

Article

Synthesis, Performance, and Mechanism of Upcycled Lithium Slag-Based Geopolymers for High-Capacity Pb(II) Elimination

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Abstract

The concurrent disposal of industrial lithium slag (LS) and the remediation of heavy-metal-contaminated water remain critical environmental imperatives. Herein, industrial lithium slag was successfully upcycled into a high-capacity geopolymer via alkali activation to systematically evaluate its Pb(II) removal mechanisms. Synthesized under optimal conditions (11 mol/L alkali concentration, 0.616 solid-to-liquid ratio), the geopolymer showed exceptional Pb(II) capture, achieving ~99% removal efficiency within 120 min for a 100 mg/L Pb(II) solution at pH 6.0. The adsorption kinetics obeyed the pseudo-first-order model, yielding a remarkable theoretical equilibrium capacity of 284 mg/g. Thermodynamic results reveal a spontaneous ($\Delta G < 0$), endothermic ($\Delta H = 17.66$ kJ/mol) process with increased interfacial randomness ($\Delta S > 0$). Integrating macroscopic performance with characterizations and density functional theory (DFT) computations elucidated a site-specific chemisorption mechanism and the precipitation of PbSO_4 caused by Pb(II) and SO_4^{2-} in LS. Ultimately, this work provides a sustainable paradigm for the value-added upcycling of industrial solid waste.

Keywords: Pb(II) adsorption; geopolymer; lithium slag; adsorption mechanism

1. Introduction

With the rapid development of the global new energy industry, the demand for lithium-ion batteries has grown exponentially, leading to the generation of massive amounts of industrial solid waste, lithium slag (LS), during the upstream extraction process [1–4]. Currently, most LS is primarily disposed of through open-air stockpiling or landfilling. This not only occupies substantial land resources but also poses a severe threat to surrounding ecosystems; once the residual alkaline substances and trace heavy metals leach out with rainwater, they can cause irreversible damage to soil and groundwater [5,6]. Although previous studies have attempted to utilize LS as cement admixtures or low-end road base materials, these disposal methods suffer from low added value and limited consumption capacity. In fact, LS is rich in silicon dioxide and aluminum oxide, providing an

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excellent material basis for its high-value upcycling into inorganic functional materials [7]. Therefore, exploring green and efficient new pathways for LS resource utilization is urgently needed.

Developing innovative, environmentally friendly, and resource-recovery-oriented methodologies has become a key paradigm in modern wastewater reclamation and environmental biotechnology [8,9]. Heavy metal pollution in aquatic environments, particularly lead (Pb(II)) pollution, poses a severe threat to the human central nervous system and ecological security due to its high toxicity, non-biodegradability, and tendency for bioaccumulation [10,11]. Currently, conventional technologies for removing Pb(II) from water include chemical precipitation, ion exchange, membrane separation, and adsorption [12]. Among these, adsorption is considered the most promising water treatment technology owing to its simple operation, low cost, and minimal generation of secondary sludge [10,13]. However, traditional adsorbents (such as commercial activated carbon and organic resins) generally suffer from high preparation costs, limited adsorption capacities, or regeneration difficulties [14–16]. Consequently, developing novel adsorbent materials with abundant sources, low cost, and an ultra-high affinity for Pb(II) remains a critical challenge in the field of environmental remediation.

Geopolymers, a class of three-dimensional network inorganic polymers cross-linked by silicon–oxygen [SiO_4] and aluminum–oxygen [AlO_4] tetrahedra, have shown immense potential in the field of heavy metal adsorption in recent years [17]. Because the substitution of Si^{4+} by Al^{3+} in the network skeleton generates a structural negative charge, geopolymers inherently possess excellent cation exchange capacity and abundant heavy metal binding sites. To further enhance their mass transfer efficiency and adsorption capacity, introducing foaming agents to fabricate porous geopolymers has emerged as an effective strategy. The porous structure not only significantly increases the specific surface area of the material but also fully exposes the internal active sites [18]. Currently, the precursors for preparing geopolymers are predominantly focused on fly ash or metakaolin [4], whereas research on utilizing bulk industrial LS as the primary raw material remains insufficient. More importantly, existing studies largely focus on macroscopic adsorption thermodynamics and kinetics, while a fundamental atomic-level understanding of the microscopic coordination mechanisms between heavy metal ions and the distinct active units ($[\text{SiO}_4]$ and $[\text{AlO}_4]$) within the geopolymer skeleton is still lacking [19].

Herein, a green strategy is proposed to treat Pb(II) pollution using industrial LS. A novel porous geopolymer adsorbent was successfully synthesized via alkali activation, aiming to achieve the following specific objectives:

- (1) Adsorption Performance Evaluation: To systematically evaluate the macroscopic Pb(II) adsorption capacity of the LS-based geopolymer under various conditions, including kinetic and thermodynamic analyses.
- (2) Spectroscopic Mechanism Characterization: To identify the functional groups and the specific adsorption mechanism for Pb(II) immobilization using characterization techniques (SEM, XPS, XRD, thermal analysis, FT-IR, and BET).
- (3) Theoretical DFT Simulation: To elucidate the atomic-scale coordination configuration and active binding sites of Pb(II) on the geopolymer surface via DFT calculations.

In summary, this study provides both a practical pathway for the high-value utilization of industrial LS and theoretical support for the design of geopolymer-based heavy metal adsorbents.

2. Materials and Methods

2.1. Materials

The LS used in this study was sourced from Tianqi Lithium Co., Ltd., Suining, China. The primary chemical composition of the LS, as determined by X-ray fluorescence (XRF) spectrometry, is summarized in Table 1. Notably, the LS is predominantly composed of SiO₂, Al₂O₃, SO₃, and CaO accounting for 56.721 wt%, 18.164 wt%, 14.642 wt%, and 6.432 wt%, respectively. All chemical reagents employed in the experiments were of analytical grade and used as received without further purification.

Table 1. Chemical multi-element analysis results of the LS sample (wt%).

SiO ₂	Al ₂ O ₃	SO ₃	CaO	Fe ₂ O ₃	K ₂ O	P ₂ O ₅	F
56.721	18.164	14.642	6.432	1.410	0.579	0.542	0.361
MgO	Na ₂ O	MnO	SnO ₂	TiO ₂	Rb ₂ O	WO ₃	Others
0.288	0.230	0.136	0.103	0.101	0.093	0.025	0.174

2.2. Preparation of the Geopolymer

As illustrated in Figure 1, the porous geopolymer was synthesized by initially mixing 15 g of pretreated (dried and ground) LS with an alkaline activator solution with different solid–liquid ratios (S/L) and NaOH concentrations, sodium silicate (19.5 g), and CTAB (0.2588 g). The different ingredient ratios and sample numbers are shown in Table 2. Samples G1–G4 and G5–G8 were designed to evaluate the effects of the S/L ratio and the alkaline activator concentration, respectively. After mechanical stirring (500 rpm, 5 min) to form a uniform slurry, H₂O₂ (1.04 g) was introduced as a foaming agent. The aerated mixture was briefly stirred for 30 s, rapidly cast into molds, and cured at 35 °C for 48 h. The resulting geopolymer solid materials were then crushed, passed through a 200-mesh (74 µm) sieve, washed thoroughly with deionized water to remove residual alkalinity, and dried at 65 °C to a constant weight, yielding the final geopolymer adsorbent.

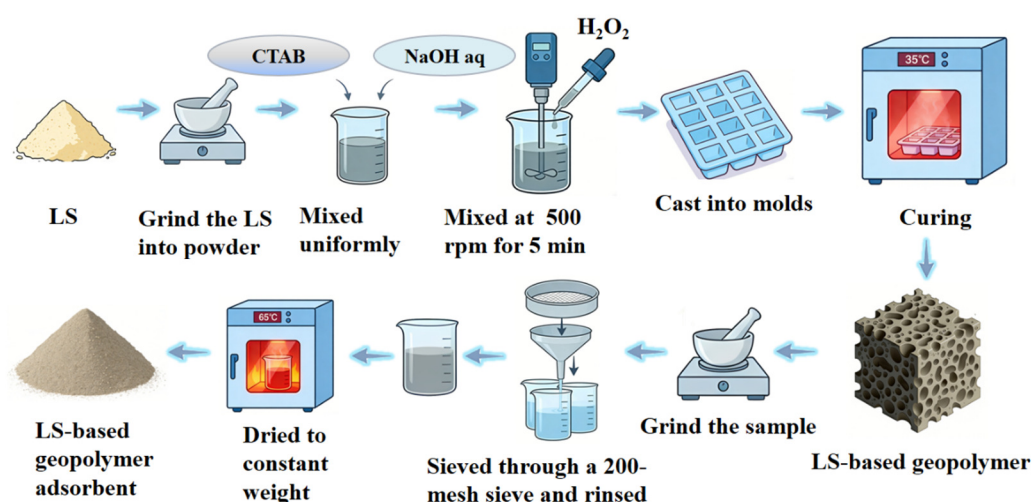


Figure 1. Schematic diagram of sample preparation process.

Table 2. Details of the geopolymer preparation.

No.	LS (g)	S/L	NaOH Concentration (mol/L)	NaOH Solution (g)	Sodium Silicate Solution (g)	CTAB (g)	H ₂ O ₂ (g)
G1	15.00	0.570	8	5.27	21.06	0.2588	1.04

G2	15.00	0.592	8	5.07	20.28	0.2588	1.04
G3	15.00	0.616	8	4.88	19.50	0.2588	1.04
G4	15.00	0.642	8	4.68	18.72	0.2588	1.04
G5	15.00	0.616	7	4.88	19.50	0.2588	1.04
G6	15.00	0.616	9	4.88	19.50	0.2588	1.04
G7	15.00	0.616	10	4.88	19.50	0.2588	1.04
G8	15.00	0.616	11	4.88	19.50	0.2588	1.04

2.3. Characterizations of the Geopolymer

The crystalline phase compositions of the samples were identified using an X-ray diffractometer (XRD, DX-2700, Dandong Fangyuan Instrument Co., Ltd., Dandong, China) operated at 40 kV and 30 mA, with a scanning range (2θ) of 5–80° and a step size of 0.06°. XRD measurements were performed using a Cu K α radiation source. Prior to testing, the powder samples were thoroughly ground and passed through a 200-mesh standard sieve. The resulting homogeneous fine powder was then uniformly packed into the recess of the sample holder for analysis.

The chemical bonding and functional groups were characterized via Fourier transform infrared spectroscopy (FTIR, FTIR-650S, Gangdong Technology Co., Ltd., Tianjin, China) over a wavenumber range of 400–4000 cm^{−1} (resolution: 1 cm^{−1}, 32 scans).

The thermal stability was evaluated utilizing a simultaneous thermogravimetric analyzer (TGA, STA 449F5, NETZSCH Instruments, Selb, Germany) from 30 to 1000 °C at a heating rate of 10 °C·min^{−1}. Approximately 7 mg of the dried powder sample was weighed into an alumina ceramic crucible. The thermal analysis was conducted under a high-purity nitrogen (N₂) atmosphere at a flow rate of 30 mL/min to prevent high-temperature oxidation.

Additionally, the surface micro-morphologies and structural variations were observed by a scanning electron microscope (SEM, ZEISS-Sigma 360, Carl Zeiss AG, Oberkochen, Germany) at magnifications of 200× and 400× under an accelerating voltage of 5 kV. Prior to SEM imaging, the sample surfaces were sputter-coated with gold to enhance conductivity.

Furthermore, the surface elemental compositions and chemical states were analyzed via X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB Xi+, Thermo Fisher, Waltham, MA, USA) equipped with a monochromatized Al K α X-ray source, operating at an anode voltage of 13.4 keV and an emission current of 6 mA.

2.4. Pb(II) Adsorption on the Geopolymer

To fully evaluate the adsorption performance of LS-based geopolymers for Pb(II), the optimal preparation parameters (S/L ratio and alkali concentration) were identified. Using the optimal sample G8, the influences of pH, dosage, contact time, temperature, and initial concentration were then systematically studied. The experimental conditions were investigated as follows: pH (2, 3, 4, 5, 6, 7), adsorbent dosage (0.3, 0.6, 0.9, 1.2, 1.5, 1.8 g/L), adsorption time (contact time) (20, 40, 60, 80, 100, 120, 160, 200, 240, 280, 320, 360 min), temperature (15, 25, 35, 45 °C), and initial Pb concentration (100, 150, 300, 400 mg/L). Furthermore, the adsorption kinetics and thermodynamics were fitted and analyzed using the adsorption data at different times and temperatures, respectively.

Batch adsorption experiments were conducted to evaluate the Pb(II) uptake capacity of the adsorbent. Prior to the tests, the granular material was ground into powder. In a typical procedure, 50 mg of adsorbent was suspended in a Pb(II) solution with a specified initial concentration. The solution pH was either maintained at its natural state or adjusted to predetermined values. The suspensions were subsequently agitated in an orbital shaker at 160 rpm for designated durations.

The concentration of Pb(II) was measured by ICP-OES (Optima 5300 V, Perkin Elmer, Shelton, CT, USA). The adsorption capacity of the adsorbent for Pb(II) Q (mg/g) and the removal rate of Pb(II) R (%) were calculated using Equations (1) and (2) [20].

$$R = \frac{C_0 - C_t}{C_0} \cdot 100\% \quad (1)$$

where C_0 is the initial concentration of Pb(II) before adsorption, and C_t is the concentration of Pb(II) after adsorption.

$$Q = (C_0 - C_t) \cdot \frac{V}{1000m} \quad (2)$$

where C_0 is the initial concentration of Pb(II) before adsorption, C_t is the concentration of Pb(II) after adsorption, V is the volume of the Pb(II) solution in the adsorption experiment (mL), and m is the dosage of the adsorbent.

Studying adsorption kinetics helps to understand the adsorption rate and pathway of pollutants by adsorbents. In this paper, four models, namely the pseudo-first-order kinetic model, pseudo-second-order kinetic model, Elovich model, and intra-particle diffusion model, were selected to fit the adsorption, as shown in Equations (3)–(6), respectively.

$$\ln(Q_e - Q_t) = -k_1 t + \ln Q_{ecal1} \quad (3)$$

$$t/Q_t = t/Q_{ecal2} + 1/(k_2 \cdot Q_{ecal2}^2) \quad (4)$$

$$Q_t = \ln(\alpha \cdot \beta) / \beta + \ln(t) / \beta \quad (5)$$

$$Q_t = k_i \cdot t^{1/2} + C_i \quad (6)$$

where k_1 and k_2 are diffusion factors, Q_e is the equilibrium adsorption capacity of the adsorbent for Pb(II) (mg/g), Q_t is the adsorption capacity at time (mg/g), Q_{ecal} is the theoretical maximum adsorption capacity, (mg/g), α is the initial adsorption rate (mg/g/min), β is the surface desorption constant of the Elovich model (g/mg), k_i is the intra-particle diffusion rate constant (mg·g⁻¹·min^{-1/2}), t is the adsorption contact time (min), and C_i is the constant related to the boundary layer thickness in the intraparticle diffusion model (mg/g).

Adsorption thermodynamic parameters, including enthalpy change (ΔH), entropy change (ΔS), and Gibbs free energy change (ΔG), were calculated using Equations (7)–(9):

$$K_d = Q_e / C_e \quad (7)$$

$$\ln K_d = \Delta S / R - \Delta H / RT \quad (8)$$

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

where K_d is the distribution coefficient (L/g); Q_e is the equilibrium adsorption capacity of Pb(II) on the adsorbent (mg/g); C_e is the concentration of Pb(II) in the solution at adsorption equilibrium, (mg/L); R is the ideal gas constant, 8.314 J/(mol·K); T is the thermodynamic temperature (K).

2.5. Computation Details

All quantum chemical calculations were performed using the Gaussian 09W software package (revision A. 02) [21]. Geometry optimizations and subsequent energetic analyses were carried out at the M06-2X/def2-TZVP level of theory [22–24]. The M06-2X functional was specifically selected for its superior performance in accurately describing weak non-covalent interactions. Concurrently, the def2-TZVP basis set, which covers elements from H to Rn, is highly suitable for modeling the coordination behavior of heavy metals,

thereby ensuring the reliability of the Pb(II) adsorption simulations. Furthermore, electrostatic potential (ESP) distributions were evaluated using the Multiwfn program [25,26], employing the highly efficient algorithm proposed by Zhang and Lu [27].

3. Results and Discussion

3.1. Morphology Characteristics of the LS-Based Geopolymer Adsorbent

G8 was selected to represent the LS-based geopolymer adsorbent for SEM, thermal analysis, FT-IR, and BET as it exhibited the optimal Pb(II) removal performance, representing the final target adsorbent structure. Figure 2a–f shows the digital photos and SEM images of the prepared LS-based geopolymer products (G8). As can be seen from Figure 2a,b, the surface of the geopolymer blocks is relatively smooth, but there are many pores with diameters of several hundred micrometers inside. Figure 2c shows the geopolymer products in a powder form, and samples in this state were used for the adsorption experiments. Figure 2d–f presented the particle size of the geopolymer adsorbent is about 30 μm , and there are many voids with diameters of less than 1 μm and cracks in the particles, which enlarged the surface area of the particles. Furthermore, there are also fibrous aggregates nearby detected by SEM.

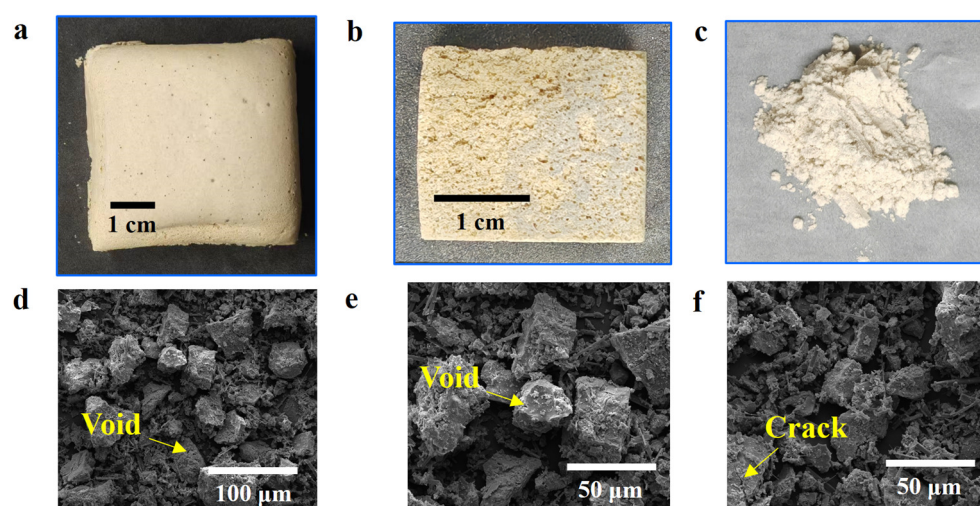


Figure 2. Comprehensive characterization of the prepared G8 geopolymer: digital photograph of (a) block, (b) profile and (c) powder; (d–f) SEM image of powder.

3.2. Chemical and Physical Characteristics of the LS-Based Geopolymer Adsorbent

Figure 3a shows the XRD patterns of the LS raw material and the geopolymers prepared under different solid–liquid ratios and alkalinity. G1 (lowest S/L) and G4 (highest S/L) were chosen to maximally show the influence of S/L, and G5 (lowest alkali concentration) and G8 (highest alkali concentration) were chosen to maximally show the influence of alkali concentration. To precisely illustrate the positions of individual peaks, the XRD spectra are shown only within the range of $2\theta = 10\text{--}40^\circ$, where all primary peaks are observed. The peaks at 24.1° , 25.7° , 26.9° and 28.6° in the XRD patterns correspond to leached spodumene (HAlSi_2O_6 , PDF#79-1982), which is the dominant phase in the LS. The peaks at 25.4° and 31.9° are attributed to CaSO_4 (PDF#37-1496), consistent with the SO_3 and CaO content detected by XRF and the fibrous aggregates detected by SEM. The formation of gypsum originates from the reaction between Li_2SO_4 and CaCO_3 during the lithium extraction process from spodumene [28]. The peak at 26.7° represents the characteristic diffraction peak of quartz (PDF#46-1045). The low intensity of the quartz reflection at 20.3° suggests a low abundance of quartz in the sample. Consequently, the overlapped

peak at 26.8° is dominated by leached spodumene rather than quartz. In order to deeply analyze the geopolymerization of LS, the relative peak intensity of leached spodumene and quartz in LS and derived geopolymers was shown in Table 3. The peak intensity ratio between the diffraction peak at 25.7° , attributed to the leached spodumene phase, and the peak at $2\theta = 26.7^\circ$, attributed to the overlapped peak of the quartz phase and the leached spodumene phase in the LS, as well as the four geopolymers, decreased substantially from approximately 1/2 to 1/5. This reduction signifies the consumption of the active silicon-aluminum constituents (HAlSi_2O_6) in the LS and the concomitant formation of an aluminosilicate gel phase, consistent with the microstructural evolution expected for a successfully formed geopolymer. In addition, compared with LS, in the XRD spectra of the geopolymer samples, a broadened peak ranging from 15° to 35° can be observed (the highlighted rectangular area in Figure 3a), which further proves that the geopolymerization reaction has occurred [29].

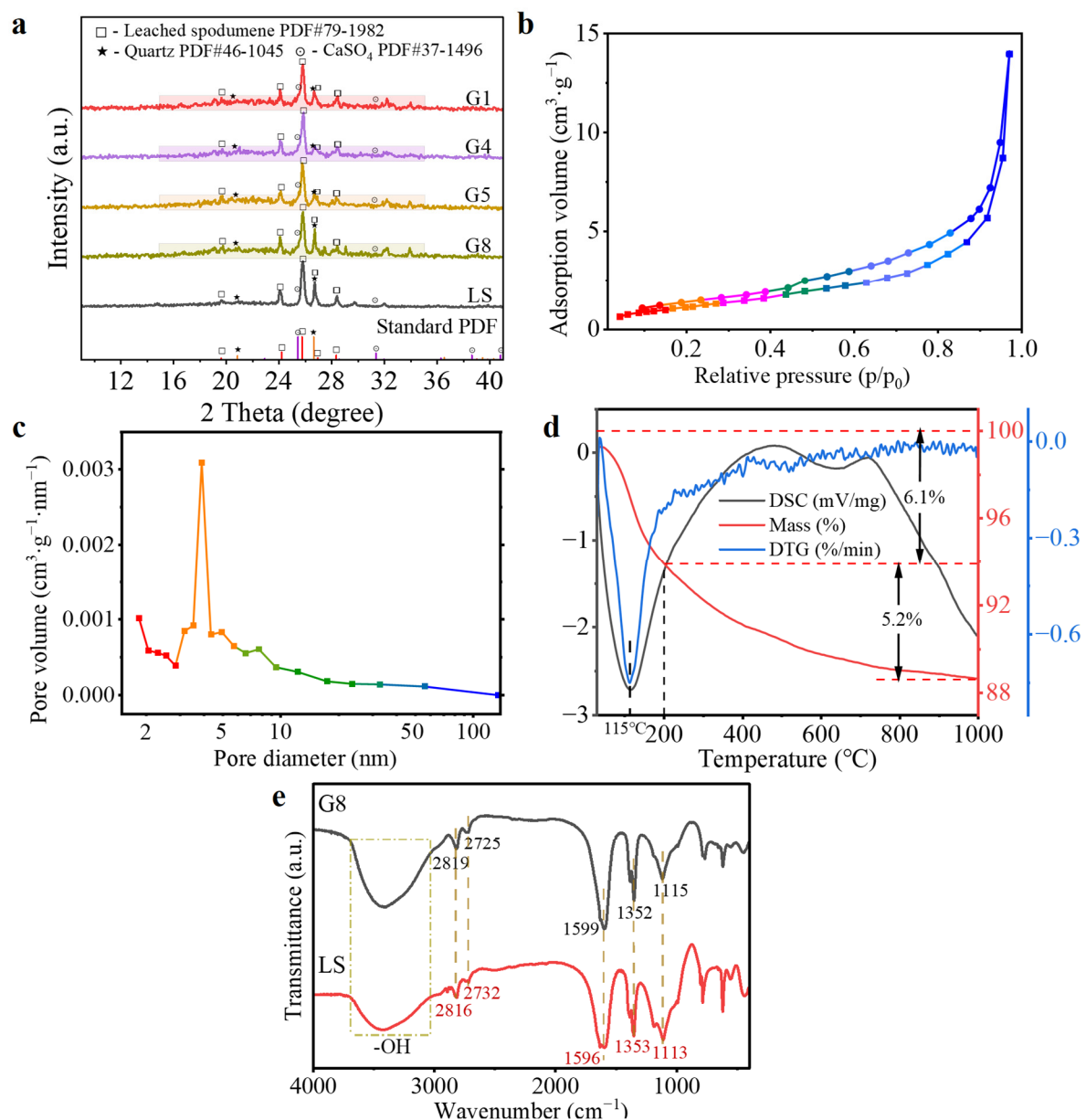


Figure 3. (a) XRD patterns under varying solid-to-liquid ratios and alkalinities, (b) N_2 adsorption-desorption isotherms, (c) pore size distribution curves, (d) thermal analysis curves, and (e) infrared spectra of samples.

Table 3. Peak intensity of different XRD patterns.

Intensity of the Main Peak	LS	G1	G4	G5	G8
25.7° (Leached spodumene)	474	246	299	261	257
26.8° (Overlapped peak)	262	113	85	91	166
I (Overlapped peak)/I (Leached spodumene)	0.553	0.459	0.284	0.349	0.646

Figure 3b,c show the BET analyses of the N₂ adsorption–desorption isotherm and pore size distribution curve of the prepared LS-based geopolymer (G8). As can be seen, the sample exhibits a type IV isotherm and an H3 hysteresis loop, indicating that the sample is rich in mesoporous structures. The data in Table 4 show that the BET specific surface area of the sample is 4.3903 m²/g, the pore volume is 0.0191 mL/g, and the average pore diameter is 17.40 nm, further confirming the well-developed mesoporous nature within the geopolymer matrix.

Figure 3d shows the thermal analysis results of the prepared geopolymer product (G8). As can be seen, the sample mass decreased by 6.1% at 30–200 °C, mainly attributed to the loss of adsorbed water. The mass continuously decreased by 5.2% between 200–1000 °C, mainly attributed to the loss of zeolitic water in the zeolite-like phase of the geopolymer and structural water from —OH in the geopolymer [30,31]. A relatively obvious peak appeared in DSC and DTG at 0–200 °C, with their peaks both at 115 °C. This indicates that a process characterized mainly by endothermic reaction and mass loss occurred in the geopolymer product near 115 °C, which is dominated by the removal of adsorbed water. These features are typical characteristics of the N-A-S-H gel structure, confirming the existence of gel pores and interlayer structures [32]. The DSC peak in the range between 600 °C and 700 °C characterizes the allotropic transformation of α -quartz to β -quartz [33].

Combined with the infrared spectrum analysis in Figure 3e, the peak of 1113 cm^{−1} in the LS corresponds to the Si—O—T (T = Si, Al) asymmetric stretching vibration peak. Aluminosilicates possess an amorphous structure defined by short-range-ordered yet long-range-disordered chains, generated through the sharing of oxygen corners between TO₄ tetrahedra (T = Si, Al). Within this tetrahedral configuration, the oxygen atoms can be distinguished by their coordination environment: bridging oxygens (BO) link adjacent T atoms to propagate the matrix, whereas non-bridging oxygens (NBO) reside at terminal positions, frequently compensating framework charges or serving as active binding sites [34]. The peak between 900–1300 cm^{−1} in Figure 3e represents the polymerization degree of tetrahedral [SiO₄] and [AlO₄] structures, respectively. Compared with LS, the sharp peak at approximately 1200 cm^{−1} of the FT-IR spectrum of the geopolymer gets dramatically weaker, which provides strong initial evidence for the dissolution and depolymerization of the geopolymer reaction [35].

Table 4. BET specific surface area, pore volume, and average pore size of the sample.

Sample	BET Surface Area/(m ² /g)	Pore Volume/(mL/g)	Average Pore Size/nm
LS-Based Geopolymer (G8)	4.3903	0.0191	17.40

3.3. Pb(II) Adsorption Performance of LS-Based Geopolymer Adsorbent

3.3.1. Influence of Preparation Conditions on the Adsorption Performance of LS-Based Geopolymer Adsorbents for Pb(II)

In order to determine the optimal preparation conditions for the LS-based geopolymer adsorbent, the effects of solid–liquid ratio and alkali activator concentration on the removal efficiency of Pb(II) by the adsorbent were investigated. Figure 4a,b show the

Pb(II) removal efficiency of geopolymer samples (G1–G8) under different S/L ratios and alkali activator conditions.

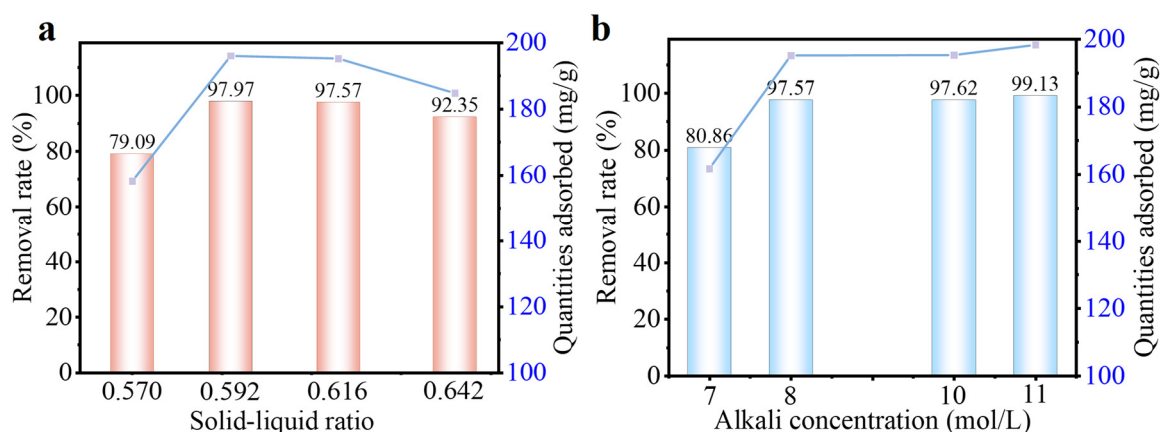


Figure 4. Effects of (a) solid-to-liquid ratio and (b) alkali concentration on adsorption performance.

(1) Effect of S/L ratios on the adsorption performance of LS-based geopolymer adsorbents for Pb(II)

As shown in Figure 4a, as the solid–liquid ratio increases from 0.570 to 0.592, the Pb(II) removal rate and adsorption capacity increase significantly, with the removal rate rising from 79% to 98% and the adsorption capacity increasing substantially and stabilizing at 196 mg/g. When the S/L ratio exceeds 0.63, both the removal rate and adsorption capacity decline slightly; the removal rate drops from a peak of 97% to 92%, and the adsorption capacity decreases to 185 mg/g. The above-mentioned phenomenon could be illustrated as follows:

The S/L ratio primarily determines the integrity of the geopolymer network structure and pore characteristics by controlling the water content and mass transfer efficiency in the reaction system. When the S/L ratio is 0.570, the relatively low ratio would cause excessive water, leading to rapid dissolution of raw materials but hindering formation of a 3D network during polycondensation, thus inhibiting geopolymerization, which reduces the number of adsorption reactive sites. However, when the S/L ratio increased into the range 0.592–0.616, the LS and alkali-activator in the system reach an ideal geopolymerization balance, generating a large amount of aluminosilicate gel with abundant negative charges and surface functional groups, while retaining suitable pore channels for Pb(II) diffusion, thereby maximizing adsorption performance. Furthermore, if the S/L ratio is too high (>0.63), the lack of alkali-activator leads to incomplete precursor dissolution, leaving behind a large amount of inert unreacted particles. Meanwhile, excessive slurry viscosity causes the product structure to become overly dense, severely blocking internal pores, which greatly increases the mass transfer resistance of Pb(II), masks effective adsorption sites, and results in a decline in adsorption capacity [36].

To balance the adsorption capacity and the saving of liquid raw materials (NaOH and sodium silicate solutions), a S/L ratio of 0.616 was chosen as the optimum, which was then kept constant in the alkali concentration optimization experiments.

(2) Effect of alkali concentration on the adsorption performance of LS-based geopolymer adsorbents for Pb(II)

The influence of the concentration of the alkaline activator on the removal efficiency of Pb(II) by the LS-based polymer adsorbent is similar to that of the solid–liquid ratio. As shown in Figure 4b, when the alkali activator concentration is below 10 mol/L, the adsorption removal rate remains at a low level of 80%, and the adsorption capacity is also low (161 mg/g). The experiment for the 8 mol/L condition in Figure 4b was conducted in the

same batch as those in Figure 4a, which may have introduced certain experimental deviations leading to the abnormally high adsorption capacity. When the alkali activator concentration increases to 10 mol/L and above, the removal rate rises directly to over 97% and remains almost unchanged, with the adsorption capacity also increasing significantly to a peak (195 mg/g). The above-mentioned phenomenon could be illustrated as follows:

The alkali activator concentration directly determines the depolymerization degree of the precursor in the geopolymerization process and the generation amount of effective ion exchange sites in the framework. Under low concentration conditions, the solution alkalinity is insufficient to completely break the Si—O—Si and Al—O—Si bonds in the raw material, leading to incomplete development of the three-dimensional network framework, and very few exchangeable alkali metal ions are available to balance the negative charge of the aluminate tetrahedra, thus limiting the adsorption capacity. When the concentration reaches the threshold (10 mol/L and above), the strong alkaline environment can deeply activate the precursor, promoting a high-intensity polycondensation reaction to construct a highly cross-linked and perfect network; this process fixes a massive amount of exchangeable ions in the structure, resulting in a qualitative leap in the material's ability to undergo ion exchange with Pb(II) in the solution, ultimately reaching a stable adsorption plateau as the material's adsorption potential is exhausted or Pb(II) in the water is completely removed.

Based on a comprehensive consideration of Pb(II) removal efficiency and the manufacturing cost of the adsorbent, a liquid-to-solid ratio of 0.616 and an alkali activator concentration of 11 mol/L were selected as the optimal preparation conditions for the adsorbent.

3.3.2. Influence of Adsorption Conditions on the Adsorption Performance of LS-Based Geopolymer Adsorbents for Pb(II)

To further evaluate and validate the actual adsorption performance and underlying mechanism of the material, the effect of different adsorption conditions on the removal of Pb(II) by this LS-based geopolymer adsorbent was investigated. G8 geopolymer was used for the batch adsorption experiments due to its excellent performance (removal rate 99.13%).

Figure 5 shows the influence of different adsorption conditions on the adsorption effect. In the experiments, the experimental conditions were fixed at room temperature ~25°C, Pb(II) initial concentration of 100 mg/L, contact time of 2 h, oscillation speed of 160 rpm, pollutant volume of 50 mL, and adsorbent dosage of 25 mg.

(1) Effect of solution pH on adsorption performance

Solution pH governs the adsorbent's surface chemistry and Pb(II) speciation. As shown in Figure 5a, Pb(II) removal efficiency and capacity surge from 16.79% and 33.58%, respectively, as the pH rises from 2.0 to 6.0, plateauing at ~96% removal efficiency and 193 mg/g capacity thereafter. The adsorption tests were limited to pH less than 7.0 to avoid Pb(OH)₂ precipitation interference. When the solution pH is beyond 7.0, the Pb(II) removal efficiency and capacity remain almost unchanged. The reasons for these can be explained as follows:

When the solution pH is 2.0, the weak Pb(II) adsorption is attributed to the severe restriction by the intense H₃O⁺ competition and electrostatic repulsion from protonated surface amine and hydroxyl groups. As the solution pH gradually increases to 6.0, the diminishing H₃O⁺ concentration alleviates this competition. Simultaneously, the progressive surface deprotonation exposes more and more abundant negatively charged sites, completely shifting the interaction from electrostatic repulsion to strong attraction, thereby increasing the Pb(II) removal efficiency and capacity. When the solution pH is

beyond 6.0, Pb(II) removal efficiency and capacity achieve thermodynamic saturation due to the complete exhaustion of active sites on the LS-based geopolymer surface [37].

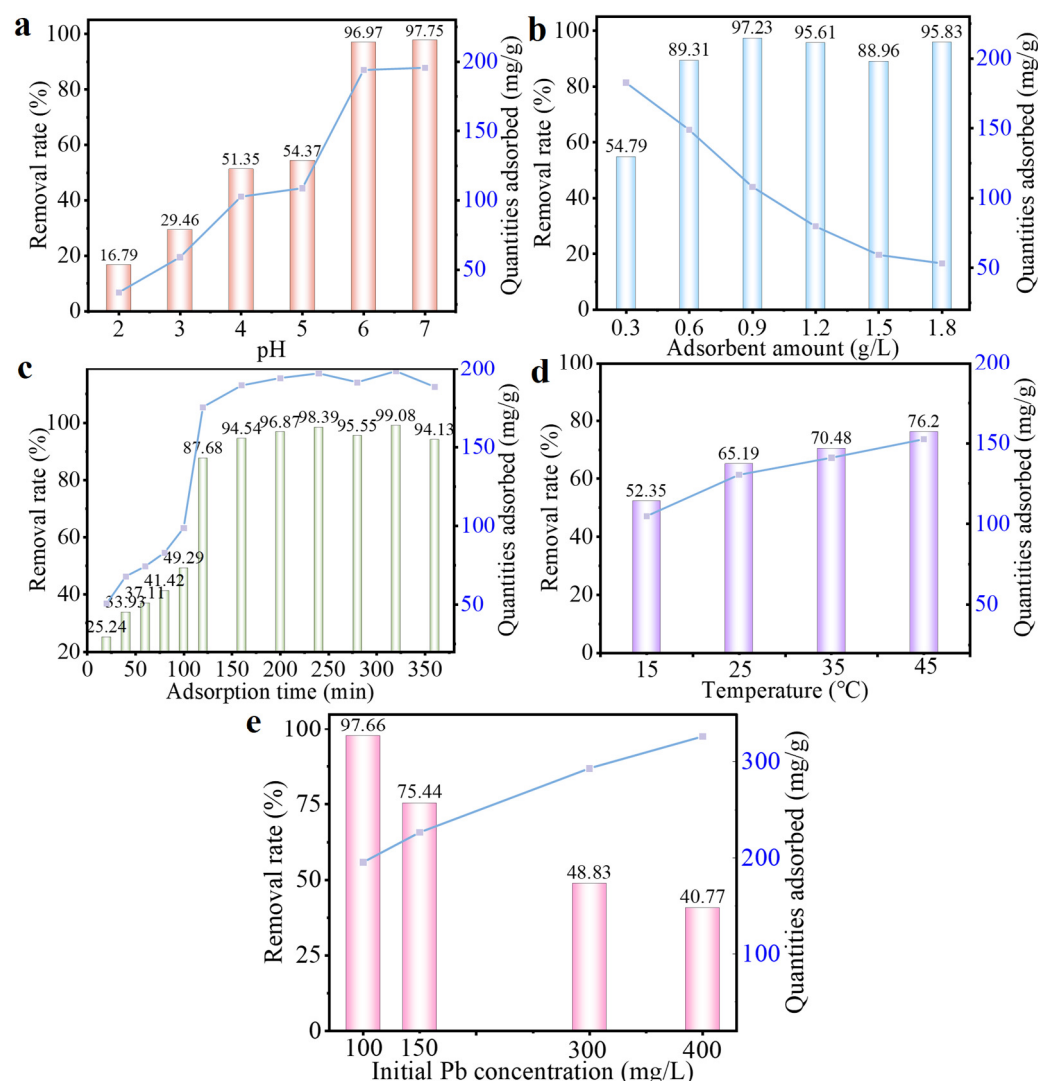


Figure 5. Effects of (a) initial pH, (b) adsorbent dosage, (c) contact time, (d) temperature, and (e) initial Pb(II) concentration on the adsorption performance.

(2) Effect of adsorbent dosage on adsorption performance

As depicted in Figure 5b, in the first stage, increasing the adsorbent dosage from 0.3 to 0.6 g/L, the removal efficiency of Pb(II) increased from 54.79% to 89.31%, but the adsorption capacity decreased. In the second stage, when the adsorbent dosage ranged from 0.6 to 1.8 g/L, the Pb(II) removal efficiency fluctuated slightly within 89.31–97.23%, with an average removal rate of 93.39%. As the adsorbent dosage increased, no significant change in removal efficiency was observed. This is because the total amount of Pb(II) was fixed; once the adsorbent was in excess, the active sites became saturated and the removal efficiency had already reached its upper limit. Further increasing the dosage merely introduced additional ineffective sites, thus causing no further variation. The slight fluctuations may be attributed to local mixing effects or particle shielding induced by dosage changes, minor perturbations in pH and interfacial conditions, as well as measurement errors [38].

The adsorption capacity exhibited a continuous decline with increasing dosage. At the lowest dosage (0.6 g/L), the adsorption capacity reached its maximum, approximately 160 mg/g. When the dosage was increased to 0.9 g/L and 1.2 g/L, the adsorption capacity

dropped to about 105 mg/g and 80 mg/g, respectively. At the highest dosage of 1.8 g/L, the adsorption capacity reached its minimum, around 38 mg/g. This trend can be explained as follows: under a fixed total amount of pollutants, increasing the adsorbent dosage means that more adsorbent competes for the same pool of Pb(II) ions, thereby reducing the average amount of pollutant allocated per unit mass of adsorbent. Moreover, excessive particles tend to agglomerate, blocking active sites, which further contributes to the continuous decrease in adsorption capacity.

(3) Effect of contact time on adsorption performance

As shown in Figure 5c, extending the contact time from 0 to 360 min reveals a two-stage adsorption profile for Pb(II): a rapid initial increase followed by eventual stabilization:

① Initial rapid stage (0–120 min): the Pb(II) removal efficiency and adsorption capacity surge to 87% and 175 mg/g, respectively. This swift capture is facilitated by an abundance of fully exposed surface active sites and a robust mass transfer driving force from the high Pb(II) concentration in the solution.

② Slow adsorption and equilibrium stage (120–300 min): In this period, the growth rate of adsorption capacity drops substantially as the external sites become saturated, finally reaching an equilibrium plateau of 198 mg/g at 300 min. In this later stage, Pb(II) ions must overcome increased resistance to diffuse into the internal porous structures of the material. Consequently, the rate-limiting step transitions to intra-particle diffusion, practically halting further adsorption.

(4) Effect of temperature on adsorption performance: As shown in Figure 5d, an increase in temperature significantly promotes adsorption. When the temperature rises from 15 °C to 45 °C, the equilibrium adsorption capacity increases from ~130 mg/g to 152 mg/g, clearly confirming that the adsorption process is endothermic. Increasing the temperature is favorable both thermodynamically and kinetically: on one hand, it provides energy for Pb(II) to overcome the diffusion activation energy barrier, enhancing its diffusion rate in the solution and material pores; on the other hand, it may increase the activity or exposure of active sites, thereby improving adsorption capacity. Although high temperatures are favorable for adsorption, considering energy consumption and practical application costs, room temperature (25 °C) is sufficient for efficient removal and is therefore selected as the optimal operating temperature.

(5) Effect of Pb(II) concentration on adsorption performance: As depicted in Figure 5e, the initial Pb(II) concentration (100–400 mg/L) exerts opposing effects on the adsorption capacity and removal efficiency. The adsorption capacity rises significantly from 195 mg/g to 326 mg/g across this concentration range. This enhancement is attributed to the steeper concentration gradient, which dramatically strengthens the mass transfer driving force, thereby facilitating the movement of more Pb(II) ions into the internal pores and active binding sites. In contrast, the removal efficiency continuously drops as the concentration increases. At 100 mg/L, the available active sites easily accommodate the low amount of Pb(II), yielding a near 100% removal. However, at higher initial concentrations, the copious amount of Pb(II) rapidly exhausts the available binding sites. Therefore, the inability of the saturated adsorbent to capture the surplus Pb(II) left in the aqueous phase inevitably causes a sharp decrease in the removal efficiency.

3.3.3. Comparison Analyses of Samples Before and After Adsorption

(1) XPS analysis

Figure 6 and Table 5 show the XPS test results of geopolymer samples before and after adsorption of Pb(II), and all curves are raw data.

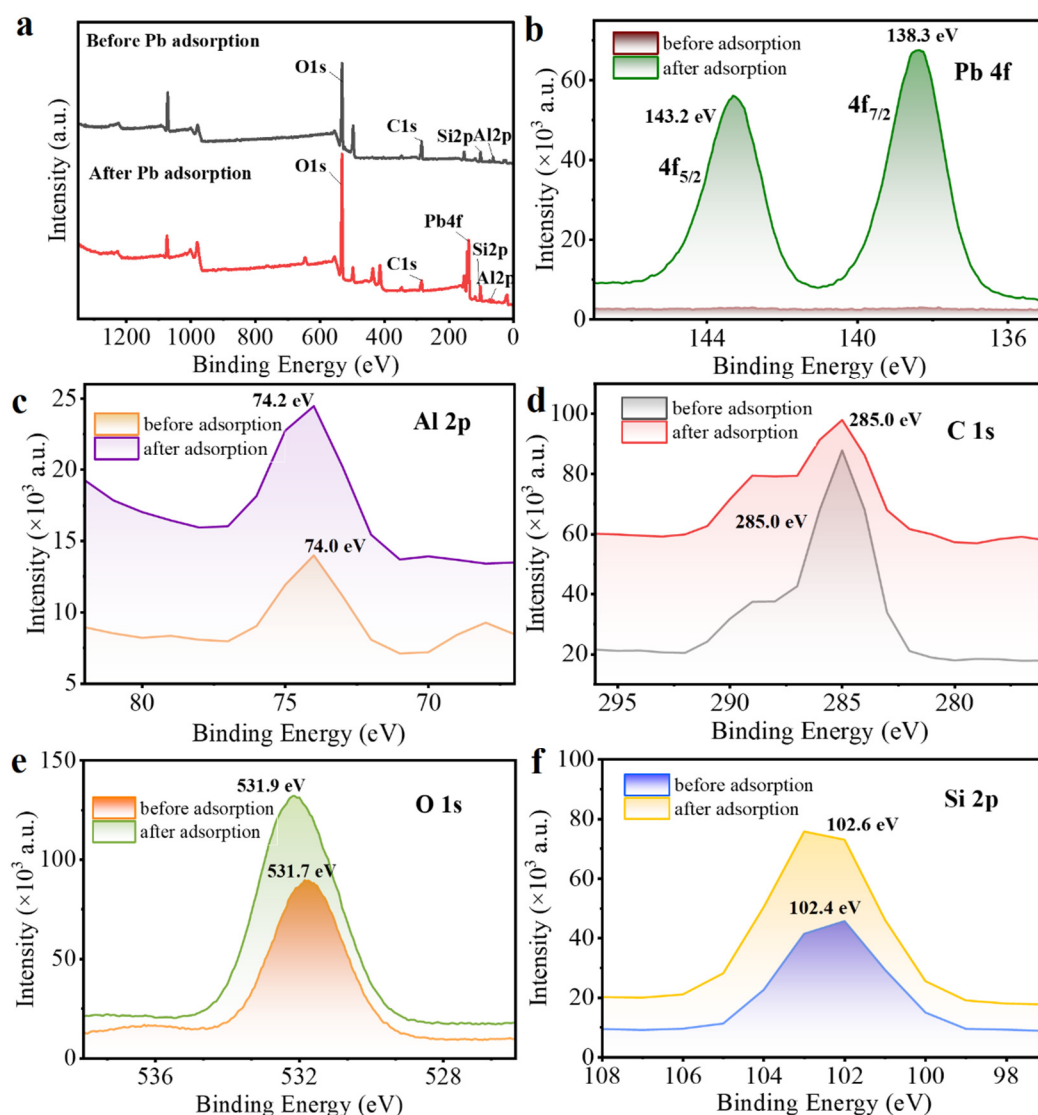


Figure 6. XPS spectra of the geopolymer before and after Pb(II) adsorption: (a) survey spectra, and high-resolution spectra of (b) Pb 4f, (c) Al 2p, (d) C 1s, (e) O 1s, and (f) Si 2p.

Table 5. EDS analyses of the LS-based geopolymer before and after Pb(II) adsorption.

Species		Before Adsorption	After Adsorption
Atomic concentration (%)	C 1s	56.77	36.47
	O 1s	18.70	24.13
	Al 2p	1.95	3.08
	Si 2p	22.58	33.38
	Pb 4f	-	2.95
Binding energy (eV)	C 1s	285.0	285.0
	O 1s	531.7	531.9
	Al 2p	74.0	74.2
	Si 2p	102.4	102.6
	Pb 4f	-	138.3 (4f _{7/2}), 143.2 (4f _{5/2})

Based on the integrated XPS peak areas and standard RSF values (Table 5), the atomic-level chemical immobilization mechanism of Pb(II) was elucidated (Figure 6). After adsorption, typical Pb(II) doublets appear at 138.3 eV (Pb 4f_{7/2}) and 143.2 eV (Pb 4f_{5/2}) with a peak separation of 4.9 eV. The surface Pb concentration reaches 2.95%, confirming successful adsorption. This process is accompanied by a decrease in C 1s (56.77% →

36.47%) due to surface coverage, alongside increases in O 1s, Si 2p, and Al 2p concentrations, hinting at new bond formation (Pb—O—Si) and surface reconstruction. Notably, the binding energies of O 1s, Si 2p, and Al 2p all upshift by +0.2 eV. This indicates that surface oxygen atoms (e.g., silanol, aluminol) donate lone-pair electrons to coordinate with Pb(II) (forming Pb—O—Si/Al bonds). The resulting electron transfer toward the electropositive Pb(II) depletes the electron cloud density around the framework O, Si, and Al atoms, increasing their effective nuclear charge and thereby increasing their binding energies.

(2) SEM and EDS analyses

The elemental distribution of the LS-based geopolymer before and after Pb(II) adsorption was analyzed via SEM and EDS mapping. As shown in Figure 7a, Pb(II) is successfully captured but exhibits a distinctly heterogeneous distribution, with localized cyan-colored enriched regions rather than a uniform dispersion. This preferential accumulation at specific microstructural sites suggests a synergistic removal mechanism driven by surface complexation, framework ion exchange, and localized precipitation at highly active sites. Furthermore, as shown in Figure 7b, Pb was detected at minimal levels in the detection area before adsorption. After adsorption, however, the analyzed region exhibited a pure Pb-enriched phase devoid of elemental interference, confirming the effective immobilization of Pb(II).

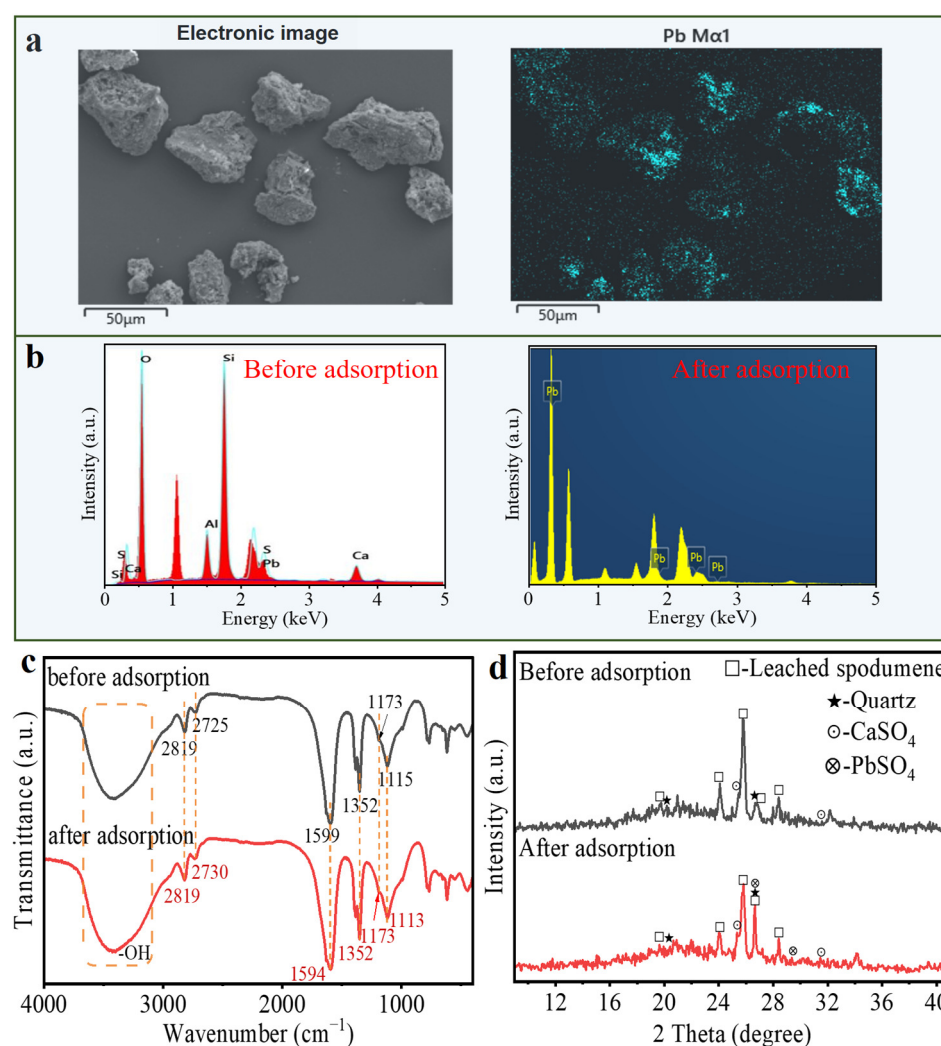


Figure 7. Morphological and structural characterization of the geopolymer: (a) SEM elemental mapping images after Pb(II) adsorption, (b) EDS spectra before and after Pb(II) adsorption, (c) FT-IR spectra before and after Pb(II) adsorption, and (d) XRD patterns before and after Pb(II) adsorption.

(3) FT-IR analyses

Figure 7c presents the FT-IR analysis results of the geopolymer products before and after Pb(II) adsorption. As shown in the figure, the geopolymer product before Pb(II) adsorption exhibits strong absorption peaks at wavenumbers such as 2819 cm⁻¹, 2725 cm⁻¹, 1599 cm⁻¹, 1352 cm⁻¹, and 1115 cm⁻¹. Among these, the characteristic peak at 1599 cm⁻¹ can be attributed to the bending vibration of adsorbed H—O—H water molecules. The characteristic peak at 1115 cm⁻¹ likely corresponds to the asymmetric stretching vibration of Si—O—Si or Si—O—Al bonds. Its appearance indicates that the silicon-aluminum phases in the raw materials have dissolved and re-polycondensed, forming a three-dimensional network structure.

After Pb(II) adsorption, the characteristic peak at 1599 cm⁻¹ red-shifted by 5 cm⁻¹, indicating that Pb(II) coordinated with the oxygen atoms in the system, lengthening the O—H bond and resulting in a decrease in the vibration frequency. The characteristic peak at 1115 cm⁻¹ red-shifted by 2 cm⁻¹, suggesting that Pb(II) interacted with the oxygen in Si—O—Si or Si—O—Al bonds. The coordination of Pb(II) pulled the electron cloud, weakening the strength of the Si—O or Al—O bonds, which consequently led to an increase in bond length and a decrease in the characteristic vibration frequency.

(4) XRD analyses

Figure 7d shows the XRD patterns of the samples before and after adsorption. The PDF card for the newly formed lead sulfate (PbSO₄) phase is PDF# 36-1461, while those of the other phases are identical to those mentioned previously. No diffraction peak was observed at 2θ ≈ 26.6° prior to adsorption; however, a new peak emerged at this position following Pb(II) loading, indicating the formation of a crystalline phase associated with the adsorption process. In the context of the Pb(II) adsorption system by lithium-slag-based geopolymer, this peak is primarily attributed to the characteristic crystalline phase of lead sulfate (PbSO₄), which is formed through the in situ precipitation and crystallization of sulfate ions and lead ions present in the system, as seen in Equation (10).



3.4. Adsorption Kinetics and Thermodynamics

As detailed in Figure 8 and Table 6, the pseudo-first-order model provides the best fit for the four adsorption kinetics models ($R^2 = 0.934$), outperforming the intra-particle diffusion (0.850), Elovich (0.841), and pseudo-second-order (0.798) models. Nevertheless, the satisfactory fits of the Elovich and intra-particle diffusion models offer critical mechanistic insights. Specifically, the Elovich model suggests a chemisorption-dominated process where the uptake rate decays exponentially with increasing surface coverage, reflecting the energetic heterogeneity of the geopolymer's active sites. Concurrently, the intra-particle diffusion model confirms that the migration of Pb(II) from the bulk solution into the internal porous network is a prominent rate-governing step.

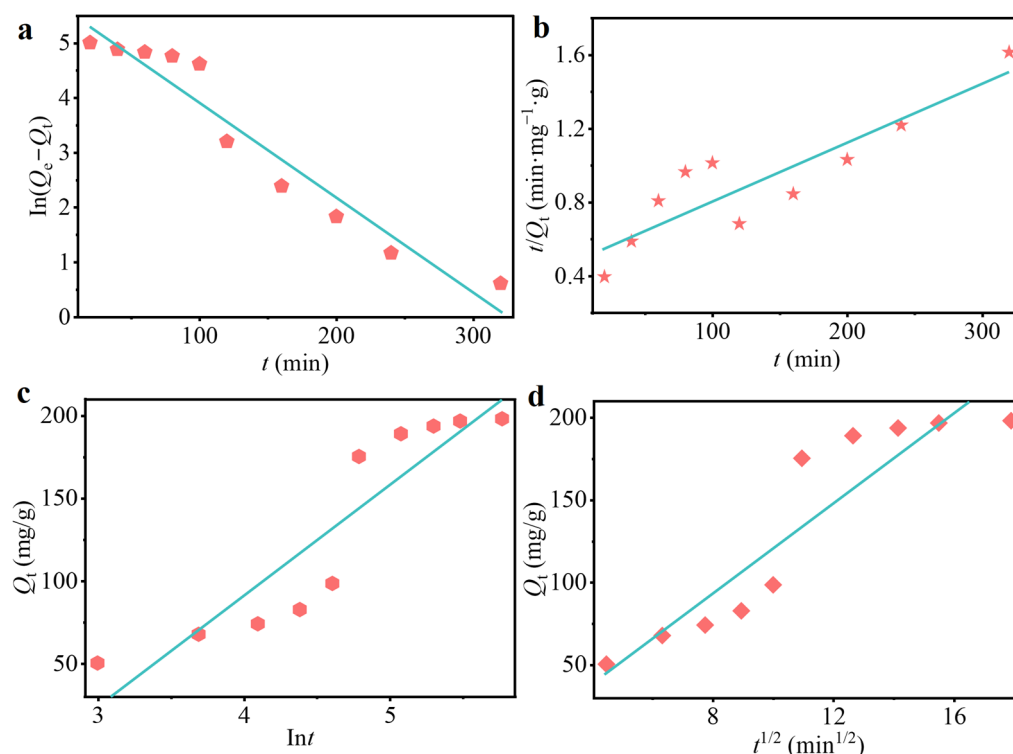


Figure 8. Fitting curves of various kinetic models for Pb(II) adsorption onto the L-based geopolymer: (a) Pseudo-first-order; (b) Pseudo-second-order; (c) Elovich; (d) Intra-particle diffusion.

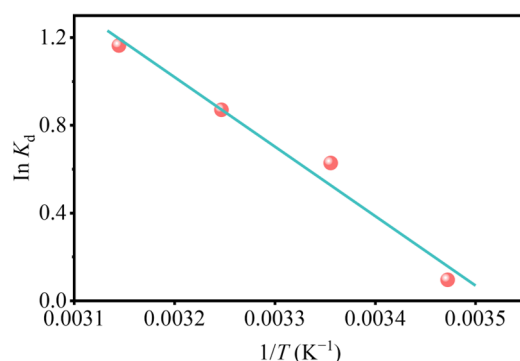
Table 6. Kinetic parameters of the adsorption of Pb(II) in our system.

Kinetics Model	Parameter	Value
Pseudo-first-order	$Q_{ecal1}/(\text{mg/g})$	284
	$K_1/(\text{min}^{-1})$	−0.01729
	R_1^2	0.9340
Pseudo-second-order	$Q_{ecal2}/(\text{mg/g})$	313
	$K_2/(\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1})$	0.0209
	R_2^2	0.7977
Elovich	$\alpha/(\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1})$	4.79
	$\beta/(\text{g} \cdot \text{mg}^{-1})$	0.0149
	R_3^2	0.8414
Intra-particle diffusion	$K_i/(\text{mg} \cdot (\text{g} \cdot \text{min}^{1/2})^{-1})$	13.65
	$C_i(\text{mg} \cdot \text{g}^{-1})$	−15.53
	R_4^2	0.8498

Thermodynamic analysis reveals the spontaneity and stability of the Pb(II) adsorption process on the geopolymer adsorbent surface. Using $1/T$ as the abscissa and $\ln K_d$ as the ordinate for linear fitting, the fitted line is shown in Figure 9, and the relevant fitting parameters are listed in Table 7. As shown in Table 7, the fitted correlation coefficient $R^2 = 0.997$, indicating an excellent linear relationship. The positive enthalpy change (ΔH°) of 17.66 kJ/mol for the adsorbent suggests that the adsorption is an endothermic process. The positive entropy change (ΔS°) of 0.0668 kJ·mol^{−1}·K^{−1} reflects an increase in the stoichiometric number at the solid–liquid interface. The Gibbs free energy change (ΔG°) is negative across the experimental temperature range (288.15 K to 318.15 K), confirming that the adsorption process is spontaneous and stable. Furthermore, the ΔG° value becomes more negative with increasing temperature, indicating that higher temperatures favor the adsorption of Pb(II).

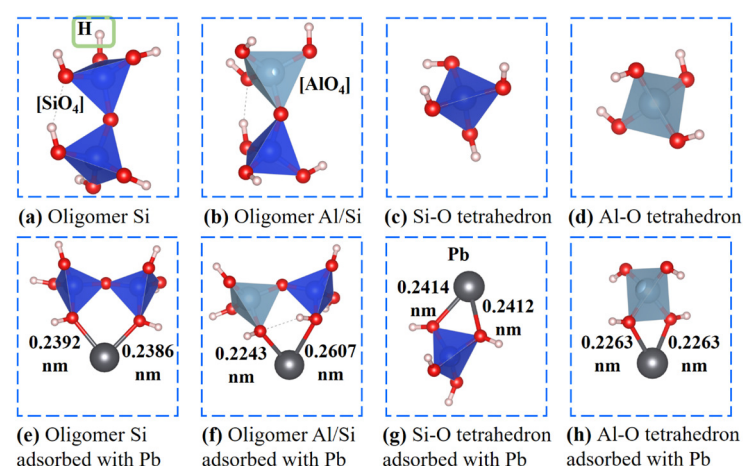
Table 7. Thermodynamic parameters for Pb(II) adsorption onto the LS-based geopolymer.

Parameter	Value
R^2	0.997
$\Delta H/(\text{kJ/mol})$	17.66
$\Delta S/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	0.0668
$\Delta G/(\text{kJ/mol})$	288.15 K
	298.15 K
	308.15 K
	318.15 K
	−1.584
	−2.230
	−2.876
	−3.523

**Figure 9.** Thermodynamic fitting curves for Pb(II) adsorption onto the LS-based geopolymer.

3.5. Quantum Chemistry Simulation of Geopolymer Before and After Pb(II) Adsorption

Figure 10 shows the optimized structural configurations of two monomer models and two oligomer models before and after Pb(II) adsorption, plotted using VESTA [39]. The RESP charges and Mulliken charges of the atoms in these configurations are provided in Supplementary Materials Tables S1–S4. The main bond lengths in the configurations are listed in Tables S5 and S6.

**Figure 10.** Optimized structural configurations of the monomer and oligomer models before and after Pb(II) adsorption.

Based on the adsorption geometry and bond parameters (Figure 10), the Pb(II) ion spontaneously approaches the two O atoms of the Al–O tetrahedron from an initial distance of approximately 0.3 nm to an identical equilibrium bond length of 0.2263 nm. This distance falls between standard Pb–O chemical bonds and van der Waals interactions, confirming the formation of definitive chemical bonds, albeit slightly elongated due to

steric hindrance. The identical Pb–O bond lengths indicate simultaneous, symmetrical bi-dentate coordination, a hallmark of stable inner-sphere surface complexation. For the Si–O tetrahedron monomer, the distance between the Pb(II) ion and the two coordinating O atoms is 0.2412 nm, which is 0.0149 nm longer than that in the Al–O tetrahedron (0.2263 nm), yet still shorter than the initial pre-optimization distance of about 0.3 nm. This confirms that the Si–O tetrahedron monomer does exhibit adsorption interaction with Pb(II), but the interaction is weaker. After Pb(II) adsorption, the O–H bonds in the Al–O and Si–O tetrahedron monomers were elongated by an average of 0.0010 nm and 0.0003 nm, respectively. The Al–O bonds and Si–O bonds were elongated by an average of 0.0003 nm and 0.0004 nm, respectively. Notably, the Al–O/Si–O bonds near the Pb(II) ion showed larger average elongations of 0.0051 nm and 0.0035 nm, respectively. The two oligomer models exhibited the same trend: the Al–O/Si–O bonds near Pb(II) were elongated by an average of 0.0050 nm and 0.0049 nm after adsorption. The two oligomer models in Figure 10 exhibit the same trend: the Al–O/Si–O bonds near Pb(II) were extended by an average of 0.0050 nm and 0.0049 nm after adsorption, again consistent with the FT-IR analysis.

A comparison of adsorption energies in Figure 11 reveals that the Al–O tetrahedron monomer has an adsorption energy of -329.8 kJ toward Pb(II), significantly stronger than that of the Si–O tetrahedron monomer (-158.2 kJ). For the mixed Al–O/Si–O oligomer, the adsorption energy (-243.2 kJ) falls between the two pure monomers, while the pure Si–O oligomer gives a value of -172.5 kJ, similar to its monomer. These energetic comparisons confirm that the Al–O tetrahedral sites dominate the strong chemisorption of Pb(II) over the Si–O sites.

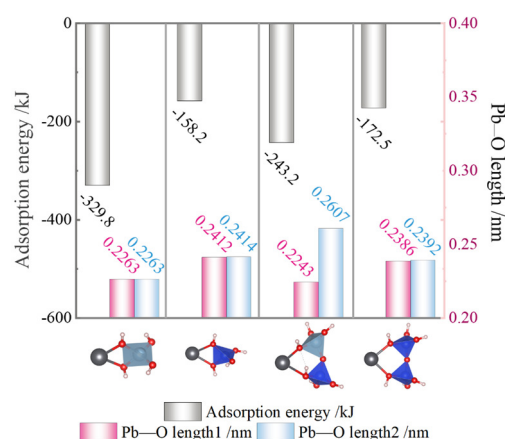


Figure 11. Calculated adsorption energies and optimized bond lengths of the different model systems.

3.6. Summary of Adsorption Mechanism

Based on the analysis above, an adsorption model as depicted in Figure 12 is proposed. In practical systems, heavy metal adsorption primarily targets localized active sites. To isolate the intrinsic adsorbate-framework interactions from interferences like long-range crystal fields, hydrogen bonding, and solvent effects, idealized $[\text{AlO}_4]$ and $[\text{SiO}_4]$ models were employed. Due to the lower electronegativity of Al (1.61) compared to Si (1.90), the Al–O bond exhibits a higher ionic character ($\approx 63\%$ vs. $\approx 51\%$). Consequently, Al–O oxygen atoms possess a more diffuse electron cloud and stronger basicity, readily donating lone-pair electrons to form robust coordination bonds with Pb(II). Computed adsorption energies confirm that the Al–O monomer exhibits stronger chemisorption toward Pb(II) than its Si–O counterpart. Furthermore, the localized 0.0050 nm elongation of proximal Al/Si–O bonds post-adsorption perfectly corroborates the downshift of the 1599 cm^{-1} FT-IR peak. Regarding material composition, the LS used in this study

contains 56.72 wt% SiO₂ and 18.16 wt% Al₂O₃, with a low-to-medium Si/Al molar ratio of 2.65. This composition provides an optimal balance: the material is rich in highly reactive Al—O sites that enhance adsorption performance, while the SiO₂ forms a stable tetrahedral network. This silica skeleton ensures the necessary mechanical strength, porous structure, and chemical stability, granting the prepared samples both high reactivity and structural integrity.

These thermodynamic and structural insights suggest that optimizing the Si/Al ratio in geopolymer design is not merely about maximizing adsorption capacity, but rather engineering a synergistic ‘adsorption-support’ framework [40]. This provides a clear guideline for tailored synthesis of geopolymer adsorbents with both high decontamination efficiency and long-term durability in practical wastewater treatment.

Kinetic analysis using four different models reveals that the pseudo-first-order model provides the best overall fit. However, the Elovich and intra-particle diffusion models also demonstrate strong correlation. The high agreement with the Elovich model suggests that the process is predominantly chemisorption, where the adsorption rate decreases exponentially as surface coverage increases—a defining characteristic of geopolymers with heterogeneous active sites.

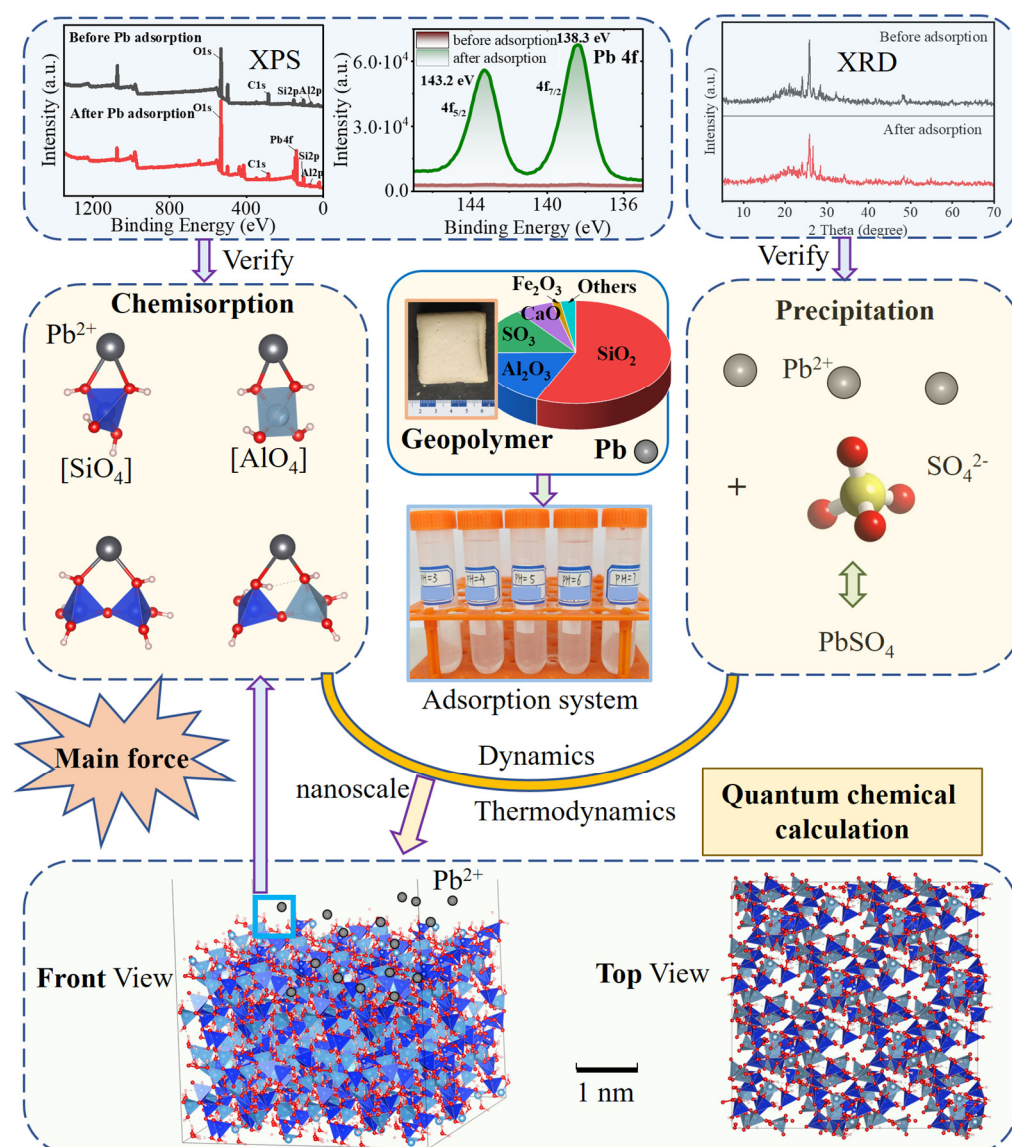


Figure 12. Proposed mechanism for Pb(II) adsorption onto the LS-based geopolymer.

Thermodynamic evaluations show an excellent linear fit ($R^2 = 0.997$). The positive enthalpy change ($\Delta H^\circ = 17.66$ kJ/mol) indicates that the adsorption is an endothermic process, while the positive entropy change ($\Delta S^\circ = 0.0668$ kJ·mol⁻¹·K⁻¹) reflects increased randomness at the solid–liquid interface. The Gibbs free energy (ΔG°) remains negative across the tested temperature range (288.15 K to 318.15 K), confirming the spontaneity and stability of the adsorption process. Additionally, ΔG° becomes increasingly negative at higher temperatures, indicating that heating thermodynamically favors the adsorption of Pb(II).

Given the slight appearance of the PbSO₄ diffraction peak in the XRD pattern, a plausible adsorption pathway is that Pb(II) is initially retained via chemisorption onto the LS surface, while the SO₄²⁻ released into solution sustains local supersaturation, which subsequently evolves into surface-induced precipitation of PbSO₄. Accordingly, the overall Pb(II) removal should be interpreted as a coupled mechanism involving both chemisorption and precipitation, and chemisorption is the main force.

Raw lithium slag indeed contains leachable trace contaminants [41]. However, once LS is converted into a geopolymer matrix, these trace elements are securely immobilized through three-dimensional N-A-S-H gel encapsulation and lattice substitution [41,42].

3.7. Adsorption Performance Comparisons Between This Work and Some Reported Adsorbents

As illustrated in Figure 13 [2,43–45], the findings of existing related studies are predominantly clustered within the region denoted by the cyan circles, where the equilibrium times generally range from 1 to 3 h. Within this specific timeframe, the maximum adsorption capacities of these previously reported materials (e.g., MT, MFA, MMB, SA@AM, and UNCAM) remain strictly below 130 mg/g. This performance is substantially lower than the exceptional adsorption capacity achieved in the present study, as highlighted by the red area. This direct comparison visually confirms that, under comparable equilibrium time conditions, the material developed in this work exhibits a vastly superior adsorption capability. Consequently, it demonstrates a prominent advantage over existing adsorbents by successfully achieving an optimal balance between high adsorption efficiency and minimal time expenditure.

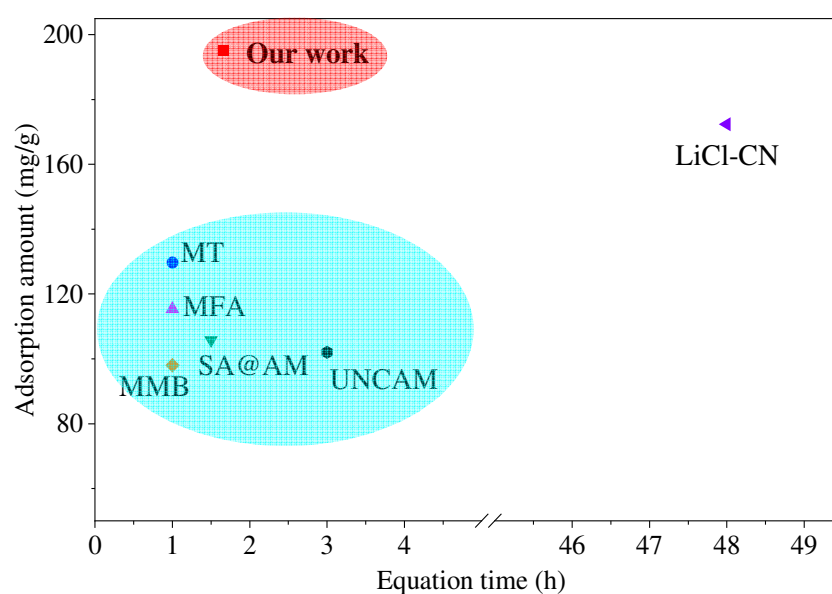


Figure 13. Comparison of the adsorption performance in the present study with other reported adsorbents [2,43–45].

4. Conclusions

In this study, a high-capacity porous geopolymer was successfully synthesized by upcycling industrial LS and systematically evaluated for its Pb(II) sequestration capabilities. The principal findings are summarized as follows:

(1) A highly porous lithium-slag-based geopolymer was fabricated via alkali activation (NaOH and sodium silicate) coupled with H₂O₂ foaming. Utilizing LS rich in SiO₂ (56.72 wt%) and Al₂O₃ (18.16 wt%) as the primary precursor, structural and performance optimizations revealed that an alkali concentration of 11 mol/L and a solid-to-liquid ratio of 0.616 yielded the most favorable porous architecture and maximum adsorption efficacy.

(2) The prepared geopolymer exhibited outstanding Pb(II) removal performance. For a 100 mg/L Pb(II) solution at pH 6.0 and room temperature, the removal efficiency approached 90% within 120 min before reaching equilibrium. The adsorption kinetics were accurately captured by the pseudo-first-order model, yielding a remarkable theoretical equilibrium capacity (Q_e) of 284 mg/g.

(3) Kinetic analysis shows the pseudo-first-order and Elovich models provide the best fits, confirming chemisorption as the dominant mechanism, characteristic of heterogeneous geopolymer surfaces. Thermodynamic results reveal a spontaneous ($\Delta G < 0$), endothermic ($\Delta H = 17.66$ kJ/mol) process with increased interfacial randomness ($\Delta S > 0$). The increasingly negative ΔG at higher temperatures indicates that elevated temperature thermodynamically favors Pb(II) adsorption. Together, these findings and the XRD peak of PbSO₄ establish that Pb(II) removal by the LS-based geopolymer is a coupled mechanism involving both chemisorption and precipitation, and chemisorption is the main force.

To further advance the practical and engineering applicability of this adsorbent, several follow-up studies will be conducted in the next phase of our research. First, systematic regeneration and cycle tests will be performed to evaluate the long-term reusability and stability of the adsorbent. Second, further experiments using real water samples are suggested, and the influence of common coexisting anions and cations could be investigated to assess the selective adsorption performance in complex aquatic matrices. Finally, leaching tests on the post-adsorption samples will be carried out to monitor the potential re-dissolution of heavy metals, thereby verifying the environmental safety and long-term stability of the exhausted adsorbents.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr14152461/s1>, Table S1: RESP charges and Mulliken charges of mono Al system (Unit: e); Table S2: RESP charges and Mulliken charges of mono Si system (Unit: e); Table S3: RESP charges and Mulliken charges of oli Si system (Unit: e); Table S4: RESP charges and Mulliken charges of oli Al/Si system (Unit: e); Table S5: Main bond length of monoAl/Si system (unit: nm); Table S6: Main bond length of oli Si and Al/Si system (unit: nm).

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Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy.

Conflicts of Interest: Authors Yang Tang, Xiaojun Yang, Chuan Guan, Binbin Tang, Wenjie Jiang, Yang Xian, Ping Jiang, Peiyuan Peng and Zhenhua Feng were employed by the Sichuan Experimental Testing and Research Center of Natural Resources (Sichuan Nuclear Emergency Technical Support Center). The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. The authors declare that this study received funding from the Research Project of Sichuan Experimental Testing and Research Center of Natural Resources. The funder was not involved in the study design, collection, analysis, interpretation of data, the writing of this article or the decision to submit it for publication.

Abbreviations

The following abbreviations are used in this manuscript:

BO	Bridging oxygens
CTAB	Hexadecyltrimethylammonium bromide
DFT	Density Functional Theory
EDS	Energy Dispersive Spectrometer
FT-IR	Fourier Transform Infrared Spectroscopy
LS	Lithium Slag
NBO	Non-bridging oxygens
SEM	Scanning Electron Microscope
S/L ratio	solid-to-liquid mass ratio
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

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