

Reactive nanoadsorbents for environmental cleanup: testing disposal sustainability

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Nano-enabled solutions are continuously being explored as an efficient and sustainable option for water clean up. Laboratory-synthesised nano-adsorbents efficiently remove heavy metal cations and oxyanions from water. However, their high contaminant sorption capacity questions their safe disposal and long-term environmental fate after disposal. We have explored different nanocomposites with varying contaminant removal mechanisms for their possible fate in soils and landfill conditions.

Ongoing research efforts are dedicated to finding strong candidates for sorption-assisted techniques in the treatment of contaminated waters. Several conventional and advanced adsorbents satisfy the bottom line sustainability criteria of being scalable, efficient, economic, and environmentally friendly. Most of the conventional and advanced adsorbents are being continuously explored for real world deployment ranging from activated carbon filters in home reverse osmosis (RO) purifiers, granulated activated carbon beds in water treatment plants, to recently deployed nano-adsorbents such as iron oxyhydroxides (FeOOH) for arsenic, nano

alumina fibres for particulates, carbon nanotube (CNT)-based membranes for desalination, zeolites for removal of ammonia and heavy metals etc¹.

High surface area and reactivity of nano-adsorbents lead to their high contaminant removal capacities, suggesting huge contaminant loads at their saturation level. This further leads to the next environmental concern, *i.e.* the fate of contaminant-sorbed adsorbent wastes in the environment and possible sustainable disposal pathways. Concerns regarding the disposal include:

(i) desorption of sorbed contaminants, (ii) dissolution of the adsorbent, (iii) release of constituent metal ions from the adsorbents, and (iv) migration of toxicants in the subsurface environment.

Disposal of nano-adsorbents in soils and landfills leads to their interaction with sunlight, air and water, including slightly acidic rainwater, and organic acids-rich soil pore water or landfill leachate waters. Organic compounds can form complexes with toxic metals, leading to their increased solubility and migration in the subsurface environment². At the same time, organic acids released by plants can also dissolve and leach contaminants from the adsorbent wastes posing the risk of their plant uptake³. Surface characteristics, composition, nature of adsorbent-adsorbate interaction, binding strength, and mechanisms are some of the factors that can play a crucial role in deciding the environmental fate of these

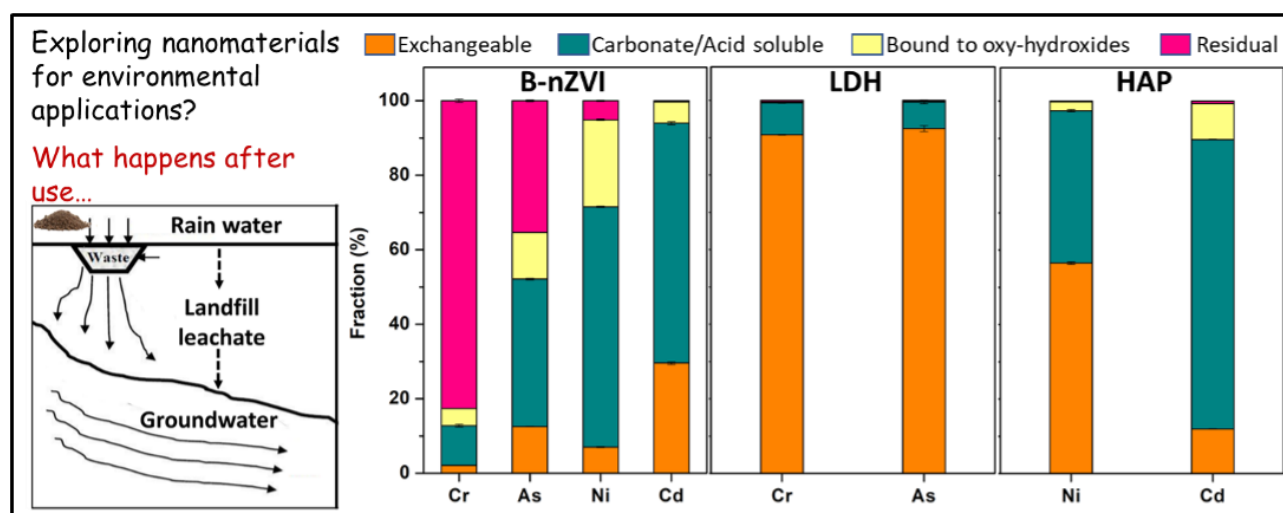


Figure 1. Sequential extraction of sorbed contaminants on different nanoadsorbents.

adsorbent wastes⁴. Current research in the field includes assessment of toxicity of various nano-adsorbents before and after the sorption of contaminants, transport of graphene or other nanomaterials in saturated porous media, and life cycle assessment (LCA) of some of the nano-adsorbents. LCA considers the use of energy and water in the processing of various raw materials to synthesise nano-adsorbents to final applications, considering the total energy utilisation in terms of equivalent CO₂ emissions and climate change⁵.

So far, knowledge is limited regarding the fate, dissolution and transport of the contaminant-sorbed nano-adsorbents in the environment. Therefore, we have focused on a variety of contaminant-loaded nanoadsorbents that can attach contaminants through distinct interaction mechanisms, *i.e.* anion-exchange (layered double hydroxides, LDHs)⁶, cation exchange, and crystal incorporation (hydroxyapatites,

HAPs)⁷ and complexation, redox transformation and coprecipitation (clay-supported nanoscale zerovalent iron composites, B-nZVIs)⁸. These collected adsorbent wastes were processed through sequential extraction procedure to probe their soil fractionation and to evaluate contaminant desorption and adsorbent dissolution in different stages (**Figure 1**). Different sorbed contaminants on B-nZVI displayed varying fractionation, with limited exchangeable fraction suggesting strong contaminant binding. Chromium showed minimal leachability with retention of > 80% in residual phase, suggesting minimal long-term leaching. LDH-sorbed contaminants exhibited over 90 % release as exchangeable fraction, emphasising disposal challenges, although research also suggests their potential in contaminant recovery and adsorbent reuse. In HAP, both nickel and cadmium showed considerable release dispersed over exchangeable and acid-soluble fractions with limited strongly-bound fractions, indicating potential soil contamination. These nuanced findings underscore the complex environmental implications, disposal considerations, and potential recovery strategies for B-nZVIs, LDHs, and HAPs in the context of contaminant interactions.

We have further explored contaminants release in simulated landfill conditions by reacting adsorbent wastes sequentially with rainwater, landfill leachate water, and groundwater in continuous column mode. The required amount of soil needed to dilute the wastes before disposal can be correlated with the total contaminant leaching in the simulated landfill environment. The safe dilution disposal factor (SDDF) was defined as total metal leaching through adsorbent waste columns in rainwater (RW), landfill leachate water (LW), and groundwater (GW) divided by the soil permissible limit (SPL) of different metals as defined by environmental protection agency⁹.

$$SDDF = (C_{RW} + C_{LW} + C_{GW}) / C_{SPL}$$

Results suggest that researchers should give equal importance to the long- and short-term environmental

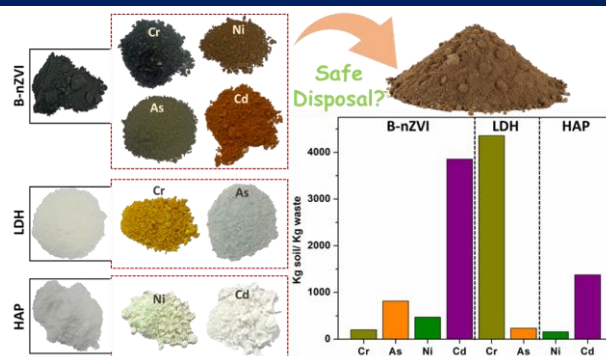


Figure 2. Contaminant-sorbed nanoadsorbent wastes and their respective soil dilution requirements .

fate of adsorbent wastes after contaminant removal. Combined understanding of their potential for soil fractionation and leaching of sorbed contaminants in landfill environment can help in defining different disposal pathways, and minimising environmental risks.

Redox-active nanoparticles like B-nZVIs lead to redox-transformation of contaminants and bind strongly, limiting their recyclability and reuse. Conversely, sorbed contaminants can be recovered from weak binders like LDHs, allowing reuse. Adsorbents showing very high contaminant removal capacities and low SDDF values or soil dilution requirements (**Figure 2**) are thus eco-friendlier compared to adsorbents with low capacity and high soil dilution requirement, while adsorbents with e-resource recovery-reuse potential should be our priority.

References

1. A. Nagar and T. Pradeep, *ACS Nano*, 2020, **14**, 6420-6435. <https://doi.org/10.1021/acsnano.9b01730>.
2. J. Namieśnik and A. Rabajczyk, *Chemical Speciation & Bioavailability*, 2010, **22**, 1-24. <https://doi.org/10.3184/095422910X12632119406391>.
3. R. A. Wuana and F.E. Okieimen, *ISRN Ecology*, 2011, **2011**, 402647. <https://doi.org/10.5402/2011/402647>.
4. S. Rawat, V. L. R. Pullagurala, I. O. Adisa, Y. Wang, J. R. Peralta-Videa and J. L. Gardea-Torresdey, *Current Opinion in Environmental Science & Health*, 2018, **6**, 47-53. <https://doi.org/10.1016/j.coesh.2018.07.014>.
5. P. Ganguly, A. Breen and S. C. Pillai, *ACS Biomater. Sci. Eng.*, 2018, **4**, 2237-2275. <https://doi.org/10.1021/acsbmaterials.8b00068>.
6. N. Khandelwal, N. Singh, E. Tiwari and G. Krishna Darbha, *Environmental Nanotechnology, Monitoring & Management*, 2022, **18**, 100754. <https://doi.org/10.1016/j.enmm.2022.100754>.
7. S. Rout, N. Khandelwal, A. K. Poswal, V. Pulhani and A. V. Kumar, *Environmental Science: Nano*, 2021, **8**, 1256-1268. <https://doi.org/10.1039/D0EN01246G>.
8. N. Khandelwal, N. Singh, E. Tiwari, R. Marsac, D. Schild, T. Schäfer and G. Krishna Darbha, *Chem. Eng. J.*, 2023, **461**, 141883. <https://doi.org/10.1016/j.cej.2023.141883>.
9. M. E. Will and I. G. W. Suter, *Toxicological benchmarks for potential contaminants of concern for effects on soil and litter invertebrates and heterotrophic process*, United States, 1995

