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Studies on Adsorption of Petroleum Products under Static Conditions

Vira Sabadash[1*], Vitaliy Lysko[1]

[1] Department of Ecology and Sustainable Environmental Management, Lviv Polytechnic National University, Viacheslav Chornovil Institute of Sustainable Development, S. Bandera St, 12, Lviv, 79013, Ukraine

* Corresponding author's e-mail: virasabadash@gmail.com

ABSTRACT

This paper provides an overview of the adsorption of petroleum products, focusing on various aspects such as adsorbent types, mechanisms of adsorption, factors influencing efficiency, kinetics, equilibrium, practical applications, and environmental implications. It explores the properties and characteristics of adsorbents, including activated carbon, zeolites, clay minerals, silica gel, and others, highlighting their interaction with petroleum products. The article delves into the theories and mechanisms governing the adsorption process, discussing physical and chemical adsorption as well as the role of forces like van der Waals, hydrogen bonding, and electrostatic interactions. The results of experimental investigations were conducted to evaluate the adsorption capacities of various adsorbents for petroleum products. The adsorption performance, kinetics, and equilibrium behavior of different adsorbents were analyzed, providing insights into their effectiveness in removing petroleum contaminants from aqueous solutions. The adsorption kinetics and equilibrium studies were explored through mathematical models like Langmuir and Freundlich isotherms. The practical applications of adsorption in the petroleum industry were discussed, including removing pollutants from wastewater, gas and diesel purification, and desulfurization. The environmental implications of adsorption technology in mitigating oil spills and reducing petroleum-related pollution were addressed. The conclusion emphasizes the significance of these studies in enhancing understanding, developing efficient solutions, and addressing environmental challenges associated with the petroleum industry. Ongoing research in this field aims to further improve adsorption processes for a more effective and sustainable approach.

Keywords: wastewaters, oil products, adsorption, zeolite, fly ash.

INTRODUCTION

Water pollution and the discharge of oil and diesel contaminants into wastewater pose significant environmental challenges worldwide (Sočo et al., 2021). Adsorption has emerged as an effective method for removing pollutants from wastewater. This study investigates the adsorption capacities of zeolites and carbon nanotubes (CNTs) for the removal of wastewater contaminants, with a focus on their application in environmental protection. The adsorption of petroleum products is critical in environmental remediation and wastewater treatment (Biswal et al., 2023). Adsorption is a fundamental phenomenon that is crucial in various industrial applications, environmental remediation, and pollution control. Factors such as temperature, pressure, contact time, surface area, and pore size are examined for their impact on adsorption efficiency (Nahursky et al., 2022). The authors aimed to shed light on the significance of adsorption, its mechanisms, and the specific interactions between petroleum products and adsorbents. The petroleum industry is one of the largest global industries, and properly handling petroleum products is paramount. Adsorption is a versatile process that removes impurities from petroleum products, such as crude oil, gasoline, and diesel (Prabhu et al., 2021).

Fly ash is a by-product of coal combustion and is widely used in various applications due to its unique chemical and physical properties. Understanding the empirical formula as well as the predominant and vital elements in fly ash is essential for assessing its potential applications and environmental impacts (Sabadash et al., 2020).

The empirical formula of fly ash represents the chemical composition of a material based on the relative abundance of its constituent elements. It provides a simplified representation of the essential elements present in fly ash. The empirical formula is typically derived from the elemental analysis of the fly ash sample (Sabadash et al., 2017). The fly ash obtained from the Dobrotvir heat power plant comprises several elements, some more prevalent than others. These predominant elements may include silicon (Si), aluminium (Al), iron (Fe), calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) (Ge et al., 2023). The specific elements and their relative abundance can vary depending on the coal composition and combustion conditions.

In addition to the predominant elements, other vital elements in fly ash may have particular significance due to their environmental or industrial implications (Sydorchuk et al., 2014). These elements might include trace elements such as arsenic (As), mercury (Hg), lead (Pb), chromium (Cr), and others. The presence of these critical elements requires careful monitoring and consideration in terms of potential environmental impacts and the suitability of fly ash for specific applications. The characteristics of fly ash from the Dobrotvir heat power plant, including its empirical formula of fly ash and understanding of any environmental implications associated with its use, were presented. By understanding the composition of fly ash, researchers, engineers, and environmentalists can make informed decisions regarding its proper utilization and potential treatment methods to ensure minimal environmental impact (Sabadash et al., 2018).

The synthesis of zeolites from fly ashes represents a promising approach to transforming an industrial waste product into a valuable resource. Zeolites synthesized from fly ashes possess unique properties that make them suitable for various applications (Hyvlud et al., 2016). This innovative and sustainable utilization of fly ash reduces environmental burdens and opens up new opportunities for the beneficial reuse of waste materials. Numerous studies have established the promising potential of ash as an effective adsorbent for removing various contaminants (Zheng et al., 2023). By undergoing chemical and physical activation, the adsorption capacity of fly ash can be significantly enhanced.

Moreover, fly ash has demonstrated considerable prospects in the construction industry. A notable application involves converting fly ash into zeolites, which offers numerous benefits, such as ion exchange, molecular sieves, and adsorbents (Zhang et al., 2019). This conversion addresses the issue of disposal and transforms waste into a valuable commodity. Furthermore, investigations have revealed the significant role of the unburned carbon component in ash, enhancing its adsorption capacity (Paliulis, 2021). The discussion also encompasses future research opportunities in these domains. Cation exchange resins derived from hydrogels synthesized from ash or other silicon-containing materials also find practical applications (Mohammed et al., 2020).

MATERIALS AND METHODS

Synthetic Sorbent Zeolite was synthesized from ash using hydrothermal synthesis and a combined two-stage approach that incorporates the "fusing" method and hydrothermal techniques.

Hydrothermal Method: In this method, the ash was mixed with 10% NaOH in a 1:4 ratio. The mixture was then crystallized at temperatures of 363K and 380K. After crystallization, the reaction mixture underwent filtration, followed by washing with distilled water to achieve a pH of 10. Subsequently, it was dried at a constant weight of 378K for 12 hours. The synthesis conditions are outlined in Table 1.

Two-Stage Method for Synthetic Zeolite Production. For this method, crystalline NaOH and fly ash were combined in a weight ratio 1.2:1. The mixture was ground and heated in a platinum crucible at 823K for one hour. After cooling to 293K, the resulting melt was ground and diluted with distilled water at a ratio of 1:4. The mixture was then subjected to crystallization at 293K in a thermostatic bath equipped with a shaker for either 12 or 24 hours. Subsequently, the reaction mixture was incubated in a thermostat for 12 hours at 373K. The crystalline phase was separated by filtration, washed multiple times with distilled water, and dried at 378K for 12 hours.

The obtained surface morphology and chemical composition of samples were studied by electron microscopic analysis according to the method presented by (Mohammed et al., 2020). The diameter of the electron beam was 1 μm, and the acceleration potential was 15 kV. Elemental analysis of the zeolite surface was performed for different areas of samples with an area of 100 μm^2

Table 1. Conditions for modification of fly ash by hydrothermal method

Samples No.	NaOH : ash ratio	Content of NaOH, %	Crystallisation time τ , hour	Crystallisation temperature T Crist., K
1	4 : 1	10	12	380
2	4 : 1	10	12	380
3	4 : 1	10	6	363
4	4 : 1	13	6	363

Table 2. Conditions for modification of removal ash by two-stage fusing method

Sample No.	NaOH : ash ratio	Fusing temperature, K	Crystallisation time, h	Hydrothermal method	
				Temperature, K	Time, h
5	1.2 : 1	823	12	373	12
6	1.2 : 1	823	24	373	12

by scanning with an electronic probe. Data on the chemical composition of the synthesised samples were derived from the average results. The adsorbents obtained by sintering (removal) of sodium TPP ash from sodium by PEM hydroxide and hydrothermal method according to the procedure presented in Section 2 contained zeolites X, Na-P1 and fayalite in the crystal structure.

Morphological Analysis Techniques: The techniques were used to analyze the morphology of fly ash and zeolites. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) are commonly employed for this purpose. SEM provides high-resolution images of the surface morphology, while TEM allows researchers to examine the internal structure and nanoscale features of particles.

Fly Ash Morphology: The morphology of fly ash particles was determined through SEM analysis. The SEM images reveal the size, shape, and surface texture of fly ash particles. Fly ash particles can vary in size and shape depending on the coal type, combustion conditions, and post-combustion treatments. The morphology of fly ash influences its reactivity, surface area, and suitability for different applications.

Zeolite Morphology: Similarly, the slide highlights the morphological analysis of synthesized zeolites using SEM and TEM. Zeolite crystals can exhibit various morphologies, such as cubical, spherical, needle-like, or irregular shapes. The crystal size and shape influence zeolites' porosity and surface area, which are crucial factors determining their adsorption and catalytic properties. Morphological analysis also aids in evaluating the porosity of both fly ash and zeolites. Pore structure plays a vital role in determining the adsorption and ion exchange capacities of these materials. Porosity is assessed using specialized techniques, such as nitrogen adsorption-desorption isotherms (BET analysis), which provide information on the surface area and pore size distribution.

For instance, fly ash with a high surface area and fine particle size may exhibit enhanced reactivity in cementitious applications. On the other hand, the zeolites with well-defined morphology and uniform crystal size are often preferred for advanced catalytic and adsorption processes.

Methodology for investigating the adsorption of diesel from wastewater

Preparation of Synthetic Zeolite: a. obtain the synthetic zeolite material and ensure it is suitable for adsorption experiments, such as powdered or granular form. b. If necessary, pretreat the synthetic zeolite according to manufacturer recommendations, such as activation or drying, to optimize its adsorption properties.

Preparation of a Diesel-Wastewater Solution: a. Prepare a stock solution of diesel by dissolving the desired amount of diesel in a suitable solvent (n-hexane) to achieve concentrations within the range of 0 to 2 g/L. b. Dilute the diesel stock solution with distilled water or wastewater to obtain the desired diesel concentrations for the adsorption experiments.

Adsorption Experiment Setup: a. Measure specific volumes of the prepared diesel-wastewater solutions into individual glass vials or containers. b. Add a predetermined amount of synthetic zeolite to each vial, ensuring a proper adsorbent-to-solution ratio (e.g., 1 g of zeolite per 100 mL of solution). c. Seal the vials or containers to maintain a static condition and prevent evaporation or contamination during the experiment.

Equilibration and Contact Time: a. Place the vials or containers in a controlled environment, such as a laboratory incubator or temperature-controlled room, at a predetermined temperature (e.g., 25°C). b. Allow the samples to equilibrate for a specific contact time, typically several hours to a few days, to ensure sufficient interaction between the diesel and synthetic zeolite.

Sample Analysis: a. After the desired contact time has elapsed, carefully remove the synthetic zeolite from the vials or containers. b. Separate the zeolite from the liquid phase by filtration or centrifugation. c. Analyze the residual diesel concentration in the liquid phase using appropriate analytical techniques, such as gas chromatography (GC) or spectrophotometry. d. Calculate the adsorbed diesel quantity per unit mass of synthetic zeolite based on the difference between the initial and residual concentrations.

Replicates and Controls: a. Conduct the adsorption experiments in replicates to ensure the reliability and reproducibility of the results. b. Include appropriate controls, such as adsorption experiments without synthetic zeolite, to account for any background adsorption or other factors that may influence the observed results.

Data Analysis: a. Analyze the adsorption data by plotting the adsorbed diesel quantity versus the initial diesel concentration. b. Fit the experimental data to relevant adsorption isotherm models, such as the Langmuir or Freundlich isotherms, to determine the adsorption capacity and other parameters. c. Perform statistical analysis, if applicable, to evaluate the significance of the observed differences between experimental conditions.

RESULTS AND DISCUSSION

The spectra of the zeolite surface are given in Figures 1 and 2. The images were obtained using a scanning electron microscope in the mode of secondary electrons, which provides

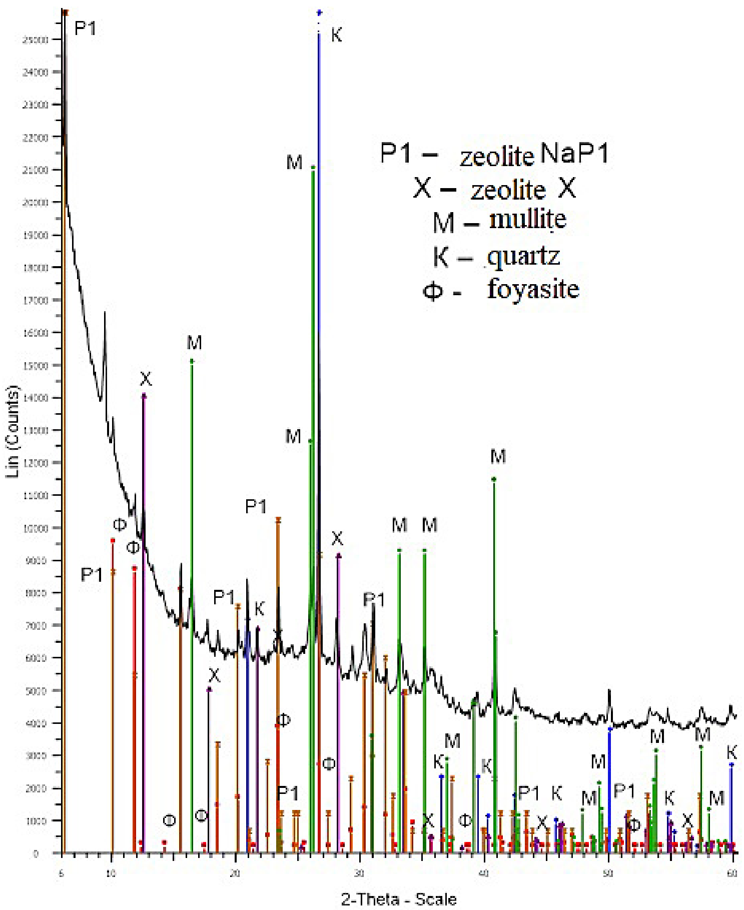

Fig. 1. Diffractogram of zeolite synthesized by hydrothermal method NaOH 3M crystallization time 12 hours

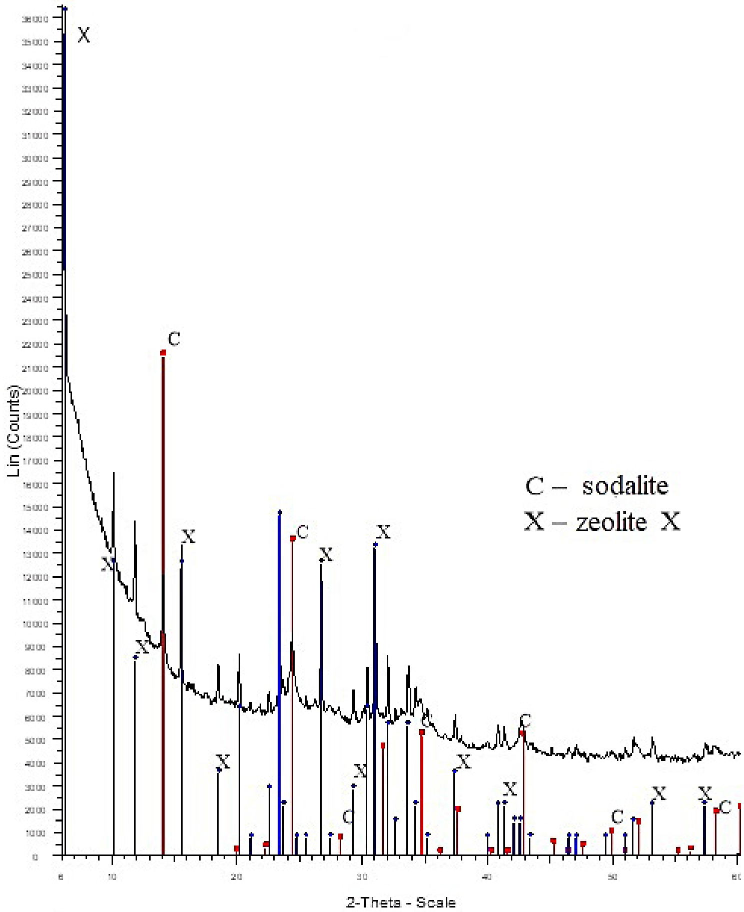

Fig. 2. Diffractogram of zeolite synthesized by fusing method NaOHcr, activation time 12 hours

proper resolution and informative results. By understanding the morphology of fly ash and zeolites, researchers can optimize the synthesis process to control the particle size, shape, and porosity, tailoring the materials for targeted applications. This knowledge also facilitates the development of novel composites or hybrid materials with improved performance characteristics. Synthetic zeolites based on TPP removal ash contain carbon. This approach allows them to be used for the adsorption of organic compounds, particularly petroleum products. The isotherm of sorption of diesel fuel by ash modified by the sintering method is typical for microporous sorbents, and the isotherm of sorption for ash modified by the hydrothermal method is typical for mesoporous sorbents. According to Hills' classification, these isotherms belong to the L-type. As an example, isotherms of adsorption of diesel fuel on synthesised sorbents based on removal ash (Fig. 3),

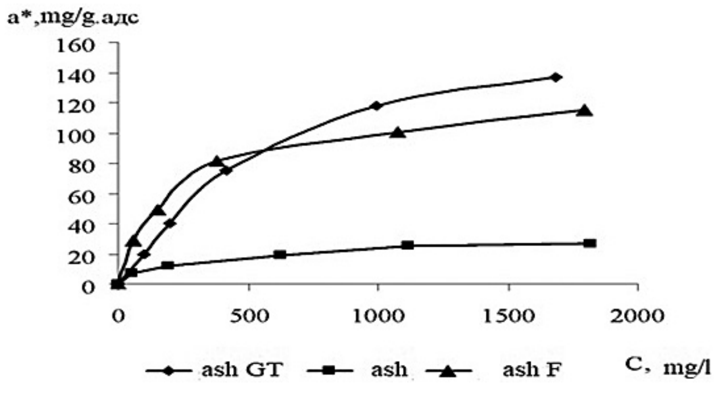

Fig. 3. Isotherms of sorption of diesel fuel by modified sorbents

which the Langmuir isotherm and the Freundlich isotherm can describe. The linearized isotherms provide valuable insights into the adsorption capacity, surface properties, and adsorption mechanisms of zeolite material. This information is crucial for designing effective adsorbents for diesel fuel removal and remediation in environmental applications. Additionally, the data obtained from the linearized isotherms can be used to optimize the synthesis process of zeolites for enhanced diesel fuel adsorption performance.

Sorption isotherms for removal of ash, ash modified by the sintering method and hydrothermal method, processed in accordance with the Langmuir model, are presented in Figure 4.

Langmuir isotherm for ash:

$$a^* = 24.5\frac{0.007C}{1+0.007C} \tag{1}$$

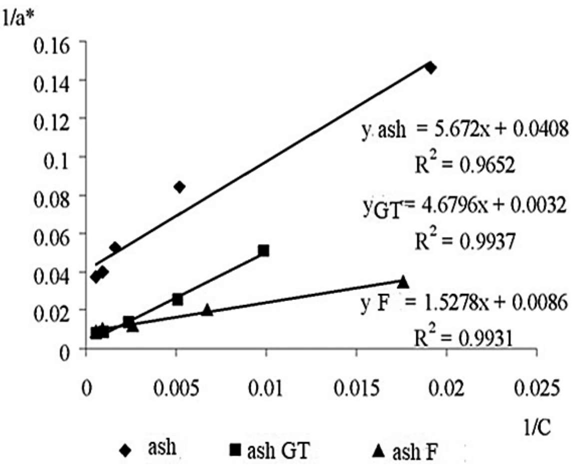

Fig. 4. Langmuir linearized isotherm for adsorption of diesel fuel by synthesized zeolites based on removal ash

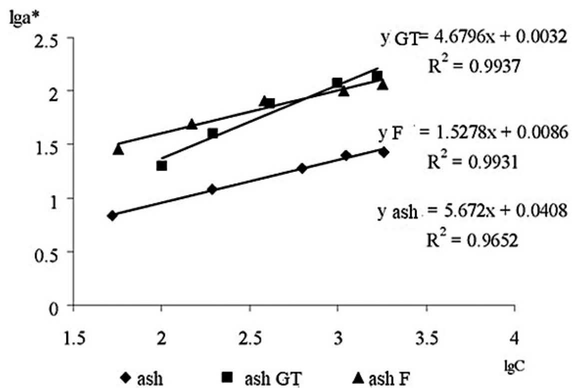

Fig. 5. Freundrich's linearized isotherm for adsorption of diesel fuel by synthesized zeolites based on removal ash

Langmuir isotherm for ash modified by the hydrothermal method:

$$a^* = 312.5\frac{6.84\cdot10^{-4}C}{1+6.84\cdot10^{-4}C} \tag{2}$$

$$a^* = 312.5\frac{6.84\cdot10^{-4}C}{1+6.84\cdot10^{-4}C} \tag{3}$$

Langmuir isotherm for ash modified by sintering:

$$a^* = 116.28\frac{0{,}0056C}{1+0{,}0056C} \tag{4}$$

Freundlich isotherm for ash:

$$a^* = 5.67s^{\ 1/0.98} \tag{5}$$

Freundlich isotherm for ash modified by hydrothermal method:

$$a^* = 4.68s^{\ 1/0.99} \tag{6}$$

Freundlich isotherm for ash modified by sintering:

$$a^* = 1.53s^{\ 1/0.91} \tag{7}$$

The value of the correlation coefficients indicates that in this range of concentrations, both isotherms well describe the statics of adsorption. The use of zeolites for adsorption has shown that there is not only physical adsorption but also ion exchange because in the structure of the zeolite are ions Na^+, K^+, Ca^{2+}, Mg^{2+}, which are able to exchange cations in solution (e.g., heavy metal ions).

CONCLUSIONS

The scientific studies on the adsorption of petroleum products provide valuable insights into this critical field's processes, mechanisms, and applications. The adsorption processes have been investigated for the removal and recovery of petroleum products under static conditions. The adsorption mechanisms of petroleum products involve complex interactions between the adsorbent material and the adsorbate molecules. Physical and chemical adsorptions play crucial roles in the overall adsorption process. Physical adsorption involves weak van der Waals forces, while chemical adsorption involves stronger chemical bonds between the adsorbate and adsorbent surface. Adsorbent materials based on fly ashes have been investigated for the adsorption of petroleum products. The selection of the appropriate adsorbent material depends on factors such as adsorption capacity, selectivity, cost-effectiveness, and ease of regeneration. The adsorption of petroleum products finds applications in various industries and environmental remediation processes. These applications include oil spill cleanup, wastewater treatment, groundwater remediation, gas separation, and recovering valuable hydrocarbons from industrial waste streams. Despite significant progress in the field of adsorption of petroleum products, several challenges remain. These challenges include developing efficient adsorbent materials with high adsorption capacity, selectivity, and stability, as well as optimizing adsorption processes for large-scale applications. Future research efforts should address these challenges and explore novel techniques and materials for enhanced adsorption performance. In summary, the studies on the adsorption of petroleum products provide a comprehensive overview of the processes, mechanisms, and applications involved. This knowledge contributes to developing efficient and sustainable solutions for removing and recovering petroleum products, with the ultimate goal of mitigating environmental pollution and achieving energy and resource efficiency.

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