani waters of the Caspian Sea. Geology, geography and global energy. 2012, № 3 (46) pp. 7
11. Agaguseinova M.M., Abdullaeva G.N., Salmanova N.I. Supramolecular metalloporphyrin catalytic systems for petrochemical synthesis.Oil refining and petrochemistry. 2010, pp. 172-175
12. Ali MF, Abbas SA Review of methods for the demetallization of residual fuel oils Fuel Process Technol. 2006, № 87, pp. 573–584
13. Hodgson G.V., Baker B.L., Pik I. Geochemistry of porphyrins. Basic aspects of petroleum geochemistry: collection. M.: Publishing house. AN USSR. 1970, pp. 172-243
14. Senge, M. O., Sergeeva, N. N. & Hale, K. J. Classic highlights in porphyrin and porphyrinoid totalsynthesis and biosynthesis. Chem. Soc. Rev. 50, 2021, pp. 730–4789
15. Akhmetov A.F., Krasilnikov Yu.V., Organyuk O.V., Parfenov M.A., Lyapina N.K. On the issue of studying metalloporphyrins in oils. Electronic scientific journal “Oil and Gas Business”. 2012, № 5, pp. 336-342
16. Ancheyta J. Modeling of Processes and Reactors for Upgrading of Heavy Petroleum. CRC Press; Taylor & Francis Group. 2013, Vol.23, 524 p
17. McKenna AM, Purcell JM, Rodgers RP, Marshall AG Identification of Vanadyl Porphyrins in a Heavy Crude Oil and Raw Asphaltene by Atmospheric Pressure Photoionization FT-ICR Mass Spectrometry. Energy & Fuels.2009, № 23, pp. 2122-2128
18. Aghahuseynova, M.M. Synthesis and properties of metallocomplex catalysts based on oil mettalloporphyrins. EURICA- physics and engineering. 2020, № 4, pp.19-28
19. Agahuseynova, M.M., Abdullaeva, G.N. Catalitic oxygenation of olefins with petroleum metalloporphyrines. Proceeding of High Education Instutution Russian Journal of “Chemistry and chemical Technology ”. 2010, 53(9), pp. 12-16
20. Milordov D.V., Abilova, G.R., Mironov, N.A., Yakubova, S.G., Yakubov, M.R., A Comparative Analysis of the Solubility of Asphaltene Fractions with Addition of Petroleum Vanadyl Porphyrins, Petroleum Chemistry. 2022, pp. 240-249
21. Mironov, N.; Milordov, D.; Abilova, G.; Tazeeva, E.; Yakubova, S.; Yakubov, M. Preparative-scale purification of petroleum vanadyl porphyrins by sulfuric acid loaded macroporous silica. J. Porphyr. Phthalocyanines. 2020, Vol.24, pp.528-537
22. Khisaa J., Derese S., Mack J., Amuhaya E., Nyokong T. J. Porphyrins Phthalocyanines. 2021, 25, pp. 794–799

23. Hugo SS, Ana CR, Sodero Jean-Pierre Korb, etc. The role of metalloporphyrins on the physical-chemical properties of petroleum fluids. Fuel. 2017, №188, pp. 374-381
24. Earl W., Bakert J., William L., Wilson L. Application of metailoporphyrin biomarkers as petroleum maturity indicators: The importance of quantitation Organic Geochemistry. 1987, Vol.11, № 4, pp. 303-309
25. Jackson AH, Kenner GW, Smith KM Pyrroles and related compounds. Mass spectrometry in structural and stereochemical problems-76. The mass spectrum of porphyrins. Tetrahedron. 1965, Vol.25. pp. 2913
26. Suboch V.P., Antipenko B.P., Titov V.I., Gurinovich T.P. Application of mass spectrometry of metastable ions to determine the chemical structure of petroleum porphyrins. Journal of Applied Spectroscopy. 1976, № 4, pp. 637
27. Hajibrahim SK Development of high pressure liquid chromatography (HPLC) for fractionation and fiшgeфrinting of petropophyrins mixtures. Journal of Liquid Chromatography. 1981, Vol.4, № 5 pp. 749
28. Serebrennikova O.B., Mozzhelina T.K., Beiko O.A., Krasovskaya L.I. High performance liquid chromatography of petroleum vanadyl porphyrins. Petrochemistry. 1985, T. 25, № 5, pp. 992
29. Rytting, B.M.; Singh, I.D.; Kilpatrick, P.K.; Harper, M.R.; Mennito, A.S.; Zhang, Y. Ultrahigh-purity vanadyl petroporphyrins. Energy Fuel. 2018, 32, pp. 5711–5724
30. Ganesh KN, Sanders JK, Waterton JC Quinone-capped porphyrins: NMR studies of static and dynamic stereochemistry and coordination properties. Journal of the Chemical Society. Perkin Transactions. 1982, №1, pp. 1617
31. Groves K. Lee J. The porphyrin handbook. 2000, Vol.4, pp.17-39
32. Serebrennikova O.V., Belokon T.V. Geochemistry of porphyrins. Novosibirsk: Nauka, 1984, 88 p
33. Hodgson J., V., Baker B.L., Pick I. Geochemistry of porphyrins. Basic aspects of petroleum geochemistry. M.: Nedra. 1970, pp. 172-243
34. Bogomolova A.I. and others. Modern methods of oil research: reference and methodological manual. L.: Nedra. 1984, 431 p
35. Serebrennikova O.V. Origin, composition and transformation of petroleum porphyrins: dissertation. doc. chem. Sci. Tomsk. 1990, 235 p
36. Proskuryakova A.E. Chemistry of oil and gas: textbook. manual for universities. M.: Chemistry. 1996, 446 p
37. Plyusnin A.N. State of research in the field of isolation and separation of heteroatomic components of oil. Improvement of methods for analyzing oils. Proceedings of IHH CO AH USSR. Tomsk: TF SO AH USSR. 1983, pp. 5-49
38. Groennings S. Detection of porphyrin aggregate in petroleum. Analytical Chemistry. 1953, Vol.11, pp. 938-941
39. Sugihara JM, Determination of vanadyl porphyrins by demetalation with hydrogen bromide-formic acid. Analytical Chemistry. 1964. Vol.36, pp. 2374 Dean RA, Girdler RB Reaction of metal etioporphyrins on dissolution in sulfuric acid. Chem. Indust. 1960, Vol.14, pp. 100-101
40. Palmer SE Baker LS, Charney JW Louda Tetrapyrrole pigments in United States humic coals. Geochimica et Cosmochimica Acta. 1982, Vol.46, pp. 1233-1241
41. Sokolova V.I., Kolbin M.A. Liquid chromatography of petroleum products. M.: Chemistry. 1984, pp. 5-23

42. Kolganova M.M., Kotorovich A.E. Organic geochemistry of Mesozoic oil and gas bearing deviations of Siberia. M.: Nedra. 1974, 40 p
43. Shostakovsky M.F., Eletsky N.P., Titov V.I. Isolation of vanadyl porphyrins from oil using complexation method. Petrochemistry, 1977, T. 17, pp. 453-454
44. Galimov R.A., Galimov R.A., Krivonozhkina L.B., Abushaeva V.V., Romanov G.V. Extraction extraction of vanadyl porphyrins from asphaltenes. Petrochemistry. 1993, T. 33, pp. 539-543
45. Nadirov R.A., Kotova A.V., Ergalieva A.K., Yagyeva S.M., Goldberg I.S. Preparation of vanadyl porphyrins from asphaltite of the Sadkinsky deposit. Chemistry and technology of fuels and oils. 1987, №4, pp. 9-10
46. Kamyanov V.F., Aksenov V.S., Titov V.I. Heteroatomic components of oils. Novosibirsk: Nauka, 1983, 239 p
47. Akhmetov S.A. Technology of deep processing of oil and gas: a textbook for universities. Ufa: Gilem. 2002, 672 p
48. Magomedov R.N., Popova A.Z., Maryutina T.A., Kadiev Kh.M., Khadzhiev S.N. State and prospects of demetallization of heavy petroleum feedstock (review). Petrochemistry. 2015, T. 55, №4, pp. 267-290
49. Technology for extracting non-ferrous metals from oil and its desulfurization. SPC "Quadra".http://npckvadra.ru/wp-content/uploads/2013/04/tehncvet_met. pdf
50. Pat. JP 53 "8315, MKI C10G32/04 dated 09/28/76; publ. 02/23/84
51. Pat. 2462501 Russian Federation. Obraztsov S.V., Orlov A.A. – 2012
52. Pat. RF 2346024. Method for transferring metals from the hydrocarbon phase to the aqueous phase, composition for implementing the method, spent hydrocarbon emulsion / Creamer L.N., Nguyen T.M., Weirs J.J. 2006
53. Wu B., Zhu J., Wang J., Jiang C.Technique for High-Viscosity Crude Oil Demetallization in the Liaohe Oil Field// Energy & Fuels. 2006, Vol.20, № 4, pp. 1345
54. Kalopi L., Mirco N., Elisabetta I., etc. Photochemical hydrogen generation with porphyrin-based systems. Coordination Chemistry Reviews. 2015, Vol.304. pp 38-54
55. Harriman A. Metalloporphyrin-photosensitized formation of hydrogen from organic and inorganic substrates. Journal of Photochemistry.1985, Vol.29, pp. 139-150
56. Mizuno O., Dinsdale R., Hawkes FR, Hawkes DL, Noike T. Enhancement of hydrogen production from glucose by nitrogen gas sparging. Bioresource Technology. 2000, Vol.73, pp. 59-65
57. Rustamov VR, Abdullayev KM, Aliyev FG, Kerimov VK Hydrogen. formation from biomass using solar energy. International Journal of Hydrogen Energy. 1998, Vol.23, pp. 649-652
58. Woodward J., Orr M., Cordray K., Greenbaum E. Enzymatic production of biohydrogen. Nature. 2000, №405, pp. 1014-1015
59. Inoue T., Kumar S.N., Kamachi T., Okura I. Hydrogen Evolution from Glucose with the Combination of Glucose Dehydrogenase and Hydrogenase from A. eutrophus H16. Chemistry Letters. 1999, Vol.28, pp. 147–148
60. Woodward J., Mattingly S.M., Danson M., Hough D., Ward N., Adams M. In vitro hydrogen production by glucose dehydrogenase and hydrogenase Nature Biotechnology. 1996, Vol.14, pp. 872-874
61. Saiki Y., Amao Y. Bio-mimetic hydrogen production from polysaccharide using

the visible light sensitization of zinc porphyrin. Biotechnology and Bioengineering. 2003, Vol.82, pp. 710-714

62. Sakai K, Ozawa H. Homogeneous Catalysis of Platinum (II) Complexes in Photochemical Hydrogen Production from Water. Coord Chem Rev. 2007, 251, pp. 2753–2766
63. Yamaguchi H., Onji T., Ohara H., Ikeda N., Harada A.Photoinduced Hydrogen-Evolution System with an Antibody–Porphyrin Complex as a Photosensitizer Bulletin of the Chemical Society of Japan. 2009, Vol.82, pp. 1341-1346
64. Zhang L., Lu Y., Du Y., Yang P., Wang X. Synthesis and photocatalytic evolution of hydrogen of meso-tetrakis(p-sulfonatophenyl) porphyrin functionalized platinum nanocomposites. Journal of Porphyrins and Phthalocyanines. 2010, Vol. 14, pp. 540-546
65. Fateeva A., Chater PA, Ireland CP, Tahir AA, Khimyak YZ, Wiper PV, Darwent JR, Rosseinsky MJ A Water-Stable Porphyrin-Based Metal–Organic Framework Active for Visible-Light Photocatalysis. Angewandte Chemie International Edition. 2012, Vol.51, pp. 7440-7444
66. Zhu M., Dong Y., Du Y., Mou Z., Liu J., Yang P., Wang X. Chemistry. A European Journal. 2012, Vol.18. pp. 4367-4374
67. Zhu M., Lu Y., Du Y., Li J., Wang X., Yang P.Photocatalytic hydrogen evolution without an electron mediator using a porphyrin–pyrene conjugate functionalized Pt nanocomposite as a photocatalyst. International Journal of Hydrogen Energy. 2011, Vol.36, pp. 4298-4304
68. Kotani H., Ono T., Ohkubo K., Fukuzumi S.Efficient photocatalytic hydrogen evolution without an electron mediator using a simple electron donor-acceptor dad. Physical Chemistry Chemical Physics. 2007, Vol.9, pp. 1487-1492
69. Semeikin A.S., Golubchikov O.A., Koifman O.I. Synthesis and application of porphyrins. Izv. universities Chemistry and chem. Technology. 2005 T.48, pp. 14-21
70. Pobedinsky S.M., Bazanov M.I., Trofimenko A.A. and others. Questions of kinetics and catalysis. – Ivanovo: Ivanovo Chemical Technology. Institute. 1974, Issue. 2, pp. 108-110
71. Tarasevich M.H., Radyushkina I.A. Catalysis and electrolysis with metalloporphyrins. M.: Nauka. 1982, 168 p
72. Bedioui F.Zeolite-encapsulated and clay-intercalated metal porphyrin, phthalocyanine and Schiff-base complexes as models for biomimetic oxidation catalysts: an overview. Coordination Chemistry Reviews. 1995, Vol.144. pp. 39-68
73. Haber J., Matachowski L., Pamin K., Poltowicz J.The effect of peripheral substituents in metalloporphyrins on their catalytic activity in Lyons system. Journal of Molecular Catalysis A. 2003, Vol.198, pp. 215-221
74. Aida T., Inoue S., Kadish KM, Smith KM, Guilard R. The Porphyrin Handbook. - San Diego: Academic Press. 1999, pp. 133
75. Oliveira DC, Sacco HC, Nascimento OR, Iamamoto Y., Ciuffi KJAmino ironporphyrinosilica hybrid materials. Journal of Non-Crystalline Solids. 2001, Vol.284, pp. 27-33
76. Gardolinski JE, Martins HP, Wypych F.,Comportamento Termico da Caulinita Hidratada. Quimica Nova. 2003, Vol.26, pp. 30-35
77. Nakagaki S., Machado GS, Halma M., Marangon AS, Castro KADF, Mattoso N.,

Wypych F.Immobilization of iron porphyrins in tubular kaolinite obtained by an intercalation delamination procedure. Journal of Catalysis. 2006, Vol.242, pp. 110-117

78. Khasanova E.T., Fetisova N.I. Application of porphyrins in medicine. Proc. report 5th All-Union Conference on coordination and physical chemistry of porphyrins. Ivanovo 1988, pp. 34
79. Hisazury H., Misaki T., Miyoshi N. Photoradiation therapy of bladder tumors. Journal of Urology. 1983, Vol.130, pp. 685-687
80. Sergeev P.V., Sviridov HK, Shimanovsky N.L. Contrast agents. M.: Medicine. 1993, 253 p
81. Drugs for the treatment of diseases caused by the human immunodeficiency virus: Application 2138212. Japan, MKI 55 O F 61 K 31/40, C 07 D 487/22 / Totani Harumasa, Kato Norika, Asanaka Yoshiyuki, Kurimura Takashi; Sawai seiyaku K.K., Madisa shinyaku K.K. - 1 1-44133; application 02.23.89; publ. 05/28/90. Kokay tokkyo koko. 199, Ser. 3 (2), №50, pp. 133-139
82. Berezin B.D., Koifman O.I. Metalloporphyrins. Advances in Chemistry.1980, T. 49, №12, pp. 2389-2417
83. Kamogawa Hiromi. Styrene polymers containing hemin residues. Japanese. Pat. class 26/3, F 116/C08F8/42, N 51-8672; publ. 03/18/76
84. Pat. class 26/3 F115/C08F 8/30, N 51-21637 Japan. Method for producing polymers containing porphyrin residues in side chains. Kamogawa H.; publ. 07/05/76
85. Pat. class 16E 64/C07D 487/22, N52-12640 Japan. Method for obtaining polymerizable porphyrin derivatives. Kamogawa Hiromi; publ. 04/21/77
86. Govorov A.G., Korzhenevsky A.B., Koifman O.I. Immobilization of pheophytin b on polyvinyl alcohol. Study of the properties of immobilizers. News of Universities. Chemistry and chem. Technology. 1993, T.36, № 3, pp. 75-81
87. Wohrte P., Paliuras M. Okura I. Polymer - bound porphyrins and their precurcops. Macromol. Chem. 1991, Vol.192, №4, pp. 819-832

СОСТАВ , СТРУКТУРА И ПРИМЕНЕНИЕ НЕФТЯНЫХ МЕТАЛЛОПОРФИРИНОВ (Обзор)

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В обзоре представлен анализ опубликованных научных работ в области металлопорфиринов, содержащихся в природном сырье — нефти. Рассмотрены существующие методы идентификации и методы определения содержания металлопорфиринов в нефтях. Проанализированы методы извлечения порфиринов из остаточных нефтей. Представлены наиболее интересные направления использования металлопорфиринов нефти в синтезе новых химических систем.

Большое внимание уделено рассмотрению возможностей использования металлопорфиринов в качестве ингредиентов в катализе, получении медицинских препаратов для диагностики и лечения различных заболеваний и создании новых композиционных материалов на основе полимеров, получении неорганико-органических гибридных материалов с ценными свойствами.

Ключевые слова: *нефтяные порфирины, методы идентификации, содержание* *порфириновых соединений в нефтяных фракциях, применение, металлопорфириновые катализаторы, новые композиционные материалы.*

NEFT METAL PORFİRİNLƏRİNİN TƏRKİBİ , QURULUŞU VƏ TƏTBİQİ. (İcmal)

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İcmal təbii xammalda - neftdə olan metalloporfirinlər sahəsində çap olunmuş elmi işlərin təhlilini təqdim edir. Mövcud identifikasiya üsulları və yağlarda metalloporfirinlərin tərkibini təyin etmək üsulları nəzərdən keçirilir. Qalıq yağlardan porfirinlərin çıxarılması üsulları təhlil edilir. Yeni kimyəvi sistemlərin sintezində neft metalloporfirinlərindən istifadənin ən maraqlı istiqamətləri təqdim olunur.

Metalloporfirinlərin katalizdə inqrediyent kimi istifadə edilməsi, müxtəlif xəstəliklərin diaqnostikası və müalicəsi üçün dərman preparatlarının alınması və polimerlər əsasında yeni kompozit materialların yaradılması, qiymətli xassələrə malik qeyri-üzvi hibrid materialların alınması imkanlarının nəzərdən keçirilməsinə böyük diqqət yetirilir.

Açar sözlər: *neft porfirinləri, identifikasiya üsulları, neft fraksiyalarında porfirin birləşmələrinin tərkibi, tətbiqi, metal porfirin katalizatorları, yeni kompozit materiallar.*

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SYNTHESIS OF BIO-NANO ADSORBENTS ON THE BASE OF HAZELNUTT SHELLS AND Fe_3O_4 NANOPARTICLES FOR THE REMEDIATION OF OIL POLLUTED WATER

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The study aimed to prepare a new bionanoadsorbent by modifying hazelnut shells (HnSh) with Fe_3O_4 *nanoparticles and evaluating its potential for extracting oil and oil products from real wastewater. The oil sorption capacity of plant-based hazelnut adsorbent and synthesized new bio-nano adsorbent was studied. Optimum time, optimum pH, and optimum adsorption capacity were determined for oil sorption of bio-nanoadsorbent synthesized based on* Fe_3O_4 *with hazelnut shell (HnSh), which is a pure plant of origin adsorbent. From the conducted experiments, it was determined that the pure hazelnut shell can adsorb 61.25% of oil in 30 minutes. To increase the capacity of adsorption, the bio-nanoadsorbent synthesized based on* Fe_3O_4 *with hazelnut shell adsorbs 92.5% of oil in 12 minutes. Synthesizing a bionanoadsorbent based on* Fe_3O_4 *increases the absorption capacity of hazelnut shell, which is a waste of plant origin, and the magnetite property of the nanoparticle enables easy separation of the bio-nanoadsorbent from water. The pH dependence of biosorbent and bionanoadsorbent was determined and studied while determining the optimal conditions of the study. pH 7.5 was determined as the optimal condition.*

Keywords: *hazelnut shell, bio-nanoadsorbent, nanoparticle, sorption, petroleum products*.

INTRODUCTION

Many processes related to the extraction, production, and transportation of oil and oil products affect the environment to varying degrees. Leaks from oil pipelines, pipelines, oil wells, underground storage tanks of gas stations, improper disposal of oil waste, and oil spills are the main sources of surface and groundwater pollution. Removal of hydrocarbons from water contaminated with oil and oil products is an important issue to prevent further water pollution due to environmental problems. The purpose of this study is to apply new technologies using modern methods for the treatment of oil-contaminated waters. Crude oil is a natural liquid that is a complex mixture of organic molecules, mainly hydrocarbons, with different chemical and physical properties [1].

The presence of oil in water bodies poses a high threat to the aquatic environment. The main objective of this study is to investigate the feasibility of using plant origin waste as a biosorbent for cleaning oil and oil products in a water basin. The biosorbent used in this study is a hazelnut shell.

The biosorption method in the treatment of oil-polluted waters is considered to be an emerging method for the treatment of industrial wastewater and the removal of various pollutants [1]. Biosorption technology involves the use of economically inexpensive biological materials that can be obtained from agricultural and plant origin waste. Thus, this technology is the most economically and environmentally friendly technology [2,3].

In our country, hazelnut shell is used more for industrial purposes. Based on literature data, it was determined that the chemical composition of hazelnut shells is different. According to the first study, it was determined that the hazelnut shell contains about 30% hemicellulose, 26% cellulose, 43% lignin, and about 3.3% extractives, while another study found that the hazelnut shell contains 25% hemicellulose, 37% cellulose, and 23% lignin. It is clear from the literature that hazelnut shell is an effective bioabsorbent based on various uses in some studies [3].

The results of our study showed that the biosorption process is pH dependent and hazelnut shell is an effective adsorbent for the absorption of oil from water contaminated with oil and oil products. Thus, the ability of hazelnut shell to absorb oil is 61.25%.

To accelerate the sorption process, a bio-nanoadsorbent modified with nanoparticles was synthesized based on a plant-derived biosorbent. Fe_3O_4 superparamagnetic nanoparticles were used as nanoparticles. Among all iron oxides, Fe_3O_4 has attracted more attention due to its superior magnetic properties. In the last two decades, research on Fe_3O_4 nanoparticles has made significant progress not only in the synthesis of magnetic Fe_3O_4 nanoparticles with a homogeneous core but also in the preparation and application of advanced nanoarchitectures (core-layer, composites, functional surfaces, etc.) [4-8]. Magnetic nanoparticles, Fe_3O_4, are widely used in the purification of water from oil and oil products, as they can be easily separated due to their high magnetism. Based on the experience of our research, it is clear that bio-nanoadsorbents based on newly synthesized hazelnut shells and Fe_3O_4 have higher absorption capacity than pure hazelnut shells of plant origin. Thus, our synthesized bio-nanoadsorbent, hazelnut shell, and Fe_3O_4 -based adsorbent absorb 92.5% of oil.

In our presented article, a new bio-nanoadsorbent based on hazelnut shell and Fe_3O_4 was synthesized, and optimal conditions for the treatment of oil-contaminated water were determined [2-8].

The aim of the dissertation work that we have presented is to apply a modern method based on low-waste and zero-waste technology in the environment. Also, prevention of pollution of the environment from plant of origin and water environment with petroleum products is considered one of the main goals of the work.

EXPERIMENTAL PART

First, to experiment, Fe_3O_4 magnetic nanoparticles were synthesized by the co-precipitation method. Fe_3O_4 magnetic nanoparticles were synthesized by co-precipitation of Fe^{3+} and Fe^{2+} ions. A 0.5% polyethylene glycol solution was added to a 100 mL solution of Fe^{3+} and Fe^{2+} in a molar ratio of 3:2, stirred vigorously for a few minutes, then 100 mL of a 25% ammonium solution was added to the initial iron salts solution under vigorous flow. The deposition was carried out at a temperature of $70\text{-}80^0$ C for 1 hour. The synthesized black precipitate is mixed in a QSonica (Q700) Sonicator ultrasonic device. The resulting black precipitate is separated based on the decantation method (PrO-Analytical by Centurion Scientific Ltd), then washed several times with distilled water and dried for several days. To prevent agglomeration of particles, the precipitated particles are exposed to ultrasonic waves for 10 minutes in an ultrasonicator device poured into a Petri dish and dried in air [2-8].

Then, for the synthesis of bio-adsorbent, the brown shell of the hazelnut is washed and after washing, it is dried in a laboratory oven at a temperature of 60^0C for 24 hours. Dried hazelnut shells are crushed, crumbled, and made into powder. Bio-nano adsorbents are synthesized based on hazelnut shells and Fe_3O_4 nanoparticles in different concentrations (1, 3.5, 10%) (pH=7.5) [1].

The obtained black bio-nano adsorbents are poured into a Petri dish and the drying process is carried out. Synthesized bio-nanosorbents are ground into powder, and the reason for this is that the absorption capacity of the ground bio-nanoadsorbents is greater than that of non-ground bio-nanoadsorbents.

RESULTS AND DISCUSSION

To adsorb oil from water with a hazelnut shell, the first 10 ml of oil is mixed in 100 ml of H_2O. 0.5 grams of ground hazelnut shell is added to the mixed solution at room temperature, and the time dependence of the oil absorption of the hazelnut shell is determined [2-8].

0.25 in addition to 0.5 grams of hazelnut shell; 1; 1.5; 3; the experiment is repeated with gram hazelnut shell.

During the experiment, the sorption was first repeated depending on both the amount of hazelnut shell and, accordingly, the time. To determine the amount and time of the optimal biosorbent in the initial stage, 0.25 as a pure biosorbent; 0.5; 1; 1.5; the oil absorption experiment of 3 g of hazelnut shell from water mixed with oil for 1, 2, 4, 5, 6, 8, 10, 12, 15, 20, 30, 60, 120 minutes was carried out. The conducted experiment is shown in figure 1 and it was determined that 0.25 g of hazelnut shell is 29.3% in 60 minutes, 0.5 g of hazelnut shell is 61.25% in 30 minutes, 1 g of hazelnut shell is 70.5% in 20 minutes, 1.5 g hazelnut shell can absorb 72.6% of oil in 15 minutes and 3 g of hazelnut shell can absorb 99.75% of oil in one minute [8-10].

The purpose of these experiments is to determine the optimal time and amount of oil absorption by the hazelnut shell. Thus, it was determined from the conducted experiment that the optimal amount of hazelnut shell is 0.5 g, and the optimal time for absorption is 15 minutes. Each experiment was conducted at room temperature (21.5^0C).

After determining the optimal amount of hazelnut shell and the absorption time, the experiment of oil adsorption through bio-nanoadsorbents synthesized and obtained bio-nanoadsorbents based on hazelnut shell+ Fe_3O_4 nanoparticles to increase the oil sorption capacity of hazelnut shell is repeated as a function of time at room temperature [9-12].

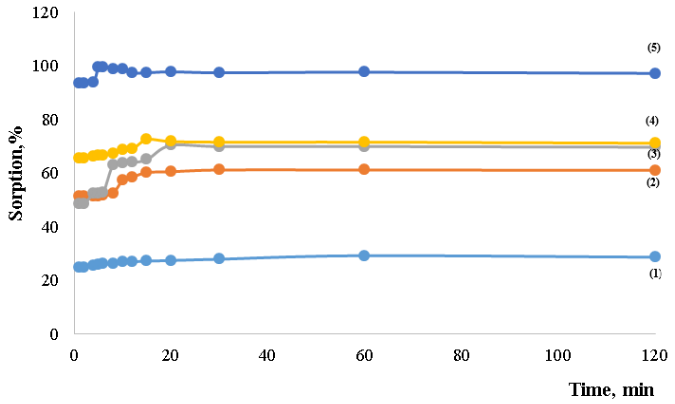


Fig.1. Dependence of the sorption on time (1) 0.25 g of HnSh; (2) 0.5 g of HnSh; (3) 1 g hazelnut shell; (4) 1.5 g of HnSh; (5) 3 g HnSh + 10 ml oil

An oil sorption experiment of pure biosorbent hazelnut shell was carried out in the oil adsorption process of newly synthesized bio-nanoadsorbents.

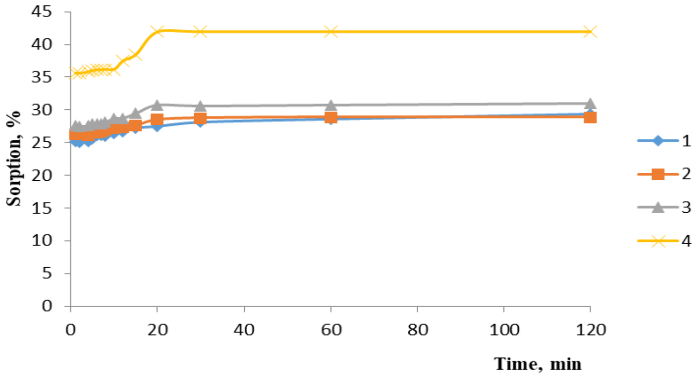


Fig.2. Optimum oil absorption time of 0.25 g bio-nanoadsorbent; (1) HnSh + 1%Fe_3O_4, (2) HnSh + 3%Fe_3O_4, (3) HnSh + 5%Fe_3O_4, (4) HnSh + 10%Fe_3O_4

Based on the synthesized biosorbent + 1, 3, 5, 10% Fe_3O_4, the time dependence of oil absorption of the new bio-nanoadsorbent was determined. The experiment is repeated for the optimal amount and time of bio-nanoadsorbent. 0.25 g 1% bio-nanoadsorbent 28.6% in 60 minutes, 3% bio-nanoadsorbent in 30 minutes, 5% and 10% bio-nanoadsorbent 30.75% and 42% oil absorption in 20 minutes have the ability.

The absorptions shown in figure 2 and mentioned above are the optimal absorption times and amounts of the bio-nanoadsorbent synthesized based on 0.25 g of different percentages of hazelnut shell+ Fe_3O_4.

After, the experiment was repeated with the amount of 1, 3, 5, 10% of 0.5 g of bio-nanoadsorbent.

It can be seen from fig.3 that for 0.5 g of bio-nanoadsorbent, 58.75% oil adsorption for 60 minutes with 1%, 81.25% for 20 minutes with 3%, 87.5% for 20 minutes with 5%, and 92.5% for 12 minutes for 10% bio nanoadsorbent. has the ability. The noted absorptions are the optimal absorption times and amounts of bioanoadsorbent synthesized based on 0.5 g of different percentages of hazelnut shell+ Fe_3O_4 [11-17].

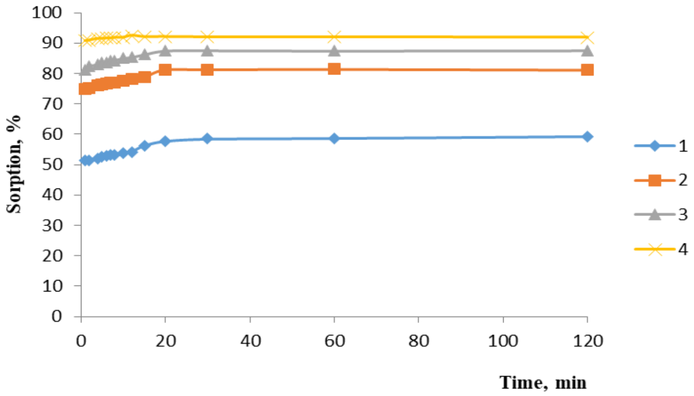
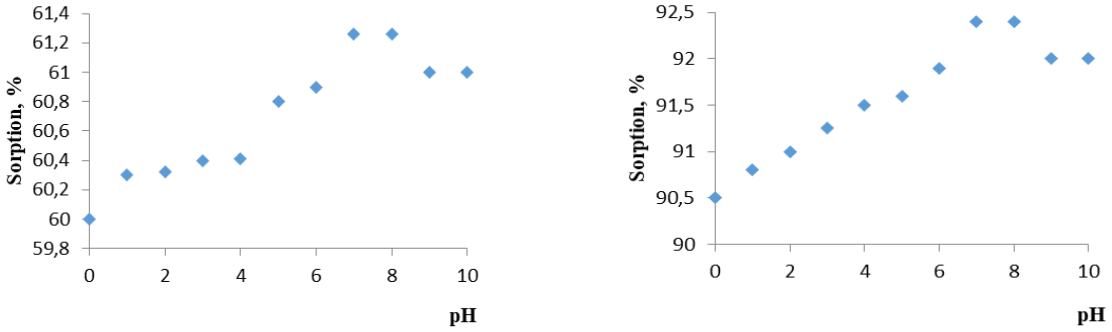


Fig.3. Dependence of optimal absorption time of 0.5 g bio-nanoadsorbent; (1) HnSh+ 1%Fe_3O_4, (2) HnSh + 3%Fe_3O_4, (3) HnSh + 5%Fe_3O_4, (4) HnSh + 10%Fe_3O_4

The pH dependence experiment of bioadsorbent and bio-nanoadsorbent was carried out [17, 18].



a) b)

Fig.4. Dependence of oil absorption of bio-nanoadsorbent on pH; a) HnSh and b) HnSh + Fe_3O_4

Figure 4 shows the pH dependence of biosorbent and bio-nanoadsorbent adsorption of oil from water. From fig.4, it was determined that at pH 0, biosorbent oil adsorption was 60%, and bio-nanoadsorbent adsorption was 90.5%. According to the conducted experiments, it was determined that pH 7.5 is the optimal environment for bio-nanoadsorbent based on hazelnut shell and hazelnut shell + Fe_3O_4 to absorb oil. So, as shown in figure 3 and at pH=7.5, hazelnut shell absorbs 61.2% of oil, and bionanosorbents based on hazelnut shell+ Fe_3O_4 sorbs about 92.5% of oil.

CONCLUSION

As a result of the research, water contaminated with oil and oil products was cleaned with newly synthesized adsorbents based on pure hazelnut shell and hazelnut shell and Fe_3O_4 nanoparticles. The optimal time, pH, and amount of oil absorption of bio-nanoadsorbents and pure hazelnut shell, that is, the optimal conditions of the adsorption process, were determined. The optimal adsorption capacity of biosorbent hazelnut shell, which is a plant origin waste, is 61.25%, and the optimal adsorption capacity of the new bio-nanoadsorbent synthesized based on hazelnut shell and Fe_3O_4 nanoparticles is 92.5%.

It was determined from the conducted experiment that Fe_3O_4 nanoparticles are the reason for increasing the adsorption capacity of the synthesized bio-nanoadsorbent. The determined results show that the main goal of the research work is the implementation of low-waste and zero-waste technology. This is explained by the fact that tons of hazelnut shells are regularly thrown into the environment every season. Oil and oil products pollute the water environment every day. Experiments show that the treatment of both environments polluted with plant origin waste and water polluted with oil is possible with the help of newly synthesized hazelnut shell Fe_3O_4 nanoparticles.

REFERENCES

1. Shartooh S.M., Shartooh S.M., Hiyaly S.A.K. Al. Pomegranate Peels as Biosorbent Material to Remove Heavy Metal Ions from Industerial Wastewater, İraqi Journal of Science. 25 October, 2018, pp.823-831
2. Ramazanov M., Shirinova H., Hajiyeva F. The impact of manufacturing technology, of the polypropylene matrix and iron oxide nanoparticles based magnetodielectric nanocomposites on electrophysical parameters. Mater. Chem. P hys. 2020, Vol.253,№ 1, pp. 123287
3. Ramazanov M., Shirinova H., Hajiyeva F., et al. The relation between the composition, structure and absorption properties of ultra-high frequency radio waves of poly (vinylidene fluoride)/magnetite nanocomposites Int. J. Mod. Phys. B, 2019, Vol.33, №10, pp.1950083, doi:10.1142/S0217979219 500838
4. Ramazanov M., Maharramov A., Ali-zada R. et al. Theoretical and experimental investigation of the magnetic properties of polyvinylidene fluoride and magnetite nanoparticles-based nanocomposites. J. Theor. Appl. Phys. 2018, Vol.12, № 1, pp. 7-13, doi:10.1007/s40094-018-0282-3
5. Ramazanov M., Maharramov A., Hajiyeva F. et al. The Effect of the Temperature–Time Mode of Crystallization on the Morphology and Thermal Properties of Nanocomposites Based on Polypropylene and Magnetite. Journal of Inorg Organomet Polym Mater. 2018, Vol.28, № 3, pp.1171-1177, https://doi.org/10.1007/s10904-017-0767-6
6. Ramazanov M, Maharramov A, Palma L et al. Negative magnetoresistance of polymer nanocomposites on the basis of PP+Fe_3O_4 and PVDF+Fe_3O_4 in the magnetic field. Ferroelectr , 2018, Vol.537, №1, pp. 191 -197
7. Ramazanov M. A., Shirinova H. A., Hajiyeva F. V., and Karimova, A. Influence of Temperature-Time mode of crystallization on electrophysical characteristics of the Polypropylene Magnetite nanocomposite. Integr. Ferroelectrics, 2019, Vol.201, №1, pp.218–223, https://doi.org/10.1080/10584587.2019.1668712
8. Ramazanov M., Shirinova H., Hajiyeva F. et al. Structure and magnetic properties of PP+Fe_3O_4 nanocomposites depending on manufacturing techniques. Int. J. Mod Phys. B, 2019, Vol.33, №27, pp.1950315, doi:10.1142/S0217979219503156

9. Valiyeva G., Bavasso I., Palma Di L., Hajiyeva S. R., Ramazanov M. A., Hajiyeva F. V., Synthesis of Fe/Ni Bimetallic Nanoparticles and Application to the Catalytic Removal of Nitrates from Water, Nanomaterials. 2019, №8, pp. 1130
10. Valiyeva G., Palma L., Hajiyeva S., Ramazanov M.A., Hajiyeva F.V., Maharramov A., Gasimov E., Rzayev F., Reuse of bimetallic nanoparticles for nitrate reduction IEEE Transactions on Nanotechnology. 2023, № 22, pp. 613–619
11. Abdullayeva E.M., Hajıyeva F.V. Catalytical removal of Coomassie Brilliant Blue R-250 dye bu Fe_3O_4 magnetite nanoparticles, Advanced Physical Research. 2021, Vol.3, №2, pp. 93-98
12. Choi H. and Cloud R. M., “Natural sorbents in oil spill cleanup,” Environmental Science and Technology. 1992, Vol.26, № 4, pp. 772-776
13. Mousavi S.M., Hashemi S. A., Esmaeili H., Amani A. M. and Mojoudi F., Synthesis of Fe_3O_4 nanoparticles modified by oak shell for treatment of wastewater containing Ni (II) Acta Chim, Slow. 2018, №65, pp. 750-756
14. Stjepanovi´c M., Veli´c N.and Habuda-Stani´ M. Modified Hazelnut Shells as a Novel Adsorbent for the Removal of Nitrate from Wastewater, Water. 2022, Vol.14, №5, pp.816
15. Botahala L, Malailak Y., Maure H. S., Karlani H., Determination of effectiveness absorption of the rice husk and hazelnut shell to purification used cooking oil, Indonesia Chimica Acta, June 2019, Vol.12. №1, pp. 19-28 doi:10.20956/ica.v12i1.6172
16. Silva V.A.J., Andrade P.L., Silva M.P.C., and et.al., Synthesis and characterization of Fe_3O_4 nanoparticles coated with fucan polysaccharides, Journal of Magnetism and Magnetic Materials. 2013, Vol.343, pp. 138-143
17. Zhuang L., Zhang W., Zhao Y., and et. al., Preparation and Characterization of Fe_3O_4 Particles with Novel Nanosheets Morphology and Magnetochromatic Property by a Modified Solvothermal Method, Scientific reports. 2015, Vol.5, № 1, pp. 9320, doi: 10.1038/srep09320
18. Richa Jain, Recent advances of magnetite nanomaterials to remove arsenic from water, RSC Adv. 2022, №12, pp. 32197–32209
19. Willard H. H., et al., Instrumental Methods of Analysis, Journal of Chemical Education, 7th edn. 1988, pp. 896
20. Yousef R. Qiblawey H. El-Naas M. H. Adsorption as a Process for Produced Water Treatment: a Review. Processes. 2020, №8, pp. 1657
21. Fawzia I. El-Dib, Dalia E. Mohamed, Omnia A.A. El-Shamy, Study the adsorption properties of magnetite nanoparticles in the presence of different synthesized surfactants for heavy metal ions removal, Egyptian journal of petroleum. 2020, Vol.29, pp. 1-7
22. Rajput, S.; Pittman, C.U., Jr.; Mohan, D. Magnetic magnetite (Fe_3O_4) nanoparticle synthesis and applications for lead (Pb^{2+}) and chromium (Cr^{6+}) removal from water. *J. Colloid* Interface Sci. 2016, Vol.468, pp. 334–346
23. Anjum M. Miandad R. Waqas M. *et al.*, Remediation of wastewater using various nano-materials. Arabian J. Chem. 2019, Vol.12, pp. 4897–4919
24. Lata S. Samadder S. R. Removal of arsenic from water using nano adsorbents and challenges: a review. J. Environ. Manage. 2016, Vol.66, pp. 387–406

СИНТЕЗ БИОНАНОАДСОРБЕНТОВ НА ОСНОВЕ СКОРЛУПЫ ФУНДУКА И НАНОЧАСТИЦ Fe_3O_4 ДЛЯ ОЧИСТКИ НЕФТЕЗАГРЯЗНЕННЫХ ВОД

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Целью исследования было получение нового био-наноадсорбента путем модификации скорлупы фундука наночастицами Fe_3O_4 и оценка его возможностей для извлечения нефти и нефтепродуктов из реальных сточных вод. Изучена нефтесорбционная способность растительного адсорбента фундука и синтезированного нового бионаноадсорбента. Определены оптимальное время, оптимальное значение pH и оптимальная адсорбционная емкость нефтесорбции бионаноадсорбента, синтезированного на основе Fe_3O_4 со скорлупой фундука, который является чистым растительным адсорбентом. В результате проведенных экспериментов установлено, что чистая скорлупа фундука обладает способностью адсорбировать 61,25% масла за 30 минут. С целью повышения способности адсорбции бионаноадсорбент, синтезированный на основе Fe_3O_4 со скорлупой фундука, адсорбирует 92,5% масла за 12 минут. Синтез бионаноадсорбента на основе Fe_3O_4 увеличивает поглотительную способность скорлупы фундука, являющейся отходом растительного происхождения, а магнетитовое свойство наночастицы позволяет легко отделить бионаноадсорбент от воды. Определена и изучена зависимость pH биосорбента и бионаноадсорбента при определении оптимальных условий исследования. pH 7,5 был определен как оптимальное состояние.

Ключевые слова: *скорлупа фундука, бионаноадсорбент, наночастицы, сорбция, нефтепродукты.*

NEFTLƏ ÇIRKLƏNMIŞ SULARIN TƏMIZLƏNMƏSI ÜÇÜN FINDIQ QABIQLARI VƏ Fe_3O_4 NANOHISSƏCIKLƏRI ƏSASINDA BIO-NANOADSORBENTLƏRIN SINTEZI

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Tədqiqatın məqsədi fındıq qabıqlarının Fe_3O_4 *nanohisəciklərlə modifikasiyası ilə yeni bionanoadsorbent hazırlamaq və onun real tullantı sularından neft və neft məhsullarının çıxarılması potensialını qiymətləndirməkdən ibarət idi. Bitki mənşəli fındıq adsorbentin və sintez olunmuş yeni bio-nanoadsorbentin nefti sorbsiya qabiliyyəti öyrənildi. Təmiz bitki mənşəli adsorbent olan fındıq qabığı və fındıq qabığı ilə* Fe_3O_4 *əsasında sintez edilmiş bio-nanoadsorbentin nefti sorbsiya edərkən optimal zaman, optimal pH və optimal adsorbsiya tutumu müəyyən edilmişdir. Aparılan təcrübələrdən müəyyən edilmişdir ki, təmiz fındıq qabığı 30 dəqiqədə 61,25 % nefti adsorbsiya etmək qabiliyyətinə malikdir. Adsorbsiyanın tutumunu artırmaq məqsədilə sintez etdiyimiz fındıq qabığı ilə* Fe_3O_4 *əsasında sintez edilmiş bio-nanoadsorbent isə 12 dəqiqədə 92,5 % nefti adsorbsiya edir.* Fe_3O_4 *əsasında bionanoadsorbentin sintez edilməsi bitki mənşəli tullantı olan fındıq qabığının uduculuq qabiliyyətinin artırılmasına və nanohissəciyin maqnetit xüsusiyyətinin olması isə bio-nanoadsorbentin sudan rahat şəkildə ayırılmasına şərait yaradır. Tədqiqatın optimal şəraiti müəyyən edilərkən biosorbentin və bionanodsorbentin pH-dan asılılığı müəyyən edilərək tədqiq edilmişdir. Optimal şərait olaraq pH 7,5 müəyyən edilmişdir.*

Açar sözlər: *fındıq qabığı, bio-nanoadsorbent, nanohissəcik, sorbsiya, neft məhsulları.*

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CATALYTICAL DEGRADATION OF ORANGE II DYE VIA FENTON REACTIONS USING IRON OXIDE NANOPARTICLES

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In this work, was investigated of catalytic oxidative degradation of the Orange II synthetic dye by hydrogen peroxide H_2O_2 *in the presence of* Fe_3O_4 *magnetite nanoparticles. After characterizing the synthesized nanoparticles by various physical methods for the degradation of dyes, we studied them as photo-Fenton catalysts and investigated their photocatalytic activity in the presence of* H_2O_2 *under sunlight. To understand the catalytic performance of* Fe_3O_4 *magnetic nanoparticles, we have chosen Orange II dye as a pollutant. We also varied the reaction parameters including solution pH and* H_2O_2 *concentration to test the effect of Orange II dye on the photocatalytic activity. Furthermore, its photocatalytic efficiency along with structural stability for* Fe_3O_4 *magnetic nanoparticles were also discussed.*

Keywords: *magnetite, Orange, hidrogen peroxide, nanoparticles, synthesis*

INTRODUCTION

The production of dye materials in the industry is increasing and developing rapidly day by day. The paint industry is a small part of the chemical industry. About 800,000 tons of paint are produced in the world annually. Synthetic dyes are used in industries such as textiles, paper printing, food, pharmaceuticals, leather and cosmetics [1, 4]. In modern times, a wide variety of dyes are formed by applying numerous chemical compounds and are used in various fields. Toxic nature of synthetic dyes has become a cause of grave concern to environmentalists. Use of synthetic dyes has an adverse effect on all forms of life [1, 2].

Sulfur, naphthol, nitrates, acetic acid, soaps, chromium compounds of enzymes, and heavy metals such as copper, arsenic, lead, cadmium, mercury, nickel, cobalt, and some auxiliary chemicals, which are the main wastes of the synthetic dye industry, are highly toxic wastes. Sulfur, naphthol, nitrates, acetic acid, soaps, chromium compounds of enzymes, and heavy metals such as copper, arsenic, lead, cadmium, mercury, nickel, cobalt, and some auxiliary chemicals, which are the main wastes of the synthetic dye industry, are highly toxic wastes.These organic materials often produce byproducts that are carcinogenic and undesirable. If these wastes enter the agricultural fields, they lose the fertility of the soil [3, 4].

Dye waste is dangerous for the environment, in particular, the presence of dye waste in environmental water bodies is of increasing concern to environmentalists. In order to prevent this pollution, methods of treatment of dye waste are being developed. Dye waste must be treated before being released into the environment to minimize severe impacts on it [4].

Orange II dye, like other Azo dyes, is a very harmful, biologically degradable toxic dye. Orange II is acidic in nature. When this paint enters water bodies, it dissolves well there, so it easily mixes with water and has a toxic effect on the aquatic biosphere. Since Orange II has an azo group, it shows the characteristics of all dyes of this group.

These groups of dyes are mixed with industrial effluents and have a harmful negative effect on the human body and aquatic organisms. In addition, it creates an ecotoxic effect in the environment. When Orange II dye enters water bodies, it reduces the transmission of sunlight in water and increases water turbidity.

Dye waste is usually discharged into the environment as production waste from the textile industry. Orange II dye is also used as a colorant in pharmaceutical and cosmetic products. The biggest disadvantage of OII is that it leaches into water bodies without undergoing degradation as a highly persistent compound in biological treatment plants [5, 12].

In wastewater treatment, various advanced oxidation processes such as photocatalysis, electrochemical catalysis and Fenton/photo-Fenton process have attracted great attention of researchers [5]. The Fenton and photo-Fenton processes are used in unison to oxidize transient species of organic pollutants by generating (·OH). The OH radical produced by the decomposition of H_2O_2 in the Fenton reaction played an important role in the treatment of refractory pollutants. Alternatively, H_2O_2 is more readily converted to ·OH during the photo-Fenton reaction in the presence of iron oxide nanoparticles [6, 13]. Therefore, to overcome the drawbacks of the slow dynamics of the traditional Fenton process, the photo-Fenton reaction is considered a smart method for the degradation of various organic dyes [7, 14, 15].

To date, there are many known catalysts for photo-Fenton reactions, however, iron-based materials exhibit good photoactivity [8]. The advantage of iron oxides is that they are non-hazardous, environmentally friendly and abundant on earth. Also, these oxides can be easily prepared in the laboratory [9, 16-18].

In many parts of the world, scientists have applied nanoparticles for the photodegradation of Orange II dyes and effective results have been achieved. Degradation studies show that nanoparticles degrade an average of 93-96% of Orange II in aqueous solution. The effects of various parameters such as initial concentration of dyes, pH, re-catalysts and catalyst dosage were also studied [9, 10, 11, 19-22].

EXPERİMENTAL PART

Materials:

Iron sulphate heptahydrate ($FeSO_4 \times 7H_2O$, 98% chemically pure, PLC 141362), ferric chloride hexahydrate ($FeCl_3 \times 6H_2O$, 98% chemically pure, PLC 141358), ammonium hydroxide (25% PLC 141129), polyethylene glycol-6000 (PEG-6000, PLC 163325), Orange II sodium salt (PLC 171545C), hydrogen peroxide (H_2O_2).

The molecular weight of Orange II dye dye used as a dye in the experiments is 350.32 g/mol and its chemical structure is shown in figure 1.

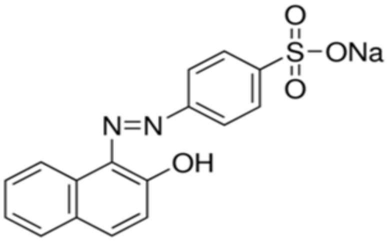

Fig. 1. Chemical structure of the Orange II sodium salt

Synthesis process flow for Fe_3O_4 magnetic nanoparticles

The preparation stage of Fe_3O_4 nanoparticles was carried out through the presence of PEG-6000 SAM (surfactant). During the process, Fe^{3+} and Fe^{2+} ions were taken in a ratio of 3:2 and co-precipitated. In the preparation process of this stage, ammonium solution was used as a precipitation agent and nanoparticles were prepared under nitrogen atmosphere. After this step, a black precipitate was formed, which was washed with distilled water until pH=7. The resulting mixture was then centrifuged in an ultracentrifuge to separate the obtained black precipitate from the main mass and then redispersed in water. Then, the magnetic nanoparticles dispersed in water were subjected to ultrasonic treatment in a VSX 500 ultrasonic device to prevent the formation of aggregates and agglomerates at the end of the chemical reaction. In such a process, the ultrasonic power was 500 W, the ultrasonic frequency was 20 kHz, and the sonication time was 10 minutes. At the last stage, the powders exposed to ultrasound were transferred to a Petri dish and air-dried for 24 hours.

About the characterization.

The sizes of nanoparticles were determined using an Integra-Prima atomic force microscope (AFM) (NT-MDT, Zelenograd). Special silicon probes coated with a gold shell with a radius of 20 nm and a resonance frequency of 87-230 kHz were used for measurements. AFM scanning was performed in a semi-contact mode with a scanning speed of 1.969 Hz. UV-spectra of the samples were carried out on a Specord 250 Plus device. The process was carried out at room temperature. The wavelength is 200-700 nm.

The process of paint degradation.

All the experiments conducted during the process of degradation of paint were checked in laboratory conditions. At this time, the pH change was taken in the range of 1÷11. The process was carried out at room temperature and on the surface of Fe_3O_4 magnetic nanoparticles catalyst. Hydrogen peroxide was used as an oxidant in the process. The kinetics of its decomposition process on the surface of the catalyst was investigated. Thus, 0.1 grams of Coomassie Brilliant blue R-250 was mixed in 100 ml volume of distilled water until completely dissolved. Then, 0.1 ml of Fe_3O_4 colloid solution, 0.5 ml of dye solution, 0.1 ml of hydrogen peroxide and the specified amount of CBB P-250 dye were added to the flasks taken (11 flasks). For each flask, different time intervals have been defined in carrying out the process. Quantitative analysis of CBB R-250 degradable dye was measured in a spectrophotometer. The spectra of the paint were studied by taking them in the interval of 0÷24 hours.

RESULTS AND DISCUSSION

As can be seen from fig.1 AFM 2D (a) and 3D (b) magnetite nanoparticles synthesized in the presence of polyethylene glycol. The scan size was 1200×1200 nm. It is evident from the AFM images that the synthesized nanoparticles are homogeneous and monodisperse. İt seems from fiq.2 the histogram of the size distribution of Fe_3O_4 nanoparticles obtained from the AFM results. According to the histogram, it is evident that the distribution of nanoparticles varies in a narrow range of particle sizes and the average size of Fe_3O_4 nanoparticles is 8-13 nm. AFM analysis proves that the nanoparticles are stabilized well enough in the presence of PEG-6000.

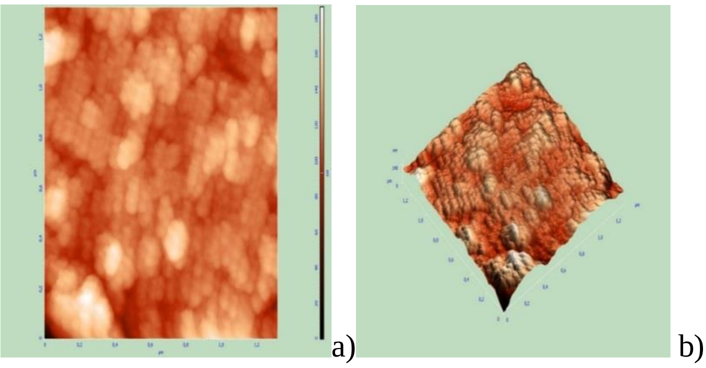
a) b)

Fig. 1. AFM 2D (a) and 3D (b) images of Fe_3O_4 nanoparticles

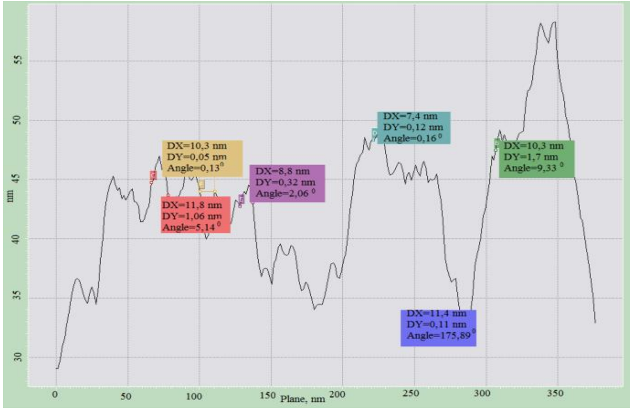

Fig.2. Histogram of nanoparticle size distribution.

Fig.3 shows the UV spectra of Orange II + H_2O_2 + Fe_3O_4 depending on the pH of the medium. As can be seen in the spectra, maxima are observed at 308 nm and 483 nm, which are characteristic maxima for the Orange II dye. As can be seen, high decomposition of the dye is observed in an acidic medium and maximum degradation is achieved at pH=3. Oxidative degradation of Orange II dye was high at low pH. This is due to an increase in the concentration of Fe^{2+} ions, which are responsible for the formation of free radicals. In an alkaline environment, the concentration of free radicals decreases at high values of pH. This leads to a decrease in the speed of paint decomposition.

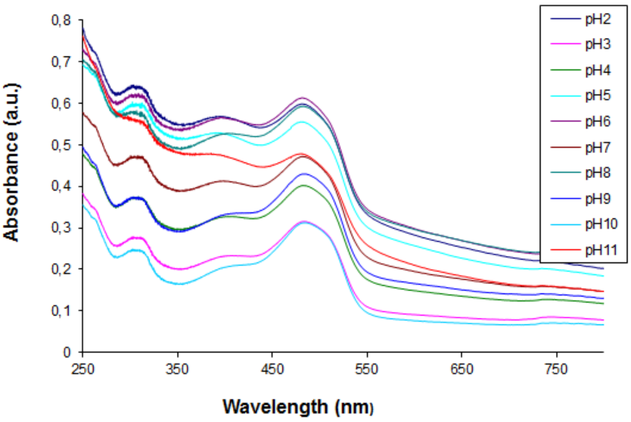

Fig.3. UV-Vis spectrum of Orange II + H_2O_2 + Fe_3O_4 depending on the pH of the medium

Fig.4 shows the UV spectra of Orange II in the presence of the oxidizer H_2O_2 depending on the concentration of magnetite nanoparticles Fe_3O_4. It seems from the figure that the maximum degradation of the paint occurs at concentrations as low as 0.2 g/l of magnetite nanoparticles.With an increase in the concentration of Fe_3O_4 nanoparticles (0.4; 0.6; 2 g/l), additional degradation almost does not occur, and at a concentration of 4 g /l, the decomposition of the dye practically slows down. The slowdown in dye degradation with an increase in the concentration of nanoparticles is explained by the agglomeration of nanoparticles due to their increase in size and, consequently, an underestimation of the catalytic activity of the nanoparticles.

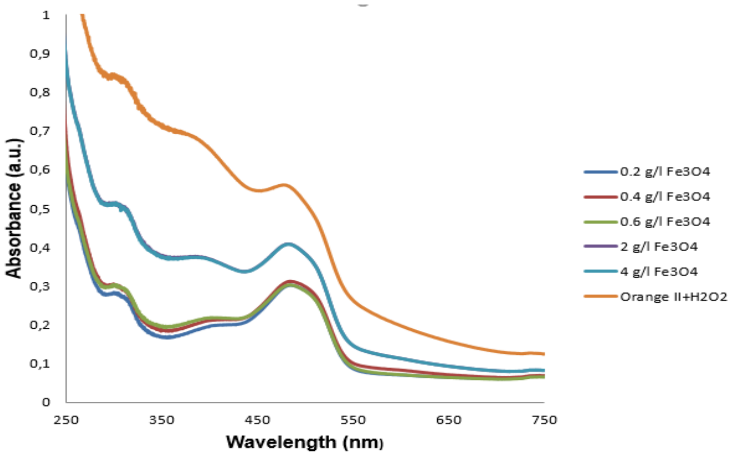

Fig.4. UV-Vis spectra of Orange II+H_2O_2 system in the dependence ofconcentration of Fe_3O_4 nanoparticles

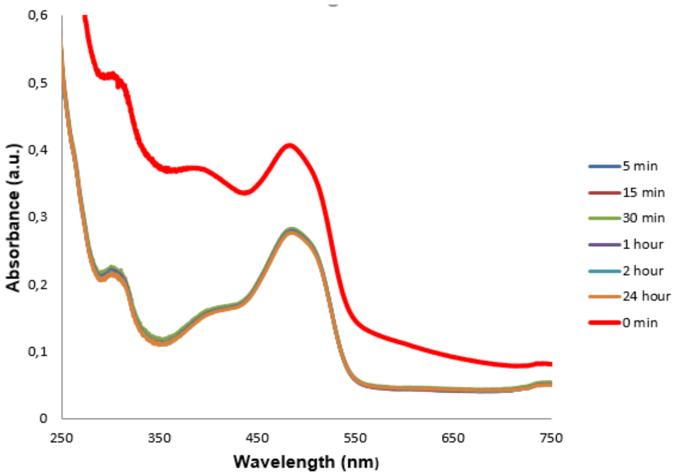

Fig.5. UV-Vis spectra of Orange II +H_2O_2+Fe_3O_4 system in the dependence of the time

Figure 5 shows the UV spectra of Orange II in the presence of H_2O_2 and Fe_3O_4 as a function of time. It was found that the degradation of Orange II during the first 5 minutes is almost 50%. Further increase in time does not affect the rate of oxidative degradation, which can be explained by the underestimation of the catalytic activity of magnetite nanoparticles over time.

CONCLUSION

The presented work presents the results of works on catalytic degradation of the dye Orange II in the presence of the oxidizer H_2O_2 and the catalyst-magnetite nanoparticles. It was found that the maximum degradation of Orange II is observed in an acidic medium at pH=3, which is explained by the increase in the concentration of free radicals. It was also determined that the dye is decomposed at low concentrations of magnetite nanoparticles of 0.2 g/l for 5 minutes and a further increase in the concentration of nanoparticles does not affect the degradation rate. A decrease in the degradation rate with an increase in the concentration of nanoparticles and time is explained by the agglomeration of nanoparticles and a decrease in their catalytic ability.

REFERENCES

1. Mohamed A. H, Ahmed E.N. Health and Environmental Impacts of Dyes: Mini Review.American Journal of Environmental Science and Engineering. 2017, Vol.1 ,№3,pp. 64-67, doi: 10.11648/j.ajese.20170103.11
2. Jiuyang L, Wenyuan Y, Ming X, Dong H.S, Jianquan L, Yinhua W, Bart V.B. Environmental impacts and remediation of dye-containing wastewater. Nature Reviews Earth & Environment. 2023, Vol.4,pp. 785–803
3. Javid M., Manoj S. Impact of Textile Dyes on Human Health and Environment. In book. Impact of Textile Dyes on Public Health and the Environment. 2020, doi: 10.4018/978-1-7998-0311-9.ch008
4. Vanitha K, Jibrail K. Efficiency of various recent wastewater dye removal methods: A review. Journal of Environmental Chemical Engineering. 2018,Vol.6, Issue 4, pp. 4676-4697
5. Tusar N.N, Maučec D, Rangus M, Arčon I, Mazaj M, Cotman M, Pintar A, Kaučič V. Manganese Functionalized Silicate Nanoparticles as a Fenton-type Catalyst for Water Purification by Advanced Oxidation Processes (AOP).Adv. Funct. Mater. 2012, pp. 820– 826, doi: 10.1002/adfm.201102361
6. Liu, Y, Jin, W, Zhao, Y, Zhang, G, Zhang, W. Enhanced Catalytic Degradation of Methylene Blue by α-Fe_2O_3/Graphene Oxide via Heterogeneous Photo-Fenton Reactions. Appl. Catal., B. 2017, pp. 642 -652
7. Arnab S, Samir K.P, Subhra J. Synthesis of Template-Free Iron Oxyhydroxide Nanorods for Sunlight-Driven Photo-Fenton Catalysis.ACS Omega. 2021, Vol.6, Issue 42, pp. 26-35
8. Wang X, Wang J, Cui Z, Wang S, Cao M. Facet Effect of α-Fe_2O_3 Crystals on Photocatalytic Performance in the Photo-Fenton Reaction. RSC Adv. 2014, pp. 34387– 34394, doi: 10.1039/c4ra03866e
9. Xinyu Z, Jianfeng M, Changhai F, Mingguo P, Sridhar K. Enhancement of photo-fenton-like degradation of orange II by MnO_2/NiO nanocomposite with the synergistic effect from bisulfite. Journal of Alloys and Compounds. 2019, Vol.785, pp. 343-349, doi.org/10.1016/j.jallcom.2019.01.197
10. Tamanna G, Shujaat A, Idrees K, Ibrahim K, Mazen A, Ahad A.A, Mamdouh A, Khalid S. Photodegradation of orange II dye using p-n junction NiO/TiO2 composite, and assessment of its biological activities. Journal of Saudi Chemical Society. 2023, Vol.27, Issue 4. pp. 101654,.https://doi.org/10.1016/j.jscs.2023.101654

11. Naseer A.K, Khalid S, Idrees K, Tamanna G, Muhammad S, Ala U, Ivar Z. Efficient photodegradation of orange II dye by nickel oxide nanoparticles and nanoclay supported nickel oxide nanocomposite. Appl Water Sci 12, 2022,pp. 131, 2022, https://doi.org/10.1007/s13201-022-01647-x
12. Zahra N, Mahboobeh D, Seyyed A.M, Neemat J, Susana S.M, Ali A. Efficient sonocatalytic degradation of orange II dye and real textile wastewater using peroxymonosulfate activated with a novel heterogeneous TiO_2–FeZn bimetallic nanocatalyst. Journal of the Iranian Chemical Society. 2023, Vol.20. pp. 1589–1603
13. Naeim E, Teng B, Hongmei L, Graeme J.M, Godwin A.A, Jianxi Z, Runliang Z, Xiaoliang L, Hongping H, Yunfei X. Catalytic degradation of Orange II in aqueous solution using diatomite-supported bimetallic Fe/ Ni nanoparticles RSC Adv. 2018, Vol.8, pp. 7687–7696
14. Razium A.S, Ayman N.S, Syed T.H.S, Nazar H.K, Mohammad R.S, Keith R.H. Catalytic Reductive Degradation of Methyl Orange Using Air Resilient Copper Nanostructures. Journal of Nanomaterials 2015, Article ID 136164
15. Masaku K., Keneiloe S., Gebhu N., Nosipho M. Degradation Kinetics of Methyl Orange Dye in Water Using Trimetallic Fe/Cu/Ag Nanoparticles Catalysts. 2021, pp. 428, https://doi.org/10.3390/catal11040428
16. Divya N, Bansal A, Jana A.K. Photocatalytic degradation of azo dye Orange II in aqueous solutions using copper-impregnated titania. J. Environ. Sci. Technol. 2013.,Vol.10 , pp. 1265–1274
17. Chih-Wei T. Study of Photocatalytic Degradation of Methyl Orange on Different Morphologies of ZnO Catalysts. Modern Research in Catalysis. 2013, Vol.2 №.2, pp. 1-6. article id:29894doi:10.4236/mrc.2013.22003
18. Honghai W, Xiaowen D, Dayi D, Yufeng G, Liguo Z, Guangping H. Decolourization of the azo dye Orange G in aqueous solution via a heterogeneous Fenton-like reaction catalysed by goethite. Environmental Technology. 2012, Vol. 3, №3 ,pp. 1545–1552
19. Vinoda B.M, Vinuth M, adav D.B. Photocatalytic Degradation of Toxic Methyl Red Dye Using Silica Nanoparticles Synthesized from Rice Husk Ash J Environ Anal Toxicol. 2015, pp. 5-6
20. Rahat J, Umair Y.Q. Catalytic Oxidation Process for the Degradation of Synthetic Dyes: An Overview Int J. Environ. Res. Public Health. 2019, Vol.16, pp. 2066
21. Mansouri M, Mozafari N, Bayati B, Setareshenas N. Photo-catalytic dye degradation of methyl orange using zirconia–zeolite nanoparticles. Bull. Mater. Sci. 2019, Vol.42, pp. 230
22. Makeswari M, Saraswathi P. Photocatalytic Degradation Of Methyl Orange From Aqueous Solution By Using Chitosan Silica Composite. 2021,Vol.10, Issue 2, pp. 2320- 2330

КАТАЛИТИЧЕСКАЯ ДЕГРАДАЦИЯ КРАСИТЕЛЯ ORANGE II ПОСРЕДСТВОМ ФЕНТОНОВЫХ РЕАКЦИЙ С ИСПОЛЬЗОВАНИЕМ НАНОЧАСТИЦ ОКСИДА ЖЕЛЕЗА

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В данной работе исследована каталитическая окислительная деградация синтетического красителя Orange II пероксидом водорода H_2O_2 в присутствии наночастиц магнетита Fe_3O_4. После характеристики синтезированных наночастиц различными физическими методами для деградации красителей, мы изучили их как фотокатализаторы Фентона и исследовали их фотокаталитическую активность в присутствии H_2O_2 под солнечным светом. Чтобы понять каталитическую эффективность магнитных наночастиц Fe_3O_4, мы выбрали краситель Orange II в качестве загрязняющего вещества. Мы также варьировали параметры реакции, включая pH раствора и концентрацию H_2O_2, чтобы проверить влияние красителя Orange II на фотокаталитическую активность. Кроме того, также обсуждались его фотокаталитическая эффективность наряду со структурной стабильностью и стабильностью магнитных наночастиц Fe_3O_4.

Ключевые слова: *магнит, Orange, пероксид водорода, наночастицы, синтез.*

ORANGE II BOYASININ FENTON REAKSİYALARLA DƏMİR OKSİD NANOHİSSƏCİKLƏRİNİN İSTİFADƏSİ İLƏ KATALİTİK DEQRADASİYASI

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Tədqiqat işində Fe_3O_4 maqnetit nanohissəciklərinin iştirakı ilə Orange II sintetik boyasının hidrogen peroksid H_2O_2 ilə katalitik oksidləşdirici deqradasiyası tədqiq edilmişdir. Sintez edilmiş nanohissəcikləri boyaların parçalanması üçün müxtəlif fiziki üsullarla xarakterizə etdikdən sonra biz onları foto-Fenton katalizatorları kimi tədqiq etdik və günəş işığı altında H_2O_2-nin iştirakı ilə fotokatalitik aktivliyini araşdırdıq. Fe_3O_4 maqnit nanohissəciklərinin katalitik performansını anlamaq üçün çirkləndirici olaraq Orange II boyasını seçdik. Orange II boyasının fotokatalitik fəaliyyətə təsirini yoxlamaq üçün məhlulun pH və H_2O_2 konsentrasiyası daxil olmaqla reaksiya parametrlərini də dəyişdik. Bundan əlavə, tədqiqat işində Fe_3O_4 maqnit nanohissəcikləri üçün struktur sabitliyi ilə yanaşı, onun fotokatalitik effektivliyi də müzakirə edilmişdir.

Açar sözlər: *maqnit, Orange, hidrogen peroksid, nanohissəciklər, sintez.*

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IN-DEPTH DETERMINATION OF İNDUSTRIAL WASTEWATER COMPOSITION FORMED IN BAKU STEEL SMELTING PLANT

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When we carried out an environmental study at the Baku Steel Smelting Plant, it was determined that one of the sources of atmospheric pollution is the industrial waste watwer formed in that plant. The results of our research work were determined by the ICP-OES GBC Quantima device, which was used in different areas of the enterprise and analyzed by the water samples taken after treatment. Based on the results of the analysis, it can be noted that the composition of the industrial waste water samples formed after the cooling system of the Electric Arc Steel Melting Furnace of the enterprise, compared to the composition of the industrial waste water samples entering the cooling system of that area, contains some metals (Mn, Cu, Al, Mo, Zn, Pb , Cr) amount has increased several times. Also, H_2S, SO_2, PH_3, *HCl,* Cl_2 *and other metal oxide compounds were found dissolved in water in the industrial waste water. At the next stages, environmental analyzes were carried out by us for the presence of a significant amount of heavy metal compounds in the water used by the plant.*

Keywords: *recycling, steel smelting, industrial wastewater, Electric Arc Steel Melting Furnace, environmental studies, cooling system.*

INTRODUCTION

According to the information and explanations given in many technical literatures[1-15], one of the main areas of the metallurgical industry is the secondary steel smelting production area. As mentioned in those literatures, a significant amount of gas, liquid and solid (slag) waste is formed during the secondary steel smelting production process compared to the primary steel smelting production areas. According to the information provided by the above literature, the amount of water used (cooling, washing, etc.) in re-smelting production areas is very high. Thus, in those industries, it is 13-15% of the total water used in other industries of the country. According to the information given in the above-mentioned literature and also in other literature[1-10], in some cases, 260 m3 of total water is used for the processing of 1 t of steel. However, up to 4% additional water is used in the steelmaking production process, despite the fact that most of the industrial wastewater is reused after it is initially collected, used and treated. According to the given explanations, 35% of the water used is subject to low pollution, that is, 5-15 m3 of that water, which is not related to pollutants, is formed during the use of 1 ton of steel in the process of processing. As mentioned in many technical literatures [2-8], industrial waste water formed in the metallurgical industry is cleaned by mechanical, chemical, physico-chemical and biological methods. The main goal of our research work is the ecological assessment of the environmental impact of industrial waste We have conducted scientific and ecological studies related to the topic. During the research, it was determined that a large amount of industrial waste water is formed during the recycling process of out-of-order steel technological equipment. According to the information given in many technical literatures, one of the main sources of pollution of natural water resources is the metallurgical industry recycling production area. During the research, it is determined that a large amount of industrial waste water is formed at the Baku Steel Smelting Enterprise. Until now, no research work has been conducted on determining the in-depth composition of industrial wastewater, like other wastes formed in that production area.water formed at the Baku Steel Smelting facility. That is why a research study was conducted on determining the environmental composition of industrial waste water entering and leaving the treatment plant in the production areas of that enterprise.

EXPERIMENTAL PART

Our research work was mainly analyzes of water samples entering and leaving the cooling system of Electric Arc Steel Melting Furnace (EASMF). In accordance with the purpose of the research work, work was done in the direction of sampling and analysis of the industrial waste water formed in the production areas of the Baku Steel Smelting Enterprise, mainly in the EASMF. The samples taken from the water entering the cooling system of EASMF and the water samples coming out of the cooling system of EASMF (that is, industrial waste water samples) were analyzed in depth by means of analytical chemical methods (photometric, photocolorimetric) which basically know the amount of metal ions. During those analyses, it was determined that some chemical indicators, mainly the amount of metal ions, were found in the inlet water entering the cooling system of EGPS. This can be explained by the fact that the amount of Cu, Mo, Mn, Al, Pb, Cr, Zn and other metals was high because most of the water entering the cooling system consisted of used water. The samples taken at the inlet and outlet of the water used in the cooling system of the mentioned production area were initially determined by the pH environment, OKT, OBT, codity. The amount of Cu, Mo, Mn, Al, Pb, Cr, Zn and other metals was determined using the ICP-OES GBC Quantima device. At the same time, the amounts of petroleum hydrocarbons, phenol and other mixed compounds contained in the samples were determined by the extraction method using a mixture of isopentane and normal hexane as an extractant reagent. The amounts of sulfate, chloride, ammonium, nitrite, nitrate and silicate salts contained in the collected water samples were also determined. The average indicators of the results of the conducted research are shown in table 1.

Table 1

The average indicators of the results of the conducted research

The name of component	Measure unit		Water entering the cooling system of EASMF (inlet water)	Water coming out of the cooling system of EASMF (outlet water)
pH		6.0-8.0	8.7	8.8
Biochemical consumption of oxygen	mqO_2/l	6.0	4.65	5.05
Chemical consumption of oxygen	mqO_2/l	6.0	6.59	7.21
Hardness	mq-ekv/l	6.0	7.43	7.88
Ca^{2+}	mq/l	16	20.1	26.4

Cont.of table 1

Mg^{2+}	mq/l	4.0	5.22	6.86
Alkalinity	mq-ekv/l	7,5	4.1	4.4
SO_4^{2-}	mq/l	50	28.6	228.8
Cl^-	mq/l	35	96.9	95.5
SiO_2^-	mq/l	10.0	14.12	13.96
Na^+	mq/l	130	137.8	222.5
K^+	mq/l	1.8	3.2	3.1
Al^{3+}	mq/l	5.0	9.49	41.4
Fe	mq/l	30	79.5	225.2
Mn	mq/l	10	0.372	7.98
Cu	mq/l	100	54.4	93.6
Mo	mq/l	20	23.7	25.0
Zn	mq/l	1.0	0.525	1.8
Pb	mq/l	0.3	0.162	0.673
Ni	mq/l	1.0	2.88	2.1
Cr	mq/l	0.5	3.44	4.68
B	mq/l	0.05	0.241	0.245
As	mq/l	0.5	<4	<4
Ba	mq/l	0.1	<0.6	<0.6
Hg	mq/l	.005	<0.02	<0.02
Se	mq/l	0.01	<0.1	<0.1

RESULTS AND DISCUSSION

As can be seen from many technical literatures and the data above, one of the most important issues is the collection of general information about the composition of raw materials and auxiliary reagents taken when environmental research work is carried out in some industrial enterprise, as well as the implementation of ecological analyzes about the composition, classification and characteristics of the products and all types of waste. Therefore, along with the determination of the composition of the raw materials and auxiliary reagents used in the above-mentioned enterprise, we have conducted an ecological research on the composition and characteristics of all types of waste received in the production process. A part of that research work was carried out on the determination of the causes, composition and characteristics of the negative impact on the environment of the industrial streams-wastewater formed at the Baku Steel Smelting Enterprise, which is considered one of the heavy industrial enterprises in Baku. As can be seen from the results of the conducted research, it was determined by us for the first time that one of the sources of atmospheric air pollution by the enterprise is the industrial flows formed in the production areas of that enterprise. The ecotoxic substances contained in those waters evaporate into the atmosphere in a short period of time, spread, change their concentration in the air, and the mentioned industrial enterprise can be considered as a source that pollutes the atmosphere.

Despite the fact that every harmful substance given in the literature is within the permitted concentration limit in the working and sanitary zones, it causes the pollution of the biosphere in the end along with the pollution of all spheres. As a result of this, it was determined that it is possible to evaluate the environment as a source of negative environmental impact on human health. As mentioned at the beginning of the article, it is possible to consider the assessment of the continuous composition of the industrial streams formed in the enterprise as an ecologically very important research work. As can be seen from the previous explanations, as a result of the use of auxiliary reagents with different composition and properties in the Baku Steel Smelting Enterprise, harmful and ecotoxic substances of various properties are released into the atmosphere. The industrial flows formed in that enterprise cause atmospheric pollution. That is why it can be considered reasonable that the cleaning of harmful substances with ecotoxic properties contained in industrial streams by the maximum possible physico-chemical method plays an important role in the fulfillment of environmental safety requirements in the modern era.

CONCLUSION

The research work conducted at the Baku Steel Smelting Plant was mainly related to determining the composition and classification of gas, liquid, and solid wastes formed in the enterprise, to justify the release of harmful substances and the impact of those wastes on the environment. As can be seen from the information given in the introduction, the recycling steel industry is considered as one of the main sources of environmental pollution. Permanent pollution of the environment by that industrial area as a result of the presence of ecotoxic substances of various composition and properties in the main production technological process of the above-mentioned enterprise, as a result of the presence of every harmful substance contained in the industrial waste water received in the form of gases - aerosols and also in liquid form is happening. Therefore, it is one of the most important issues to repeatedly carry out environmental research work on the determination of the composition of harmful substances released into the atmosphere from the areas mentioned by us, as well as the composition of industrial waste water formed. Explanations about the creation of ecological problems that lead to the destruction of the fauna of water resources as a result of the heavy metal compounds contained in the industrial waste water formed in that production, despite the purification of those waters in accordance with ecological norms, are thrown into the water basins. One of the bases of our research work determination, identification and classification of liquid waste generated at Baku Steel Smelting Plant. According to the results of the conducted research, it is possible that deep cleaning of reused water is important. That is why, based on the results of our research, the following explanations can be given:

The main reason for the presence of various non-metallic, alkaline and heavy metals in the industrial waste water formed in the mentioned areas with different composition and characteristics is due to the presence of various metal compounds in the recycled steel equipment used as raw materials, above 15000^0 C. it can be assumed that a part of the metals released during the melting process at the temperature is quickly transferred to the content of the water used in the cooling system.

Many mixed metal compounds are obtained as a result of high temperature decomposition of many components (coal, coke, ferromanganese, ferrosilicomanganese) used in the recycling process of recycled steel equipment, cast iron and even non-ferrous metal scraps. During the cooling process of these alloys, their part separated from the main alloys enters the water used for cooling and creates industrial waste water. That is why it causes the creation of mixtures containing sulfur, phosphorus, coal and other halogen compounds and pollution of the water used. Thus, the content of harmful substances with ecotoxicant properties increases several times in the water received and reused during the cooling of steel alloys in the Electric Arc Steel Melting Area. That's why it can be considered that the cleaning of reused industrial waste water in several stages by physico-chemical methods plays an important role in preventing the ecological stress in the working area of the enterprise.

REFERENCES

1. R.A.Aliyeva, S.R.Hajiyeva. Weighing and analysis of samples. Baku, 2009, pp. 116
2. G.İ.Bayramov, A.A.Samadova, N.M.Jafarova. Methods of analysis of harmfull substances in the industrial waste water produced in the oil industry. 2019, pp. 26
3. Mukuldev Khunte, Process Waste Generation and Utilization in Steel Industry, International Journal of Industrial and Manufacturing Systems Engineering. May 11, 2018, Vol.3, Issue, pp. 432
4. M. Sh. Barkan, E.I. Kabanov. Prospects for recycling and metallurgical enterprises during the extaction and processing of iron ore raw materials. Modern problems of complex processing of refractory raw materials (Plaksin Readings-2017) mat.. Inter.scientific conf. Krasnoyarsk, 12– 15 september 2017, pp. 452
5. Birman Y.A,Voordova N.G Secondary resources generated in the Metallurgical Industry, Engineering environmental protection ed. M: Publishing house of yhe Association of Construction Universites. 2002, pp. 269
6. Letimin, V.N., Dust and sludge from gas purification plants of metallurgical plants and analysis of ways of their disposal. Theory and technology of metallurgical production. V.N. Letimin. 2015, №1, (16), pp. 82–86
7. Y. A. Filipp, Current state and development of environmental protection in ferrous metallurgy. Ferrous metals. 2000, №4, pp. 26–35
8. AMCOM L. L.C. [Official website]. RL:http://www.amcom-usa.com/ru/ (date of access: 24.10.2019).
9. Garvilovski M, Kamberovic Z, Filipovic M, Majinski N. Optimization of Integrated Steel Plant Recycling: Fine-Grain Remains and By-Products Synergy Strojarstvo. 2011, №53 (5), pp. 359–365
10. Sehiselo, Ndlow. G. S. Simate, E. Matinde. Waste Production and Utilization in the Metal Eaxtraction Industry Sehiselo Ndlow. CRC Press, 274. Sehiselo, Ndlow. Waste Production and Utilization in the Metal Eaxtraction Industry.Sehiselo Ndlow, G. S. Simate, E. Matinde. CRC Press. 2017, pp. 512
11. G.I. Bayramov, A.A. Samadova, N.M. Jafarova "Methods of analysis of harmful substances in the industrial waste water produced in the oil industry", methodological manual, Baku 2019, pp. 26
12. ArcelorMittal [official website]. URL: https://corporate.arcelormittal.com/ (accessed: 24.10.2019)
13. Mukuldev Khunte, International Journal of Industrial and Manufacturing Systems Engineering 3,Process Waste Generation and Utilization in Steel Industry, may 11, 2018, Vol.3, №1, pp. 1-5

14. Luma A H Al-Kindi and 1Wadood K K Al-Ghabban, Reducing steel scrap in fabrication of steel storage tanks, IOP Conf. Series: Materials Science and Engineering 737. 2020, pp. 1-10
15. Chamling, P.K.; Haldar, S.; Patra, S. Physico-Chemical and Mechanical Characterization of Steel Slag as Railway Ballast. Indian Geotech. Journal. 2020, 50, pp. 267
16. Vadim Romanov, R.Romanova, Emissions of harmful substances and their dangers to living organisms Lit Res. 23 July. 2020, pp. 220
17. Sehliselo Ndlovu, Geoffrey S. Simate, Elias Matinde, Waste Production and Utilization in the Metal Extraction Industry, eBook-Boca RatonTaylor & Francis, CRC Press, 2017, pp. 501

УГЛУБЛЕННОЕ ОПРЕДЕЛЕНИЕ СОСТАВА ПРОИЗВОДСТВЕННЫХ СТОЧНЫХ ВОД, ОБРАЗУЮЩИХСЯ НА БАКИНСКОМ СТАЛЕПЛАВИЛЬНОМ ПРЕДПРИЯТИИ

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При проведении нами экологических исследований на Бакинском сталеплавильном комбинате, обнаружено что, промышленные сточные воды, формирующиеся на этом предприятии, являются одним из источников загрязнения атмосферы. Пробы, взятые из воды, используемой на разных участках предприятия, при поступлении на предприятие и после очистки, исследованы при помощи прибора ICP-OES GBC Quantima. По результатам анализа можно отметить, что количество некоторых металлов (Mn, Cu, Al, Mo, Zn, Pb, Cr) в составе проб производственных сточных вод, образовавшихся после системы охлаждения электродуговой сталеплавильной печи предприятия, возросло в несколько раз по сравнению с составом проб производственных сточных вод, поступающих на охлаждение. Также в этих промышленных сточных водах были обнаружены растворенные H_2S, SO_2, PH_3, HCl, Cl_2 и оксиды металлов. На следующих этапах нами были проведены экологические анализы на наличие в воде, используемой предприятием.

Ключевые слова: *переработка, выплавка стали, промышленные сточные воды, электродуговая сталеплавильная печь, экологические исследования, система охлаждения.*

BAKI POLAD ƏRİTMƏ MÜƏSSİSƏSİNDƏ FORMALAŞAN İSTEHSALAT TULLANTI SULARININ TƏRKİBİNİN DƏRİNDƏN MÜƏYYƏNLƏŞDİRİLMƏSİ.

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Tərəfimizdən Bakı Polad Əritmə müəssisəsində ekoloji tədqiqat aparılan zaman müəyyən edilmişdir ki, atmosferin çirklənmə mənbələrindən biri olan həmin müəssisədə formalaşan sənaye tullantı sularıdır. Apardığımız tədqiqat işinin nəticələri həmin müəssisənin ayrı - ayrı *sahələrində istifadə olunan müəssisənin daxil olan və təmizləndikdən sonra götürülən həmin su nümunələrinin analizləri İCP-OES GBC Quantima cihazı vasitəsi ilə müəyyən edilmişdir. Aparılan analizlərin nəticələrinə əsasən qeyd etmək olar ki, müəssisənin Elektik Qövslü Polad Əritmə Sobasının soyutma sistemindən sonra formalaşan sənaye tullantı suyu nümunələrinin tərkibi həmin sahənin soyutma sisteminə daxil olan təkrar istifadə olunmuş sənaye tullantı suyu nümunələrinin tərkibinə nisbətən bəzi metalların (Mn, Cu, Al,Mo, Zn, Pb, Cr) miqdarı bir neçə dəfə çox olmuşdur. Həmçinin həmin sənaye tullantı sularının tərkibində suda həll olmuş şəkildə* H_2S, SO_2, PH_3, *HCl,* Cl_2 *və digər metal oksid birləşmələri tapılmışdır. Sonrakı mərhələlərdə də müəssisə tərəfindən işlədilən suyun tərkibində xeyli miqdarda ağır metal birləşmələrinin olması tərəfimizdən ekoloji təhlilləri aparılmışdır.*

Açar sözlər: *təkrar emal, polad əritmə, sənaye tullantı suları, Elektrik Qövslü Polad Əritmə Sobası, ekoloji araşdırmalar, soyutma sitemi.*

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STUDY OF COMPLEX FORMATION OF COPPER (II) WITH 3 - ((E) -2-HYDROXYBENZYLIDENE) HYDROZONE) INDOLINE-2-ONE IN THE PRESENCE OF A THIRD COMPONENTS

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In the present study, we investigated the formation of the complex Cu (II) with 3 - ((E)-2-hydroxybenzylidene)hydrozone)indoline-2-one (R) in the presence of diphenylguanidine (DPG) and triphenylguanidine (TPG). The reagent has been synthesized from salicylic aldehyde. The dissociation constant of the reagent was determined by the potentiometric method in an aqueous-ethanol medium: pК=9,48± 0,03. The optimal conditions for complex formation have been established. The major spectrophotometric characteristics of the complexes are calculated. Studied intreraction of Cu(II) with 3-((E)-2-hydroxybenzylidene)hydrozone)indoline-2-one (R) in presence and absence of a third components - diphenylguanidine (DPG) and triphenylguanidine (TPG). The maximum light absorption of the processed complex compounds is λ_{max} *=440 nm for Cu(II)-R,* λ_{max} *=456 nm for Cu(II)R-DPG and* λ_{max}*=482 nm for Cu(II)R-TPG. The optimal pH for complexation was found to be at pH 5.0 (Cu(II)-R), 4.0 (Cu(II)R-DPG) and 3.0 (Cu(II)R-TPG) respectively. The ratio of the reacting components in the composition of binary-ligand (1: 2) and mixed-ligand (1:2:1)complexes are established. The interval of obedience to Beer's law is determined:* 0,26-2,56 *mkg/mL (Cu(II)-R), 0,128-2,048 mkg/mL (Cu(II)R-DPG) and 0,128-3,07 mkg/mL (Cu(II)R-TPG) respectively. The molar absorption coefficients of the complexes were calculated from saturation curves: 18000 (Cu(II)-R), 22500 (Cu(II)R-DPG) and 27000(Cu(II)R-TPG) respectively. The Astakhov method was used to determine the number of separated protons (n).The influence of foreign ions on complexation of Cu(II) with R in the absence and in the presence of third components was studied. The developed technique was used to determine the trace amounts of copper in wastewater.*

Keywords: *spectrophotometric metod, copper(II) comlexformation, salicylaldehyde, homogen and mixed-ligand complexes.*

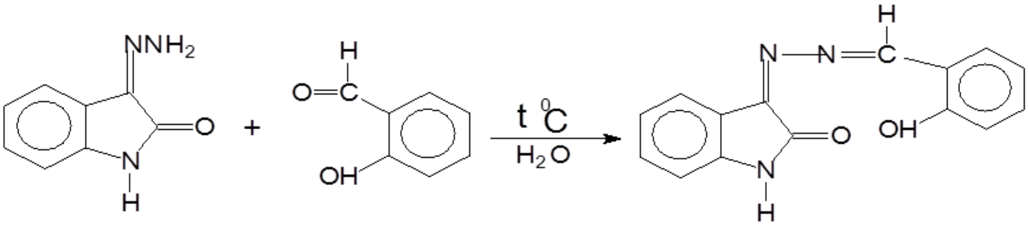
INTRODUCTION

Salicylaldehyde is a key precursor to various chelating agents. Salicylic aldehyde is a common arene and is used as an organic reagent for the production of various chemicals: condensation with ethylenediamine forms the ligand of salen, and hydroxylamine forms salicylaldoxime. As a result of the condensation of aromatic amines, salicylic aldehyde is chelated into ligands, forming a Schiff bases. In these compounds, the carbonyl group is replaced by an azomethine or imine group.The presence of an azomethine linkage in aromatic compounds makes these reagents acts as a chromogenic in determined the trace amount of transition metals in some natural food samples. Also their tendency as ligands to coordinate with many metal ions was reported especially on these ligands having two or more donor atoms were concentrated in coordination chemistry. Coordination compounds are formed by the combination of metal ions and neutral molecules or anions called ligands. They are able to donate electrons to the d-orbitals of the metal ion and as a result a bond is formed. In this chemistry of coordination the bioligands have great attention because of their potential activities of transition metal complex. Schiff base compounds and their metal complexes are widely used as catalysts in various biological environments, polymers, dyes, as well as in medicine and pharmaceuticals [1–11]. Consequently, the synthesis of new salicylic aldehyde derivatives, the spectrophotometric study of the complex compounds they form with metal ions, the study of their physicochemical properties, the development of sensitive and selective methods for determination in various objects are considered theoretically and practically relevant. A vital micronutrient for a lot of important processes is copper. Copper is found in many enzymes that play a role in electron transfer, activation of oxygen and superoxide disproportionation. Excess copper is too toxic, while copper deficiency may contribute to the development of severe diseases. Copper also has antimicrobial activity [12-13]. The importance of copper in industrial and medical processes, in healthcare, requires scientists to develop new methods that allow the determination of trace amounts of copper. Photometric methods for the determination of copper remain one of the most widespread due to the relative cheapness of the necessary equipment and a wide range of organic reagents that form light absorbing compounds with copper ions.

The present study delves into the complexation of copper(II) with 3-((E)-2-hydroxybenzylidene)hydrozone)indoline-2-one (R) in the presence and in the absence of diphenylguanidine (DPG) and triphenylguanidine (TPG) utilizing a photometric method to assess the interactions. A highly selective method for determining the trace amount of copper in wastewater has been developed.

EXPERIMENTAL PART

Solutions and reagents: Based on salicylaldehyde, the organic reagent 3-((E)-2-hydroxybenzylidene)hydrazone)indoline-2-one was synthesized according to the following scheme:



The corresponding unsymmetrical azin (R) was synthesized by the condensation reaction of N-unsubstituted hydrazone with salicylic aldehyde.

The reagent is good soluble in ethanol. We used $2\cdot10^{-3}$ M ethanolic solution of the reagent, $1\cdot10^{-4}$ M water-ethanol solutions of diphenylguanidine (DPG) and triphenylguanidine (TPG). The initial ($1\cdot10^{-1}$ M) copper solution was prepared by dissolving the salt $CuSO_4\cdot5H_2O$ [14]. Working solutions with less copper were prepared by reducing the concentration of the initial solution. To achieve the required acidity, fixanal HCl (pH 1–2) and ammonia acetate solutions (pH 3–11) were used.

Apparatus: The absorbances of the solutions was measured on a Lambda 40 spectrophotometer (Perkin Elmer) and a KFK-2 photocolorimeter in a cuvette with a layer thickness of 1 cm. The pH of the solutions was monitored using a pH-121 potentiometer with a glass electrode.

RESULTS AND DISCUSSIONS

We have synthesized a new reagent on the basic of salicylaldehyde and monohydrazon isatin according to known method [1], its composition and structure established by NMR methods. [(2-hydroxybenzaldehyde) -3-isatin] -bishydrozone:

NMR ^{1}H(DMSO-d_6, δ, д.м.) 11.45(d, OH-Ph), 8.81(d, N=CH), 9.91(d, NH), 6.81-7.71(m, 4H, Ar).

Observed signals in 11,25 p.m., which show that the proton of OH group promotes to the formation a strong hydrogen bonding. Proton of azomethine group is observed in the 8,81p.m. (d), and the NH proton of the indole ring in 9.91 p.m (d). Proton of the aromatic ring observed in the range of 6,81-7,71 p.m.

The dissociation constant of the reagent was determined using a potentiometric titration in an aqueous ethanol medium (1:2) taking into account the Bates correction [15]. The volume of titratable 10^{-3} M solutions is 50 ml, the titrant is $2\cdot10^{-2}$ M KOH solution free of carbon dioxide. The ionic strength was kept constant by adding the calculated quantity of KCl. Calculated dissociation constants of the reagent: pK=9,48± 0,03.

Cu(II) forms a red complex with reagent R. To determine the optimal conditions for the formation of complex compounds, absorption spectra were built based on the pH of the system (pH 1-14). The change in the optical density of the copper (II) complex compound with the reagent at the maximum wavelength depending on pH is shown in figure1.

As can be seen from fig.1, the optimum pH of the Cu(II)-R binary complex is 5. The study of complex compounds in the presence of diphenylguanidine (DPG) and triphenylguanidine (TPG) shows that the optical properties increase sharply, and the optimal pH of complex formation shifts to a more acidic medium with the formation of mixed ligand complexes. The optimum pH of the Cu(II)-R- DPG and Cu(II)-R-TPG complexes are 4 and 3.

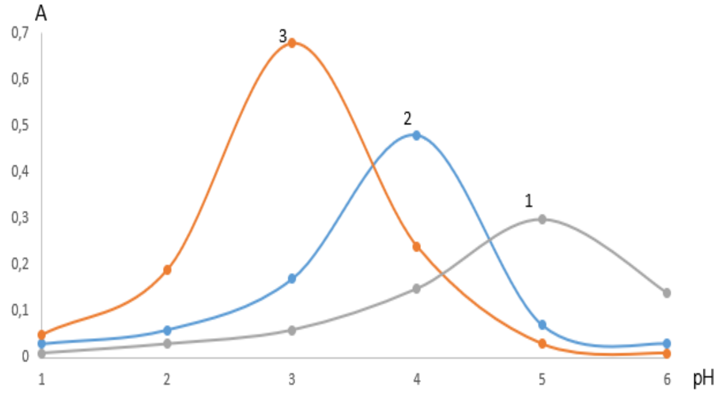


Fig.1. The dependence of the absorbances of solutions of the complexes of Cu(II) on pH: 1 – Cu(II) R, 2- Cu(II) R-DPG, 3- Cu(II) R-TPG, C_{Cu} =1,0 x10^{-3} M, C_R =2 x10^{-3} M, C_{III}=1,0 x10^{-4} M, Lambda-40, ℓ=1,0 sm

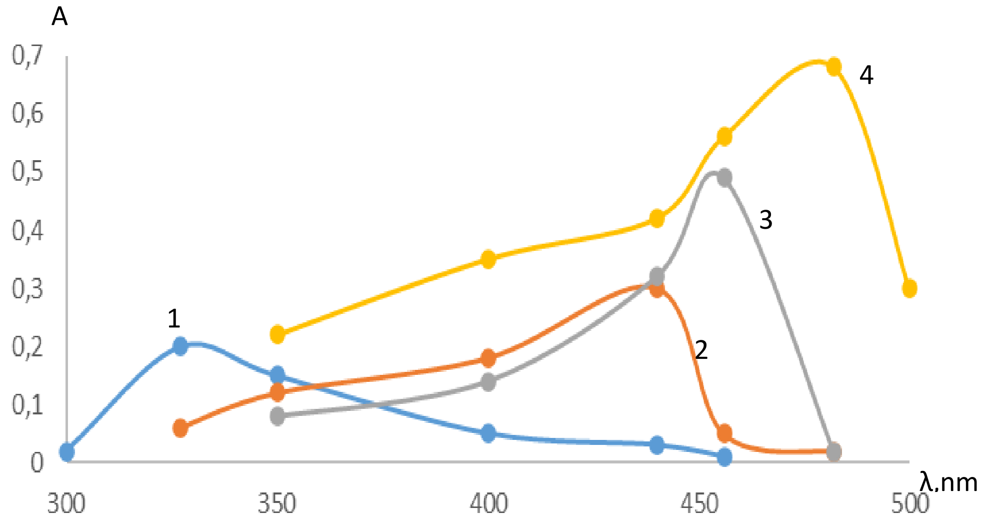


Fig.2. Absorption spectra of solutions of complexes with copper (II): 1 –R, 2- Cu(II) R, 3- Cu(II) R-DPG, 4- Cu(II) R-TPG C_{Cu} =1,0 x10^{-3} M ; C_R =2 x10^{-3} M, C_{III}=1,0 x10^{-4} M, Lambda-40, ℓ=1,0 sm

The maximum light absorption of the processed complex compounds is λ_{max} =440 nm for Cu(II)-R, λ_{max} =456 nm for Cu(II)R-DPG and λ_{max}=482 nm for Cu(II)R-TPG,. The maximum light absorption of the reagent itself is observed at λ_{max} = 327 nm (fig.2).

It was determined that in the presence of the third components mixed-ligand complexes are formed, during the formation of which a batochromic shift is observed compared to the spectrum of the binary complex.

The study revealed that the optimal conditions for the formation of the binary and mixed-ligand complexes depended on the temperature and time. These complex compounds studied are formed straightaway after blending the solutions of the components. If the Cu(II)-R binary complex is stable for 2 hours and up to heating to 70°C, then the Cu(II)R-DPG and Cu(II)R-TPG complexes are stable for 48 hours and when heated to 80°C.

The ratio of the reacting components in the complexes was established by the methods of isomolar series, the relative yield of Starik-Barbanel, and the shift of equilibrium [16]. All methods showed that the ratio of components in binary complexes Cu(II)-R is 1:2, and in mixed-ligand complexes Cu(II)R-DPG = 1:2:1 and Cu(II)R-TFG=1:2:1. The molar light absorption coefficients of the complexes were calculated from the saturation curves [17]. Concentration intervals were established where Beer's law is observed (table 1).

The Astakhov method [19] was used to determine the number of separated protons (n). A series of solutions was prepared, maintaining a constant concentration of the metal and varying the concentration of the reagent. Based on the results obtained, a dependence graph is constructed. The optimal pH of the CuR system is 5. As a result of research, complex formation according to the Astakhov complex formation method at pH 4.0 4.2; 4.4; 4.6; 4.8, 5.0 it is established that the angular coefficient of dependence is equal to tgα=2. This indicates that 2 protons are separated upon complexation. For other systems, the number of separated protons during complex formation was studied accordingly (fig.3).

Table 1

Spectrophotometric characteristics of copper (II) complexes

Complex	pH	λ_{max}, nм	ε, L/mol·sm	Me:R	Obedience to Beer`s law, mkg/mL
Cu(II)R	5	440	18000	1:2	0,26-2,56
Cu(II)R- DPG	4	456	22500	1:2:1	0,128-2,048
Cu(II)R- TPG	3	482	27000	1:2:1	0,128-3,07
4-(4'-chlorobenzylideneimino)-3-methyl-5-mercapto-1,2,4-triazole[18].	4	414	3381	1:2	0,256-1,536

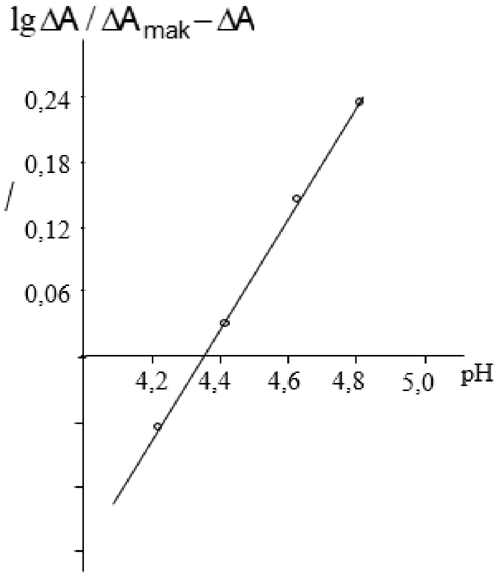


Fig.3. The number of separated protons during complex formation in the Cu(II)R system.

The effect of foreign ions on the complexation of copper(II) with R in the absence and in the presence of third components has been studied [20]. It was found that in the presence of third components, the selectivity of complexation reactions significantly increases (table 2).

The study of the effect of foreign ions and masking substances on the photometric determination of copper (II) in the form of binary and mixed-ligand complexes showed that the selectivity of the reaction increases in the presence of diphenylguanidine (DPG) and triphenylguanidine (TPG). Selectivity data make it possible to apply the developed method for the photometric determination of copper (II) in the form of mixed ligand complexes for the determination of its microquantities in complex objects. A technique has been developed for the spectrophotometric determination of microquantities of copper in the wastewate

Table 2

Permissible ratios of foreign ions to copper (II) when it is determined in the form of binary- and mixed-ligand complexes (error 5%)

Foreign ions	Cu(II)-R	Cu(II)-R-DFG	Cu(II)-R-TFG	2,7-bis(azo 2-hydroxy-3-sulfo-5-nitrobenzene)-1,8-dihydroxynaphthalene-3,6-disulfonate sodium salt [21]
Na(I)	*	*	*	*
K(I)	*	*	*	*
Ca(II)	*	*	*	625
Ba(II)	*	*	*	43
Zn(II)	1:480	1:600	1:1000	609
Cd(II)	1:280	1:350	1:380	813
Mn(II)	1:1620	1:1800	1:1810	172
Ni(II)	1:220	1:200	1: 220	18
Co(II)	1:220	1:600	1:600	19
Al(III)	1:1920	1:2010	1:2050	422
Bi(III)	1:77	1:50	1:160	
Sn(III)	1: 210	1: 160	1:430	
Ti(IV)	1:42	1:180	1:326	
Mo(VI)	1:300	1:360	1:800	
W(VI)	1: 50	1:80	1:100	
Carbamide	*	*	*	
Thiocarbamide	1:485	1:500	1:510	
F^-	1:250	1:300	1:250	100
Wine acid	*	*	*	
Lemon acid	1:980	1:800	1:500	

Note: * does not interfere

Analysis technique. They take 1 liter of waste water (Azerneftyag) and evaporate it without boiling until a precipitate forms. The treated precipitate is dissolved in 5 ml of nitric acid and transferred to a 50 ml flask, diluted with distilled water to the line. Take a 1 ml aliquot of the solution into a flask and pour into a 25 ml flask, add 2 ml of $1 \cdot 10^{-3}$ M R, 1 ml of $1 \cdot 10^{-4}$ TPG and wash with pH=3 buffer solution to the line. The absorbance of the solution is measured in KFK-2 at λ=490 nm (l=1 cm) after 5 minutes. Copper was found by photometric method (4.04±0.01) 10^{-5}%, atomic absorption method (4.02±0.02) 10^{-5}%. [22]

CONCLUSION

1. To determine copper by spectrophotometric method, the derivative of salicylaldehyde was used in the presence of third components.
2. The complex compounds of copper with a reagent in the presence of third components were studied spectrophotometrically, the optimal conditions for complex formation and characteristics of the complexes (pHopt, molar absorption coefficients, composition of

complexes, interval of obedience to Beer's law, stability constant) were determined. It was determined that in the presence of the third component, some analytical reaction parameters increase.

3. The Astakhov method was used to determine the number of separated protons (n).

4.The effect of foreign ions and masking substances on complexation reactions was studied. It was found that reactions with modified forms of the reagents are characterized by higher selectivity. These methods are highly sensitive and selective. It is a very rapid and a simple technique.

REFERENCES

1. Jamaluddin A.M., Tasnima Z.A. Simple Spectrophotometric Method for the Determination of Copper in Some Real, Environmental, Biological, Food and Soil Samples Using Salicylaldehyde Benzoyl Hydrazone. Pak.J.Anal.Environ.Chem. 2012, № 1, pp. 22-35
2. Kareem E.K., Sajid M. Lateef Abbas, Abid Ali Drea. Synthesis and Characterization of Some Transition Metal Complexes with New Schiff Base Ligand Derivative from Isatin. Journal of Kufa for Chemical. 2015, Vol.1, № 10, pp. 74-85
3. Omer B. Ibrahim, M,A. Mohamed and Moamen S. Refat. J. Canadian chemical Transactions. 2014, pp. 108-121
4. Reddy T., Reddy P.N. Kumar, Reddy N.C. Gangi, Sangita D. Kumar and Reddy A.V. A rapid extractive spectrophotometric determination of Cu (II) in biological, geological and pharmaceutical samples using o-hydroxyacetophenone isonicotinoylhydrazone cholars Research Library Der Pharmacia Lettre. 2015, 7 (3), pp. 274-286
5. Barazandeh T.M.. Synthesis of 6-(2-Methoxynaphthyl)-2,3-dihydro-1,2,4-triazine-3-thione as a New Reagent for Spectrophotometric Determination of Copper. Int J Anal Chem. 2014, pp. 1-6
6. Tsintsadze G.V., Mamedova Ch.A., Alieva F.S.. 2-((E)-(((E)-1-(pyridin-2-yl)ethylidene)hydrozono)methyl)phenol as reagent for spectrophotometric determination of copper(II). Chemical Journal of Georgia. 2015, 1, pp. 16-20
7. Kuliev K.A., Verdizade N.A., Suleymanova G.S.. Study of complex formation of copper (II) with 2,6-dithiol-4-tert-butylphenol and hydrophobic amines. Irkutsk: Izvestia Universities. Applied Chemistry and Biotechnology. 2017, Vol.7, № 2, pp. 21-32
8. Alieva F.S., Mamedova F.O., Bakhmanova F.N.. Photometric determination of trace amounts of copper(II) in pyrite. Factory Laboratory. Diagnostics of Materials, − Moscow. 2019, №. 10, Vol.85, pp. 23
9. Rishu Katwal, H.K.a.B.K.K. Applications of Copper – Schiff's Base Complexes: A Review.Sci. Revs. Chem. Commun. 2018, 3(1), pp. 1-15
10. Zoubi, W.A.Biological Activities of Schiff Bases and Their Complexes: A Review of Recent Works.International Journal of Organic Chemistry. 2019, 3, pp.73-95
11. Shrestha S., Sudha M. Synthesis and Characterization of Copper Complex of Salicylaldehyde Benzoyl Hydrazone. J. Nepal Chem. Soc. 2012, Vol.29, pp. 11-17

12. R. Gyawali, S. A. Ibrahim, S. A. Abu Hasfa, S. Q. Smqadri, and Y. Haik, “Antimicrobial activity of copper alone and in combination with lactic acid against Escherichia coli O157:H7 in laboratory medium and on the surface of lettuce and tomatoes,” Journal of Pathogens, Vol.2014, Article ID 650968, 9 p
13. L. Zhu, J. Elguindi, C. Rensing, and S. Ravishankar, “Antimi- crobial activity of different copper alloy surfaces against copper resistantand sensitive Salmonellaenterica,” Food Microbiology. Vol.30, № 1, pp. 303–310
14. Korostelev P.P. Preparation of solutions for chemical analytical work. M.: Chemistry. 1964, pp. 386
15. Beyts R.G. Determination of pH. Theory and practice. L.: Chemistry. 1972, 400 p
16. Barbanel Y.A. Diagram of the relative yield of a reaction as a means of physicochemical analysis of solutions. Journal of Inorganic Chemistry. 1964, T.9, pp. 437-446
17. Nemodruk A.A., Abalakina V.M., Moreyskaya L.V., Burmistrov M.T. Guide to methods of analytical control in intensive metallurgy. M.: 1983, T. 9, 92 p
18. Umesh B., A.Shaikh [et al.]. An efficient, cost effective, sensing behaviour liquid-liquid extraction and spectrophotometric determination of copper (II) incorporated with 4-(4′-chlorobenzylideneimino)-3-methyl-5-mercapto-1,2,4-triazole: Analysis of food samples, leafy vegetables, fertilizers and environmental samples. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2018, Vol. 189, pp. 443 – 453
19. Astakhov K.B. Spectrophotometric study of complex formation of some rare earth elements with nitriloacetic acid. V.B. Verinikin, V.I. Zimin, A.D. Zvereva. Journal of Inorganic Chemistry. 1961, №6, pp. 2069-2076
20. Bulatov M.I., Kalinkin I.P. A practical guide to photometric and spectrophotometric methods of analysis. L.: Chemistry. 1972, 407 p
21. Mardanova V.I., Gadzhieva S.R., Chiragov F.M. Study of complex formation of copper (II) with 2,7-bis(azo-2-hydroxy-3-sulfo-5-nitrobenzene)-1,8-dihydroxy-naphthalene-3,6-disulfonate salt in the presence of third components. Irkutsk: Izvestia universities Applied chemistry and biotechnology. 2019, 9 (3), pp. 385-394
22. Mamedova Ch.A., Gadzhieva S.R., Chiragov F.M., Shikhaliev N.K. Determination of copper in wastewater. X Republican scientific conference “Current problems of ecology and soil science in the 21st century”, dedicated to the 98th anniversary of the birth of national leader Heydar Aliyev. Baku, 2021, pp. 25

ИССЛЕДОВАНИЕ КОМПЛЕКСООБРАЗОВАНИЯ МЕДИ (II) С 3-((E)-2-ГИДРОКСИБЕНЗИЛИДЕН)ГИДРОЗОНО)ИНДОЛИН-2-ОНОМ В ПРИСУТСТВИИ ТРЕТЬИХ КОМПОНЕНТОВ

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В представленной работе изучено комплексообразование меди (II) с 3-((E)-2-гидроксибензилиден)гидрозоно)индолином-2-оном в присутствии и в отсутствие третьих компонентов - дифенилгуанидина и трифенилгуанидина. Реагент синтезирован *на основе салицилового альдегида, его константа диссоциации определена методом потенциометрического титрования в водно-спиртовой среде: рК=9,48±0,03. Установлено, что медь (II) с реагентом образует окрашенные разнолигандные комплексы в присутствии третьих компонентов. Найдены оптимальные условия комплексообразования (λ_{opt}, pH_{opt}). Определено соотношение реагирующих компонентов в однолигандных (1:2) и разнолигандных (1:2:1) комплексах. Максимальное светопоглощение однолигандного комплекса составляет λ_{max}=440 нм для Cu(II)-R, для разнолигандных комплексов λ_{max}=456 нм Cu(II)R-ДФГ и λ_{max}=482 нм Cu(II)R-ТФГ. Оптимальный рН комплексообразования был определен как рН 5,0 (Cu(II)-R), 4,0 (Cu(II)R-ДФГ) и 3,0 (Cu(II)R-ТФГ) соответственно. Определен диапазон подчинения закону Бера: 0,26-2,56 мкг/мл (Cu(II)-R), 0,128-2,048 мкг/мл (Cu(II)R-ДФГ) и 0,128-3,07 мкг/мл (Cu(II)R-ТФГ) соответственно. Молярные коэффициенты поглощения комплексов рассчитаны на основе градировочного графика и равны 18000 (Cu(II)-R), 22500 (Cu(II)R-ДФГ) и 27000 (Cu(II)R-ТФГ) соответственно. Методом Астахова определялось число отделившихся протонов (n). Изучено влияние некоторых ионов и маскирующих веществ на комплексообразование Cu(II) с R в отсутствие и в присутствии третьих компонентов. Установлено, что в присутствии третьих компонентов избирательность реакции значительно увеличивается. Разработанная методика применена для определения микроколичеств меди в сточных водах.*

Ключевые слова: *синтез, комплексообразования меди (II), спектрофотометрический метод, салицилового альдегид, бинарные и разнолигандные комплексы.*

MİSİN (II) 3-((E)-2-HİDROKSİBENZİLİDEN)HİDROZONO) İNDOLİN-2-ON İLƏ ÜÇÜNCÜ KOMPONENTLƏR İŞTİRAKINDA KOMPLEKSƏMƏLƏGƏTİRMƏSİNİN TƏDQİQİ

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Təqdim olunan işdə misin (II) 3-((E)-2-hidroksibenziliden)hidrozono)indolin-2-on ilə üçüncü komponentlər – difenilquanidin və trifenilquanidin iştirakında və iştirakı olmadan kompleksəmələgətirməsi tədqiq edilmişdir. Reagent salisil aldehidi əsasında sintez edilmiş, onun davamlılıq sabiti potonsiometrik titrləmə metodu ilə su-spirt mühitində müəyyən edilmişdir: pK=9,48± 0,03. Kompleks əmələgəlmənin optimal şəraiti tapılmışdır (λ_{opt}, pH_{opt}). Eyniliqandlı (1:2) və qarışıqliqandlı (1:2:1) komplekslərin tərkibində reaksiyaya girən komponentlərin nisbəti müəyyən edilmişdir. Eyniliqandlı kompleks birləşmənin maksimum işıq udması Cu(II)-R üçün λ_{max} =440 nm, qarışıqliqandlı komplekslərin Cu(II)R-DFQ üçün λ_{max} =456 nm və Cu(II)R-TFQ üçün λ_{max}=482 nm-dir. Kompleksəmələgəlmənin optimal pH-ı müvafiq olaraq pH 5.0 (Cu(II)-R), 4.0 (Cu(II)R-DFQ) və 3.0 (Cu(II)R-TFQ) müəyyən edilmişdir. Ber qanununa tabelik intervalı müəyyən edilmişdir: 0,26-2,56 mkg/mL (Cu(II)-R), 0,128-2,048 mkg/mL (Cu(II)R-DFQ) və 0,128-3,07 mkg/mL (Cu(II)R-TFQ) müvafiq olaraq. Komplekslərin molyar udma əmsalları dərəcəli qrafik əsasında hesablanmışdır və müvafiq olaraq, 18000 (Cu(II)-R), 22500 (Cu(II)R-DFQ) və 27000 (Cu(II)R-TFQ) bərabərdir. Ayrılmış protonların (n) sayını təyin etmək üçün Astaxov metodundan istifadə edilmişdir. Misin(II) eyniliqandlı və qarışıqliqandlı komplekslərinin əmələ gəlməsinə bəzi ionların və pərdələyici maddələrin təsiri tədqiq edilmişdir.Müəyyən olunmuşdur ki, üçüncü komponentlər iştirakında reaksiyanın seçiciliyi əhəmiyyətli dərəcədə artır.

Hazırlanmış metodika tullantı sularında misin (II) mikromiqdarını təyin etmək üçün tətbiq edilmişdir.

Açar sözlər: *spektrofotometrik metod, misin(II) kompleksəmələgətirməsi, salisil aldehidi, eyniliqandlı komplekslər, müxtəlifliqandlı komplekslər.*

ATTENTION FOR AUTHORS!

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