Exploring unconventional approaches to sediments decontamination

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Introduction: Sediments are soil particles found at the sea bottom and comprised of organic matter, iron oxides, carbonates, sulfides, clay, sand, silt and interstitial water. Natural organic matter is derived from humus, decomposed plant and animal residues and other organic matter such as woody or plant material, garbage, dead organisms and other debris. Sediments are heterogeneous and their composition significantly varies from site to site. Accumulation of pollutants during long periods and multiple pollutant sources at the harbors are the reasons that the sediment is a complex mixture of multiple types of pollutants including Persistent Organic Pollutants (POPs), microplastics and heavy metals among others.
The technologies for decontamination of multiply-polluted sediments must be improved to address the whole complex of contaminants. The existing technologies are frequently incompatible for different mixtures of pollutants, for example for microplastics and biochar on the removal of polycyclic aromatic hydrocarbons and phthalate esters.

Methods: A plausible and potentially more efficient alternative to the current decontamination paradigm relies on the application of unconventional ways for triggering chemical reactions. The new approach, to be done within the spanish project "Exploration of unconventional reactional pathways for an integrated and sustainable decontamination of dredged sediments (UNIDEC), intends to employ, in a concerted way, different types of energy including mechanical energy, sonication, electrokinetics, electromagnetic radiation, microwave and UV light. Such reactions usually have different reaction pathways and unusual reaction products, which are unattainable by conventional thermally driven chemical reactions [1].

This approach is ambitious but is grounded on solid experimental evidences obtained in investigation of synergistic enhancement of chemical reactions by non-thermal driving forces. For instance, piezoelectric materials with photocatalytic activity may employ the piezoelectric field directly for separating photo-generated charge carriers during the light/piezo-excitation increases the lifetime of generated charges and the overall catalytic effectiveness [2].

Results: To tackle this problem a multistage research plan, which involves understanding the fundamental mechanisms of non-thermally driven chemical reactions on various components of real sediments, exploration of the possibility to use the non-thermally driven reactions for decontamination purposes and tuning the technological parameters of such reactions, was developed.
At the first stage, we analyzed tribochemical activation of mineral and organic components of sediments using the measurement of rates of electron emission and radical generation. In parallel, an original tribo-mass-spectrometry method was developed to quantify the rate of organic contaminants and plastics decomposition under a combination of mechanical energy and UV light. Model organic contaminants can be used to simulate typical POPs.
At the second stage, real sediment is subjected to various combinations of non-thermal treatment processes including mechanochemically and electrokinetically assisted photocatalysis. The reaction rate is assessed *operando* using coupled mass-spectrometry.
At the third stage, socio-economic impact of the new technology is analyzed and the measures to increase its acceptance by general public and stakeholders are developed.

Summary: The alternative non-thermally driven chemical reactions are very promising to face the problem of sediment contamination and revalorization in the frame of the paradigm of circular economy, though much research is still needed to scale this technology to industrial level.

References: [1] Ares et al. (2019) *ChemPhysChem* **20**:1248-1260; [2] Tu et al. (2020) *Adv Functional Mater* **30**:2005158.