Functionalized chitosan for solid-phase extraction of Germanium

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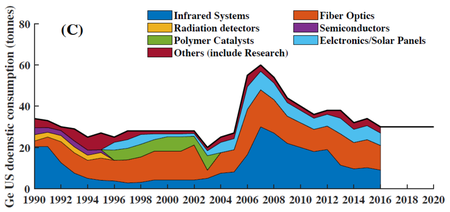
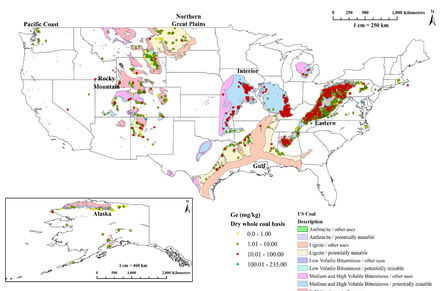
ABSTRACT

Germanium is one of the critical elements because of its growing demand, supply risk, and inefficient production. Solid-phase extraction using selective adsorbent can result in efficient and economical production process. In the current study, a functionalized chitosan adsorbent was developed and tested for selective solid-phase extraction of germanium. The adsorbent was characterized by FTIR for presence of functional groups. The adsorbent showed Langmuir maximum Ge adsorption capacity of 25.9 mg/g at optimum pH of 3. The Ge adsorption is monolayer, expected in case of surface complexation mechanism of adsorption. The adsorption kinetics is pseudo 1st order due to limited number of surface site compared to the initial Ge concentration. The adsorbent performed better than commercial adsorbent in terms of Ge adsorption in presence of other ions.

INTRODUCTION

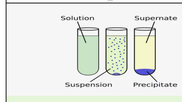
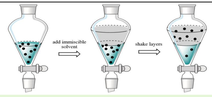
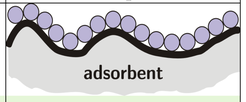




- Germanium is used in infrared systems, fiber optics, polymer catalysis, semiconductors, electronics, and solar panels.
- It is one of critical elements due to high tech applications, lack of substitute, and supply risk.
- It lacks mineral resources and is recovered from zinc refinery residue and coal fly ash.
- Due to inefficient production processes, the zinc refinery residue produced in the US is exported for Ge recovery and at the same time the US reserve of coal contains 1.6 Mt Ge but is non-viable due to low concentration (Patel & Karamalidis, 2021).

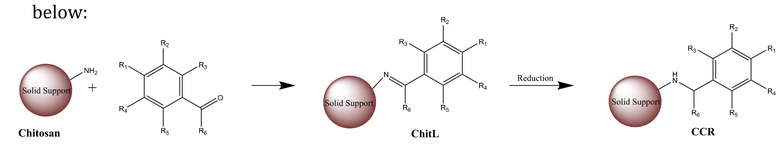
➢ **Solid-phase extraction using selective adsorbent can solve the issue of inefficient production. An efficient and economical production process can result in domestic production from Zn refinery residue and coal fly ash.**

Zn refinery residue or coal fly ash → Leach Ge to solution → Separation and recovery → Conversion to desired form

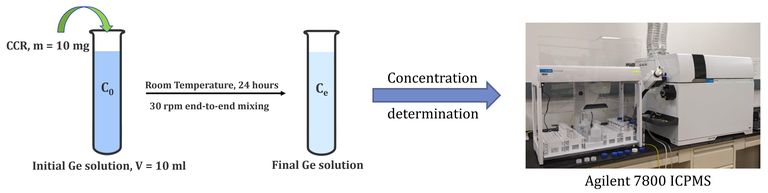
Precipitation	Solvent extraction	Adsorption
		
Energy intensive	Energy intensive	Energy efficient
Chemical intensive	Chemical intensive	Low chemical requirement
High waste generation	High waste generation	Low waste generation
High Ge conc. required	High Ge conc. required	Can work with low conc.
Industrial use exist	Industrial use exist	Lab scale so far due to lack of good materials

EXPERIMENTAL METHODS

- Chitosan is used as solid support for functionalization with ligand (not disclosed) as below:



- The adsorbent was characterized by FT-IR spectroscopy.
- Batch adsorption experiments: optimum pH, adsorption isotherm, adsorption kinetics, and distribution coefficient in presence of other ions.
- Batch adsorption experiments: adsorbent dose of 10mg/10ml, room temperature, 24 hours, mixed end-to-end at 30 rpm, pH 3 for isotherm, kinetic, and multi-element adsorption.
- The dissolved ion concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS).



Adsorption (mg/g)

$$q_e\left(\frac{mg}{g}\right) = \frac{C_0 - C_e}{m} * V$$

Adsorption (%)

$$Ads\ (\%) = \frac{C_0 - C_e}{C_0} * 100$$

Distribution Coeff. (K_d)

$$K_d\left(\frac{ml}{g}\right) = \frac{C_0 - C_e}{C_e} * V/m$$

Langmuir isotherm

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

Freundlich isotherm

$$q_e = K_F {C_e}^{1/n}$$

Pseudo 1st order kinetics

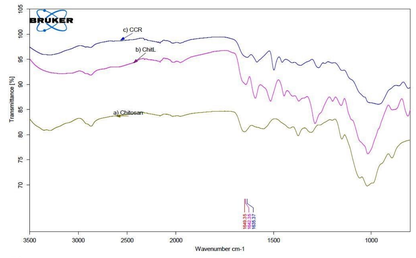
$$q_t = q_e(1 - \exp(-k_1 t))$$

Pseudo 2nd order kinetics

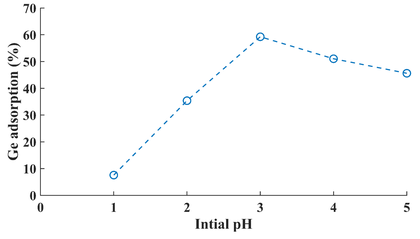
$$q_t = \frac{{q_e}^2 k_2 t}{(1 + q_e k_2 t)}$$

- C_0 = initial conc. (mg/l)
- C_e = equilibrium conc. (mg/l)
- V = solution volume (in l)
- m = adsorbent mass (in g)
- q_m= maximum adsorption (mg/g)

RESULTS

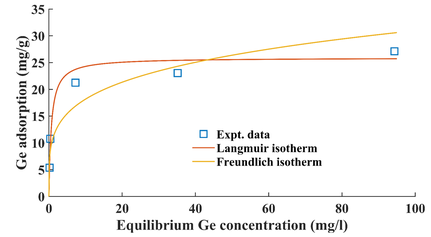


- C=N vibration peak appeared at 1642 cm^{-1} in chitL (Peng et. al., 1998).
- C=N peak signifies chitosan functionalization.
- The C=N peak at 1642 cm^{-1} reduces in CCR due to reduction.

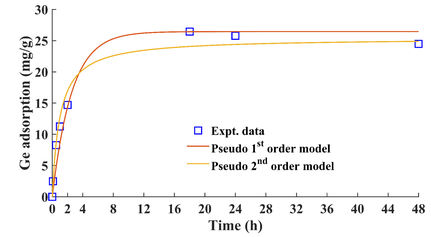


- The optimum pH for adsorption is pH 3.
- At lower pH, the ligand does not complex with germanium (Patel & Karamalidis, 2021).

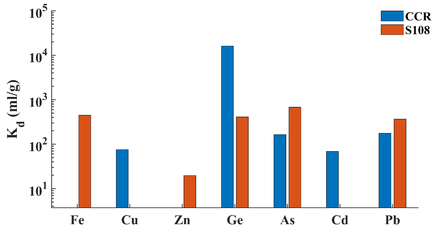
RESULTS



- The Langmuir maximum adsorption capacity is 25.9 mg/g.
- Langmuir isotherm better explains the expt. data than Freundlich isotherm.
- It suggests that the adsorption is monolayer, expected in surface complexation mechanism (Ayawei et. al. 2017).



- The maximum adsorption was reached at 18 hour.
- Pseudo 1st order explains the data better than pseudo 2nd order.
- It implies that the C_0 > adsorption sites (Wang & Guo, 2020)



- The adsorbent is highly selective for Ge (K_d ~ 16000 ml/g) against other elements (K_d <200 ml/g).
- The adsorbent CCR is more selective than commercial Ge adsorbent Purolite S108 (Ge K_d ~ 410 ml/g)

CONCLUSIONS

- The ligand functionalized chitosan was able to adsorb Ge with maximum capacity of 25.9 mg/g at pH 3.
- The Ge adsorption is monolayer, expected in case of surface complexation mechanism of adsorption.
- The adsorption sites are limited and thus, pseudo 1st order kinetics is followed during adsorption.
- The adsorbent is highly selective for Ge. It performed better than commercially available Ge adsorbent in terms of distribution coefficient (K_d).
- The adsorbent can be used for solid-phase extraction of germanium.

REFERENCES

- Ayawei, N., Ebelegi, A. N., & Wankasi, D. (2017). Modelling and Interpretation of Adsorption Isotherms. *Journal of Chemistry*, *2017*. doi.org/10.1155/2017/3039817
- Patel, M., & Karamalidis, A. K. (2021). Germanium: A review of its US demand, uses, resources, chemistry, and separation technologies. *Separation and Purification Technology*, 118981. doi.org/10.1016/j.seppur.2021.118981
- Peng, C., Wang, Y., Tan, S., & Cheng, G. (1998). Preparation of Chitosan Derivatives. Synthesis of N-Schiff Base Type and N-Secondary Amino Type Chitosan-Crown Ethers. *Polymer Journal*, *30*(10), 843–845.
- Wang, J., & Guo, X. (2020). Adsorption kinetic models: Physical meanings, applications, and solving methods. *Journal of Hazardous Materials*, *390*, 122156. doi.org/10.1016/J.JHAZMAT.2020.122156

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