Novel Anionic Clay Adsorbents for Boiler Blow-down Waters Reclaim and Re-use

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Overview

- Project Background
- Problems and Solutions
- Project Objectives
- Experimental Aspects
- Results and Discussion
- Conclusions

Background

- **Water Demand:** The electric power generation industry will find itself in direct competition for water with the other growing sectors of the economy

- **Solution:** Reclaiming and reusing power plant spent-waters are likely to reduce the pressure for finding additional sources of traditional cooling water

- **Contaminants of Concern:** Renewed concerns exist today about the environmental fate of heavy metals (As and Se) that are found in many of the power plant effluents, which negatively impact their disposal
  - **Arsenic (As) - future MCL of 0.01 ppm (Jan 2006)**
  - **Selenium (Se) - MCL of 0.05 ppm (USA), MCL of 0.01ppm (Europe, Japan)**

Problems and Solutions

Adsorption is the simplest and most direct approach

- **Problems**
  - **Traditional adsorbents suffer from low adsorption capacity and selectivity towards these heavy metal contaminants**
- **Solutions**
  - **Developing and using novel materials**
    - **Layered double hydroxides (LDH)**

Hydrotalcite

- **Formula**

$[M_{1-x}^{II}M_x^{III}(OH)_2]^{x+}A_{x/n}^{n-}\cdot yH_2O$

Trivalent metal (e.g., Al,Fe)

Divalent metal(e.g.Mg, Zn)

Interlayer anions (e.g., CO_3^{2-},Cl^-)

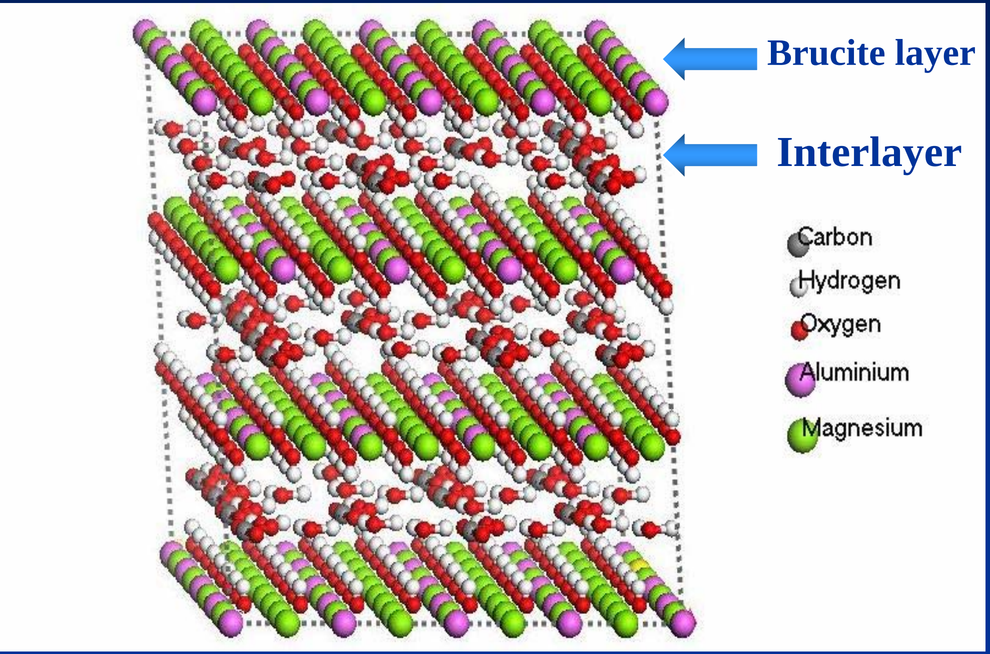


Fig. 1 Computer generated structure of the LDH

- **Uptake mechanism**
  - Adsorption
  - Intercalation by anion exchange
  - Intercalation by reconstruction of the structure of the calcined LDH
- **Applications**

Project Objectives

- **Systematic study of the adsorption of As and Se by calcined and uncalcined LDH from model power plant streams**
  - **Adsorption kinetics**
  - **Adsorption/desorption isotherms**
  - **Effect of pH**
  - **Effect of the As and Se oxidation states**
  - **Effect of competitive ions (NO_3^-, CO_3^{2-}, SO_4^{2-}, HPO_4^{2-})**
  - **Effect of particle size**

As: As(III) and As (V)
Se: Se(IV) and Se(VI)

Experimental Aspects

- **Adsorbent preparation**
  - **Mg-Al-CO_3-LDH**
  - **Co-precipitation method**
- **Characterization**
  - **FT-IR**
  - **X-ray diffraction (XRD)** ------ The structure of LDH
  - **BET------surface area of LDH**
    - 47 m^2/g for uncalcined LDH
    - 198 m^2/g for calcined LDH
  - **ICP-MS------**As and Se concentration in the aqueous solution
    - The instrument detection limit (using the EPA 200.8 method): 0.043 μg/l for As and 0.172μg/l for Se
- **Adsorption experiments – Batch technique**

FT-IR Spectra of Calcined and Uncalcined LDH

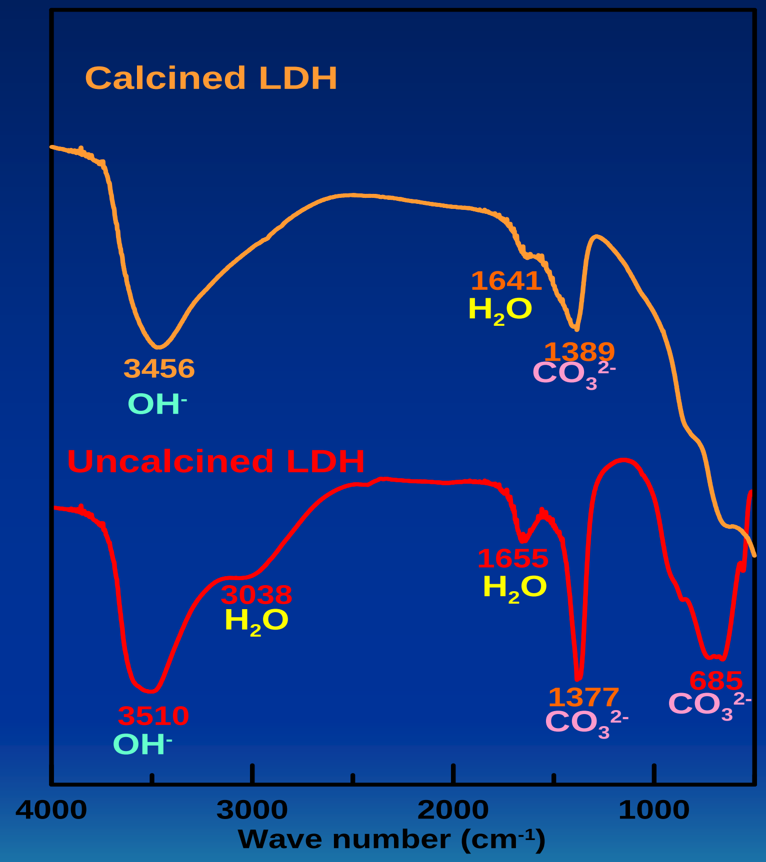


Fig. 2 FT-IR spectra of calcined and uncalcined LDH

Adsorption Kinetics

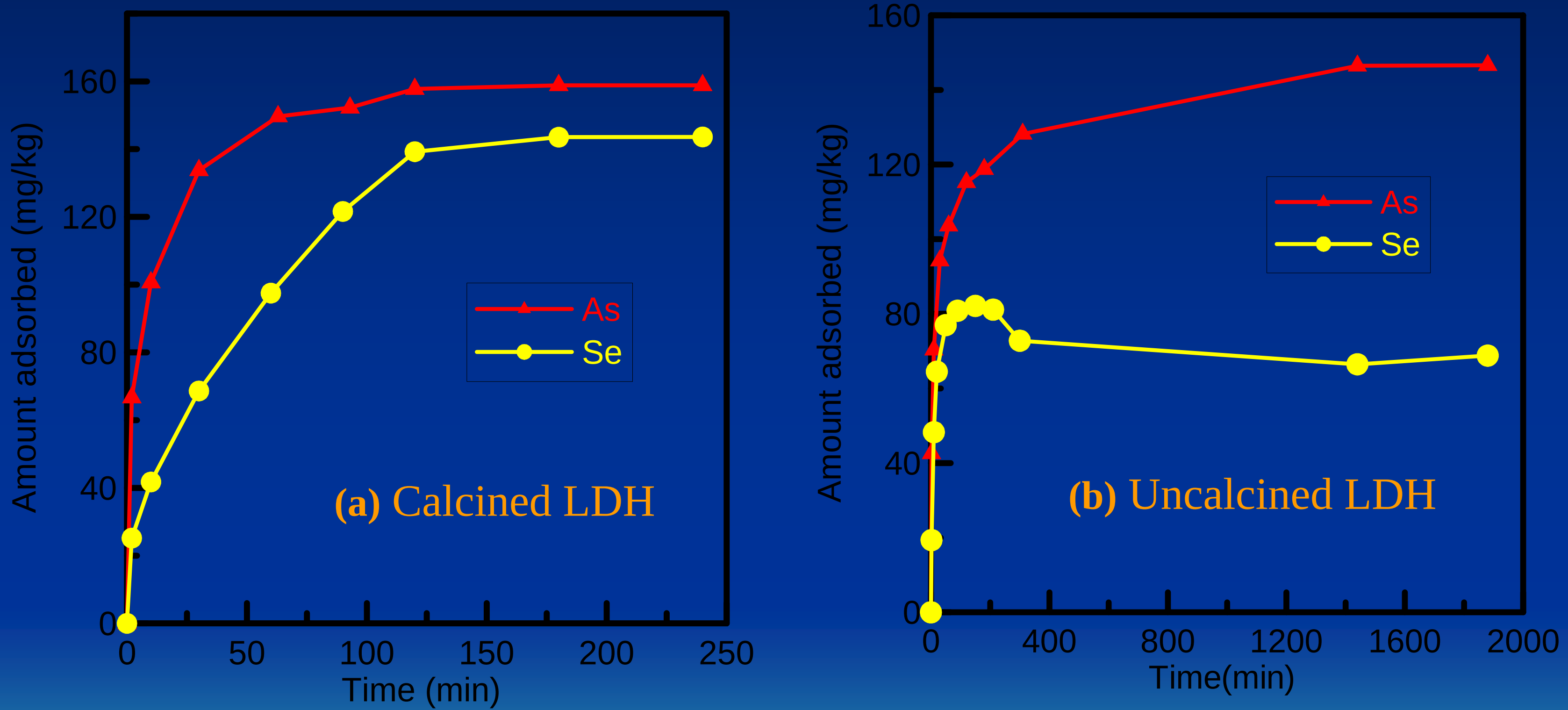


Fig. 3 Adsorption kinetics of As(V) and Se (IV) on (a) calcined and (b) uncalcined LDH in 20 ppb solution

Kinetic Model

A m^th order kinetic rate equation:

$$dq_t / dt = k_1 (q_e - q_t)^m \qquad (1)$$

The mass balance equation for the batch reactor system:

$$V \frac{dC}{dt} = -W \frac{dq_t}{dt} \qquad (2)$$

Equation 1 and 2 must be coupled with the adsorption equilibrium relations (Freundlich):

$$q_e = KC^{1/n} \qquad (3)$$

Table 1 Kinetic parameters for adsorption

	k_1	m	R^2
As/calcined	1.00E-6	2.14	0.941
Se/calcined	1.01E-2	0.98	0.936
As/uncalcined	1.26E-6	2.24	0.901
Se/uncalcined	2.00E-3	1.98	0.975

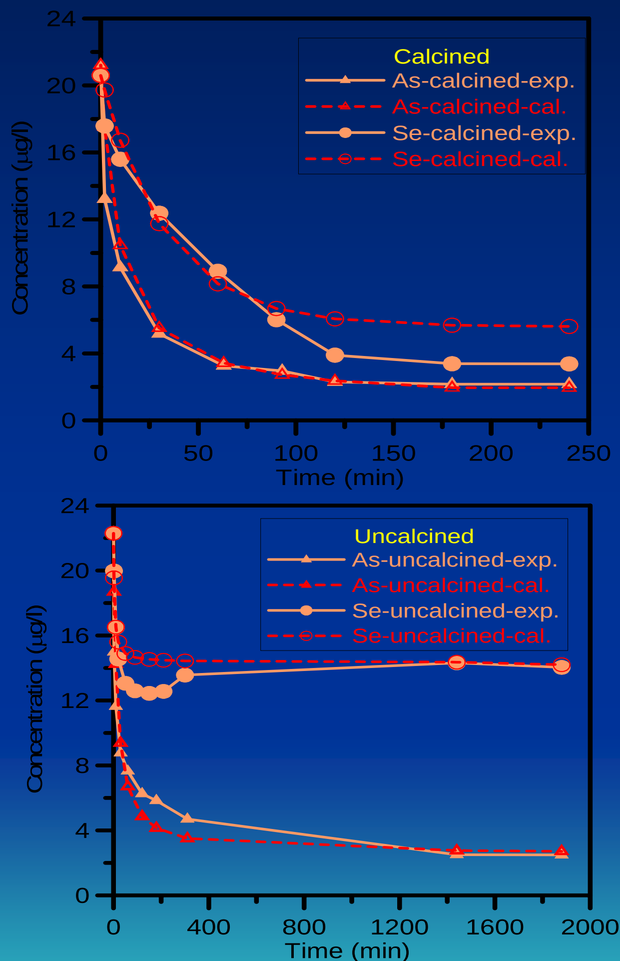


Fig. 4 Comparison between the measured and modeled time profiles for adsorption of As (V) and Se(IV) on uncalcined and calcined LDH

Adsorption Isotherms

Freundlich isotherm: $q_e = KC^{1/n}$

Table 2 Freundlich adsorption constants

	K	1/n	R^2
As(V)/calcined	194.4	0.880	0.956
Se(IV)/calcined	25.1	0.934	0.952
As(V)/uncalcined	79.4	0.870	0.920
Se(IV)/uncalcined	6.99	0.845	0.989

- **As (V) has a larger adsorption capacity and affinity than Se (IV) for both uncalcined and calcined LDH**
- **The adsorption capacity of As (V) and Se (IV) on the calcined LDH is higher than that on the uncalcined LDH**

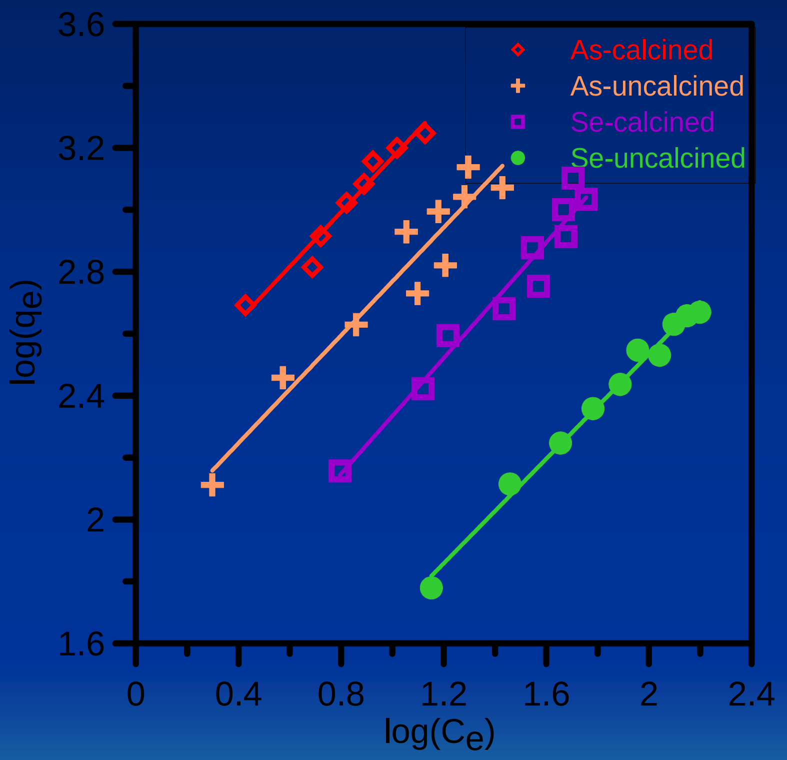


Fig. 5 Adsorption isotherm of As(V) and Se (IV)

Effect of the Initial pH

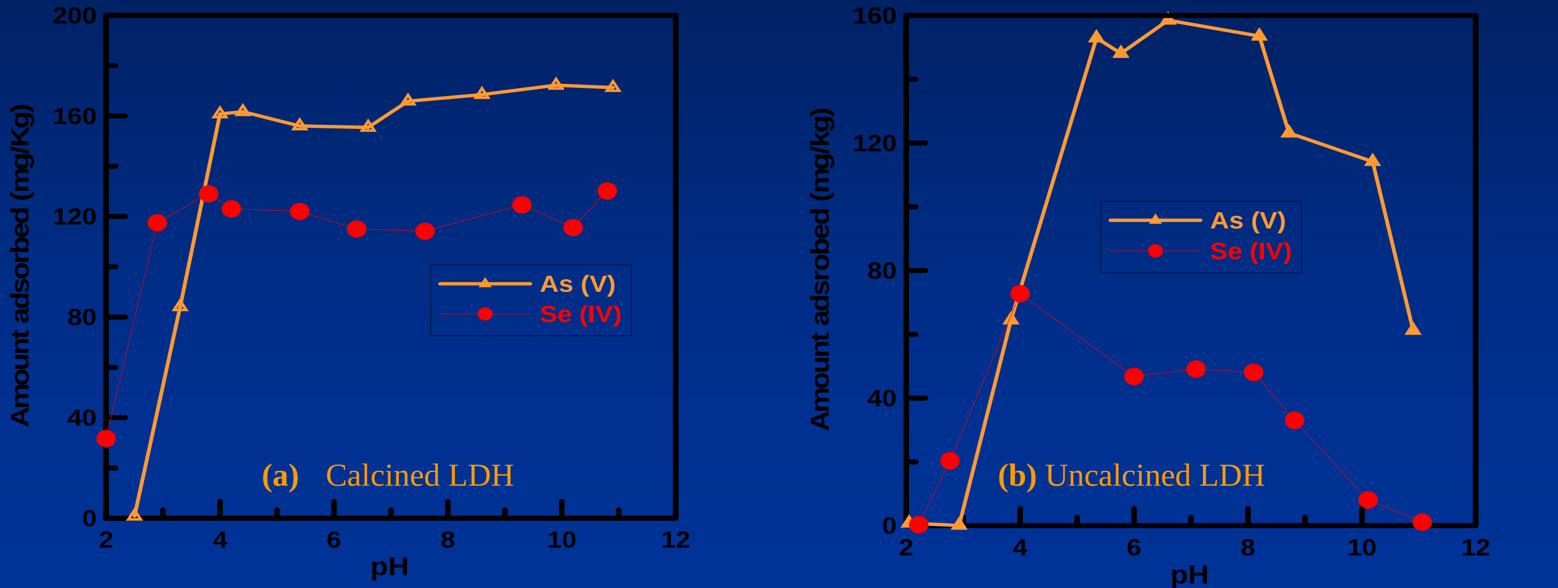


Fig. 6 The effect of pH on the uptake of As(V) and Se (IV) in 20 ppb solutions

pH does not significantly influence the adsorption of As and Se on calcined LDH when above 4; As and Se adsorption on uncalcined LDH is more sensitive to variations in pH.

Effect of As Oxidation State

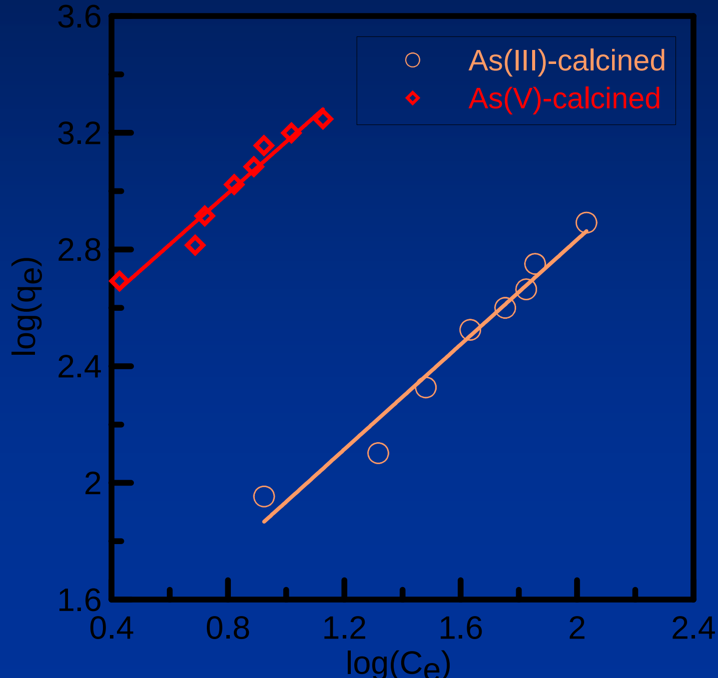
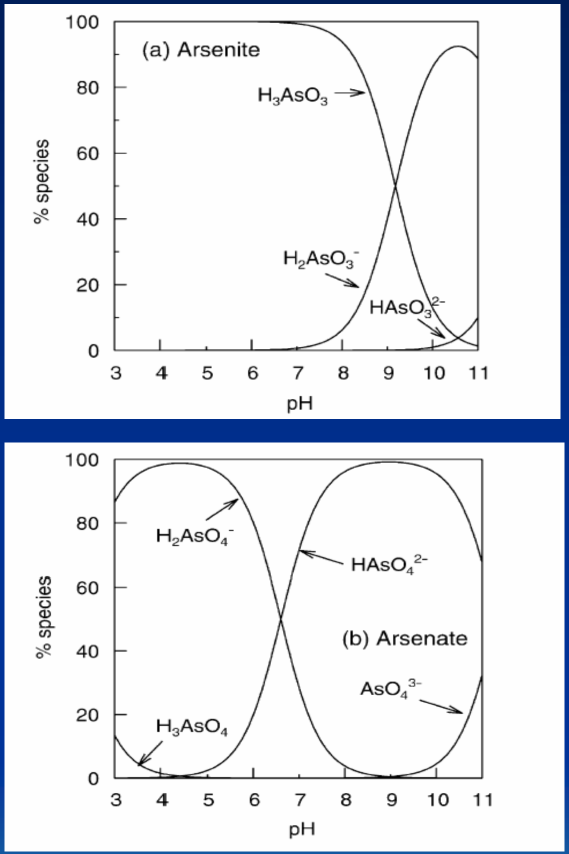


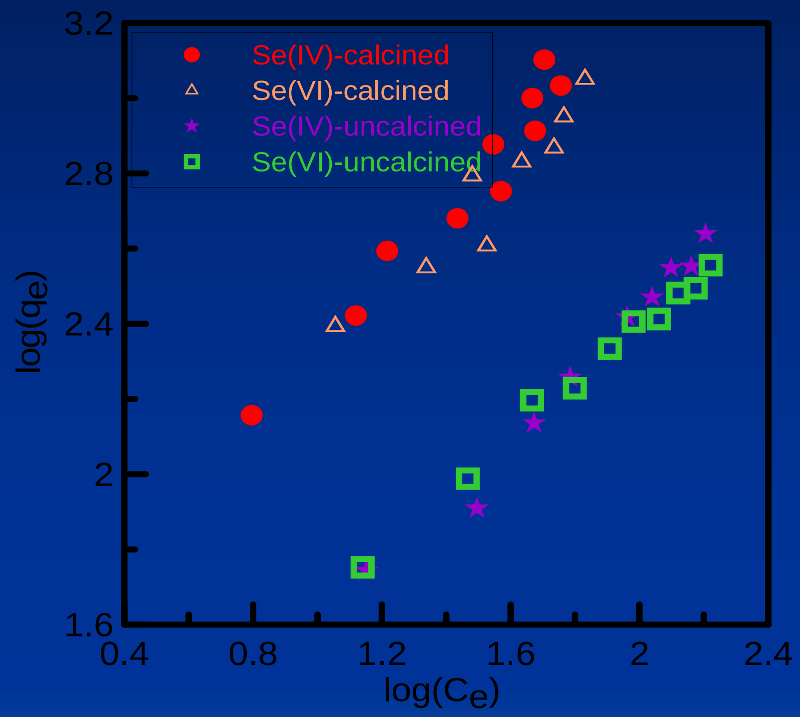
Fig. 7 The effect of As oxidation state on adsorption



➤**As (III) is more difficult to remove than As (V)**

Arsenate : $H_2AsO_4^-$ or $HAsO_4^{2-}$
Arsenite : H_3AsO_3

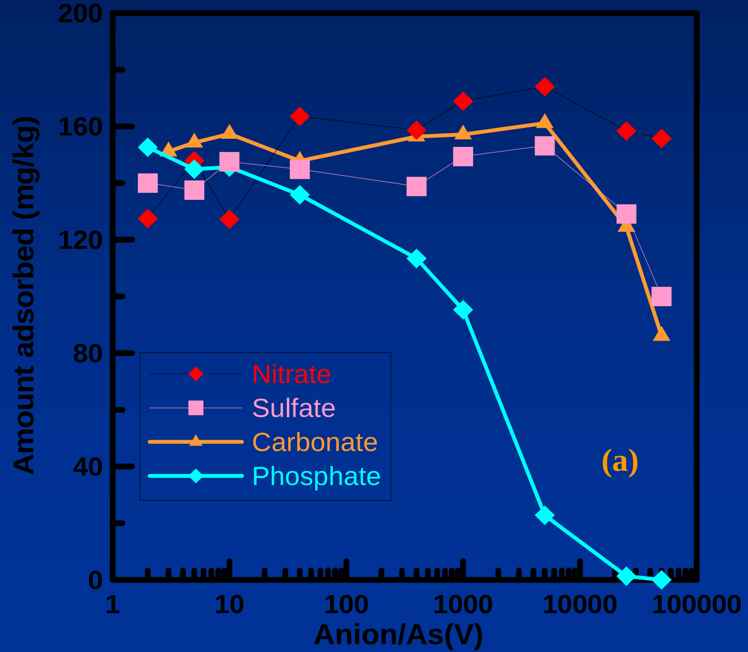
Effect of Se Oxidation State



The adsorption of Se(IV) and Se(VI) is relatively similar on both calcined and uncalcined LDH

Fig. 8 The effect of Se oxidation state on adsorption

Effect of Competitive Anions



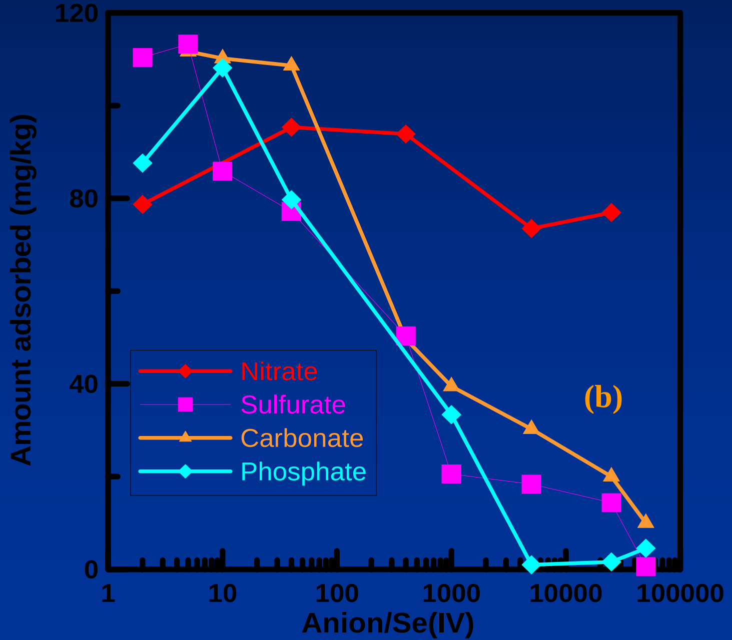


Fig. 9 The effect of competitive anions on uptake of (a) As(V) and (b) Se (IV) in 20 ppb solutions on calcined LDH

Competitive anions have a greater effect on Se (IV) uptake than on As (V) uptake

$HPO_4^{2-} > CO_3^{2-} \sim SO_4^{2-} > NO_3^-$

Desorption

-As/calcined LDH

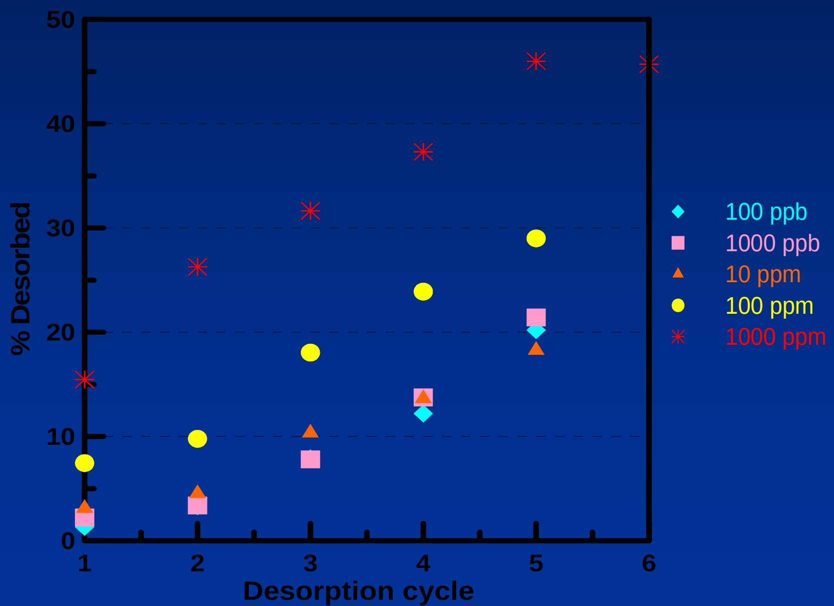


Figure 10 SO_4^{2-} concentration effect on As(V) desorption

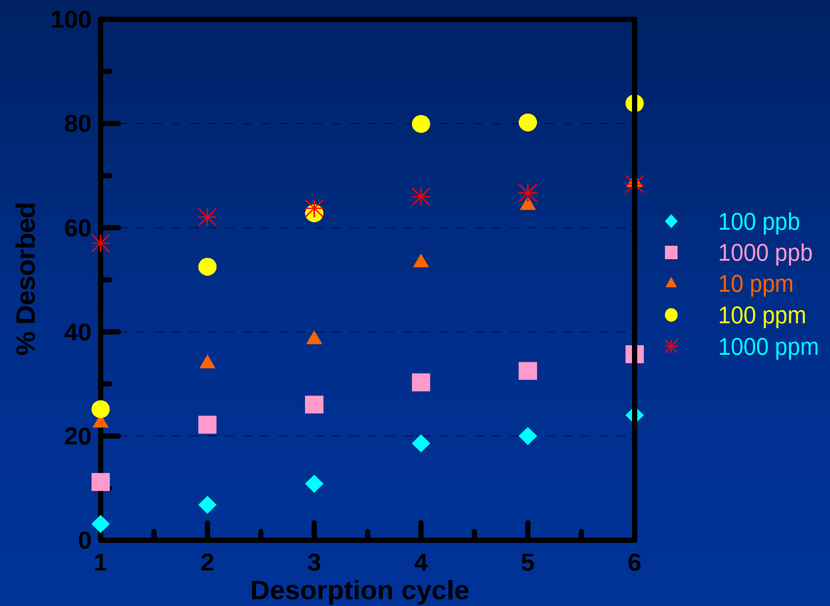


Fig. 11 HPO_4^{2-} concentration effect on As(V) desorption

- **Desorption depends on the type of ion species and their concentration**
- **The difference of As (V) desorption in these anion solutions related to their affinities to LDH. $HPO_4^{2-} > CO_3^{2-} \sim SO_4^{2-} > NO_3^{-}$**

Desorption

-Se/calcined LDH

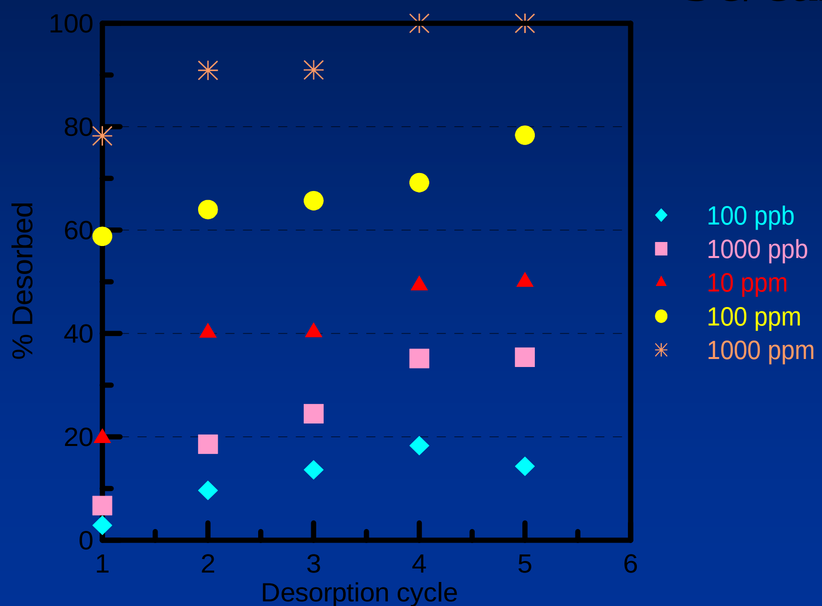


Figure 12 SO_4^{2-} concentration effect on Se(IV) desorption

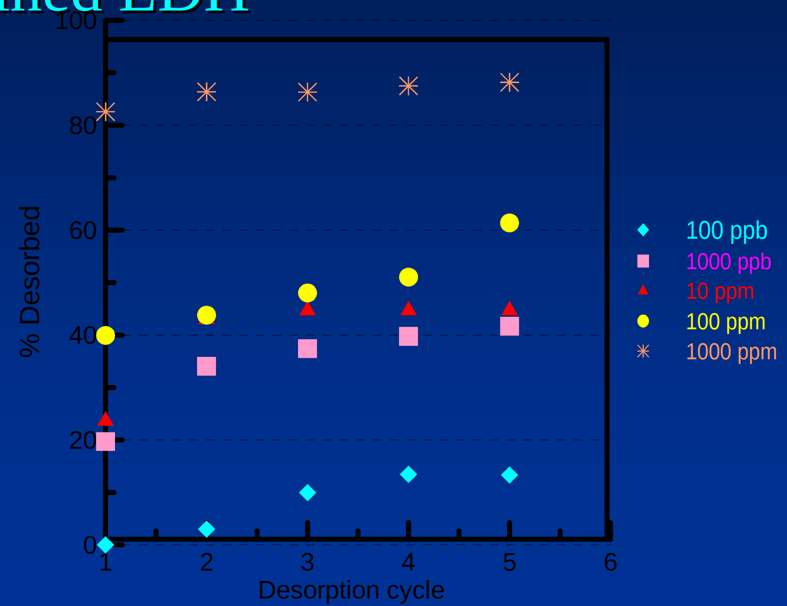


Fig. 13 HPO_4^{2-} concentration effect on Se(IV) desorption

- **The desorption rate and amount of Se(IV) desorbed from calcined LDH is higher than As(V), which is consistent with the lower sorption affinity of Se towards the calcined LDH.**
- **The difference of Se(IV) desorption in these anion solutions follows: $HPO_4^{2-} > CO_3^{2-} \sim SO_4^{2-} > NO_3^-$**

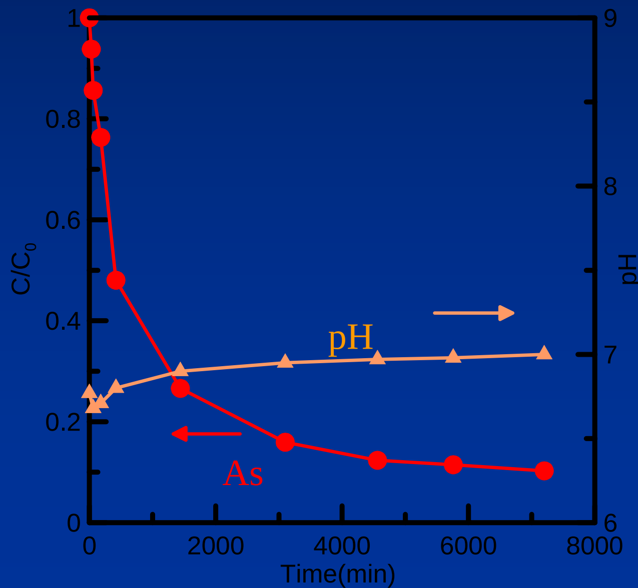
84% of adsorbed As (V) and 100% of Se(IV) can be desorbed after 6 desorption cycles

Adsorption Kinetics-Conditioned Calcined LDH

-pH, Mg, Al as a function of time

Secondary Drinking Water Regulations (EPA)- Al: 0.05 to 0.2 mg/l

Conditioning the adsorbent: Washing and allowing the calcined LDH standing in water for 24 h



C_0=205 ppb
d=75-90 μm
Dose=0.04g/l

Figure 14 pH change as a function of time

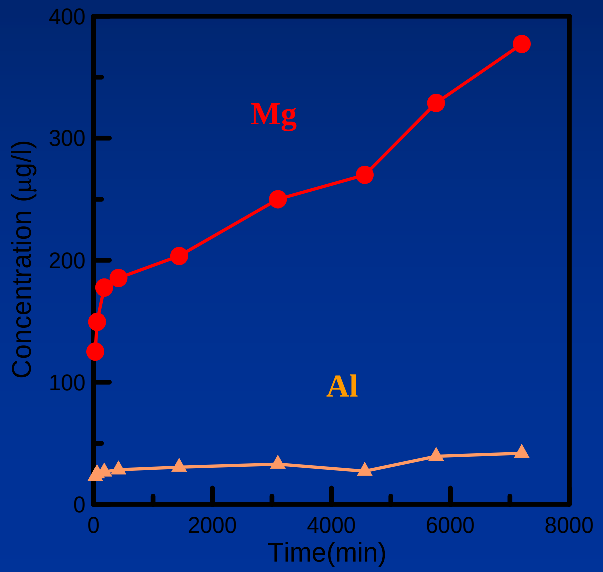


Fig. 15 Mg and Al in the solution as a function of time

Effect of Particle Size

-on conditioned calcined LDH

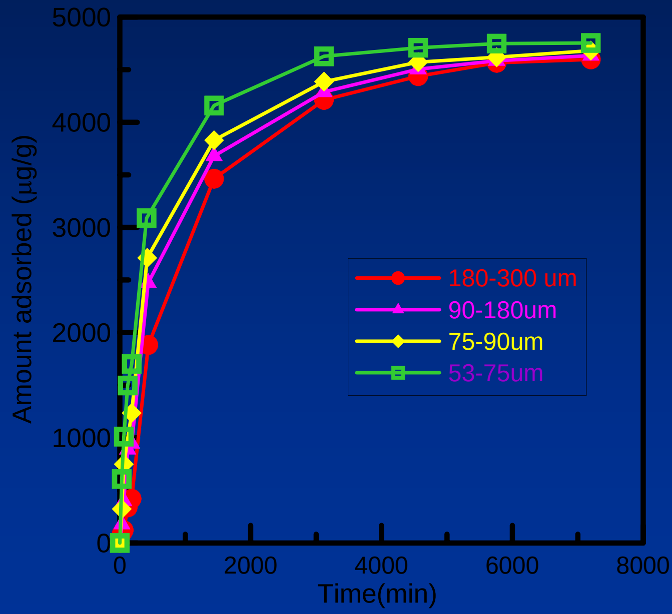


Figure 16 Effect of particle size on adsorption kinetics

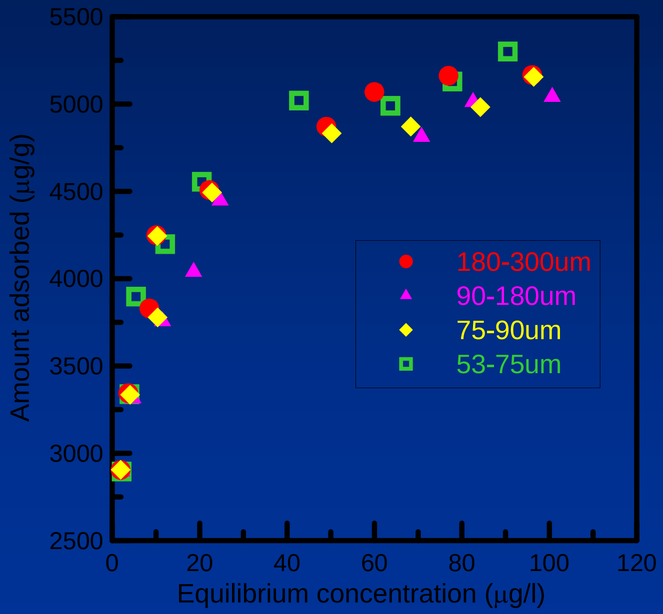


Fig. 17 Effect of particle size on adsorption isotherm

- The As(V) adsorption rate on conditioned LDH increases with decreasing particle size of the adsorbent.
- The adsorption capacity of As(V) on conditioned LDH is independent of particle size

Conclusions

- $Mg\text{-}Al\text{-}CO_3$-LDH shows promising capacity for the removal of trace levels of As and Se from aqueous solutions.
- The calcined LDH showed higher adsorption capacity and efficiency than uncalcined LDH for both As (V) and Se (IV).
- The starting solution pH does not significantly influence the adsorption of As and Se on calcined LDH, as long as it is higher than 4; As and Se adsorption on uncalcined LDH is, however, more sensitive to variations in the initial pH.
- As (III) is more difficult to remove than As (V) by both the calcined and uncalcined LDH; the adsorption of Se(IV) and Se(VI) is relatively similar on both calcined and uncalcined LDH.
- Competing ions have a greater effect on Se (IV) rather than on As (V) uptake.
- The desorption of As (V) and Se (IV) from the LDH depend on the type of ion species and their concentration in the desorbing solutions.
- The As(V) adsorption rate on conditioned calcined LDH increases with decreasing particle size, while the adsorption capacity LDH is independent of particle size.

Thanks!

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