UNIVERSITY of OULU
OULUN YLIOPISTO

NITRATE REMOVAL BY MODIFIED LIGNOCELLULOSE

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A FEW WORDS ABOUT OULU

- located 500 km (310 miles) north of capital Helsinki
- 194 000 inhabitants

- University of Oulu
  - founded in 1958, 3rd largest in Finland
  - 16 000 students, 3 000 staff members
  - focus areas
    - biosciences and health
    - information technology
    - cultural identity and interaction
    - environment, natural resources and materials
  - arctic expertise
- Chemical Process Engineering research group

CONTENTS

NITRATE REMOVAL BY MODIFIED LIGNOCELLULOSE

- Hazards of nitrate pollution in waterways
- Nitrate removal methods
- Modified lignocellulose
- Results of sorption studies
    - synthetic solutions
    - industrial wastewaters
- Chemical resistance of resin
- Future plans

NITRATE POLLUTION

- sources: agriculture, sewage, explosives in mining

NO_3^-

- problems:
  - drinking water: formation of carcinogens, fatal to infants
  - water systems: eutrophication
- removal methods
  - biological/chemical treatment
  - electrodialysis
  - reverse osmosis
  - adsorption
  - ion exchange

AIMS AND OBJECTIVES

- biobased platform for anion exchanger preparation (OH-groups)
- lignocellulose + chemical modification
  → quaternary anion exchanger
- what's new: application of resins in industrial processes

1. Chemical modification of lignocellulose
2. Sorption studies on synthetic and industrial wastewaters
3. Desorption and reuse
4. Chemical resistance
5. Disposal of used resin
6. Development of modification method

CHEMICAL MODIFICATION

- pine sawdust, pine, spruce and birch bark and peat
- particle size 90–250 µm
- chemical modification enables anion sorption
  - ➢ epichlorohydrin, triethylamine, ethylenediamine and N,N-dimethylformamide

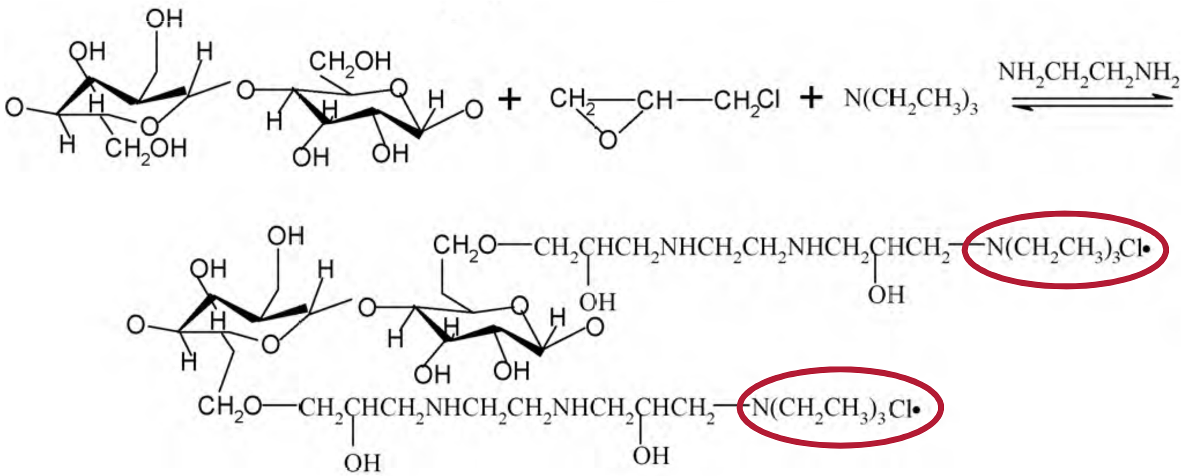
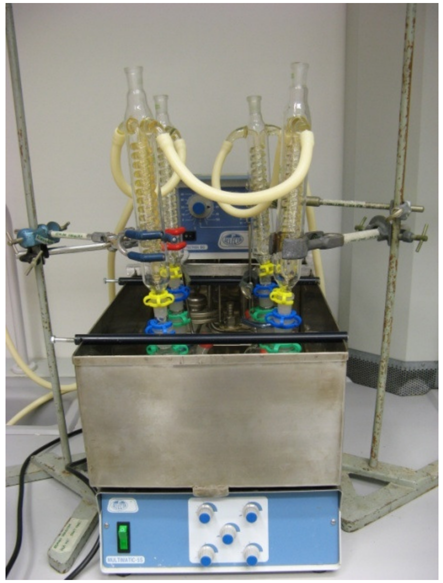


Fig. 1. Schematic presentation of the synthesis of modified lignocellulose. Source: Xu et al., Carbohyd. Polym. 82 (2010), 1212–1218.



PREPARED RESINS

- 2 g of lignocellulose yielded 8—12 g of resin (mass increase 300—500%)
- increased porosity
  - ➢ surface area increased about 1.7—4.9-fold
- nitrogen content increased from ~1% to ~9%
- positive surface charge
  - ➢ quaternary ammonium groups

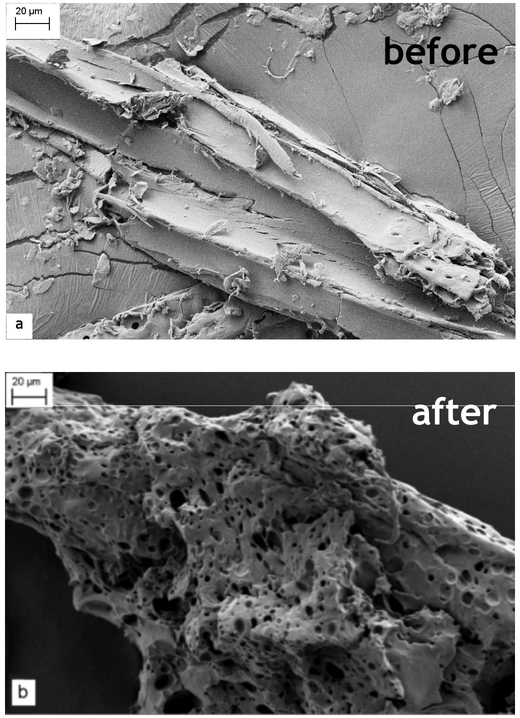


***Fig. 2.** FESEM micrographs of untreated pine sawdust (above) and quaternized pine sawdust (below) at 1000x magnification.*

RESULTS

SYNTHETIC SOLUTIONS – NITRATE

- over 80% nitrate reductions from 30 mg N/l (typical in mining ww)
- maximum binding capacity 30 mg N/g (fig. 3)
- efficient sorption at pH 3–10 (fig. 4)

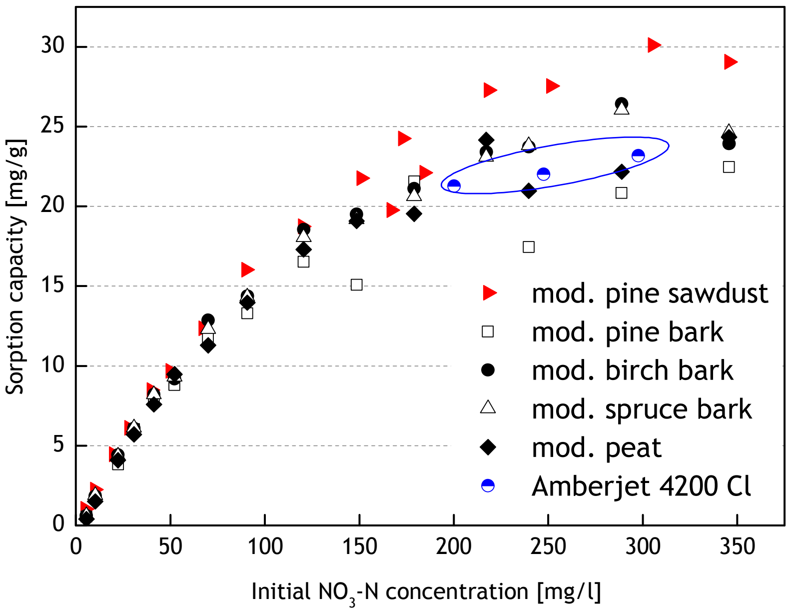


Fig. 3. Maximum nitrate binding capacity. Commercial anion exchange resin, Amberjet 4200 Cl, as a reference. Resin dose 4 g/l.

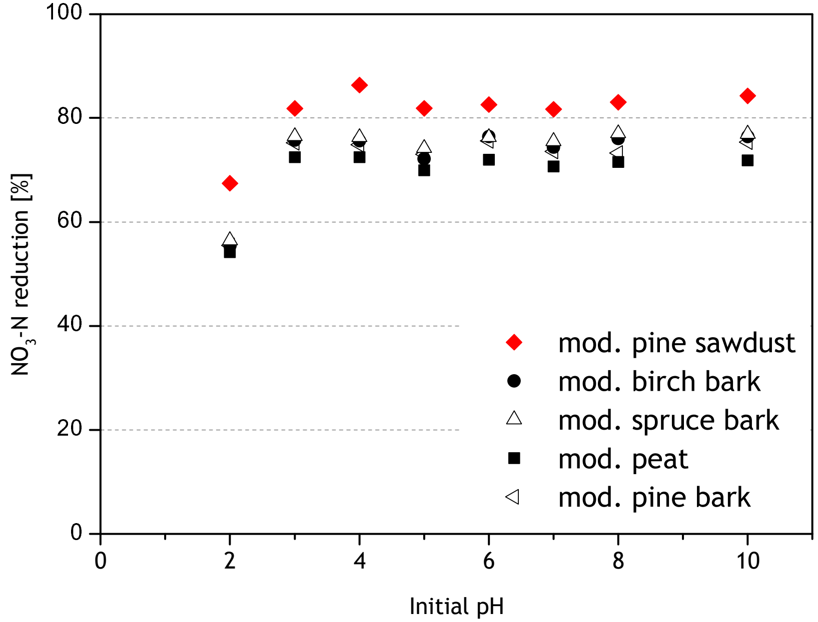


Fig. 4. Effect of pH on nitrate sorption. Initially 30 mg N/l. Resin dose 3 g/l.

RESULTS

SYNTHETIC SOLUTIONS – NITRATE

- wide temperature range for mod. pine sawdust: 5–70 °C
  - applicable for both cold mining ww and warm industrial ww

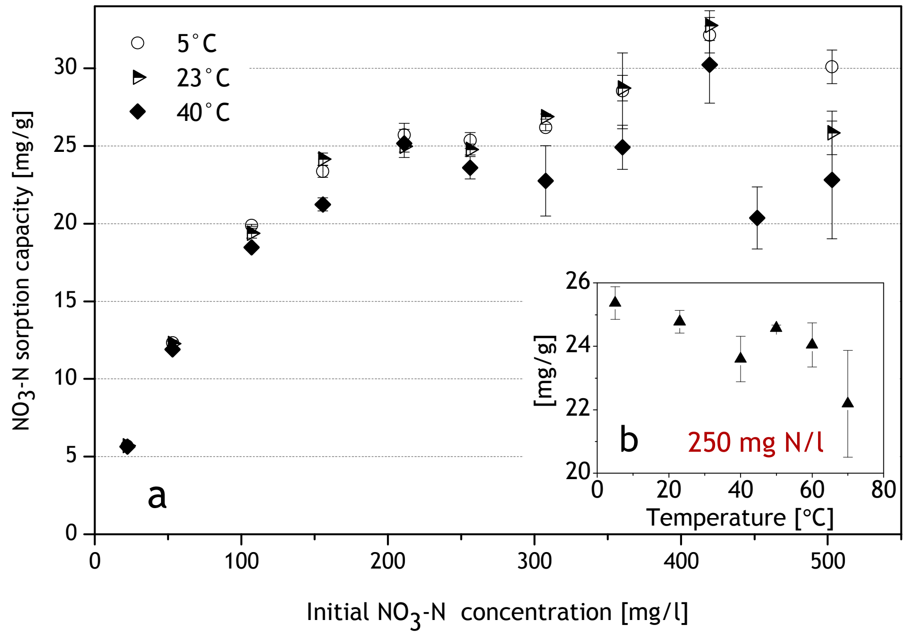
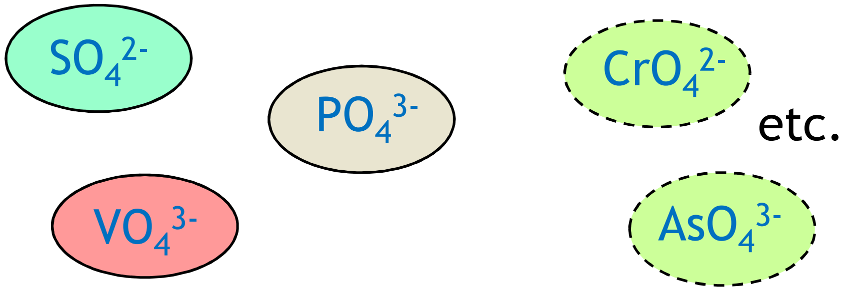


Fig. 5. (a) Nitrate sorption capacity at 5-40 ℃ and (b) comparison of sorption capacities at 5-70 ℃ at 250 mg N/l. Resin dose 3 g/l.

RESULTS

OTHER ANIONS

- sulphate, phosphate
- anionic metals
    - vanadate
    - chromate
    - arsenate



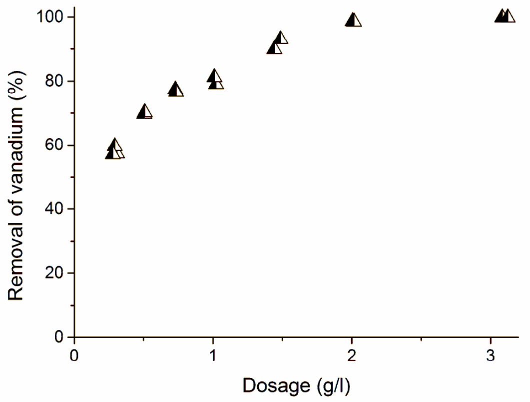


Fig. 6. *Effect of resin dosage on vanadium removal from industrial wastewater. Initially 50.4 mg V/l.*

- high affinity for vanadium(V) (fig. 6)
- sorption capacities
    - ➢ 130 mg V/g for synthetic solution
    - ➢ 103 mg V/g for industrial wastewater (initial conc. 50.4 mg V/l)
- uptake of sulphate and phosphate

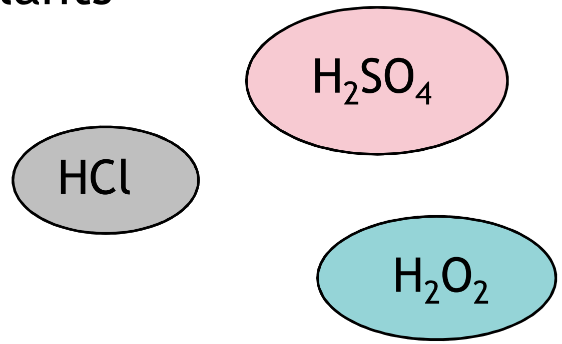
MINING WASTEWATERS

- ongoing sorption tests with mining wastewater
- batch tests
  - effects of dose, contact time and temperature
- column test series
  - 3 sorption-desorption cycles, maintenance cycle, 3 sorption-desorption cycles, maintenance cycle, 2 sorption-desorption cycles
- contaminants:
  - nitrate (9 mg N/l)
  - sulphate (8000 mg/l)
  - Sb, As, Ni, V, Cr, Zn,...
- sorption of cations?

Fig. 7*. Column apparatus for tests on mining wastewater.*

CHEMICAL RESISTANCE OF RESIN

- in real processes, ion exchange resins require maintenance
  - removal of accumulated impurities and foulants by acids or disinfectants



- modified pine sawdust exhibited good resistance towards acids

- some physical degradation with H_2O_2 was observed

FUTURE PLANS

- alternative modification method
  - less hazardous chemicals, cost-efficient process
- disposal of used resin

Publications

Keränen A., Leiviskä T., Gao B.-Y., Hormi O., & Tanskanen J. (2013). *Preparation of novel anion exchangers from pine sawdust and bark, spruce bark, birch bark and peat for the removal of nitrate*. ***Chem. Eng. Sci.***, *98*, 59–68.

Keränen A., Leiviskä T., Hormi O., & Tanskanen J. (under review) *Removal of nitrate by modified pine sawdust: Effects of temperature and co-existing anions.*

Leiviskä T., Keränen A., Vainionpää N., Al Amir J., Hormi O. & Tanskanen J. (accepted) *Vanadium removal from aqueous solution and real wastewater using quaternized pine sawdust.* ***IWA World Water Congress & Exhibition***, Lisbon, Portugal, September 21–26, 2014.

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WATER RESEARCH IN THE CHEMICAL PROCESS ENGINEERING RESEARCH GROUP

- coagulation and flocculation (1), adsorption, ion exchange (2)
- total surface charge (3), zeta potential (4)
- dissolved air flotation (5)
- TOC, BOD, UV absorbancy