# INNOVATIVE TECHNOLOGIES FOR WASTEWATER TREATMENT, REUSE AND RESOURCE RECOVERY

# - STRUCTURED ADSORBENTS

vito Elena M. Seftel, Bart Michielsen | September 27-28, 2023 | INDIA

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PAVITRA GANGA

WORKSHOP

Innovative technologies for wastewater treatment, reuse and resource recovery

# TABLE OF CONTENTS




This project has received funding from the *European Union's Horizon 2020 research and innovation programme* under grant agreement No 821051.
This project has been co-funded by Department of Biotechnology (DBT), Government of India.

# INTRODUCTION – CHROMIUM (Cr)

- Heavy metal with multiple oxidation states (-II → +VI)
- Stable forms: Cr(III) and Cr(VI)
- Usages in industry: dyeing, tannery industry, metallurgy…





*Is used as Cr(III)*  *which becomes dangerous when oxidizing at Cr(VI)* 

10 FEB 2022 **Is Hexavalent Chromium Present In Your Industry?**


https://www.airex-industries.com/en/media-centre/327-is-hexavalent-chromium-present-in-your-industry

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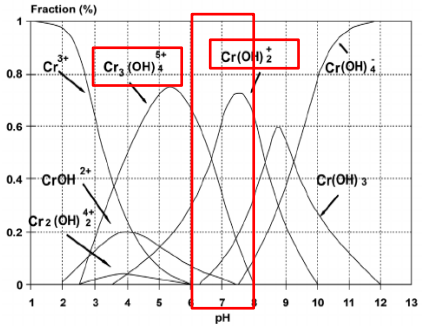
# INTRODUCTION – CHROMIUM (Cr)

- Heavy metal with multiple oxidation states (-II → +VI)
- <u>pH – dependent distribution</u>

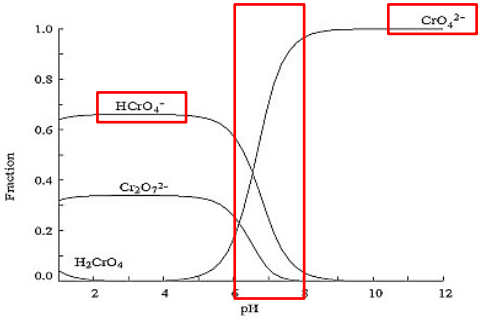
→ pH ~7 → Cr(III)-species: positively charged
→ Cr(VI)-species: negatively charged

*Trivalent chromium (CrIII)*




Santos, V.C.G.D., et al., *Highly improved chromium (III) uptake capacity in modified sugarcane bagasse using different chemical treatments.* Química Nova, 2012. **35**(8): p. 1606-1611.

*Hexavalent chromium (CrVI)*




Sampaio Cde, G., et al., *Chitosan/mangiferin particles for Cr(VI) reduction and removal.* Int J Biol Macromol, 2015. **78**: p. 273-9.

*Is used as Cr(III)*  *which becomes dangerous when oxidizing at Cr(VI)* 

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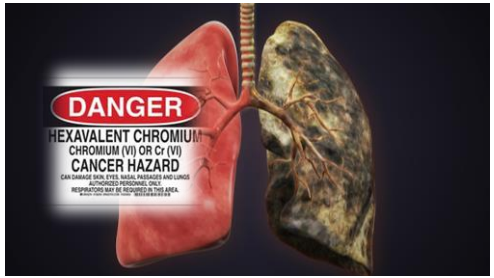
# INTRODUCTION – CHROMIUM (Cr)

- Toxicity: Cr(VI)

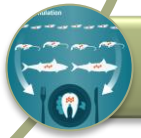



Dermatitis

Cancer

Decrease of plant growth

Adaptation plant morphology



Accumulation in aquatic life

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# STRUCTURED ADSORBENTS – WHY?

- Waste streams:
  - **Large** volumes with **low** concentrations of valuables or undesirable compounds
- Treatment technologies:
  - Chemical precipitation, ion-exchange, electrocoagulation… → Disadvantage: not viable for **low** concentration of metals and production of chemical sludges

**Adsorption** = key technology to recover/remove **low** concentrations of valuables/undesirable compounds from complex, low-grade matrices

- Good sorption material:
  - Stable → choice of material
  - Selectivity → composition/surface modification
  - Low costs → regenerable
  - Permeability → structured materials

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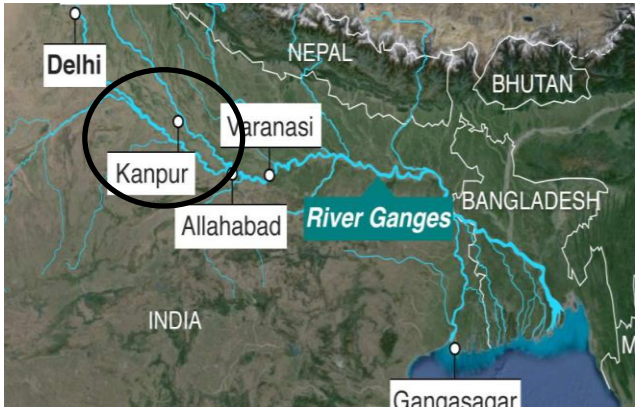
# STRUCTURED ADSORBENTS - MAIN OBJECTIVE

- Remove heavy metals (Cr) from the polluted wastewater (in Kanpur)

- Resource recovery





Uses Cr salts as tanning substance[1]


1.Abreu, Ceramics International, 2009, 35(6), 2225-2234
2.EPA (Safe Drinking Water Act)
https://www.epa.gov/sdwa/chromium-drinking-water

→ pH ~neutral and $Cr^{3+}$ & $Cr^{6+}$ ($CrO_4^{2-}$)
→ wastewater discharge limit for Chromium is 100 ppb (100µg/L)[2].

→ Adsorption using structured adsorbents to reduce Cr concentration and reuse of wastewater (secondary use)

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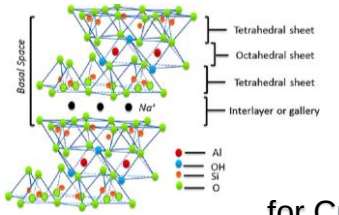
# METHODOLOGY

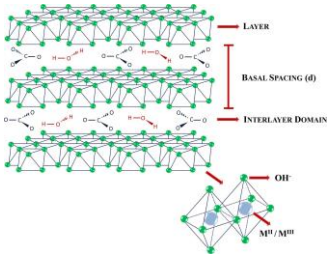
## ***Structured sorbents with specific structure designed at VITO:***

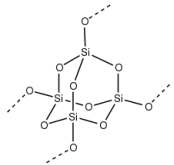
- ✓ High loading capacity
- ✓ Capable to uptake both positive and negative charged Cr species
- ✓ Regenerable
- ✓ Structured (shaped – apply in columns set-ups)

Layered Phyllosilicates
(Bentonite - B)




Layered Double Hydroxides (LDHs)



for $Cr^{3+}$ for $Cr^{6+}$ for mechanical stability

Structured adsorbents

*Granulation by Intensive mixing*

Powdered adsorbents

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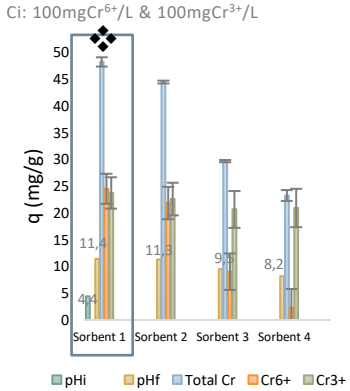
# PRELIMINARY RESULTS

## *Structured sorbents with specific structure:* ***variation in LDH:B ratio***

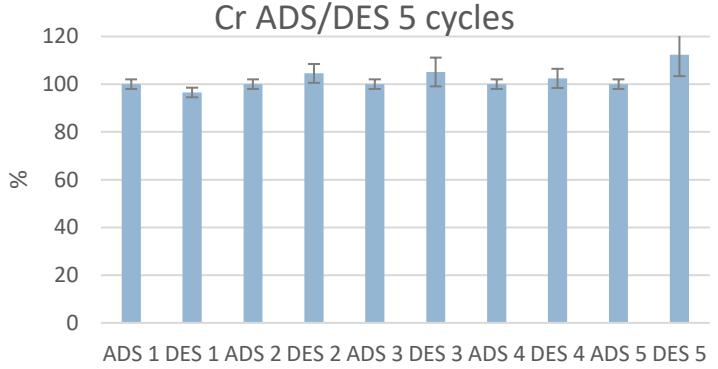
- Composition screening in synthetic Cr solutions at VITO:

Thesis Ms. Mitra De Geest (2022) – VITO and University of Antwerp




❖ Sorbent1: LDH and Bentonite are in the ratio of 80:20

- Desorption optimization and multicycle tests at VITO:




❖ 2M NaCl at neutral pH


**Reference:**
De Geest, M.; Michielsen, B.; Ciocarlan, R.-G.; Cool, P.; Seftel, E.M. Structured LDH/Bentonite Composites for Chromium Removal and Recovery from Aqueous Solutions. Molecules 2023, 28, 4879. https://doi.org/10.3390/molecules28124879



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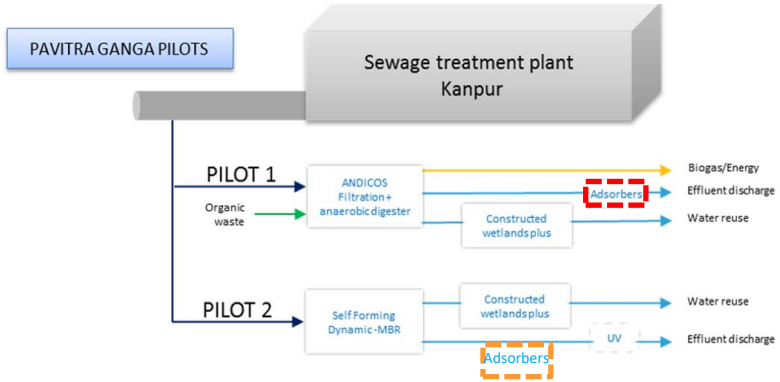
# THE PROCESS FLOW DIAGRAM / PILOT SETUP - MAIN OBJECTIVE

- Remove heavy metals (Cr) from the polluted wastewater (in Kanpur)
- Resource recovery


- Experiments using the Wastewater effluent from STP at Jajmau that has been passed through IPC membrane
- Scale:
  - Small batch experiments → validate Structured sorbent selected composition (Sorbent 1), investigate the adsorption equilibrium parameters and kinetic parameters
  - Larger column tests to validate the small-scale experiments and modeling

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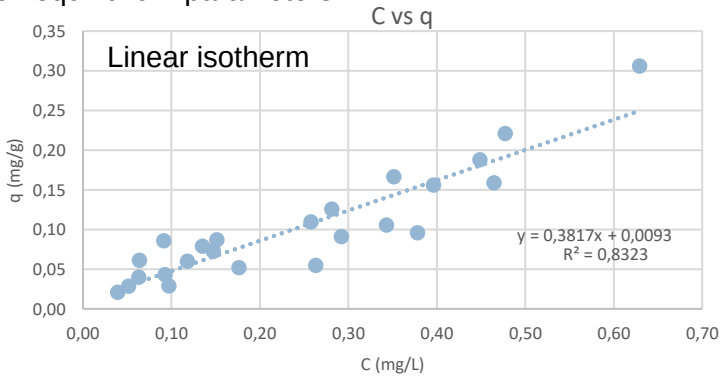
# THE PROCESS VALIDATION VIA SMALL SCALE EXPERIMENTS

## Tests – validation (IIT Kanpur)

Sorption tests performed with low Cr concentrations, e.g. of 0.5 – 2 mgCr/L in permeate (IPC membrane filtration)

- Master thesis:
  - Mr. Mohit Vaid (2022) → Validation of selection of sorbent composition: **Sorbent 1**
  - Ms. Henna Shaji (2023) → small scale batch tests and column testing
    - Isotherm experiment: investigate the adsorption equilibrium parameters

| Dosages (g/100mL) | Removal Efficiency |
|---|---|
| 0.5 | 49-68 % |
| 0.75 | 66-78 % |
| 1 | 77-81 % |
| 1.5 | 76-87 % |
| 2 | 91-94 % |
| 2.5 | 93-96 % |




→ At low concentrations, the Cr removal % is dependent of S/L ratio
→ Complete removal can be achieved with increased S/L ratio

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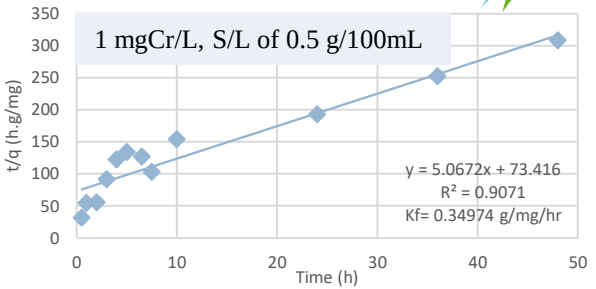
# THE PROCESS VALIDATION VIA SMALL SCALE EXPERIMENTS

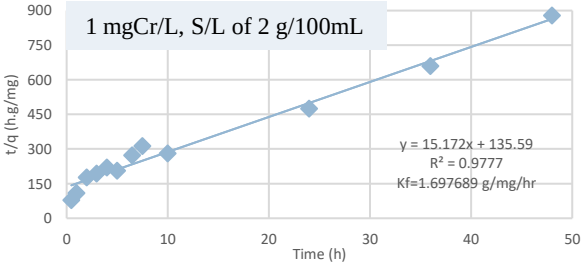
## Kinetic tests (IIT Kanpur)

- At various S/L ratios, e.g. 0,5, 1 and 2gSorbent 1/100mL permeate
- low Cr concentrations, e.g. 1 and 2 mgCr/L in permeate

→ The data points were found to follow pseudo 2nd order kinetics

- The rate constant i.e., $K_f$ obtained in the range 0.1 to 2 g/mg/hr
- The majority of Cr removal was achieved within first:
  - 24h of the addition of adsorbent in case the dosage is 0.5 g / 100 mL
  - 10 h of the addition of adsorbent in case the dosage is 1 – 2 g / 100 mL




Thesis Ms. Henna Shaji (2023)

→ Results were used for modelling studies and predict the behaviour under flow conditions which indicated that the **U = Hydraulic loading rate (m³/m²/h)** is the main parameter affecting the column performances

$$U = \frac{Q}{A_{CS}}$$

Q = Flowrate in m³/h
$A_{CS}$ = Area of cross-section of Column

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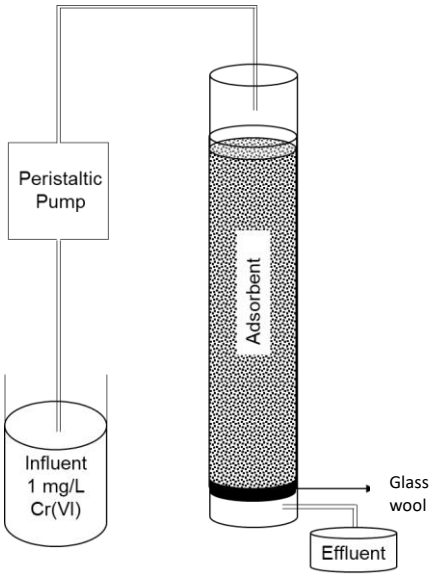
# THE PROCESS FLOW DIAGRAM / COLUMN DESIGN

## Column design and experimental plan (IIT Kanpur)




- IPC Permeate with concentration of 1mg/L Cr(VI) will be passing through the column.
- Peristaltic pump used for controlling influent flow
- Flow rate chosen is 2ml/min → 4mL/min
- Based on the values of **U (0.5, 1 and 1.5 $m^3/m^2/d$)** and the minimum flow rate (2mL/min) 3 columns were prepared:
  - Diameter columns: 5cm, 6cm and 8cm
  - Column height: 75cm
- Support material such as glass wool - for the support of adsorbents (Columns with inbuilt support)
- Sample collection daily until saturation
- Analysis using ICP-MS

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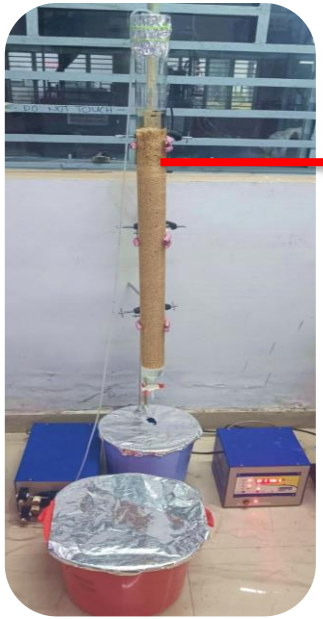
# THE PROCESS FLOW DIAGRAM / COLUMN EXPERIMENTS

## Column design and experiments(IIT Kanpur)

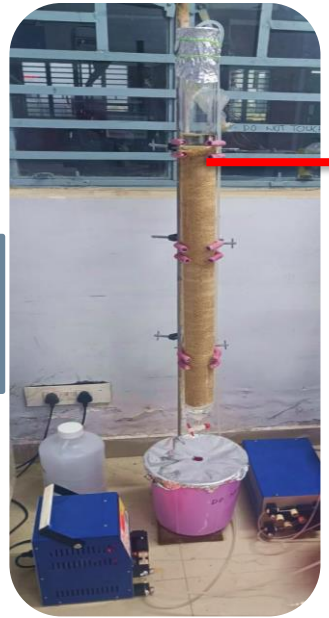
- Based on the values of U (0.5, 1 and 1.5 $m^3/m^2/d$) and the minimum flow rate, 2 to 4 mL/min

Column 1



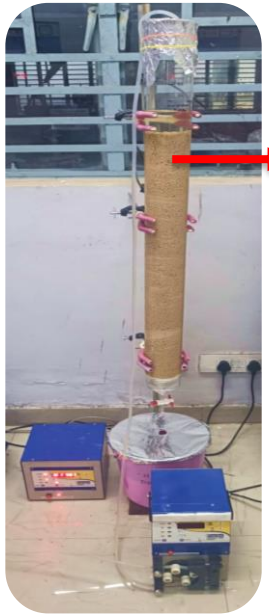
U= ~1.5 $m^3/m^2/d$
H = 0.75m
D= 5cm

Column 2



U= ~1 $m^3/m^2/d$
H = 0.75m
D= 6cm

Column 3



U= ~0.5 $m^3/m^2/d$
H = 0.75m
D= 8cm

Thesis Henna Shaji 2023

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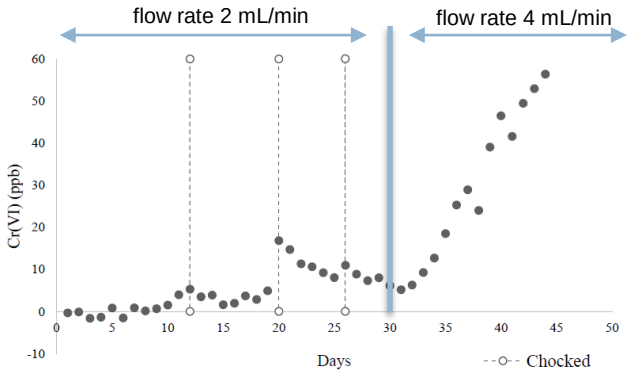
# COLUMN EXPERIMENTS

**Breakthrough curves of Cr(VI) adsorption on structured adsorbent:**

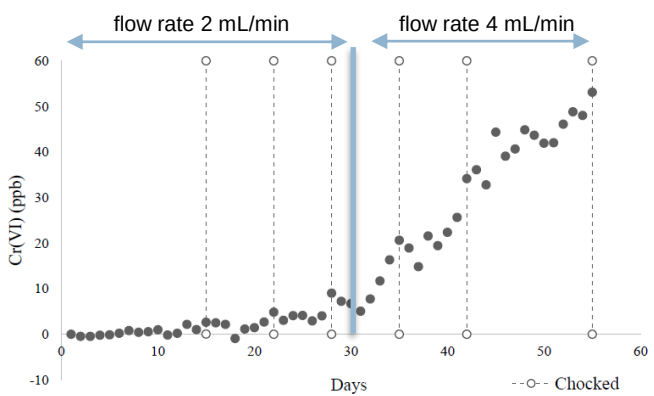
Column 1_D 5cm




Conditions: bed depth 0.75 m: U = 1.5 $m^3/m^2/h$
- pH variation: 8.3-8.6 → 12

- Breakthrough > 50ppb after ~ 42days
~165 L of wastewater treated

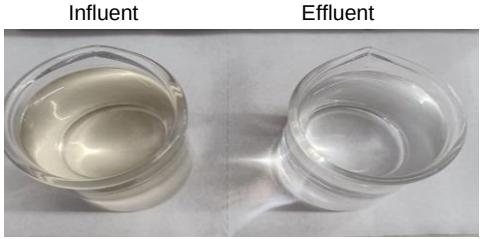
Column 2_D 6cm




Conditions: bed depth 0.75 m; U = 1 $m^3/m^2/h$
- pH variation: 8.3-8.6 → 12

- Breakthrough > 50ppb after ~ 55days
~270 L of wastewater treated

* Color change observed:




→ wastewater discharge limit for Chromium is 100 ppb (100µg/L)[1].

1.EPA (Safe Drinking Water Act)
https://www.epa.gov/sdwa/chromium-drinking-water

Thesis Henna Shaji 2023

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# OPERATIONAL PROBLEMS AND APPROACHES FOR TROUBLE SHOOTING

- As the solutions contain chromium, the appropriate precautions have to be taken
- Support material such as glass wool is used when packing the columns: it is advised to use protective equipment:
    - protective gloves and a face mask when handling the glass wool

- As the columns chocked during long time operation:
    - The mechanical stability of the structured sorbents should be further improved by increasing the silica content during the granulation procedure

- pH observed to increase during operation ($pH_i$ 8.3 – 8.6 → $pH_f$ 12):
    - Before further usage or disposal, the pH of effluent should be altered.

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# CONCLUSIONS

- Structured sorbents with specific composition for both $Cr^{3+}$ & $Cr^{6+}$ adsorption were prepared
- Structured sorbent with LDH:Bentonite of 80:20 performed the best
- The regeneration of the Sorbent after Cr adsorption, namely Cr elution, was optimized: 2M NaCl solution with neutral pH
- The potential for resource recovery (Cr) was demonstrated at lab scale at VITO over 5 cycles
- The selected composition was tested and validated at with real permeates at IIT Kanpur
  - At low concentrations, the Cr removal % is dependent of S/L ratio
  - Complete removal can be achieved with increased S/L ratio
- The small-scale results allowed us to design the larger-scale column set-up and the experimental testing
  - Breakthrough study allows to estimate the long-term performance of the Structured adsorbents

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# FUTURE RESEARCH PERSPECTIVES

- Optimization of operational parameters under flow conditions
- Validation of desorption procedure on the larger columns setups for multicycle use
- Testing of various Cr containing wastewater sources (various Cr concentrations)
- Investigation on use/regeneration/disposal of exhausted Structured adsorbents

# OPTIONS FOR SCALE UP

- Up-scalable technology:
  - Materials side: Structured sorbent production: commercially available clays (LDH & Bentonite) and granulation technique
  - Application side: Possibility to work with larger columns or multiple columns installations

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# PUBLICATIONS FROM THIS RESEARCH

*molecules*

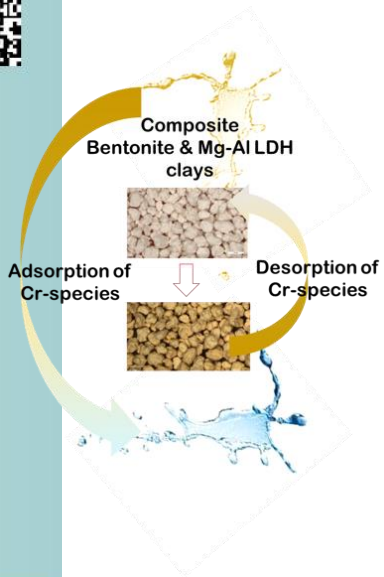
an Open Access Journal by MDPI

## Structured LDH/Bentonite Composites for Chromium Removal and Recovery from Aqueous Solutions

Mitra De Geest; Bart Michielsen; Radu-G. Ciocarlan; Pegie Cool; Elena M. Seftel

*Molecules* **2023**, Volume 28, Issue 12, 4879

https://doi.org/10.3390/molecules28124879

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- EU H2020 Pavitra Ganga project No. 821051 and consortium partners
- vito Dr. Bart Michielsen
- Universiteit Antwerpen Prof. Pegie Cool
    - Ms. Mitra De Geest (Master thesis 2022)
- IIT KANPUR Indian Institute of Technology Kanpur Prof. Purnendu Bose
    - Mr. Mohit Vaid (Master thesis 2022) and
    - Ms. Henna Shaji (Master thesis 2023)

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