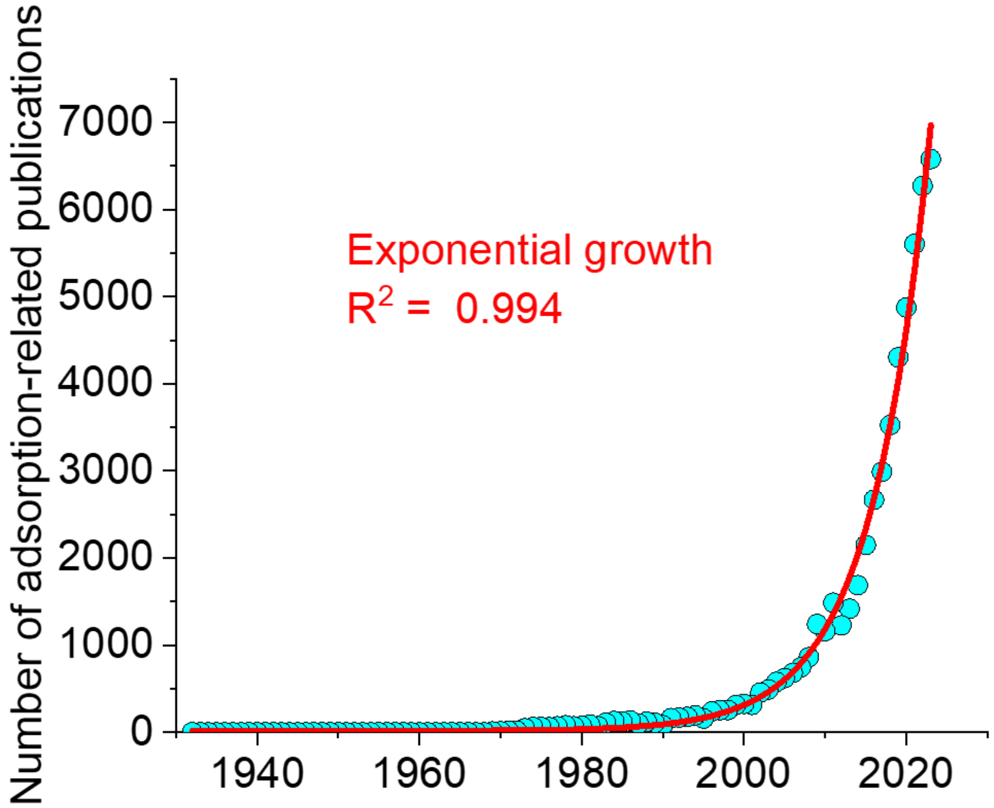
Recent advances in using geopolymers and alkali-activated materials as adsorbents

14.2.2025

Tero Luukkonen, University of Oulu

Use of geopolymers/AAMs as adsorbent binder



Scopus: "(adsorbent OR adsorption) AND ("water treatment" OR "wastewater treatment")"

- Adsorption-related research is increasing exponentially.
- Very few adsorbents end as commercial products.
- One challenge: **how to develop practical granular materials from adsorbent powders?**

Hybrid Advances 5 (2024) 100134

Contents lists available at ScienceDirect

Hybrid Advances

journal homepage: www.journals.elsevier.com/hybrid-advances

Research Article

Porous metakaolin geopolymer as a reactive binder for hydroxyapatite adsorbent granules in dye removal

Aghilas Brahmi[a,b], Salima Ziani[a,c], Salima AitAli[a,c], Bachir Nadir Benkhaoula[d], Yangmei Yu[b], Hania Ahouari[e,f], Hafit Khireddine[c], Tero Luukkonen[b,g,*]

Chemical Engineering Research and Design 212 (2024) 485–492

Contents lists available at ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

Regeneration of metal-containing alkali-activated adsorbent granules from a field experiment

Nusrat Kabir[a], Jenna Finnilä[b], Johanna Laukkanen[c], Tero Luukkonen[a,d,*]

High-shear granulation:

Metakaolin + sodium metasilicate powder (SiO_2/Na_2O = 0.9) + hydroxyapatite

\+

H_2O_2 solution

Pan granulation:

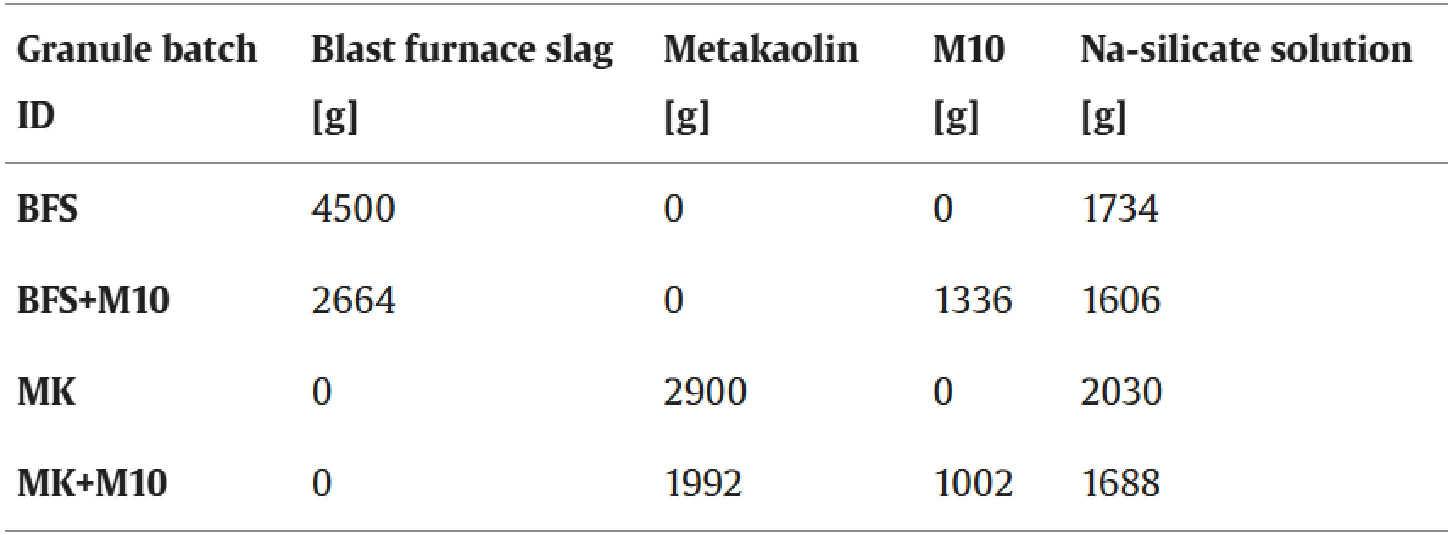
Metakaolin/BFS + M10 adsorbent ($MgCO_3/MgO/Mg$ silicate)

\+

Sodium silicate solution (SiO_2/Na_2O = 1.2)

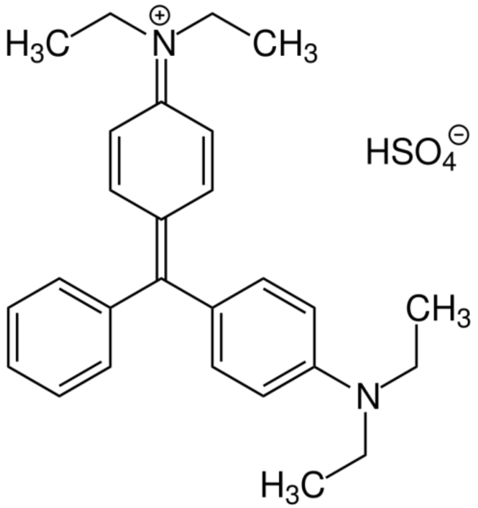
Granule compositions

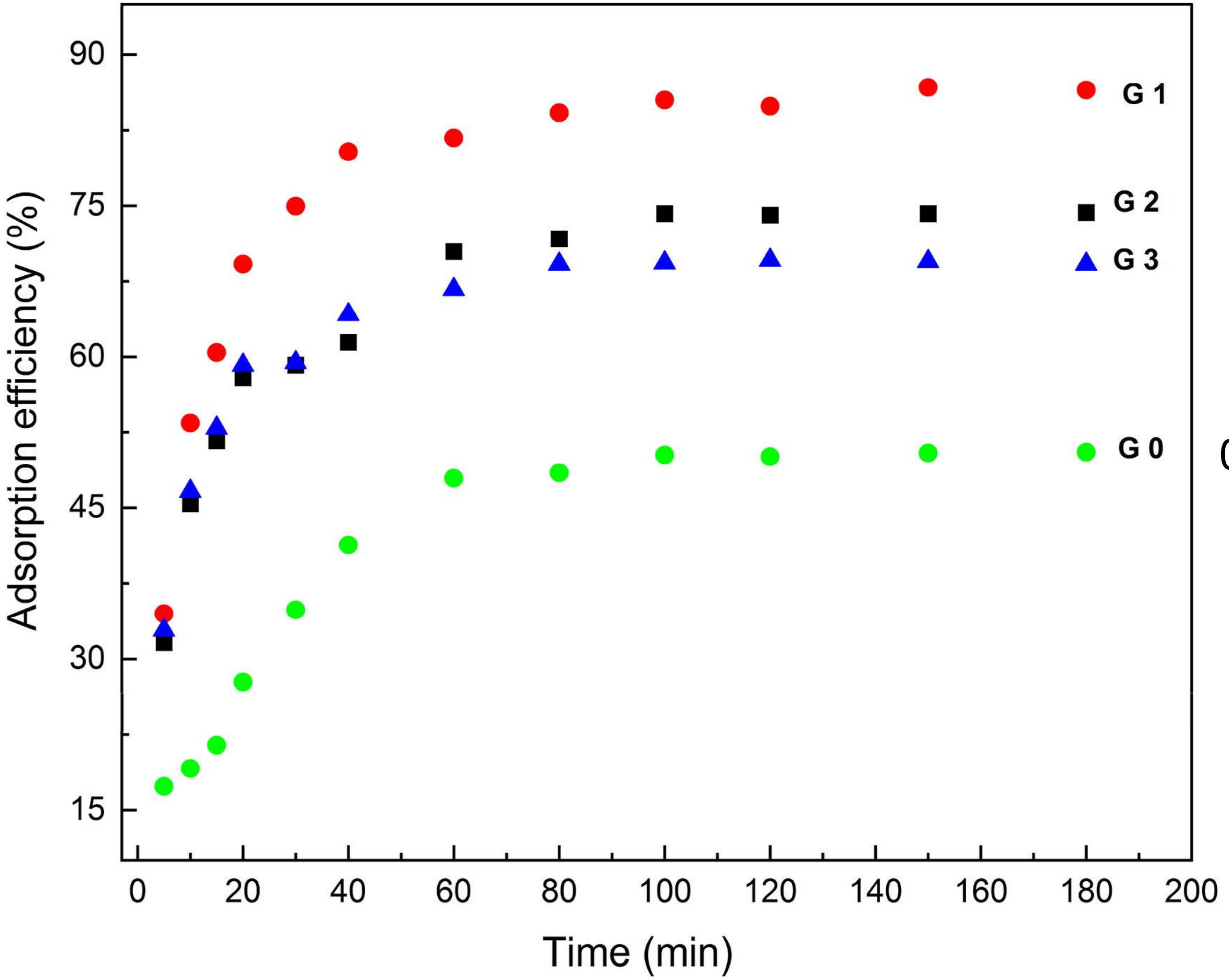
- **Hydroxyapatite granules:** Metakaolin (28.0 wt%) + sodium metasilicate powder (14.6 wt%) + hydroxyapatite (57.4 wt%) + H_2O_2 solution (dosing amount 18 wt% of solids)
- **M10 granules:**



Granule batch ID	Blast furnace slag [g]	Metakaolin [g]	M10 [g]	Na-silicate solution [g]
BFS	4500	0	0	1734
BFS+M10	2664	0	1336	1606
MK	0	2900	0	2030
MK+M10	0	1992	1002	1688

Hydroxyapatite granules





5 wt% concentration H_2O_2

7.5 wt% concentration H_2O_2

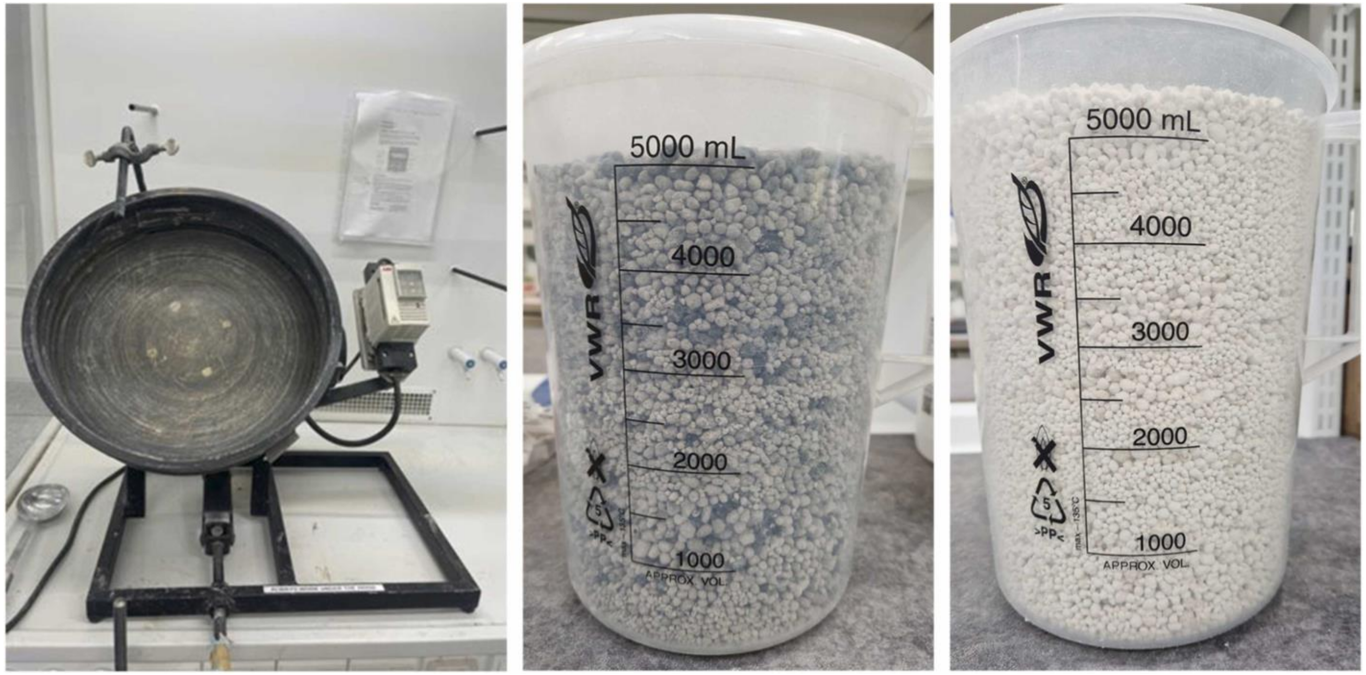
10 wt% concentration H_2O_2

0 wt% concentration H_2O_2

Conditions: [dye] = 15 mg/L, adsorbent dose = 2 g/L, pH = 5, granule diameter = 2 mm, agitation speed = 350 rpm, and T = 25 C

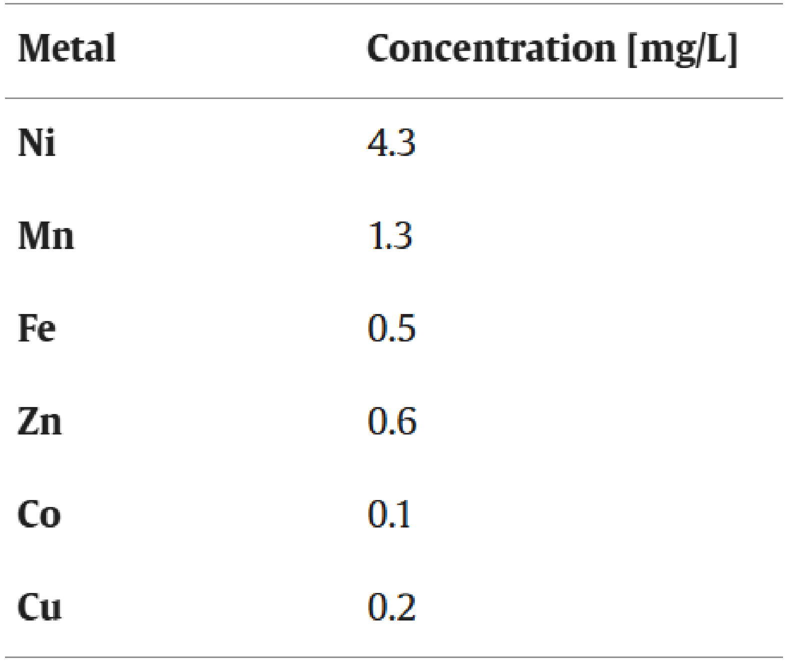
M10 granules

- On site mine water treatment
- 3 adsorption cycles
- Regeneration with 0.3 M HNO_3 (L/S = 10, 3 h)
- Granule amount: 5 L (cycle 1), 0.18 L (cycles 2 & 3)
- Contact time: 5 – 30 min (cycle 1), 30 min (cycles 2-3)

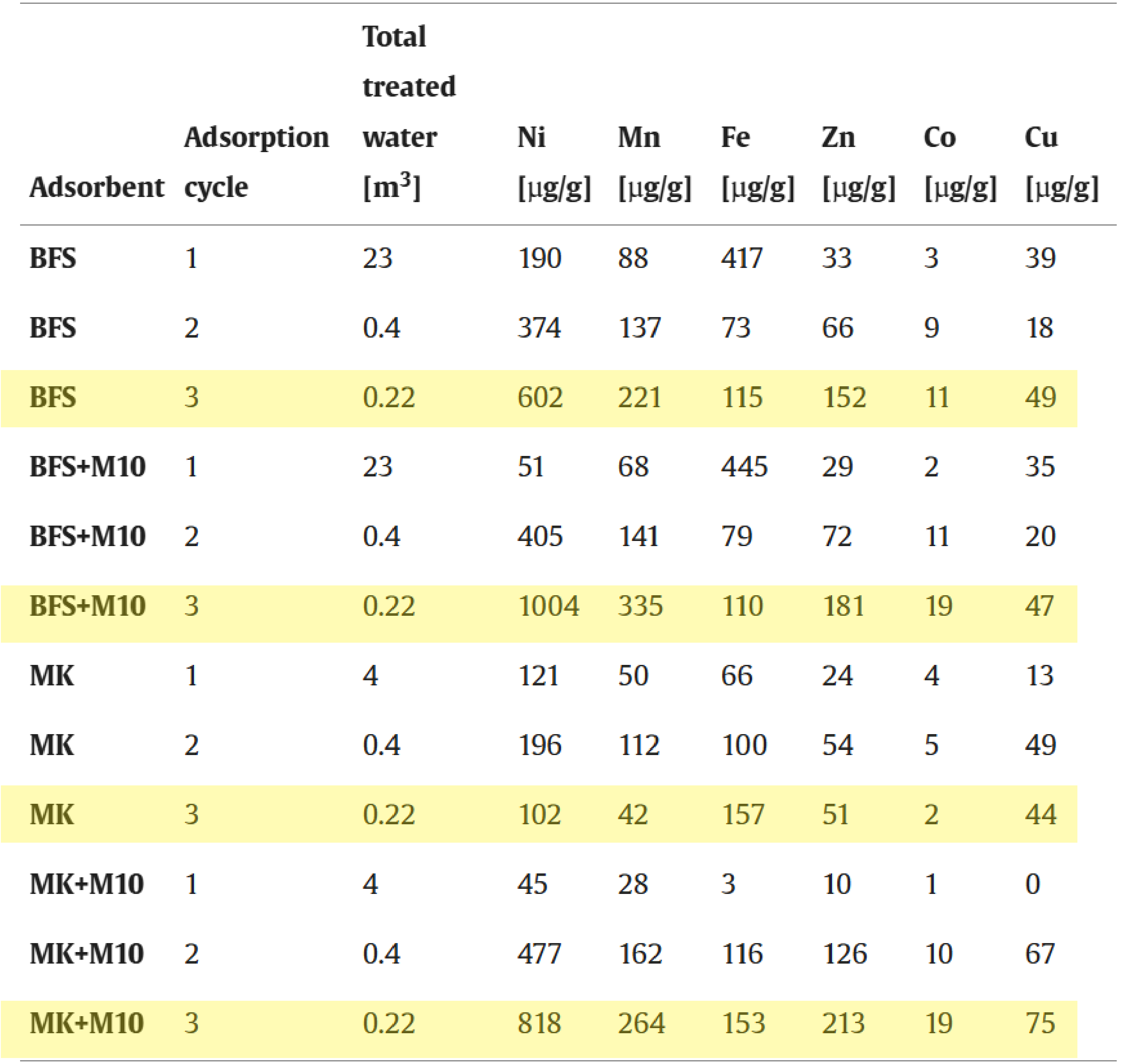


M10 granules

Closed mine, waste rock storage area seepage water (pH = 5.2)



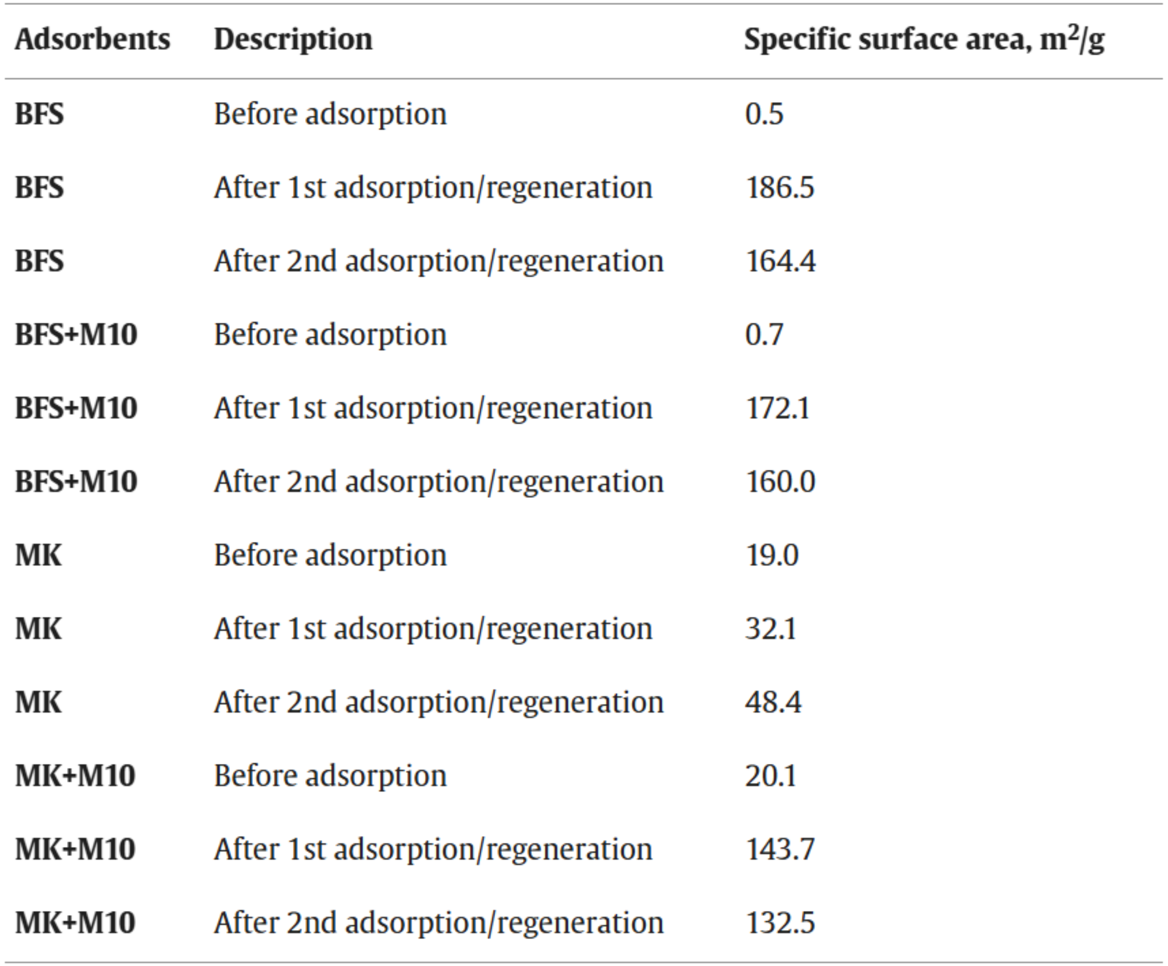
Metal	Concentration [mg/L]
Ni	4.3
Mn	1.3
Fe	0.5
Zn	0.6
Co	0.1
Cu	0.2



Adsorbent	Adsorption cycle	Total treated water [m^3]	Ni [µg/g]	Mn [µg/g]	Fe [µg/g]	Zn [µg/g]	Co [µg/g]	Cu [µg/g]
BFS	1	23	190	88	417	33	3	39
BFS	2	0.4	374	137	73	66	9	18
BFS	3	0.22	602	221	115	152	11	49
BFS+M10	1	23	51	68	445	29	2	35
BFS+M10	2	0.4	405	141	79	72	11	20
BFS+M10	3	0.22	1004	335	110	181	19	47
MK	1	4	121	50	66	24	4	13
MK	2	0.4	196	112	100	54	5	49
MK	3	0.22	102	42	157	51	2	44
MK+M10	1	4	45	28	3	10	1	0
MK+M10	2	0.4	477	162	116	126	10	67
MK+M10	3	0.22	818	264	153	213	19	75

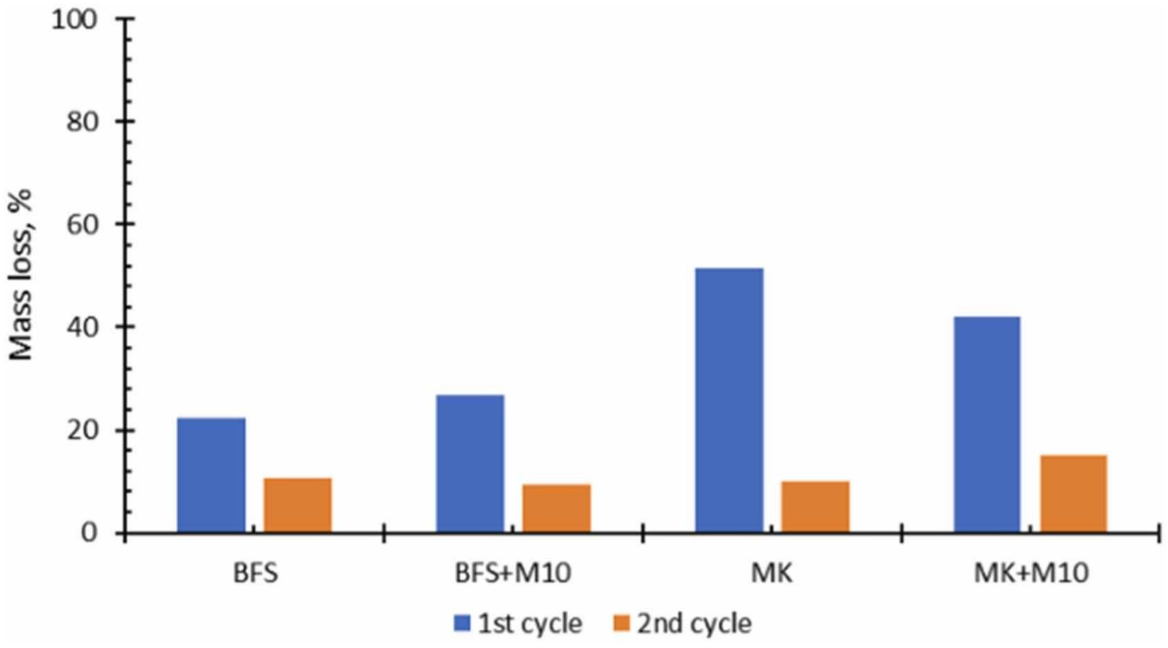
Regeneration: 0.3 M HNO_3

Granules after adsorption



Adsorbents	Description	Specific surface area, m^2/g
BFS	Before adsorption	0.5
BFS	After 1st adsorption/regeneration	186.5
BFS	After 2nd adsorption/regeneration	164.4
BFS+M10	Before adsorption	0.7
BFS+M10	After 1st adsorption/regeneration	172.1
BFS+M10	After 2nd adsorption/regeneration	160.0
MK	Before adsorption	19.0
MK	After 1st adsorption/regeneration	32.1
MK	After 2nd adsorption/regeneration	48.4
MK+M10	Before adsorption	20.1
MK+M10	After 1st adsorption/regeneration	143.7
MK+M10	After 2nd adsorption/regeneration	132.5

- Regeneration caused mass loss:



Microplastics separation

Separation and Purification Technology 339 (2024) 126709

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Separation of microplastics from water using superhydrophobic silane-coupling-agent-modified geopolymer foam

M.A.H. Bhuyan [a,b,c,*], R. Busquets [b,c], L.C. Campos [c], T. Luukkonen [a,d]

[a] *Fibre and Particle Engineering Research Unit, University of Oulu, Erkki Koiso-Kanttilan Katu, Oulu 90014, Finland*
[b] *Department of Chemical and Pharmaceutical Sciences, Kingston University, Penrhyn Road, Kingston Upon Thames KT1 2EE, United Kingdom*
[c] *Civil Environmental & Geomatic Engineering, University College London, Gower Street, London WC1E6BT, United Kingdom*
[d] *Department of Chemical Engineering Technology, University of Johannesburg, P.O Box 17011, Doornfontein 2088, South Africa*

ARTICLE INFO

Keywords:
Geopolymer
Hydrophobicity
Microplastics
Silane coupling agent
Wastewater treatment

ABSTRACT

Microplastics are a topical environmental problem that requires urgent solutions. They are ubiquitously present in various wastewaters and are discharged into aquatic environments because of difficulties in their removal. In this study, a novel filtration medium, superhydrophobic geopolymer foam, was prepared and investigated for the separation of microplastics from water. The foam was prepared using metakaolin, sodium silicate, sodium hydroxide, hydrogen peroxide, and Triton X-100 surfactant as raw materials and superhydrophobized with a silane coupling agent, triethoxy(octyl)silane. The purpose of the superhydrophobization was to improve the attachment of hydrophobic microplastic particles to the foam surface via chemical interactions. The modified geopolymer foam exhibited a water contact angle of 152°, and the presence of octyl chains on its surface was confirmed using Fourier transform infrared and X-ray photoelectron spectroscopies. When applied as a filter, the modified foam separated 53-63-µm sized polyethylene microspheres with ~99 % removal efficiency, and no change in its separation efficiency was observed for ~200 bed volumes of treated water. A comparison with an unmodified foam filter confirmed that the removal mechanism was not based on physical separation at higher flow rates, because the performance of the unmodified foam began to degrade after treating ~5 bed volumes of wastewater. The performance of the modified foam was also validated with laundry washing effluents (particle size of microplastics varied roughly within 2–2000 µm), achieving ~84 % separation efficiency for ~50 bed volumes of wastewater. This study provides proof of concept of using superhydrophobic geopolymers as efficient, easy-to-prepare, and potentially low-cost separation media for microplastics from water effluents.

1. Introduction

The global production of plastics was estimated to be 391 million metric tons in 2021 [1]. A significant fraction of this amount ends up in the aquatic environment, where weathering eventually degrades plastic items into microplastics (MPs, particles with a diameter between 1 µm and 5 mm) and subsequently nanoplastics (NPs, particles with a diameter between 1 nm and 1 µm) [2]. Some important direct discharge sources of MPs/NPs include industrial and municipal wastewater and tire or bitumen wear [3–7]. It has been estimated that approximately 2.3 million tons of plastic waste float in oceans [8].

Conventional wastewater treatment processes (such as coagulation and flocculation) can separate more than 90 % of the MPs in raw wastewater [9–11]. However, the amount of MPs in treated wastewater has been estimated to be on the order of 10^{11}–10^{12} particles per day from a single wastewater treatment plant (WWTP) [12,13]. The estimated MP/NP amounts are highly uncertain, especially when data from different measurements are combined [14]. The presence of MPs is ecotoxicologically alarming because most fish are contaminated by them in the areas affected by WWTPs [15,16]. MP ingestion can have several negative impacts on aquatic organisms, including a reduction in growth rate, difficulty in digestion, and intestinal abrasion [17]. MPs can also adsorb persistent organic pollutants, pathogenic microbes, and toxic metals on their surfaces, acting as carriers of these pollutants into aquatic organisms and releasing them into the digestive system [18].

To improve wastewater treatment for MP separation, various approaches are studied. For instance, conventional pressure-driven membrane separation processes, such as microfiltration, ultrafiltration, or

---

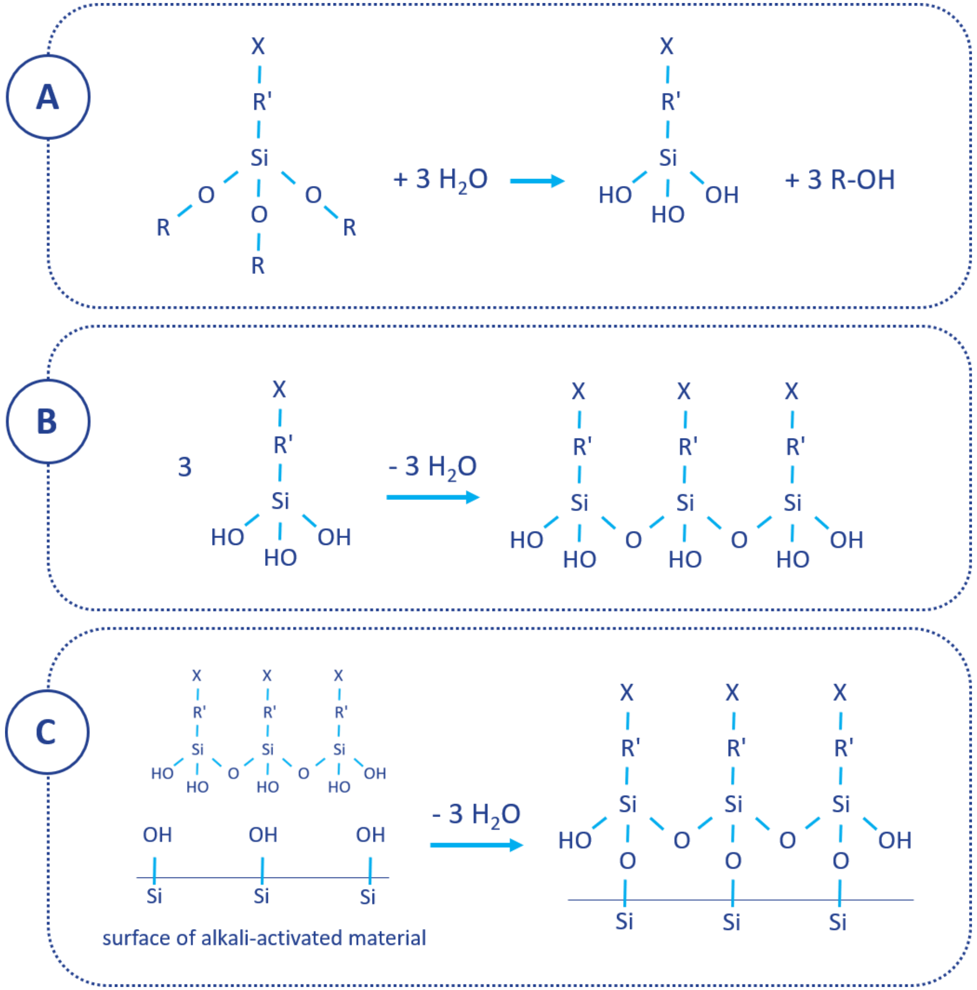
[*] Corresponding author.
E-mail address: mohammad.bhuyan@oulu.fi (M.A.H. Bhuyan).

https://doi.org/10.1016/j.seppur.2024.126709
Received 19 December 2023; Received in revised form 25 January 2024; Accepted 5 February 2024

Microplastics: diameter of 1 µm to 5 mm
Nanoplastics: diameter of 1 nm and 1 µm

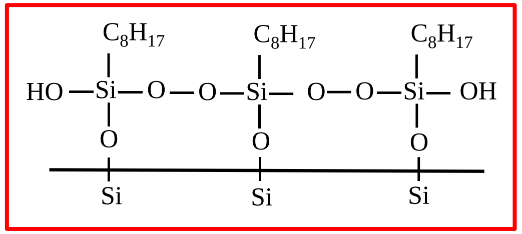
Unmodified geopolymer surface
→ hydrophilic

PE microspheres
45–50 µm

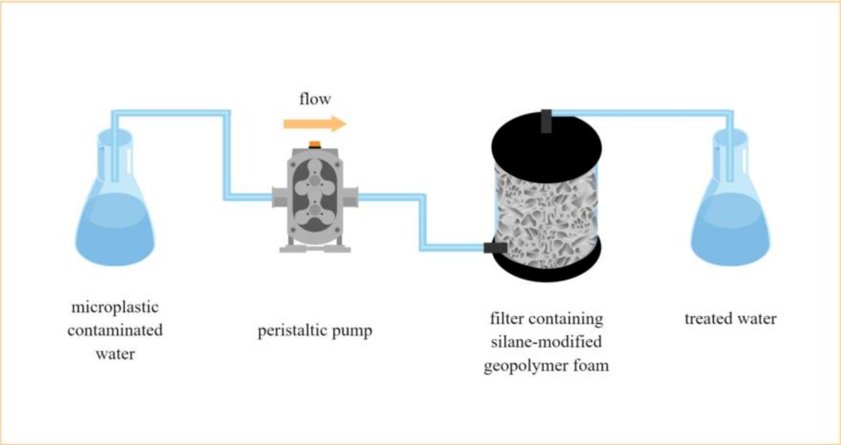


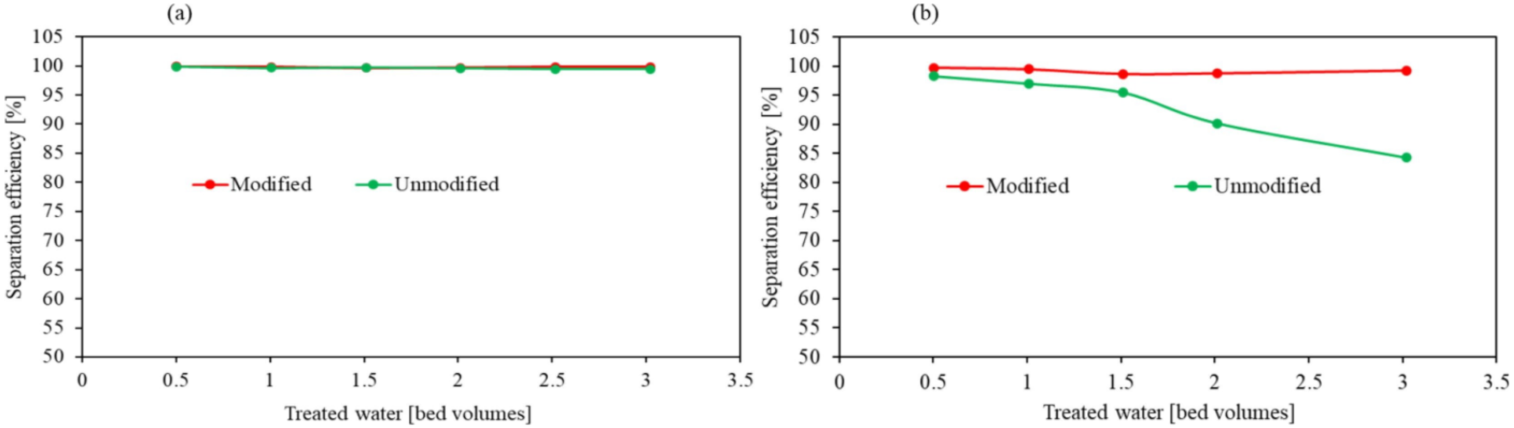
Luukkonen, T. (2022). Surface chemistry of alkali-activated materials and how to modify it. In Alkali-Activated Materials in Environmental Technology Applications (pp. 113-140). Woodhead Publishing.

Geopolymer surface modified with triethoxy(octyl)silane
→ superhydrophobic
(water contact angle 153 °)

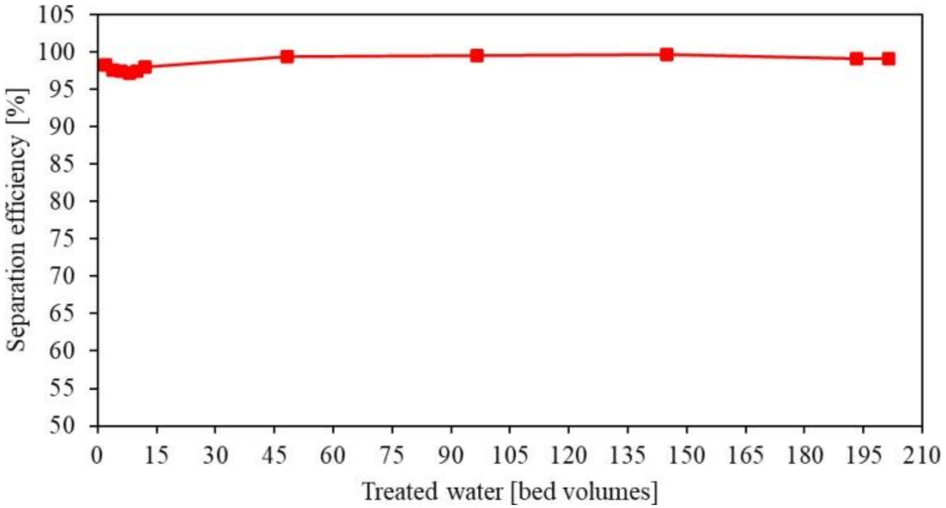


XPS → Si-C bond

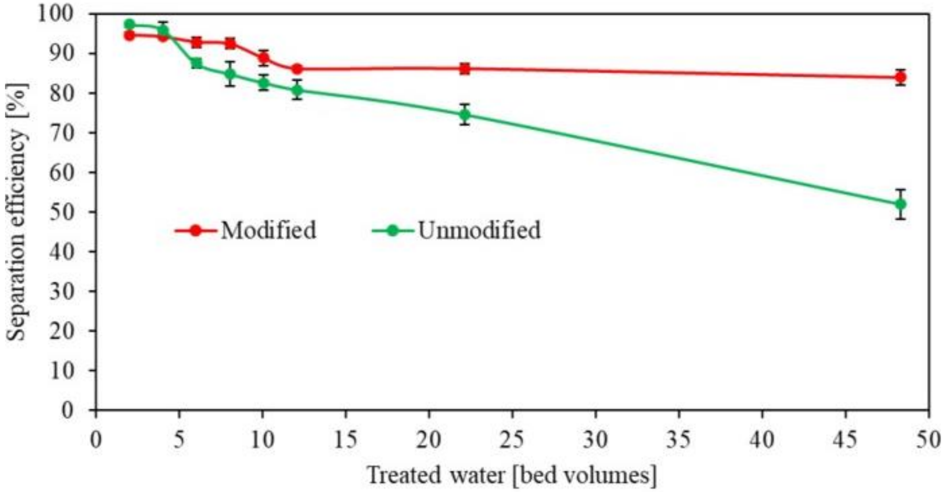




Synthetic wastewater (5 mg/L of PE = 65000 particles per L)
(a) Flow rate = 3 mL/min (contact time ≈ 50 min)
(b) Flow rate = 5 mL/min (contact time ≈ 30 min)



Synthetic wastewater
Flow rate = 5 mL/min (contact time ≈ 30 min)



Laundry wastewater (9000 MPs/L, 2 µm–2 mm)
Flowrate 5 mL/min

Acknowledgements

Funded by
the European Union

PhD Researchers:

Mohammad Bhuyan

Postdoc

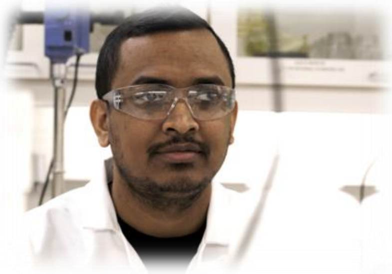
Caroline (Yangmei) Yu

Sima Kamali

Mehedi Rabbil

Marco Fazzini

Exchange from
Uni. Bologna



Faysal Hossain

Akram Hossain

Somayeh Karandish Marvasti

Teknologiateollisuuden
100-vuotissäätiö

BUSINESS
FINLAND

Research Council
of Finland

UNIVERSITY
OF OULU