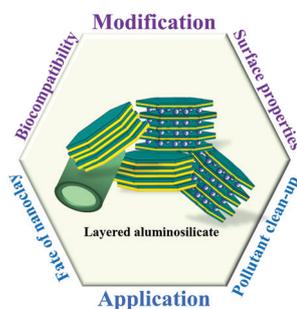


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Biocompatible functionalisation of nanoclays for improved environmental remediation

Bhabananda Biswas,* Laurence N. Warr, Emily F. Hilder, Nirmal Goswami, Mohammad M. Rahman, Jock G. Churchman, Krasimir Vasilev, Gang Pan and Ravi Naidu*

This review presents a summary of modified nanoclays and new perspective of producing biocompatibly functionalised nanoclays for environmental remediation.

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10 **Biocompatible functionalisation of nanoclays for improved environmental remediation** Q2

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Among the wide range of materials used for remediating environmental contaminants, modified and functionalised nanoclays show particular promise as advanced sorbents, improved dispersants, or biodegradation enhancers. However, many chemically modified nanoclay materials are incompatible with living organisms when they are used in natural systems with detrimental implications for ecosystem recovery. Here we critically review the pros and cons of functionalised nanoclays and provide new perspectives on the synthesis of environmentally friendly varieties. Particular focus is given to alternatives to conventional surfactants used in the modified nanoclay products, and strategies in synthesising nanoclay-supported metal and metal oxide nanoparticles. A large number of promising nanoclay-based sorbents are yet to satisfy environmental biocompatibility *in situ* but opportunities are there to tailor them to produce “biocompatible” or regenerative/reusable materials.

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15 **1. Introduction**

30 **1.1 Background**

Clay minerals are layered aluminosilicate phases formed as natural, poorly-crystalline products of water–rock interaction in surface and near-surface environments of the Earth. In terms of particle size, they are typically <2 μm in equivalent spherical diameter. Due to their nanoscale (<100 nm) structure in at least one dimension, clay minerals are often technically referred to as nanoclays (Fig. 1). Montmorillonite (a mineral of the smectite group typical of bentonite clay), kaolinite, halloysite, and palygorskite (also known as attapulgite) are the most common nanoclay minerals used in environmental applications.^{1,2} These mineral phases have been well studied in clay science and extensively documented

elsewhere.³ In this review, we focus on the rapidly evolving topic of nanoclay utilisation for the purpose of environmental remediation in an eco-friendly manner. Due to their natural occurrence and abundance, clay minerals and related minerals, such as zeolites are generally viewed as environmentally friendly and inexpensive materials.^{4,5} However, as remediating agents, natural nanoclays often require some form of physicochemical modification to obtain engineered nanoclays or nanocomposites that are suitable to carry out a specific functional task in relation to the sorption or dispersion of toxic substances.^{6,7} Such treatments usually require the use of less environmentally desirable chemical compounds, such as strong salts, acids, bases, and various types of organic modifiers. As a result, the properties of the nanoclays are no longer those natural to the environment and application may constitute adding an additional polluting agent. Therefore, the compatibility of these functional materials to the ecosystem remains a key question of importance. Clearly, there is a need to weigh up the benefits against the risks of using remediating products prior to their application in combating the effects of anthropogenic pollution.

Due to the increasing awareness of the negative impact of chemical pollution in an overpopulated world,^{9,10} there is an urgent need to develop more environmentally compatible functionally modified nanoclays for advancing remediation efforts. This article provides a state-of-the-art review of current progress and highlights the key issues that remain in this advancing field of research.

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1.2 Scope of this review

Over the last ten years (2008–2018), the research on clay minerals, in particular, the development of chemically reactive nanoclays, has vastly increased due to their promising applications in a multitude of areas (Fig. 2).

Among these, ~10% of the reported research has been conducted in the field of environmental science and ~35% in the subject areas, such as material science, engineering and chemistry that covers a range of new sorbents used for remediating environmental contaminants (Source: Scopus, retrieved date: 16 April 2019) (Fig. 2). However, one commonly overlooked aspect is that the modified clay products (e.g., organically modified clay minerals – organoclays) often contain conventional surfactants and other chemicals that have poor biocompatibility, and can prove toxic to environmental flora and fauna.¹¹

To date the biocompatibility of a modified nanoclay is well studied in terms of its biomedical use^{12–15} and its

environmental compliance for goods (e.g., packaging material).^{16,17} For example, environmentally friendly clay–polymer nanocomposites were developed by the Toyota research group, and the trend was followed for many applications.^{18–20}

In contrast, the advancement of such and other modified nanoclays for environmental remediation in an eco-safe manner is still a young field of research. Application of clay-based sorbents detrimental to the functioning of biological resources (e.g. microorganisms) can slow or stop the rate of natural attenuation of contaminants (e.g., biodegradation) in the surface environment and therefore affect the biotic health of soil and water. Very few review articles have addressed the potential application and secondary pollution risk of these modified products and possible routes to mitigate these risks (e.g., through a modification process). Recently Lazzara *et al.*²¹ reviewed the potential toxicity and compatibility of halloysite nanotubes and their modified materials for agricultural uses. To the best of our knowledge, no review article has presented a



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Laurence N. Warr

Laurence N. Warr received his PhD in geology in 1991 at the University of Exeter (UK) and habilitated in geology and mineralogy at the University of Heidelberg (Germany) in 1998. He was awarded a number of scholarships (habilitation and Heisenberg grants) between 1996 and 2003 from the German Research Council (DFG) to research on the mineralogy and geochemistry of clay minerals and continued his work 2003–2007 as a CNRS researcher at the “Centre de Géochimie de la Surface” in Strasbourg (France). Since 2007 he holds the chair of Economic Geology and Geochemistry at the University of Greifswald (Germany).



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holistic approach to the biocompatibility of modified nanoclays for environmental applications. Here we also highlight a new perspective on this issue linked to potential research outcomes and outline a future research direction to achieve acceptable biocompatibility. To fulfil this goal, a range of criteria during the preparation of modified nanoclays that rule out any negative impact on biological activity is proposed; namely non-toxic, non-carcinogenic or mutagenic, no detriment to respiration systems or the supply of nutrients and no direct or indirect physical damage to life-sustaining ecosystems. Only under such conditions can the application of functionalised nanoclays be safe to use for remediating environmental pollution.

2. Functionalised nanoclays and their biocompatibility used in environmental remediation

2.1 The structure and reactivity of nanoclays

A reaction model for two dominant types of natural nanoclay (1 : 1 and 2 : 1 sheet silicates) is presented in Fig. 1, showing the location of internal surface (interlayer) sites, the fixed negatively charged surfaces and variably charged particle edges, and the sites of metal cation substitution in the tetrahedral ($M_{\text{Tet}}\text{O}_4$ where $M_{\text{Tet}} = \text{Si}$ or Al), and octahedral layers ($M_{\text{Oct}}\text{O}_6$ where $M_{\text{Oct}} = \text{Al}$, Mg or Fe) (Fig. 1).³ Nanoclays represent a group of very small, partly ordered and disordered minerals that typically occur as sheets or fibres with an imbalance in electrostatic charge. The most common building block used is that of montmorillonite, which consists of ~ 1 nm thick two-dimensional aluminosilicate layers (2 : 1 types), comprising one aluminium octahedral (AlO_6) sheet sandwiched between two silicon tetrahedral (SiO_4) sheets and two expandable interlayers (Fig. 1). The 2 : 1 montmorillonite type differs from that of

palygorskite which has a ribbon structure of 2 : 1 aluminosilicate with a fibrous form and non-expandable layers. Similarly, zeolite also differs from montmorillonite with a three-dimensional connected aluminosilicate framework. On the other hand, 1 : 1 clay minerals, such as kaolinite are formed as hexagonal to pseudo-hexagonal plates with alternating octahedron and tetrahedron layers. Halloysite, similar in composition to kaolinite, contains a water monolayer in adjacent layers and often forms as a tubular shape.

Depending on structural variation, clay minerals possess moderate to large specific surface area ($\sim 5\text{--}750\text{ m}^2\text{ g}^{-1}$), low to high cation exchange capacity (CEC) ($\sim 3\text{--}1500\text{ cmol}_c\text{ kg}^{-1}$), good mechanical and chemical stability, and a layered structure. Their surface charges are typically heterogeneous in nature and are controlled by cationic substitutions in the tetrahedral or octahedral framework that make up these thin particles.⁸ Hydrated nanoclays are characterised by a variety of reaction sites where diverse types of surface complexation can occur dependent on surface layer charge, pH and ionic concentration (Fig. 1). Inner sphere complexes with intermediate bond strengths between ionic and covalent forces are commonly developed on the variably charged edge sites.² In contrast, electrostatically bonded outer-sphere complexes typically characterise the diffuse double layers of permanently charged external surfaces and the surfaces of nanopores within the interlayer space. More diffuse ion complexation can also develop further afield within the diffuse double layer held by long-range electrostatic forces. The reactivity of nanoclays is used to tailor them with functional molecules (*e.g.*, surfactants, biopolymers) to produce new properties that are essential for environmental decontamination, such as enhanced surface area, porosity and hydrophobicity (Fig. 3).² In the case of shape, various nanoclay minerals provide a unique physical architecture. For example, smectite can expand using its interlayer



Jock G. Churchman

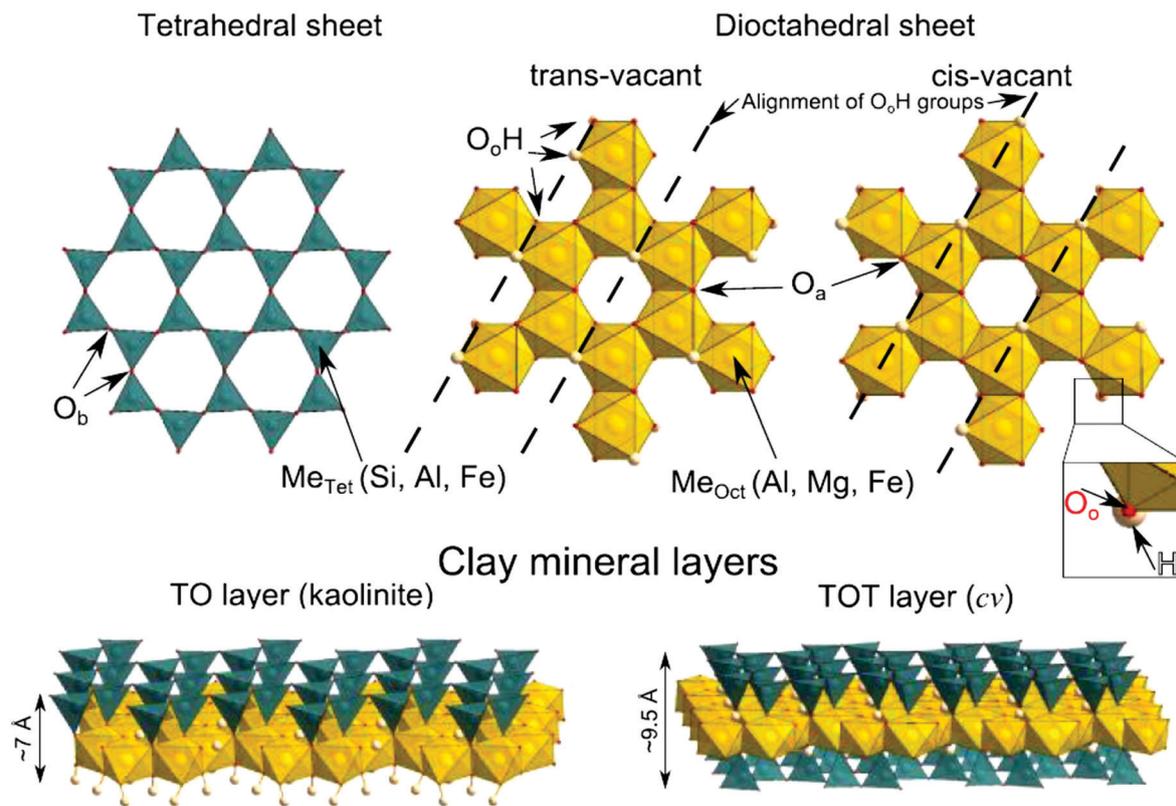
Jock Churchman is an Adjunct Senior Lecturer at the University of Adelaide and Adjunct Professor at the University of South Australia. A chemistry PhD from Otago University was followed by several prestigious research positions in USA, New Zealand and Australia. His research has included halloysite, clay mineral genesis, acid dissolution and organic complexes, clays and soil physical properties, and their environmental applications.



Ravi Naidu

Ravi Naidu is the Global Innovation Chair and Director of the GCER at The University of Newcastle, Australia. He has been a global leader in interdisciplinary research over two decades in chemistry of various sorbents and their 'risk-based' applications to managing contaminated sites. He received a PhD and DSc in environmental science from Massey University, New Zealand and is the highest cited environmental scientist from Australia. He is an elected Fellow of many professional organisations including the Australian Academy of Technological Sciences and Engineering. He won the Richard Pratt – Banksia CEO Award recognising his contributions towards environmental sustainability.

Clay mineral sheets



Clay mineral particles

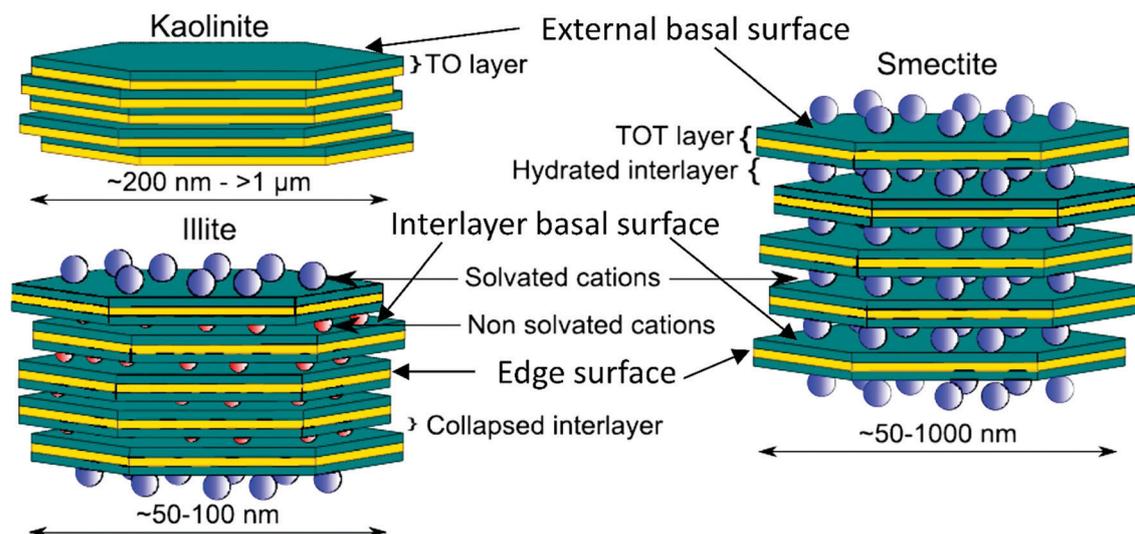


Fig. 1 Tetrahedral (T) and octahedral (O) sheets, TO (e.g., kaolinite) and TOT layers (smectite), and clay mineral particles. The figure is used after Tournassat et al.⁸ Copyright (2015) Elsevier.

spaces (Fig. 1), while single platelets of kaolinite can be used as nanosheets. In contrast, halloysite or palygorskite provide forms of tubular/hollow structures, whereby, halloysite, widely known as the halloysite nanotubes (HNTs), has become a material of diverse application due to its unique nanotube

structure. HNTs have layers of exterior sheets of siloxane (Si-O-Si) and interior sheets of Al-(OH)₃ and the rolling of these layers create exterior, interlayer and lumen surfaces.²² The size of the lumen for each individual HNT is about 15 nm and the external diameter is ~50 nm, whereas the tube length typically

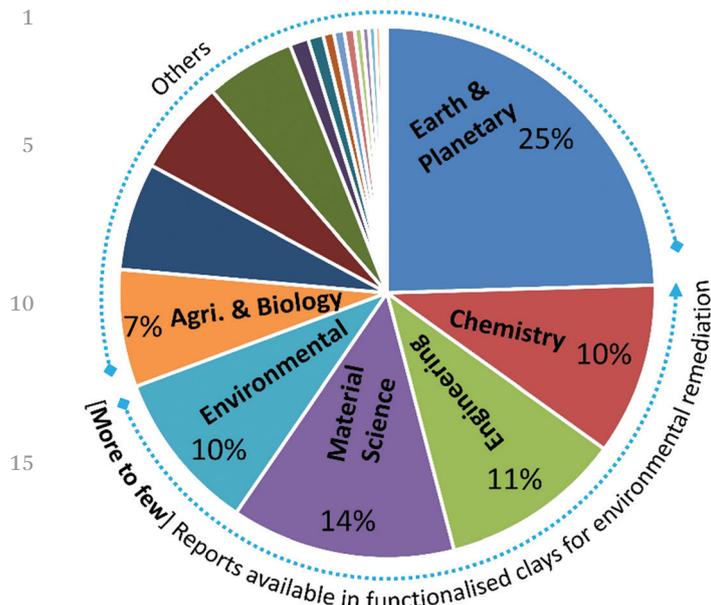


Fig. 2 The subject area-wise research on clay minerals in the last 10 years of time (2008–2018; data retrieved on 16 April 2019 using “Scopus” database; search criteria: search word “clay minerals”, limit: article, abstract, keywords).

varies from ~300–1000 nm. Due to the presence of such a hollow structure, these tubes have been used as a storage system for pesticides applied in agriculture and holding surfactants for their controlled release to combat environmental contaminants.

A major advantage of most of the nanoclays is that they allow functionalisation with an array of chemicals as illustrated in Fig. 3. Such treatment produces acid or alkali-treated clay, pillared clay, clay-supported nanoparticles, organoclay and a number of other types of clay modified with surfactants or other chemicals.⁷ These functional properties are required to sorb targeted contaminants²³ or slowly release toxic chemicals for agricultural purposes, such as pesticides, in a controlled manner.^{24,25} Heavy metal(loid)s (*e.g.*, cadmium, arsenic, lead, *etc.*) and organic contaminants (*e.g.*, polycyclic aromatic hydrocarbons (PAHs), oil, pesticides) have been successfully removed from water, soil and sediments following such applications.^{26–28} The disadvantage is that the modifying chemicals that reside within the clay mineral structure are also commonly toxic to the essential (micro)organisms when applied to the contaminated sites.^{29–34}

Over the last two decades, two parallel research topics have evolved related to environmental remediation using modified nanoclay products: (i) the preparation of sorbents for the immobilisation, catalysis and transformation of contaminants, and (ii) the development of materials for enhancing biodegradation of contaminants. The first topic aims to improve the efficiency of remediation by direct removal of target contaminants but often ignores the impact of sorbents on the biotic population (*e.g.*, microorganism, worms) and risks introducing a secondary pollutant to the environment. The second topic is

based on models and empirical research that allows for micro-organisms, in particular bacteria, to reside intertwined with the minerals.³⁵ This is made possible by the addition of natural or some modified clays that are known to support bacterial activity through close interactions with clay mineral surfaces, which maintains nutrient supply within a clay-modulated bacterial network.^{36–39} These interactions may lead to the formation of protective “clay-hutches”⁴⁰ and finally, the production of biofilms,^{41–43} which are favourable for the bioremediation of contaminants.⁴⁴ With either topic, limited attempts have been made to achieve satisfactory compatibility and eco-compliance with the environmental flora and fauna. The specific functionalisation and their environmental compliance are discussed in the following sections.

2.2 Organoclay: surfactant-modified nanoclays

Organically modified clay minerals, often referred to as organoclays, are predominantly prepared by modification using surfactants.^{46,48} Due to their diverse properties, organoclays have moved beyond laboratory development, and are in the stage of field testing for remediation purposes.^{33,49–51} Organoclays also serve as the precursors for many other types of modified nanoclays and related products as discussed elsewhere in this paper.^{52–55} As there is a growing number of organoclay applications for combating environmental pollution, their bio-/environmental compatibility is particularly important but is often overlooked. Typically the organic compounds are hosted on the outer surfaces, interlayers or interparticle pore space of nanoclay particles (Fig. 4).^{48,56} The intercalation and surface adsorption of surfactants depends on the charge density of accessible surfaces, the type of layer-to-layer bonding and associated cations (Fig. 4).⁸ For example, certain cations in swelling tetrahedral–octahedral–tetrahedral type clay minerals (*e.g.*, smectite) favour the complexation of cationic surfactant within interlayer sites by increasing cationic exchange, but adsorption of such amines by tetrahedral–octahedral type non-swelling clay minerals (*e.g.*, kaolinite) may require grafting with a precursor molecule, such as 1,3-butanediol, or di(ethylene) glycol methyl ether.^{8,57} Surfactants are used in environmental clay science generally for two purposes: (i) to functionalise nanoclays to produce a newly synthesised material used for sorbing the target pollutants, and (ii) to controlled release of these surfactants using the confinement of nanoclays. The biocompatibility of these types of organically-modified nanoclays has been discussed in more detail in the following sections.

2.2.1 Cationic surfactant-modified nanoclays. Cationic surfactant-modified clays and zeolites are the common candidates in environmental applications.^{34,46,59–61} Widely used surfactant cations are hexadecyltrimethylammonium (HDTMA, $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3$), octadecyltrimethylammonium (ODTMA, $\text{CH}_3(\text{CH}_2)_{16}\text{N}^+(\text{CH}_3)_3$), dodecyltrimethylammonium (DDTMA, $\text{CH}_3(\text{CH}_2)_{10}\text{N}^+(\text{CH}_3)_3$), dioctadecyldimethylammonium (DDDMA, $[\text{CH}_3(\text{CH}_2)_{17}]_2\text{N}^+(\text{CH}_3)_2$), and similar ammonium cations.^{62,63} These are intercalated into the clay mineral structure through cationic exchange and grafted onto the nanoclay surface.^{46,48} Generally heat

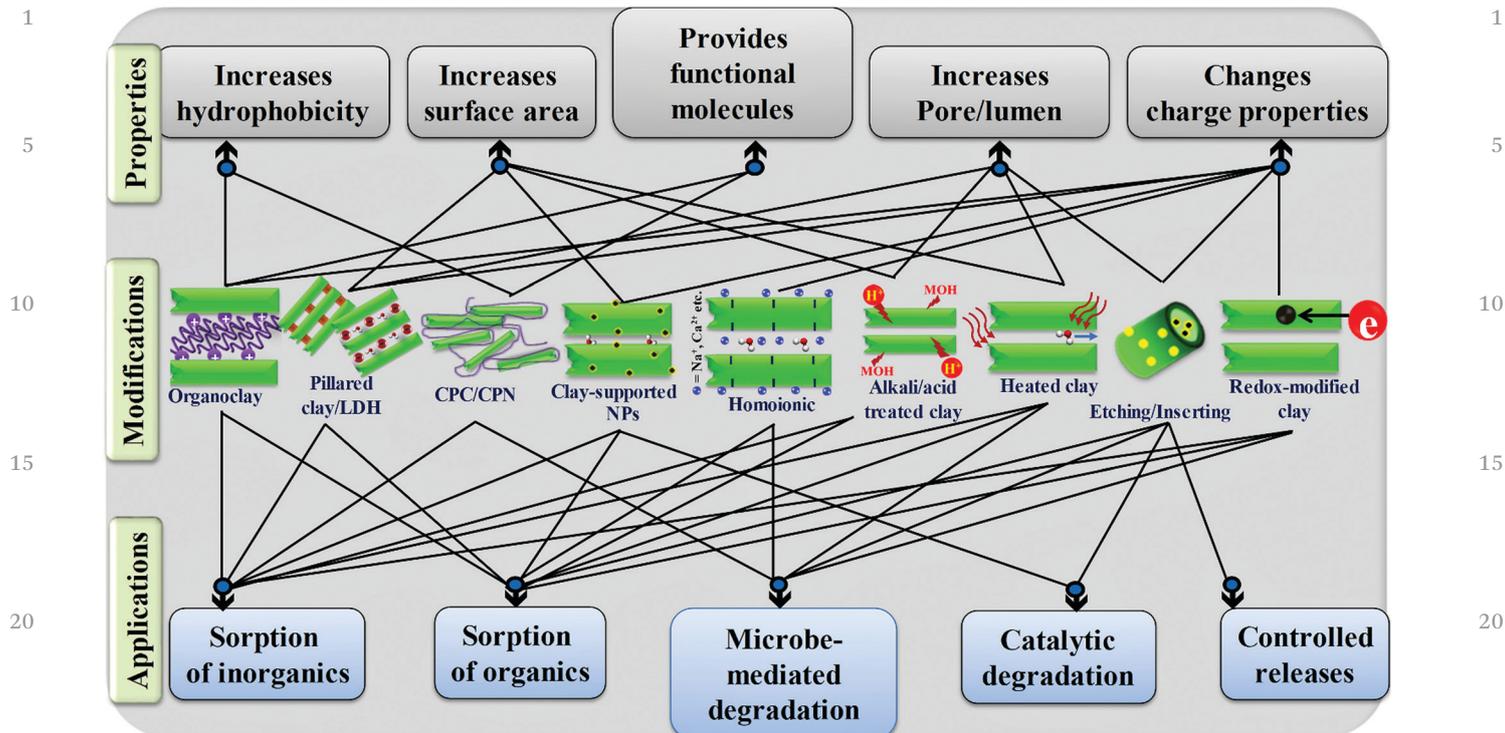


Fig. 3 A scheme of potential networks showing modified clay minerals with their important properties and environmental applications. Their preparation and technical details can be found elsewhere.⁴⁵ From left to right, brief terminology of the modified clay is: (i) organoclay representing clay minerals, particular those with expandable layers are modified with organic compounds, commonly in the form of surfactants,⁴⁶ (ii) LDH is layered double hydroxide, which can be a synthetic and natural anionic clay and is often modified to replace interlayer anions with desired anions; the term "pillared clay" is often used to indicate "pillared interlayer clay" that should ensure the pillaring species increase the interlayer space and maintain accessible porosity without collapsing upon heating,⁴⁷ (iii) CPC/CPN, clay–polymer composite or clay–polymer nanocomposite, (iv) clay-supported nanoparticles (NPs), for instance, those used as the carrier or supportive material of other inorganic nanoparticles, such as metal or metal oxide NPs, (v) "Homoionic" clay, generally mono-, di- or tri-valent elemental cations are saturated on cationic nanoclay minerals (e.g., smectite), (vi) acid or alkali-treated clay, commonly HCl and H₂SO₄ are used as acid or NaOH and KOH as alkali to modify clay and to manipulate pores and surface area, (vii) heated clay or thermally activated clay to manipulate hydration states, (viii) etching/inserting, commonly produced by the modification of halloysite and palygorskite where the size of lumen/pore and decorating with desired functional components are customised, and (ix) redox-modified clay, the manipulation of oxidation and reduction states of Fe-rich clay. The most frequently used clay and nanoclay products are discussed in this article.

(~80 °C) and mechanical stirring enhance the reaction for ~3 h and the loading of surfactant is dependent on the CEC of the nanoclay and the mass ratio of water/clay (~10:1 to 20:1) (Box 1).^{46,64} Quaternary ammonium compounds, (QACs), more simply known as "quats", contain nitrogen cations (N⁺) supported by four species of alkyl or aryl groups. They are commonly used to

manipulate clay properties but a primary concern as a source of toxicity. These compounds can persist in the environment, and increase the secondary pollution concern.⁶⁵ In some cases, they have been documented to introduce toxicity to natural biota.^{66–68} Other toxic QACs belong to gemini-type surfactants,⁶² where two hydrophilic heads and two hydrophobic tails are bridged by a

Box 1: Amount of surfactants in organoclays

Surfactant loading to nanoclay is calculated by the f fraction of its CEC that is replaced by the surfactant cation, following the equation:

$$M_c = f \cdot \text{CEC} \cdot X \cdot M_w$$

where, M_c is the mass of surfactant required to satisfy f fraction of the CEC of clay. X is the mass of clay (g) and M_w is the molecular weight of the surfactant (g mol⁻¹).

For example, HDTMA has a molecular weight of 364.45 g mol⁻¹. If a montmorillonite's CEC is 110.5 cmol_c kg⁻¹, then to synthesise 1 g of organoclay 0.40 g of HDTMA is required.

In such cases with a maximum of 0.5% organoclay used in the remediating bulk media *in situ* (e.g., water or soil), 1 kg of water or soil would receive 2.0 g of HDTMA. However, based on the reports, if a maximum 5% of the intercalated surfactant is released back during the clean-up application, 0.1 g surfactant per kg environmental media (e.g., soil or water) is the amount for potential toxicity caused directly by the surfactant.

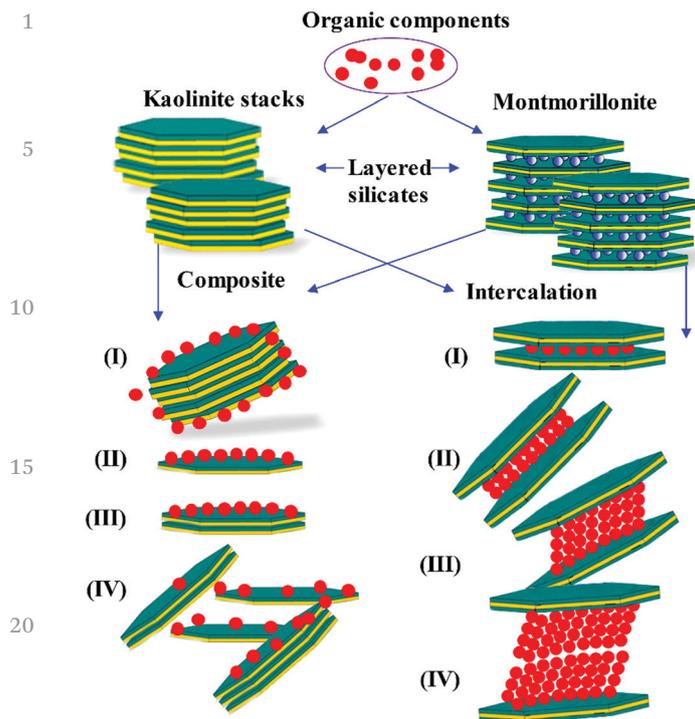


Fig. 4 Most commonly occurring arrangements of surfactant-modified clay. Left: Various clay mineral platelets with the surfactants forming "traditional/conventional" composite (I–IV). Right: Surfactant intercalated layered nanoclay (e.g., montmorillonite), (I) lateral monolayer, (II) lateral bilayer, and (III) & (IV) paraffin-type mono and bi-layer, respectively. The detailed mechanism of such arrangements can be found elsewhere.^{8,48,56,58}

spacer.⁶⁹ Microbial performance in natural conditions is governed by their physiological activities. These synthetic compounds used for modifying clay products may cause disturbance at the genetic level and thus influence these physiological activities.⁷⁰ Perhaps direct exposure of QACs to the soil, sediment and water impose such detrimental effects;⁷¹ however, usually QACs are protected in the clay structure, especially in the interlayer spaces of the swelling nanoclays (Fig. 4). In these cases, the loading of QACs and desorption from the nanoclay will be the determining factors that induce organoclay-induced ecotoxicity.

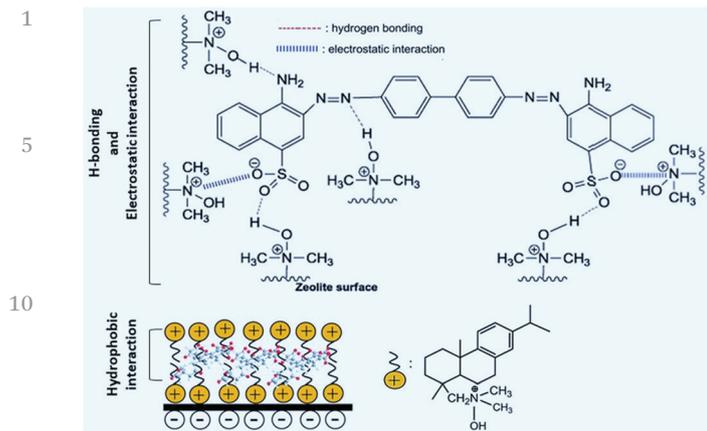
Among QACs, HDTMA is the most widely used for material modification and is a concern in terms of its potential ecotoxicity. There appears to be a significant gap in organoclay research between detailed toxicological studies and the claims that QAC-organoclays are harmful or safe for the environment. Limited reports are available documenting that organoclays produced by synthetic cationic surfactants are toxic to the natural biotic community.^{71–74} Sarkar *et al.*⁷² concluded that few QAC (e.g., HDTMA, ODTMA)-modified clay minerals exhibit toxicity to soil microbes by affecting their enzymatic functions such as dehydrogenase and nitrification. These organoclays are also noxious to earthworms as indicated by up to 62% body-weight loss in the presence of organoclays (loading rate: 1% in soil). However, some organoclay types may result in low toxicity to the microflora and fauna; for example, Arquad[®]

(hydrogenated tallow form of DDDMA) modified smectite is considered to be less toxic than HDTMA and ODTMA-modified smectite.⁷² Whether these materials are compatible with native microorganisms at their genomic level over the long term remains inconclusive or has been ignored as a topic. Abbate *et al.*²⁹ showed that QAC-modified smectite (commercially available alkyl quaternary ammonium-modified smectite) can either inhibit or stimulate different types of microorganisms. In a later work using 16S-rRNA of a cultured bacterial population from a compost soil, they claimed that organoclays do not have any repressive effect on the original microbial community.⁷⁵ However, a culture-independent and different microorganism assemblages and contrasting environmental conditions play a significant role in environmental process.⁷⁶ These should be considered before diagnosing any detrimental effects due to the introduction of foreign materials (e.g., organoclays).

Box 1 represents an estimation of the amount of surfactant required to synthesise organoclays and shows that the CEC plays a key role in controlling the ecotoxicity when the material is applied at a polluted site. During preparation, the loading of QACs can be optimised to minimize the ecotoxicity to produce more biocompatible material. Witthuhn *et al.*⁷⁷ synthesised organoclay using DDDMA and reported that $\leq 40\%$ loading of DDDMA relative to a clay's CEC produced a material supportive to a potential 2,4 dichlorophenol-degrading bacterium. The organoclay was loaded at 1 g L^{-1} in a liquid medium and during testing resulted in $\sim 50\%$ degradation of the pollutant. The absence of free QAC cations other than these adsorbed within the interlayer space should achieve such biocompatibility.^{77–79}

While we have been observing the invention and re-invention of several surfactant cations to generate enhanced nanoclays useful to pollutant adsorption or desorption,^{80–82} the long-term fate and effect of such surfactants in soil and water are not fully known. There are compelling reasons to introduce "greener" cationic surfactants than those currently used to modify materials for real-world applications.^{83–85} Goursaud *et al.*⁸³ synthesised biodegradable surfactants using betaine glycine as the reactant, which was subsequently degraded up to 70% by aerobic microorganisms within 28 days of incubation. Our review finds that these "green" surfactants have not been used to synthesise organoclays for environmental applications, which warrants further investigation regarding the material's performance and cost.

As the use of long-chain cation amines negates the environmental sustainability, alternatives to the cationic amine surfactants, have been searched for and used to modify clay and related materials.⁸⁶ For example, a rosin-based surfactant in the form of an amine oxide such as *N,N*-dimethyl dehydroabietylamine oxide (DOOA) was synthesised *via* alkylation and oxidation of dehydroabietylamine.⁸⁷ A zeolite modified with a loading of twice of its external CEC could effectively adsorb anionic contaminants such as Congo red dye⁸⁶ and humic acid⁸⁸ from aqueous solutions. This material was sustained in a wide range of pH (5–9), and it lost only a maximum 5% of the loaded surfactant. The mechanism of anionic contaminant



15 Fig. 5 Mode of adsorption of anionic dye (e.g., Congo red) with cationic surfactant-modified zeolite. The figure is adapted and modified with permission from Liu *et al.*⁸⁶ Copyright (2014) Elsevier.

removal from the natural system occurs *via* the zeolite-supported surfactant's reactive sites.^{86,88} Interactions involve H-bonding between the N- and O-containing groups of contaminants and the H atoms from $\text{-N}^+(\text{CH}_3)_2 \rightarrow \text{OH}$ groups of DOOA with electrostatic interaction between the negatively charged group of contaminants (e.g., SO_3^- of Congo red dye) and the positively charged surfactants (e.g., $\text{R-N}^+(\text{CH}_3)_2 \rightarrow \text{OH}$ in the case of a DOOA modified zeolite surface). Interaction between contaminants hydrophobic sites and the modified zeolite is another mechanism used to explain contaminant adsorption (Fig. 5).^{86,88}

2.2.2 **Modification using anionic surfactants.** Anionic surfactants, such as sodium dodecyl sulfate (SDS) or dioctyl sodium sulfosuccinate (DOSS) are mostly available as commercial oil dispersants. In clay science, they are mostly used to synthesise types of organoclay. However, it is yet an unfavourable practice due to the low driving force for the intercalation of these anionic major compounds into the interlayers of 2:1 smectites.⁸⁹

The free anionic surfactants are toxic for aquatic ecosystems,^{90,91} although relatively less than that the cationic types, such as QACs. Several of these anionic candidates might

be readily biodegraded in aerobic conditions but are likely to persist in anaerobic environments.⁹⁰ This was shown by the negligible rates of surfactant biodegradation when applied to the deep-water horizon oil spill as a dispersant.^{92,93} However, controlled release of these surfactants using a confined carrier, such as HNT, could be used as the oil dispersant. This leads to oil biodegradation and such slow release complies with the slow degradation of the surfactant itself. For instance, an anionic surfactant such as DOSS showed relatively strong bonding with the positively charged inner surface of HNT lumen and was released more slowly than a non-ionic equivalent such as Tween[®] 80. As DOSS is more toxic than Tween[®] 80 and the coupling chemistry of this clay-anionic surfactant is useful for mitigating such surfactant toxicity (Fig. 6).^{94,95} A successful loading of surfactant into the clay lumen might require vacuum suction for the batch reaction (e.g., methanol-soluble surfactant with 0.2% HNT (w/v) with mechanical stirring).⁹⁵ The HNT interwoven with DOSS smeared around the oil droplets reduces the net interfacial energy to stabilise the emulsion (Fig. 6).⁹⁵

In the case of anionic surfactant-modified 2:1 smectite nanoclay, the complete adsorption of anions within the inter-layer is important to prevent the release of the "toxic" molecules into the soil and water habitat. However, their intercalation process is different from that of cationic surfactants. For example, SDS-montmorillonite intercalation occurs mainly through ion-dipole interactions with structural and exchangeable protons or cations (e.g., H_3O^+ , Ca^{2+} , Na^+).⁸⁹ In contrast, an anion exchange mechanism applies for the anionic nanoclays, such as layered double hydroxide (LDH) (e.g., hydro-talcite), and complete intercalation of surfactants, such as sulfonate compounds can be achieved. Depending on the type of target pollutants, the intercalated surfactants trap can immobilise them in soil, by so-called complete sequestration of pollutants⁹⁶ or by their controlled release, such as for pesticides to minimise environmental issues.⁹⁷

Although these types of organoclays show significant potential application for environmental remediation, there has been little toxicological study concerning their application.^{98–100}

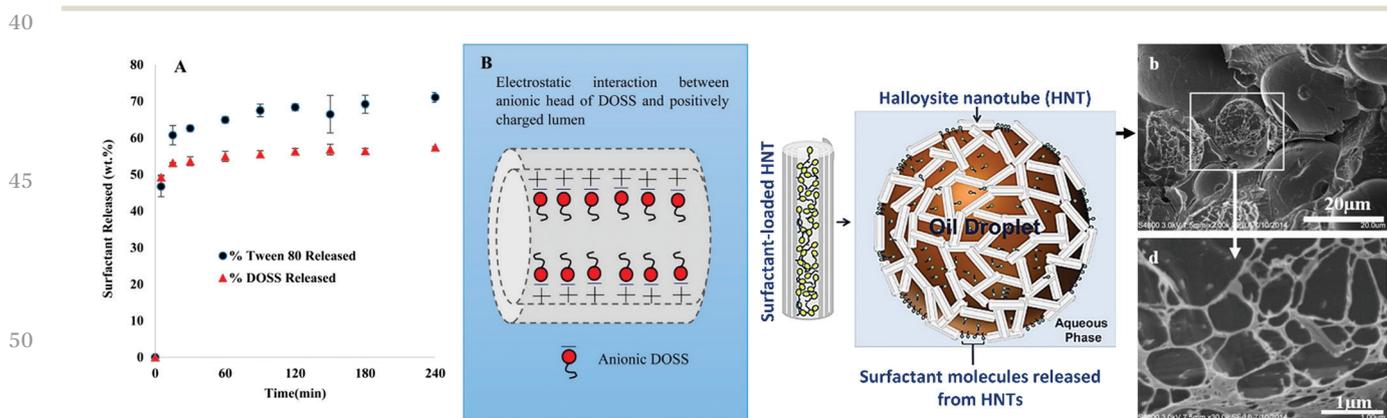


Fig. 6 (left) (A) Desorption kinetics of dioctyl sodium sulfosuccinate (DOSS) and Tween[®] 80 from halloysite nanotubes. (B) Electrostatic interaction between the anionic head of DOSS and the positively charged lumen. (right) Cryo-SEM images of dodecane-in-water emulsion (ratio 1:3) stabilized by DOSS-loaded HNT at 12.4 wt% DOSS loading (total HNT 0.1 wt%). The figure is reprinted (adapted) with permission from Nyankson *et al.*⁹⁴ (left) and Owoseni *et al.*⁹⁵ (right). Copyright (2014, 2015) American Chemical Society.

2.2.3 Modification using non-ionic surfactants. Fatty acid esters of sorbitol (*e.g.*, Span[®] 80 and Tween[®] 80, chemically known as sorbitan monooleate and its polyethoxylated form, respectively) and alkylphenol ethoxylates (*e.g.*, Triton X-100) are widely used as non-ionic surfactants for modifying nanoclays. These surfactants are complexed in the interlayer of the montmorillonite type clay minerals by H-bonding and ion-dipole interactions.^{101,102} Compared to ionic surfactants, non-ionic species offer a unique property to the modified nanoclays by enhancing the hydrophobicity of the material without changing its charge characteristics.¹⁰¹ Interestingly, the hydrophobic components of these organoclays are prone to be biodegradable, thus, the material was considered “biocompatible”.^{103,104} In the environmental application of these materials, “biocompatible” or “bio-organoclay” was claimed because of the known “nontoxicity” of Tween[®] 80 but without testing the actual biocompatibility of the synthesised organoclays.^{103,104} This type of organoclay is also considered to have a high thermal and chemical stability.¹⁰⁵ Despite the potential of non-ionic surfactant-modified nanoclays as environmentally friendly products, their adsorption capabilities are not as good as ionic and zwitterionic counterparts, and their hydrophobicity not a favourable property in hydrous conditions. However, there is a chance that non-ionic surfactant-modified nanoclays can be improved with choosing the appropriate types of nanoclays and by doping other functional compounds (*e.g.*, biopolymer) to introduce more contaminant binding sites.

2.2.4 Modification using zwitterionic surfactants. Zwitterionic surfactants are amphoteric, often the derivatives of QACs, holding both cationic and anionic functional groups in their structure. Due to their availability, low cost and low toxicity, zwitterionic surfactants are an interesting modifier for the materials applicable to natural environments.^{106–109}

Compared to cationic (*e.g.*, alkyl trimethyl ammonium salts), anionic (*e.g.*, linear alkyl benzene sulphonates with the number of $C = 11.5–11.8$) and non-anionic ($C_{12}–C_{15}$; mean C value < 14) surfactants, amphoteric species (*e.g.*, alkyl betaines, alkylamido betaines and alkyl imidazoline derivatives with all $C_{12}–C_{14}$) are readily biodegradable in both aerobic and anaerobic environments.¹¹⁰ The compatible nature of the sulfobetaine type zwitterionic surfactants first received attention to modify nanoclays and related minerals for their uses as remediating materials.^{109,111} Complete intercalation of these surfactants is essential for minimising ecotoxicity caused by such chemicals. Recently a new intercalation mechanism has been proposed to prepare an organoclay with a betaine type surfactant.¹⁰⁶ They have a certain advantage over QACs. Unlike the cationic surfactants, zwitterionic 3-(*N,N*-dimethylpalmitylammonio)propane sulfonate, which has both a quaternary ammonium cation and a SO_3^- ($M_w = 462.73 \text{ g mol}^{-1}$), is intercalated into montmorillonite *via* ion-dipole attraction instead of ion exchange. This enables the novel synthesis of organoclays following the cross-coupling intercalation mechanism (Fig. 7).¹⁰⁶

Mixed contaminations are of particular concern in real-world clean-ups.^{112,113} Zwitterionic surfactant-modified nanoclays show particular promise in combating mixed inorganic-

organic contaminations of soil and water systems. Instead of using cationic HDTMA, Ma *et al.*¹⁰⁸ employed a zwitterionic hexadecyldimethyl (3-sulphonatopropyl)ammonium to modify montmorillonite and observed that it could remove mixed inorganic-organic contaminants (Cu(II)-phenol) much more effectively than cationic organoclay. Recently Lazorenko *et al.*¹¹⁴ used two zwitterionic surfactants, namely oleylamidopropyl betaine and hydroxyethylalkyl imidazoline to synthesise organo-montmorillonite and reported that with only 100% equivalent to the clay's CEC they produced better products in terms of expansion of interlayer space (4.63 nm and 4.40 nm, respectively) and the adsorption of contaminants.

As presented in Fig. 4, the interlayer spaces can be expanded by surfactants without exceeding the clay's CEC, but toxicity remains minimal. Since zwitterionic products can also contain quaternary ammonium cations, direct contact of these surfactants can induce significant toxicity for planktonic aquatic organisms.¹¹⁵ After controlled and packed loading of zwitterionic surfactants into layered nanoclays,¹⁰⁹ they are no longer expected to impact the planktonic or higher ranked organisms in water, sediment and soil environments. Using “zwitterionic” L-carnitine intercalated montmorillonite (100% clay's CEC equivalent) as the carrier of atrazine produced efficient post-delivery biodegradation of this pesticide compared to cationic HDTMA-modified species.¹¹⁶ The weak basic nature of atrazine ($\text{pK}_a = 1.7$) is favourable for acid-base interaction with the acid group ($-\text{COOH}$) of L-carnitine, which is prone to breakdown in an alkaline soil environment. Under such conditions, desorption-driven microbial breakdown of atrazine is known to occur.¹¹⁶ A contrasting result was reported when pH-resistant hydrophobic bonding of atrazine-HDTMA was activated.¹¹⁶ Also, the longer alkyl chain of these surfactants might prime to the toxicity; thus, employing shorter chained species in nanoclay modification may be less damaging to ecosystem health.

Instead of using potential environmental noncompliant surfactant cations, natural organic cations that may or may not contain polar functional groups are likely to provide a greener approach for the adsorption of contaminants with polar sites. Cruz-Guzmán *et al.*¹¹⁷ synthesised organo-montmorillonite using L-carnitine, L-cystine dimethyl ester and thiamine. These are structurally zwitterionic compounds; however, in acidic conditions during organoclay synthesis ($\text{pH} \sim 3.0$), they exhibit protonation and ensure participation in cation exchange with the interlayers of nanoclays.^{116,117} Depending on the targeted pollutant, the mode of adsorption might not rely on such cations, rather on the counterpart anions. To synthesise these cation-modified montmorillonites, an acidic medium was maintained using 1 mM HNO_3 (1 : 50 v/v clay/solution ratio) and with up to 150% modifier loading of the clay's CEC. Carnitine@montmorillonite showed complete adsorption of pesticide (*e.g.*, simazine) followed by cystine dimethyl ester and thiamine counterparts and raw nanoclay (Fig. 8). For Carnitine@montmorillonite, this adsorption was favoured by either the: (i) increase of ionisation of $-\text{COOH}$ groups involving proton transfer, or (ii) H-bonding of N atoms

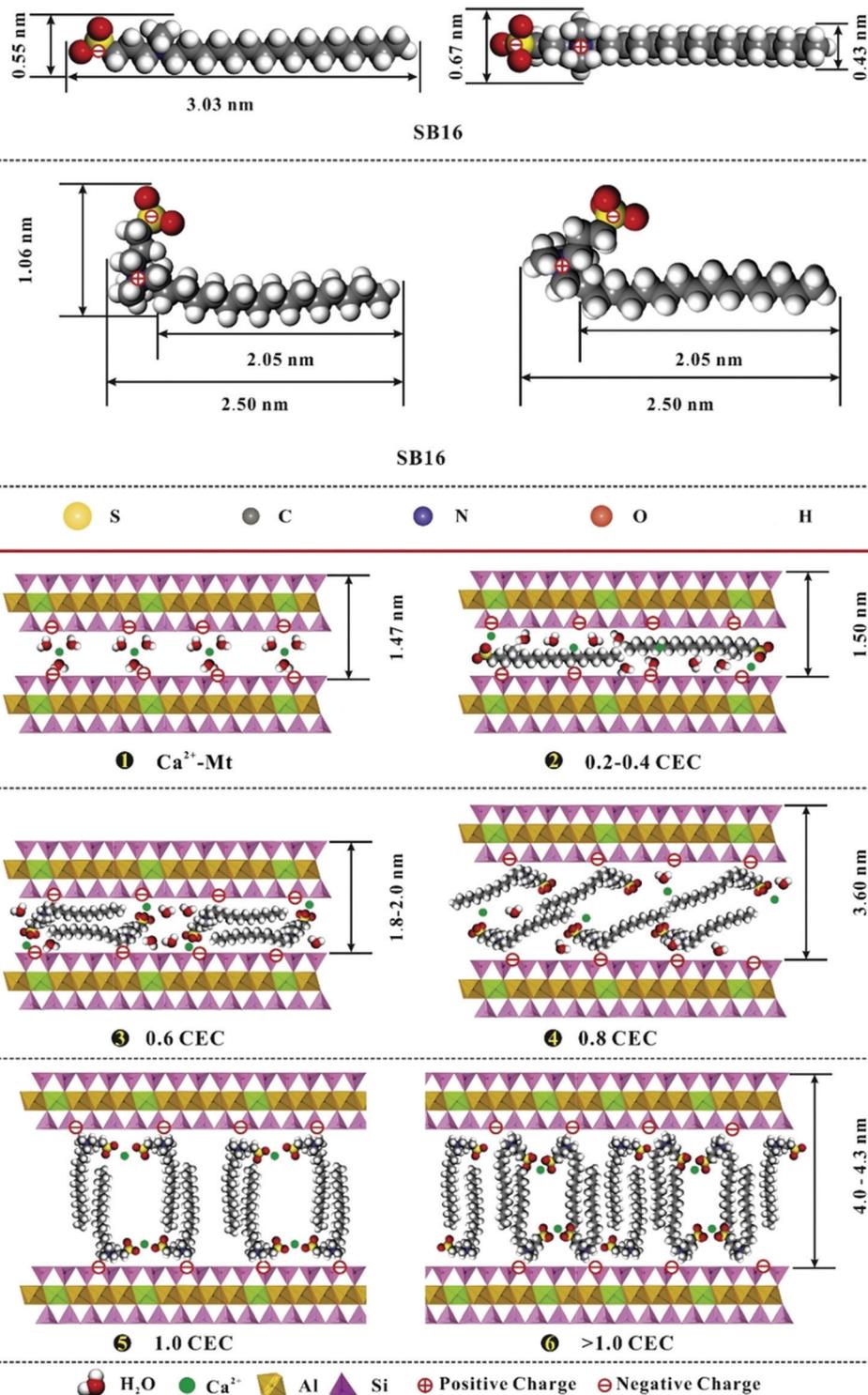


Fig. 7 Intercalation mechanisms of zwitterionic sulfobetaine surfactant into the interlayer of smectite nanoclay. SB16 denotes sulfobetaine containing tail of 16 C behind the N cation. Figure is adapted with permission from Zhu *et al.*¹⁰⁶ Copyright (2017) Elsevier. 1.0 CEC means that the loading of surfactant is 100% equivalent to the cation exchange capacity of nanoclay; similarly, 0.6 CEC = 60% of CEC and so on.

of simazine and the $-\text{COOH}$ groups.¹¹⁸ Promisingly, 100% CEC or 150% CEC loading was similarly effective to adsorb the target pollutants with carnitine@montmorillonite, which provides an easy selection of $\leq 100\%$ CEC approach to avoid

loss of modifying agents during their application in the environment.

2.2.5 Surface-tailoring of organoclays, surfactants mixtures and regeneration and recycling of organoclays. With the

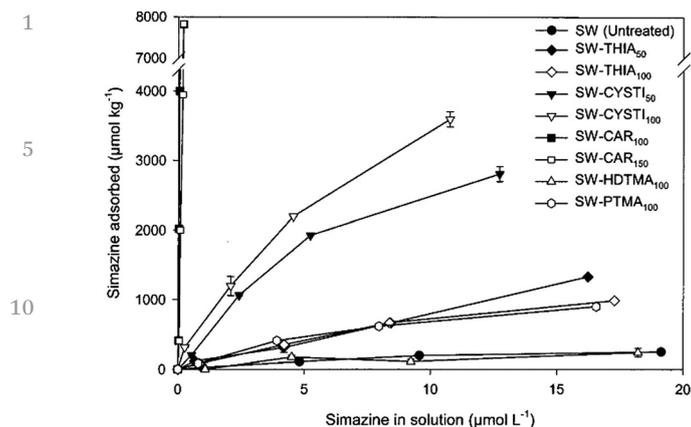


Fig. 8 Simazine adsorption on modified montmorillonite. SW = Wyoming montmorillonite, THIA = thiamine, CYSTI = L-cystine dimethyl ester, CAR = L-carnitine, HDTMA = hexadecyltrimethylammonium, PTMA = phenyltrimethylammonium. The number after the modified clay (e.g., SW-CAR₁₀₀) is the amount of surfactant equivalent to clay's CEC. The figure is reprinted with permission from Cruz-Guzmán *et al.*¹¹⁷ Copyright (2004) American Chemical Society.

prospect of enhancing clay-microbial interaction for environmental remediation,^{37,38} QAC-modified clay requires further surface-tailoring to eliminate the chemical residues or suppress functional molecules that are toxic to (micro)organisms.^{112,119} Surface-tailored organoclays (fatty acid@QAC-modified clay) have been developed for this purpose, in contrast to QAC-modified organoclays.^{112,120} The material showed a selective

binding capacity for heavy metals (e.g., Cd) and PAHs (e.g., naphthalene, phenanthrene) in a mixed contaminated scenario.¹¹² This clay-based product also showed more biocompatibility to bacteria in an aqueous suspension¹²¹ and a field soil.¹¹⁹ When applied to originally contaminated soil, the sorbent-mediated biodegradation of PAHs revealed that the modified organoclay also performed well under natural conditions.¹²² In a microcosm study, the modified organosmectite (fatty acid@QAC-modified clay) increased bacterial growth by 5–7 fold more than its parent clay and enhanced the biodegradation of phenanthrene from the soil. Considering this potential, Fig. 9 proposes a model of an effective sorbent for target contaminants, whereby the organoclay remains neutral or positive to the growth and function of the natural microbial community.

In these studies, the net cationic charged organoclay (Arquad[®]-modified smectite) was converted into a net negatively-charged organoclay when palmitic acid (CH₃(CH₂)₁₃CH₂COOH) was further introduced into the organoclay.^{112,119} The authors argued that the insertion of a low amount of surfactant ($\leq 100\%$ equivalent to the CEC of clay) and exposure to the biocompatible fatty acid of natural microorganisms could be the key mechanism for mitigating the toxicity of its parent nanoclay (QAC-modified smectite). The long alkyl chain of palmitic acid was attached to the alkyl chain of cationic surfactant (Arquad[®]) and the carboxyl groups remain exposed to contribute their negative charge within the modified form of organoclay (Fig. 9). Such an arrangement of

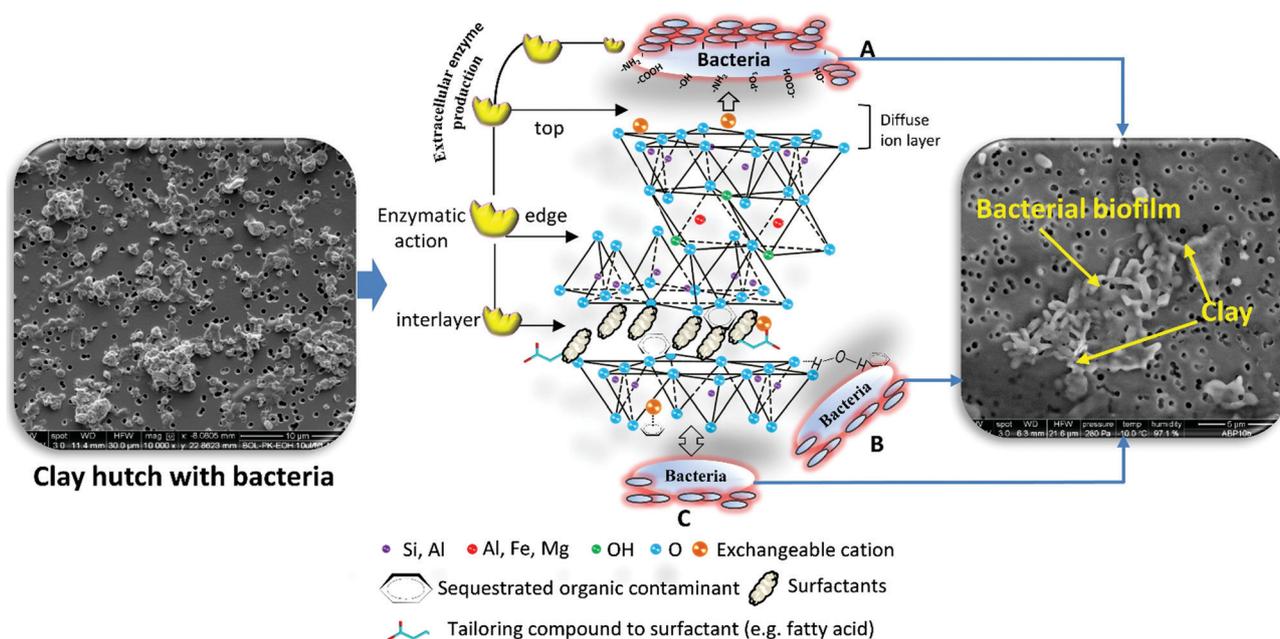


Fig. 9 Mechanism of possible biocompatible (surface-tailored) organoclay and its application in contaminated soil. Once bacteria are compatible with modified clay as forming a hutch-like structure, the extracellular enzyme produced by bacterial biofilm may also enter the interlayer to facilitate sequestered organic contaminants. A, B and C represent electrostatic attachment of bacteria by cation-bridging, hydrogen-bonding and van der Waals interaction, respectively. The scheme is modified from Biswas *et al.*,³⁸ Warr *et al.*⁴² and Secundo *et al.*¹²³ SEM image of clay-hutch is taken from Biswas¹²⁴ as an oil-modified smectite-*Pseudoxanthomonas* sp. and clay-bacterial biofilm from Mandal *et al.*¹²¹ with the copyright permission of Elsevier. The size of item (clay mineral structure, bacteria and chemical compound) in the sketch is not proportional to each other.

1 **Table 1** Various halloysite nanotube-based formulations of different surfactants for an effectively controlled dispersant of soil remediation from water. The table is adapted with permission from Nyankson *et al.*⁹⁴ Copyright (2015) American Chemical Society

Dispersant formulation ^a	Total wt% of anionic surfactant	Total wt% of nonionic surfactant	Dispersion effectiveness (vol%)
HNT-40 wt% DOSS-20 wt% Lecithin FPI-40 wt% Tween [®] 80	60	40	100
HNT-20 wt% DOSS-60 wt% Lecithin FPI-20 wt% Tween [®] 80	80	20	
HNT-40 wt% DOSS-20 wt% Span [®] 80-40 wt% Tween [®] 80	40	60	96.2
HNT-40 wt% DOSS-20 wt% Span [®] 80-40 wt% Tween [®] 80	20	80	
HNT-40 wt% Span [®] 80-20 wt% Lecithin FPI-40 wt% Tween [®] 80	20	80	99
HNT-20 wt% Span [®] 80-40 wt% Lecithin FPI-40 wt% Tween [®] 80	40	60	

10 ^a HNT, halloysite nanotube; DOSS, dioctyl sodium sulfosuccinate-an anionic surfactant; Lecithin FPI, anionic fraction of crude lecithin; Tween[®] 80 and Span[®] 80 are nonionic surfactant.

15 coupling surfactant with fatty acids could be a promising way of adsorbing both hydrophobic pollutants (*e.g.*, PAH) and heavy metals (*e.g.*, Cd) simultaneously.^{112,120} Based on the competitive adsorption of phenanthrene and Cd on this type of nanoclay, Biswas *et al.*¹¹² suggested that the adsorption sites for inorganic and organic compounds were different. Metal cations are more likely to complex with the carboxyl end of fatty acids whereas phenanthrene is probably adsorbed on the tetrahedral sites through H-bonding with silanol groups, by cation- π bonding and by trapping at particle edges (Fig. 9). Such mechanisms allow microorganisms to be hosted on the surface on the clay sheet, and hence they can avoid direct contact with toxic metals like Cd (Fig. 9).¹¹²

20 Although such fatty acid-tailored Arquad[®]-modified smectite was relatively biocompatible and allowed more growth of soil bacteria, there is evidence that it can alter the native microbial community structure.¹²⁵ Using an ecological marker (16S rRNA), this study reported that a few groups of bacteria (*e.g.*, *Proteobacteria*, *Actinobacteria* and *Firmicutes*), which are dominant during petroleum hydrocarbon degradation, changed in their relative abundance. The study was the first research showing the soil microbial community structure after applying potentially microbe-supported clay products (*e.g.*, palmitic acid@QAC-modified smectite). Therefore, it is highly prudent to study further as it is unclear whether alteration of the microbial community structure has any long-term detrimental effects on the ecosystem.

30 In the case of surfactants used to fabricate the surface properties of clay minerals, the effect of their head groups and alkyl properties is another factor in the arrangement of the surfactant in the clay mineral interlayer and its subsequent ecotoxicity.^{62,77,126} This also dictates the adsorption of contaminants, such as that of heavy metals from aqueous solution. Wang *et al.*¹²⁶ tested a series of alkyl ammonium surfactants ranging from primary (NH₂-R) to quaternary cation ((CH₃)₃N⁺-R) species for the modification of smectite and the sorption of Cs. In the remediation of metals from aqueous solutions, metal cations, such as Cs are adsorbed onto cationic organoclays by cation-exchange and hydrophobic interactions, and the hydrated NH₃⁺-R heads bring water molecules and Cs ions better into the surfactants than (CH₃)₃N⁺-R heads.¹²⁶ The benefit is greater adsorption along with the complete exclusion of relatively more toxic quaternary heads. Also, the monomeric

15 forms of QACs induce greater toxicity than their dimeric analogues, but this toxicity can be minimised by tailoring a heteroatom to the spacer or a hydroxyethyl group to the polar head groups, which can provide hydrophilicity to these gemini surfactant-modified materials.⁶²

20 The selection of surfactant or doping of surfactant with relatively non-toxic compounds is an approach that might achieve environmental compatibility, but effective formulations are required and remain under-explored. Nanoclays packed with various surfactants might be useful for dispersing these active agents effectively in natural systems. For example, Owoeni *et al.*⁹⁵ and Nyankson *et al.*⁹⁴ inserted three surfactants into HNT. These included non-ionic (Tween[®] 80 or Span[®] 80) and anionic species (dioctyl sodium sulfosuccinate (DOSS) or Lecithin FPI as an anionic fraction of crude lecithin). They found that such ternary surfactants are more effective in breaking down oil droplets in water by a controlled release mechanism (Table 1). Such release of HNT-laden surfactants is important not only for the continuous supply of the surfactant molecules in the water-oil interface that accelerates oil remediation, but also minimises the loss of surfactants that are redundant and harmful to the ecosystem.⁹⁴ These dispersants are considered “effective” when they are utilised more than 50 \pm 5% in the oil clean-up process.¹²⁷ Only with the support of HNTs, Nyankson *et al.*⁹⁴ reported that batteries of Tween[®] 80, DOSS and Lecithin FPI in HNT lumen were useful for as much as 100% of dispersion (Fig. 10 and Table 1). The oxyethylene “hairs” of Tween[®] 80 might offer steric stabilisation whereas DOSS and Lecithin FPI are ionic at the oil-water interface (Fig. 10D and E). In such a formulation, DOSS was substituted with a non-ionic food grade surfactant (Span[®] 80), and the composite was slightly less effective (99%) but close to 100% (Table 1) due to the inhibition of oil droplet breakup caused by Span[®] 80.¹²⁸ Considering the eco-benefits of using food grade non-ionic surfactants (Section 2.2.3) they could be equally useful to clean-up oil spills without damaging environmental habitats and organisms.^{94,95}

35 Since the uncontrollable desorption of surfactants from organoclays is a critical constraint during application of such materials,⁷⁴ retrieval of pollutant-adsorbed organoclays could be another green strategy. For example, ethyl hexadecyl dimethyl ammonium bromide (EHDAB, CH₃(CH₂)₁₄CH₂N⁺(CH₃)₃)-metal hexacyanoferrate composite could be an effective material for

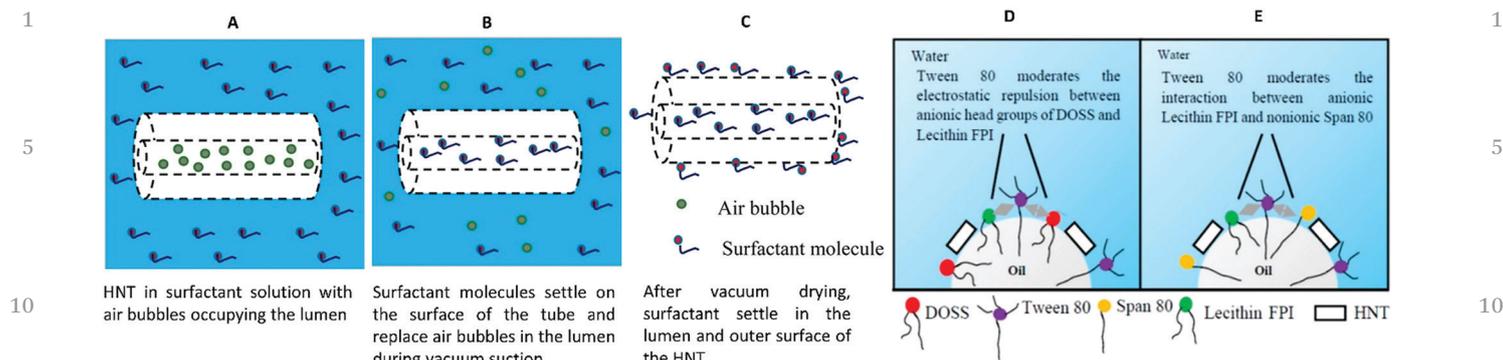


Fig. 10 Sketch of a mixture of surfactants inserted into the hallosite nanotube (A–C, sequence of loading method). (D and E) Mode of action during oil remediation. The figure is reprinted (adapted) with permission from Nyankson *et al.*⁹⁴ Copyright (2015) American Chemical Society.

adsorbing radioactive pollutant (Cs^+). This material can be readily retrieved as it floats on the wastewater once it complexes with the metal.⁸¹ On the other hand, repetitive use of synthesised organoclays offers a more sustainable approach to minimising the use of potential secondary pollutants (*i.e.* organoclay).^{129,130} To achieve this, two methods are followed, they are: (i) regeneration of organoclays, *i.e.* re-use of used organoclays following desorption of laden pollutants, and (ii) recycling of organoclays, *i.e.* the modifying agents (*e.g.*, surfactants) can be lost but the clay template can be further used for synthesising organoclays.^{131,132} Regeneration is preferred over recycling unless the controlled release of surfactants is the principal mode of action when using nanoclay as the carrier.⁹⁴ HDTMA-modified montmorillonite, which was toxic to environmental microorganisms and earthworm,⁷² could be used sustainably following chemical and biological regeneration of these clay products.¹³³ In the chemical regeneration process, desorption of the adsorbed contaminant in a controlled manner (pH, temperature and mechanical centrifugation) is followed, often accompanying with potential electrolysis.^{56,129,133} For example, phenol adsorbed organo-montmorillonite (HDTMA loading 100% of clay CEC) was regenerated by a vigorous shaking in an alkaline pH medium (conditions: pH 13, duration 120 min, shaking speed 150 rpm, 4 cycles).¹³³ Since pH plays a key role in regenerating that organoclay, it would not be feasible for *in situ* remediation but rather in a controlled wastewater remediation plant. Depending on the application site, other means of regeneration, such as using supercritical fluid, photo-assisted oxidation or thermal desorption can be followed.^{131,134} In the case of organism (*e.g.*, fungi, bacteria)-mediated regeneration of organoclay, its application can be extended to the field scale. In other words, some types of microorganisms can tolerate the potential toxicity of the clay modifier (*e.g.*, surfactants) and simultaneously degrade the adsorbed pollutants from the organoclay bioreactor. This provides a system suitable for repeated use of the organoclay. Yang *et al.*¹³³ employed highly phenol tolerable yeast (*Yarrowia lipolytica* Y103) and reported that in a HDTMA-intercalated nanoclay (CEC equivalent $\leq 100\%$) the yeast could regenerate the organoclay for subsequent use. This occurs by enhancing desorption of adsorbed phenol along with its degradation. While the yeast potentially degrades either

pronated or deprotonated phenol in the aqueous phase, the desorption of bound-phenol accelerates to achieve the sorption-desorption equilibrium.¹³³ In another approach, the natural microbiota can be immobilised and packed into the organoclay capsules, and the whole assembles can act as the bioreactors in a similar regenerative fashion.⁵⁶

Table 2 summaries key issues regarding the synthesis of surfactant-modified nanoclays.

Although various types of surfactants, including ionic, non-ionic or amphoteric compounds may impose toxicity to the natural environment, the degree of acute and chronic effects and minimisation of toxicity should be considered when designing organoclays. In such cases, cationic surfactants can be replaced with zwitterionic ones^{108,116} or cationic gemini surfactants rather than their monomeric counterparts and non-oxygen-containing gemini species. Instead of chemically synthesised surfactant, biologically derived surfactant, known as “biosurfactant” can readily add value to the biocompatibility to the nanoclay products; detailed aspects of biosurfactant-modified nanoclays have been discussed in Section 2.3.3.

2.3 Polymer and biomass modified nanoclays

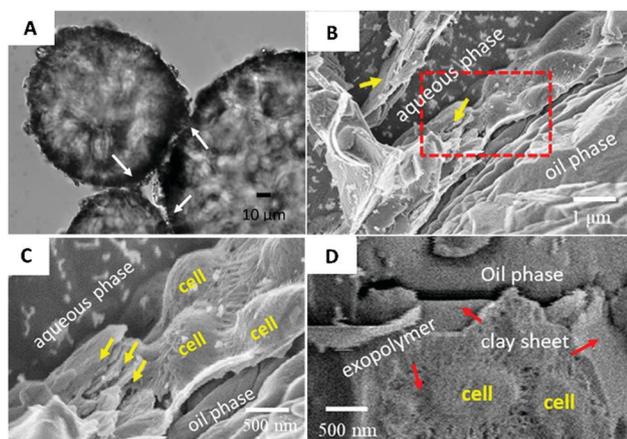
2.3.1 Clay-polymer nanocomposites (CPN). The hybrids of polymer and layered silicates have over the last decade led to a wide range of promising materials with diverse applications.^{18,19} This is mainly due to the stability of functional groups that is achieved by their strong interaction with the surfaces of nanoclay platelets.^{137,138} While the drive to synthesise eco-compliant CPN materials for several uses including biomedical and applications in devices is high,^{18,139} their use in pollution remediation is less well studied. Polymer modification of the surface properties of nanoclay minerals is a promising technique for environmental remediation,^{140–142} but the non-biodegradability of polymers may create a further hazard in nature when delivered as a clay-polymer composite to contaminated sites. With sustainability concerns driving the development of a range of new biodegradable polymers, more green “clay-biopolymer nanocomposite” materials offer significant potential for environmental remediation due to their biodegradability.^{143–147} These polymers are degradable by means of enzymatic digestion and chemical breakdown

1 Table 2 Summary of key issues regarding surfactant-modified nanoclays 1

Types	Examples of surfactant	Major modified nanoclays	Key advantages/disadvantages	Key consideration for biocompatibility	Ref.
5 Cationic QAC & gemini surfactant	Hexadecyltrimethylammonium (HDTMA), octadecyltrimethylammonium (ODTMA), dodecyltrimethylammonium (DDTMA), dioctadecyldimethylammonium (DDDMA), 1,3-bis(dodecyldimethylammonio)-propane dibromide, 1,3-bis(dodecyldimethylammonio)-2-hydroxypropane dichloride, 3-oxa-1,5-tetramethylene-bis(<i>N</i> -dodecyl- <i>N</i> -hydroxyethyl- <i>N</i> -methylammonium)dichloride	Organoclay of smectite, palygorskite	Advantage: • Highly hydrophobic, • Cationic charged material, • Regeneration of materials can be achieved for the control wastewater treatment. Disadvantage: • Toxicity is high due to the presence of QACs, • Leaving these modified clays in the environment might cause leaching of toxic surfactants.	• CEC equivalent of loading of surfactant should be ≤100%, • Regeneration of materials is recommended, • Betaine and derivative types of surfactants can be tested as alternatives, • Oxygen functionalisation of gemini surfactant can reduce toxicity.	29, 71–74, 77, 83, 135 and 136
20 Anionic	Sodium dodecyl sulfate (SDS), dioctyl sodium sulfosuccinate (DOSS)	Organoclay of smectite, LDH and controlled release by HNTs	Advantage: • Effective oil dispersant, • Anionic clay can be further modified using surfactants. Disadvantage: • High toxicity for the aquatic ecosystem, • Poor intercalation in smectites.	• Toxicological studies required, • Toxicity can be minimised using a mixture of surfactants.	89–91 and 95
30 Zwitterionic	Sulfobetaine and betaine types, <i>L</i> -carnitine, <i>L</i> -cystine dimethyl ester and thiamine	Organoclay of smectite	Advantage: • Less toxic compared to QACs, • Can be useful for the mixed contaminants with contrasting charge properties, • Regeneration can be achieved during wastewater treatment. Disadvantage: • Relatively difficult to intercalate into the nanoclays, • Leaving these modified clays in the environment may lead to leaching of toxic surfactants.	• Can be tested as an alternative use of cationic QACs, • During synthesis, pH controlling is important to obtain desired intercalation into nanoclays • CEC equivalent of loading of surfactant should be ≤100%.	106–109, 111 and 117
45 Non-ionic	Span [®] 80, Tween [®] 80, Triton X-100	Organoclay of smectite	Advantage: • “Reportedly” non-toxic to environmental receptors, • Highly hydrophobic Disadvantage: • Difficult to intercalate due to non-ionic nature of functional groups, • Hydrophobicity is not favoured in hydrous condition	• If hydrophobicity is the target function, it is more eco-safe to use, • Can be tailored with bio-polymer.	103 and 104

1 associated with living organisms.¹⁴⁸ Enzyme digestion usually
occurs when polymers contain an oxygen atom in the backbone
chain. This chemical structure may contain either ether (R-CO-
R') or ester (R-CO₂-R') and therefore can be biodegraded by the
5 enzymatic functions of microorganisms. Both natural and
synthetic polymers can possess this chemical structure, for
instance, starch and cellulose (natural biopolymer) and poly-
lactic acid (PLA) (synthetic) are biodegradable in the natural
environment. Biodegradable polymers can be derived from
10 renewable resources, so are considered environmentally
friendly.¹⁴⁸

The pyrolysed chitosan@kaolinite (prepared at 700 °C for
1 h under a nitrogen atmosphere) proved biocompatible during
crude oil bioremediation.¹⁴⁹ Omarova *et al.*¹⁴⁹ synthesised
15 carbonised kaolinite (0.46% added carbon) using a biopolymer
(*i.e.* chitosan) at 0.01 of chitosan-to-clay weight ratio. Carboni-
sation of kaolinite platelets added more hydrophobicity (con-
tact angle = 89 ± 4° *vs.* its unmodified counterpart = 31 ± 3°)
and the composite material armoured the oil droplets and
20 attracted the oil-degrading bacterium *Alcanivorax borkumensis*
at the oil-water interface (Fig. 11). At a laboratory scale, clay-
assisted biofilm formation enhanced bioremediation of oil spill
and prevented freedom of oil movement.¹⁴⁹ This suggests that
application of this material could protect coastal eco-receptors,
25 such as marsh plants from the random migration of toxic oils
towards the coast.¹⁴⁹ Chitosan@clay or sand has also been used
as flocculants to mitigate nutrient pollution in fresh and
marine waters.^{150–153} The underlying mechanism is to generate
large flocs of toxic algal cells by their cell-cell 'network' bridged
30 by environmentally safe chitosan. Clay or sand particles serve
as the framework and bulk material that should sink to prevent



35 Fig. 11 (A) Microscope image of emulsion droplets connected by the
biofilm produced by carbonised kaolinite-stabilized *Alcanivorax borku-*
40 *mensis*. Cryo-SEM image of (B) the "crust" of the droplet shows bacterial
cells and kaolinite particles, (C) closer view of (B) shows individual cells and
kaolinite sheets at the oil surface, and (D) bacterial cells attached to the
particles that form armour around oil droplets. Emulsions were prepared
with 2.5% w/v particle suspension in a seawater mineral salt medium. Oil to
aqueous suspension volume ratio, 1 : 30. The figure is reprinted (adapted)
55 with permission from Omarova *et al.*¹⁴⁹ Copyright (2015) American
Chemical Society.

rejuvenation of buried nutrient from the cells to the lake
1 surface water (Fig. 12). However, toxicity caused by the compo-
site flocculants cannot be completely ruled out but is expected
to remain minimal compared with the raw chitosan or starch
(table inset, Fig. 12). Using biotic candidates such as planktons,
5 lake worm and fish, the ecotoxicological assessment concluded
that inorganic material (*e.g.*, sand, clay)-supported biopolymers
(*e.g.*, chitosan, starch) are 31–124 times less toxic than the raw
polymers (table inset, Fig. 12).¹⁵⁴

Other carbonaceous material coupled to nanoclays have
10 become effective sorbents for environment pollutants.^{157–159}
Although direct evidence of *in situ* biocompatibility of these
materials is rare, a sustainable use with regeneration of these
composites is a favourable aspect of these nanoclays. For
example, HDTMA-modified montmorillonite or 3-aminopropyl
15 triethoxysilane (APTES)-pillared montmorillonite was used as a
precursor to synthesise a graphene oxide@nanoclay composite
material (Fig. 13). Both materials showed regeneration effi-
ciency due to shuttling between adsorption and desorption of
Cr(vi) with the change in pH of the reaction medium.^{155,156} In
20 both cases, Cr(vi) is adsorbed in acidic solution (pH ~ 3.0) by
intra-particle diffusion, surface adsorption, complexation and
boundary layer diffusion processes.¹⁵⁶ In the case of composite
material 1 (Fig. 13), the Cr(vi)-laden composite (0.1 g) was
reused after treatment with 50 mL of 0.3 mol L⁻¹ NaOH for
25 2 h (total ~4 cycles) following by reactivation with 1 mol L⁻¹
HCl for 3 h.¹⁵⁵ For composite material 2 (Fig. 13), Cr(vi)-loaded
adsorbent (0.15 g) was treated with 20 mL of 0.1 mol L⁻¹ NaOH
at 30 °C for 90 min (total ~6 cycles).¹⁵⁶ In both cases, the
complete desorption was irreversible due to the strong electro-
30 static interaction between Cr(vi) and the functional sites of the
composites but the guest OH⁻ from the alkali treatment could
weaken bonding favourable for desorption-mediated reusabil-
ity of the material.^{155,156}

Conversion of potentially "incompatible" QAC-modified
35 nanoclays using biopolymer treatment can also be another
approach to form biocompatible products. Biopolymer@organo-
clay, such as chitosan@organoclay or cellulose@organoclay
can be used as reusable metal sorbents with minimal toxicity
compared to that caused by organoclay.^{160,161} Chitosan@QAC-
40 modified montmorillonite was used and the removal of Cr(vi)
was achieved with up to 128.43 mg per g of material extracted
with a good desorption response. Because its regeneration
capacity is promising but its biocompatibility is not yet known,
the applicability of these nanoclays could be limited to waste-
45 water plants instead of for direct use in soil and water
systems.¹⁶⁰

One approach of using nanoclay modified products is to
engineer mixtures that are considered to enhance bacterial
50 activity to combat hydrocarbon pollution. Using, Fullers Earth
(palygorskite and Ca-montmorillonite, total 71.8% of compo-
site) with sodium carboxymethyl cellulose (7.1% of composite),
organoclay (quaternary ammonium salt modified montmoril-
lonite, commercially known as Tixogel[®] VP, 7.1% of composite)
and N, P, K fertiliser (14% of composite), clay flakes were
55 developed that attach to floating oil phases in water.¹⁶² The

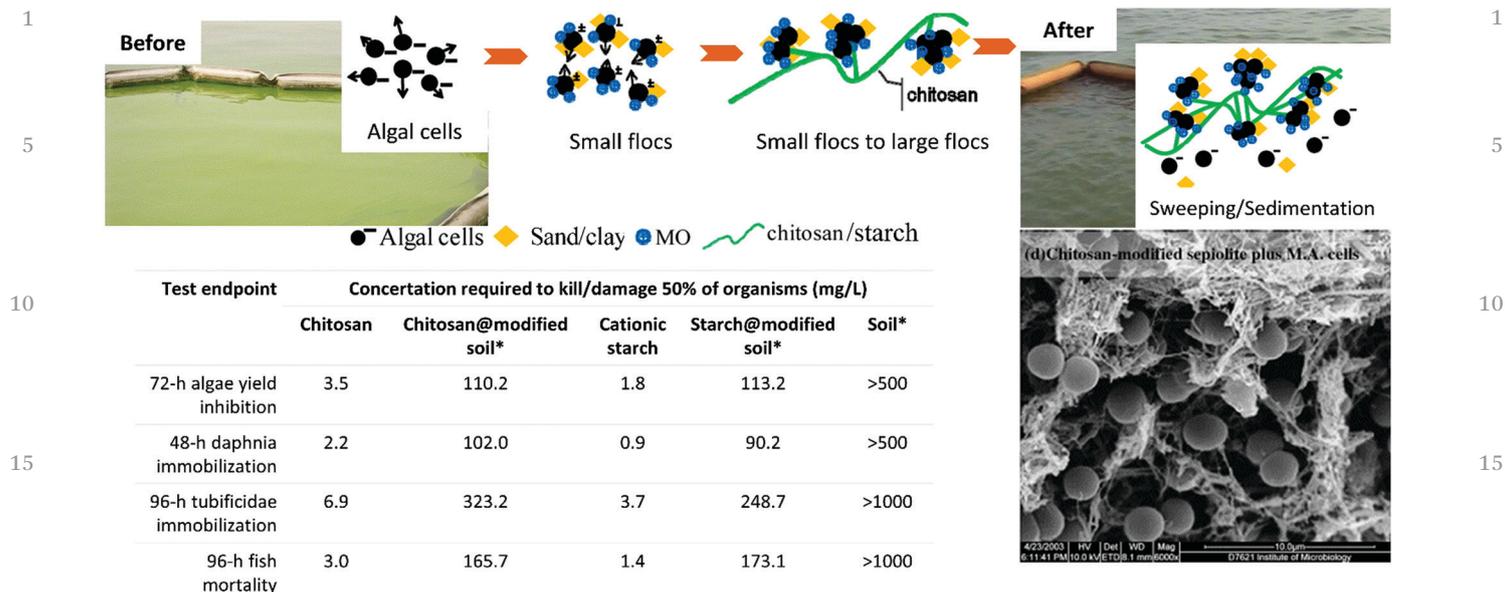


Fig. 12 Polluted toxic water containing bloomed algal cells (before) are cleaned with biopolymer@clay and sand along with a plant (*Moringa oleifera*) derived natural coagulant (MO) (after). The SEM image shows typical flocs of algal cells attached to the chitosan@sepiolite composite. The table in the figure shows the toxicological profile tested with such clay and sand-based flocculants. Details of the toxicological index have been discussed in the relevant section. The figure is modified with permission from Li and Pan¹⁵⁰ (Copyright (2013) American Chemical Society), Zou et al.¹⁵³ and Pan et al.¹⁵² (Copyright (2006) Elsevier). Results in the table were taken from Wang et al.¹⁵⁴ (Copyright (2016) Elsevier).

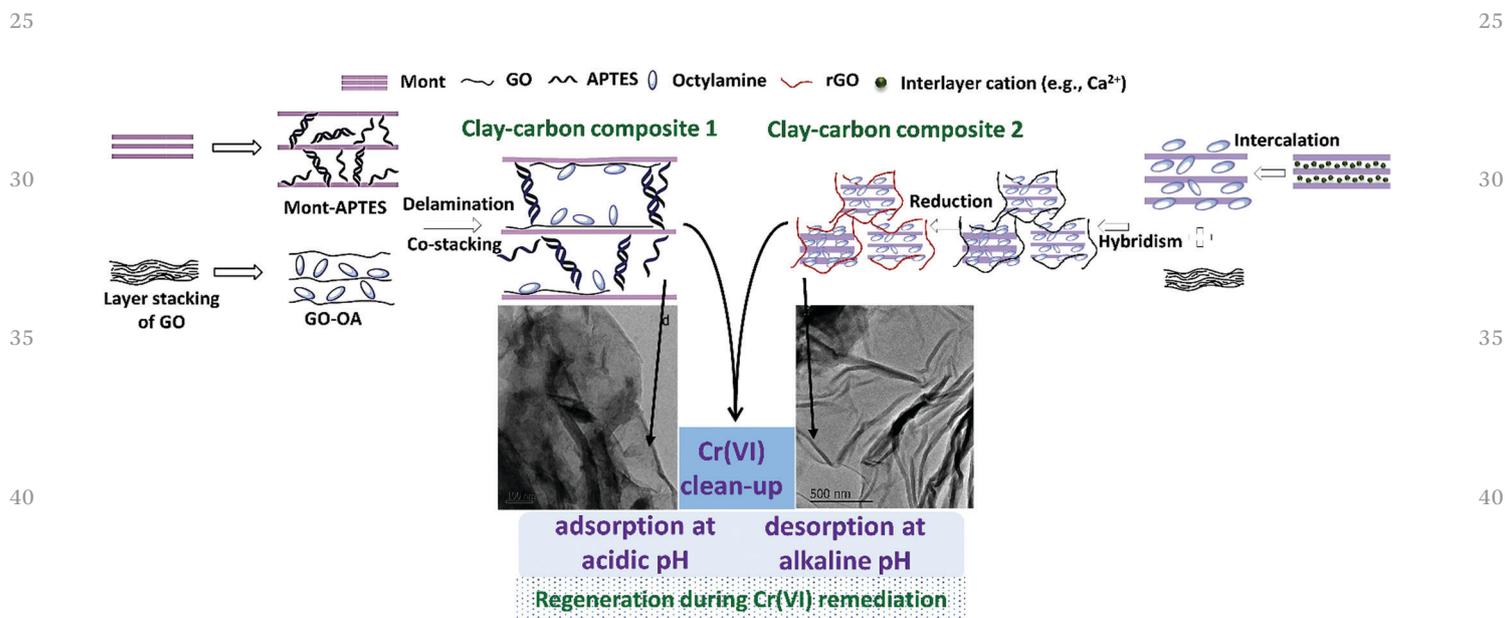


Fig. 13 The reusability of two carbon@nanoclay materials. The composite 1 is APTES-modified montmorillonite (Mont) with octylamine (OA)-modified graphene oxide (GO) while composite 2 is OA-modified Mont with reduced GO (rGO). The mechanism of reusing these materials has been discussed in the relevant section. The figure is modified with permission after Chen et al.¹⁵⁵ (Copyright (2017) Elsevier[®]) and Zhang et al.¹⁵⁶ with permission from The Royal Society of Chemistry.

composite served as a substrate for landing and hosting oil-degrading bacteria and simultaneously formed flocculants containing oil droplets. Such experiments indicate that the ecotoxicity of oil spills caused by wide migration across the water horizon could be mitigated through controlled *in situ* flocculation and biodegradation (Fig. 14). Using a similar approach, various compositions of nanoclays, such as kaolinite,

montmorillonite, palygorskite and nontronite have been experimentally investigated for oil spill remediation.³²

2.3.2 CPN hydrogels. Hydrogels, both organic and inorganic, are usually produced by chemical and physical cross-linking. Due to their highly porous structure, high specific surface area and wettability, hydrogels have attracted diverse usage in drug delivery, agriculture and sewage treatment.^{163,164}

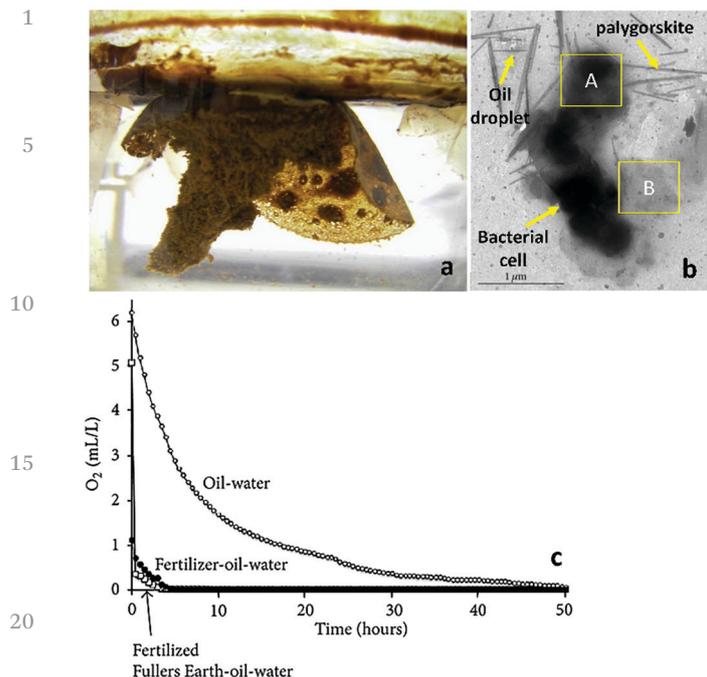


Fig. 14 (a) Photograph of a floating fertilised Fuller Earth clay flake within Deepwater Horizon oil and Gulf coast water after 3 weeks of experimental agitation. The brown furry mass attached to the flake consists of biofilm–clay–oil flocculates that slowly sink to form an organic-rich bottom mud; (b) TEM image of the clay-treated oil showing relationships between bacteria, oil, and clay mineral (palygorskite) particles. A (bacterial cell) and B (biofilm) in the composite-based bio-flocculants; (c) the O_2 depletion curves ($mL L^{-1}$) showing the bacterial activity in the bio-flocculants compared to the control (oil–water and only fertiliser–oil–water systems). Images and figure are taken from Warr *et al.*¹⁶²

Many of the gels containing nanoclay become superabsorbent for environmental contaminants^{165–167} and exhibit eco-compliance.¹⁶⁶ For example, the use of montmorillonite nanosheets is an ideal material for hydrogel fabrication as it improves the total performance of hydrogels, providing more strength, toughness and excellent thermal stability. They are also easily recycled and thus environmentally compliant.¹⁶⁸ Use of biopolymer instead of polymer in these nanoclay-based hydrogels has been advocated to avoid environmental burden during application.¹⁶⁹ For example, cellulose, a naturally available biopolymer, can be used to synthesise hydrogels.¹⁶⁹ In a study, cellulose–clay nanocomposite hydrogel with superabsorbent properties was used for the removal of dyes such as methylene blue from water (removal efficiency 96–98%, sorbent = 1.5 g in 8 mL solution of maximum $100 mg L^{-1}$ dye).¹⁶⁹ This hydrogel was prepared using chemical cross-linking of cellulose, carboxymethyl cellulose (CMC), and alkylamine intercalated clay in NaOH or urea aqueous solution.¹⁶⁹ Fig. 15 represents cellulose–clay nanocomposite hydrogels networks with (a) unmodified clay and (b) modified clay (alkyl amine modified).

In the cross-linking process of hydrogel formation, carboxy cellulose can be used instead of carboxymethyl cellulose, to act as a “green” solvent for the cellulose.¹⁷⁰ Fig. 15b shows that montmorillonite is exfoliated by using alkyl amine. However,

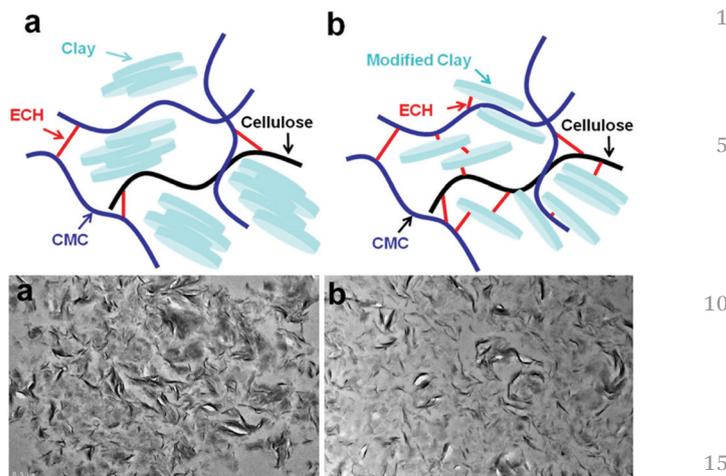


Fig. 15 Scheme of the synthesis of cellulose–clay nanocomposite hydrogels. (a) Hydrogel network containing unmodified clay with TEM image. (b) Epoxidized clay (modified clay) cross-linked in the hydrogel networks with TEM image. In either case, clay loading was 15 wt%. The figure is modified with permission from Peng *et al.*¹⁶⁹ Copyright (2013) American Chemical Society.

without using this amine, only ultrasonic irradiation can also provide similar nanosheets, which can be used for synthesising clay-based hydrogel¹⁶⁸ in the presence of “biocompatible” chitosan as a crosslinking agent (Fig. 16). The formation mechanism of the self-assembly hydrogels relies on the hydrogen bonds ($-OH \cdots +NH_3-$), and the electrostatic interaction between the montmorillonite-nanosheet and chitosan (Fig. 16).¹⁶⁸

Using HNT as an inorganic tube, a nanosponge of a cyclodextrins-like compound such as cucurbit[8]uril or heptakis-6-(dimethyl-*tert*-butylsilyl)-6-deoxy- β -cyclodextrin has been synthesised,^{171,172} which has proven effective for the removal of water and air pollutants (Fig. 17).

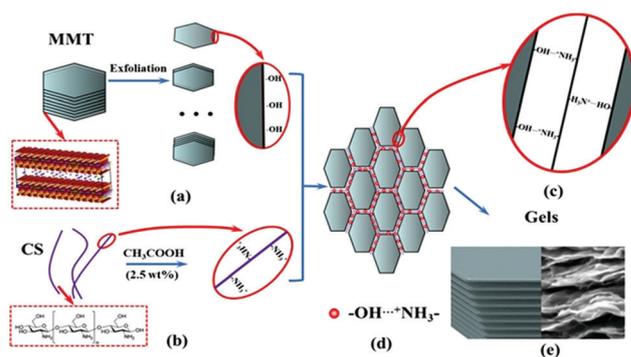


Fig. 16 Schematic sketch showing the self-assembly mechanism of montmorillonite nanosheet–chitosan hydrogels, (a) montmorillonite was exfoliated to nanosheets and dispersed with $-OH$ on the edges, (b) chitosan presented as electropositive with $-NH_3^+$ groups in acidic solution, (c) hydrogen bonds formed on the edges of montmorillonite particles, and (d) montmorillonite nanosheet–chitosan building thick layered stacks. The figure is modified with permission from Wang *et al.*¹⁶⁸ Copyright (2017) IOP publishing.

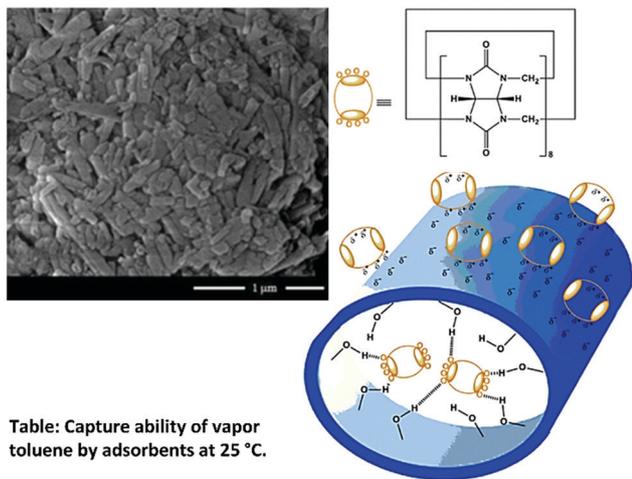


Table: Capture ability of vapor toluene by adsorbents at 25 °C.

	HNT/CB[8]*	HNT	CB[8]
Time (h)	W_{oil}	W_{oil}	W_{oil}
2	72.0±0.8	0.37±0.01	21.1±0.3
3	147.6±1.6	1.38±0.04	23.3±0.4
20	154.4±1.6	10.7±0.1	37.3±0.4

* W_{oil} , mg toluene/g adsorbent expressed as mg toluene/gCB[8] in the hybrid

Fig. 17 The interaction of cucurbit[8]uril with HNT and the toluene adsorption capacity of this hybrid compared with those of the separate components. Figure is modified with permission from Massaro et al.¹⁷¹ Copyright (2016) Wiley-VCH.

The preparation method is simple (~15 min sonication of HNT–cucurbit[8]uril aqueous mixture), and the major benefit of this hybrid material is linked to the biocompatibility of the components.¹⁷¹ The interaction between HNTs and cucurbit[8]uril occurs by positively charged alumina on the inside of the lumen forming H-bonds with the portal carbonyl of cucurbit[8]uril as Al–OH–O=C–), and by electrostatic interaction of siloxane on the outer surface of HNT with the partial dipole of carbonyl of the guest compound (Fig. 17). This hybrid offers tuneable properties of the hydrophilic/hydrophobic interfaces thus, greater dispersibility of cyclodextrin derivatives is achieved to capture more hydrophobic pollutants, such as toluene (table inset in Fig. 17)¹⁷¹ and other organic dyes.¹⁷²

2.3.3 Nanoclay-supported biomass/biosurfactant and biomass-modified nanoclays. Several sources of biodegradable biopolymers represent biomass that can be used directly for clay modification to satisfy environmental compliance. This has been discussed in Section 2.3.1. However, in recent years, conventional biomass, such as that produced from bacteria, fungi, straw, plant leaves, seeds and plant-based oil has been used to decorate nanoclays for targeted applications. The interest in these approaches is growing due to their low or non-toxic nature and low input cost.^{173,174} Developing composite materials to enhance the synergy between microbes and clay minerals is also becoming particularly relevant for environmentally friendly applications.³⁸

Biomass-modified nanoclays can help in two main ways: (i) supporting microorganisms, where the microbes take part in

the biodegradation of contaminants, and (ii) as clay–biomass composites, where the biomass operates as a sorbent; in this case, functional molecules within the biomass offer additional adsorption sites to those of the clay minerals. Since the abiotic and biotic components intertwine with each other, the clay minerals act as substrates,¹⁷⁵ protective shields,¹⁷⁶ and provide essential minerals and cations.¹⁷⁷ At the same time, microbes, especially bacteria and fungi, play a significant role in enhancing the rate of transformation and degradation of inorganic and organic pollutants.^{178,179} This clay mineral–microbe coupling can thus enhance the removal efficiency of both inorganic^{37,180–185} and organic^{176,186–189} contaminants. Recently, a few studies have been carried out on the biocompatibility of clay minerals using a biosurfactant-producing bacterium *Pseudoxanthomonas* sp. and the potential EPS-producing bacterium *Mycobacterium gilvum*.^{121,190} These studies reported that *Pseudoxanthomonas* sp. grew more efficiently with smectite when olive oil (0.1% w/v) was present.¹⁹⁰ Additionally, Biswas¹²⁴ modified kaolinite and montmorillonite using olive oil and molasses (clay:biomass = 1:9 w/w) and tested the compatibility with the native microorganisms of uncontaminated and hydrocarbon-contaminated soils. They reported that the modified products were also not inhibitory to the native microbial consortia; rather, they contributed to the bacterial count by up to 179% and 46% more than in uncontaminated and PAH-contaminated soil, respectively (Fig. 18).

Such biomass-modified clay also induced biosurfactant production in a liquid culture of *Pseudoxanthomonas* sp., which strengthens the green approach to hydrocarbon remediation when biocompatible modified clays are used in soils and water. In such cases, bacterial growth activity modifies the structural and elemental properties of the clay mineral, such as the dissolution of Si, Al, Fe and Mg.^{190–192} Biological exploitation

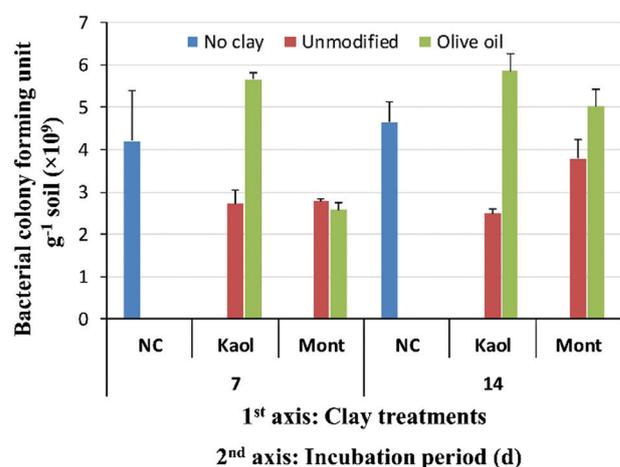


Fig. 18 Results of a bacterial viability test after 14 days of incubation in PAH-contaminated field soil. The olive oil-modified montmorillonite or kaolinite-amended soil was more biocompatible than raw soil. NC = no clay soil; Kaol = kaolinite and Mont = montmorillonite. The graph is replotted from Biswas (2016) with permission from the University of South Australia.

of clay minerals can also lead to changes in the iron redox state, which has been discussed under Section 2.7.

As an alternative to chemical surfactants (Section 2.2), biosurfactants offer benign conditions in real-world applications.^{193,194} However, clay-based materials, such as organoclay produced using (micro)organism-derived biosurfactants are not common practice in environmental remediation. The limitation lies in the cost associated due to the high amount of biosurfactants required to obtain equivalent surface properties of nanoclays when compared to chemical surfactants. Biosurfactant-modified (*Pseudomonas aeruginosa*-produced rhamnolipid) LDH has successfully been synthesised as a potential “bio-organoclay”.¹⁹⁵ This was synthesised following prolonged reaction of 2:1 LDH with rhamnolipid (conc. 1000 mg L⁻¹) at 0.5 g L⁻¹ soil to liquid ratio (reaction condition: 3 days, 65 °C). In either case (SDS-LDH and rhamnolipid-LDH), ion-exchange mechanisms were applied to intercalate organo-molecules into the LDH. Rhamnolipid-LDH was more effective for removing hydrophobic organic pollutants, such as naphthalene (by 1.3 times higher than SDS-LDH). Although the mode of real-world application of this “bio-organoclay” is unclear, the good adsorption capabilities add value to its potential compatibility in natural systems.¹⁹⁵

Along with bacterial biomass and EPS, fungal biomass has also been used to remediate pollutants by bio-sorption¹⁹⁶ with

clay minerals acting as the abiotic support for the biomass.^{197,198} Fungal biomass@clays can be synthesised *in situ* where fungal species are grown with a supplement of clay particles (loading: 1–5% of clay (w/v) in a liquid culture medium with the equivalent mass of fungal inoculum). Heavy metal cations, such as uranium and cadmium were adsorbed sustainably using the fungal biomass.^{197,199,200} Electrostatic interaction occurs between the negative sites of biomass containing carboxylic, amino or phosphate groups, and the target pollutant cations.²⁰⁰ Cation exchange was another mode of adsorption in the interlayer of 2:1 type nanoclay.¹⁹⁷ Because no toxic chemicals are used to synthesise fungal biomass@nanoclay composite, these sorbents are considered as eco-friendly additives to soil or water systems. Moreover, in a controlled remediation set-up, another non-chemical treatment can bring about the reusability of these materials. Olivelli *et al.*¹⁹⁸ reported that the dehydration–rehydration of the fungal biomass@montmorillonite cycle could switch between the adsorption and desorption of U(v) and therefore offer sustainable reusability (Fig. 19). In fact, the cation binding sites are dominant in the dried form of a composite rather than in wet composite. Also, the composite pelletability is useful to construct reusable columns for the adsorption of toxic metals in any reactor-based remediation system.¹⁹⁷

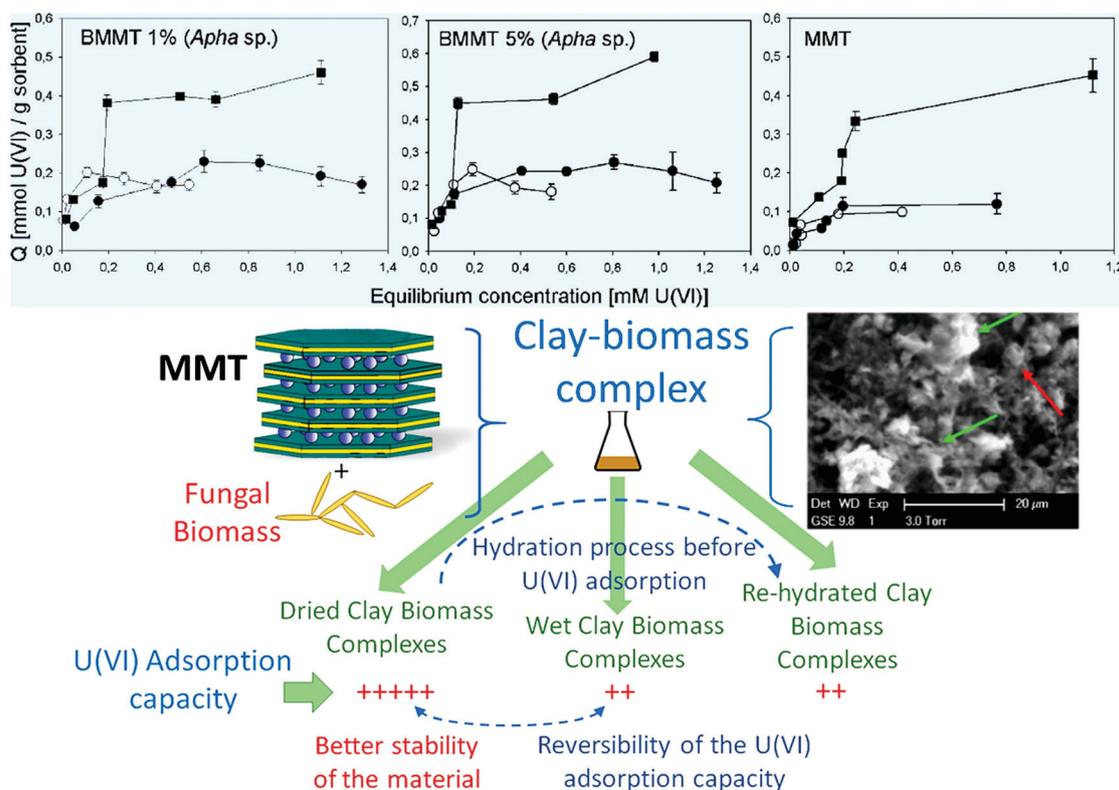


Fig. 19 Fungal biomass@montmorillonite used to clean-up uranium (U). BMMT represents the biomass (B)–montmorillonite (MMT) couple. The upper adsorption curve represents the U(vi) adsorbed on biomass@MMT (*Aphanocladium* sp.) and MMT. Isotherms performed with wet samples (○), dried samples (■), or dried and rehydrated samples (●). The lower scheme shows the relationships between the hydration state of the composite materials and their reusability for the removal of uranium. The SEM image shows the nanoclay bulk (red arrow) and the fungal biomass (green arrow). The figure is modified and reprinted (adapted) with permission from Olivelli *et al.*¹⁹⁷ and Olivelli *et al.*¹⁹⁸ Copyright (2013, 2017) American Chemical Society.

2.4 Metal and metal oxide nano-particles (NPs)–nanoclay composites

In addition to nanoclays, we have witnessed dramatic growth in nanotechnology using metal and metal oxides, here referred to as nanoparticles (NPs). This has occurred due to their increased demand in various sectors such as optoelectronics, catalysis, sensing imaging, medicine and the remediation of environmental pollutants. Indeed, there are many potential advantages and enormous benefits of NPs used in the remediation of environmental contaminants; however, at the same time, their use has also raised public concerns about possible negative effects on environment.^{201–203} Many NPs are either intrinsically toxic or with time release toxic by-products. Once released and mobile, they undergo many possible reactions and interactions in the environment.^{204–207} To circumvent this problem, various support materials have been proposed. NP supported on nanoclay minerals have attained significant attention in their design and synthesis mainly due to clay's ability to control or stabilise these agents during application as composites.²⁰⁸ These materials often provide new functionalities which are not characteristics of either of the individual components of the composite. These functionalities can be exploited when clay–NPs are used in environmental applications and work by catalysis, photocatalysis and sorption.^{209,210} However, the effect of the composite itself to the biotic health of the environment often remains unknown or in many cases, it is claimed to be “eco-friendly” and “biocompatible” without sufficient ecotoxicity testing.^{208,211} Indeed, concern was raised by recent research showing that several NPs such as zinc (Zn) or silver (Ag) NPs are more toxic to aquatic organisms when attached to smectite.^{212,213} In the following section, we exemplify several widely used clay-supported NPs and discuss their functionalities in relation to their efficiency as depolluting agents while also considering their ecotoxicity and environmental compliance.

2.4.1 Iron-based NPs-seeded nanoclays. For environmental remediation, widely used metal (oxide) NPs are iron-based. Representative examples of nanoclay-based iron (Fe) NPs used for the removal of various toxic chemicals from soil and water include the clay–iron (zero valent) composite (used for the removal of Cr(vi), Co(II), Pb(II), Cu(II), and others),^{214–217} the α -Fe₂O₃@smectite (excellent Cr(vi) adsorbent used in wastewater treatment),^{218,219} the composite of Fe₂O₃–palygorskite (for the removal of pesticides),²²⁰ and the Fe₃O₄@HNT (for pentachlorophenol degradation).²²¹ In most cases, the pollutant removal capacity of the composite materials was more than when the parent nanoclay or the NP were used alone.²⁰⁸

Nanoscale zero-valent iron (nZVI) is typically synthesised using reducing Fe-salts together with a reducing agent such as sodium borohydride, which in its pure form can cause cellular damage to environmental bacteria.²²² However, this toxicity could be reduced by controlling the duration of exposure²²² and the loading concentration²²³ applied to contaminated sites. In both the cases, the use of nanoclay could help reduce the ecotoxicity of those NPs, mainly by providing stability under

diverse environmental conditions.^{224,225} The clay–nZVI composites are efficient in removing various pollutants because of the combined mechanisms of adsorption, precipitation and redox changes.^{208,217} However, the ecotoxicological status of clay-supported nZVI during *in situ* application is not yet fully clear. There are only a few passive examples that have highlighted the “green” synthesis of smectite-supported nZVI mainly by replacing harsh chemicals (*e.g.*, sodium borohydride, organic solvents) with less harmful chemicals as reducing agents (*e.g.*, biological extracts).^{211,226} Comparing green (plant) and semi-green (industrial grade chemicals such as sodium dithionite instead of borohydride) reducing agents, Kozma *et al.*²²⁷ reported them to be environmentally benign. However, nZVIs derived from these safe chemicals were shown to be poor catalysts for the degradation of the volatile chlorinated compound studied when compared to the nZVI obtained by borohydride treatment. Interestingly, these “green” nZVIs when supported by smectite can be efficient remediating material. For example, Tandon *et al.*²¹¹ reported that a smectite-supported nZVI (clay = 2 g for 10 mL of nZVI (0.1 M Fe(NO₃)₃ and tea extract (1:1 v/v)) removed up to 99% of As(III) from wastewater at extreme pH conditions (2.75 and 11.1). Similarly, an organic dye such as malachite green was removed up to 95.16% by using smectite-supported “green” nZVI.²²⁶ Moreover, the toxicity of malachite green to a soil-growing plant was reduced by four times more when the composite was added to the soil.²²⁶ This indicates that clay-supported nZVI is not an additional burden to environmental biota such as plants but instead can be beneficial.²²⁶

Introducing a carbon source and biopolymer may also enhance the stability of nZVI on the nanoclay template and prevent its release into the natural system during groundwater remediation.²²⁸ In a similar approach using rosin-derived biochar, the stability of smectite- α -Fe₂O₃ NPs or alginate-based Fe₃O₄ NPs on LDH was achieved and the composites removed Cr(vi) and fluoride ions efficiently without risk of the release of the NPs to the environment.^{218,229} The detailed function of carbon source and biopolymer in the synthesis of biocompatibly modified nanoclay has been discussed in Section 2.3. Along with stability, extracting the polluted composite after the sorption of pollutants from the natural system and the reusability of sorbent would add value to achieving environmental compliance.²²⁰ For example, clay-supported magnetic properties of NPs (*e.g.*, Fe₂O₃, Fe₃O₄) facilitated the retrieval of the clay–NP composite during the application of these composites in wastewater treatment, such as the removal of pesticide,²²⁰ or phenolic compounds.^{221,230}

2.4.2 Other NPs-seeded nanoclays. The degradation of organic pollutants is often assisted by photocatalysts. Photocatalytic nanomaterial such as cadmium sulphide (CdS), which is usually ecotoxic,²³¹ has been immobilised onto HNT and used for controlling various photocatalytic reactions in a manner so that the bare CdS is not toxic to the environment. For achieving better performance, CdS NPs are often doped by metal ions (*e.g.*, Zn²⁺, Bi³⁺, Cr³⁺, and Ni²⁺) before they are conjugated to HNTs.²³² However, without doping, CdS can also

1 be immobilised to the HNT surface *via* ligand linkage, and the material exhibits high activity and stability under visible light irradiation.²³³ Similar *modus operandi* was also reported in NiO or TiO₂@palygorskite, TiO₂@HNT, TiO₂ or antimony-doped tin oxide (Sb-SnO₂)@kaolinite for the degradation of organic pollutants.^{234–239} Some of the metal oxide composites (*e.g.*, nanoclay-supported TiO₂, silver (Ag)-TiO₂ or ZnO) also have efficient antibacterial properties, which can be used to treat harmful bacterial contamination in wastewater.^{240,241} However, such metal or metal oxide NPs when attached to the surface of nanoclay (*e.g.*, montmorillonite) may be detrimental to the non-targeted natural biota.^{212,213} Gupta *et al.*²¹³ reported that the heteroagglomeration of ZnO increases with the presence of clay particles in the aquatic system by seeding aggregated numbers of ZnO on the surface of single clay particle. When a single clay particle invaded into the biological systems (*e.g.*, protozoan cells), the multiple numbers of toxic ZnO NPs were delivered along with it (Fig. 20). However, this toxicity was dependent on the concentration of both such NPs and the supportive clay particles. For example, 100 μg mL⁻¹ of montmorillonite (particle size 0.3–1.0 μm) mixed with 100 μg mL⁻¹ of ZnO NPs was

significantly toxic to the aquatic protozoan cells while 5 μg mL⁻¹ of ZnO NPs with the same clay amount proved to be nontoxic (Fig. 20).⁹²

The agglomeration of NPs determines the ecotoxicity of these materials in natural systems mainly by controlling their bioavailability to environmental organisms.^{242,243} For example, homoagglomeration of NPs with clay particles tends to form larger aggregates that are likely to sediment faster than heteroagglomerated grains. As a result, homoagglomerated NPs are then less available to organisms living in the surface water. Although clay-supported metal and metal oxide NPs (*e.g.*, ZnO@montmorillonite and Ag NPs@montmorillonite) were ecologically toxic,^{212,213} the environmental safety of these materials can be achieved by controlling their aggregation behaviours. Labille *et al.*²⁴² reported that pH and salinity are the driving forces of agglomeration of such metal oxide NPs onto clay mineral surfaces in aqueous suspension. For example, at fixed pH values (5 and 8), low salinity (NaCl ~ 10⁻³ M) heteroagglomeration of TiO₂ NPs occurred at an NP to clay particle ratio of 0.5 or more. In contrast, a much lower number of NPs are required to achieve similar agglomeration in more saline water (NaCl ~ 10⁻¹ M).²⁴² In these cases, clay-supported NPs showing homoagglomeration are favoured over heteroagglomeration during wastewater treatment so that the composite materials can be recollected by sedimentation during remediation treatment.²⁴⁴

While exposure of non-complexed NPs and the use of harsh reducing agents are a concern regarding environmental health, several interesting clay-based NPs have been developed and used as catalysts for the degradation of pollutants in a controlled manner.^{245,246} In such cases, costly NPs (ruthenium (Rh), palladium (Pd), gold (Au), Ag, among other metals) have been immobilised with the nanoclays and used as effective catalysts for the removal of pollutants at an industrial scale, especially for the groundwater remediation of organic pollutants.^{245,247} For example, smectite-Fe/Pd NPs were used for the dechlorination of *p*-chlorophenol from aqueous solution.²⁴⁸ While the structure of nanoclay plays an important role in controlling the immobilisation of NPs, use of HNTs or the kaolinite nanosheet has increased dramatically in recent years. The lumen of HNTs were first utilised as a nanoreactor by Lvov *et al.* for the synthesis of calcium carbonate (CaCO₃) using a bio-catalytic reaction.²⁴⁹ Following this work, both the interior and outer surfaces of HNT were decorated with various NPs for application in catalysis and for the photocatalysis of pollutants. An HNT-Rh NP catalyst was developed by a wet impregnation method for the production of CO_x-free hydrogen from ammonia²⁵⁰ and hydrogenation of phenol and cresols.²⁵¹ These materials can be extremely useful for removing these toxic compounds from contaminated water. Since the binding energy between Rh NPs with the external surface of the HNT structure is relatively weak, efforts have been made to incorporate these nanoparticles into the lumen of HNTs²⁵² to provide more stability. Approximately, 3–4 nm Rh NPs were incorporated in this way when incubated with RuCl₃ and subsequently reduced by sodium borohydride.²⁵²

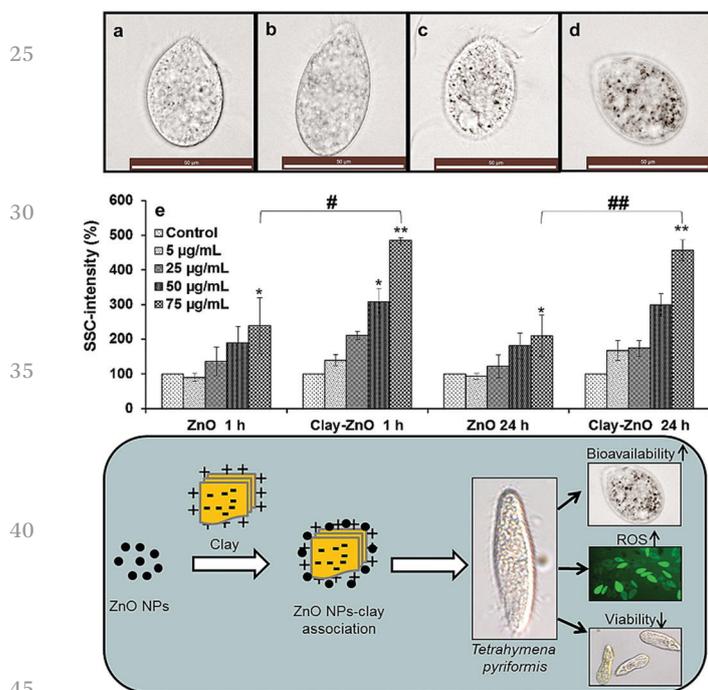


Fig. 20 A concentration dependent ecotoxicity of montmorillonite-attached ZnO on an aquatic protozoan *Tetrahymena* sp. Optical microscopy of *Tetrahymena* cells after 1 h of exposure: (a) control without clay, (b) control with clay, (c) treatment with unattached ZnO NPs, (d) treatment with ZnO NP-clay association. Time and concentration-dependent change in the cellular granularity of *Tetrahymena* determined by flow cytometry (e). Values represented are the mean \pm SE of three independent experiments. **p* 0.05 with 95% confidence interval was considered as statistically significant. #*p* 0.05, significance between unattached-ZnO NPs and ZnO NPs-clay association. The schematic sketch shows the overall toxicity to protozoan cells caused by the clay-attached ZnO in the aquatic system. The figure is adapted with permission from Gupta *et al.*²¹³ Copyright (2017) Elsevier.

1 Noble metal NPs such as Ag and Au have also been deposited
on kaolinite surfaces for increasing the stability of NPs, which is
considered an important step in the material synthesis for
environmental application. The most common approach for Ag
5 NP deposition is by reducing silver ions adsorbed on kaolinite
and the composite can be used as a catalyst for the degradation
of dyes or volatile compounds.^{253,254} Typical reducing agents
used are sodium borohydride, EDTA or ionising radiation. Such
kaolinite-based metal NPs are often fabricated by a post-
10 synthetic method whereby the metal nanoparticles are first
prepared and then immobilised on the kaolinite surface. Kaoli-
nite is often functionalised with organic ligands to improve
composite stability by strong binding to the kaolinite surface.
For example, a study showed that when kaolinite internal and
15 external surfaces were modified with 2-amino-2-methyl-1,3-
propanediol, the deposition of Au NPs was enhanced.²⁵⁵

2.4.3 Nanobubble-trapped nanoclays. In some cases, applica-
tion of nanobubbles instead of nanomaterials has proved useful for
remediation, for example, to alleviate anoxia/hypoxia in nutrient-
polluted waters. Due to excessive nutrients and pollution from
various anthropogenic activities, dead zones at the sediment–water
interface are often encountered²⁵⁶ with extremely unfavourable
hypoxia/anoxia conditions for aquatic organisms. In such dead
zones, sediment releases various inorganic nutrients such as N and
25 P and these cause eutrophication, a phenomenon of nutrient
pollution.²⁵⁶ Recently, oxygen nanobubble-conceived nanoclay,
zeolite or other related minerals have been developed to supply
oxygen to bottom water²⁵⁶ and the sediment–water interface.²⁵⁷
Another threat of algae-induced anoxia/hypoxia in the environment
30 is through the emission of greenhouse gases, especially
methane.²⁵⁸ Studies indicate that algae-induced anoxia/hypoxia
could be reduced or reversed after oxygen nanobubble loaded
zeolite was added to anoxic sediment and methane emission was
reduced by 3.2 times compared to the control.²⁵⁸

35 Nanoclays or zeolites carrying nanobubbles are particularly
useful because this technique offers a controlled and contin-
uous supply of oxygen to the affected environment over a
sustainable time period. Zhang *et al.*²⁵⁶ reported that the
application of nanobubble@clay particles on lake sediment
40 (~2 cm height with 100 g material) could increase dissolved
oxygen in the sediment–water interface from 4 mg L⁻¹ to 6 mg
L⁻¹, which was sustained for ~127 days. Nanobubble trapped
clays or zeolites are usually prepared without any chemicals
and as a result, there is little risk of exogenous chemicals
45 entering the environment during application. For preparation,
a vacuum is applied to the bulk of carrier materials to vacate
pore spaces (pressure -0.08 to -0.1 MPa for ~2 h), followed by
the intrusion of pure O₂ (pressure 0.12 to 0.15 MPa for ~4
h).²⁵⁷ For full saturation of the pores in the clays or zeolites,
50 repeating cycles of O₂ intrusion are usually required.²⁵⁶

2.5 Cation-saturated nanoclays

It is well established that the type of interlayer cation in the 2 : 1
smectite (*e.g.*, montmorillonite) plays an important role in the
55 hydration behaviour and nature of chemical complexation in
hydrous environments. Montmorillonite is most commonly

1 occupied by the exchangeable cations of Na⁺, K⁺, Ca²⁺ or
Mg²⁺, which can be replaced by one of these metals ions or
others such as Ba²⁺, Sr²⁺, Cu²⁺, Mn²⁺, Ni²⁺ and Zn²⁺, although
pH specific adsorption at edge sites or surface precipitation are
important additional mechanisms.^{2,259} “Homoionic” nanoclay
5 is prepared using corresponding chloride or nitrate salts, and
the process involves dispersion of nanoclays in a salt solution
for ~24 h and exchanged at least three times.²⁵⁹ Removal of
residual ions (*e.g.*, Cl⁻ or NO₃⁻) and surplus cations other than
the desired exchangeable cation is important to obtain purified
10 “homoionic” nanoclay that minimises the toxicity of these ions
to natural microbial assemblages. However, it is often hard to
achieve complete exchange of interlayer cations with an
exchangeable cation, even if the concentration in the solution
is 20 times greater than the clay's CEC.²⁵⁹ Care is taken in the
15 selection of cations because an excessive amount of many
cations used for synthesising homoionic nanoclays are consid-
ered as environmental pollutants or ecotoxic, such as Cu and
Zn.²⁶⁰

Recent experimental insights into the biocompatibility of
20 homoionic smectites revealed that divalent cations (*e.g.* Ca²⁺,
Fe²⁺) increased the activity of hydrocarbon-degrading bacteria
in crude oil when compared to monovalent cation (Na⁺, K⁺)
exchange (Fig. 21a).^{32,42,261,262} The homoionic interlayer cation
plays a key parameter in the absorption of both hard and soft
25 proteins, such as lysozyme and bovine serum albumin.²⁶³ The
adsorption of protein was overall more in the presence of
divalent interlayer cations like Ca²⁺ or Mg²⁺ than with mono-
valent Li⁺ or Na⁺. This feature was attributed to the lowering of
the kinetic barrier for adsorption associated with increasing
30 interlayer space and the number of water molecules in the ion
coordination shell. Such adsorption effects are likely to be of
particular relevance to organic–inorganic interactions in soil,
such as the immobilisation of enzymes or attachment of
bacterial cells.²⁶⁴ Although links to protein adsorption has
35 not yet been made, this feature is attributed largely to enhanced
cation-bridging between the bacteria and clay minerals surfaces
that favours the bacteria-mediated removal of contaminants
(Fig. 21). The mechanism of cation-bridging in seawater was
also proposed to explain the higher rates of oxygenase reactions
40 that led to the enhanced breakdown of alkanes and selected
alkylate PAHs compounds by *Alkanivorax borkumensis* and the
addition of iron-rich nontronite (Fig. 21b).²⁶² In a similar way,
it is the divalent cations of Ca²⁺, Fe²⁺ and perhaps Mg²⁺ that
favour closer proximity between clay mineral surface, the
45 bacteria cell and the hydrocarbon micelles.

2.6 (Hydro)thermally (acid, alkali and heat) modified nanoclays

50 These modified nanoclays (Fig. 3) are the products of treatment
with only dry heat or are hydrothermally altered in the presence
of acid or alkali compounds. These treatments increase surface
area, porosity, lumen diameter, and often modify the materials
elemental composition.^{265–267} With the need of the multi-
55 functionalities of clay-based sorbents for decontamination,
hydrothermal treatments are often performed to obtain the

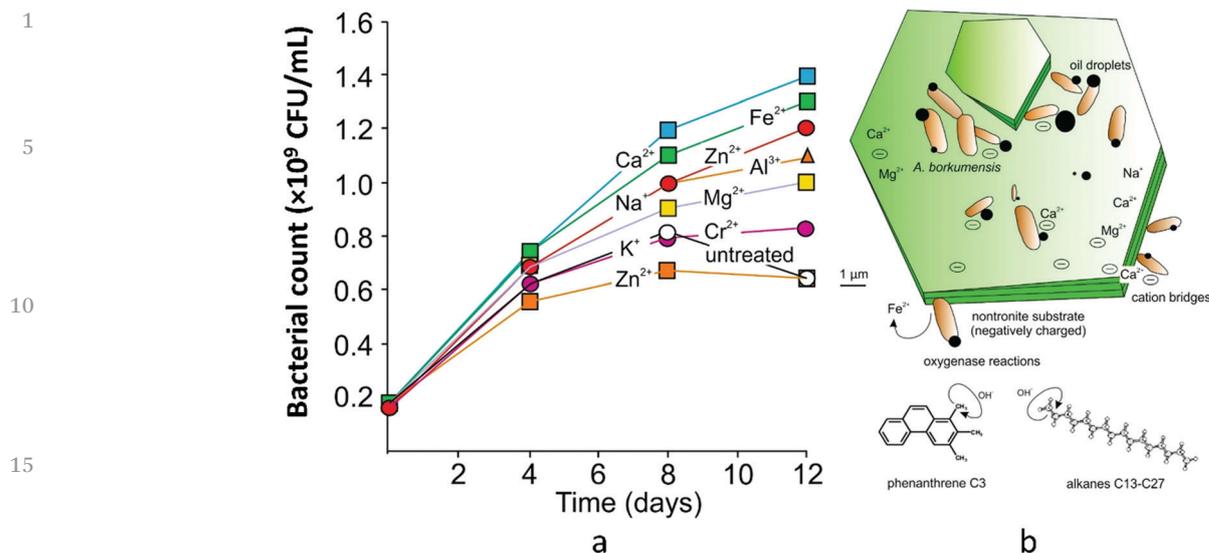


Fig. 21 (a) Bacteria-growth curves of oil-degrading species in the presence of different types of homoionic smectite, (b) model for clay-enhanced biodegradation of hydrocarbons by cation bridging between bivalent ions on nontronite clay surfaces, *Alkanivorax borkumensis* and oil droplets in a seawater medium. The results are extracted from Ugochukwu *et al.*²⁶¹ and the schematic is adapted from Warr *et al.*²⁶² Copyright (2014, 2018) Elsevier.

precursor materials for secondary modification, such as nanoparticle-decorated nanoclays or clay-polymer nanocomposite.^{16,268–273} Modified clay precursors (*e.g.*, organo-clays) are also used in hydrothermal treatment to tailor desired functional groups.²⁷⁴

If properly washed, nanoclays modified by acid or alkali reactive species are expected to be environmentally compliant because they do not host any environmentally persistent chemicals or long-chain hydrophobic compounds, such as surfactants. However, Ugochukwu *et al.*²⁷⁵ and Ugochukwu and Fialips³⁰ reported that acid-treated clays produced an inhibitory effect on the aerobic biodegradation of crude oil in an aqueous solution mainly because of a pH decrease in the remediation medium (*e.g.*, water or slurry). Protonation of silanol and aluminol groups located at variable charged edge sites of the acid-activated smectite was responsible for increasing acidity in the final product.^{275,276} However, by control of the pH, Biswas *et al.*²⁷⁷ demonstrated that acid or alkali treated nanoclays can be biocompatible and supportive to the natural and augmented microbial community for removing PAHs from soil. The key principles were (i) lowering the concentration of acid or alkali, and (ii) complete removal of residues from the materials prior to application.²⁷⁷ The natural substrate can also influence toxicity; for example, soil has a high pH buffering capacity compared with water,²⁷⁸ therefore pH-related nanoclay ecotoxicity in soil is expected to be minimal. Biswas *et al.*²⁷⁷ treated 2:1 nanoclays such as smectite and palygorskite with no more than 3 M HCl or NaOH (conditions: 1:5 of clay to solution ratio (w/v), shaking 100 strokes min⁻¹ in a water bath at 75 °C for 45 min). The authors reported increased bacterial growth in soil (sorber loading was 1–5% of soil) when 0.5 M HCl treated smectite and palygorskite were spiked with soil; this increased biodegradation of PAH by 5–8% more than its controls (Fig. 22).

Acid-activated nanoclays are characterised by significantly enhanced specific surface areas²⁷⁹ that are favourable for the increased dissolution of cations beneficial for the metabolism of functional microorganisms. The increased surface area and porous nature of these nanoclays is also likely to provide a congenial physical microenvironment that acts as a protective shield.³⁸ Whereas Al is less likely to be favourable to bacterial activity and in higher concentration is toxic, Si in the aqueous medium²⁸⁰ and elemental cations, such as Mg²⁺, Ca²⁺ and Fe²⁺

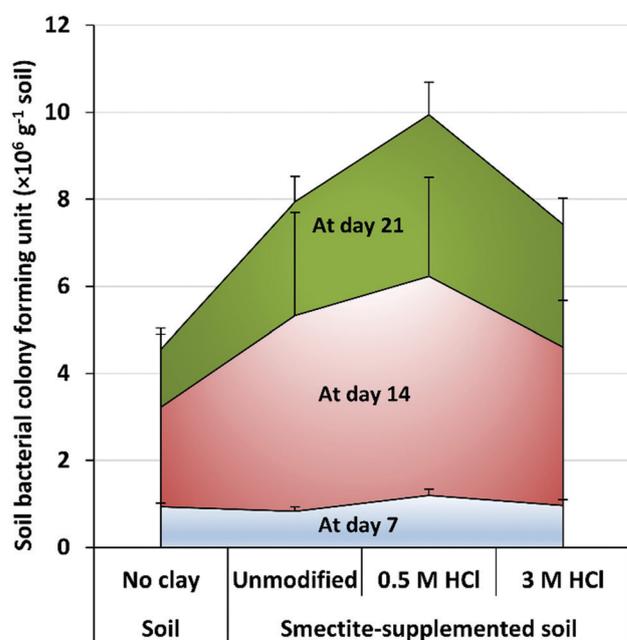


Fig. 22 In a bacterial viability test in a PAH-contaminated field sandy soil, the mild acid-modified smectite enhanced soil bacterial growth. The graph is replotted after Biswas *et al.*²⁷⁷ with permission of Elsevier.

are considered to be favourable for bacterial attachment to material surfaces *via* cation-bridging and subsequent biofilm formation.⁴² In 2:1 type swelling nanoclays (*e.g.*, smectite), dissolution of structural Si or Al did not vary significantly with the concentration of HCl (0.5–3.0 M) but exchangeable Mg²⁺ and Ca²⁺ underwent a dramatic shift (~ 3535 vs. $22\,394$ Mg²⁺ $\mu\text{g g}^{-1}$ by the action of 0.5 M vs. 3.0 M HCl; $11\,664$ vs. $67\,067$ Ca²⁺ $\mu\text{g g}^{-1}$ for 0.5 M vs. 3.0 M HCl treatment).^{277,281} In the case of strong acid-treated nanoclay products, the decrease in pH accompanying the loss of cations essential for bacteria–clay interaction induces bio-incompatibility during the clay-mediated bioremediation of soil contaminants (Fig. 22).^{30,277}

Some beneficial properties were formed by the acid treatment of HNTs when agitated with 0.1 M HCl or H₂SO₄ at 60 °C for ~ 8 h.^{16,268} The potentially biocompatible HNTs lose Al favourably during acid etching, therefore the size of lumen increases to accommodate guest molecules.²⁸² This effect is utilised to adsorb dyes and other contaminants.²⁸³ In contrast, alkali treatment modifies the outer edges of HNTs by leaching Si; a reaction that can be employed for imposing surface functionalisation at the point of interest. Like most natural nanoclay, HNTs are also potentially eco-safe. A recent laboratory scale study on a soil nematode (*Caenorhabditis elegans*) reported that these organisms remain unaffected by contact with HNTs and ingesting up to 1 mg mL⁻¹ of HNTs in aqueous solution.²⁸⁴ Similarly, HNTs remain compatible with soil-grown plants.²⁸⁵ However, whether a modification of the HNT structure by heat, acid or alkali treatment causes any incompatibility to such organisms in soil or water is not fully known. Calcined halloysite (at ~ 650 °C) was used to improve the plant-assisted remediation of heavy metals from soil through the adsorption of toxic metals while keeping them immobilised in the plant roots.²⁸⁶ However, the study did not consider the microbial health of the rhizosphere (*i.e.*, plant roots microenvironments) in order to enable assessment of the biocompatibility of the heat-treated HNT materials.

In the case of certain types of clay minerals, for instance palygorskite, the surface area and pore volume can be reduced by alkali treatment due to structural collapse caused by an excessive alkali/clay (14 : 1) ratio and longer treatment time (> 4 h).²⁸⁷ However, surface area and pore volume increased with a lower alkali/clay (3 : 1) ratio at the same alkali (NaOH) concentration and a shorter reaction duration (45 min), and these features could offer more biocompatibility by nurturing clay–microbe interactions during the bioremediation process.^{277,288,289} Similarly, acid treatment of palygorskite undergoes leaching of Al and Mg from the structure that leads to an increase in surface area, and the opening of pores, channels and grooves. However, both alkali and acid treatment can be avoided and replaced with dry heat treatment to obtain properties that are helpful for pollution remediation. During biodegradation, the bioavailability of organic pollutants is crucial to maximising their mineralisation, and often organic matter associated with minerals restrains bioavailability.²⁹⁰ A mild heat treatment of palygorskite (< 400 °C) has been shown to damage the binding sites between organic matter and

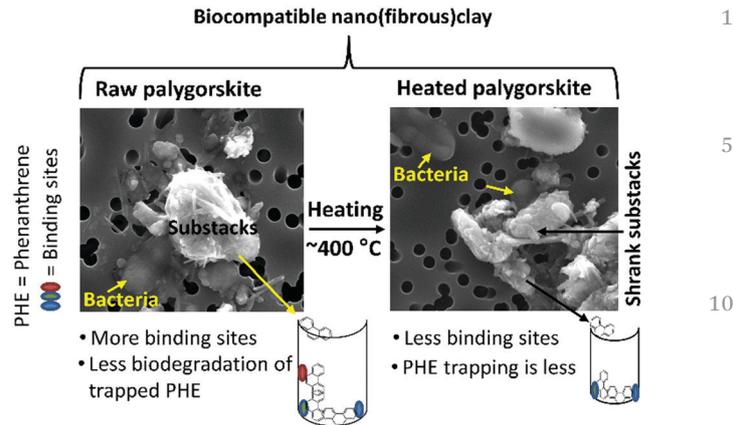


Fig. 23 Thermally modified nano(fibrous)clay (palygorskite) and its bacterial interaction during biodegradation of phenanthrene. The schematic is redrawn after Biswas *et al.*²⁹¹ with permission of Elsevier.

associated clay particles, which may increase bioavailability of organic pollutant (*e.g.*, clay bound to phenanthrene), and lead to a clay-assisted biodegradation of such organic pollutants in soils or slurries (Fig. 23).²⁹¹ On the other hand, structural damage of particles and changes in the fabric of clays caused by only their thermal modification at high temperatures (≥ 400 °C for ~ 2 h) is not expected to be favourable for supporting microbial viability in soil or water.¹⁹¹

2.7 Redox-modified nanoclays

Iron species and Fe(II)/Fe(III) redox couple reactions play a pivotal role in removing various contaminants present in the environment, especially from groundwater.^{292–294} Manipulating iron species using nanoclay templates, such as Fe-bearing nontronite is a useful way of developing environmentally favourable materials.^{295–301} Redox-manipulated clay minerals have a role in adding microbial functions to aid iron-mediated contaminant removal.³⁰² These modified nanoclays are obtained by using chemical compounds or microorganism. For example, chemically reduced iron-bearing clay minerals prepared using sodium dithionite degrade nitro-aromatic compounds such as nitrobenzene²⁹⁶ at a faster rate than biologically reduced counterparts (reducing bio-agent (bacteria): *Shewanella putrefaciens*). However, microbe-mediated slow and indirect reduction of groundwater pollutants might have long-term benefits for the environment.²⁹⁸ In the absence of O₂, anaerobic microorganisms may maintain their energy using redox pathways.³⁰³

In natural soil and sediment environments, clay structural Fe can also be oxidised by nitrate-dependent Fe(II)-oxidising bacteria and reduced by Fe(III)-reducing bacteria under the ambient temperature and geochemical conditions.³⁰⁴ The study of Zhao *et al.*³⁰⁴ showed that the structural Fe in nontronite was able to undergo multiple redox cycles mediated by those bacteria, and this process was sustained over an extended period because of the nature of solid-state Fe-redox cycling. These bacteria can possibly form a syntrophic relationship to

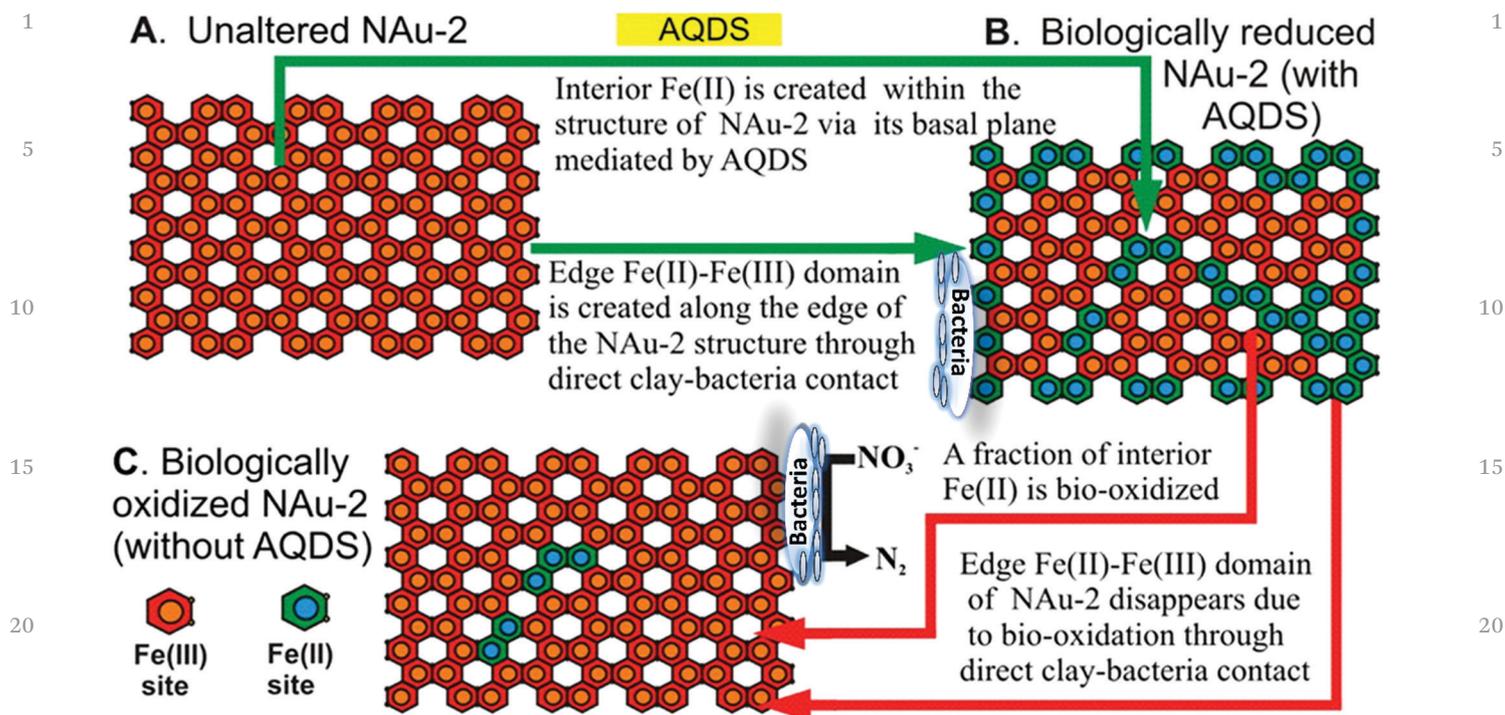


Fig. 24 Microbially redox cycling in Fe-bearing clay minerals for the remediation of nitrate pollutants. AQDS = anthraquinone-2,6-disulfonate, which acts as electron shuttle, NAu-2 = nontronite. The figure is reprinted (adapted) with permission from Zhao *et al.*³⁰⁴ Copyright (2015) American Chemical Society.

support each other's growth whereas clay minerals act as a supportive medium (Fig. 24).

In redox-modified nanoclay developed for an environmental application, the redox states play a critical role in determining the fate of target pollutants and associated microbial health.³⁰⁵ The fraction of redox-active structural Fe ($\text{Fe}^{2+}/\text{Fe}_{\text{total}}$) in Fe-bearing smectite varies with E_{h} -values between -0.6 V and $+0.6$ V.³⁰¹ Care should be taken in the application of these materials because some redox conditions induced more ecotoxicity of contaminants instead of mitigating them. For example, the toxicity of pesticide residues to mammals and environmental biota is influenced by the redox state of Fe in smectite. A ferruginous smectite reduced by sodium dithionite diminished the geno-/cyto-toxicity of pesticides, namely alachlor and oxamyl. In contrast, dicamba became more cytotoxic in the presence of reduced smectite and 2,4-D remained neutral.^{306,307} Therefore, application of redox-modified clay minerals need to consider the specific pollutants involved as we aim to maintain environmental biota free from material-induced cytotoxicity.

3. Conclusions, recommendation and future outlook

Modified nanoclays are promising materials for environmental remediation but their biocompatible and eco-compliance when used in natural systems is not yet guaranteed. In many cases, we do not have sufficient data to conclude whether the

modified nanoclay products are environmentally biocompatible. Considering the potential of both modified clay products and (micro)-organisms in environmental remediation, it is critically important to seek a compromise between attaining the necessary functional properties of the materials used to remediate contaminants and minimising any adverse impact of the materials on the natural flora and fauna. This review has highlighted a wide range of modified nanoclays, techniques for their preparation and *modus operandi* to obtain more biocompatibility when applied to the natural environment. Among these, use of surfactants and polymers (*e.g.*, quaternary ammonium type surfactant) to produce organoclays or clay-polymer composites might lead to concerns for environmental safety from eco-toxicity. However, alternatives in the form of biodegradable and "green" chemicals (*e.g.*, betaine, zwitterion surfactants, biopolymer) showed similar functionalisation of nanoclays with minimal environmental toxicity. Additionally, several types of composites of metal or metal oxide nanoparticles and nanoclays have been reported as eco-toxic particularly for aquatic organisms. Only some frequently used modified nanoclays such as heat, acid or alkali-activated nanoclay, Ca^{2+} , Na^{+} or Mg^{2+} -saturated nanoclay or Fe-based redox-modified clay were found to be non-toxic or less harmful when applied directly to the environment.

From a material synthesis perspective, the following key principles are proposed: (i) removal of any excess and unused chemical residues after synthesis of the modified clay product, (ii) during ion exchange, the amount of chemical such as surfactant should not exceed the CEC of the clay mineral, (iii)

1 increase the stability and homoagglomeration of metal and
 metal oxide NPs when synthesising nanoclay-supported NPs,
 (iv) maximise use of nontoxic surfactants to achieve similar
 5 performance, such as biosurfactants instead of synthetic sur-
 factants, and natural cations instead of QACs, (v) use of
 secondary non-toxic compounds that can bind the free mole-
 cules of synthetic surfactant – for example, long-chain fatty
 acids that bind the alkyl chain of QACs, and (vi) co-delivery of
 10 surfactant-modified clay products and the surfactant-degrading
 microorganism to the contaminated sites with the aim of
 reducing the toxicity of released surfactant from the interlayers
 of the nanoclays in the environment.

In conclusion, there is evidence of ecotoxicity caused by
 several modified nanoclays but also the possibility of obtaining
 15 “low-toxic” or “eco-friendly” functionalised nanoclay products.
 Therefore, the concept of ‘biocompatibly modified nanoclays’
 should be advocated in the development of nanoclay-based
 materials designed for more effective remediation practices.
 Application of new generation environmentally friendly nano-
 20 clays should not result in the potential loss of living organisms
 at a contaminated site.

Conflicts of interest

25 There are no conflicts of interest to declare.

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