

Selective Sorption of Ge(IV) Oxoanion by Composite Sorbent Based on Hydrous Oxide of Zirconium

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ABSTRACT

In this work, a composite sorbent based on hydrous zirconium oxide was used for selective removal of Ge(IV) oxoanions. Experiments were carried out by batch equilibrium tests and dynamic column sorption. The best sorption capacity was reached at the pH of 9, when about 4.3 g of Ge by liter of composite. The negative effect of the concentration of chlorides and sulfates was observed when their concentration was higher than 500 mg/L. The optimal specific solution flow rate for sorption by ZrO₂-PAN sorbent was determined to be 6 BV/h. For regeneration, 15 BV of 0.5 M HCl solution saturated with NaCl was used.

Keywords: germanium; sorption; zirconium oxide; composite sorbent; PAN

INTRODUCTION

Germanium has many applications in semiconductors, as a dopant in the fiber optics for communication networks, infrared vision systems, and silicon solar panels and as a polymerization catalysts in PET plastics production¹⁻⁴. Certain Ge compounds are often used in drugs and nutriment⁵. These applications can be the source of Ge contamination in surface and waste waters.

Germanium is a trace element in the Earth's crust, averaging about 1 mg/kg in whole rocks and minerals^{6,7}. It is naturally occurring in argyrodite [Ag₈GeS₆], zinc ores and coal (coal ash contains as much as 20 – 280 mg/kg)^{8,9}, coal combustion or gasification ash may be a potential source of valuable elements (recovery entails acidic and alkaline extraction procedures)¹⁰. The majority of germanium is produced as a by-product of zinc refining. This element exists in seawater as hydroxyacid, i.e., Ge(OH)₄¹¹, which dissociate in alkaline media Ge(OH)₄/GeO(OH)₃⁻/GeO₂(OH)₂²⁻ - pK₁ ~ 8.98; pK₂ ~ 11.8^{12,13}.

The general toxicity of germanium compounds is low, except for the germanium tetrahydride (germane). Few observations on the toxicity of germanium in man exist. Germanium is not carcinogenic and even appears to inhibit cancer development. It is used in the form of the organometallic compound (spiro germanium) to destroy cancer cells. Ge is almost completely absorbed after oral exposure and excreted from the human body within 3 days^{14,15}.

Commonly, the recovery of germanium is done by means of hydrometallurgy, where the process is combined with another process such as solvent extraction^{16,17}, flotation¹⁸ and adsorption^{19,20}. Recovery of germanium from aqueous solution with adsorption processes can be achieved by polymeric sorbents containing N-methylglucamine functional group²¹⁻²⁶, or sorbents based on chitosan or cellulose. Breakthrough capacities of glucamine sorbents were found to be about 0.32 mmol/mL for Diaion CRB 02²⁴ and 0.15 mmol/mL for Purolite D-4123²⁵, while adsorption capacities of the 2,3-dihydroxypropyl chitosan resin²⁷ were up to 1.4

mmol/g; of branched-saccharide chitosan resin²⁸ were about 2 mmol/g, cellulose²⁹ adsorption capacities (pH 9) were up to 1.8 mmol/g. The adsorption mechanism was ascribed to a complex formation between Ge(IV) and hydroxyl groups. Different biosorbents^{20,30}, activated carbon³¹, inorganic sorbents, such as hydrous oxides of Al, Fe, Zr, and Ti³² or Ce can also be used; the breakthrough capacity of composite sorbent CeO₂/XAD-7 was about 15 mmol/L³³.

In this work, the composite sorbent based on zirconium hydrous oxide was used for selective removal of Ge oxoanion.

EXPERIMENTAL

Sorbent

Sorbent ZrO₂-PAN is a composite of zirconium oxide and polyacrylonitrile matrix (prepared at Department of Nuclear Chemistry, CTU Prague, Czech Republic). Composite sorbents were prepared according to the following modification of the general procedure³⁴⁻³⁶. Fibrous polyacrylonitrile (PAN) was dissolved in dimethylsulfoxide, powdered ZrO₂ was gradually added to PAN solution, and suspension was carefully mixed. The homogeneous suspension was then dispersed into a water bath. Coagulated beads were washed with distilled water and sieved. Swollen fraction with grain size 0.4 – 1.0 mm was separated and used without drying. According to the procedure used, the granulated beads contain about 57 wt. % of zirconium oxide.

The sorbent has amphoteric character. Prior the sorption of Ge oxoanion, the sorbent was conditioned with five bed volumes (BV) of 0.1 M sodium hydroxide solution.

Experimental conditions

Dynamic column sorption (Figure 1): The loading solution passed through the column (inner diameter 10 mm) containing 10 mL of sorbent with the flow rate of 3 to 24 BV/h.

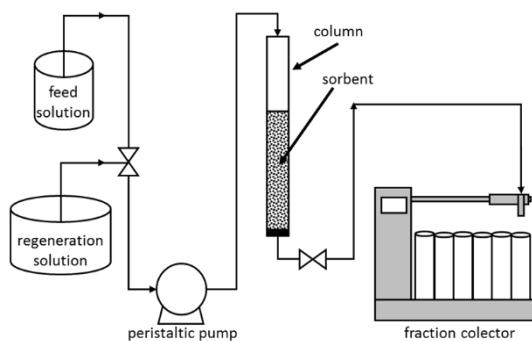
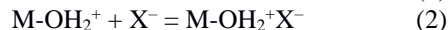


Figure 1 Experimental setup – dynamic column sorption

Fractions of filtrate were collected and metal concentrations were analyzed with ICP-OES technique (PerkinElmer Instruments – Optima 2000 DV), LOQ = 5 µg/L.

For the experiments, the weight concentration (shown here after as ρ) of Ge(IV) in the feed solution was 1 – 3 mg/L and the concentration of chlorides and sulfates was 100 – 1000 mg/L. The experimental pH values were 6, 9, and 11. The effects of pH, flow rate, concentration of accompanying anions in the feed solution, and desorption procedure of Ge(IV) were studied.

It is supposed that the mechanism of sorption is similar to the mechanism of sorption of arsenic oxoanions in a similar composite sorbent ZrO₂/XAD-7³⁷:



Where M is Zr, X⁻ is an exchangeable anion (e.g. Cl⁻), and Y⁻ is the target oxoanion.

For the sorption run, the limiting breakthrough concentration of metal was decided to be 0.1 mg/L. The breakthrough capacities of the sorbent q were therefore calculated according to the following equation (4):

$$q = \frac{V \cdot (\rho_0 - \rho_e)}{V_0} \quad [\text{mg/L}] \quad (4)$$

Vvolume at the breakthrough point [mL]

V_0volume of the sorbent [mL]

ρ_0metal concentration in the feed solution [mg/L]

ρ_emetal concentration in the eluent [mg/L]

Regeneration: As a regeneration solution, varying volumes of HCl (concentration 0.5; 1.0 and 2.0 M), 1.0 M NaOH, and a solution of 0.5 M HCl saturated with NaCl were used.

Equilibrium batch sorption: For the batch experiments, the concentration of Ge(IV) in the feed solution was selected to be 15 mg/L, the concentration of chlorides, nitrates, and sulfates was in the range 0 – 1000 mg/L and the pH was 9. One liter of the solution was contacted with 0.5 mL of conditioned sorbent and mixed with an overhead stirrer (IKA RW 11 Basic). At time 0.5; 1; 2; 4; 6; 24; 48 and 72 hours, samples for analysis were taken. The effect of accompanying anions (Cl⁻; SO₄²⁻) in the initial solution on the sorption kinetic were studied.

RESULTS AND DISCUSSION

Influence of pH

The influence of pH on the Ge(IV) oxoanion sorption, when $\rho(\text{Ge}) = 3 \text{ mg/L}$, $\rho(\text{Cl}^-; \text{SO}_4^{2-}) = 100 \text{ mg/L}$ and specific flow rate $s = 6 \text{ BV/h}$, was studied at pHs = 6, 9 and 11. The sorption capacity of Ge(IV) anion was highest at the pH of 9 (Table 1), when the sorption capacity of 4.3 g/L (13.8 mg/g) was obtained. At pH 6, it decreased by 18 % and at pH 11 by 28 %. Therefore, the pH of the feed solution was kept at 9 in all the consequent sorption runs.

Table I Breakthrough capacities - influence of pH

pH	breakthrough capacity q [mg/L]	breakthrough capacity q [mg/g]
6	3570	11.4
9	4330	13.8
11	3410	10.9

Influence of concentration of Ge(IV)

When the weight concentration of germanium(IV) in the feed solution was increased from 1 mg/L to 2 and 3 mg/L at pH = 9 in dynamic column experiments, the sorption cycles were shorter, but sorption capacities (Table 2 and Figure 2) increased by about 60 % and 80 %, respectively.

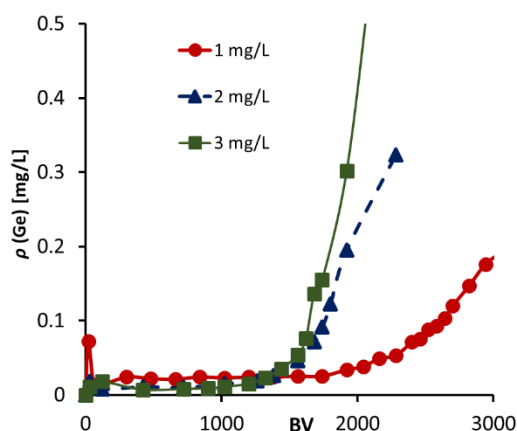


Figure 2 Sorption of Ge(IV) on ZrO₂-PAN - Effect of concentration Ge(IV) in the feed solution $\rho(\text{Ge}) = 1 - 3 \text{ mg/L}$, $\rho(\text{Cl}^-; \text{SO}_4^{2-}) = 100 \text{ mg/L}$, $s = 6 \text{ BV/h}$, pH = 9

The positive effect of higher concentration of Ge(IV) was observed, showing that the maximum sorption capacity was not reached. For the consequent sorption runs in this

work, Ge(IV) concentration of 3 mg/L was used in the feed solution.

Table II Breakthrough capacities - influence of concentration Ge(IV) in the feed solution

$\rho(\text{Ge})$ [mg/L]	breakthrough capacity q [mg/L]
1	1530
2	2430
3	4330

Influence of concentration of accompanying anions

When the concentration of sulfates and chlorides in the feed solution was increased from 100 mg/L to 1000 mg/L at pH 9, the breakthrough sorption capacity of dynamic column experiments (Table 3) decreased from 4.3 g/L to 2.3 g/L. The negative effect of chlorides and sulfates was observed when the concentration was higher than 500 mg/L (sorption capacity decreased by 15 %). The selectivity of ZrO₂-PAN was very high, between 100 and 500 mg/L of accompanying anions (sorption capacities were similar to the 4.3 g/L observed in the absence of competing anions).

Table III Breakthrough capacities - influence of concentration of accompanying anions

$\rho(\text{Cl}^-; \text{SO}_4^{2-})$ [mg/L]	breakthrough capacity q [mg/L]
100;100	4330
500;500	4280
750;750	3640
1000;1000	2330

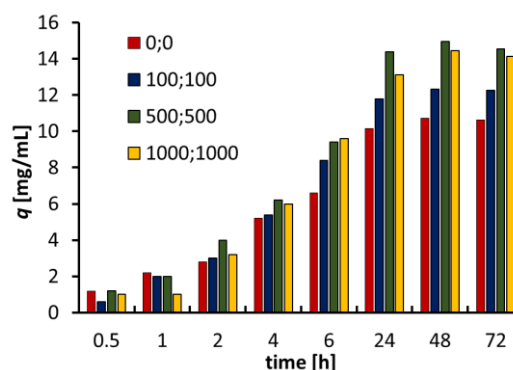


Figure 3 Kinetics of Ge(IV) sorption on ZrO₂-PAN - effect of concentration of accompanying anions; $\rho(\text{Ge}) = 15 \text{ mg/L}$, $\rho(\text{Cl}^-; \text{SO}_4^{2-}) = 0 - 1000 \text{ mg/L}$, pH = 9

The results obtained in batch experiments (Figure 3) for short contact time were similar, during in the first 30 minutes 4.5 % of

Ge(IV) was removed from the solution without chlorides and sulfates and about 2 % was removed in the presence of accompanying anions. Up to 6 hours this trend was change. Within 72 hours about 45 % of Ge(IV) (14 mg of Ge with 1 mL of sorbent) and 39 % (11 mg/mL) was removed from the feed solution containing 15 mg/L Ge and 500 – 1000 mg/L and 0 – 100 mg/L chlorides and sulfates, respectively, at pH 9.

Influence of flow rate

The effect of flow rate was studied at specific flow rates ranging from 3 BV/h to 24 BV/h ($\rho(\text{Ge}) = 3 \text{ mg/L}$, $\rho(\text{Cl}^-; \text{SO}_4^{2-}) = 100 \text{ mg/L}$ and at pH 9). The difference between sorption capacities, specific flow rate at 3 and 6 BV/h was minimal, and the decrease of sorption capacities from 6 to 24 BV/h was gradual – about 15 % in every step (Table 4 and Figure 4). The optimal flow rate for sorption of Ge(VI) by sorbent $\text{ZrO}_2\text{-PAN}$ was 6 BV/h because experiments at the flow rate of 3 BV/h are time consuming.

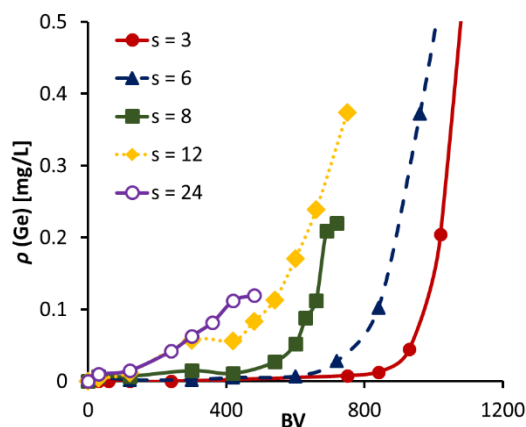


Figure 4 Sorption of Ge(IV) on $\text{ZrO}_2\text{-PAN}$ - Effect of specific flow rate
 $\rho(\text{Ge}) = 3 \text{ mg/L}$, $\rho(\text{Cl}^-; \text{SO}_4^{2-}) = 100 \text{ mg/L}$,
 $\text{pH} = 9$, $s = 3 - 24 \text{ BV/h}$.

Table IV Breakthrough capacities - influence of flow rate

s [BV/h]	breakthrough capacity q [mg/L]
3	2825
6	2700
8	1930
12	1440
24	1230

Regeneration

Recovery of Ge(IV) from $\text{ZrO}_2\text{-PAN}$ with different regeneration solutions was studied.

As the first regeneration solution, 10 BV of 1 M HCl ($s = 3 \text{ BV/h}$) was used. Recovery of Ge(IV) was only 48 % and the concentration of Ge at the beginning of the next sorption cycle was about $50 \mu\text{g/L}$. For the second regeneration, 10 BV of 1 M NaOH was used. The recovery of Ge was only 40 % and, therefore, the second step using 10 BV of 1 M HCl had to be used, but the concentration of Ge was still higher than $25 \mu\text{g/L}$ at the start of the next sorption cycle.

In the third regeneration attempt, the volume of 1 M HCl was increased to 15 BV and the recovery of Ge increased to 88 %. It was sufficient, but a problem with chemical stability of the sorbent was found at longer contact times with 1 M HCl.

For good recovery of Ge and better chemical stability of the sorbent, a new regeneration solution, 15 BV of 0.5 M HCl saturated with NaCl (solution of 0.5 M HCl in equilibrium with NaCl) was evaluated. The reproducibility of this method of regeneration is shown in Figure 5. For every part (A, B, C), 10 ml of sorbet was used and sorption conditions were $\rho(\text{Ge}) = 3 \text{ mg/L}$; $\rho(\text{Cl}^-; \text{SO}_4^{2-}) = 100 \text{ mg/L}$; $\text{pH} = 9$; $s = 6 \text{ BV/h}$. Regeneration was the same for all the cases (15 BV, 0.5 M HCl saturated with NaCl).

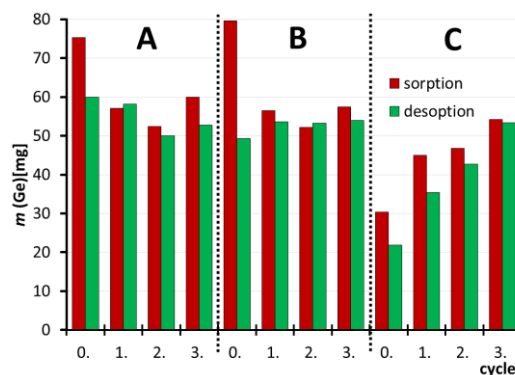


Figure 5 Repeatability of sorption and desorption of Ge(IV) on $\text{ZrO}_2\text{-PAN}$ –
 (A; B – same sorption condition; C – other sorption condition); regeneration solution 0.5 M HCl saturated with NaCl (15 BV, $s = 3 \text{ BV/h}$)

Set A and B represent the conditions of sorption, the sorption cycles were terminated after exceeding the limit concentration. The 0th cycles were longer (about 2600 BV = 430 hours of sorption) than other cycles and recovery was only 70 %. In set C, shortening of the 0th cycle time (1000 BV = 167 hours) was tried to solve the problem with desorption after the 0th cycle (Figure 5 – part C), but the problem with desorption was

similar. The 1st and the 2nd cycles were terminated after 1500 BV (250 hours) and the 3rd sorption cycle was terminated after exceeding the limit concentration and was similar as in set A and B. In all the cases (A, B, and C) the 4th cycles had similar sorption and desorption parameters, and termination of the sorption phase of the 0th cycle before exceeding the limit concentration did not improve the regeneration efficiency.

CONCLUSIONS

The composite sorbent based on zirconium oxide (ZrO₂-PAN) was successfully used for selective removal of Ge(IV) oxoanions. The pH value of 9 was determined to be optimal for the removal of germanate oxoanion from aqueous solution. At this pH, the breakthrough capacity was about 4.3 g/L (60 mmol/L). Similar breakthrough capacities were observed when the concentration of accompanying anions (sulfates and chlorides) was below 500 mg/L. When the concentration of accompanying anions was increased to 1000 mg/L, the breakthrough capacity decreased by about 40 %. Breakthrough capacities were decreasing with the increasing the specific flow rate s in the studied range of 6 to 24 BV/h. Optimum sorption conditions were $\rho(\text{Ge}) = 3 \text{ mg/L}$; $\rho(\text{Cl}^-; \text{SO}_4^{2-}) = 100 \text{ mg/L}$; pH = 9; $s = 6 \text{ BV/h}$. Regeneration with 15 BV of 0.5 M HCl saturated with NaCl was optimal. About 90 % of Ge was recovered and Ge leakage in the following cycle did not exceed the limit concentration of 25 $\mu\text{g/L}$.

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