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Study of lignite as the raw material for adsorption of Pb(II) and Cd(II) ions from aqueous solution

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Abstract: The adsorption of two heavy metal ions, lead and cadmium, from an aqueous solution was investigated using Kosovo's lignite as the raw material. The material's properties, including nature, functional groups, surface shape, and charge, were investigated using FTIR, XRD, SEM, and pHZPC techniques. The objective of determining parameters such as initial concentration, pH, contact time, adsorbent dosage, and temperature was to understand how these variables influence adsorption. Under optimal conditions (0.125g/50cm³, 30 mg/dm³, 30 min, 200 rpm, and pH 6), the removal efficiency of Pb(II) was 97.22 %, and 90.04% for Cd(II) under optimal conditions (0.125g/50cm³, 30 mg/dm³, 30 min, 200 rpm, and pH 6). To investigate the achievement of equilibrium between lignite and metal ions, two key isotherm models - s, Langmuir and Freundlich -, were applied. Based on the Langmuir isotherm model, the maximum adsorption capacities for lead and cadmium were 55.55 mg/g and 48.78 mg/g, respectively, at 288 K. The best medium for removing metal ions from lignite (desorption) is was found to be 0.5M HCl. Standard enthalpy change, standard entropy change, and Gibbs free energy indicated that the adsorption of heavy metals with onto lignite is a favorable, exothermic, and spontaneous process and is spontaneous. This investigation study shows that this lignite from Kosovo is highly effective in adsorbing lead and cadmium these two heavy metals from aqueous solutions.

Introduction

Water is a fundamental resource essential for the survival and development of all living organisms; therefore, protecting water sources from contamination is of paramount importance (Moyo et al. 2017). The rapid expansion of industrial activities has been a significant contributor to environmental pollution, encompassing processes such as smelting, electroplating, alloy production, photographic development, battery manufacturing, metallurgical operations, and other industrial activities (Kumar et al. 2022). Heavy metals, due to their lack of natural biodegradability, pose a substantial threat to the environment. Many of these metals display high levels of toxicity, carcinogenic potential, and a propensity for bioaccumulation, thus posing serious hazards to both environment and human health (Wang et al. 2021). The critical issue of heavy metal contamination necessitates prompt and effective mitigation strategies to reduce associated risks as much as possible (Canhua et al. 2023).

Lead exposure can bring a range of health issues, such as thrombosis, arteriosclerosis, hypertension, and cardiovascular

disease (Mitra et al. 2022). Cadmium ranks among the most common inorganic pollutants and is extensively used in industries such as cadmium plating, alkaline battery manufacturing, copper alloy production, and the production of paints and plastics (Wang et al. 2022). It is widely recognized as a carcinogen that impacts multiple organs, including the kidneys, bones, lungs, pancreas, and prostate (Wang et al. 2021). Consequently, numerous research methodologies have been developed to assess the adsorption of metal ions, especially lead and cadmium (Thaçi et al. 2021). Common methods for treating water contaminated with heavy metals include precipitation, ion exchange, reverse osmosis, ultrafiltration, electrochemical treatment, etc. (Madadgar et al. 2023). Nevertheless, these procedures have significant disadvantages, such as high maintenance costs, energy consumption, and use of toxic materials that may cause secondary contamination during disposal (Wei et al. 2016).

Adsorption is considered one of the best methods of a well-known surface phenomenon that has been shown till now (Senthil and Senthil 2021). One of the main advantages of this technique is its ability to reduce sludge generation (Senthil

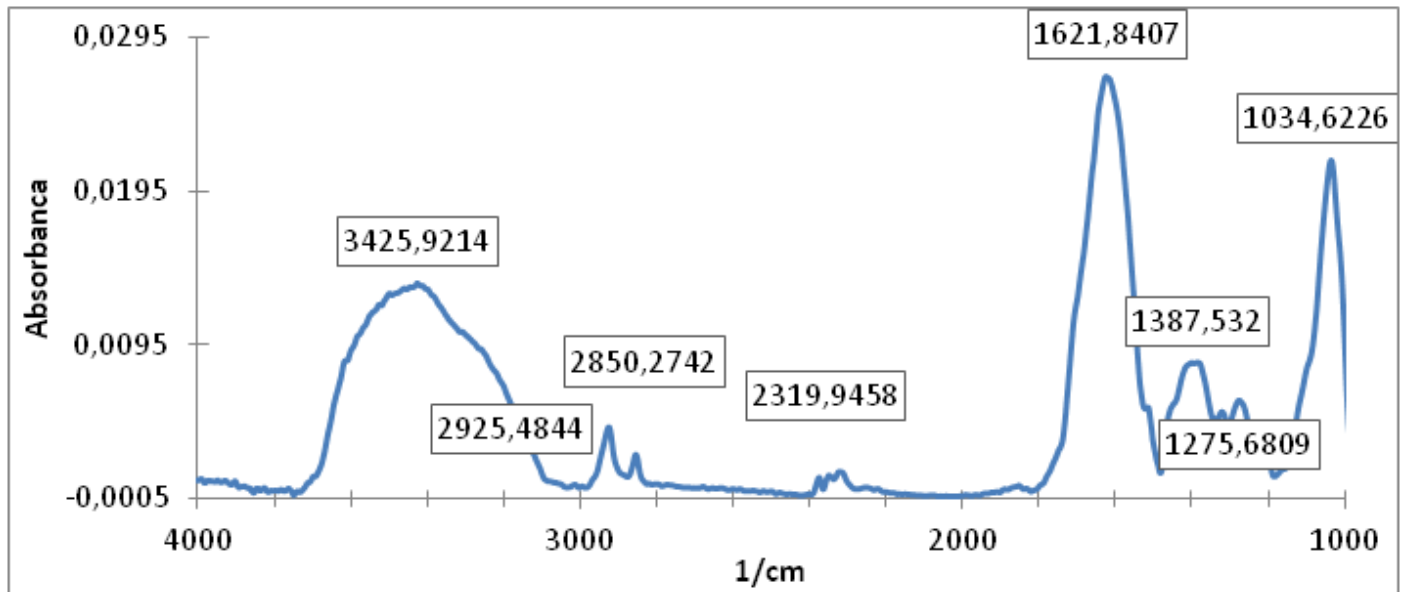


Fig. 1. FTIR spectrum of lignite.

and Senthil 2021). Furthermore, adsorption is cost-effective, environmentally friendly, and simple to implement (Fouad et al. 2022), particularly when using biodegradable and readily available biomasses. The selection of a suitable adsorbent is a crucial factor in the efficiency of heavy metal ion adsorption. A wide variety of adsorbents are currently being used (He et al. 2020, Phaenark et al. 2023, Thaçi et al. 2023, Thaçi et al. 2024).

Coal is formed over time as vegetation decomposes underground. It is categorized into lignite, bituminous, sub-bituminous, and anthracite based on the degree of plant matter decomposition and the concentration of carbon (Ezeokonkwo et al. 2018). Lignite is the primary energy source for thermal power plants globally, contributing significantly to environmental pollution. A similar situation exists in Kosovo, where a large share of energy production depends on lignite. Burning lignite generates substantial amounts of mineral elements that form bottom ash, further exacerbating environmental pollution (Daci-Ajvazi et al. 2018). In addition to its use in energy generation, lignite has been tested for

its ability to adsorb various pollutants (both organic and inorganic) from contaminated water (Kus'mierek et al. 2020; Nazari et al. 2018). In particular, the main emphasis has been on its effectiveness in removing heavy metals from aqueous solutions (Zherebtsov et al. 2020).

This study highlights a different aspect of lignite, presenting it not merely as an environmental pollutant but also as an effective adsorbent. Untreated lignite from Kosovo was used as a raw material for removing lead and cadmium from contaminated waters. To examine the composition and characteristics of the lignite, several analytical techniques were employed, including elemental analysis, FTIR, XRD, SEM, and pH_{pzc} measurements.

Material and methods

Preparation of adsorbent and methods

Lignite was collected across Bardhi i Madh in Obiliq (Republic of Kosovo). It was rinsed with distilled water and

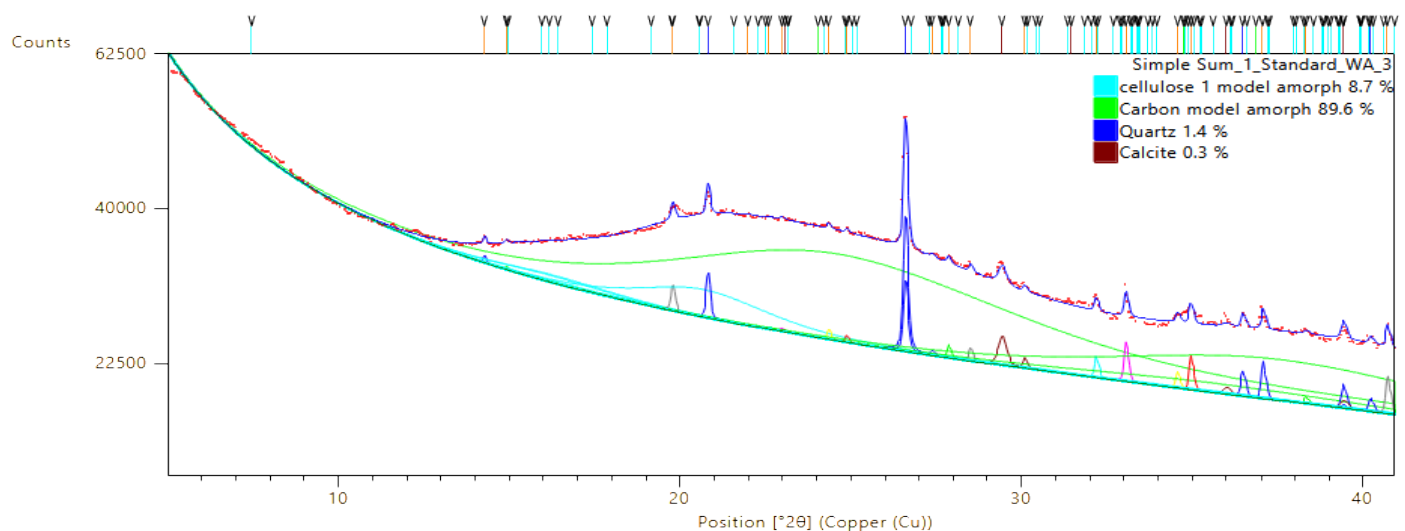


Fig. 2. XRD of lignite.

Table 1. Elementary analysis of lignite.

Elements	C	H	N	S	O	Mg	Al	Cl	Si	K	Ca	Fe
(%)	50.4	4.85	1.66	0.77	34.25	0.407	0.567	<0.01	1.03	0.06	2.19	0.52

heated at 105 °C every two hours until a constant mass was reached. The lignite was then pulverized, sieved, and particles smaller than 0.1 mm were used in the study. The FTIR spectra of lignite were recorded using a SHIMADZU FTIR 8400S with KBr discs, covering a scan range of 1000 to 4000 cm⁻¹. The surface properties and morphology of the material were examined using scanning electron microscopy (SEM; ZEISS Supra 55 VP, Jena) operated at an accelerating voltage of 2 kV. The sample was recorded using an Empyrean Powder Diffractometer. All measurements were continuous scans in the range of 5 - 41 degrees in 2θ, with a step size of 0.039 degrees and a counting time of 10 times 55 seconds per step. The scans did not show significant variations, the sum of all was used for calculations. The point of zero charge (pH_{pzc}) was also determined.

Methodology

The removal of heavy metals (Pb²⁺, Cd²⁺) by lignite was investigated using a batch method. Stock solutions of the metals were prepared at concentrations of 15, 30, 60, and 100 mg/dm³. Four different amounts of lignite (0.05, 0.125, 0.25, and 0.50 g) were used and mixed with 0.050 dm³ of the metal ion solutions. To determine the optimal contact time, experiments were conducted at various intervals: 5, 10, 20, 30, 60, 90, and 120 minutes. The studies were performed at four different temperatures (318, 308, 298, 288 K) and under six different pH conditions (2, 3, 4, 5, 6, and 7). The pH was adjusted using 0.1 M HCl or 0.1 M NaOH with a HANA pH-meter (HI 98130). All experiments were conducted in a thermostatic shaker bath at 200 rpm. The concentrations of lead and cadmium ions were quantified using Atomic Absorption Spectroscopy (AAS, flame Contra AA 300, Analytik Jena). Two key parameters, adsorbent capacity (q_e) and removal efficiency (% A), were calculated using the following equations:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$\%(A) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where C_0 denotes the initial concentration, C_e represents equilibrium concentrations of metal ions (mg/dm³), respectively, V is the volume of the solution (dm³), and m is the mass of the adsorbent (g).

Adsorbent Regeneration

The regeneration of lignite is essential to maintain its effectiveness as a raw material (Lavado-Meza et al. 2023). Heavy metal ion desorption was performed using various desorption media such as 0.5M HCl, 0.5M HNO₃, 0.5M CH₃COOH, and distilled water. Lignite loaded with metal ions was placed in the desorption media mentioned above and stirred at 200 rpm for a duration of 2 hours at 298 K.

Results and Discussion

Characterization of adsorbent

Elementary analysis is a crucial factor in assessing the properties of carbon-based materials. The results (Table 1) indicate that the primary elements identified in the lignite sample are carbon, oxygen, hydrogen, and nitrogen, each contributing more than 1.00% to the overall composition. It is important to note that this lignite has a lower carbon content (50.44%) compared to lignite from other countries, which typically ranges from 60 to 80 % (Mishra et al. 2023), indicating a low degree of carbonation. Additionally, the amount of ash produced from the combustion of 1000 mg of lignite was quantified, resulting in the formation of 122.20 mg of ash. Table 1 displays the elementary composition data for Kosovo's lignite.

The FTIR spectrum of lignite

Fourier Transform Infrared (FTIR) spectroscopy was employed to identify the main functional groups present in lignite, which may play a key role in the binding of lead and cadmium ions through interactions with adsorbent surface (Saranda et al. 2017). The spectrum is shown in Fig. 1.

Analysis of the lignite spectrum shown in Fig. 1 confirms the presence of functional groups such as carbonyl, amine, and hydroxyl. Broad and intense peaks at 3425.92, 2925.48, and 2850.27 cm⁻¹ correspond to the stretching vibrations of O-H, N-H, and C-H, respectively (Mishra et al. 2023, Thaçi et al. 2023). The substantial peak at 1621.84 cm⁻¹ is attributed to C=O and N-H stretching vibrations, respectively (Mishra et al. 2023). Additionally, peaks at 1275.68 and 1387.53 cm⁻¹ indicate C-N and C-O stretching vibrations, respectively (Thaçi et al. 2024). Furthermore, a significant adsorption band at 1034.62 cm⁻¹ confirms the presence of C-O stretching vibrations.

X-ray diffraction

Lignite XRD shows only a small ratio of crystalline material. Quartz and Calcite were identified using Rietveld Fitting. Several other peaks could not be identified seriously. The remaining unidentified peaks were analyzed exclusively to quantify the amorphous content in the sample. The amorphous phase was modeled by including two starting conditions that should be part of the sample. Carbon and Cellulose 1 were introduced as amorphous phases and refined using Rietveld Fitting. However, the amorphous content attributed to the two phases, Carbon and Cellulose 1 alone does not fully account for the composition determined by elemental analysis. This discrepancy suggests the presence of other unidentified organic materials in the amorphous matrix, particularly in light of the observed carbon-to-oxygen ratio. The background of the XRD pattern was calculated using a combination of constant, 1/x, and 1/x² functions. The X-ray diffraction pattern of lignite is presented in Fig.2.

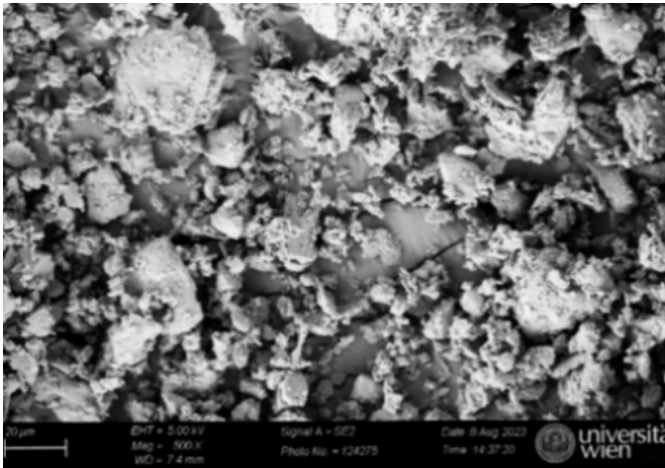


Fig. 3. SEM image of the lignite.

SEM method

This approach provides qualitative insight into the surface structure, which is essential for material characterization (Jiao et al. 2017). This adsorbent possesses various heterogeneous porous structures, indicating a favorable environment for the adsorption of lead and cadmium ions. The SEM picture of lignite is shown in Fig. 3.

Determination of pH_{PZC} and impact of pH

The pH_{PZC} value was computed using the equation $\Delta pH = pH_f - pH_o$, where pH_f denotes the final pH and pH_o refers to the initial pH. The results are shown in Fig. 4 (a).

As illustrated in Fig. 4, lignite exhibits a pH_{PZC} of 5.6. When the pH is below 5.6, the adsorbent surface carries a positive charge, above this value, it becomes negatively charged. At lower pH levels, the elevated concentration of hydrogen ions in the solution competes with metal ions for adsorption sites (Fouad et al. 2022).

pH is the most important component in adsorption, determining how adsorbents interact with metal ions. Functional groups present in lignite, such as carbonyl, hydroxyl, and amino, play important roles in binding mechanisms (Zheng et al. 2010). Fig. 4(b) shows the association between different pH levels and the percentage adsorption of lead and cadmium ions. The data indicate that adsorption efficiency increases with rising pH up to pH 4 for Pb(II) and pH 5 for Cd(II). The pH range of 6 to 7 was shown to be optimal for the maximal

adsorption of Pb(II) and Cd(II) ions. Fig. 4(b) illustrates the relationship between varying pH levels and the percentage adsorption of lead and cadmium ions. The data presented in this figure indicate that as the pH of the medium increases, the adsorption percentage also increases. This trend was evident up to pH 4 for lead and pH 5 for cadmium, while the maximal adsorption was at pH 6 and 7 for these two metal ions. At pH 2, lignite removed 72.47% lead and 52.09% cadmium, whereas at pH 6, these rates climbed sharply, reaching 97.22% for lead and 90.04% for cadmium. Furthermore, at pH7, the maximum cadmium adsorption reached 91.07%. At low pH, the high concentration of hydrogen ions increases competition for binding sites on the lignite surface, reducing lead and cadmium adsorption due to electrostatic repulsion (Fouad et al. 2022). As the pH increases, the surface charge of lignite becomes more negative, enhancing the adsorption of positively charged metal ions (Thaçi et al. 2024).

Effect of contact time

The study examined this parameter on the adsorption of Pb(II) and Cd(II) ions by lignite over a period ranging from 5 to 120 minutes. Experiments were conducted under controlled conditions: pH 5.0, 0.125g of adsorbent, at a temperature of 298K. The findings are presented in Fig. 5.

According to the results presented in Fig. 5, it can be inferred that lead ion binding is particularly intensive in the first five minutes, followed by a very slight increase up to 30 minutes. Specifically, the adsorption capacity of Pb(II) was 11.22 mg/g at 5 minutes, increasing marginally to 11.58 mg/g at 30 minutes. In contrast, Cd(II) adsorption was less intense in the initial 5 minutes but increased significantly between 5 and 30 minutes, before reaching equilibrium. As a result, extending the contact time from 5 to 30 minutes (about 500%) enhanced the adsorption capacity by only 0.36 mg/g (Pb^{2+}) and 5.26 mg/g (Cd^{2+}). These findings indicate that equilibrium was reached for both metal ions after 30 minutes, and the adsorption capacity remained constant thereafter.

Effect of metal ion concentration

To explore the maximum adsorption capacity of lignite for lead and cadmium ions, different initial metal concentrations were tested, such as 15, 30, 60, and 100 mg/dm³, as shown in Fig. 6.

Fig. 6 demonstrates the increased adsorbent capacity with rising concentrations of metal ions. The experimental results

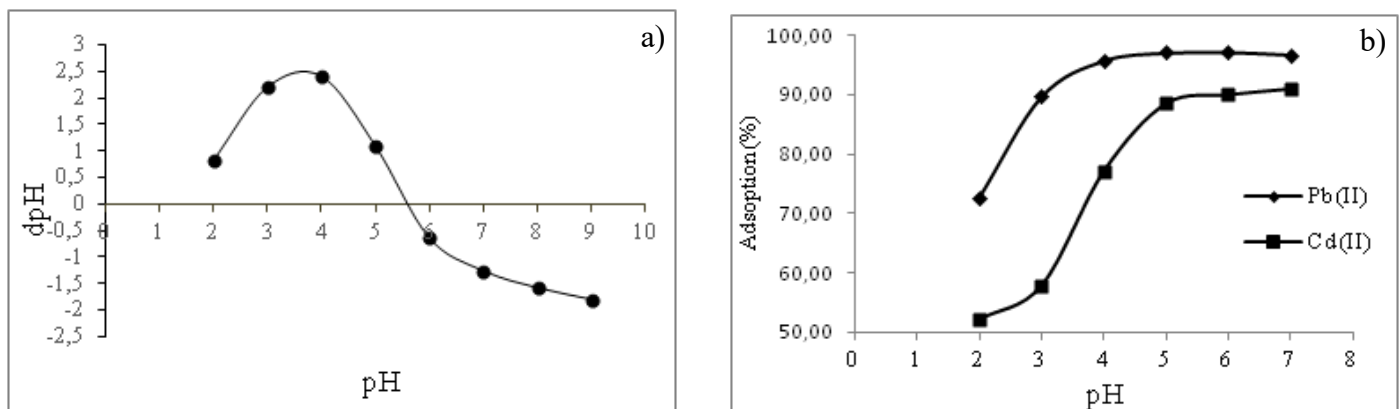


Fig. 4. a) Determination of pH_{PZC} and b) Percentage of lead and cadmium adsorption vs pH.

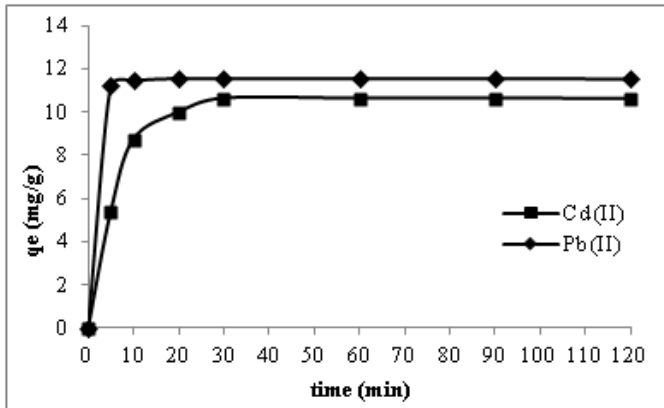


Fig. 5. Effect of contact times on adsorption of lead and cadmium ions with lignite.

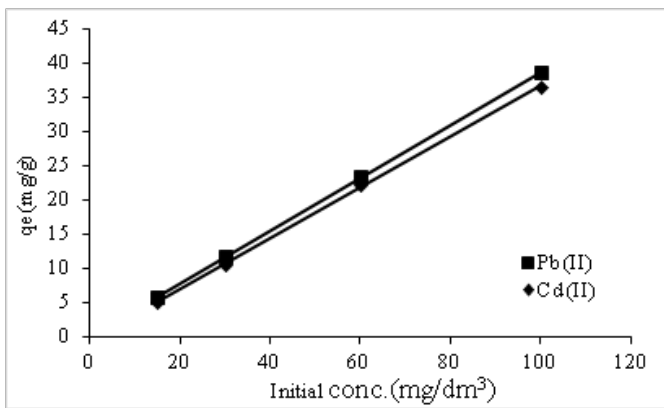


Fig. 6. The effect of initial conc. on adsorption of lead and cadmium with lignite.

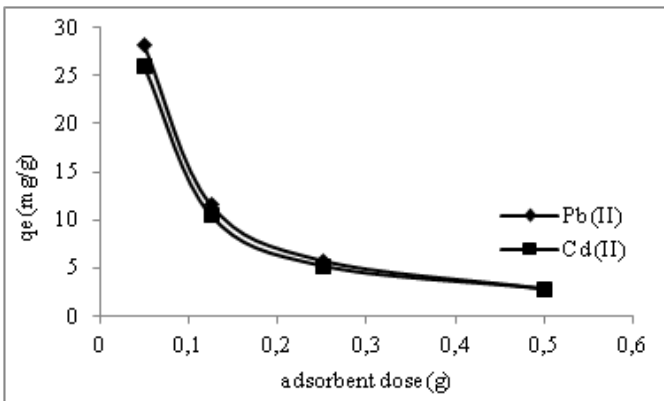


Fig. 7. Effect of adsorbent dose on removing Pb²⁺ and Cd²⁺ ions with lignite.

show that as the initial concentration of Pb²⁺ increases from 15 to 100 mg/dm³, the adsorption capacity rises to 32.98 mg/g. Similarly, for cadmium, the adsorption capacity increases to 31.50 mg/g over the same concentration range. At lower metal concentration, the actual maximum capacity of the adsorbent may not be observed, as numerous active binding sites remain unoccupied (Phaenark et al. 2023). On the other hand, higher metal concentrations provide a stronger driving force for ion transfer toward the adsorbent surface, leading to the saturation of all available binding sites and revealing the full adsorption potential (Ramin et al. 2018).

Effect of adsorbent dose

The adsorbent dosage directly influences the availability of binding sites for removing metal ions (Saranda et al. 2017). The impact of adsorbent dosage was studied under specific conditions: an initial concentration of 30 mg/dm³, a temperature of 298 K, and pH of 5.0. Fig. 7 illustrates how varying adsorbent doses (0.05, 0.125, 0.250, and 0.500 g/50cm³ of solution) affect the adsorption process.

Based on the experimental results, the capacity of the adsorbent decreases with increasing adsorbent mass, especially between 0.05 and 0.25 g. This observation may be attributed to the formation of aggregates, which subsequently reduce the total surface area available for binding metal ions (Nouri et al. 2007).

Equilibrium isotherms

One of the most essential approaches for analyzing the equilibrium between heavy metal ions in the liquid and solid phases is through equilibrium isotherms (Saranda et al. 2017). To explain the phenomenon of adsorption of two heavy metals, we used two adsorption isotherm models: the Langmuir and Freundlich models.

According to the Langmuir model, each adsorption site can accommodate only a single molecule from the solution, leading to monolayer adsorption (Nassef and Eltaweel 2019). The linear form of the Langmuir equation is given below:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \quad (3)$$

Where, q_m is the maximum adsorbent capacity in a monolayer (mg/g); K_L (dm³/mg) is a parameter that indicates the affinity of the adsorption process, linked to the adsorption energy; C_e is the equilibrium concentration of metal ions in solution (mg/

Table 2. The R_L parameter of lignite for lead and cadmium ions.

Temp.(K)	Concentration of Pb ²⁺ (mol/dm ³)				Concentration of Cd ²⁺ (mol/dm ³)			
	15	30	60	100	15	30	60	100
318	0.165	0.090	0.047	0.029	0.434	0.277	0.161	0.103
308	0.133	0.071	0.037	0.022	0.407	0.256	0.147	0.093
298	0.128	0.068	0.035	0.021	0.397	0.248	0.141	0.091
288	0.103	0.054	0.028	0.017	0.377	0.232	0.131	0.083

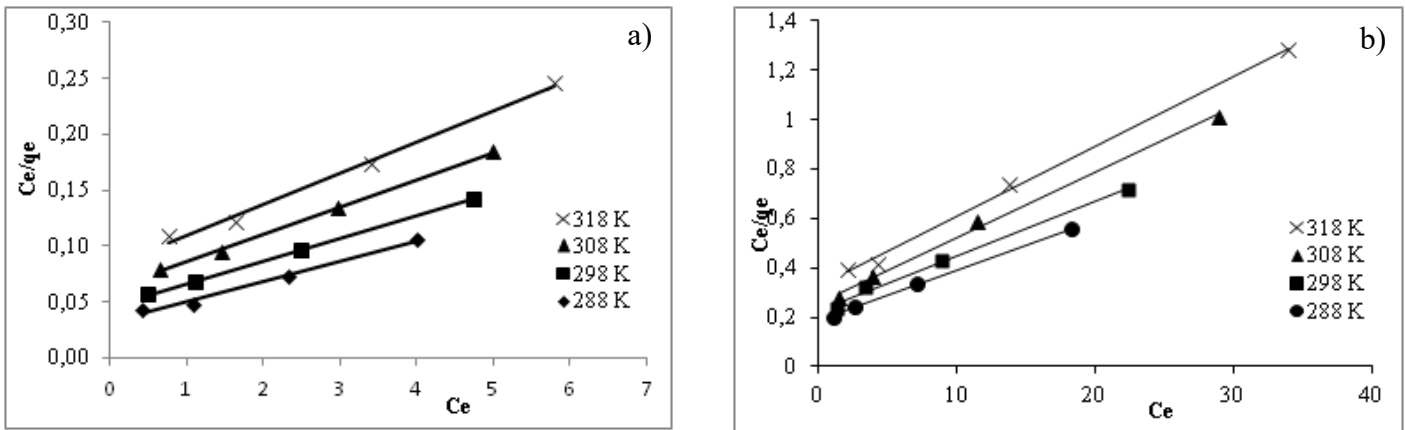


Fig. 8. Langmuir model isotherms of a) Pb(II) and b) Cd(II) ions.

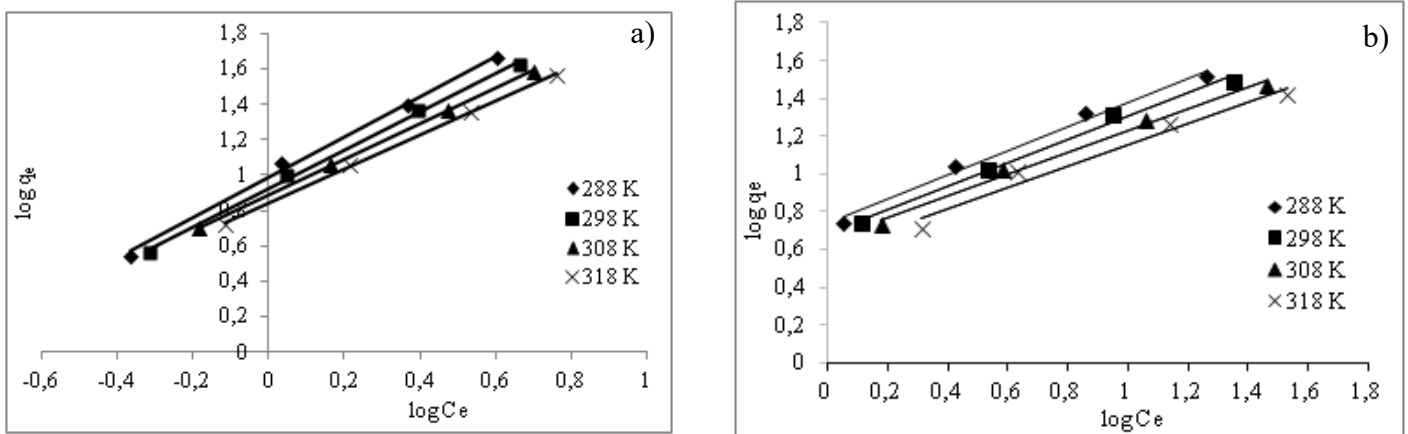


Fig. 9. Freundlich model isotherms of a) Pb(II) and b) Cd(II).

dm^3) and q_e , is the equilibrium concentration of Pb^{2+} and Cd^{2+} ions adsorbed onto the coal (mg/g).

Plotting Ce/q_e versus Ce yields a straight line, where the slope corresponds to $1/q_m$ and the intercept to $1/(K_L q_m)$. The Langmuir isotherm results for Pb^{2+} and Cd^{2+} ions are shown in Fig. 8 a) and b), respectively.

The key characteristics of the Langmuir model can be described using a separation factor (R_L) or equilibrium parameter (Fouad et al. 2022):

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

For adsorption to be deemed favorable, the condition must be $0 < R_L < 1$ (Manoj et al. 2020). The data of the separation factor are presented in Table 2.

The values of the separation factor R_L for coal, observed at various concentrations and temperatures, range from 0 to 1, indicating that the adsorption of lead and cadmium ions in this study is favorable. As shown in Table 2, increasing the concentration of Pb^{2+} ions from 15 to 100 mg/dm^3 at 288 K leads to a decrease in R_L from 0.103 to 0.017. Similarly, for cadmium, it decreases from 0.377 to 0.083 under the same conditions. In contrast, increasing the temperature from 288 K to 318 K at a concentration of 30 mg/dm^3 results in an increase in the R_L value from 0.036 to 0.045 for lead ions and

from 0.036 to 0.045 for cadmium ions. The Freundlich model isotherm provides an alternative model based on different underlying assumptions. Unlike the Langmuir model, it does not restrict adsorption to a monolayer, thus offering another view of the adsorption processes (Nazari et al. 2018). The Freundlich equation is presented below:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

Where, K_F (mg/g) is the Freundlich isotherm constant, $1/n$ is the adsorption intensity, reflecting the material's heterogeneity. The Freundlich isotherms are presented in Fig. 9 and in Table 3.

Table 3 shows that the Pb^{2+} adsorption onto coal fits the Freundlich isotherm better, while Cd^{2+} adsorption aligns more closely with the Langmuir isotherms, based on the linear coefficient value. These results indicate that the loading of Pb^{2+} on lignite occurs in multilayers, whereas Cd^{2+} adsorption is monolayer in nature. This difference may contribute to the higher adsorption capacity observed for lead compared to cadmium. The observed decrease in both q_{max} and K_L values with rising temperature confirms that the adsorption of both lead and cadmium onto lignite is an exothermic process.

The maximum adsorption capacities at 288K were 55.55 mg/g and 48.78 mg/g for Pb^{2+} and Cd^{2+} , respectively. The higher sorption of lead compared to cadmium by lignite is likely due to lead's smaller hydrated radius ($\text{Pb}^{2+} = 0.401 \text{ nm}$,

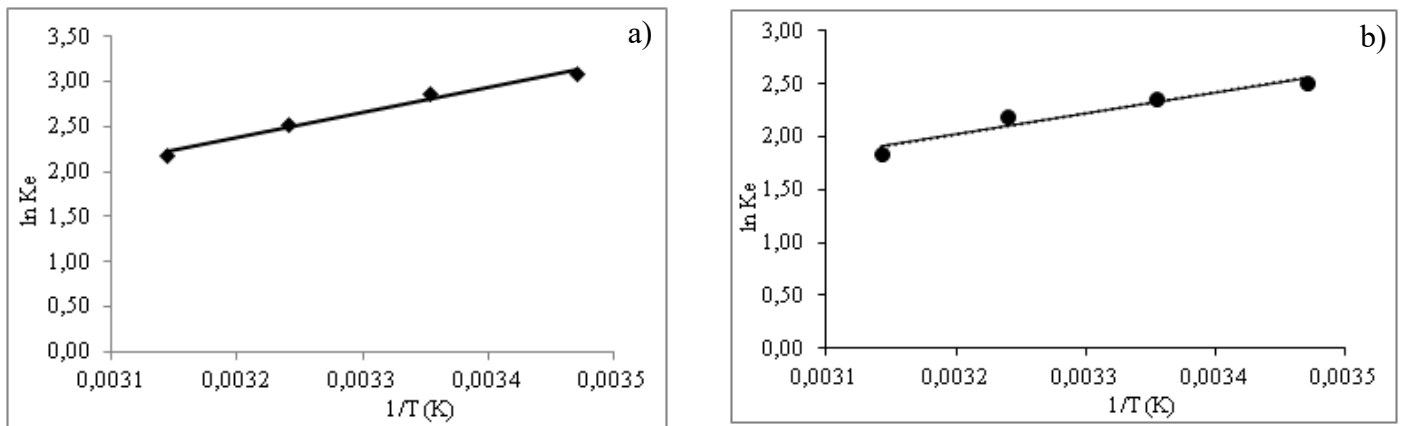


Fig. 10. The plot of $\ln K_e$ vs $1/T$ of a) Pb^{2+} and b) Cd^{2+} .

$Cd^{2+} = 0.426$ nm) and lower hydration energy ($Pb^{2+} = 1481$ kJ/mol, $Cd^{2+} = 1807$ kJ/mol) (Boulaiche et al. 2019).

Thermodynamic parameters

Temperature plays a key role in interpreting the interaction between adsorbents and adsorbates (Saranda et al. 2017). The study examined the adsorption of Pb^{2+} and Cd^{2+} at temperatures ranging from 15 °C to 45 °C. In this study, we determined thermodynamic parameters such as standard enthalpy change, standard entropy change, and Gibbs free energy. A negative Gibbs free energy value signifies that the adsorption process is spontaneous, otherwise, the process is not spontaneous (Saranda et al. 2017). These three parameters can be calculated using the following equation:

$$\Delta G^\circ = -RT \ln K_e \quad (6)$$

$$K_e = \frac{(C_o - C_e)}{C_e} \quad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (8)$$

$$\ln K_e = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (9)$$

Where, K_e represents the equilibrium constant, R is the universal gas constant, and T represents absolute temperature. A plot of

$\ln K_e$ vs $1/T$ showed a linear relationship, from where ΔH° and ΔS° can be calculated. These values are depicted in Fig. 10.

Table 4 clearly shows that temperature adversely affects the adsorption of Pb^{2+} and Cd^{2+} on lignite, indicating that higher temperatures have a negative effect. As the temperature increased, a rise in the ΔG value was observed, suggesting that the process was more favorable at lower temperatures. The negative values of ΔH° for lead and cadmium ions indicate that the adsorption process is exothermic. The ΔH° value for Cd^{2+} suggests that the adsorption primarily involves a physical process characterized by weak attractive forces. In contrast, the adsorption of lead appears to involve both physical and chemical interactions, as evidenced by surface complex formation (Fouad et al. 2022). The negative values of ΔS° for Pb^{2+} (-53.442 J/molK) and Cd^{2+} (-35.646 J/molK) indicate a decrease in the system's degree of freedom during the adsorption of the metal ions (Saranda et al. 2017). The thermodynamic parameters of the metal ions are presented in Table 4.

Desorption and regeneration

In this study, various agents were used to desorb metal ions from lignite, enabling its reuse. The results for the two metal ions are presented in Fig. 11.

Fig. 11 shows that lignite can be effectively regenerated using 0.5M HCl, 0.5M HNO_3 , and 0.5M CH_3COOH , resulting in recoveries of 94.88%, 93.13%, and 90.74% for $Pb(II)$,

Table 3. Langmuir and Freundlich isotherm data for lead and cadmium ions.

Isotherm	Parameter for Pb(II)					Parameter for Cd(II)			
	Temp. (K)	288	298	308	318	288	298	308	318
	q_{max} (mg/g)	55.55	50.00	41.67	37.04	48.78	45.05	37.74	35.21
Langmuir	KL (dm ³ /mg)	0.581	0.453	0.434	0.337	0.110	0.101	0.097	0.087
	R^2	0.992	0.994	0.993	0.991	0.998	0.995	0.996	0.997
	K_F (mg/g)	13.13	11.91	10.05	9.162	5.520	4.853	4.529	3.908
Freundlich	1/n	0.985	0.926	0.889	0.839	0.639	0.618	0.577	0.566
	R^2	0.995	0.997	0.999	0.999	0.988	0.992	0.992	0.968

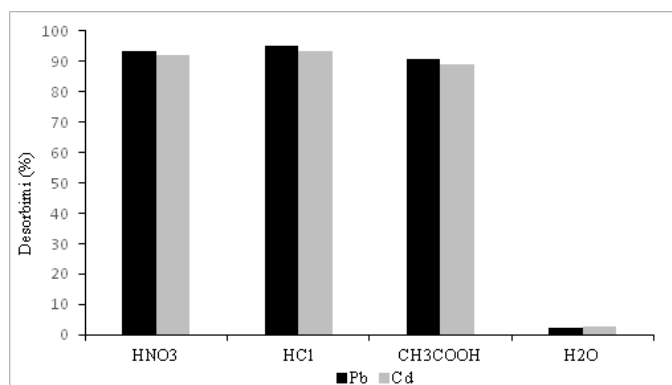


Fig. 11. Desorption of Pb²⁺ and Cd²⁺ in different mediums.

and 93.15%, 92.22%, and 89.03% for Cd(II), respectively. In contrast, desorption using distilled water led to minimal recovery of lignite. Therefore, it can be concluded that 0.5M HCl is the most effective agent in the lignite desorption process, while distilled water has little impact. This trend suggests that lignite is both stable and reusable, making it a viable and economically beneficial option for removing metals from wastewater (Ramin et al. 2018).

Conclusions

Lignite, in its natural form, is an effective absorbent for removing lead and cadmium ions from aqueous solutions and wastewater due to its widespread availability, low cost, high efficiency, and minimal energy requirements. FTIR spectral analysis confirmed the presence of functional groups such as amine, hydroxyl, and carbonyl in lignite, which play a key role in the adsorption of lead and cadmium. The Langmuir isotherm model best described cadmium ion adsorption, while the Freundlich isotherm model was more suitable for lead ion adsorption. Optimal adsorption conditions were achieved at pH 6 for lead and 7 for cadmium.

Among the desorbing agents tested, 0.5M hydrochloric acid proved most effective for regenerating the adsorbent. The standard enthalpy changes for lead and cadmium were -22.896 kJ/mol and -16.396 kJ/mol, respectively, indicating a stronger interaction between lignite and lead ions. Negative Gibbs free energy values at all tested temperatures for both metal ions confirmed the spontaneity of the adsorption process. Finally, lignite proves to be an excellent material for the adsorption of these two metal ions.

References

- Boulaiche, W., Belhamdi, B., Hamdi, B. & Trari, M. (2019). Kinetic and Equilibrium Studies of Biosorption of M(II) (M=Cu, Pb, Ni, Zn and Cd) onto Seaweed Posidonia Oceanica Fibers. *Applied Water Science*, 9, 173, pp. 1-11. DOI:10.1007/s13201-019-1062-1.
- Daci-Ajvazi, M., Thaçi, B., Daci, N. & Gashi, S. (2018). Evaluation of packed adsorption column for lead, cadmium, and zinc removal using different biosorbents. *Journal of Environmental Protection and Ecology*, 19, 3, pp. 997–1007.
- Ezeokonkwo, M. A., Ofor, O. F. & Ani, J. U. (2018). Preparation and Evaluation of Adsorbents from Coal and Irvingia gabonensis Seed Shell for the Removal of Cd(II) and Pb(II) Ions from Aqueous Solutions. *Frontiers in Chemistry*, 5, 132, pp. 1-14. DOI:10.3389/fchem.2017.00132.
- Fouad, M. B., Abdelghani, B., Aicha, Ch., Belgacem, T. & Djelloul, A. (2022). Comparative study of Pb (II) adsorption from water on used cardboard and powdered activated carbon. *Membrane and Water Treatment*, 13, 2, pp. 73-83. DOI:10.12989/mwt.2022.13.2.073.
- He, X., Jiang, J., Hong, Z., Pan, X., Dong, Y. & Xu, R. (2020). Effect of aluminum modification of rice straw-based biochar on arsenate adsorption. *Journal of Soils Sediments*, 20, 8, pp. 3073–3082. DOI:10.1007/s11368-020-02595-2.
- Jiao, Y., Han, D., Lu, Y., Rong, Y., Fang, L. & Liu, Y. (2017). Characterization of Pine-Sawdust Pyrolytic Char activated by phosphoric acid through microwave irradiation and adsorption property toward CDNB. *Desalination and Water Treatment*, 77, pp. 247-255. DOI:10.5004/dwt.2017.20780.
- Kumar, R., Verma, S., Harwani, G., Paridar, D. & Mishra, S. (2022). Adsorptive and kinetic studies of toxic metal ions from contaminated water by functionalized silica. *Membrane and Water Treatment*, 13, 5, pp. 227-233. DOI:10.12989/mwt.2022.13.5.227.
- Kusmierek, K., Sprynskyy, M. & Swiatkowski, A. (2020). Raw lignite as an effective low-cost adsorbent to remove phenol and chlorophenols from aqueous solutions. *Separation Science and Technology* 55, 1, pp. 1741–1751. DOI: 10.1080/01496395.2019.1607384
- Lavado-Meza, C., Fernandez-Pezua, M.C., Gamarra-Gómez, F., Sacari-Sacari, E., Angeles-Suazo, J. & Dávalos-Prado, J. Z. (2023). Single and binary removals of Pb(II) and Cd(II) with chemically modified Opuntia ficus indica Cladodes. *Molecules*, 28, 11, pp. 1-17. DOI:10.3390/molecules28114451.

Table 4. Thermodynamics parameters of lead and cadmium ions with lignite.

Pb ²⁺				Cd ²⁺		
Temp. (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
318	-5.901			- 5.075		
308	-6.436	-22.896	-53.442	- 5.431	- 16.396	- 35.646
298	-6.970			- 5.775		
288	-7.505			- 6.129		

- Li, C., Wei, S., Li, Z., Li, M. & Zha, Y. (2023). Study on the adsorption performance of steel slag and manganese slag composite materials for lead. *Desalination and Water Treatment*, 304, pp. 150–161. DOI:10.5004/dwt.2023.29806.
- Madadgar, S., Doultai, A. F., Boroumand, Z., Sadeghpour, H., Taherdankoo, R. & Butscher, C. (2023). Biosorption of aqueous Pb(II), Co(II), Cd(II) and Ni(II) ions from Sungun Copper Mine wastewater by *Chrysopogon zizanioides* Root powder. *Minerals*, 13, 106, pp. 1–19. DOI:10.3390/min13010106.
- Manoj, K., Debendra, R., Rajendra, K. & Ajaya, B. (2020). Determination of point zero charges (PZC) of homemade Charcoals of *Shorea Robusta* (Sakhuwa) and *Pinus Roxburghii* (Salla). *International Journal of Engineering Research & Technology*, 9, 10, pp. 152–155. DOI:10.17577/IJERTV9IS100046.
- Mishra, S., Prasad, A.K., Shukla, A., Vinod, A., Preety, K. & Varma, A.K. (2023). Estimation of Carbon Content in High-Ash Coal Using Mid-Infrared Fourier-Transform Infrared Spectroscopy. *Minerals*, 13, 938. DOI:10.3390/min13070938.
- Mitra, S., Chakraborty, A. J., Tareq, A. M., Emran, T. B., Nainu, F., Khusro, A., Idris, A. M., Khandaker, M. U., Osman, H., Alhumaydhi, A. F. & Simal-Gandara, J. (2022). Impact of heavy metals on the environment and human health: Novel therapeutic insights to counter the toxicity. *Journal of King Saud University Science*, 34, 3, pp. 1–12. DOI:10.1016/j.jksus.2022.101865.
- Moyo, M., Pakade, V. E. & Modies, J. S. (2017). Biosorption of lead(II) by chemically modified *Mangifera indica* seed shells: Adsorbent preparation, characterization and performance assessment. *Process Safety and Environmental Protection*, 111, pp. 40–51. DOI:10.1016/j.psep.2017.06.007.
- Nassef, E. & Eltaweel, Y. (2019). Removal of Zinc from aqueous solution using activated Oil shale. *Journal of Chemistry*, ID 4261210, pp. 1–9. DOI:10.1155/2019/4261210.
- Nazari, M. A., Mohaddes, F., Pramanik, B.K., Othman, M., Muster, T. & Bhuiyan, M.A. (2018). Application of Victorian brown coal for removal of ammonium and organics from wastewater. *Environmental Technology*, 39, 2, pp. 1–33. DOI: 10.1080/09593330.2017.1319424
- Nouri, L., Ghodbane, I., Hamdaoui, O. & Chiha, M. (2007). Batch sorption dynamics and equilibrium for the removal of cadmium ions from aqueous phase using wheat bran. *Journal of Hazardous Materials*, 149, 1, pp. 115–125. DOI:10.1016/j.jhazmat.2007.03.055.
- Phaenark, Ch., Harn-asa, P., Paejaroen, P., Chunchob, S. & Sawangproh, W. (2023). Removal of Pb(II) and Cd(II) by biomass derived from Broadleaf Cattail and Water Hyacinth. *Journal of Water and Environmental Technology*, 21, 4, pp. 191–203. DOI:10.2965/jwet.22-138.
- Ramin, M., Hamid, M., Ehsan, A. & Ramezan, A. T. (2018). Adsorption of cadmium from aqueous solutions by novel Fe₃O₄-newly isolated *Actinomucor* sp. Bionanoadsorbent: functional group study. *Artificial Cell Nanomedicine, and Biotechnology*, 46, 3, pp. 1092–1101. DOI:10.1080/21691401.2018.1533841.
- Sarada, B., Prasad, M. K., Kumar, K. K. & Murthy, Ch. V. R. (2017). Biosorption of Cd²⁺ by Green Plant Biomass, *Araucaria Heterophylla*: Characterization, Kinetic, isotherm and thermodynamic studies. *Applied Water Science*, 7, 9, pp. 3483–3496. DOI:10.1007/s13201-017-0618-1.
- Senthil, R. B. & Senthil, K. P. (2021). Application of adsorption process for effective removal of emerging contaminants from water and wastewater. *Environmental Pollution*, 280, 1, 116995. DOI:10.1016/j.envpol.2021.116995.
- Thaçi, B. S., Daci-Ajavazi, M., Daci, N. & Gashi, S. (2023). Removal of Zinc (II) ions by Wheat Bran and Waste Coffee as low-cost biosorbents. *Iranian Journal of Chemistry and Chemical Engineering*, 42, 1, pp. 111–122. DOI:10.30492/IJCCE.2022.541673.4995.
- Thaçi, B. S., Gashi, S.T., Daci, N. M., Podvorica, F. I. & Sopaj, F. (2024). A versatile study of single and binary removals of Pb(II) and Cd(II) ions from aqueous solutions using pine cone as biosorbent. *Desalination and Water Treatment*. 319, 100465. DOI:10.1016/j.dwt.2024.100465.
- Thaçi, B. S., Gashi, S., Daci, N. & Daci-Ajavazi, M. (2021). Hybrid processes evaluation of Pb(II) removal from wastewater effluents. *Polish Journal of Environment Studies*, 30, 4, pp. 3261–3267. DOI:10.15244/pjoes/130457.
- Wang, P., Huang, Zh., Fu, Zh., Zhao, P., Feng, Z., Wang, Y. & Li, F. (2022). Adsorption mechanism of Cd(II) by calcium-modified lignite-derived humin in aqueous solutions. *International Journal of Coal Science & Technology*, 9, 37, pp. 1–11. DOI:10.1007/s40789-022-00492-2.
- Wang, P., Liu, W., Xu, H. & Liu, G. (2021). Adsorption of Pb(II) cation from aqueous solution by acid modified low-rank coal: An experimental study and simulation. *Water Science & Technology*, 84, 12, pp. 3726–3737. DOI:10.2166/wst.2021.462.
- Wei, W., Wang, Q., Li, A., Yang, J., Ma, F., Pi, S. & Wu, D. (2016). Biosorption of Pb(II) from aqueous solutions by extracellular polymeric substance extracted from *Klebsiella* sp. J1: “Adsorption behavior and mechanism assessment”. *Scientific Reports*, 6, 1, pp. 1–10. DOI:10.1038/srep31575.
- Zheng, L., Dang, Z., Yi, X. & Zhang, H. (2010). Equilibrium and kinetic studies of adsorption of Cd(II) from aqueous solution using modified corn stalk. *Journal of Hazardous Materials*, 176, 1–3, pp. 650–656. DOI:10.1016/j.jhazmat.2009.11.081.
- Zherebtsov, S. I., Malysenko, N.V., Votolin, K.S. & Ismagilov, Z. R. (2020). Sorption of Metal Cations by Lignite and Humic Acids. *Coke and Chemistry*, 63, 3, pp. 142–148. DOI: 10.3103/S1068364X20030096