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Application of soil-zeolite column to immobilization of selected pollutants, including metals, contained in municipal landfill leachate

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ABSTRACT

This study aimed to assess the possibility of clay and clay-synthetic zeolite substrates application to immobilization of elements available in municipal landfill leachate. The experimental sorption tests were carried out using the column method to best reflect the actual conditions of elements sorption from percolating leachate in the soil. The leachate sampled in Rokitno, Lublin, Poland, municipal landfill cell was used in the study. Four sorbent substrates were tested: sandy loam sampled in Chotyłów, Poland, its mixture with 10 and 20% by mass of synthetic zeolite NaP1, and synthetic zeolite NaP1. The following elements identified in the leachate were selected for the study: Al, P, Mn, Fe, Sn, and Ba. The elemental concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS) in accordance with the procedure EPA 6020. The studied sorbents showed good sorption efficiency, however, accompanied by relatively low sorption capacity.

Keywords: sorbents, sorption properties, heavy metals, landfill leachate, synthetic zeolite, clay soil.

INTRODUCTION

Landfill leachate is a liquid by-product of the decomposition of municipal waste deposited in landfills, a mixture of infiltrated rainwater, water resulting from waste biodegradation, and water contained directly in the waste. Thus, it poses a serious environmental threat, illustrating the problems of modern waste management and the need for environmental protection (Wang et al., 2024; Teng and Chen, 2023; Lindamulla et al., 2022; Teng et al., 2021; Arunbabu et al., 2017).

The amount of created leachate is mainly related to precipitation depth, evapotranspiration, surface run-off, groundwater infiltration to the landfilled waste mass and the deposited waste degree of compaction(Lindamulla et al., 2022; Fu et al., 2019). Thus, landfill leachate is characterized by a very high concentration of chemical oxygen demand (COD), ammonium nitrogen, persistent organic pollutants (POP),and heavy metals (Genethliou et al., 2023; Vaverková et al., 2020).

According to the European Waste Catalogue, landfill leachate is considered hazardous or non-hazardous waste (European Commission, 2000). Thus, landfill leachate is commonly considered toxic and poses a potential threat to the surrounding environment and ecosystems (Teng et al., 2021). The penetration of metals, including heavy metals, into groundwater through leachate may lead to long-term contamination, posing ecological and health risks.

The release of phosphorus and nitrogen from leachates to soil, water, and groundwater can negatively impact the environment, as phosphorus can cause eutrophication of water, resulting in excessive algae growth and disruption of aquatic ecosystems. The presence of nitrate and ammonium compounds negatively impacts water quality and human health (Pazoki et al., 2012).

Heavy metals are persistent pollutants able to accumulate in soil, groundwater, plants and animals organisms as a result of various processes. On a global scale, heavy metals play a special role as being considered one of the most dangerous

categories of pollutants, mainly due to their persistence, toxicity, migration in the environment, and lack of biodegradability. Their carcinogenic ability through skin contact or ingestion has been documented, along with numerous diseases with serious consequences (Kaur et al., 2020; Agrawal et al., 2021; Parvin et al., 2021; Wang et al., 2020; Flieger et al., 2020; Franus et al., 2014). There was indicated that harmful substances contained in leachate cause pathological changes in human cells, aquatic organisms, and plants (Jabłońska-Trypuć et al., 2021; Pereira et al., 2016).

Understanding the characteristics of pollutants contained in leachates provides opportunities to control and prevent environmental hazards resulting from the last element of waste management chain, landfilling (Fu et al., 2019).

To prevent the migration of harmful substances contained in the landfill leachate, various types of sealing, including compacted earthen liners, are used, often using soils with a low permeability, characterized by a coefficient of saturated hydraulic conductivity, not greater than $1 \cdot 10^{-9}$ m·s^{-1} (Minister of the Environment, 2003; Czop et al., 2017; Wysocka, 2015). Various additives are sometimes used to improve the sealing properties and immobilize harmful substances contained in leachate. The use of alternative materials is primarily aimed at increasing the sorption capacity of mineral insulating liners (Phanikumar et al., 2016; Myowig et al., 2006; Franus et al., 2014). The literature indicates that synthetic zeolites are exceptionally effective sorbents for removing metals from aqueous solutions due to their high surface area, porosity, and ion exchange capacity (Flieger et al., 2020; Panek et al., 2021). Furthermore, the use of synthetic zeolites obtained from waste products is consistent with the concept of sustainable development.

Moreover, natural zeolites often require expensive processing before use; therefore, there is growing interest in cheaper and more readily available synthetic zeolites produced from recycled materials (Widomski et al., 2021). Their properties can be modified during the synthesis stage, making them valuable functional materials. Synthetic zeolites are commonly used as sorbents to remove metal ions, metalloids, phosphates, ammonium ions, and radioactive elements from wastewater and landfill leachate (Bilardi et al.,2019; Panek, Medykowska and Szewczuk-Karpisz, 2021; Velarde et al., 2023). The literature (Adamczyk et al., 2012, Elboughdiri, 2020) studies deliver research on metal sorption using natural and synthetic zeolites conducted under static conditions, where the adsorbate remains in contact with the adsorbent without forced flow, for a specified period of time under controlled pH, temperature, and concentration conditions.

Adamczyk et al. (2012) studied the sorption of selected metals (Zn, Ni, Pb, and Mn) under batch conditions using synthetic NaP1 zeolite. Based on the obtained results, the authors concluded that equilibrium of the sorption reaction was established after two hours, and the percentage reduction of the analyzed metals ranged from 71.41% for Ni to over 97% for the remaining metals. Elboughdiri (2020) investigated the removal efficiency of copper, lead, and cadmium ions from synthetic wastewater using natural zeolites. The results indicated that the removal efficiency of the analyzed metals was influenced by the initial solution concentration, solution pH, stirring speed, and adsorbent mass. As the amount of adsorbent, solution pH, and stirring speed increased, the sorption efficiency of the analyzed metals increased.

However, such studies do not fully reflect the actual conditions of contaminant migration and retention in the porous medium environment. Therefore, the main aim of this study was to investigate element sorption under dynamic conditions using soil-zeolite columns. Column studies allow for the determination of the immobilization efficiency of contaminants contained in landfill leachates and the assessment of the sorption capacity of the tested materials under dynamic conditions, which better reflect the environmental conditions occurring in landfills, compared to static methods.

This study investigated the potential use of soils and mixtures of soils and synthetic zeolites to immobilize elements contained in landfill leachates. The experimental studies utilized clay soil from the decommissioned Chotyłów ceramic clay deposit and locally produced synthetic zeolite NaP1. Particular attention was paid to the effectiveness of immobilizing elements such as aluminum, phosphorus, manganese, iron, tin, and barium. These elements are commonly identified in landfill leachate as products of waste decomposition and components of anthropogenic origin (Frisbie et al., 2015; Ahmad et al., 2022).

Furthermore, the selection of these elements is supported by the literature, as landfill leachate contains a wide spectrum of inorganic constituents, including metals. The choice of the analyzed elements is also justified by their environmental relevance and potential toxicity. Manganese may

exhibit neurotoxic effects and influence cognitive functions, barium affects the cardiovascular and muscular systems, while tin compounds, especially organotin compounds, are characterized by toxic and endocrine - disrupting effects (Frisbie et al., 2015; Lehmler et al., 2018; Ahmad et al., 2022). Aluminum has been associated with potential neurotoxic effects, whereas excessive iron may lead to oxidative stress and organ damage (Health Canada, 2019; Abed et al., 2023). In turn, phosphorus, as a biogenic element, contributes to eutrophication of water bodies and degradation of aquatic ecosystems (Pazoki et al., 2012).

This study therefore aims to identify effective and efficient methods for removing contaminants from landfill leachates.

MATERIALS AND METHODS

Sorbent substrates characteristics

The clay substrate studied was sampled from the village of Chotyłów, from a location of the decommissioned ceramic clay deposit, located in the northern part of the Łuków Plain, southeast of Biała Podlaska. Sampling was performed at an appropriate depth below the ground surface (i.e., 0.8–1.0 m) to avoid the presence of vegetation and roots. The soil was then air-dried and crushed using a rubber mallet. The prepared specimens were then dried at 105 °C for 24 hours. The particle size distribution of the applied clayey substrate was determined according to standards ASTM C136/C136M-19 and PN-B-04481:1988 (ASTM International, 2019, Polish Committee for Standardization 1988). The substrate texture type was recognized as sandy loam, according to USDA (United States Department of Agriculture) classification (USDA Natural Resources Conservation Service, 2019).

Regionally produced zeolite NaP1 was used as an additive to clayey soil to investigate the sorption of elements contained in landfill leachate. It was obtained by the hydrothermal reaction of fly ash from coal combustion with sodium hydroxide (NaOH) using a patented zeolite synthesis installation (Wdowin et al., 2014). Fly ash collected from the Jaworzno III Power Plant (Poland) served as the raw precursor. Hydrothermal synthesis of zeolite was carried out using 20 kg of fly ash, 90 L 3.3 M NaOH aq (12 kg of solid NaOH in 90 L H_2O), at a temperature of 80 °C. The NaP1 zeolite synthesis process lasted 24 h (Bandura et al., 2017; Panek et al., 2017; Widomski et al., 2021). The obtained synthetic NaP1 zeolite is a representation of a structure similar to gismodine (GIS), as defined in current structural classifications. This structure is composed of 8-membered channels formed from 2-4-membered aluminosilicate rings (Malinowski et al., 2024).

The described sandy loam was mixed with NaP1 zeolite at ratios of 10 and 20% by mass, after drying at 105 °C for 24 hours. The particle size distribution, pH, specific surface area, and t-plot micropore surface area were determined. The pH of prepared samples was determined by the potentiometric method using pH/conductivity meter CPC-501 Elmetron (Zabrze, Poland), in accordance with the national standard PN-ISO 10390:1997 (Polish Committee for Standardization 1997). The granulometric composition of sandy loam and sandy loam mixed with NaP1 zeolite at 10 and 20% by mass was determined using the aerometric method specified by the PN-B-04481:1988 standard (Polish Committee for Standardization 1988). The particle size distribution of NaP1 zeolite was determined by laser diffraction using a Mastersizer 3000 analyzer (Malvern Panalytical, United Kingdom). The distribution was performed using an ultrasonic probe to break up larger particle aggregates in a demineralized water dispersing liquid. To determine the sorption properties, the BET specific surface area, t-plot micropore surface area, and adsorption and desorption isotherms were determined using 3Flex analyzer (Micromeritics, Norcross, GA, USA). The phase compositions of the sorbents were analyzed using X-ray diffraction, (Panalytical, Almelo, Netherlands) (Figure 1).

Landfill leachate characteristics

The applied landfill leachate was collected from the Rokitno landfill, located in the Lubartów commune, close to Lublin, Poland. The landfill has been in operation since 1994 and is located on the site of a decommissioned aggregate mine. Table 1 presents the physicochemical parameters of landfill leachate.

Column studies

Sorption tests were conducted using the column method to better reflect the actual conditions of element sorption from percolating leachate in the soil environment.

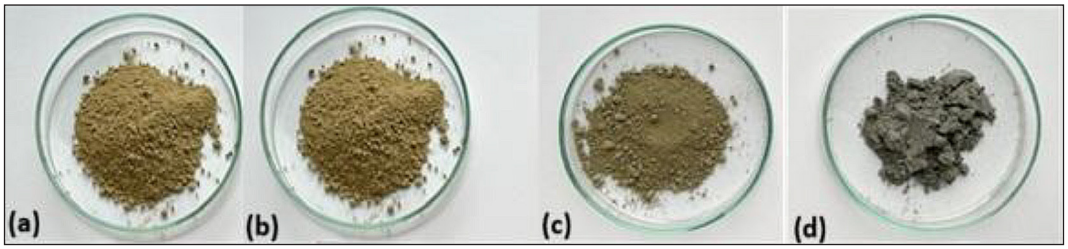

Figure 1. Samples of studied substrates: (a) Chotyłów, (b) Chotyłów with addition of 10% NaP1 zeolite, (c) Chotyłów with addition of 20% NaP1 zeolite, and (d) NaP1 zeolite

Table 1. Physicochemical characteristics of the leachate from the Rokitno landfill

pH	EC	COD	TC	IC	TOC	Cl^-	Na	Ca	Mg	K	Al	P	Mn	Fe	Sn	Ba
–	mS	mg·L^{-1}														
7.84	12.56	1125	1620	1122	498	1775	1268.7 ±9.23	142.9 ±2.83	74.6 ±2.07	764.4 ±17.3	1.133 ±0.01	11.44 ±0.11	0.225 ±0.003	2.122 ±0.03	0.024 ±0.001	0.362 ±0.04

Empty polypropylene SPE columns, 65 mm long and 12 mm wide, were loaded with 4 g of each of the studied sorbents, dried at 105 °C for 24 h, and each end of the column was protected with a layer of glass wool. The sorption materials used included: clay soil, a soil mixture with 10% NaP1 by mass, and a soil mixture with 20% NaP1 by weight. For NaP1 zeolite, 3 g of material was used because its low density allowed for complete filling of the column volume.

A 20 mL sample of the landfill leachate containing the elements mixture (the elemental composition is presented in Table 2) was passed through the bottom of the column using a Medima S1 (Warsaw, Poland) syringe infusion pump at a rate of 0.5 mL min^{-1}. The duration of experiment was 40 minutes. The experiment was performed in triplicate for each sorbent. After contact with the sorption bed, the solution was collected and filtered using a 0.45 µm PTFE filter (Alfatec Technology). The goal of this step was to remove any fine sorbent particles that might have been washed out by the landfill leachate. An identical filtration process was applied to the initial leachate solution after mineralization to determine the elements contained in the leachate. This ensured consistent analytical conditions and excluded the influence of possible adsorption on the filter itself. The obtained filtrate was then acidified with HNO_3 and stored at 4 °C until mineralization in accordance with the national PN-ISO 5667-10:2021-11 standard (Polish Committee for Standardization, 2021). Figure 2. presents the experimental system employed for sorption testing using a Medima S1 infusion pump.

Wet digestion of each 5 mL sample was performed by adding 5 mL of 69% nitric acid (HNO_3) Super Purity (Romil, USA). Then, the samples were heated to 190 °C in sealed Teflon vessels in a TOPEX microwave digestion system (PreeKem, Shanghai, China). The samples were then diluted to 25 mL with ultrapure water obtained from a Milli-Q purification system with a specific resistivity of 18.2 MΩ·cm (Millipore, Darmstadt, Germany). To avoid contamination, the assay glass was specially prepared by etching in 10% HNO_3 Super Purity (Romil, USA) for at least 24 h and then rinsed several times with ultrapure water obtained from a Milli-Q purification system.

Elemental analysis of both the initial effluent solution and the sorption effluent was performed using an Agilent 8900 ICP-MS Triple Quadrupole mass spectrometer (Agilent, Santa Clara, CA, USA) equipped with an inductively coupled plasma (ICP). Measurements were conducted in helium mode (He mode) with a helium flow rate of 5.5 mL·min^{-1}. The plasma was operated in general-purpose mode at RF power of 1.550 kW, nebulizer gas flow of 1.07 L·min^{-1}, auxiliary gas flow of 0.9 L·min^{-1}, and plasma gas flow of 15 L·min^{-1}. The integration time ranged from 0.1 to 1 s, depending on the expected element concentration. Commercial ICP analytical standards (Agilent Technologies, Santa Clara, CA, USA, and Merck Millipore, Darmstadt, Germany) were used for the analyses. The ISTD internal standard (Sc, Y, Lu) at a concentration of 0.5 mg·L^{-1} was used for analysis. The obtained recoveries were in the range of 80–120%. The elements were quantified before and after sorption using

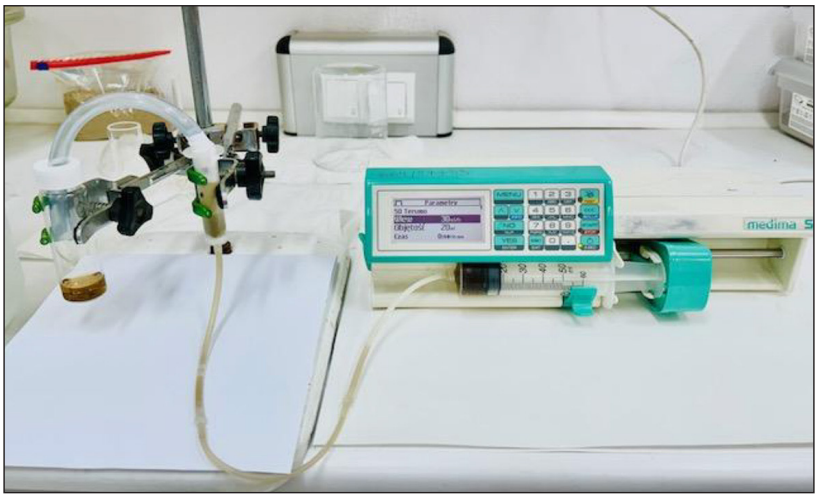

Figure 2. Experimental setup for sorption testing using a Medima S1 infusion pump

calibration curves determined separately for each element. The element removal efficiency from the landfill leachate was calculated using the following formula:

$$Adsorption\ efficiency\ (\%) = \\ = \frac{C_0 - C_{eq}}{C_0} \cdot 100\% \quad (1)$$

where: C_0 – initial concentration of an element in leachate [mg·L^{-1}], C_{eq} – concentration of an element at equilibrium [mg·L^{-1}].

The efficiency of the sorbents was calculated using the following formula:

$$q = (C_0 - Ceq) \cdot \frac{V}{m} \quad (2)$$

where: q – amount of adsorbed metal (mg·g^{-1}), C_0 – initial concentration of an element in leachate [mg·L^{-1}], C_{eq} – concentration of an element at equilibrium [mg·L^{-1}], V – solution volume [L], m – adsorbent mass [g].

RESULTS AND DISCUSSION

Characteristics of the mineral sorbents

The analyzed sorbents were characterized in terms of granulometric composition, specific surface area, microporous surface area, and adsorption/desorption isotherms. An increase in the percentage content of NaP1 zeolite resulted in an increase in the specific surface area of the analyzed sorbents by 17.9% for soil with 10% NaP1 and by 40.1% for soil with 20% NaP1.

Table 2 presents the basic characteristics of the tested substrates, including sandy loam sampled in Chotyłów and its 10% and 20% by mass mixtures with NaP1 zeolite and the sole NaP1.

The granulometric analysis of the clay and clay samples with 10 and 20% by mass addition of zeolite NaP1 showed that a sandy fraction predominated in the samples, while the proportion of the clay fraction was 9–11%.

The particle size distribution of the synthetic NaP1 zeolite is presented in Figure 3. The particle size distribution of NaP1 was multimodal, with two clearly marked peaks. The first

Table 2. The basic characteristics of the studied substrates

Parameter	pH	Particle size composition [%]			BET surface area [m^2·g^{-1}]	t-plot micropore area [m^2·g^{-1}]
		Sand 2-0.05 mm	Silt 0.05-0.002 mm	Clay <0.002 mm		
Chotyłów	7.29±0.19	55	34	11	19.99±0.16	5.48
Chotyłów+10%NaP1	8.58±0.20	55	35	10	23.56±0.09	4.83
Chotyłów+20%NaP1	9.03±0.04	55	36	9	28.00±0.17	4.25
NaP1	10.20±0.02				48.85±0.13	2.49

corresponds to particle sizes of 5–10 μm, the second maximum corresponds to particles in the range 50–100 μm. A small proportion of particles below 1 μm, as well as larger particles of 500 μm are also observed. This means that the sorbent contains both a finer and a coarser fraction, with the predominant fraction in the 5–100 μm range.

The adsorption–desorption isotherms of the investigated sorbents are presented in Figures 4 a-d.

The shape of the adsorption-desorption isotherm and hysteresis loop provide valuable information about the physical mechanism of the adsorption process and can be used to qualitatively determine the type of pores present in the sorbent (Kuila and Prasad, 2013).

All analyzed sorbents exhibit a type IV N_2 adsorption/desorption isotherm according to IUPAC (International Union of Pure and Applied Chemistry), which is characterized by the presence of an adsorption-desorption loop, called a hysteresis loop, associated with capillary condensation in mesopores. The hysteresis loop appears in pores wider than 4 nm. This type of isotherm indicates the presence of mesopores (Thommes et al., 2015). All the analyzed sorbents were characterized by an H3 hysteresis loop according to the IUPAC classification, indicating that the tested sorbents were characterized by pores of different sizes and connectivity (Barsotti et al., 2020). The H3 hysteresis loop indicates the presence of platelet particles that form slit pores (Frank et al., 2022). The type IV isotherm, characteristic of mesoporous materials (pores with a diameter of 2–50 nm), however, in the initial part of the isotherm (at low relative pressures) corresponds to adsorption on the surface and in micropores (pores with a diameter < 2 nm). This indicates high efficiency of heavy metal sorption due to the combination of micropores and mesopores (Grozdov and Zinicovscaia, 2023).

Figure 5 a-d show the XRD diffractograms of the analyzed sorbents. The diffractograms obtained for Chotyłów soil, soil mixtures with 10 and 20% by mass of NaP1 zeolite, and NaP1 zeolite provide data enabling the identification of mineral phases and the assessment of changes in the crystal structure after modification of the material. In the case of the diffractogram for Chotyłów clay soil, the following mineral phases were identified: illite, kaolinite, montmorillonite, quartz, and calcite. Montmorillonite, a mineral of the smectite group, exhibits a high cation exchange capacity (CEC) and significant metal ion adsorption capability (Malandrino et al., 2006; Ijagbemi et al., 2009). The adsorption of metal cations occurs at negatively charged sites on clay minerals (Ikegami et al., 2025). The addition of synthetic NaP1 zeolite to the soil mixture resulted in the appearance of new mineral phases, including mullite and sodium-aluminum silicate hydrate, indicating a restructuring of the crystal structure and partial mineralogical activation of the material. In the case of NaP1 zeolite, characteristic reflections corresponding to the NaP1 zeolite were observed, as well as reflections originating from other phases such as mullite and quartz.

Sorption tests

The study was conducted to investigate the removal of elements present in landfill leachate, such as Al, P, Mn, Fe, Sn, and Ba. Their selection

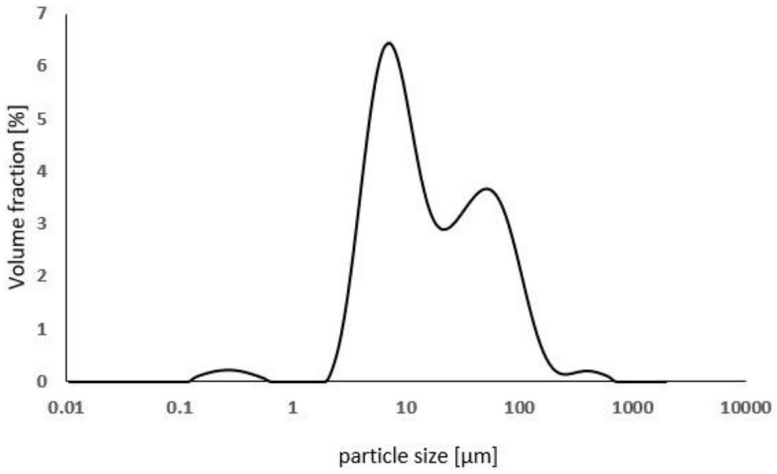

Figure 3. Particle size distribution of the synthetic NaP1 zeolite

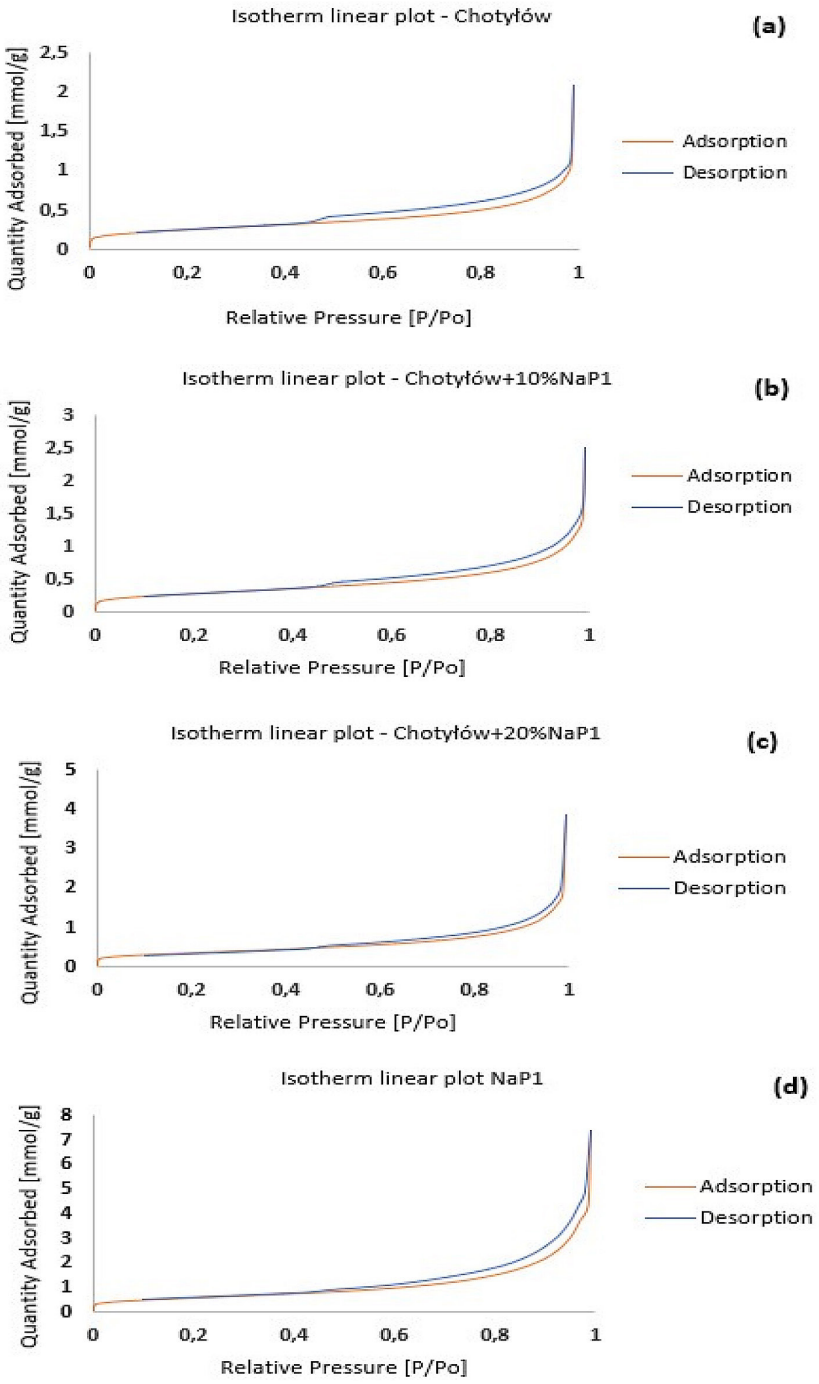

Figure 4. Adsorption–desorption isotherms for: (a) Chotyłów, (b) Chotyłów with addition of 10% NaP1 zeolite, (c) Chotyłów with addition of 20% NaP1 zeolite, and (d) NaP1 zeolite

was based on their relatively high concentrations in the analyzed leachate, their potential toxicity, and the sorption efficiency observed for the applied materials..

Table 3 shows the sorption efficiency of individual elements and the calculated efficiency of the sorbents used in this experiment.

The sorption process of the tested elements was effective for all tested sorbents, demonstrating high efficiency for most of them. The lowest sorption level was recorded for Ba on clayey soil, at only 3.9%. Such low sorption may be attributed to the presence of strongly competing Na^+ ions in the landfill leachate. These results are consistent with the observations made by Chikkamath et al. (2021), who found that the decrease in Ba sorption on clay minerals is influenced by an increase in the concentration of the NaCl electrolyte used. The addition of zeolite significantly improved the sorption capacity of this element: at

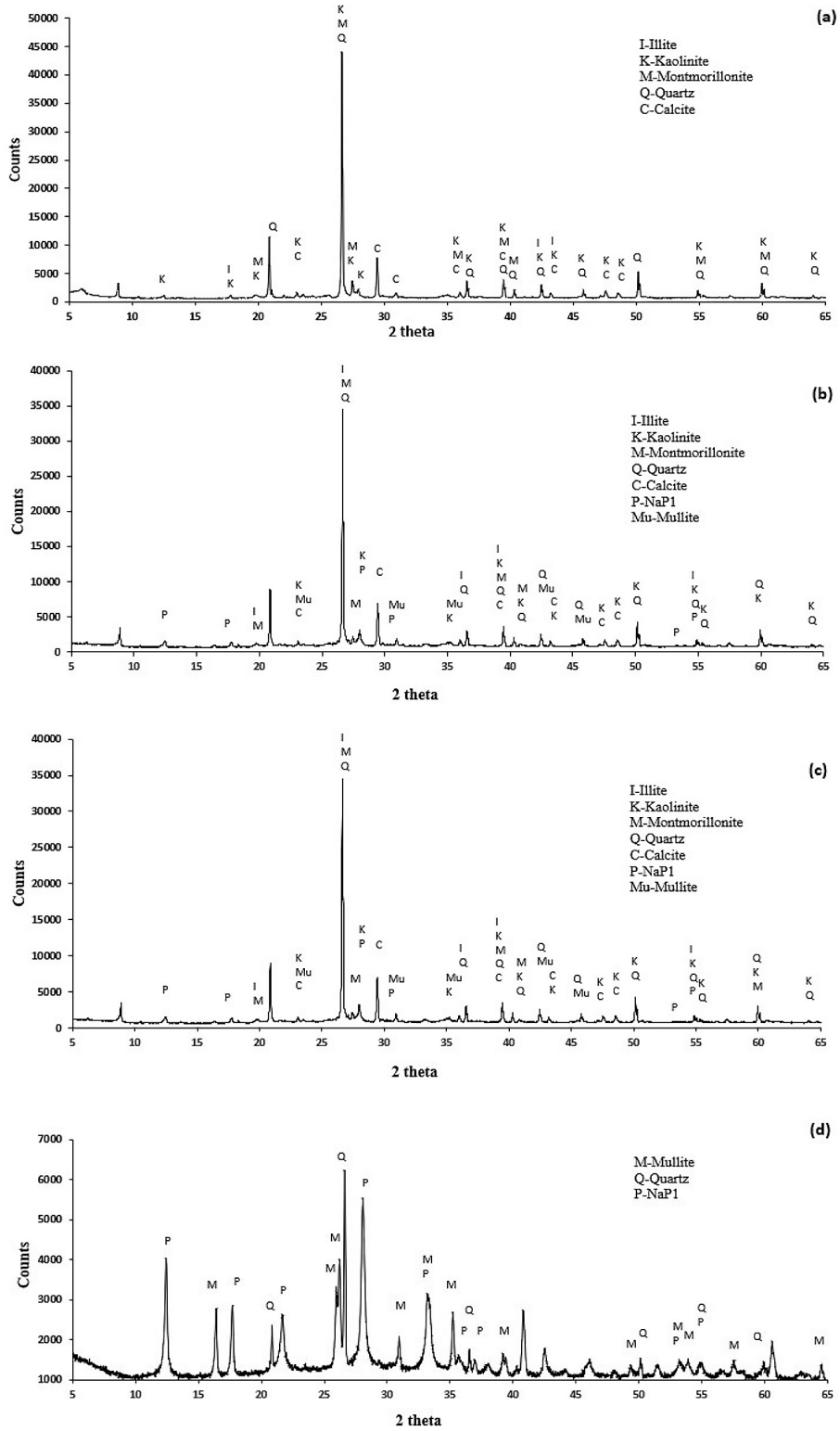

Figure 5. XRD diffractograms for: (a) Chotyłów, (b) Chotyłów with addition of 10% NaP1 zeolite, (c) Chotyłów with addition of 20% NaP1 zeolite, and (d) NaP1 zeolite

10% zeolite NaP1 addition, sorption was 47.4%, and with 20% it increased to 53.9%, while zeolite alone showed the highest value, reaching 69%. Similar observations were reported by Araissi et al., (2016), who studied the efficiency of barium and strontium removal from aqueous solutions on the synthetic zeolite 4A, with the efficiency being higher for strontium, and the sorption process occurs mainly through ion exchange. The sorption efficiency decreased in the presence of both ions.

In turn, sorption of elements such as Al, P, Fe, and Sn was determined as the most effective

Table 3. Summary of the sorption efficiency and sorption capacity of the tested elements

Sample name	27 Al	Sorption Al	Sorption capacity
	Conc. [mg·L^{-1}]	[%]	[mg·kg^{-1}]
Chotyłów	0.151±0.03	86.71±2.32	4.92±0.13
Ch+10%NaP1	0.193±0.01	82.99±0.61	4.71±0.03
Ch+20%NaP1	0.238±0.05	79.00±4.39	4.48±0.25
NaP1	0.418±0.08	68.41±7.57	4.47±0.57
min		68.41	4.48
max		86.71	5.17
Sample name	31 P	Sorption P	Sorption capacity
	Conc. [mg·L^{-1}]	[%]	[mg·kg^{-1}]
Chotyłów	4.29±0.58	62.50±5.05	35.74±2.89
Ch+10%NaP1	5.42±0.32	52.65±2.83	30.11±1.62
Ch+20%NaP1	6.28±0.41	45.11±3.60	25.79±2.06
NaP1	5.94±0.11	48.03±0.95	36.62±0.72
min		45.11	25.79
max		62.50	36.62
Sample name	55 Mn	Sorption Mn	Sorption capacity
	Conc. [mg·L^{-1}]	[%]	[mg·kg^{-1}]
Chotyłów	0.103±0.02	54.47±9.18	0.61±0.10
Ch+10%NaP1	0.079±0.01	64.91±2.95	0.73±0.03
Ch+20%NaP1	0.075±0.01	66.71±4.23	0.75±0.04
NaP1	0.051±0.00	77.47±0.10	1.16±0.01
min		54.47	0.61
max		77.47	1.16
Sample name	56 Fe	Sorption Fe	Sorption capacity
	Conc. [mg·L^{-1}]	[%]	[mg·kg^{-1}]
Chotyłów	0.815±0.10	61.60±4.70	6.54±0.50
Ch+10%NaP1	0.955±0.03	55.01±1.30	5.84±0.14
Ch+20%NaP1	1.098±0.03	48.28±1.47	5.12±0.16
NaP1	1.052±0.01	50.43±0.69	7.14±0.10
min		48.28	5.12
max		61.60	7.14
Sample name	118 Sn	Sorption Sn	Sorption capacity
	Conc [mg·L^{-1}]	[%]	[mg·kg^{-1}]
Chotyłów	0.012±0.002	48.91±6.80	0.06±0.01
Ch+10%NaP1	0.013±0.0004	43.59±1.60	0.05±0.002
Ch+20%NaP1	0.015±0.000	35.92±0.82	0.04±0.001
NaP1	0.014±0.000	41.58±0.44	0.07±0.001
min		35.92	0.04
max		48.91	0.07
Sample name	137 Ba	Sorption Ba	Sorption capacity
	Conc. [mg·L^{-1}]	[%]	[mg·kg^{-1}]
Chotyłów	0.348±0.012	3.87±1.19	0.07±0.02
Ch+10%NaP1	0.190±0.006	47.44±1.77	0.86±0.03
Ch+20%NaP1	0.167±0.005	53.90±1.44	0.98±0.025
NaP1	0.112±0.0001	69.00±0.05	1.67±0.001
min		3.87	0.07
max		69.00	1.67

on the clay soil, reaching values of 83.79% for Al, 62.5% for P, 61.6% for F,e and 48.9% for Sn, respectively. As the zeolite in the bed increased, the sorption of these elements decreased slightly, reaching a still satisfactory value of almost 50%. This may indicate the specific affinity of these elements for the mineral components of the clay fraction (Idris and Sirelkhatim Ahmed, 2012), or, in the case of aluminum, it may have been "washed out" from the zeolite, as zeolites contain aluminum in their crystalline structure (Klika et al., 2005).

Similar results regarding phosphorus removal were obtained by Ciosek et al., (2016), who investigated the efficiency of phosphorus removal from synthetic wastewater using clay-zeolite columns, achieving a sorption efficiency of 72% after 3h to 88% after 12h.

In the case of Mn, sorption on clay soil was 54%, while with the addition of 10% NaP1 zeolite it increased to 65%, and with the addition of 20% zeolite it reached 67%. The highest sorption efficiency, at 77.5%, was observed on NaP1 zeolite alone. In an article published by Wang et al., (2025), the authors emphasized in their study that clay minerals present in clay soils are excellent adsorbents, mainly due to their unique structural and chemical properties. Such materials have a large specific surface area, high cation exchange capacity (CEC), and the ability to swell (Zhao, 2011). In addition, clay soils exhibit a negative charge on their surface, which facilitates the electrostatic adsorption of ions (Chen et al., 2018). Additionally, an increase in pH increases the negative surface charge of the adsorbents, and thus the sorption efficiency (Markiewicz-Patkowska et al., 2004; Yu et al., 2023). The sorbents used for the experiment were characterized by a pH of 7.29 for the Chotylów soil, 8.58 for the soil mixture with the addition of 10% NaP1, 9.03 for the mixture with the addition of 20% NaP1, and 10.2 for the NaP1 synthetic zeolite. Moreover, the efficiency of the sorption process is also influenced by the pH of the solution. Literature data report that for many metals, optimal sorption conditions occur at a solution pH close to neutral (Ďuricová et al., 2024). The leachate used for the sorption experiment had a slightly alkaline pH of 7.84.

Figure 6 shows a graphical presentation of the sorption efficiency of the sorbents for individual elements.

Despite the good observed sorption efficiency, the calculated sorption capacity was relatively low for most of the studied elements. The exception was phosphorus, whose sorption capacity ranged from 25.76 mg·kg^{-1} for the soil mixture with 20% NaP1 zeolite to 36.62 mg·kg^{-1} for the zeolite alone.

For the remaining studied elements, the low sorption capacity may be due to several factors: relatively low concentrations of the elements contained in the landfill leachate, and the use of too high amount of sorbent relative to the element being determined The use of such a large amount of sorbents in the experiment resulted from the fact that the analyzed leachate contained high concentrations of strongly competitive ions, the content of which in the leachate was, respectively: (Na^+ 1268.7 mg·L^{-1},

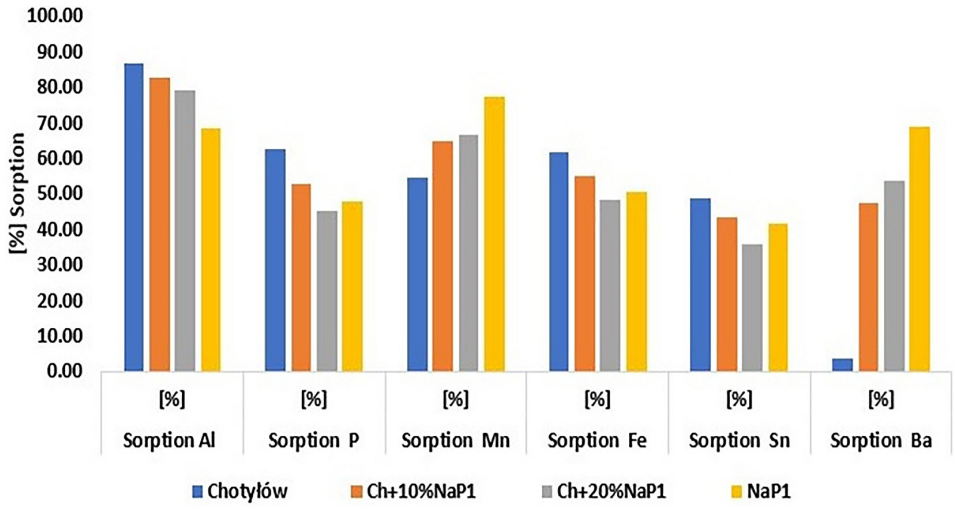

Figure 6. Comparison of the sorption efficiency of the analyzed elements on different sorbents

Mg^{2+} 74.6 mg·L^{-1}, Ca^{2+} 142.9 mg·L^{-1}, K^{+} 764.4 mg·L^{-1}). These ions compete for the occupation of active sites available on the sorbent surface, thus influencing the sorption of the analyzed elements. Moreover, ionic competition is one of the key factors limiting the sorption process in real landfill leachates. In the presence of multiple ions with similar charge and ionic radius, competition for the same sorption sites occurs, leading to a decrease in the removal efficiency of trace elements. This phenomenon is particularly significant in complex multicomponent systems such as landfill leachates, where the presence of dominant ions (e.g., Na^{+}, Ca^{2+}, Mg^{2+}, K^{+}) can substantially reduce the sorption of elements by occupying active sites and altering the surface properties of the sorbent (Mirzaei et al., 2013).

Additionally, high electrical conductivity, i.e. increased ionic strength of the solution, leads to a decrease in sorption efficiency of elements by limiting electrostatic interactions and reducing the number of available sorption sites due to particle aggregation. The presence of high concentrations of electrolytes may also "shield" the sorbent surface and restrict the transport of metal ions to active sites, which particularly affects elements whose sorption is governed by electrostatic mechanisms (Musso et al., 2019).

The content of organic matter in landfill leachate is an important factor influencing the efficiency of the sorption process. In the analyzed leachate, its level, expressed as TOC (498 mg·L^{-1}), indicates a moderate content of organic compounds. Under such conditions, organic matter may partially complex metal ions, affecting their mobility in solution. Simultaneously, its impact on the sorption process is likely less significant compared to leachates characterized by high TOC levels (Yu et al., 2022).

CONCLUSIONS

The research on the possibilities of using soils and soil mixtures with varying amounts of synthetic zeolites added to immobilize the elements contained in landfill leachates allowed the following conclusions to be drawn:

The nitrogen adsorption–desorption isotherms indicated that all sorbents were characterized by a moderate specific surface area and the presence of both micropores and mesopores, the presence of which affects the sorption efficiency of the elements.

The analysis of the sorption experiment was based primarily on the assessment of the percentage of element removal from the landfill leachate solution and the amount of the element adsorbed on the sorbent. Particular attention was paid to the sorption experiments for elements such as Al, P, Mn, Fe, Sn, and Ba. The selection of elements was dictated by their relatively high abundance in the actual landfill leachate. Based on the obtained results, the sorption efficiency was satisfactory for most elements, with the lowest sorption observed for barium. The addition of zeolite significantly improved the sorption of this metal.

The study was conducted using a dynamic column method to better represent the actual landfill conditions. Unlike static methods, this study allowed for the assessment of the sorption properties of experimental materials during actual landfill leachate flow through the porous medium.

The obtained results allowed us to conclude that the tested sorbents may be promising materials for the immobilization of pollutants contained in landfill leachates, which are raw materials for the construction of isolation barriers.

The proposed technique for immobilizing elements from landfill leachate is noteworthy because it utilizes natural sorbents, as well as mixtures of natural sorbents with sorbents derived from waste, such as fly ash. These materials ensure effective sorption even without prior modification of the sorption material. Furthermore, the use of zeolites derived from waste fly ash can be considered an ecological solution that aligns with the principles of sustainable development. Adsorption isotherms were not determined in the conducted studies due to the use of actual landfill leachate with a specific concentration of elements.

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