UiO : Department of Chemistry
University of Oslo

Removal of Cd from nitrophosphate solutions

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Occurrence of Cd in our food chain via fertilizers

Cadmium (Cd) is a non-nutritive toxic heavy metal

Cd occurs naturally in apatite with sedimentary origin which is often used as a raw material in production of phosphate-based fertilizers

Cd from fertilizers can accumulate in soil and, thus, can be absorbed by crops, which will lead consumers to ingest Cd.

EU ENVI Committee supports Cd limits

On 30 May 2017 the European Parliament Committee on the Environment, Public Health and Food Safety voted to support the use of safer phosphate-based fertilizers for EU countries. The proposed regulations:

- Max 60 mg Cd per 1 kg P_2O_5 from the date of application of the regulation
- Max 40 mg Cd per 1 kg P_2O_5 after 3 years
- Max 20 mg Cd per 1 kg P_2O_5 after 9 years

https://cdn2.hubspot.net/hubfs/2828618/downloads/saferphosphates-environment-committee-news.pdf?t=1497547064952

Our mission

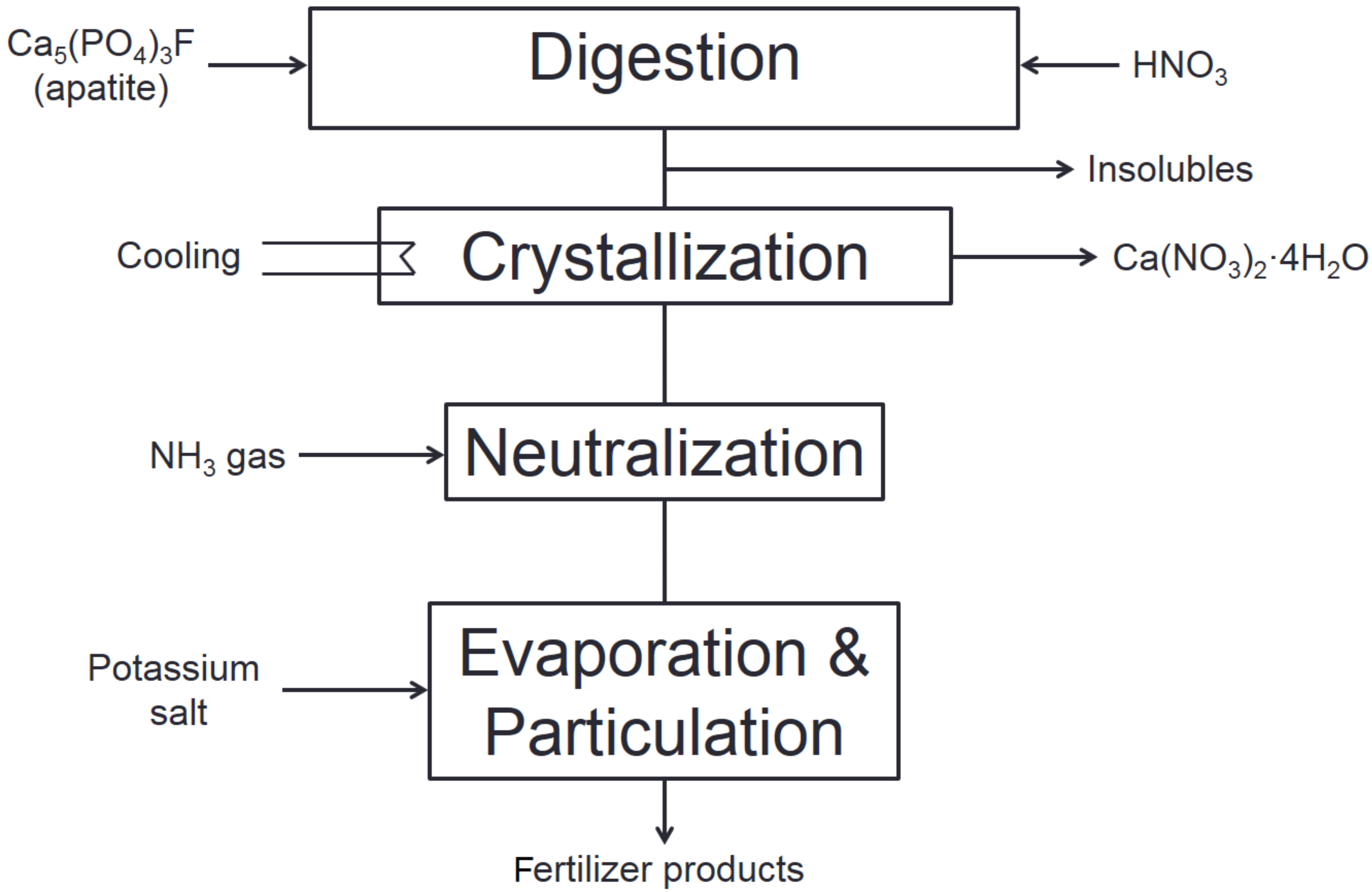
-New regulations enforce decreased use of fertilizers with Cd; and hence diminished crops

-Removing Cd from phosphate-based fertilizers allows for their continuous use, which in turn provides sustained crops;

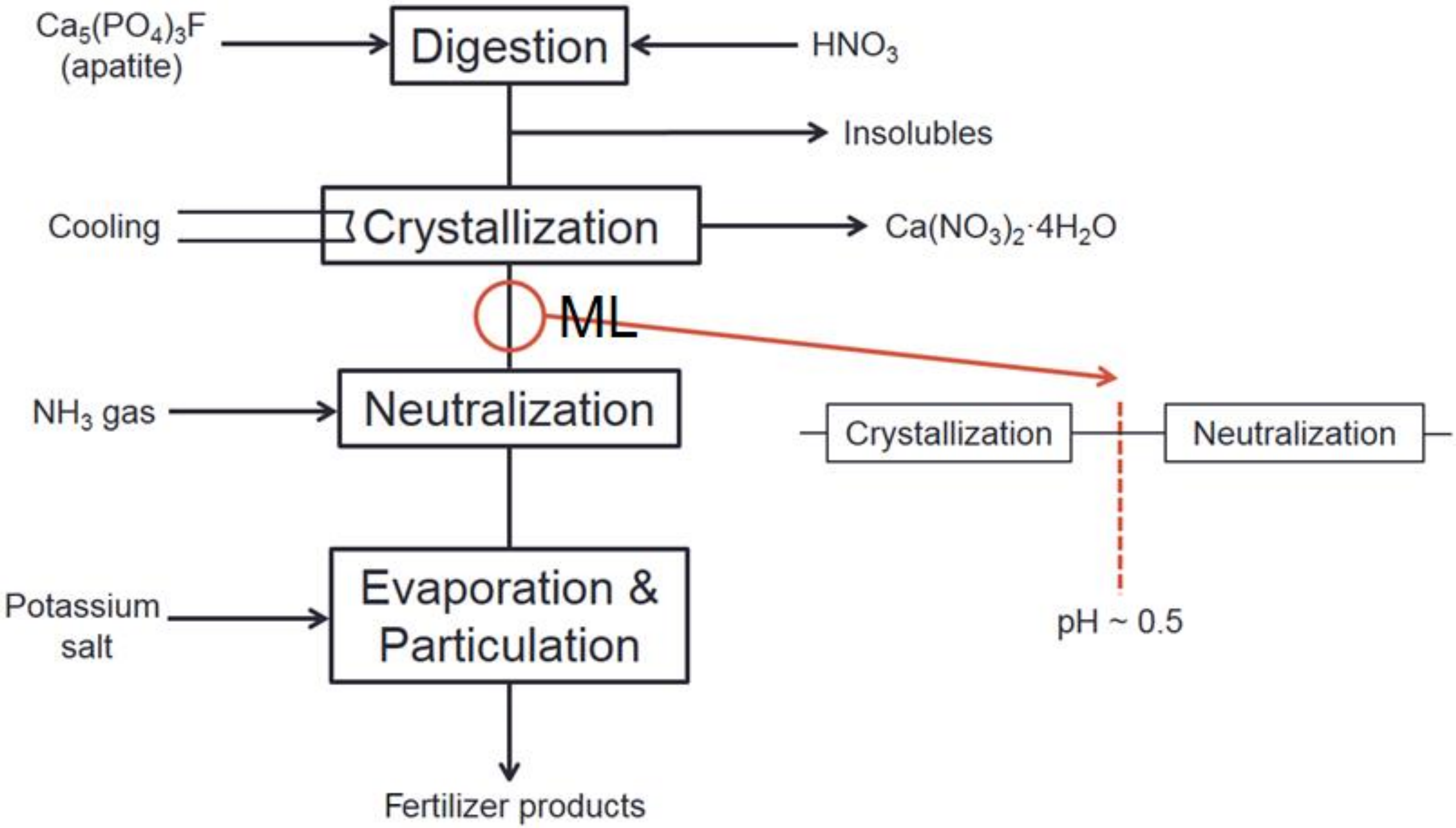
and saves the world from hunger!

«The nitrophosphate process»

Erling Johnson, Odda, Norway, 1927



Cd removal step from mother liquor (ML)



Extraction

Solid phase or liquid phase?

In industry:

2 000 000 ton per year

5 480 ton per day

228 ton per hour

Solid takes up less physical space relative to liquid, and is more feasible at industrial scale

Choice of an adsorbent for ion exchange

Previous work of Alessio Vascon and Alexander Krivokapic showed that impregnated resins can function as efficient ion exchangers in industrial solutions like our ML

Previous impregnation studies

Resins:

- Purolite MN 200 👍
- Amberlite XAD-7 👍
- Amberlite XAD-2 👎

Extractants:

- Cyanex 301 👍
- Kelex 100 👎

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ICP-OES, or ICP-MS, that is the question

TECHNICAL REPORTS: HEAVY METALS IN THE ENVIRONMENT

A Comparison of Reliability of Soil Cadmium Determination by Standard Spectrometric Methods

M. B. McBride*

Inductively coupled plasma emission spectrometry (ICP–OES) is the most common method for determination of soil Cd, yet spectral and matrix interferences affect measurements at the available analytical wavelengths for this metal. This study evaluated the severity of the interference over a range of total soil Cd by comparing ICP–OES and inductively coupled plasma mass spectrometry (ICP–MS) measurements of Cd in acid digests. Using the emission

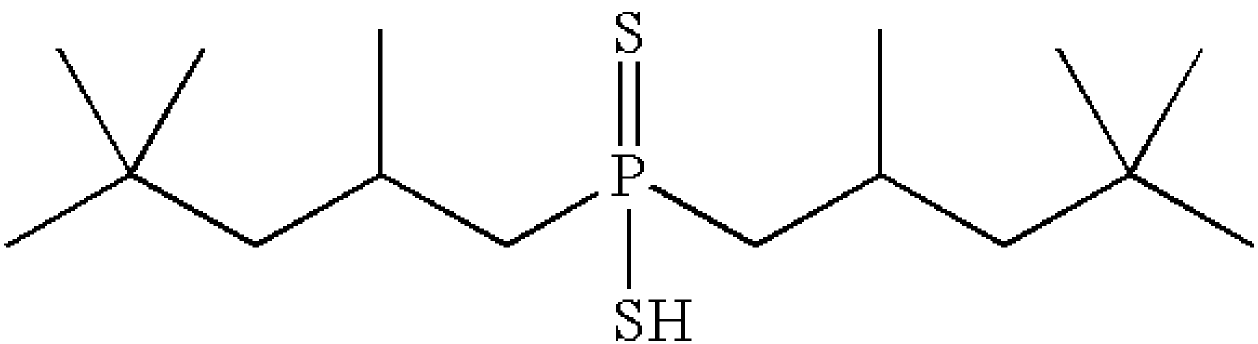
ANALYTICAL ERROR AND BIAS in determ
ments at low levels in soils and plant
frequently unrecognized limitation in quan
sure to toxic metals (McBride, 1998). In fac
are the most difficult of environmental sar
analysis by spectrometric methods such as I
and Boevski, 1999). Inductively coupled pla

J. Environ. Qual. 2011, 40, 1863 -1869

ICP-MS is more accurate technique than ICP-OES for determination of Cd-content in soil samples because of Fe, Ca, and Mg which are also present in apatite

In this presentation

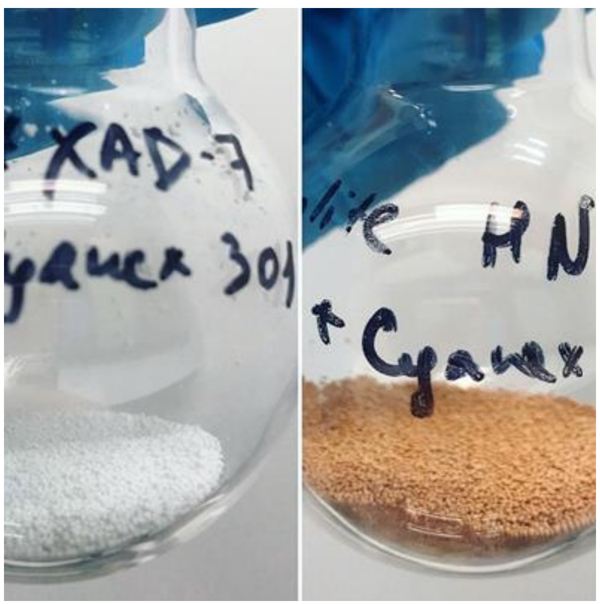
Extraction results of impregnated resins: Amberlite- XAD-4 and XAD-7, and Purolite MN 200 impregnated with extractant Cyanex 301

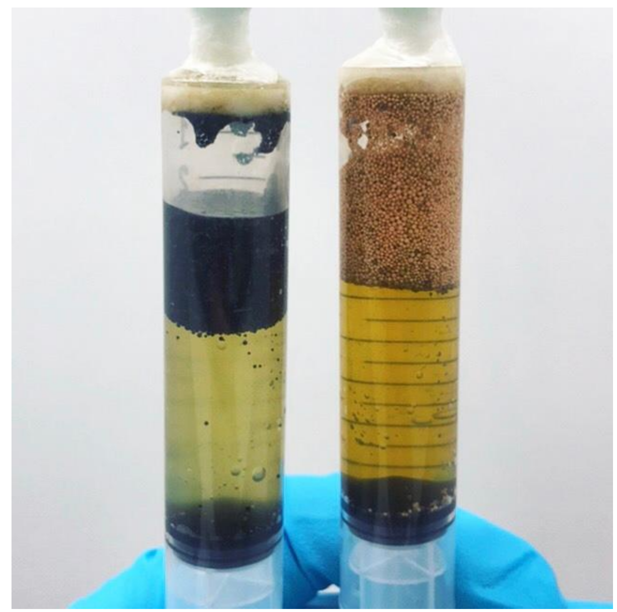


Bis(2,4,4-trimethylpentyl)dithiophosphinic acid (CYANEX 301)

Extraction process

1 g of impregnated resin + 5 mL of ML adjusted to pH ≈ 0.5 → raffinate





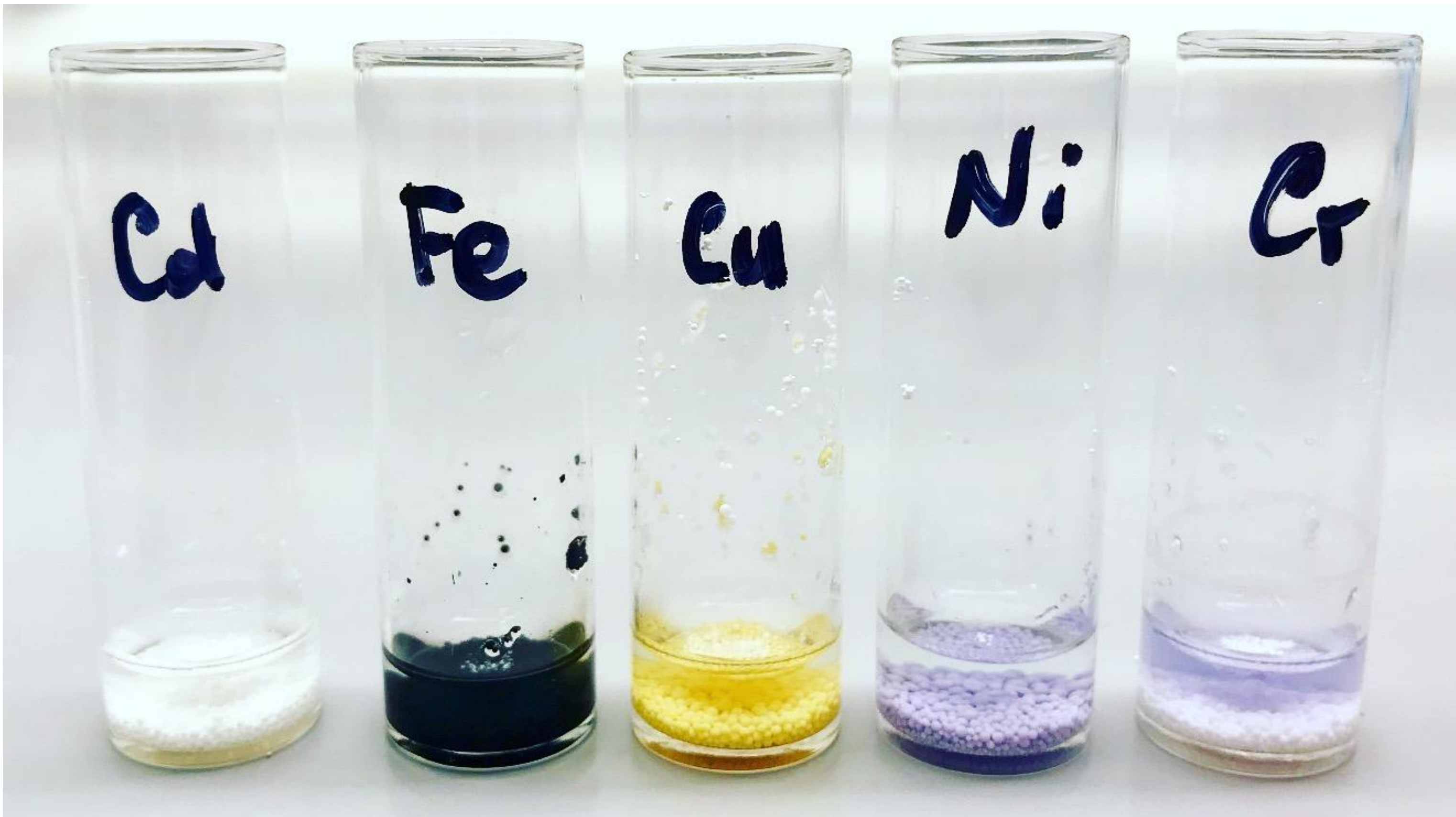
Comparison of impregnated Amberlite-XAD-7 and XAD-4

Concentration, ppm			
Sample	Amberlite		ML
Element	Raffinate XAD-7	Raffinate XAD-4	
Cu	19	21	31
Cd	5	7	11
Ni	19	24	28
Fe	176	517	735
Zn	321	280	379

Comparison of impregnated Purolite MN 200 and Amberlite XAD-7

Concentration, ppm			
Element	Raffinate Purolite MN 200	Raffinate Amberlite XAD-7	ML
Cu	14	13	27
Cd	6	6	11
Ni	24	15	23
Fe	429	192	499
Zn	273	240	314

Why do Amberlite- XAD-7 and XAD-4 turn black?



The winner of metal extraction is…

Amberlite- XAD-4 and XAD-7, and Purolite MN 200: Particle properties

Resin	Description	Particle size, µm	Surface area, m^2/g	Pore diameter, Å
Amberlite XAD-4	Polystyrene divinylbenzene	250 - 841	725	40
Amberlite XAD-7	Non ionic aliphatic acrylic polymer	250 - 841	450	90
Purolite MN 200	Polystyrene divinylbenzene	535 ± 85	900	Micropores ≈ 15, meso- and macropores ≈ 800

https://www.sigmaaldrich.com/chemistry/chemical-synthesis/learning-center/technical-bulletins/al-142/amberlite-amberlyst.html#A2
http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_097e/0901b8038097ef0b.pdf?filepath=liquidseps/pdfs/noreg/177-02319.pdf&fromPage=GetDoc
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http://www.purolite.com/product/mn200

Cd extraction by impregnated Purolite MN 200 and Amberlite XAD-7

Cd standard solution (1000 ppm) in 2.5 % HNO_3 with pH = 0.45 was used for extraction to find out how much Cd is adsorbed by impregnated Purolite MN 200 and Amberlite XAD-7 without other metals present

Cd extraction results

Concentration of Cd, ppm		
Raffinate Purolite MN 200	Raffinate Amberlite XAD-7	Cd standard solution
651	5	1000

How is it possible?

Concentration, ppm			
Element	Raffinate Purolite MN 200	Raffinate Amberlite XAD-7	ML
Cu	14	13	27
Cd	6	6	11
Ni	24	15	23
Fe	429	192	499
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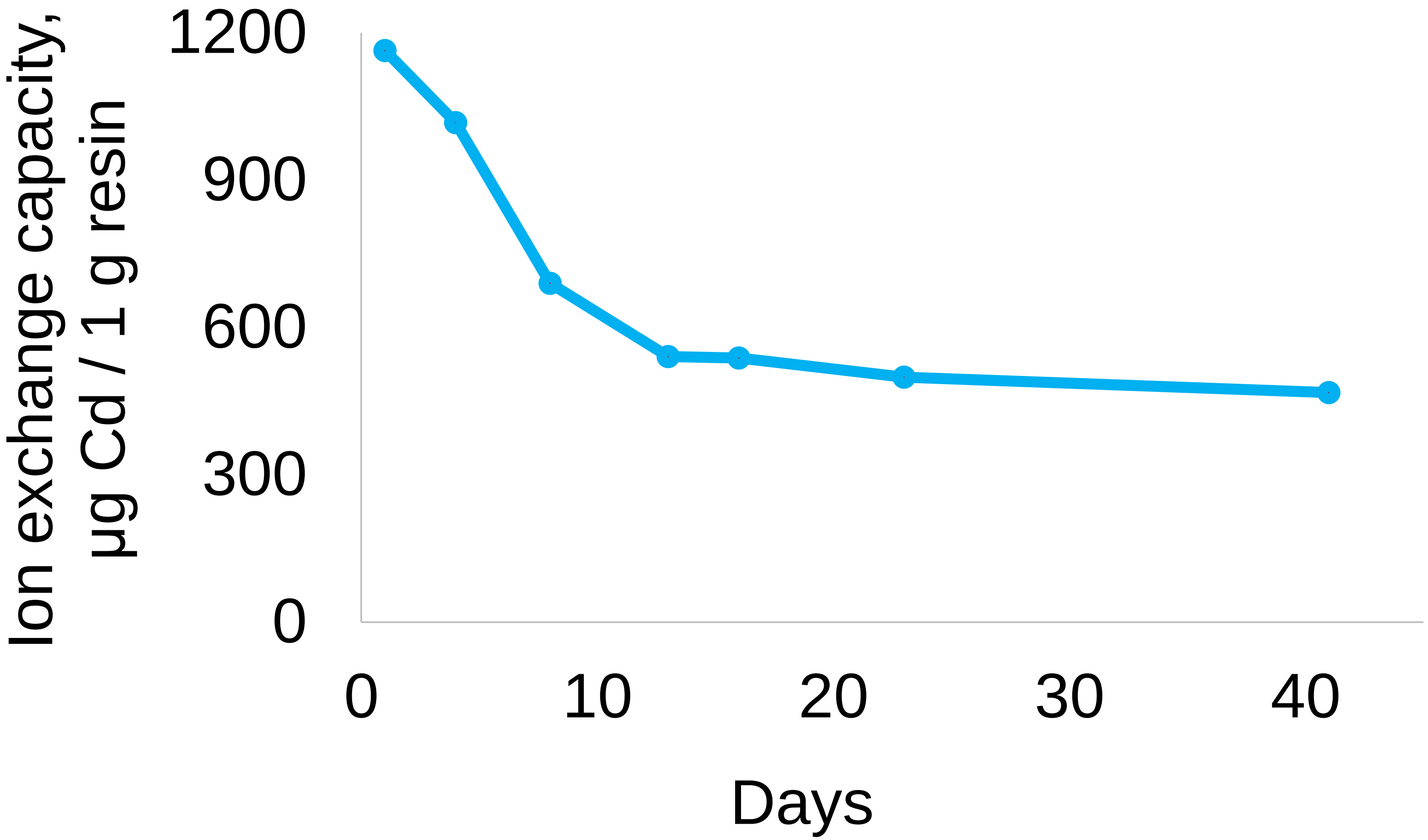
Concentration of Cd, ppm		
Raffinate Purolite MN 200	Raffinate Amberlite XAD-7	Cd std solution
651	5	1000

Stability of Purolite MN 200 ion exchange capacity

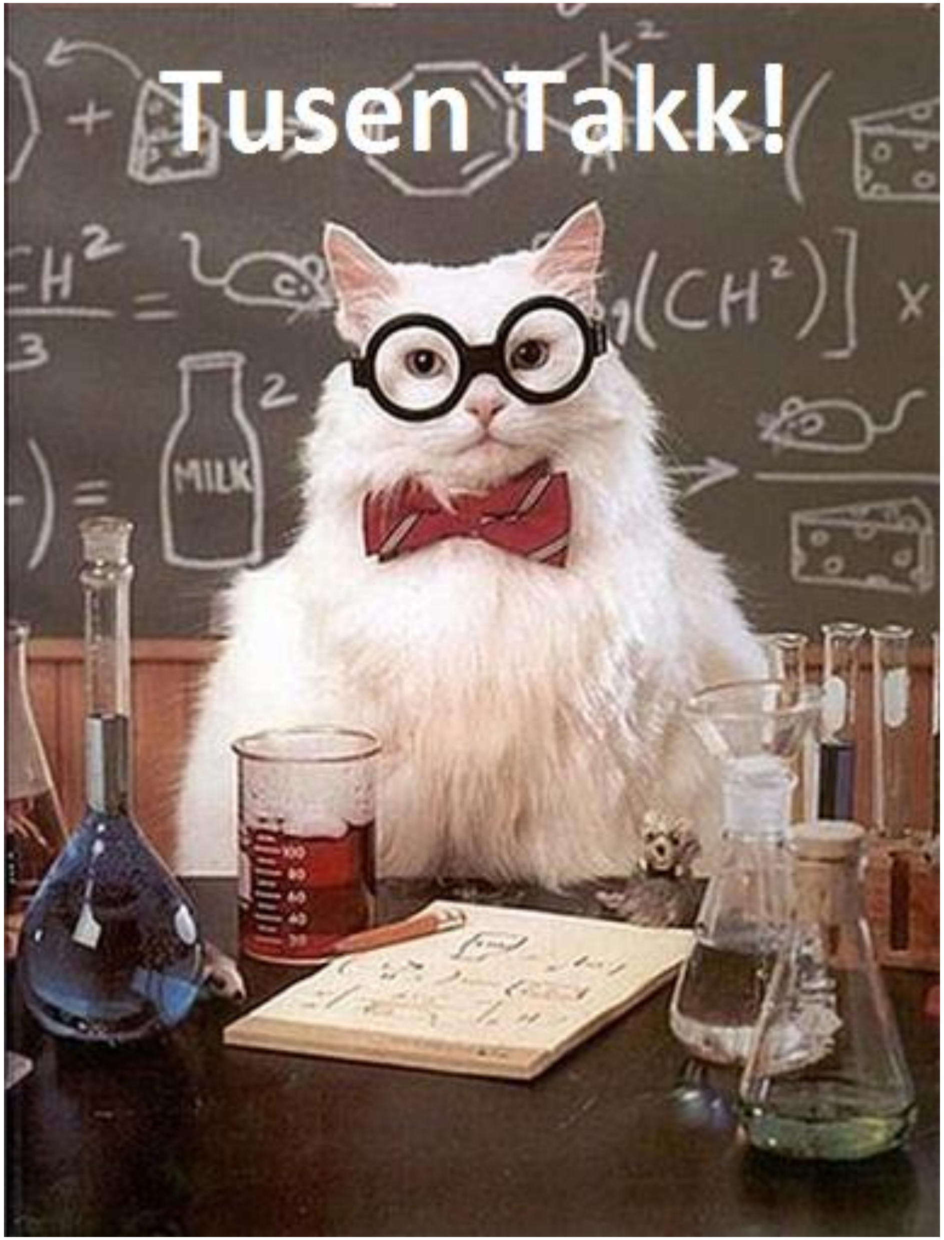


Conclusion

- Our impregnated resins extract Cd from solutions with oxidizing properties
- Purolite MN 200 and Amberlite XAD-7 in combination with Cyanex 301 give the highest Cd extraction yield

Work in progress

- Elution step
- Reuse of impregnated resins


Tusen Takk!
MILK