Regeneration of HDTMA-modified minerals after sorption with chromate anions


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Research objectives

- the regeneration study of various HDTMA-Br-modified minerals after their saturation with chromate anions

**Stages:**

1) to investigate Cr(VI) desorption possibility from organically modified-minerals using four different desorption agents (deionized H₂O, NaCl, KCl and NaCN)
2) to examine Cr(VI) desorption kinetics
3) to evaluate the stability and reuse possibility of minerals employed after successive adsorption/desorption cycles
Cr(VI) is of high toxicity and a suspected carcinogenic agent.

Cr(VI) is among the most common polluting metal anions in industrial effluents (steel production, paint manufacturing, leather tanning, electric and electronic components, pulp processing etc).

Toxic effects on humans and aquatic ecosystems.

Degradation of water quality.

Treatment processes for Cr\textsuperscript{6+} removal:

- Chemical precipitation
- Ion exchange / Adsorption
- Chemical reduction
- Membrane separation
Modification of minerals and Cr(VI) adsorption (1/3)

- Aluminosilicate natural minerals employed: Zeolite, exfoliated Vermiculite, Bentonite and Attapulgite (Palygorskite)

- Pre-treatment (modification) of these adsorbents is a necessary process for Cr(VI) removal from contaminated waters

- Modification by organic salt HDTMA-Br (hexadecyltrimethylammonium bromide) → modification results in positively charged mineral surface → Uptake of negative charged groups (e.g. HCrO$_4^-$)
Modification of minerals and Cr(VI) adsorption/desorption (2/3) Mechanisms

- HDTMA<CMC => monolayer coat => neutralization of mineral surface
- HDTMA>CMC => bilayer coat => positively charged mineral surface
- Cation exchange between 1\textsuperscript{st} cation charged hydrophil HDTMA layer and negatively charged mineral
- Van Der Waals forces and hydrophobic bonding between 1\textsuperscript{st} and 2\textsuperscript{nd} layer
- Anion exchange between Br\(^-\) of 2\textsuperscript{nd} HDTMA layer and chromate anions
- Regeneration process: Anion re-exchange between Cr(VI) and Cl\(^-\)

![Diagram showing modification mechanisms and Cr(VI) adsorption/desorption processes.](image-url)
Modification of minerals and Cr(VI) adsorption (3/3)

**Modification optimum parameters**

- **pH**
  3 for vermiculite and bentonite, 6 for zeolite and 8 for attapulgite

- **HDTMA-Br concentration**
  1g/L for zeolite, 6g/L for vermiculite, 2g/L for bentonite and 7g/L for attapulgite

**Cr(VI) adsorption optimum parameters**

- **pH = 4** for all minerals

- **Mineral dosage:** 10 g L⁻¹ for all minerals (maximum Cr(VI) removal)

- **Kinetics:** 1) $t_{eq} = 3-4$ hours, 2) Pseudo-second-order model

- **Isotherms:** 1) Langmuir model → zeolite, bentonite and vermiculite, Freundlich → attapulgite, 2) maximum adsorption capacities order ($q_m$):
  Verm. (27 mg/g) > Bent. (24 mg/g) > Attap. (15 mg/g) > Zeolite (13 mg/g)
HDTMA-mineral characterization (1/2)

- **SEM** => Structure differences between natural and modified minerals

- **Confirmation of modification**

- **TOC**: Presence of organic carbon on modified minerals

- **FTIR**: Appearance of characteristic CH$_2$ peaks

- **XRD**: Lessening of the intensity of the majority of characteristic peaks for zeolite and expansion of $d$ spacing (001) for vermiculite

- **EDX**: Increase of carbon and bromium while reducing exchangeable ions (e.g. Ca$^{2+}$)

- **ζ-potential**: natural minerals (negatively charged) => modified minerals (positively charged), confirmation of the optimal modification pH, vermiculite => more effective modification
HDTMA-mineral characterization (2/2)

FTIR bentonite

XRD bentonite

ζ-potential of natural and modified minerals
**Desorption solutions evaluation**

- **Desorption agents:** H₂O, NaCl, KCl, NaCN
- **Salts concentrations under investigation:** 0.1, 0.5, 1, 3 M

- **Desorption percentages:**
  - H₂O (< 10%)
  - NaCl-3M (>64%)
  - KCl-3M (>66%)
  - NaCN-0.1M (>38%)

- **Highest desorption percentages:**
  - Bentonite-NaCl (3M) (96%)
  - Attapulgite-KCl (3M) (93%) (mineral dosage = 10 g L⁻¹)

- **Increase of salt concentration => increase of Cr(VI) desorption percentage**
- **Comparative performance of salts employed:** NaCl > KCl > NaCN
- **NaCl optimum concentration = 1M** (equivalent of 3M, lower cost)
Kinetics models under investigation:

1) Pseudo-first-order, 2) Pseudo-second-order, 3) Elovich

Kinetic models were employed:
- to examine the adsorption process
- to describe and predict the adsorption rate
- to select the optimum operating conditions for the batch process

Experimental procedure:
- 5 g of each mineral + 500 ml NaCl (1M), 600rpm, 24h, T=25 °C
Pseudo-second order kinetic model fits best to the experimental data for all minerals ($R^2 \approx 0.97-0.99$)

- $q_{ed}$ row for minerals employed:
  - zeolite (2.5 mg g$^{-1}$) > vermiculite (2.2 mg g$^{-1}$) > bentonite (2.1 mg g$^{-1}$) > attapulgite (1.9 mg g$^{-1}$)
- $k_{2d}$ row occurred: attapulgite > zeolite > bentonite > vermiculite
- very high Cr(VI) desorption rate at the initial stages (t=0-15 min)
- Equilibrium time ($t_{eq}$) => 40 min for attapulgite, 50 min for zeolite, 60 min for bentonite and 75 for vermiculite $t_{eq}$ vermiculite > $t_{eq}$ bentonite > $t_{eq}$ zeolite > $t_{eq}$ attapulgite
Mineral regeneration cycles (1/2)

- Desorption agent: NaCl (1M)
- Evaluation of performance and stability of modified minerals in successive Cr(VI) adsorption/desorption cycles
Regeneration process (5/6)

Mineral regeneration cycles (2/2)

Zeolite - Cr(VI) adsorption

Zeolite - Cr(VI) desorption

Vermiculite - Cr(VI) adsorption

Vermiculite - Cr(VI) desorption
Regeneration process (6/6)

Mineral regeneration cycles - Conclusions

- Bentonite: 14 cycles → 73% / 25% of its initial Cr(VI) adsorption / desorption capacity
- Attapulgite: 12 cycles → 69% / 12% of its initial Cr(VI) adsorption / desorption ability
- Zeolite: 8 cycles → Loss of adsorption – desorption ability
- Vermiculite: 4 cycles → Loss of adsorption – desorption ability
- Maintenance of organic modification (bilayer structure) for bentonite and attapulgite
- Bentonite → Higher stability in successive adsorption – desorption cycles
- Final regeneration performance order of the examined minerals:

  Bentonite > Attapulgite > Zeolite > Vermiculite
Regeneration and reuse of HDTMA-Cr(VI)-modified minerals is a feasible process using the suitable desorption solution.

NaCl was the most effective of the solutions used attaining significant desorption efficiencies (~96% for bentonite).

Comparative performance of salts employed: NaCl > KCl > NaCN.

Pseudo-second-order model fitted better in the experimental data for Cr(VI) desorption.

Bentonite exhibited the highest Cr(VI) adsorption capacity (96%) and also the highest stability at the regeneration process (after 14 cycles it maintains 73% of its initial adsorption capacity).
Thank you
for your attention!