WaterPro project

Adsorption experiments

Kokkola Material week
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Programme for Sustainable Growth and Jobs
Leverage from the EU 2014–2020
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WaterPro project: New processes of the economy in water and wastewater treatment

WP1: Processing industrial side streams and other materials for water purification applications

Task 1-1. Selection of raw materials, characterization
Task 1-2. Developing and preparation of geopolymers
Task 1-3. Thermal or chemical treatment of inorganic industrial waste materials

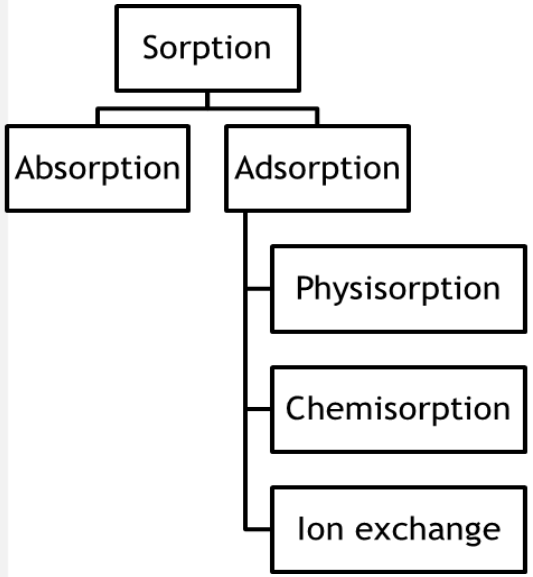
WP3: Removal or uptake of harmful substances, lab scale experiments

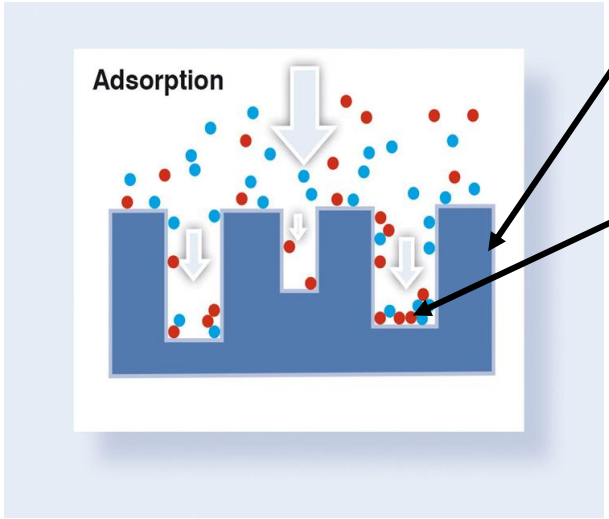
Task 3-1. Uptake of ammonium nitrogen and phosphorous
Task 3-2. Removal of sulphate
Task 3-3. Removal of metals

Background

Adsorption

Process where molecules from an ambient fluid phase are adhered to a solid surface





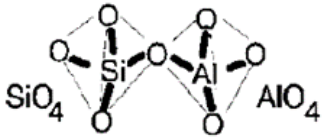
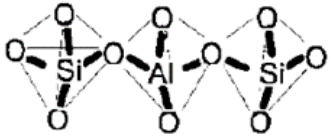
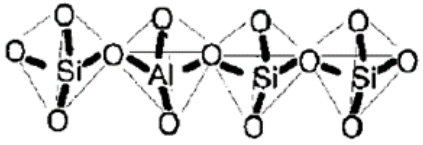
Adsorbent: Material which adsorb atoms, molecules or ions from the solution

Adsorbate: Substance which is adsorbed in the material.

→ Adsorbent can be regenerated e.g. with HCl

Alkali activated materials (AAM), geopolymers

- Joseph Davidovits in 1970's: "mineral polymers resulting from geochemical reactions" → geopolymers
- **Amorphous, three-dimensional, inorganic materials, consisting of aluminosilicate framework (most commonly)**
- Synthesis in alkaline media (NaOH + Na silicate or KOH + K silicate):

Si:Al=1	Poly(sialate) (-Si-O-Al-O-)	
Si:Al=2	Poly(sialate-siloxo) (-Si-O-Al-O-Si-O-)	
Si:Al=3	Poly(sialate-disiloxo) (-Si-O-Al-O-Si-O-Si-O-)	

- Would be expected to have the unique properties as well as zeolite adsorbents

Content

- Biomass-based activated carbon from lignocellulosic material: metals removal
- Slag based geopolymers. Column experiments, Ni adsorption-desorption studies
- Analcime for the uptake of NH_4^+ from synthetic and real agricultural slurry via adsorption

Biomass-based activated carbon from lignocellulosic material: metals removal

Target: To study is it possible to produce biomass-based activated carbon from lignocellulosic material and utilize it for the removal of metals

Experiment:

- Raw material: Lignocellulosic biomass: ubiquitous worldwide, formed as a waste material e.g in sawmills.
  - Spruce sawdust → for the removal cobalt, nickel, and zinc
  - Birch sawdust → for the removal of zinc
- Carbonization and activation of sawdust: single-step process by using 800 °C temperature and steam as a physical activation agent.
- Reference sample: commercial activated carbon
- Batch adsorption experiments: the effect of pH, initial metal concentration, adsorbent dosage and adsorption time was studied
- Desorption studies:
  - Spruce sawdust: with 0.1 M HCl (one cycle)
  - Birch sawdust: with 0.1 M HCl, HNO_3, H_2SO_4 (three cycles)

Characterization of produced samples:

Adsorbent	m^2/g
Birch carbon	860
Spruce carbon	1010

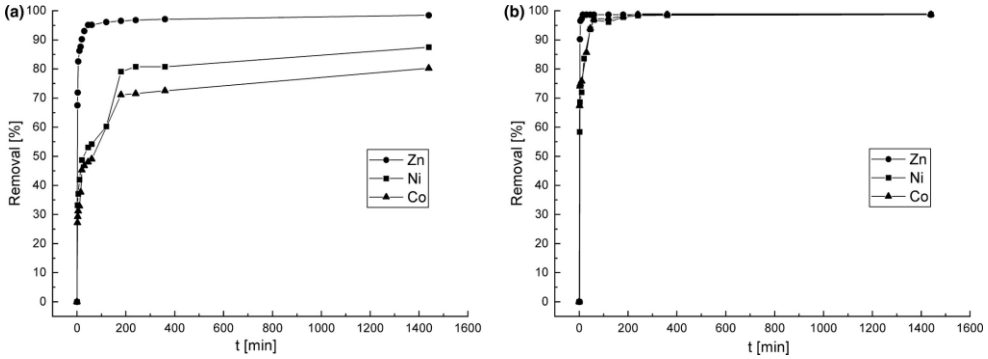
Biomass-based activated carbon from lignocellulosic material: metals removal

Results:

- **Birch carbon**

Optimum adsorption conditions for the zinc removal:

- pH: 4
- initial concentration 75 mg/L
- adsorbent dosage 3 or 5 g/L
- adsorption time 24 h.



Results:

- The maximum experimental adsorption capacity: 21.44 mg/g.

- **Spruce carbon**

Optimum adsorption conditions for the zinc, nickel and cobalt removal:

- pH: 7
- initial concentration 30 mg/L (10 mg/L for each metal)
- adsorbent dosage 10 g/L
- adsorption time 24 h.

Results:

- The order of the maximum adsorption capacity was zinc > nickel > cobalt.
- Zn: 17.2 mg/g, Ni: 6.6 mg/g, Co: 4.5 mg/g

Summary: Regenerable activated carbon towards metals from lignocellulosic biomass was produced in laboratory scale by using steam as a physical activating agent. No harmful chemicals were used during the production.

Tuomikoski S, Kupila R, Romar H, Bergna D, Kangas T, Runtti H, Lassi U (2019) Zinc Adsorption by Activated Carbon Prepared from Lignocellulosic Waste Biomass, Applied sciences, 9 (21), 4583. https://doi.org/10.3390/app9214583
Tuomikoski S, Runtti H, Romar H, Lassi U, Kangas T (2021) Multiple heavy metal removal simultaneously by a biomass-based porous carbon, Water Environment Research, published online 20 January. https://doi.org/10.1002/wer.1514

Slag-based geopolymers
Column experiments, Ni adsorption-desorption studies

Target: to prepare slag based geopolymers and test to remove nickel(II) from aqueous model solutions in fixed-bed column studies.

Experiment:

- Adsorbent: Alkali-activated adsorbents prepared by mixing three different slags from the steel industry:
  - Blast furnace slag (BFS)
  - Ladle slag (LS)
  - Linz–Donawitz converter slag (LD).
- pH: 6 using a phosphate buffer
- Initial Ni concentration: 50 mg/L
- Flow rate: 5 mL/min
- Bed height: 0.5 cm
- Samples: at time intervals of between 5 and 90 min.
- Three adsorption–desorption cycles

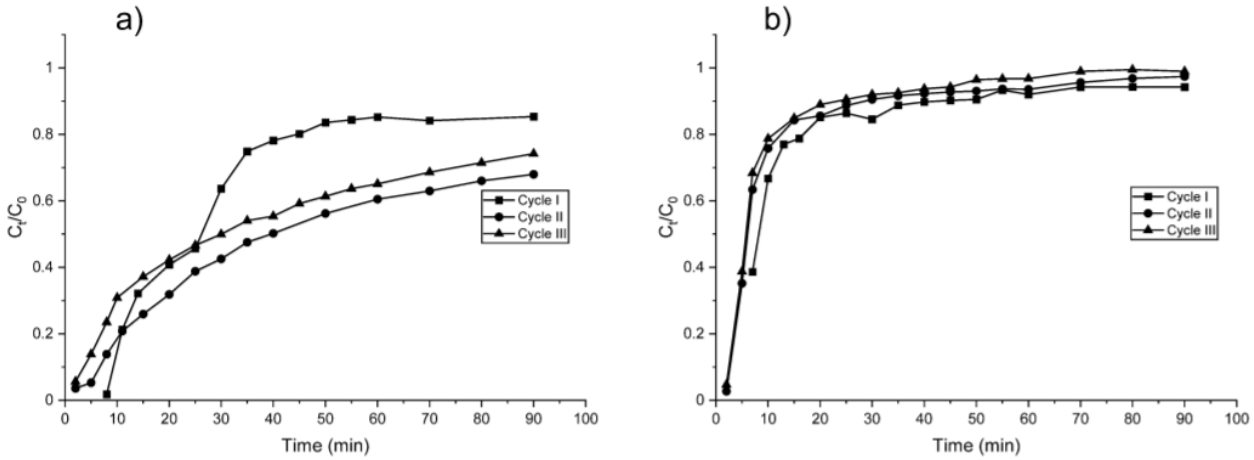
Slag based geopolymers
Column experiments, Ni adsorption-desorption studies

Results:

- Adsorption capacities

- GP(BFS,LS): 2.92 mg/g (1st ads. cycle)

- GP(LD,BFS,LS): 1.34 mg/g (1st ads. cycle)



Summary: Non-traditional slags from steel industry can be used as a raw material for geopolymer production and material was regenerable at least 3 adsorption-desorption cycles.

Sudhararasu E., Tuomikoski S., Runtti H., Hu T., Varila T., Kangas T., Lassi U. (2021) Alkali-Activated Adsorbents from Slags: Column Adsorption and Regeneration Study for Nickel(II) Removal. ChemEngineering, 5, 13. https://doi.org/10.3390/chemengineering5010013

Analcime for the uptake of NH_4^+ from synthetic and real agricultural slurry via adsorption

Target:

To study if analcime could be utilized as soil enhancer

Experiment:

- Raw material: Analcime (from the mining industry)
- Batch adsorption experiments with synthetic solution

  Effect of

  - Adsorbent dosages
  - Effect of initial concentrations of NH_4^+
  - Effect of adsorption time
  - Effect temperature

- Batch adsorption experiments with real agricultural slurry

Analcime for the uptake of NH_4^+ from synthetic and real agricultural slurry via adsorption

Results

Synthetic solution

- Effect of contact time:
  - Adsorption occurred during the first 20 minutes
- Effect of analcime dose:
  - Dose increased → NH_4^+ uptake improved
- Effect of initial NH_4^+ concentration:
  - When increased above 150 mg/L → NH_4^+ uptake decreased
- Effect of temperature:
  - Not clear impact on the NH_4^+ removal, when temperature increased up to 90 °C.
  - When temperature was 120 °C, the NH_4^+ uptake increased considerably → NH_4^+ concentration in analcime: 2.85 m% (ammonioleucite)

Real agricultural slurry:

- NH_4^+ removal percentages were small

Summary:

- Removal mostly caused by adsorption
- Analcime releases NH_4^+ slowly during a long period → analcime could be mixed directly to soil together with NH_4^+ containing fertilizer to reduce ammonia losses

Pesonen, J., Tuomikoski, S., Näppä, J., Prokkola, H., Hu, T., Lassi, U., Runtti, H., Ammonium uptake over analcime and its soil enhancer potential, 8th International Conference on Sustainable Solid Waste Management, 2021.
http://uest.ntua.gr/thessaloniki2021/pdfs/THESSALONIKI_2021_Pesonen_et_al.pdf.

Conclusions

- Regenerable activated carbon towards metals from lignocellulosic biomass was produced in laboratory scale by using steam as a physical activating agent.

- Non-traditional slags from steel industry can be used as a raw material for geopolymer production and material was regenerable at least 3 adsorption-desorption cycles.

- Analcime could be mixed directly to soil together with NH_4^+ containing fertilizer to reduce ammonia losses.

Thank you!

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