New improved nanofiber material for the recovery of metals from spent lithium-ion batteries

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Outline

- Introduction
- Application and growth of nanofiber material
- Preparing functional nanofibers
- Prepared adsorbents and applications
- Conclusions

Why recycle spent batteries ?

- The increasing production of different electronic devices such as mobile phones, laptop computers, and electric cars has greatly increased the utilization of lithium-ion batteries (LIBs).
- The production of batteries and subsequent discarded waste has increased dramatically but on the other hand, there are many valued metals in the spent LIBs.
- Batteries contain heavy metals such as mercury, lead, cadmium, and nickel, which can contaminate the environment when batteries are improperly disposed of.
- Recycling of these spent batteries is necessary and important from both economical aspects as well as for environmental protection.
- The major recycling approaches for spent LIBs are mechanical treatment, pyrometallurgy, hydrometallurgy, and biotreatment.
- Hydrometallurgical recycling offers greater value, but comes at a higher cost
- New and improved technologies involved in the recovery of metals from battery wastes are therefore required.

Search for novel materials

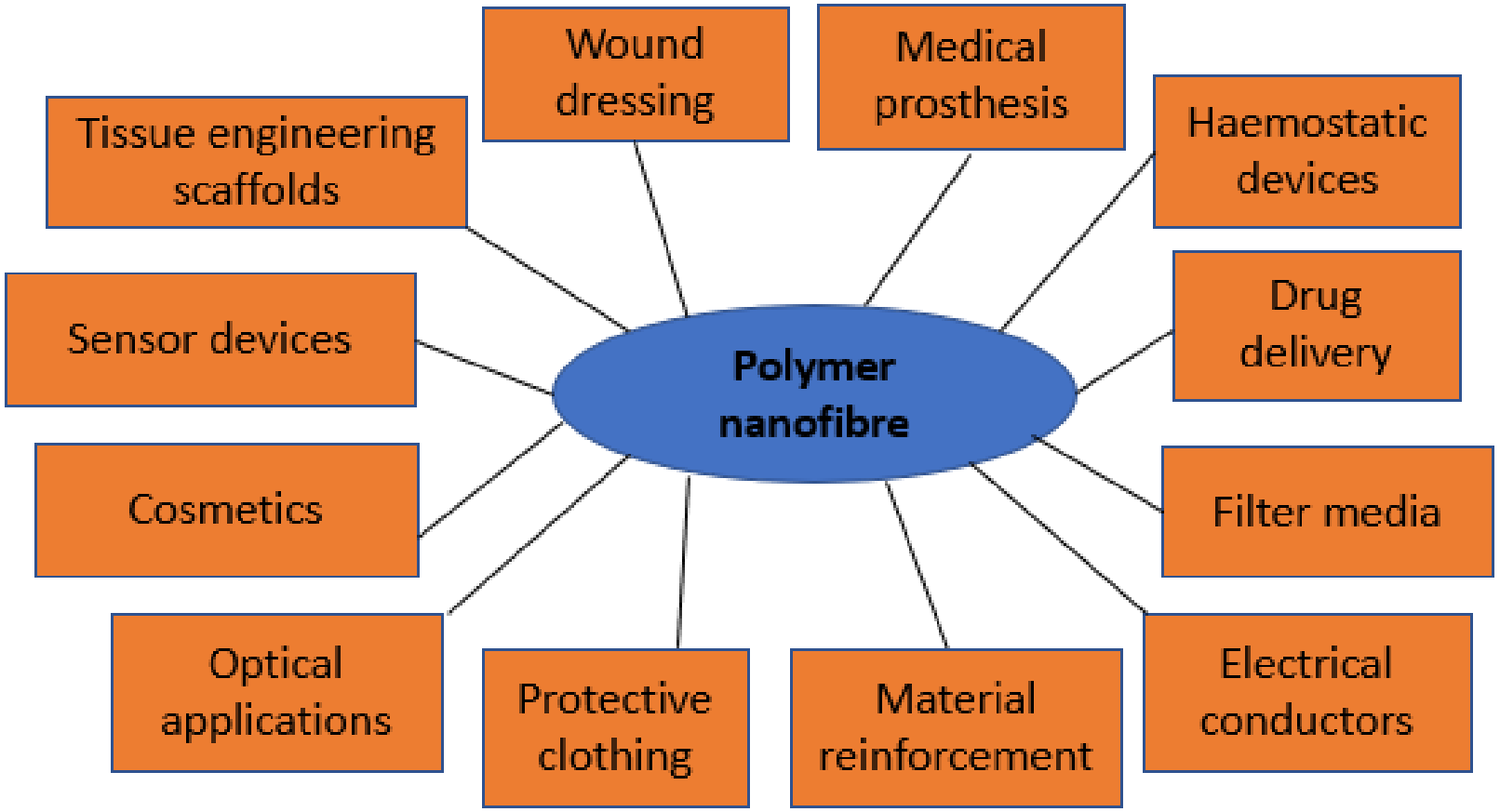
- Nanofibres are emerging as new material suited for adsorption of metals and have structural characteristics such as

- ❑ high surface area to volume ratio
- ❑ high porosity and interconnectivity
- ❑ good structural stability
- ❑ low basis weight
- ❑ cost effectiveness
- ❑ controllable scaffold thickness of the electrospun scaffold

- Fibres with diameters below 100 nm are generally classified as nanofibers

- Altering the surface chemistry, or coat techniques, nanofibers can be applied to chelate target metal ions from solution

Applications of nanofibers



Interest in Nanofibres for metal removal

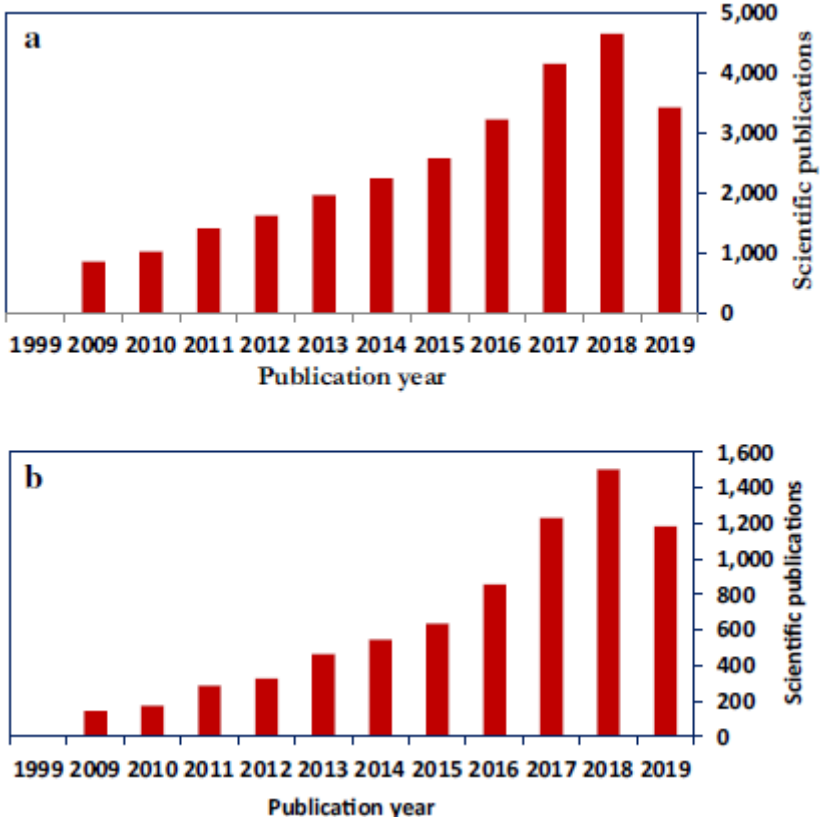


Fig 1: Annual number of scientific publications (1999–2019)
a when the terms ‘‘polymer nanofiber’’ was used
b when the terms “polymer nanofiber metal ion adsorption” were used as keywords.
Data analysis was completed using Science Direct search system 2019

Electrospinning

- Electrospinning has been recognized as an efficient technique for the fabrication of polymer nanofibres and is currently the most promising technique used for the production of continuous nanofibres on a large scale
- There are many other different methods of making nanofibers such as drawing, self-assembly, template synthesis, and thermal-induced phase separation

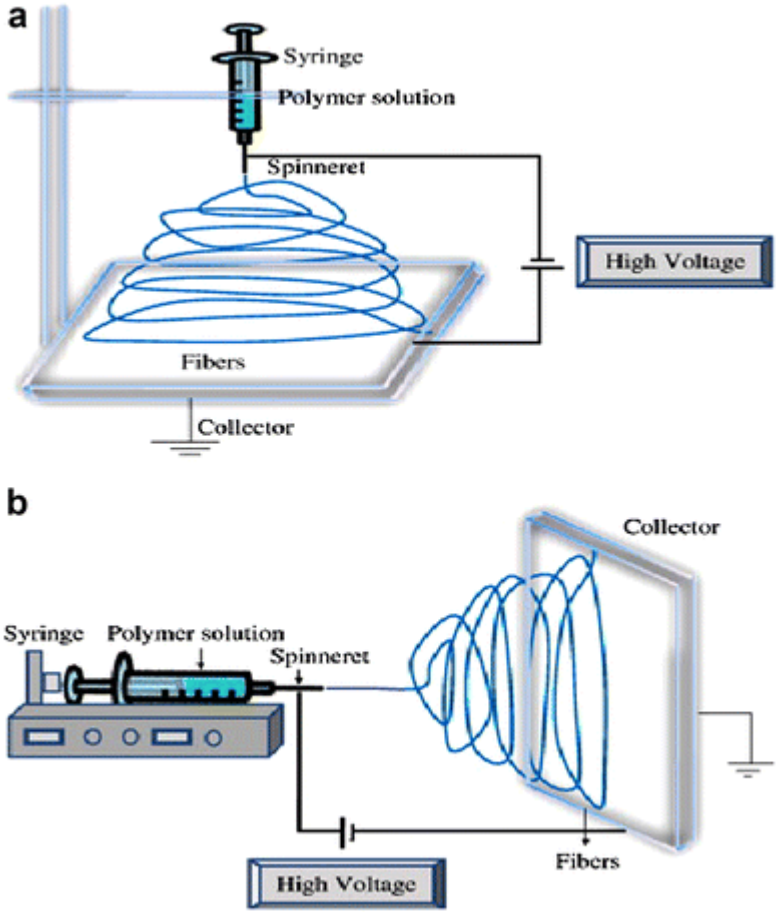


Fig 2: Typical electrospinning apparatus

Electrospinning parameters

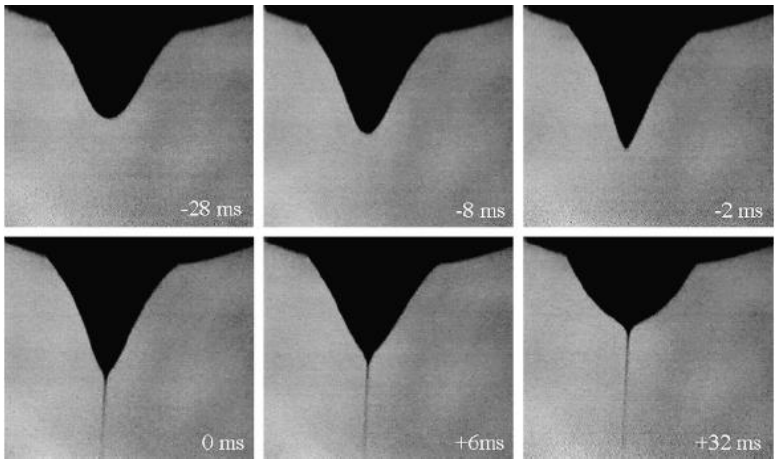


Fig 3: The impact of **applied voltage** on Taylor cone formation, jet elongation, thinning and persistent flow towards the collector (Reneker and Yarin, 2008)

Process parameters include:

Applied voltage impacts Taylor cone formation, jet elongation, thinning and persistent flow towards the collector

Flow rate to sustain the equilibrium between the exiting polymer jet and the replacement solution for the sustenance of continuous flow

Needle tip to collector distance varies with polymer type, affects flight time and stretching of the jets within the electric field

Ambient conditions including humidity, temperature

Solution parameters include:

Concentration, solubility, viscosity, surface tension, solution conductivity, type and ratio of solvent used

Preparing functional nanofibers

- Pre-electrospinning - modify a functional polymer followed by electrospinning into a nanofiber
- Blending and co-electrospinning the polymer blend using special spinning techniques
- Post-functionalisation i.e., fiber preparation followed by introduction of functional groups
- Modification of any polymer support can be done chemically (through covalent bonding of the ligand to the matrix) or physically (via sorption of a chelant into the matrix)

Functional groups

The starting materials must have the following characteristics:

- **Polymers**
  - **The polymers must have reactive functional groups as branched chain. Polymer with reaction functional group as part of chain is difficult to work with.**
- **Ligands**
  - **The ligands must have reactive functional group that can react with the functional group of the polymer support.**

Modification using Imidazole, pyrazole and pyridine-based ligands

Getting the starting materials with the characteristics above may be challenging especially when targeting selectivity

- **Recovery of Li, Co, and Ni from typical spent battery waste**

Published studies and applications

Adsorption of nickel(II) on polyacrylonitrile nanofiber modified with 2-(2′-pyridyl)imidazole

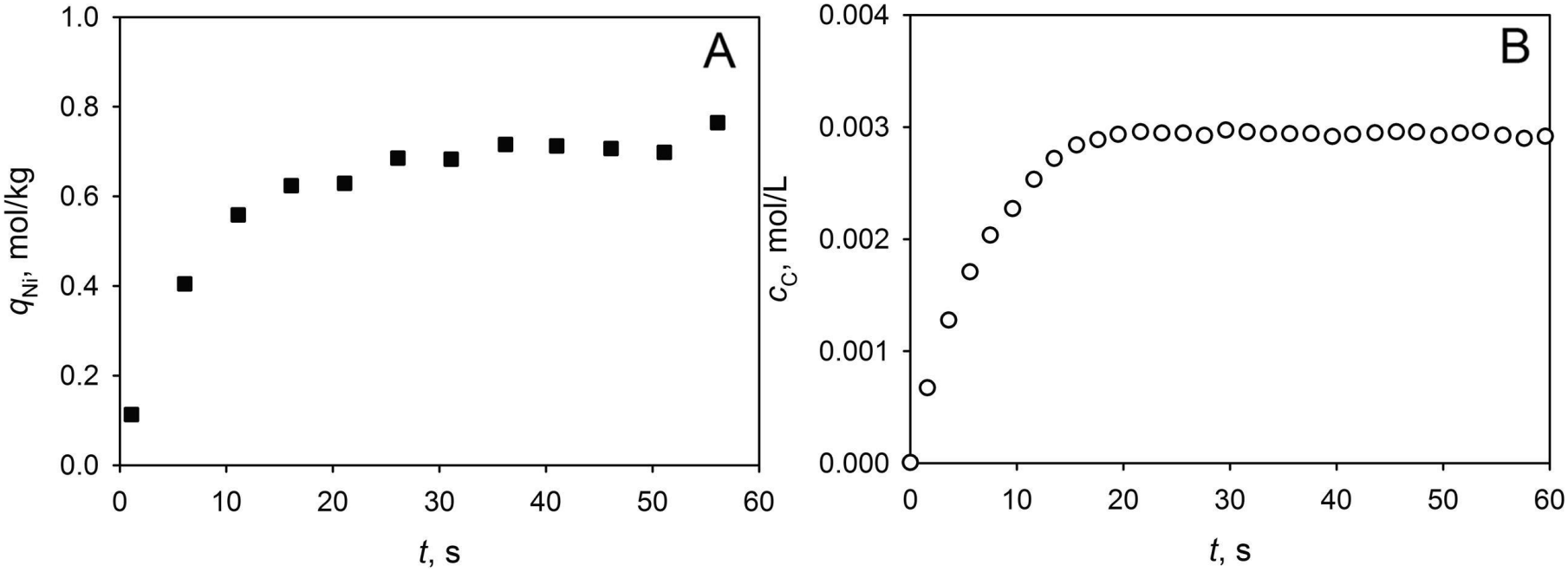


Fig. 4: Kinetics of nickel uptake in PAN–pim (A) and nickel complexation with pim in bulk solution (B). T = 22 ± 1 °C and pH 5.0 ± 0.3. (A) c_{Ni}^0 = 0.0033 mol/L, m_{ads} = 0.143 g, V_L = 75 mL. (B) c_{Ni}^0 = 0.005 mol/L, c_{pim}^0 = 0.005 mol/L.

Adsorption of nickel(II) on polyacrylonitrile nanofiber modified with 2-(2′-pyridyl)imidazole

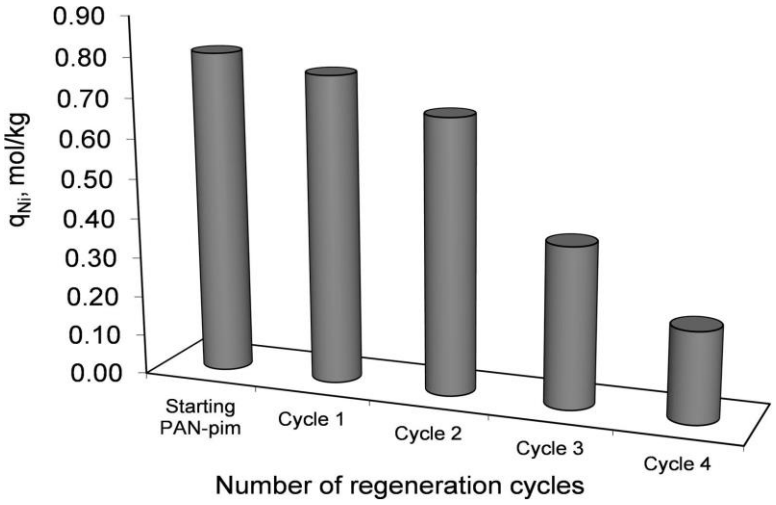


Fig. 5: The regeneration cycles of PAN–pim nanofibers for the adsorption of nickel at pH 5.0.

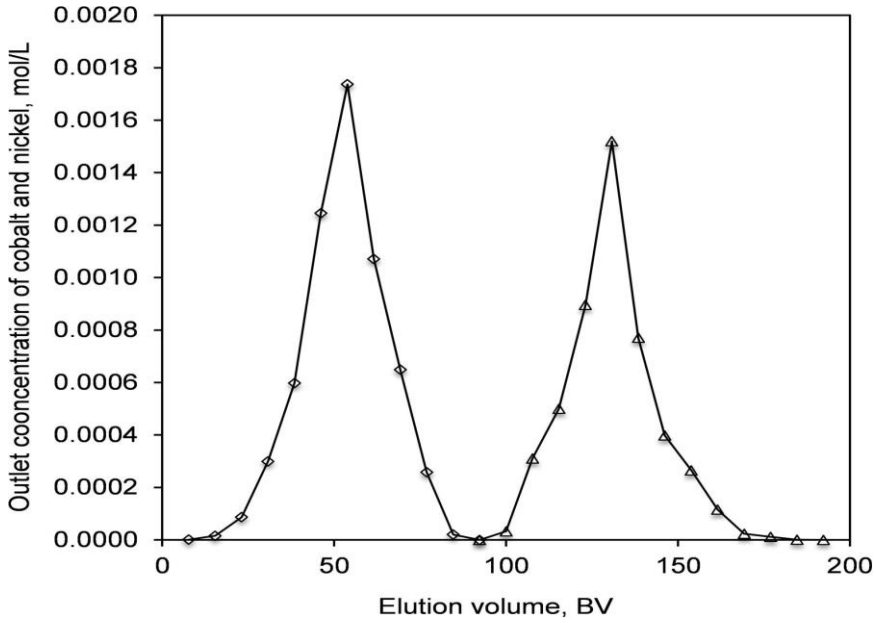
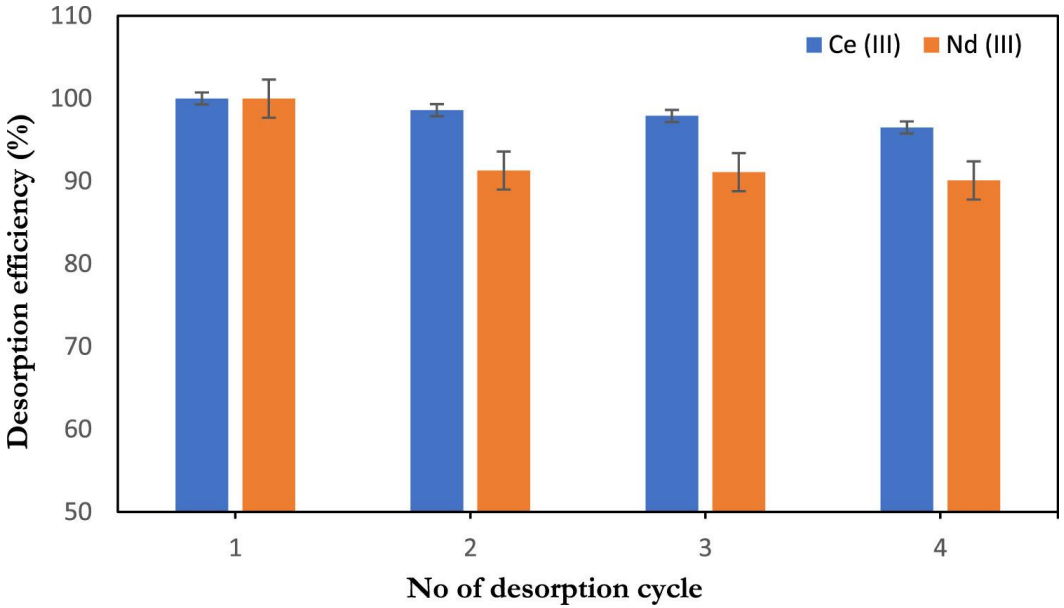


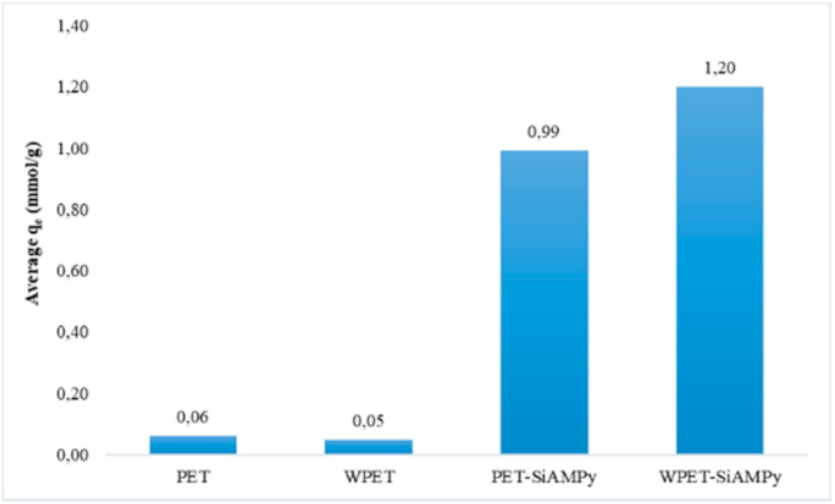
Fig. 6. Elution of nickel (triangles) and cobalt (diamonds) from PAN–pim equilibrated at pH 5 with a mixed solution of 0.005 M $NiSO_4$ and $CoSO_4$. The metal ions were eluted using a series of EDTA solutions (0.01 M fraction 1, 0.02 M fraction 2, 0.04 M fraction 3, 0.06 M fraction 4, 0.08 M fraction 5, and 0.1 M fractions 6–25). Bed volume = 1.3 mL, flowrate = 1 mL/min and T = 22 ± 1 °C.

Synthesis and characterisation of diglycolic acid functionalised polyethylene terephthalate nanofibers for rare earth elements recovery



- Fig. 7. Desorption efficiency over four cycles for Ce^{3+} or Nd^{3+} using PET-DGAnf (adsorbent mass - 0.0075 g; initial concentration - 100 mg/L; stripping agent - 1 M HNO_3; desorption time - 60 min; capacity – 136 and 124 mg/g).

Adsorptive Recovery of Cu^{2+} from Aqueous Solution by Polyethylene Terephthalate Nanofibres Modified with 2-(Aminomethyl)Pyridine



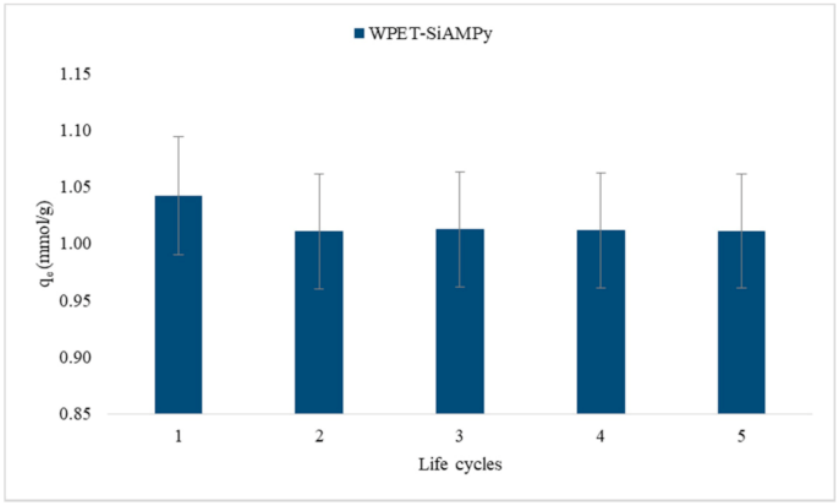
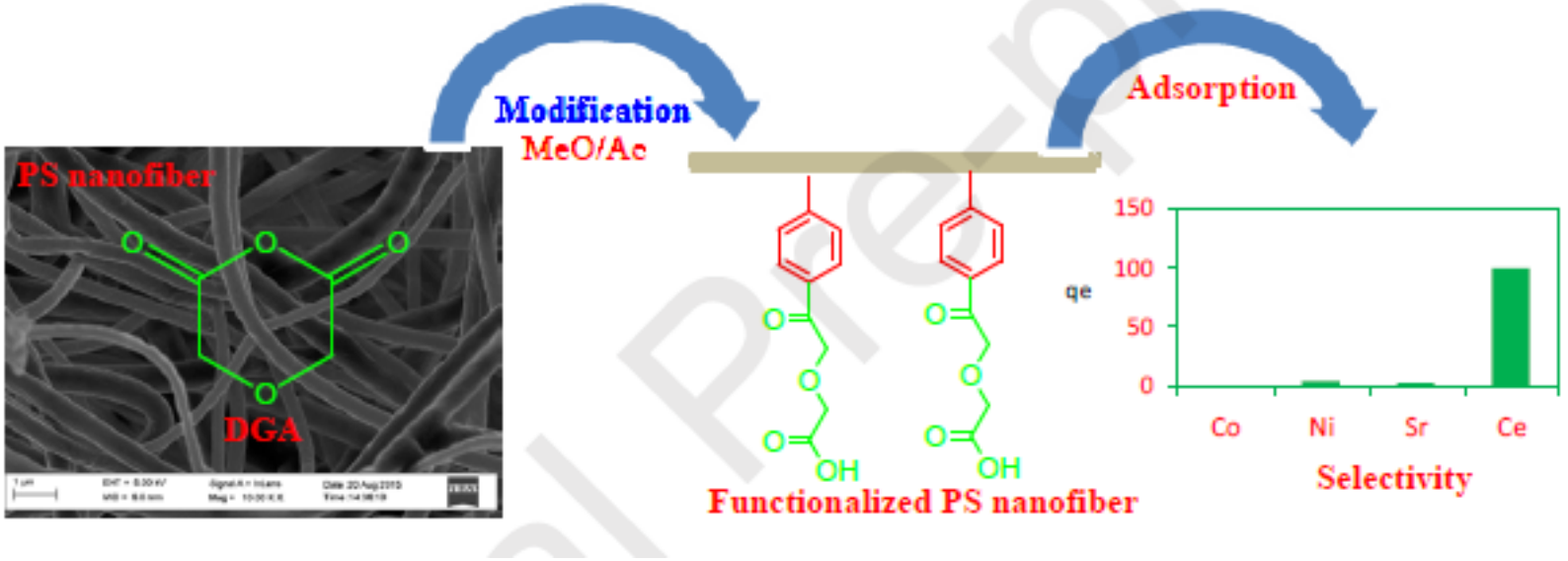


Fig 8: Average adsorption capacity of Cu^{2+} from aqueous solution using PET, WPET, PET-SiAMPy, and WPET-SiAMPy nanofibres (Cu^{2+} concentration 100 mgL^{-1}, pH 5, dosage 0.01 g, 120 min).

Fig 9: Five adsorption–desorption/regeneration cycles of Cu^{2+} using WPET-SiAMPy nanofibres

Adsorption of Ce^{3+} and Nd^{3+} by diglycolic acid functionalised electrospun polystyrene nanofiber from aqueous solution



. Sorption capacities of different sorbents in comparison to PS-DGAnf

Sorbent	Metal	pH	time (h)	Adsorption capacity (mg g^{-1})	Reference
Aminomethylphosphonic acid modified chitosan	Nd^{3+}	5	7	30.32	[41]
Calcium alginate–poly glutamic acid	Nd^{3+}	3.5	24	237.99	[42]
Phosphoric acid on silica matrix	Nd^{3+}	6	24	160	[43]
Aspartic acid grafted Cellulose	Nd^{3+}	5	3	81.2	[34]
Extractant impregnated alginate microcapsules	Nd^{3+}	4	20	149.3	[44]
chitosan/ polyvinyl/Alcohol/3-mercapto Beads	Ce^{3+}	5	6	251.41	[45]
EDTA and DTPA-functionalised chitosan	Nd^{3+}	4	3	74 77	[46]
Phosphorous functionalized nanoporous carbon	Nd^{3+}	-	1	335.5	[47]
4-dodecyl-6-((4-(hexyloxy)phenyl)diazenyl) benzene-1,3-diol mesoporous silica nano-composite	Ce^{3+}	2.5	2	150.37	[48]
PS-DGAnf	Nd^{3+}	6	0.4	146.2	This work
PS-DGAnf	Ce^{3+}	6	0.4	152.5	This work

O. Pereao, K. Laatikainen, C. Bode-Aluko, Y. Kochnev, O. Fatoba, A.N. Nechaev, L.Petrik, Adsorption of Ce3+ and Nd3+ by Diglycolic acid functionalised electrospun polystyrene nanofiber from aqueous solution, *Separation and Purification Technology* (2019), doi: https://doi.org/10.1016/j.seppur.2019.116059

Conclusions

- Functionalised nanofibers offer a technological alternative to classical adsorbents
- Show promise for selective recovery of valuable metals
- Show effective binding capacities toward different metal ions
- Nanofibres have high kinetics and selectivity
- There are many chemical and morphological modification techniques
- Good structural stability, high porosity, high surface area to volume ratio
- Strategies for the functionalization are required
- Understand the nanofiber ligand stability, nanofiber adsorption isotherms, kinetics, and thermodynamics for developing efficient new nanofiber adsorbents

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Thank you

Any Questions?