Novel Magnetic Covalent Organic Framework Composites for Adsorption of Diarrhetic Shellfish Poisoning Toxins

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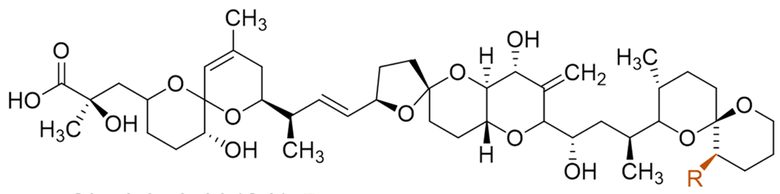
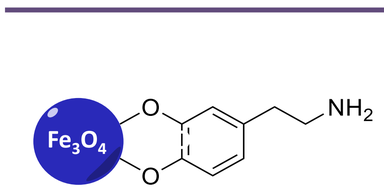
Purpose

Control of environmental pollution is mandatory for the protection of human health and the development of efficient monitoring and capturing techniques is urgently needed.[1] Diarrhetic shellfish poisoning toxins (DSP), such as okadaic acid (OA) and its analogs, such as dinophysistoxin-1 (DTX-1), are produced by marine and freshwater microalgae during harmful algal blooms (HABs) raising concerns about their potential negative effects for human health and to the environment.[1] In order to monitor the presence of these contaminants, the development of efficient approaches for pre-concentration is required. Adsorption on high-binding sorbents is an attractive approach, being one of the most useful tools for isolation and preconcentration.[2,3]

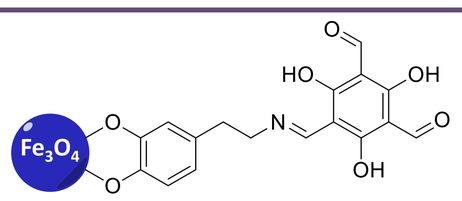
Two-dimensional covalent organic frameworks (COFs), crystalline nanoporous materials formed by the self-assembly of purely organic building blocks into sheets, which undergo stacking interactions in the third dimension, have shown promise as adsorbents, since they fulfil the requirements of high crystallinity, water-stability, and large surface area.[4] We found water-stable COF derivative TpBD-Me_2 to adsorb okadaic acid from seawater over 30 times more efficiently than the commonly used polystyrene resin HP-20.[5] To allow for easier collection of the adsorbent, we developed a magnetic COF composite.



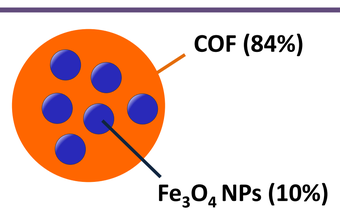
Preparation of magnetic TpBD-Me_2 COF composite



Amino-functionalized magnetite nanoparticles

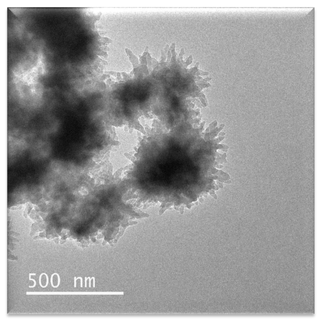


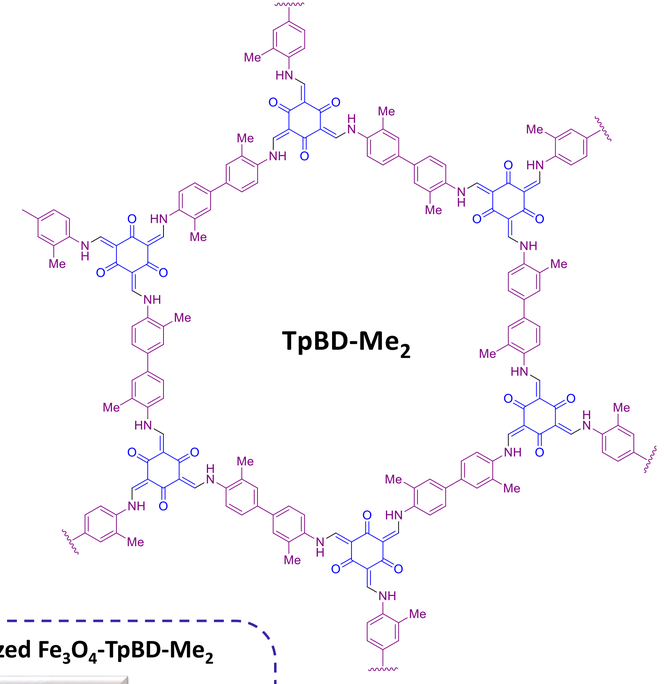
Pre-functionalization with Tp



$TpBD\text{-}Me_2$ COF composite

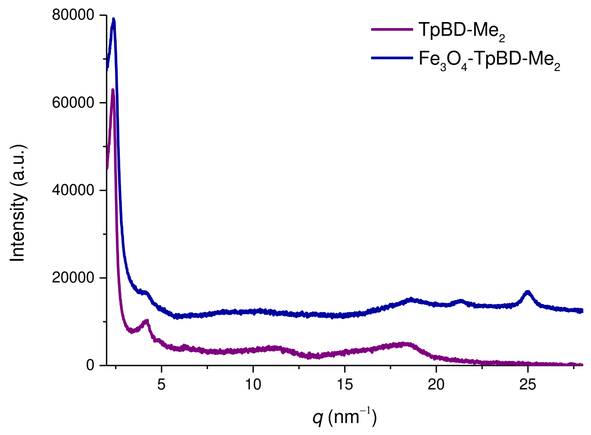
TEM image of Fe_3O_4-TpBD-Me_2



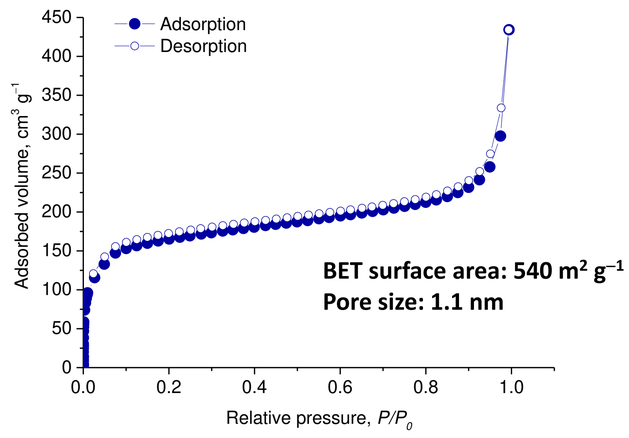


$TpBD\text{-}Me_2$ COF & Fe_3O_4-TpBD-Me_2 Characterization

SAXS pattern of $TpBD\text{-}Me_2$ and Fe_3O_4-TpBD-Me_2 composite



N_2 adsorption-desorption isotherms at 77 K of Fe_3O_4-TpBD-Me_2

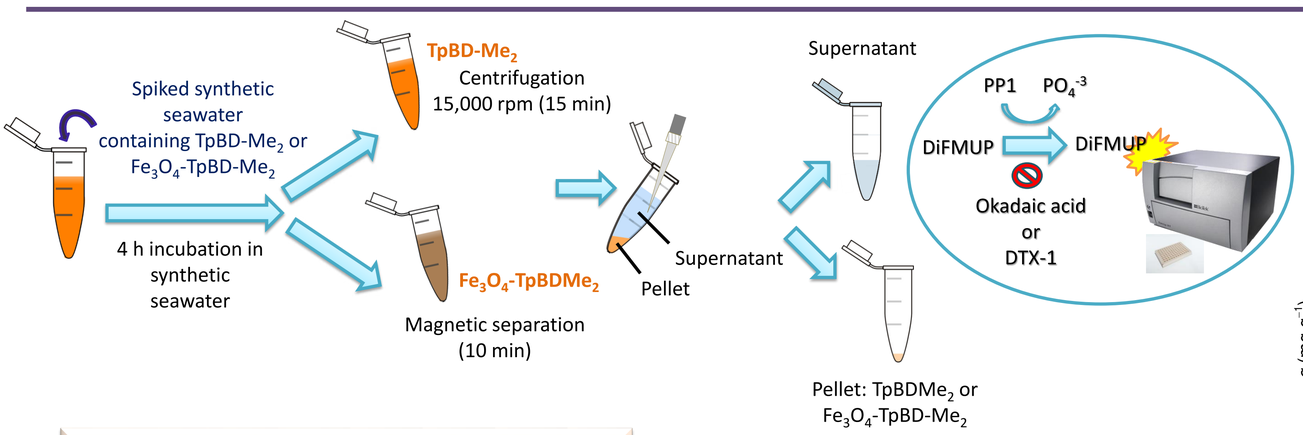


As-synthesized Fe_3O_4-TpBD-Me_2

Magnetic separation of Fe_3O_4-TpBD-Me_2

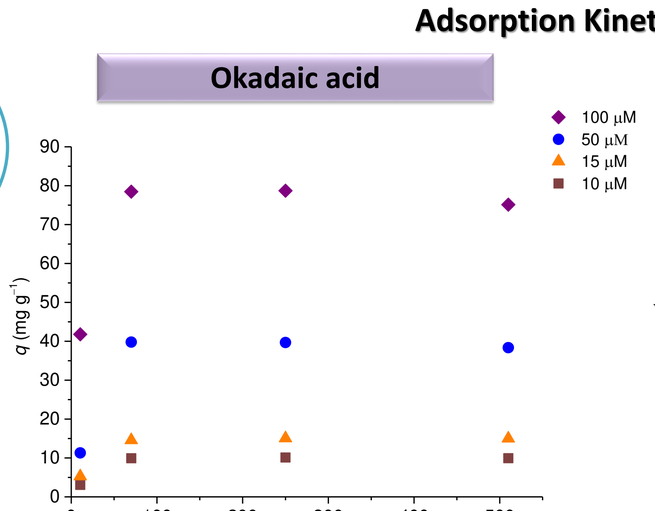
External magnetic field (Nd-Fe-B magnet)

Toxin Adsorption Capacity of $TpBD\text{-}Me_2$ and Fe_3O_4-TpBD-Me_2

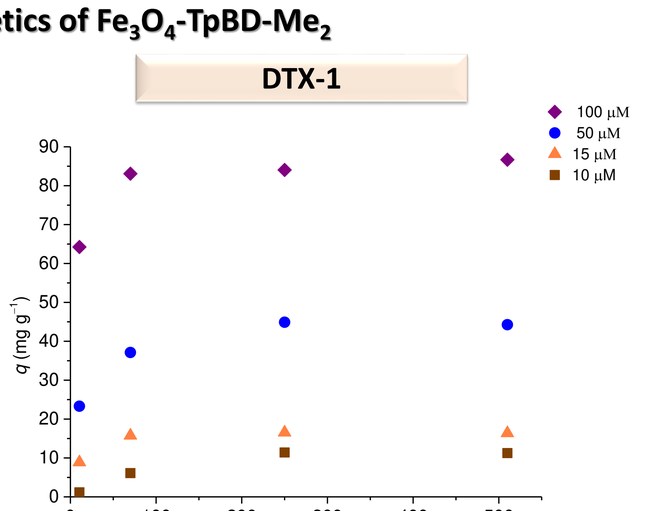


Adsorption Kinetics of Fe_3O_4-TpBD-Me_2

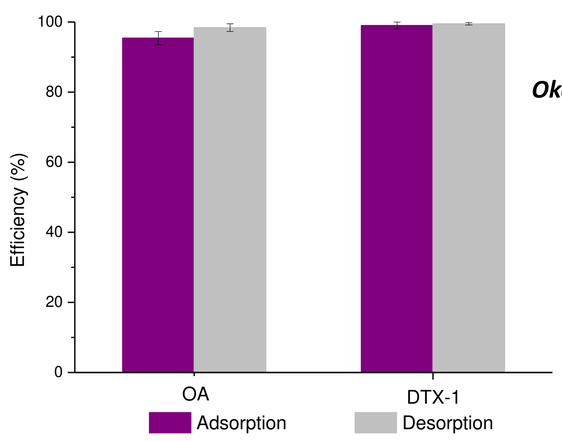
Okadaic acid



DTX-1



Adsorption-Desorption efficiency of Fe_3O_4-TpBD-Me_2



Okadaic acid and DTX-1 concentration: 10 µM;

COF concentration: 1mg mL^{-1};

Desorption with 2-propanol;

Good efficiency of desorption – capacity to be reused.

	$TpBD\text{-}Me_2$[5]	Fe_3O_4-TpBD-Me_2	DIAION 1 HP-20[6]
Surface area	592 m^2/g	538 m^2/g	500 m^2/g
Pore size	1.7 nm	1.1 nm	26 nm
Time to reach adsorption equilibrium	60 min	60 min	225 min
Activation step needed?	No	No	Yes
Adsorption capacity (q_e) OA	61 mg/g	79 mg/g	1.6 mg/g
Adsorption capacity (q_e) DTX-1	--	83 mg/g	2.9 mg/g
Separation process	Centrifugation	Magnetic	Filtration
Separation time	15 min	10 min	-

- **Adsorption equilibrium reached after 60 min in seawater at 19 °C with both sorbents;**
- **At the highest okadaic acid concentration studied (100 µM), 61 mg/g of OA was adsorbed with $TpBD\text{-}Me_2$ and 79 mg/g with Fe_3O_4-TpBD-Me_2;**
- **At the highest DTX-1 concentration studied (100 µM), 83 mg/g of DTX-1 was adsorbed with Fe_3O_4-TpBD-Me_2.**

COF concentration: 1 mg/mL

Conclusions

- **Fe_3O_4-TpBD-Me_2 adsorbs DSP toxins okadaic acid and DTX-1 more efficiently than the reported macroporous resin, HP-20;**
- **A short time is needed for Fe_3O_4-TpBD-Me_2 to reach the adsorption equilibrium;**
- **Okadaic acid and DTX- 1 can be easily and efficiently desorbed from Fe_3O_4-TpBDMe_2;**
- **The magnetic properties of Fe_3O_4-TpBD-Me_2 allow its easy collection, using an external magnetic field, highlighting their potential application for solid-phase extraction;**

References

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Acknowledgements

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