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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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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

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.

1. Introduction

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. These mineral phases have been well studied in clay science and extensively documented elsewhere. 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. 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. 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, 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.
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 use12–15 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...
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 (\(\text{MTetO}_4\) where \(\text{MTet} = \text{Si} \text{ or Al}\)), and octahedral layers (\(\text{MOctO}_6\) where \(\text{MOct} = \text{Al}, \text{Mg} \text{ or Fe}\)) (Fig. 1). 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 [\(\text{AlO}_6\)] sheet sandwiched between two silicon tetrahedral [\(\text{SiO}_4\)] 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 (\(~5–750 \text{ m}^2 \text{ g}^{-1}\) ), low to high cation exchange capacity (CEC) (\(~3–1500 \text{ cmol}, \text{ kg}^{-1}\) ), 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, \(\text{pH}\) 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.\(^9\) 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).\(^3\) In the case of shape, various nanoclay minerals provide a unique physical architecture. For example, smectite can expand using its interlayer...
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. 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. 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. Copyright (2015) Elsevier.
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, CH₃(CH₂)₁₅N+(CH₃)₃), octadecyltrimethylammonium (ODTMA, CH₃(CH₂)₁₆N+(CH₃)₃), dodecyltrimethylammonium (DDTMA, CH₃(CH₂)₁₀N+(CH₃)₃), dixoctadecyldimethylammonium (DDDMA, [CH₃(CH₂)₁₇]₂N+(CH₃)₃), and similar ammonium cations.62,63 These are intercalated into the clay mineral structure through cation exchange and grafted onto the nanoclay surface.46,48 Generally heat

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 metalloid(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.19–24

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 microorganisms, 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.

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).

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B801C and mechanical stirring enhance the reaction for B3h 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:

\[ M_c = \frac{f \times CEC \times X}{M_w} \]

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 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 surfactant. 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.
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, ArquadR (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.79 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 ≤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 ~50% degradation of the pollutant. The absence of free QAC cations other than those adsorbed within the interlayer space should achieve such biocompatibility.77–79

While we have been observing the invention and reinvention of several surfactant cations to generate enhanced nano-clays 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.85 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 dye88 and humic acid89 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
removal from the natural system occurs via the zeolite-supported surfactant’s reactive sites. Interactions involve H-bonding between the N- and O-containing groups of contaminants and the H atoms from –N+(CH3)2–OH groups of DOOA with electrostatic interaction between the negatively charged group of contaminants (e.g., SO3− of Congo red dye) and the positively charge surfactants (e.g., R–N+(CH3)2–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).

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. The free anionic surfactants are toxic for aquatic ecosystems, 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. This was shown by the negligible rates of surfactant biodegradation when applied to the deep-water horizon oil spill as a dispersant. 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 Tween80. As DOSS is more toxic than Tween80 and the coupling chemistry of this clay-anionic surfactant is useful for mitigating such surfactant toxicity (Fig. 6). 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). The HNT interwoven with DOSS smeared around the oil droplets reduces the net interfacial energy to stabilise the emulsion (Fig. 6). In the case of anionic surfactant-modified 2:1 smectite nanoclay, the complete adsorption of anions within the interlayer 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., H3O+, Ca2+, Na+). 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 pollutants or by their controlled release, such as for pesticides to minimise environmental issues.

Although these types of organoclays show significant potential application for environmental remediation, there has been little toxicological study concerning their application.
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. 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. Interestingly, the hydrophobic components of these organoclays are prone to be biodegradable, thus, the material was considered “biocompatible”. 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. This type of organoclay is also considered to have a high thermal and chemical stability. 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 hydro 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 amphoterically, 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. 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_{12–15} mean C value < 14) surfactants, amphoteric species (e.g., alkyl betaines, alkylamido betaines and alkyl imidazole derivatives with all C_{12–14}) are readily biodegradable in both aerobic and anaerobic environments. The compatible nature of the sulfobetaine type zwitterionic surfactants first received attention to modify nanoclays and related minerals for their uses as remediating materials. 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. They have a certain advantage over QACs. Unlike the cationic surfactants, zwitterionic 3-(N,N-dimethylammonio)propane sulfonate, which has both a quaternary ammonium cation and a SO_3^- (M_w = 462.73 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).

Mixed contaminations are of particular concern in real-world clean-ups. 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. employed a zwitterionic hexadecyldimethyl (3-sulphonatopropyl)ammonium to modify montmorillonite and observed that it could remove mixed inorganic–organic contaminants (Cu(n)-phenol) much more effectively than cationic organoclay. Recently Lazorenko et al. used two zwitterionic surfactants, namely oleylamido-propyl 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. After controlled and packed loading of zwitterionic surfactants into layered nanoclays, 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. The weak basic nature of atrazine (pK_a = 1.7) is favourable for acid–base interaction with the acid group (–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. A contrasting result was reported when pH-resistant hydrophobic bonding of atrazine–HDTMA was activated. 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. synthesised organo-montmorillonite using l-carnitine, l-cystine dimethyl ester and thiamine. These are structurally zwitterionic compounds; however, in acidic conditions during organoclay synthesis (pH ~ 3.0), they exhibit protonation and ensure participation in cation exchange with the interlayers of nanoclays. 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 w/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 –COOH groups involving proton transfer, or (ii) H-bonding of N atoms.
of simazine and the –COOH groups. Promisingly, 100% CEC or 150% CEC loading was similarly effective to adsorb the target pollutants with carnitine@montmorillonite, which provides an easy selection of ≤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. 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. 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.
prospect of enhancing clay–microbial interaction for environmental remediation. QAC-modified clay requires further surface-tailoring to eliminate the chemical residues or suppress functional molecules that are toxic to (micro)organisms. Surface-tailored organoclays (fatty acid@QAC-modified clay) have been developed for this purpose, in contrast to QAC-modified organoclays. The material showed a selective binding capacity for heavy metals (e.g., Cd) and PAHs (e.g., naphthalene, phenanthrene) in a mixed contaminated scenario. This clay-based product also showed more biocompatibility to bacteria in an aqueous suspension and a field soil. When applied to originally contaminated soil, the sorbent-mediated biodegradation of PAHs revealed that the modified organoclay also performed well under natural conditions. In a microcosm study, the modified organo-smectite (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. 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 clay–bacterial biofilm from Mandal et al. 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.

![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. Copyright (2004) American Chemical Society.

![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 sequestrated 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., Warr et al. and Secundo et al. SEM image of clay-hutch is taken from Biswas as an oil-modified smectite-Pseudoxanthomonas sp. and clay–bacterial biofilm from Mandal et al. 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.]

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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.\(^\text{112,120}\) Based on the competitive adsorption of phenanthrene and Cd on this type of nanoclay, Biswas \textit{et al.}\(^\text{112}\) 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).\(^\text{112}\)

Although such fatty acid-tailed Arquad\(^\text{8}\)-modified smectite was relatively biocompatible and allowed more growth of soil bacteria, there is evidence that it can alter the native microbial community structure.\(^\text{125}\) Using an ecological marker (16S rRNA), this study reported that a few groups of bacteria (e.g., \textit{Proteobacteria}, \textit{Actinobacteria} and \textit{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.

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.\(^\text{62,77,126}\) This also dictates the adsorption of contaminants, such as that of heavy metals from aqueous solution. Wang \textit{et al.}\(^\text{126}\) tested a series of alkyl ammonium surfactants ranging from primary (NH\(_2\)-R) to quaternary cation ([CH\(_2\)_\(_x\)]N\(^+\)-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 NH\(_3\)-R heads bring water molecules and Cs ions better into the surfactants than ([CH\(_2\)_\(_x\)]N\(^-\)-R heads.\(^\text{126}\) The benefit is greater adsorption along with the complete exclusion of relatively more toxic quaternary heads. Also, the monomeric 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.\(^\text{62}\)

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, Owoseni \textit{et al.}\(^\text{95}\) and Nyankson \textit{et al.}\(^\text{94}\) inserted three surfactants into HNT. These included non-ionic (TWEEN\(^\text{8}\) or Span\(^\text{8}\)) 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 reme- diation, but also minimises the loss of surfactants that are redundant and harmful to the ecosystem.\(^\text{94}\) These dispersants are considered “effective” when they are utilised more than 50 ± 5% in the oil clean-up process.\(^\text{127}\) Only with the support of HNTs, Nyankson \textit{et al.}\(^\text{94}\) reported that batteries of TWEEN\(^\text{8}\), 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\(^\text{8}\) 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\(^\text{8}\)), 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\(^\text{8}\).\(^\text{80,138}\) 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.\(^\text{94,95}\)

Since the uncontrollable desorption of surfactants from organoclays is a critical constraint during application of such materials,\(^\text{74}\) retrieval of pollutant-adsorbed organoclays could be another green strategy. For example, ethyl hexadecyl dimethyl ammonium bromide (EHDAB, CH\(_3\)(CH\(_2\))\(_{16}\)N(CH\(_3\))\(_2\)–metal hexacyanoferrate composite could be an effective material for

| 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 \textit{et al.}\(^\text{94}\) Copyright (2015) American Chemical Society |
| --- | --- | --- |
| Dispersant formulation* | Total wt% of anionic surfactant | Total wt% of nonionic surfactant | Dispersion effectiveness (vol%) |
| HNT–40 wt% DOSS–20 wt% Lecithin FPI–40 wt% Tween\(^\text{8}\) & 60 & 40 & 100 |
| HNT–40 wt% DOSS–60 wt% Lecithin FPI–20 wt% Tween\(^\text{8}\) & 80 & 20 & |
| HNT–40 wt% Span\(^\text{8}\)–20 wt% Lecithin FPI–40 wt% Tween\(^\text{8}\) & 40 & 60 & 96.2 |
| HNT–40 wt% Span\(^\text{8}\)–80 wt% Lecithin FPI–20 wt% Tween & 20 & 80 & 99 |
| HNT–20 wt% Span\(^\text{8}\)–80 wt% Lecithin FPI–40 wt% Tween & 80 & 40 & 100 |
| HNT–20 wt% Span\(^\text{8}\)–80 wt% Lecithin FPI–60 wt% Lecithin FPI–20 wt% Tween & 80 & 80 & 100 |

* HNT, halloysite nanotube; DOSS, dioctyl sodium sulfosuccinate-an anionic surfactant; Lecithin FPI, anionic fraction of crude lecithin; Tween\(^\text{8}\) and Span\(^\text{8}\) are nonionic surfactants.
adsorbing radioactive pollutant (Cs	extsuperscript{+}). This material can be readily retrieved as it floats on the wastewater once it complexes with the metal.\textsuperscript{81} On the other hand, repetitive use of synthesised organoclays offers a more sustainable approach to minimising the use of potential secondary pollutants (\textit{i.e.} organoclays).\textsuperscript{129,130} To achieve this, two methods are followed, they are: (i) regeneration of organoclays, \textit{i.e.} re-use of used organoclays following desorption of adsorbed pollutants, and (ii) recycling of organoclays, \textit{i.e.} the modifying agents (\textit{e.g.}, surfactants) can be lost but the clay template can be further used for synthesising organoclays.\textsuperscript{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.\textsuperscript{94} HDTMA-modified montmorillonite, which was toxic to environmental microorganisms and earthworm,\textsuperscript{72} could be used sustainably following chemical and biological regeneration of these clay products.\textsuperscript{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.\textsuperscript{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).\textsuperscript{133} Since pH plays a key role in regenerating that organoclay, it would not be feasible for \textit{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.\textsuperscript{131,134} In the case of organism (\textit{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 (\textit{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 \textit{et al.}\textsuperscript{133} employed highly phenol tolerant yeast (\textit{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 pronounced or deprotonated phenol in the aqueous phase, the desorption of bound-phenol accelerates to achieve the sorption-desorption equilibrium.\textsuperscript{133} In another approach, the natural microbiota can be immobilised and packed into the organoclay capsules, and the whole assemblies can act as the bioreactors in a similar regenerative fashion.\textsuperscript{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\textsuperscript{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.\textsuperscript{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.\textsuperscript{137,138} While the drive to synthesise eco-compliant CPN materials for several uses including biomedical and applications in devices is high,\textsuperscript{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.\textsuperscript{140–142} put 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.\textsuperscript{143–147} These polymers are degradable by means of enzymatic digestion and chemical breakdown.

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**Fig. 10** Sketch of a mixture of surfactants inserted into the halloysite 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 \textit{et al.}\textsuperscript{94} Copyright (2015) American Chemical Society.
## Table 2  Summary of key issues regarding surfactant-modified nanoclays

<table>
<thead>
<tr>
<th>Types</th>
<th>Examples of surfactant</th>
<th>Major modified nanoclays</th>
<th>Key advantages/ disadvantages</th>
<th>Key consideration for biocompatibility</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cationic</td>
<td>Hexadecyltrimethylammonium (HDTMA), octadecyltrimethylammonium (ODTMA), dodecyldimethylammonium (DDDMA), 1,3-bis(dodecyldimethylammonio)-propylene dibromide, 1,3-bis(dodecyldimethylammonio)-2-hydroxypropane dichloride, 3-oxa-1,5-tetramethylene-bis(N-dodecyl-N-hydroxyethyl-N-methylammonium)dichloride</td>
<td>Organoclay of smectite, pyrophyllite</td>
<td>Advantage: ● Highly hydrophobic, ● Cationic charged material, ● Regeneration of materials can be achieved for the control wastewater treatment.</td>
<td>● 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.</td>
<td>5</td>
</tr>
<tr>
<td>QAC &amp; gemini surfactant</td>
<td>Sodium dodecyl sulfate (SDS), dioctyl sodium sulfosuccinate (DOSS)</td>
<td>Organoclay of smectite, LDH and controlled release by HNTs</td>
<td>Advantage: ● Effective oil dispersant, ● Anionic clay can be further modified using surfactants. Disadvantage: ● High toxicity for the aquatic ecosystem, ● Poor intercalation in smectites.</td>
<td>● Toxicological studies required, ● Toxicity can be minimised using a mixture of surfactants.</td>
<td>20</td>
</tr>
<tr>
<td>Anionic</td>
<td>Sulfobetaine and betaine types, L-carnitine, L-cystine dimethyl ester and thiamine</td>
<td>Organoclay of smectite</td>
<td>Advantage: ● Less toxic compared to QACs, ● Can be used 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.</td>
<td>● Can be tested as an alternative use of cationic QACs, ● During synthesis, pH controlling is important to obtain desired intercalation into nanoclays</td>
<td>30</td>
</tr>
<tr>
<td>Non-ionic</td>
<td>Span® 80, Tween® 80, Triton X-100</td>
<td>Organoclay of smectite</td>
<td>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</td>
<td>● If hydrophobicity is the target function, it is more eco-safe to use, ● Can be tailored with bio-polymer.</td>
<td>45</td>
</tr>
</tbody>
</table>
Enzyme digestion usually occurs when polymers contain an oxygen atom in the backbone chain. This chemical structure may contain either ether (R–CO–O) or ester (R–CO2–O–R’) and therefore can be biodegraded by the enzymatic functions of microorganisms. Both natural and synthetic polymers can possess this chemical structure, for instance, starch and cellulose (natural biopolymer) and polyactic acid (PLA) (synthetic) are biodegradable in the natural environment. Biodegradable polymers can be derived from renewable resources, so are considered environmentally friendly.

The pyrolysed chitosan@kaolinite (prepared at 700 °C for 1 h under a nitrogen atmosphere) proved biocompatible during crude oil bioremediation. Omarova et al. synthesised carbonised kaolinite (0.46% added carbon) using a biopolymer (i.e. chitosan) at 0.01 of chitosan-to-clay weight ratio. Carbonisation of kaolinite platelets added more hydrophobicity (contact angle = 89 ± 4° vs. its unmodified counterpart = 31 ± 3°) and the composite material armoured the oil droplets and 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. This suggests that application of this material could protect coastal eco-receptors, such as marsh plants from the random migration of toxic oils towards the coast. Chitosan@clay or sand has also been used as flocculants to mitigate nutrient pollution in fresh and marine waters. The underlying mechanism is to generate large flocs of toxic algal cells by their cell–cell ‘network’ bridged by environmentally safe chitosan. Clay or sand particles serve as the framework and bulk material that should sink to prevent rejuvenation of buried nutrient from the cells to the lake surface water (Fig. 12). However, toxicity caused by the composite 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, 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).

Other carbonaceous material coupled to nanoclays have become effective sorbents for environment pollutants. 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 triethoxysilane (APTES)-pillared montmorillonite was used as a precursor to synthesise a graphene oxide@nanoclay composite material (Fig. 13). Both materials showed regeneration efficiency due to shuttling between adsorption and desorption of Cr(vi) with the change in pH of the reaction medium. In both cases, Cr(vi) is adsorbed in acidic solution (pH ~ 3.0) by intra-particle diffusion, surface adsorption, complexation and boundary layer diffusion processes. 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 2 h (total ~4 cycles) following by reactivation with 1 mol L⁻¹ HCl for 3 h. 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). In both cases, the complete desorption was irreversible due to the strong electrostatic 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 reusability of the material.

Conversion of potentially “incompatible” QAC-modified nanoclays using biopolymer treatment can also be another approach to form biocompatible products. Biopolymer@organoclay, such as chitosan@organoclay or cellulose@organoclay can be used as reusable metal sorbents with minimal toxicity compared to that caused by organoclay. Chitosan@QAC-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 wastewater plants instead of for direct use in soil and water systems.

One approach of using nanoclay modified products is to engineer mixtures that are considered to enhance bacterial activity to combat hydrocarbon pollution. Using, Fullers Earth (pyalgorskite and Ca-montmorillonite, total 71.8% of composite), organoclay (quaternary ammonium salt modified montmorillonite, commercially known as Tixogel VP, 7.1% of composite) and N, P, K fertiliser (14% of composite), clay flakes were developed that attach to floating oil phases in water.

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**Fig. 11** (A) Microscope image of emulsion droplets connected by the biofilm produced by carbonised kaolinite-stabilized Alcanivorax borkumensis. 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) with permission from Omarova et al. Copyright (2015) American Chemical Society.
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. 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.
Many of the gels containing nanoclay become superabsorbent for environmental contaminants and exhibit eco-compliance. 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. Use of biopolymer instead of polymer in these nanoclay-based hydrogels has been advocated to avoid environmental burden during application. For example, cellulose, a naturally available biopolymer, can be used to synthesise hydrogels. 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). This hydrogel was prepared using chemical cross-linking of cellulose, carboxymethyl cellulose (CMC), and alkylamine intercalated clay in NaOH or urea aqueous solution. This hydrogel was prepared using chemical cross-linking of cellulose, carboxymethyl cellulose (CMC), and alkylamine intercalated clay in NaOH or urea aqueous solution. 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. Fig. 15b shows that montmorillonite is exfoliated by using alkyl amine. However, without using this amine, only ultrasonic irradiation can also provide similar nanosheets, which can be used for synthesising clay-based hydrogel 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 (\(-\text{OH} \cdots \text{NH}_3^+\)) and the electrostatic interaction between the montmorillonite-nanosheet and chitosan (Fig. 16). 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-\(\beta\)-cyclodextrin has been synthesised, which has proven effective for the removal of water and air pollutants (Fig. 17).
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. 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–OQ→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) and other organic dyes. These studies reported that Pseudoxanthomonas sp. grew more efficiently with smectite when olive oil (0.1% w/v) was present. Additionally, Biswas 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. Biological exploitation of 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, protective shields, and provide essential minerals and cations. 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. This clay mineral–microbe coupling can thus enhance the removal efficiency of both inorganic and organic 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. These studies reported that Pseudoxanthomonas sp. grew more efficiently with smectite when olive oil (0.1% w/v) was present. Additionally, Biswas 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).

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. Developing composite materials to enhance the synergy between microbes and clay minerals is also becoming particularly relevant for environmentally friendly applications.

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, protective shields, and provide essential minerals and cations. 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. This clay mineral–microbe coupling can thus enhance the removal efficiency of both inorganic and organic 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. These studies reported that Pseudoxanthomonas sp. grew more efficiently with smectite when olive oil (0.1% w/v) was present. Additionally, Biswas 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).
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. 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 \textit{(Pseudomonas aeruginosa)-produced rhamnolipid} LDH has successfully been synthesised as a potential “bio-organoclay”. This was synthesised following a 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 \(^\circ\)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.

Along with bacterial biomass and EPS, fungal biomass has also been used to remediate pollutants by biosorption with clay minerals acting as the abiotic support for the biomass. Fungal biomass@clays can be synthesised \textit{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. Electrostatic interaction occurs between the negative sites of biomass containing carboxylic, amino or phosphate groups, and the target pollutant cations. Cation exchange was another mode of adsorption in the interlayer of 2:1 type nanoclay. 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 \textit{et al.} reported that the dehydration–rehydration of the fungal biomass@montmorillonite cycle could switch between the adsorption and desorption of U(VI) 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 pelletibility is useful to construct reusable columns for the adsorption of toxic metals in any reactor-based remediation system.

![Fig. 19](image-url) 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 \textit{(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 \textit{et al.} and Olivelli \textit{et al.} Copyright (2013, 2017) American Chemical Society.
2.4 Metal and 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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{208,211} Indeed, concern was raised by recent research and “biocompatible” without sufficient ecotoxicity showing that several NPs such as zinc (Zn) or silver (Ag) NPs are more toxic to aquatic organisms when attached to smectite.\textsuperscript{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(\text{VI}), Co(\text{II}), Pb(\text{II}), Cu(\text{II}), and others),\textsuperscript{214–217} the \(\alpha\)-Fe\(_2\)O\(_3\)@smectite (excellent Cr(\text{VI}) adsorbent used in wastewater treatment),\textsuperscript{218,219} the composite of Fe\(_2\)O\(_3\)-palygorskite (for the removal of pesticides),\textsuperscript{220} and the Fe\(_2\)O\(_3\)@HNT (for pentachlorophenol degradation).\textsuperscript{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.\textsuperscript{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.\textsuperscript{222} However, this toxicity could be reduced by controlling the duration of exposure\textsuperscript{222} and the loading concentration\textsuperscript{223} 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.\textsuperscript{224,225} The clay–nZVI composites are efficient in removing various pollutants because of the combined mechanisms of adsorption, precipitation and redox changes.\textsuperscript{208,217} However, the ecotoxicological status of clay-supported nZVI during \textit{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).\textsuperscript{211,226} Comparing green (plant) and semi-green (industrial grade chemicals such as sodium dithionite instead of borohydride) reducing agents, Kozma \textit{et al.} 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 \textit{et al.}\textsuperscript{211} reported that a smectite-supported nZVI (clay = 2 g for 10 mL of nZVI (0.1 M Fe(NO\(_3\))\(_3\)) and tea extract (1 : 1 v/v)) removed up to 99% of As(\text{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.\textsuperscript{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.\textsuperscript{226} This indicates that clay-supported nZVI is not an additional burden to environmental biota such as plants but instead can be beneficial.\textsuperscript{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.\textsuperscript{228} In a similar approach using rosin-derived biochar, the stability of smectite-\(\alpha\)-Fe\(_2\)O\(_3\) NPs or alginate-based Fe\(_2\)O\(_3\) NPs on LDH was achieved and the composites removed Cr(\text{V}) and fluoride ions efficiently without risk of the release of the NPs to the environment.\textsuperscript{218,229} The detailed function of carbon source and biopolymer in the synthesis of biocompatible 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.\textsuperscript{220} For example, clay-supported magnetic properties of NPs (e.g., Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\)) facilitated the retrieval of the clay–NP composite during the application of these composites in wastewater treatment, such as the removal of pesticide,\textsuperscript{230} or phenolic compounds.\textsuperscript{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,\textsuperscript{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., Zn\(^{2+}\), Bi\(^{3+}\), Cr\(^{3+}\), and Ni\(^{2+}\)) before they are conjugated to HNTs.\textsuperscript{232} However, without doping, CdS can also...
to be immobilised to the HNT surface via ligand linkage, and the material exhibits high activity and stability under visible light irradiation. Similar *modus operandi* was also reported in NiO or TiO$_2$@palygorskite, TiO$_2$@HNT, TiO$_2$ or antimony-doped tin oxide (Sb–SnO$_2$)@kaolinite for the degradation of organic pollutants. Some of the metal oxide composites (e.g., nanoclay-supported TiO$_2$, silver (Ag)–TiO$_2$ or ZnO) also have efficient antibacterial properties, which can be used to treat harmful bacterial contamination in wastewater. 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. Gupta *et al.* 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).

The agglomeration of NPs determines the ecotoxicity of these materials in natural systems mainly by controlling their bioavailability to environmental organisms. 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, the environmentally safety of these materials can be achieved by controlling their aggregation behaviours. Labille *et al.* 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 TiO$_2$ 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). 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.

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. 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. For example, smectite-Fe/Pd NPs were used for the dechlorination of p-chlorophenol from aqueous solution. 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 *et al.* for the synthesis of calcium carbonate (CaCO$_3$) using a bio-catalytic reaction. 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$_2$-free hydrogen from ammonia and hydrogenation of phenol and cresols. 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 HNTs to provide more stability. Approximately, 3–4 nm Rh NPs were incorporated in this way when incubated with RuCl$_3$, and subsequently reduced by sodium borohydride.

**Fig. 20** A concentration dependent ecotoxicity of montmorillonite-attached ZnO on an aquatic protozoan *Tetrahymena* sp. Optical microscop 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 ± 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.* Copyrigth (2017) Elsevier.
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 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. Typical reducing agents used are sodium borohydride, EDTA or ionising radiation. Such kaolinite-based metal NPs are often fabricated by a post-synthetic method whereby the metal nanoparticles are first prepared and then immobilised on the kaolinite surface. Kaolinite 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 external surfaces were modified with 2-amino-2-methyl-1,3-propanediol, the deposition of Au NPs was enhanced.

2.4.3 Nanobubble-trapped nanoclays. In some cases, application 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 encountered with extremely unfavourable hypoxia/anoxia conditions for aquatic organisms. In such dead zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones, sediment releases various inorganic nutrients such as N and P and these cause eutrophication, a phenomenon of nutrient zones. As dead zones are created in the vicinity of the North Sea, especially during the summer season.

**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 hydration behaviour and nature of chemical complexation in hydrous environments. Montmorillonite is most commonly 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. “Homoionic” nanoclay 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. Removal of residual ions (e.g., Cl⁻ or NO₃⁻) and surplus cations other than the desired exchangeable cation is important to obtain purified “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. Care is taken in the selection of cations because an excessive amount of many cations used for synthesising homoionic nanoclays are considered as environmental pollutants or ecotoxic, such as Cu and Zn.

Recent experimental insights into the biocompatibility of 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). The homoionic interlayer cation plays a key parameter in the absorption of both hard and soft proteins, such as lysozyme and bovine serum albumin. The adsorption of protein was overall more in the presence of divalent interlayer cations like Ca²⁺ or Mg²⁺ than with monovalent Li⁺ or Na⁺. This feature was attributed to the lowering of the kinetic barrier for adsorption associated with increasing 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. Although links to protein adsorption has 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 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). In a similar way, it is the divalent cations of Ca²⁺, Fe²⁺ and perhaps Mg²⁺ that favour closer proximity between clay mineral surface, the bacteria cell and the hydrocarbon micelles.

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

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. With the need of the multifunctionalities of clay-based sorbents for decontamination, hydrothermal treatments are often performed to obtain the...
precursor materials for secondary modification, such as nanoparticle-decorated nanoclays or clay–polymer nanocomposite. Modified clay precursors (e.g., organo-clays) are also used in hydrothermal treatment to tailor desired functional groups.

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. and Ugochukwu and Fialips 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. However, by control of the pH, Biswas et al. 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. The natural substrate can also influence toxicity; for example, soil has a high pH buffering capacity compared with water, therefore pH-related nanoclay ecotoxicity in soil is expected to be minimal. Biswas et al. 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 (sorbent 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 areas 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. Whereas Al is less likely to be favourable to bacterial activity and in higher concentration is toxic, Si in the aqueous medium and elemental cations, such as Mg²⁺, Ca²⁺ and Fe²⁺...

![Fig. 21](image-url) (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. and the schematic is adapted from Warr et al. Copyright (2014, 2018) Elsevier.

![Fig. 22](image-url) 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. with permission of Elsevier.
are considered to be favourable for bacterial attachment to material surfaces via cation-bridging and subsequent biofilm formation. 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 Mg$^{2+}$ and Ca$^{2+}$ underwent a dramatic shift (≈3535 vs. 22 394 Mg$^{2+}$ μg g$^{-1}$ by the action of 0.5 M vs. 3.0 M HCl; 11 664 vs. 67 067 Ca$^{2+}$ μg g$^{-1}$ for 0.5 M vs. 3.0 M HCl treatment). 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). Some beneficial properties were formed by the acid treatment of HNTs when agitated with 0.1 M HCl or H$_2$SO$_4$ at 60 °C for ~8 h. The potentially biocompatible HNTs lose Al favourably during acid etching, therefore the size of lumen increases to accommodate guest molecules. This effect is utilised to adsorb dyes and other contaminants. 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. Similarly, HNTs remain compatible with soil-grown plants. 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. 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). 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. 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. A mild heat treatment of palygorskite (< 400 °C) has been shown to damage the binding sites between organic matter and 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). 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.

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. Manipulating iron species using nanoclay templates, such as Fe-bearing nontronite is a useful way of developing environmentally favourable materials. Redox-manipulated clay minerals have a role in adding microbial functions to aid iron-mediated contaminant removal. These modified nanoclays are obtained by using chemical compounds or microorganisms. For example, chemically reduced iron-bearing clay minerals prepared using sodium dithionite degrade nitro-aromatic compounds such as nitrobenzene 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. In the absence of O$_2$, anaerobic microorganisms may maintain their energy using redox pathways.

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. The study of Zhao et al. 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...
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. The fraction of redox-active structural Fe (Fe\(^{2+}/\text{Fe}_{\text{total}}\)) in Fe-bearing smectite varies with \(E_{\text{h}}\) values between −0.6 V and +0.6 V. 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. 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 \textit{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)
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 performance, such as biosurfactants instead of synthetic surfactants, and natural cations instead of QACs, (v) use of secondary non-toxic compounds that can bind the free molecules of synthetic surfactant – for example, long-chain fatty acids that bind the alkyl chain of QACs, and (vi) co-delivery of 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 “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 nanoclays should not result in the potential loss of living organisms at a contaminated site.

Conflicts of interest
There are no conflicts of interest to declare.

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Notes and references

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Chem Soc Rev, 2019, 00, 1–32 | 27
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