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ELECTRIC DISCHARGE METHODS IN REMOVAL OF HEAVY METAL IONS FROM INDUSTRIAL WASTEWATER

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Abstract- Economic development and industrialization have consistently led to significant environmental challenges, particularly in the form of heavy metal contamination in industrial wastewater. The removal of toxic heavy metals from wastewater has become a critical global concern. Industrial effluents containing hazardous metals such as Fe, Hg, Cr, Co, Ba, Mn, As, Cu, Cd, Ni, Pb, and Zn pose substantial risks to both aquatic and terrestrial ecosystems, contributing significantly to environmental degradation. When untreated, these effluents exacerbate the contamination of water bodies and ecosystems. Consequently, there is a pressing need to effectively eliminate these toxic, non-biodegradable metal ions from industrial effluents. Over the past several decades, extensive research has focused on developing efficient and cost-effective methods for heavy metal removal. Traditional approaches, including chemical precipitation, ion flotation, ion exchange, coagulation, and electrochemical treatments, are commonly employed for this purpose. However, these methods have notable limitations, such as the generation of precipitates requiring additional processing, low removal efficiencies, and high operational costs. In response to these challenges, innovative, cost-efficient, and environmentally sustainable technologies are being introduced to enhance wastewater treatment processes. This includes the modernization of treatment plants and the incorporation of water-saving technologies. Among the emerging techniques, high-voltage activation via electrical discharge has gained significant attention due to its potential to improve the adsorption efficiency of sorbents, enhancing the overall treatment process. Adsorption has become a widely adopted method for industrial wastewater treatment due to its high efficiency, ease of operation, selectivity for heavy metals, and environmental compatibility. Unlike traditional methods that rely on mechanical, chemical, or thermal modifications, high-voltage electrical discharge offers distinct advantages, such as operational safety, effective removal of toxic substances, and energy efficiency.

In this study, mass spectrometric (MS) analysis was employed to investigate the reduction of heavy metal ions in industrial wastewater. The MS analysis provided valuable insights into the chemical composition of the wastewater and demonstrated how the modification of electrical discharge impacts the surface properties of adsorbents, thereby improving adsorption efficiency. The experimental investigations focused on high-voltage electrical discharges as a means to enhance the adsorption process for more efficient heavy metal removal from industrial wastewater. The study also evaluated the technological advancements and the relationship between the process parameters and the removal efficiency achieved.

Keywords: Heavy Metals, Adsorption, Adsorbent, High-Voltage Discharges, Industrial Waters, Charges.

1. INTRODUCTION

Water pollution is an important component of all life on Earth - a global problem. With its rapid development, the chemical industry is creating more and more problems for living organisms and the environment. One of the most pressing environmental problems in the world is the pollution of the hydrosphere with industrial wastewater. Currently, the main cause of water pollution is the discharge of untreated or insufficiently treated wastewater from industrial, textile and leather processing enterprises into water bodies [1]. Wastewater treatment from ecotoxicants is an important stage of the technological process for any industrial enterprise. Polluted industrial wastewater poses a threat to the state of water bodies, as it contains highly toxic substances, the most dangerous of which are heavy metal compounds. The latter, entering natural water bodies and interacting with other elements, form highly toxic compounds, which, even in small quantities, can negatively affect human health and the state of the environment [2].

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The formation of large volumes of wastewater contaminated with heavy metals, the high solubility of which in the aquatic environment poses a serious threat to all living organisms. The most common wastewater pollutants are cadmium (Cd), zinc (Zn), lead (Pb), chromium (Cr), nickel (Ni), copper (Cu), vanadium (V), platinum (Pt), silver (Ag), lead (Sn) and titanium (Ti) [3], [4], [5], [6]. The listed heavy metals are toxic and can act as carcinogenic agents and are usually formed during galvanic, electrolytic deposition, conversion coating, milling and etching, classified with a density of more than 5 g/cm3 [4]. The toxic metals Sn, Pb, Ni, As, which contribute significant amounts, include the printed circuit board (PCB) industry and the wood processing industry, oil refineries containing Ni, V and Cr in their effluents from conversion catalysts. The presence of these pollutants in water bodies is dangerous for both humans and the environment as a whole [7].

In the conditions of modern development of social progress, wastewater from chemical, petrochemical, industrial, textile, and leather processing industries are the most dangerous sources of pollution of surface water bodies. The development of modern science and technology leads to an increase in industrial production, as a result of which the amount of waste discharged into the environment in the form of wastewater increases accordingly. Typical pollutants of wastewater are ions of heavy metals, pollutants such as oil, oil products, phenols, pesticides, various organic substances included in oil and oil products, and discharge of untreated or insufficiently treated wastewater from industrial enterprises into water bodies. Harmful chemical elements and substances enter water bodies, worsen their sanitary condition and create the need for special deep purification of water before its use for domestic, drinking, and some industrial purposes [8], [9].

Many pollutants are not mechanically removed from water, are not neutralized during biological treatment, and are not removed by traditional water treatment methods such as sedimentation, coagulation, and flotation. This necessitates the inclusion of a post-sorption treatment stage in the flow diagram of an integrated water treatment process. As a rule, this stage is the last stage in the water treatment process [10]. Heavy metals are also classified as persistent chemical pollutants with a cumulative effect, which have specific toxic properties. The most environmentally dangerous heavy metals are chromium, lead, mercury, and cadmium. When processing ores, burning energy sources, and consuming heavy metals, a very large amount of them enters the atmosphere and water bodies as waste. Heavy metals entering the aquatic environment interact with other components of the environment, forming hydrated ions, oxyhydrates, ion pairs, and complex inorganic and organic compounds. The specific form of the existence of metals depends on their nature, the nature of the ions and molecules competing for the ligand site, the pH, the temperature and ionicity of the environment. Many heavy metals form synergistic mixtures that have a toxic effect on aquatic organisms that significantly exceed the sum of the actions of the individual components. Therefore, the flow of heavy metals into the atmosphere, water bodies and agricultural areas must be stopped and strictly controlled. All sources of heavy metals can be eliminated by organizing wastewater treatment and reuse systems at enterprises [11], [12], [13].

The relevance of the work lies in the need to purify the aquatic environment containing heavy metals and reduce the concentration of the pollutant to a very low level [11], [14]. Adsorption is a method of industrial water purification that allows solving the problem of neutralizing wastewater containing heavy metal ions to the required parameters, at the scale of an industrial enterprise, while minimizing costs. In order to increase the efficiency of the adsorption process, the article describes the process of electro-discharge treatment of adsorbents [1].

2. METHOD OF ANALYSIS

Among modern methods that provide effective treatment of wastewater from various pollutants, including heavy metal ions, physicochemical technologies occupy a special place [10], [14]. Currently, methods of water purification from heavy metals and other pollutants using adsorption and electrical methods for wastewater treatment are known in industry [15]. The main criterion for the adsorption method of wastewater treatment is the choice of material, or rather, it is based on its sorption qualities, porous structure and efficiency. The electrical discharge method is more economical, efficient and provides a high degree of removal of heavy metals from industrial wastewater [1], [16], [17]. Porous adsorbents of various natural origins are the object of research. The natural adsorbent mass was powdered to a particle size of 60 μm, heat-treated, dried and pressed into tablets with a diameter of 5.5 mm at room temperature under a pressure of P=100 atm. The pressed samples of the adsorbent were annealed in vacuum at T=300 °C for 3 hours, then electrified by electric discharge. Electrodischarge method - is based on the electrical cleaning of adsorbents under the influence of electric fields and discharges. Electrodischarge treatment of adsorbents is one of the promising reagent-free methods of wastewater treatment to the required parameters. Electrodischarge treatment of adsorbents for wastewater treatment provides: removal of the vast majority of toxic components, including heavy metal ions, as well as organic reagents. The mechanism of wastewater treatment by electrical discharge is determined by the processes occurring on the surface and structure of natural adsorbents under the influence of electric discharges [1], [18].

Activation by electric discharge was carried out with different types of discharges, such as corona, barrier and torch, at a selected voltage for 1 hour, with a discharge current of 60 μA. For corona discharge at a voltage of U=13.5 kV, barrier discharge at an alternating voltage of U=14 kV, torch discharge at U=14 kV. The effect of electric discharge on the adsorbent allows us to study the fact of the formation of a charge in them.

The thermostimulated relaxation method allows us to determine the charge state of the material under study, as well as to study its most important electrical properties by determining the depth of charge, the density of charge traps and their energy [15], [16], [17]. The resulting graph of the time dependence of the thermostimulated current reveals a certain set of peaks, the analysis of which provides information about the electrophysical properties of the sample material. The area under the curve of the TSR current as a function of time corresponds to the total charge discharged in the sample. The charges of the sample, which are immobile at low temperatures, acquire higher mobility when heated [1], [18]. Based on the experimental data obtained, graphs of the time dependence of the thermostimulated current were constructed, which are presented in Figures 1-6.

When processing a material by electrical discharge, the internal charge of the thermally stimulated relaxation is introduced into the sample, which is recorded by a current recorder connected in series with the sample during the heating process. Based on the time-coordinate dependence of the discharge current, we determine the value of the introduced charge, the kinetic dependence of the relaxation.

Figure 1 shows the spectra of thermally stimulated relaxation temperature diapason t_1=250 °C, t_2=300 °C, t_3=400 °C, t_4=550 °C for montmorillonite in a corona discharge. Figure 2 shows TSR curves temperature diapason t_1=200 °C, t_2=220 °C, t_3=300 °C, t_3=350 °C, t_4=400 °C, t_5=450 °C for montmorillonite in a barrier discharge. Figure 3, TSR curves temperature *diapason* t_1=250 °C, t_2=350 °C, t_3=400 °C, t_4=550 °C of montmorillonite in a torch discharge of alternating voltage. The presence of peaks in the spectrum indicates high-temperature relaxation of the electrical discharge in the adsorbent sample. The charge is calculated accordingly for each peak, which is presented in Table 1.

Table 1. Values of the accumulated charge of montmorillonite at various discharges and temperature [25]

Discharge type	*Q* (Cl) values for montmorillonite Temperature °C			
Crown discharge	250	300	400	550
	4.1×10^{-6}	1.2×10^{-5}	2.7×10^{-5}	5.2×10^{-5}
Barrier discharge	220	350	400	450
	3×10^{-5}	2.7×10^{-5}	3×10^{-6}	3.3×10^{-6}
Torch discharge	250	350	450	550
	3.8×10^{-6}	1.9×10^{-6}	7.1×10^{-6}	2.5×10^{-6}

Figure 4 shows the TSR spectra of bentonite in a corona discharge in the temperature diapason t_1=300 °C, t_2=370 °C, t_3=420°, Figure 5 TSR curves the temperature *diapason* t_1=300 °C, t_2=380 °C, t_3=420 °C for bentonite in a barrier discharge, figure 6 TSR curves at t_1=270 °C, t_2=320 °C, t_3=420° for a torch discharge of alternating voltage. Indicators of the amount of accumulated charge during electrification are presented in Table 2.

Table 2. Values of the accumulated charge of bentonite at various discharges and temperature [26]

Discharge type	*Q* (Cl) values for bentonite Temperature °C		
Crown discharge	300	370	420
	4.1×10^{-7}	2.6×10^{-7}	2.2×10^{-6}
Barrier discharge	300	380	420
	1.1×10^{-6}	4.1×10^{-7}	5.6×10^{-7}
Torch discharge	270	320	420
	4.5×10^{-7}	7.8×10^{-7}	2.8×10^{-6}

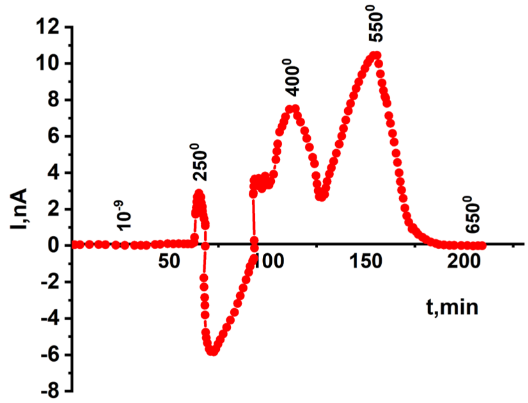


Figure 1. Temperature-stimulated current versus time for montmorillonite treated with corona discharge [24], [25]

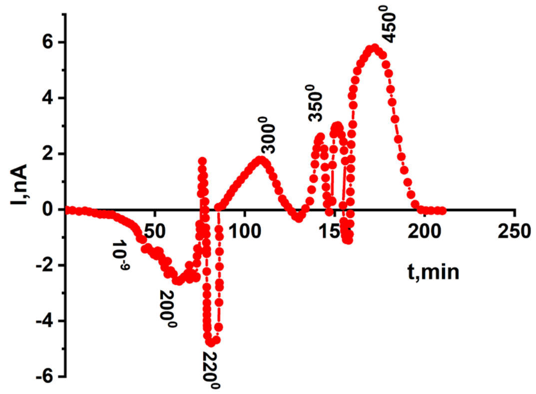


Figure 2. Dependence of thermally stimulated current on time for montmorillonite treated with a barrier discharge [24], [25]

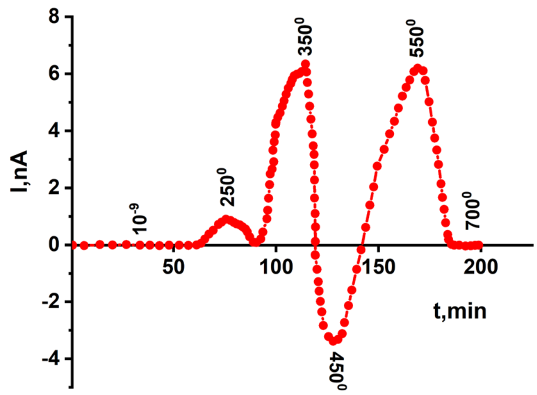


Figure 3. Dependence of thermally stimulated current on time for montmorillonite treated with a torch discharge [24], [25]

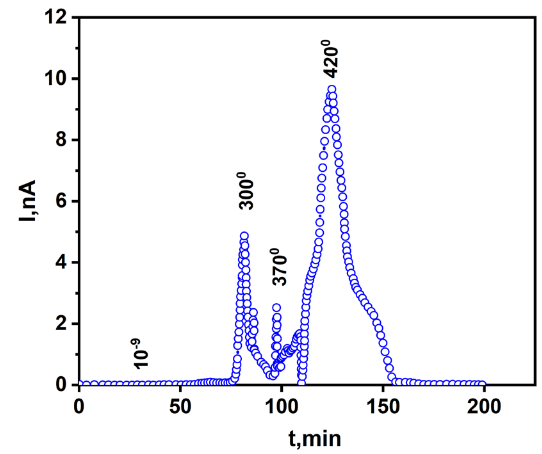


Figure 4. Curve of thermally stimulated current versus time for bentonite treated with corona discharge [24], [25]

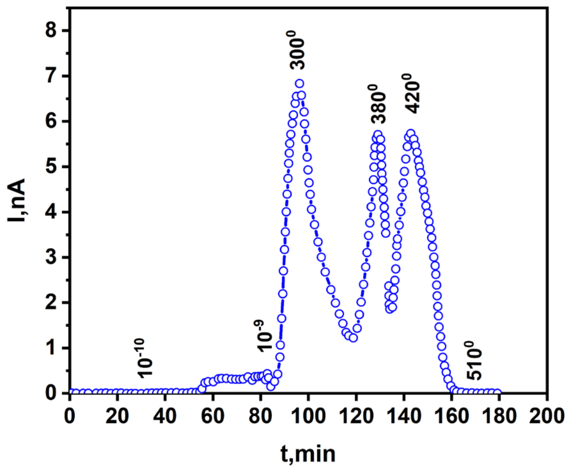


Figure 5. Dependence of thermally stimulated current on time for bentonite treated with a barrier discharge [24], [25]

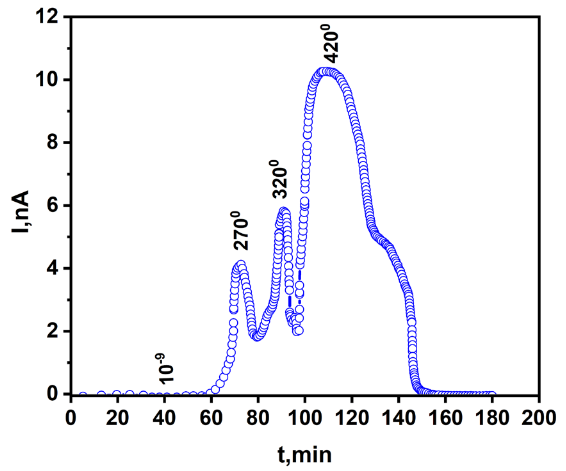
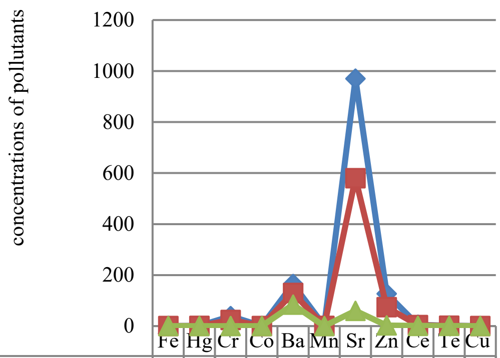


Figure 6. Dependence of thermally stimulated current on time for bentonite treated with a torch discharge [24], [25]

The formation of a charged state in the studied porous dielectric adsorbents showed that the charged state is formed due to the diffusion mechanism of the introduction of charges into the structure of the material. The process of activation of the adsorbent, in accordance with which the ions captured by the outer surface of the adsorbent diffuse into the depth of the adsorbent along the pores, bringing it to a charged state. The obtained values of the diffusion coefficient in the studied adsorbents are in the interval between the diffusion values of neutral materials and the diffusion of ions in the same non-porous materials [18]. The proposed model of the adsorbent loading process made it possible to experimentally determine the fact of the intensification of adsorption processes under the indicated effects, which is manifested in a change in their selectivity towards various components and a change in their maximum sorption capacity [15], [16], [17], [18].

To assess the influence of electrical discharge modification on the surface properties of adsorbents and their efficacy in heavy metal ion removal, MS analysis was conducted on treated industrial wastewater. The MS results revealed significant alterations in both the chemical composition of the wastewater and the surface characteristics of the adsorbents, which contributed to the enhanced adsorption capacity. This study aims to explore the molecular-level impact of high-voltage electrical discharges, such as corona, barrier, and torch discharges, on the adsorbents' structure. Specifically, it investigates how electrical discharge treatment modifies the chemical properties of montmorillonite and bentonite and improves their adsorption performance. The findings demonstrate that electrical discharges can effectively remove contaminants and introduce new molecular features, thereby enhancing the adsorbents' ability to capture heavy metals. In Figure 7, spectra comparisons of untreated and treated adsorbents show a reduction in contaminants, alongside shifts in molecular bonding and ion distribution. These results support the hypothesis that high-voltage electrical discharges significantly alter the physical and chemical properties of adsorbents, leading to more reactive surfaces and improving their adsorption efficiency [19-23].



	Fe	Hg	Cr	Co	Ba	Mn	Sr	Zn	Ce	Te	Cu
Source wate	0.8	0.9	39	0.8	165	1.2	970	127	5.2	2	0.2
without the use of EDP	0.4	0.6	24	0.5	130	0.8	580	74	4	1.2	0.1
using EDP	0.1	0.2	0.1	0.2	84	0.1	60	2.5	1	0.7	0.1

Figure 7. Industrial wastewater pollutant concentration curve [1]

It can be seen from the figure that the reduction of the content of heavy metals in wastewater occurs due to the formation of a charged state in the studied porous adsorbents. With an increase in the duration of the electric discharge treatment in the field of various discharges in the selected voltage range, the degree of purification of the crystal framework from impurities due to the emission process from the surface of the adsorbent increases, which leads to an increase in the adsorption activity of the process [16], [17]. The results obtained on the basis of experimental studies show that it is possible to increase the quality and efficiency of adsorption by treating porous adsorbents with various types of electric discharge, which allows reducing the content of heavy metals in industrial wastewater [18].

Experimental data showed that the electrical discharge method compares favorably with others in terms of simplicity of apparatus design, low energy consumption, and efficiency of the adsorption process. This method can be used as a cheap and effective method for the treatment of industrial wastewater from heavy metals [26].

3. CONCLUSIONS

This study introduces a novel approach for enhancing the adsorption capacity of natural adsorbents, such as montmorillonite and bentonite, through high-voltage electrical discharges, specifically corona, barrier, and flare discharges. By activating these adsorbents with electrical discharges, we propose a sustainable method for the removal of heavy metals from wastewater, offering an environmentally friendly alternative to traditional chemical adsorption processes. This approach significantly reduces the environmental impact of industrial effluents while improving treatment efficiency.

TSR and MS analysis to examine the effects of electrical discharge treatment on the structural and chemical properties of the adsorbents and the chemical composition of industrial wastewaters. TSR quantifies the impact of electrical discharges on the adsorption materials, while MS provides insights into the heavy metal content and chemical changes in treated wastewater. By integrating TSR with different types of electrical discharges, this methodology enables a deeper understanding of charge redistribution and structural modifications at varying voltages and temperatures, providing a more comprehensive evaluation of adsorption capacity.

In contrast to traditional methods such as chemical precipitation, ion flotation, ion exchange, electrodialysis, and photocatalysis, this study explores the molecular-level changes induced by electrical discharges, which have not been extensively investigated for adsorption applications. This work offers new perspectives on improving adsorption efficiency without relying on harmful chemicals, using cost-effective adsorbents even at low concentrations of heavy metals.

While methods like membrane filtration and biosorption have proven effective, their high operational costs limit widespread adoption. In this paper, we discuss the challenges associated with scaling electrodischarge treatments for industrial applications, including safety concerns and equipment costs. We propose optimizing discharge parameters and incorporating automated control mechanisms to make the process more feasible at scale.

Finally, we compare our findings with recent data on adsorption efficiency, validating our approach within the broader context of wastewater treatment technologies. We also suggest avenues for improving adsorption efficiency further, including the development of low-cost organic adsorbents and minimizing the toxicity of sludge produced during treatment. These improvements could lead to a more sustainable and cost-effective solution for the removal of heavy metals from industrial wastewater, addressing pressing environmental challenges.

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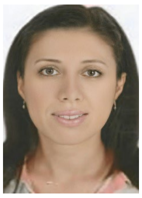
BIOGRAPHIES



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Scientific Publications: 26 Papers, 1 Patent, 3 Projects, 6 Theses