

Article

Efficient and Direct Recovery of Germanium from Optical Fiber Solid Waste via Low-Modulus Alkaline Leaching and Customized Meglumine Resin Adsorption

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Abstract

A large amount of germanium-containing waste is generated during optical fiber preform production, representing a critical secondary germanium resource. To address recovery challenges from low germanium content, high silicon content and complex occurrence states in optical fiber solid waste, this study proposes a short-flow clean hydrometallurgical process based on low-modulus alkaline leaching coupled with direct adsorption using customized meglumine resin. Results show that under low-modulus ($M = 1$) strong alkaline conditions, the system achieved a maximum germanium release concentration of 331.25 mg/L and exhibited excellent anti-gelation stability. The self-synthesized alkali-resistant NMG resin was applied for direct adsorption in raw $M = 1$ leachate without pH adjustment. The adsorption process follows pseudo-second-order kinetics and the Langmuir isotherm, with a maximum theoretical adsorption capacity of 3.529 mg/g. Spectral analysis indicates that the ortho-cis-diol groups of the resin can specifically chelate with germanate, overcoming competitive interference from strong alkali and high silicon. This process provides a theoretical basis for the green recycling of high-silicon germanium-containing secondary resources.

Keywords: optical fiber solid waste; heated alkaline leaching; silicon–germanium separation; resin adsorption; germanium recovery

1. Introduction

Germanium (Ge), as a typical dispersed metal, plays an irreplaceable role in strategic fields such as optical fiber communication, infrared optics, aerospace, and high-frequency electronic devices. With the explosive growth of global communication computing infrastructure, the demand for high-bandwidth, low-loss optical fibers in optical networks has surged. According to statistics, optical fiber communication accounts for more than 30% of the global Germanium consumption structure [1–4]. However, during the high-temperature co-oxidation process of optical fiber preform production, approximately 30% to 50% of germanium is lost in the form of vapor deposition by-products or waste/defective products [5,6], resulting in a large amount of solid waste characterized by “high silicon and low germanium” ($w(\text{SiO}_2) > 95\%$, $w(\text{Ge}) < 1\%$). Achieving efficient recovery of such secondary resources is of urgent practical significance for ensuring the security of key strategic metal supply chains [7–13].



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Regarding the recovery of high-silicon germanium-containing materials, traditional physical beneficiation and conventional acid leaching processes generally yield extremely low germanium leaching rates due to their inability to effectively disrupt the dense silicon-oxygen tetrahedral network. Meanwhile, the pyrometallurgical chlorination distillation process suffers from drawbacks such as high energy consumption, large slag volumes, and low direct recovery rates [14–20]. In contrast, the alkaline leaching process can release the encapsulated germanium atoms through the nucleophilic attack of strong alkali on the Si-O-Ge skeleton, making it an effective method for treating high-silicon materials [21–23]. However, the alkaline leaching process has long faced a dilemma: if a lower alkalinity is controlled (e.g., modulus $M = 3$ or 4). The modulus (M) here refers to the molar ratio of SiO_2 to Na_2O in the sodium silicate system, a widely used metric to characterize the relative alkalinity of silicate solutions: a lower M value corresponds to higher free OH^- concentration and stronger alkalinity), although it can mitigate interference in subsequent processing, the release of germanium is incomplete, and high-silicon solutions are highly prone to silicic acid dehydration and condensation during transfer, forming macromolecular silica gels that block pipelines or trigger “silicon poisoning” of adsorption materials [24]. Conversely, if the alkalinity is increased (e.g., $M = 1$), although the leaching rate is significantly improved, the extremely strong alkaline environment induces intense competitive adsorption, and most organic adsorption materials cannot withstand such harsh conditions, leading to difficulties in process integration. Traditional long-flow processes usually require multi-stage pH adjustment prior to extraction or adsorption, which not only consumes a large amount of acid and alkali reagents but also easily induces silica gel precipitation during the adjustment process (see Figure 1 for process comparison) [25–28].

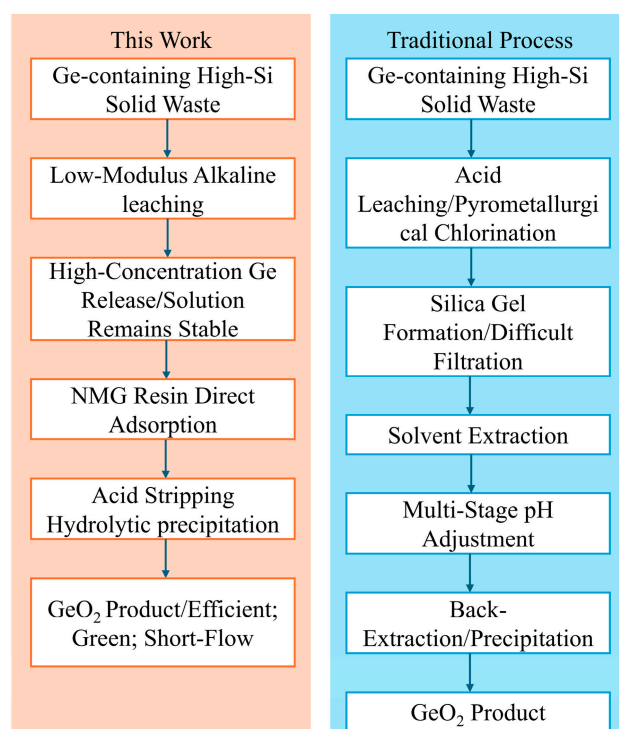


Figure 1. Schematic diagram comparing the traditional recovery process for germanium-containing high-silicon solid waste with the short-flow process proposed in this paper.

N-methyl-D-glucamine (NMG)-functionalized resins are well-known for their specific chelation ability toward cis-diol-binding species. Initially developed for boron removal from aqueous solutions, NMG resins have been further extended to the recovery of germanium due to the similar coordination chemistry of Ge(IV) with vicinal diol groups [29,30].

Virolainen et al. first demonstrated the selective recovery of germanium from sulfate solutions using NMG-functionalized chelating resins, and confirmed that the binding mechanism relies on the formation of five-membered chelate rings between ortho-cis-diol groups and germanate species. Subsequent studies further modified the resin matrix to enhance adsorption capacity and alkali resistance, yet few studies have reported their direct application in concentrated strong-alkaline sodium silicate systems. This gap motivates the present work to evaluate the feasibility of NMG resin for direct germanium adsorption from low-modulus alkaline leachates.

Based on the aforementioned issues, this paper proposes the following specific research questions (RQs): (1) Under an extremely strong alkaline ($M = 1$) environment, what are the dissociation pathways of the silicon–oxygen skeleton and the phase evolution laws of polysilicic acid? (2) How does the customized meglumine resin (NMG-Resin) achieve the specific recognition and adsorption of germanate in a complex competitive environment of strong alkali and high silicon?

To answer these questions, this study independently prepared an NMG resin with excellent alkali resistance and systematically evaluated the phase stability of the low-modulus alkaline leaching system. The study found that in a high alkalinity system with modulus $M = 1$, the system possesses excellent anti-gelation stability, and the inhibitory effect of electrostatic repulsion on polymerization was quantitatively demonstrated through Zeta potential and particle size evolution analysis. Building upon this, the resin was directly applied to the $M = 1$ raw solution. Combined with kinetic and thermodynamic model calculations, the molecular mechanism of the ortho-diol chelating with germanate to form a five-membered ring was elucidated, constructing an efficient short-flow recovery process free from pH adjustment.

2. Experiment

2.1. Experimental Materials and Reagents

The raw material utilized in this study was germanium-bearing high-silicon dust, this dust is a waste by-product generated during the manufacturing process of optical fiber preforms by a commercial optical fiber enterprise in Hubei Province, China. The dust is generated during the high-temperature vapor-phase deposition process and naturally exists in the form of fine amorphous silica particles. The samples were freshly collected from the production exhaust collection system, stored in a dry environment to avoid moisture absorption and carbonation. To ensure sample representativeness and homogeneity, the bulk dust was first homogenized via mechanical mixing for 30 min using a planetary ball mill at 200 rpm. The homogenized powder was then sieved through a 200-mesh standard sieve, and the undersize fraction was collected as the experimental feed material. The quartering method was applied to reduce the sample size stepwise to obtain representative subsamples for each leaching and adsorption test. All sampling operations were performed in triplicate to guarantee the consistency of feed composition across parallel experiments.

The chemical reagents employed in the experiments included sodium hydroxide (NaOH, analytical grade, AR), hydrochloric acid (HCl, analytical grade, AR), absolute ethanol (C_2H_5OH , analytical grade, AR, methanol-free), anhydrous sodium carbonate (Na_2CO_3 , analytical grade, AR), and N-methylglucamine (NMG, 99% purity). Deionized water with a resistivity of $\geq 18.5 M\Omega \cdot cm$ was used for all experimental procedures.

2.2. Preparation of Customized Meglumine-Type Resin

Using macroporous chloromethylated polystyrene microspheres (CMPS, chlorine content 3.5~4.5 mmol/g, particle size 100~200 mesh) as the skeleton, N-methylglucamine functional groups were grafted via a bimolecular nucleophilic substitution (SN_2) reaction.

10 g of pretreated CMPS microspheres, 25 g of NMG, 50 mL of deionized water, 50 mL of ethanol, and 6 g of anhydrous sodium carbonate were added to a three-necked flask. The mixture was stirred at 200 r/min in an 80 °C constant temperature water bath for 12 h. After the reaction, it was alternately washed with deionized water and absolute ethanol. Subsequently, it was soaked in a 5% HCl solution for 30 min to convert the amine groups into the hydrochloride form, washed with water until a neutral pH was achieved, and dried at 60 °C to obtain the customized alkali-resistant NMG resin.

2.3. Modulus Regulation and Phase Stability Testing of Sodium Silicate Solutions

The modulus (M) of the sodium silicate system is defined as the molar ratio of SiO₂ to Na₂O ($M = n(\text{SiO}_2)/n(\text{Na}_2\text{O})$), which is a standard parameter to characterize the relative alkalinity of the solution: a lower M value corresponds to a higher free OH[−] concentration and stronger alkalinity. Accurately weighed germanium-bearing high-silicon dust was mixed with calculated amounts of solid NaOH and deionized water according to the preset moduli (M = 1, 2, 3, 4). The detailed formulation parameters of each leaching system are listed in Table 1.

Table 1. Formulation parameters of leaching systems with different moduli.

Serial Number	NaOH/g	SiO ₂ /g	Germanium-Bearing Dust	Modulus	H ₂ O/g	Total Weight/g
1	13.33	10	10.42	1	76.25	100
2	6.67	10	10.42	2	82.91	100
3	4.44	10	10.42	3	85.14	100
4	3.33	10	10.42	4	86.25	100
5	6.67	5	5.21	1	38.12	50
6	3.33	5	5.21	2	41.46	50
7	2.22	5	5.21	3	42.57	50
8	1.67	5	5.21	4	43.12	50

The germanium concentration in the resulting supernatant was quantified via the phenylfluorone ultraviolet spectrophotometric method [31,32]. To assess the dynamic stability of the leaching system, the temporal evolution of solution absorbance (turbidity) was systematically monitored over 0–3 h within the wavelength range of 600–700 nm. In parallel, the hydrodynamic particle size distribution of each stabilized system was characterized using dynamic light scattering (DLS).

2.4. Resin Adsorption Experiments and Model Fitting

Firstly, 50 mL of supernatant under M = 1, 2, 3, and 4 conditions were taken respectively. Then, 5 g of pretreated self-made NMG resin was added. The mixture was magnetically stirred at room temperature, and samples were taken periodically to determine the germanium concentration.

Adsorption Kinetics Models: Pseudo-first order (PFO) and pseudo-second order (PSO) kinetic models were employed to fit the concentration decay data over time.

Pseudo-first-order kinetic equation:

$$q_t = q_e \left(1 - e^{-k_1 t}\right) \quad (1)$$

Pseudo-second-order kinetic equation:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (2)$$

where q_e and q_t are the adsorption capacities at equilibrium and at time t (mg g^{-1}), respectively; k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1}\text{min}^{-1}$) are the rate constants.

Adsorption Isotherm Models: Germanium-containing solutions with different initial concentrations were prepared, and an equal amount of resin was added for adsorption until equilibrium. Langmuir and Freundlich models were used for fitting.

Langmuir equation:

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

Freundlich equation:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where C_e is the equilibrium concentration (mg L^{-1}), q_m is the maximum theoretical adsorption capacity (mg g^{-1}), and K_L , K_F , and n are relevant constants.

3. Results and Discussion

3.1. Microstructural Characterization of Solid Waste Raw Materials and Self-Made Resin

The micro-morphology and elemental distribution of the germanium-containing high-silicon dust are shown in Figure 2. The dust particles exhibit a regular spherical shape with diameters ranging from 100 to 300 nm. EDS analysis reveals that the dust is primarily composed of O (63.2 wt%), Si (36.3 wt%) and trace amounts of Ge (0.5 wt%). The elemental mapping indicates that Ge elements are highly uniformly dispersed within the amorphous matrix, and no independent phases were observed. This strong physical encapsulation state determines that a strong alkaline medium is required to break the silicon–oxygen skeleton and release the encapsulated germanium.

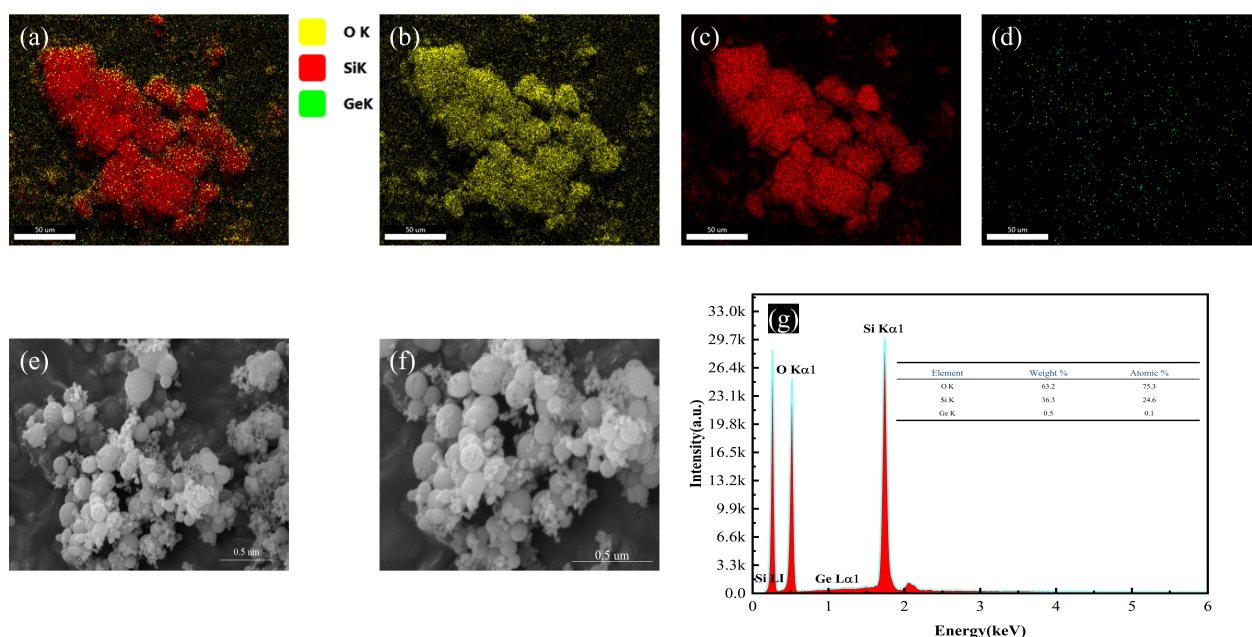


Figure 2. Germanium-containing dust EDS mapping (a–d,g) and SEM morphology (e,f).

The successful grafting of the self-made NMG resin was confirmed by Fourier transform infrared spectroscopy (FT-IR) (Figure 3). Compared with the original chloromethyl resin, the modified resin exhibited a broad and strong absorption peak attributed to -OH and -NH- near 3404 cm^{-1} , and a C-N bond stretching vibration peak appeared at 1070 cm^{-1} , indicating that the NMG molecules were successfully anchored onto the polystyrene skeleton. The high density of tertiary amines and ortho-diols not only provides binding sites for

germanate, but its robust cross-linked skeleton also endows the material with exceptional physical stability in extreme alkaline environments.

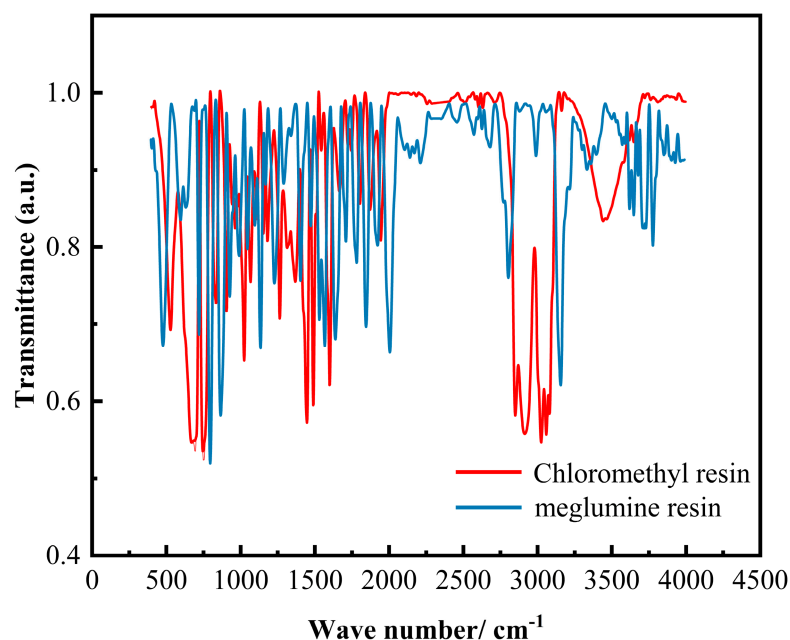


Figure 3. FT-IR comparison of chloromethyl resin and meglumine resin (X-axis: Wavenumber/ cm^{-1}).

3.2. Strong Alkali-Induced Deconstruction of Silicon–Oxygen Skeleton and Phase Stability of Polysilicic Acid

Figure 4 illustrates the effect of leaching systems with different moduli on the germanium release concentration. As the modulus of sodium silicate decreases, the leaching concentration of germanium exhibits a significant increase. When the modulus drops to $M = 1$, the germanium concentration in the leachate climbs from approximately 120 ppm to 331.25 ppm. The significant increase in germanium leaching concentration under low-modulus conditions can be reasonably explained by the alkaline etching mechanism of silicate materials. It is hypothesized that excess free OH^- ions attack the Si–O–Si and Si–O–Ge covalent bonds in the amorphous silica network via nucleophilic reaction, breaking the dense encapsulation structure and releasing the encapsulated germanate species. This mechanism is consistent with the leaching behavior observed in this work and the widely reported alkaline dissolution law of silica-based materials.

The colloidal stability of silicic acid directly determines the smooth operation of the subsequent adsorption process. In this work, dynamic light scattering (DLS) and multi-wavelength turbidity monitoring were combined to systematically evaluate the stability of leachates with different moduli.

Figure 5a–d presents the hydrodynamic particle size distributions of leachates with $M = 1$ to 4. For the $M = 1$ system, a single narrow distribution peak with a hydrodynamic diameter of approximately 1000 nm was observed, and the three parallel tests showed high consistency. This result indicates that silicic acid monomers are fully deprotonated under strong alkaline conditions, and the strong electrostatic repulsion between negatively charged silicate species effectively inhibits polymerization and aggregation, endowing the system with excellent colloidal stability. As the modulus increased to 2 and 3, a bimodal distribution appeared: in addition to the small particle peak at ~ 1000 nm, a large aggregate peak at ~ 10 – 12 μm emerged, and the discrepancy between parallel samples increased. This phenomenon demonstrates that the decrease in alkalinity weakens electrostatic repulsion, and silicic acid begins to polymerize into metastable large aggregates, leading to reduced system stability. For the $M = 4$ system, the large particle peak almost disappeared and only

the small particle peak remained. This is not a sign of restored stability; on the contrary, silicic acid polymerizes rapidly and forms large precipitates that settle quickly under low alkalinity. Only fine suspended particles remain in the supernatant tested by DLS, resulting in the observed single small-particle distribution.

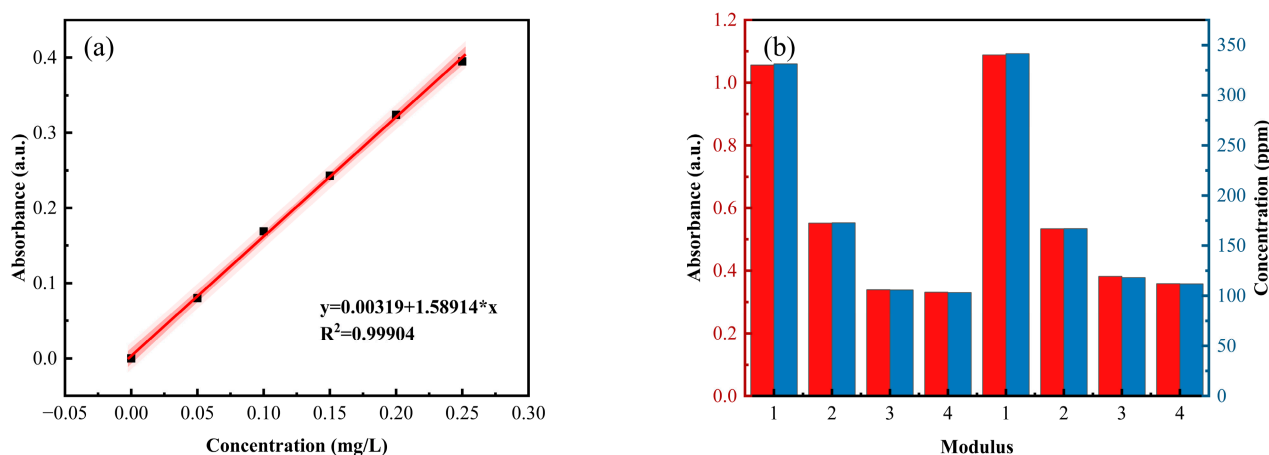


Figure 4. (a) Germanium standard curve and (b) Effect of modulus ($M = 1\sim 4$) in the leaching system on germanium release concentration (Note: Red bars represent absorbance, blue bars represent concentration).

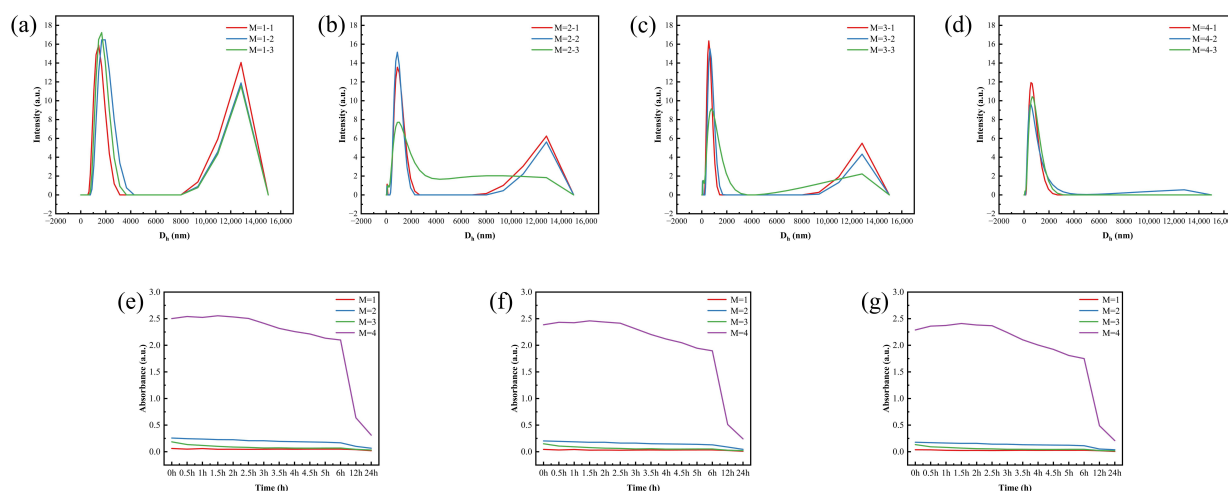


Figure 5. Hydrodynamic particle size distributions of leachates with different moduli: (a) $M = 1$, (b) $M = 2$, (c) $M = 3$, (d) $M = 4$ (each modulus was tested in triplicate). Time-dependent absorbance (turbidity) evolution of leaching systems monitored at different wavelengths: (e) 600 nm, (f) 660 nm, (g) 700 nm.

To further verify the macroscopic stability evolution, the absorbance (turbidity) of the systems was continuously monitored for 24 h at three wavelengths (600 nm, 660 nm and 700 nm), as shown in Figure 5e–g. The variation trends of absorbance at the three wavelengths were highly consistent, confirming that the turbidity change reflects the real colloidal stability evolution rather than wavelength-dependent optical interference. For $M = 1, 2$ and 3 systems, the absorbance remained at an extremely low level without obvious increase within 24 h, indicating that no large-scale aggregation or sedimentation occurred during the test period. In contrast, the $M = 4$ system showed a much higher initial absorbance, followed by a sharp drop after 5 h, and dropped to near the baseline at 24 h. This corresponds to the rapid gelation and sedimentation of silicic acid aggregates, which is in good agreement with the DLS results [22,23].

The above results collectively demonstrate that the low-modulus ($M = 1$) strong alkaline system can maintain excellent anti-gelation stability while efficiently releasing germanium, which provides a feasible premise for the subsequent direct adsorption process without pH adjustment.

3.3. Direct Resin Adsorption Kinetics and Thermodynamic Mechanism

Note: Most reported adsorbents were tested in simulated pure germanium solutions with optimized pH and high initial concentrations. The adsorption capacity in this work was obtained directly from the raw strong-alkaline high-silicon leachate without pH adjustment, with an initial Ge concentration of only 331.25 mg/L. The self-made NMG resin was directly introduced into the $M = 1$ raw leachate for adsorption. Table 2 summarizes the germanium content of module 1 solution at different adsorption time.

Table 2. Germanium content of module 1 solution at different adsorption time.

Adsorption Time	Absorbance	Germanium Content/ppm
$t = 0$	1.056	331.25
$t = 10$	0.444	138.69
$t = 20$	0.160	49.34
$t = 30$	0.138	42.42
$t = 40$	0.114	34.86
$t = 50$	0.098	29.83
$t = 60$	0.039	11.27

Figure 6 presents the adsorption kinetics and isotherm fitting results with error bars from three parallel experiments, and the specific fitting parameters are listed in Table 3. Experiments show that the resin reduces the germanium concentration from 331.25 mg L⁻¹ to approximately 11 mg L⁻¹ within 60 min. The recovery rate of germanium is over 96%. The kinetic fitting parameters are summarized in Table 3. Both the pseudo-first-order (PFO) and pseudo-second-order (PSO) models provide acceptable fits to the experimental data. The PFO model yields a slightly higher correlation coefficient ($R^2 = 0.9458$) and a smaller root mean square error (RMSE = 0.182 mg g⁻¹), and its calculated equilibrium adsorption capacity ($q_{e,cal} = 3.147$ mg g⁻¹) is closer to the experimental value. This result indicates that the adsorption process is jointly affected by both external mass transfer and chemical binding interaction [33,34].

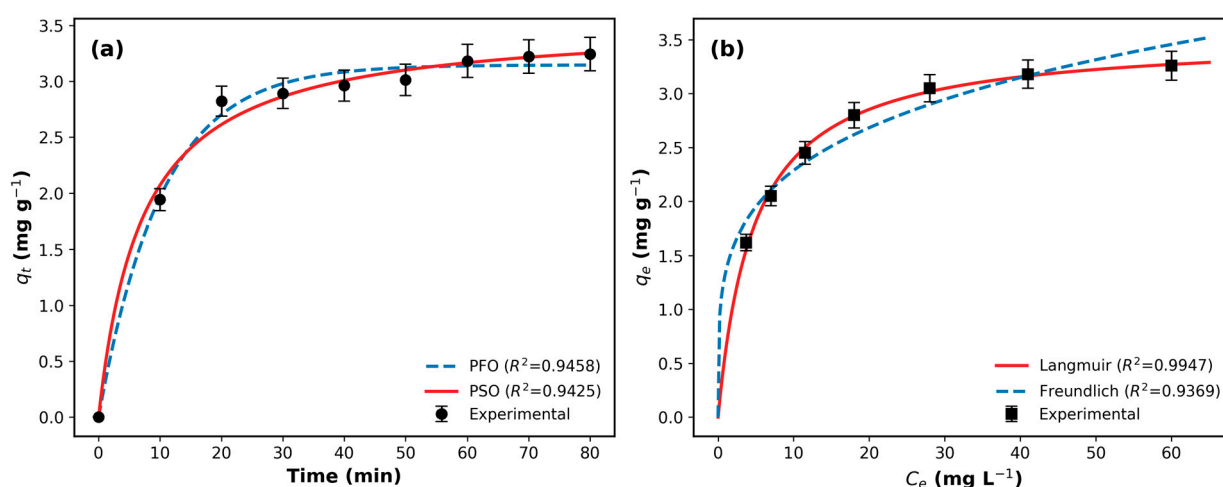


Figure 6. Adsorption kinetics (a) and adsorption isotherms (b) of the resin in the $M = 1$ raw solution (Data points are the averages of three parallel experiments with error bars).

Table 3. Adsorption kinetics and isotherm model fitting parameters.

Kinetics Model	Parameter	Value	Isotherm Model	Parameter	Value
PFO	q_e (mg g ⁻¹)	3.147	Langmuir	q_m (mg g ⁻¹)	3.529
	k_1 (min ⁻¹)	0.0978		K_L (L mg ⁻¹)	0.211
	R^2	0.9458		R^2	0.9947
	RMSE (mg g ⁻¹)	0.182		RMSE (mg g ⁻¹)	0.076
PSO	q_e (mg g ⁻¹)	3.541	Freundlich	K_F	1.345
	k_2 (g mg ⁻¹ min ⁻¹)	0.0398		n	4.338
	R^2	0.9425		R^2	0.9369
	RMSE (mg g ⁻¹)	0.215		RMSE (mg g ⁻¹)	0.324

The adsorption isotherm fitting results show that the Langmuir model ($R^2 = 0.9947$, $RMSE = 0.076$ mg g⁻¹) exhibits a much better fitting effect than the Freundlich model within the investigated concentration range. This result is consistent with the assumptions of homogeneous adsorption sites and monolayer coverage, but it cannot independently confirm the chemical nature of the adsorption interaction, as the Langmuir model essentially provides a mathematical description of equilibrium behavior. The model calculates a maximum theoretical adsorption capacity q_m of 3.529 mg g⁻¹. The maximum adsorption capacity of 3.529 mg g⁻¹ obtained in this work is limited by the low initial germanium concentration of the raw leachate (331.25 mg/L) and the harsh strong-alkaline high-silicon environment. The core advantage of this material and process lies in its excellent specific selectivity for germanium under extreme conditions, which enables direct adsorption without pH adjustment, rather than ultra-high adsorption capacity.

3.4. Specific Coordination Behavior and Comparative Analysis with Literature

To quantitatively evaluate the adsorption selectivity, the concentrations of Ge in the solution before and after adsorption were determined. The initial M = 1 leachate contains 331.25 mg/L Ge, while the equilibrium solution contains 11.27 mg/L Ge. The calculated distribution coefficient of Ge reaches 14.2 L/g. The EDS characterization of the adsorbed resin (Figure 7) further provides intuitive surface elemental evidence: Ge is significantly enriched on the resin surface, while the Si signal is weak. It should be noted that EDS is a local semi-quantitative technique, and the above weight percentage only reflects the local surface composition, which serves as auxiliary evidence for selective enrichment. The quantitative separation coefficient based on solution composition will be further tested and supplemented in subsequent work to fully evaluate the selectivity.

The FT-IR spectra of the NMG-functionalized resin before and after germanium adsorption are compared in Figure 7f, and the spectral changes provide molecular-level evidence for the adsorption behavior. The characteristic peaks of the resin skeleton, including the aliphatic C-H stretching vibration at ~2920 cm⁻¹ and the benzene ring skeleton vibration at ~1600 cm⁻¹ and ~1500 cm⁻¹, show no significant changes in peak position or intensity after adsorption. This result confirms that the polystyrene backbone and alkyl structure of the resin remain intact in the strong-alkaline adsorption environment, exhibiting excellent structural stability. The weak peak at ~1655 cm⁻¹ is attributed to the bending vibration of adsorbed water, which shows no obvious difference before and after adsorption and does not participate in the adsorption reaction. For the functional groups related to adsorption, two key changes are observed. First, the broad absorption band in the range of 3200–3600 cm⁻¹ (centered at ~3404 cm⁻¹), which corresponds to the stretching vibration of ortho-cis-diol O-H groups and N-H groups, shows significantly reduced inten-

sity and a narrower peak shape after adsorption. This phenomenon is consistent with the deprotonation of partial vicinal diol groups under alkaline conditions and the subsequent coordination with Ge(IV), which reduces the number of free hydroxyl groups and weakens intermolecular hydrogen bonding. Second, the absorption band in the 1000–1200 cm^{-1} region (centered at $\sim 1070 \text{ cm}^{-1}$), dominated by C-O stretching vibration of vicinal diols and superimposed with C-N stretching vibration, exhibits an obvious peak shift and shape change after adsorption. This indicates that the chemical environment of the C-O bond is altered due to the formation of O-Ge coordination bonds. In addition, a new characteristic peak appears at $\sim 574 \text{ cm}^{-1}$ after adsorption, which is assigned to the stretching vibration of the Ge-O bond. This peak directly proves that germanium is loaded on the resin surface via chemical bonding rather than physical adsorption.

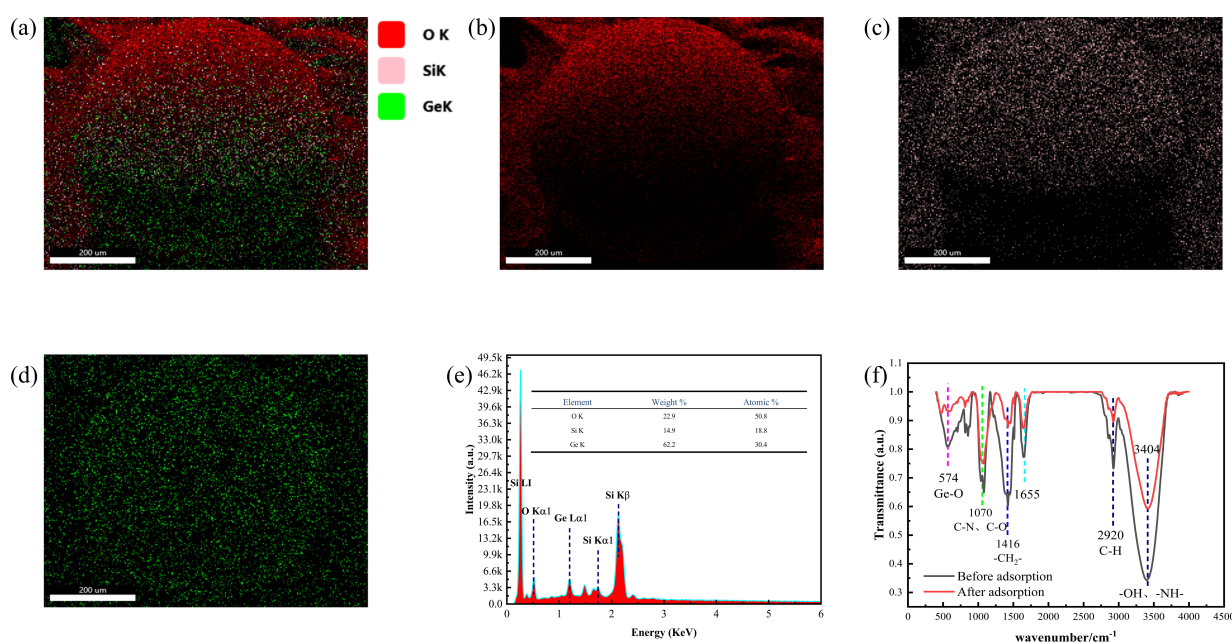


Figure 7. EDS spectrum of the resin after adsorption (a–e) and FT-IR comparison before and after adsorption (f).

Overall, the above spectral changes are consistent with the hypothesized chelation mechanism: the ortho-cis-diol groups on the resin surface coordinate with germanate to form five-membered chelate rings, which is the molecular basis for the selective adsorption of germanium in strong-alkaline high-silicon systems.

Based on the above characterizations, this paper proposes the molecular mechanism of NMG resin adsorbing Germanium (Figure 8). In a strong alkaline environment, the ortho-cis-diols on the resin overcome the competition from abundant free OH^- and monomeric silicate radicals, undergoing dehydration condensation with germanate to form an extremely stable five-membered $-\text{C}-\text{O}-\text{Ge}-\text{O}-\text{C}-$ chelating ring. Simultaneously, the adjacent tertiary amine nitrogen atom and the hydrogen atom on the hydroxyl group provide a synergistic stabilization effect through hydrogen bonding, further enhancing the binding stability [35].

To highlight the advantages of this process, Table 4 lists the performance comparison between this study and germanium adsorption materials reported in the recent literature. Although some novel materials (such as MOFs or polymer resins) exhibit high theoretical adsorption capacities in pure water or weakly acidic systems, their applications are all limited by stringent pH requirements (usually needing adjustment to pH 3–6) and the necessity of adding complexing agents such as tartaric acid [36]. The NMG resin in

this study can not only operate directly in the $M = 1$ strong-alkali raw solution but also completely eliminates the acid-adjustment and back-titration procedures, significantly shortening the process flow.

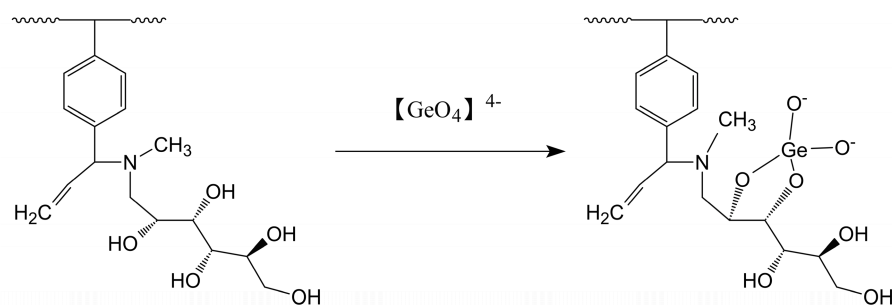


Figure 8. Molecular evolution mechanism diagram of the five-membered chelating ring formed by the ortho-diols of NMG resin and germanate.

Table 4. Performance comparison of the process in this paper with other germanium adsorption materials in the literature.

Adsorbent Material	System Environment	Optimal pH	pH Adjustment/Complexing Agent Required	Max Adsorption Capacity (mg/g)	Reference
IRA-743 commercial resin	Sulfate solution	3.0	Required	N/A	[37]
D201 $\times$ 7 anion resin	Sulfuric acid solution	Weakly acidic	Required + Tartaric acid	214.0	[38]
Ma-Zr-MOF	Pure water simulated solution	6.0	Required	82.06	[39]
Catechol-functionalized material (A-Cat-N)	Dilute acid solution	3.0	Required	39.14	[40]
Catechol-chitosan (C-Cat)	Dilute acid solution	3.0	Required	22.72	[41]
NMG-Resin (This work)	High-silicon strong-alkali raw solution	Extreme strong alkali ($M = 1$)	No pH adjustment/No complexing agent	3.53 (At low concentration)	This study

4. Conclusions

Targeting the recovery challenges of germanium-bearing high-silicon dust from optical fiber preform manufacturing, this study proposed and validated a novel short-flow process consisting of low-modulus alkaline leaching coupled with direct adsorption using a customized meglumine-functionalized resin. The main conclusions are as follows:

The low-modulus condition of $M = 1$ serves as the optimal window for the efficient dissociation and release of germanium, with the leaching concentration reaching 331.25 mg/L. Combined analysis of hydrodynamic particle size distribution and multi-wavelength turbidity evolution demonstrates that this strongly alkaline environment effectively inhibits the polymerization of polysilicic acid and maintains excellent colloidal stability of the system. This stability is attributed to enhanced electrostatic repulsion between fully deprotonated silicate species under high OH^- concentration, which is inferred from the suppressed particle aggregation and long-term suspension stability.

Kinetic and thermodynamic fitting results indicate that the adsorption of germanium by the self-synthesized NMG resin follows pseudo-second-order kinetics and the Langmuir isotherm model ($R^2 = 0.9947$), confirming that the adsorption process is dominated by monolayer chemical adsorption. The maximum theoretical adsorption capacity is calculated to be 3.529 mg/g, and the overall germanium recovery yield of the full leaching-adsorption process reaches above 96%.

This work achieves short-flow direct adsorption using the raw $M = 1$ strong-alkaline leachate without intermediate pH adjustment. Based on FT-IR spectral changes and EDS elemental characterization, it is hypothesized that the ortho-cis-diol groups on the resin surface can selectively coordinate with germanate to form a five-membered C-O-Ge-O-C chelate ring, which accounts for the specific binding behavior even in strong-alkaline and high-silicon environments. Compared with conventional processes, this method effectively avoids the cumbersome pH adjustment steps and silica gel precipitation risks in traditional routes, significantly shortens the process flow, and presents promising engineering application potential.

It should be noted that this work focuses on the feasibility verification of the short-flow leaching-adsorption separation process. The subsequent elution of loaded germanium, resin regeneration and multi-cycle performance will be systematically investigated in follow-up work. For NMG-functionalized resins, acidic elution with dilute hydrochloric acid is a mature and feasible route for germanium stripping and resin regeneration, which has been widely verified in previous studies on germanium adsorption. Subsequent work will further investigate the elution performance, resin regeneration and multi-cycle stability to complete the full germanium recovery process.

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