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Review article

Recent advances on nanohybrid systems constituting clay–chitosan with organic molecules – A review

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ABSTRACT

Bionanocomposites include matrices and dispersed phases that combine two or more biomolecules on a nanometric scale to enhance some nanomaterial properties such as biocompatibility and biodegradability. Nowadays, chitosan (CS), a cationic polysaccharide, is one of the most commonly used bioconstituent in the preparation of bionanocomposites with several other materials, such as clay. CS–clay nanocomposites are extensively explored in applications such as drug delivery systems, dressings, food packaging, and contaminant adsorption, due to their improved physicochemical, barrier, and mechanical properties. Recently, the association of organic molecules alongside CS–clay nanocomposites emerged due to the ability of adding new and specific properties for these materials. In this context, we reviewed recent advances on nanohybrid systems composed of CS–clay with organic molecules and discussed their structural interactions, enhanced properties, synthesis method, applications, and toxicological implications. Furthermore, challenges and future perspectives were considered to establish parameters for conducting future research in this field.

1. Introduction

Composites are structures constituted by a matrix and dispersed phases that can enhance physicochemical properties as flexibility (Corrado and Polini, 2019), catalytic efficiency (Ouyang et al., 2018; Wang et al., 2019), and thermal stability of materials (Bocci et al., 2020). Composites can be called nanocomposites when at least one dimension has a nanometer scale measure (1–100 nm) or a property derived from a nanometric material (Youssef and El-Sayed, 2018). Furthermore, nanocomposites have large specific surface area and high carrier capacity, making them attractive for delivery systems (Piao et al., 2020).

Nanocomposites can have an inorganic background, but when a biological molecule is introduced on these nanohydrids, they become bionanocomposites (BNCs) (Youssef and El-Sayed, 2018; Saranti et al., 2021). Hence, with the advancement of nanotechnology, several BNCs have been developed to address the issues involved in several fields, such as health, energy, electronics, and agri-food (Kord and Roohani, 2017; Liu et al., 2019; Chen et al., 2020). BNCs made from clay–chitosan (CS) have recently gained prominence (Fig. 1a) because they may have the ability to improve properties of materials (including tensile strength, thermal stability, and elongation) (Azmana et al., 2021; Cavallaro et al., 2021).

CS is a semisynthetic biopolymer derived from chitin used in several bionanotechnological applications. It comprises β-(1–4)-linked d-glucosamine (deacetylated unit) and *N*-acetyl-d-glucosamine (acetylated unit) (Dash et al., 2011; Elsabee and Abdou, 2013; Kravanja et al., 2019; Neji et al., 2020; Rodríguez-Rodríguez et al., 2020; Cavallaro et al., 2021). CS coexists with clay because it has high miscibility with layered silicates in acidic medium (Moussout et al., 2018; Ali and Ahmed, 2018; Cankaya and Sahin, 2019; Mujtaba et al., 2019; Saheed et al., 2021). Furthermore, CS is used in clays due to its mechanical, thermal, and barrier properties, which are typically derived from synthetic polymers (Futalan et al., 2011; Pongjanyakul and Suksri, 2009), with the intrinsic characteristics of biocompatibility, low toxicity, and biodegradability provided by biopolymers (Han et al., 2010). Although several CS products have been developed, their properties can be further improved. Thus, bionanocomposites (BNCs) with clays have emerged as

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a viable solution for modifying some CS properties (Han et al., 2007).

The interaction among clays and chitosan is intrinsically related to their surface ions groups and may change according to (i) type and/or modification of clays, and (ii) chitosan chemical modification. For example, chitosan can be chemically modified by PEGylation, carboxymethylation and quaternization, configurating new properties to the bionanocomposite systems. Otherwise, different types of clays configure different types of surface interactions/properties with chitosan (Awad et al., 2019; Lei et al., 2020; Yu et al., 2022).

Clays are fine-grained structures from alkaline volcanic ashes, they are classified on their position, location, mineral content, and essentially consisted of crystal minerals: definite crystalline structures composed of tetrahedral $[SiO_4]^{4-}$ and octahedral $[AlO_3(OH)_3]^{6-}$ sheets. Some clays minerals characteristics (as porosity) are essential to form an excellent BNC, but the main one is cation exchange capacity (CEC). Due to their structures, most clays have an anion exchange (depending of pH medium) that can interact with a diversity of cations, from organics or inorganic molecules (Silva et al., 2012; Lazaratou et al., 2020; Mukhopadhyay et al., 2020; Murugesan and Scheibel, 2020).

Therefore, in an acidic medium, the amine of CS can be modified through protonation and the clay–CS interaction is easily noticed (Fig. 1b) (Boch and Niepce, 2010; Silva et al., 2012). There are two main clay–CS nanostructure morphologies: (i) CS can penetrate the clays interlayer space (intercalation) or (ii) envelop the clay, leaving BNC freer (exfoliation) (Darder et al., 2012; Mahdavinia et al., 2013; Zhan et al., 2015). Both BNC morphologies have been extensively investigated due to their distinct properties of swelling, excellent retention of drugs, high adsorption capacity, as well as improved barrier and mechanical properties (Fig. 1c) (Da Costa et al., 2016; Dziadkowiec et al., 2017; Awad et al., 2019). On the other hand, tactoidal morphology has limited exfoliation and the layered retain their stacked form, which staying at a larger size. There are several reviews providing information about clays and their applications in BNC with CS (Mittal, 2009; Pavlidou and Papaspyrides, 2008; Cavallaro et al., 2021).

Even though these BNCs are well known and studied, clay–CS BNCs have limitations, and ternary or quaternary compositions with additional organic molecules (OMs) can extend the length of their applications. It may occur due to two reasons: (i) to enhance an existing property or/and ii) to achieve new characteristics. Thus, the growing development of clay–CS with OMs offers new opportunities for attaining new discussions and the development of new hybrid materials for different sectors. Therefore, this review will provide an overview of recent studies that have reported the use of these bionanocomposites and discuss the toxicological frameworks and future developments in this promising research field.

2. Types and applications of nanohybrid systems constituting clay–CS with organic molecules

Several studies have been conducted to develop new clay–CS BNCs with different types of molecules, including inorganic molecules (Wang et al., 2021a; Liu et al., 2021a; Rusmin et al., 2022). Nevertheless, OMs are structures mainly composed of carbon and known to be more biodegradable than inorganic structures, making them excellent materials for interacting with clay (Mazumder et al., 2019). Furthermore, try to elucidate the interaction among clays-CS-OM is quite interesting.

For instance, most polymers are made up of carbon–hydrogen larger molecules that can form blends. Blends (Fig. 2a1) are components that physically coexist to improve the physicochemical, mechanical, and biological properties of materials. Moreover, they can provide exemplary configurations and new properties to BNCs (Kausar, 2017; Giannakas et al., 2020; Iqbal et al., 2020). Other method to achieve the ideal BNC between two polymers is through crosslinking; and the use of this technique can be observed in the preparation of CS (Fig. 2a2) or in the other OMs; moreover, there is the case where both polymers are crosslinked (Fig. 2a3). Crosslinking can involve different forms of synthesis; however, it can be performed to improve specific properties such as swelling and the tensile strength of the materials. Another technique is graft copolymerization (grafting) (Fig. 2a4). In this technique, CS surface is directly modified with a union to the OMs; consequently, this synthesis is only possible if the two organic molecules present reactive functional groups under the right conditions (Murugesan and Scheibel, 2020). Electrostatic interactions are another common apparatus used to obtain BNCs (Fig. 2a5). Modifications in the additional organic molecule/CS or clays can be seen mainly through chemical treatment and conjugation of functionalized groups.

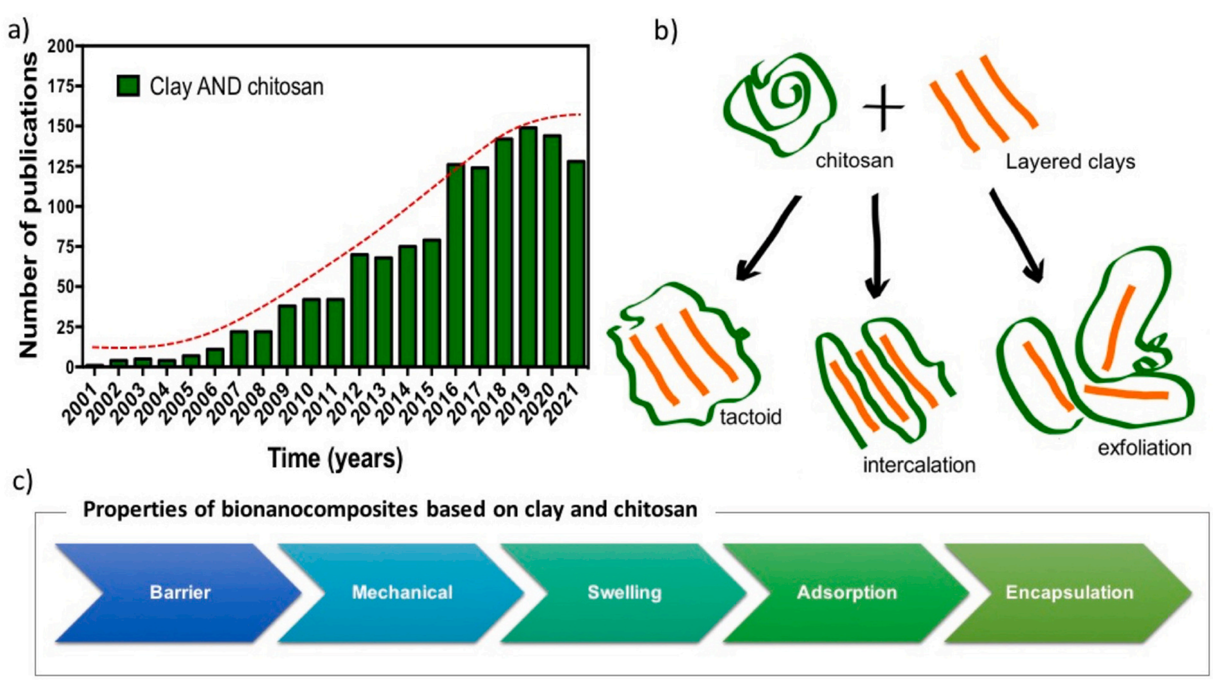

Fig. 1. (a) Number of papers published in the ISI Web of Knowledge database annually regarding the interaction of clay and chitosan. (b) Schematic representation of the potential interaction between CS molecules and layered clay. (c) Some properties improved by clay in bionanocomposites with chitosan.

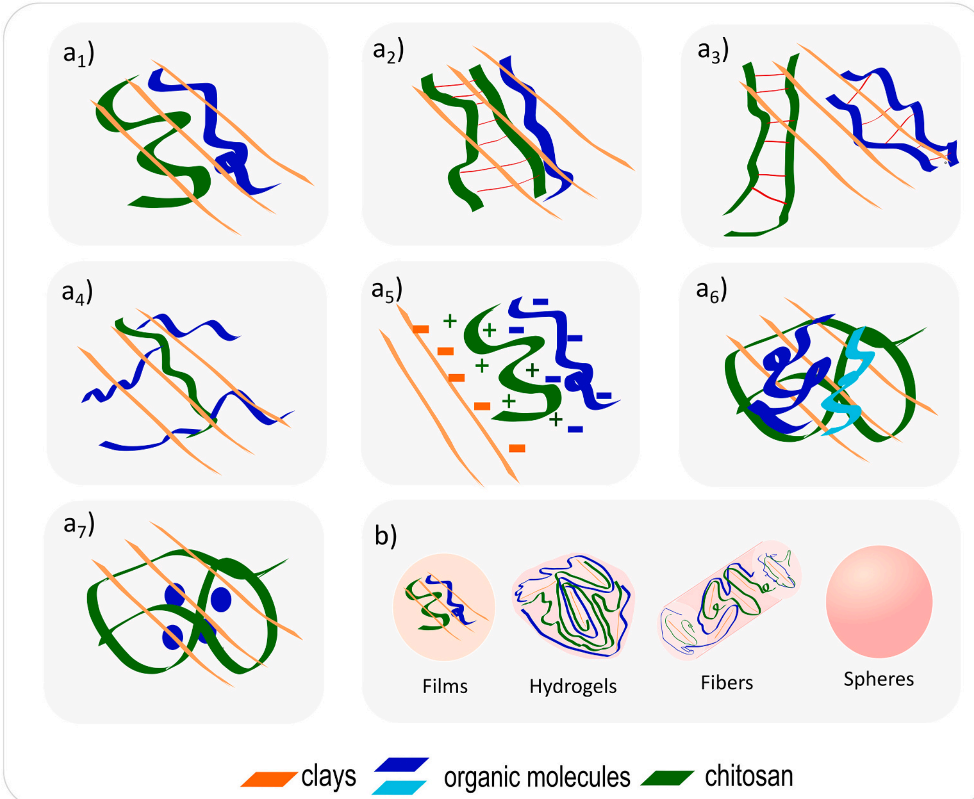

Fig. 2. The main clay/CS/organic molecular conformations: (a1) physical polymeric blend, (a2) chemical crosslinking between CS molecules, (a3) chemical crosslinking between CS and other OMs, (a4) graft copolymerization, (a5) electrostatic interaction, (a6) OM1-OM2-clay-CS, (a7) plasticizers (small molecules). (b) Different morphologies/types of BNCs.

Additionally, there are reports of two organic molecules in quaternary compositions with clay–CS; however, the OMs–clay–CS nanomaterials (Fig. 2a6) are reported with less frequency. Finally, there are bionanocomposites with nonpolymeric OMs, they have a small molecular mass, as in the case of plasticizers (Fig. 2a7). All these components may enhance properties of BNCs and new characteristics may appear depend on the different arrangements (Giannakas et al., 2020; Cui et al., 2021; Liu et al., 2021b).

As observed, clays play an essential role in BNCs with CS-organics. They can incorporate a nanosize-scale compounds or act as a nanofiller (providing a nanoproperty). Among all clays, montmorillonite (Mt) is the most prevalent within CS–organic nanohybrids. It is a layered silicate mineral clay with plasticizer ability, swelling ability, mechanical resistance, and low cost (Souza et al., 2018). Mt shares two essential subgroups with CS–organics: cloisite (CL) and bentonite (Bent). CL has potent antibacterial properties (Butnaru et al., 2016); however, Bent exhibits highly hydrophilic characteristics due to exchangeable cations (sodium) and may selectively control BNC adsorption at several pH concentrations (Wang et al., 2014). As a nanofiller, Mt has outstanding properties, such as lower toxicity compared with other nanoparticles (silica/graphene oxide) (Anirudhan and Parvathy, 2018). Moreover, Mt nanoplatelet/nanosheets are potent tools for providing good mechanical and physical properties to CS–organic BNCs (Pires et al., 2018).

Kaolinite is another clay used as a nanofiller in BNCs development (Khan et al., 2021). Nevertheless, halloysite (Hal) has unique nanotubes that shows outstanding reinforcement properties (Huang et al., 2012; Wang et al., 2020a; Govindasamy et al., 2020). Sepiolite (Sep) is a fibrous clay with a needle shape, which is used for delivering drugs (Mahdavinia et al., 2016). Another clay is Laponite (Lap), a synthetic clay with structure similar to Hal, that can be used in BNCs with CS–organics. For instance, hydrogels of Lap can improve the swelling ability of bionanocomposites (Oliveira et al., 2014). Moreover, palygorskite (Pal) is another clay with BNC potential due to its high specific surface area, moderate CEC, and selective adsorption (Sun et al., 2017). Additionally, layered double hydroxide (LDH) is a class of synthetic clay exhibiting the same characteristics as the raw clay; their properties can be tuned, unlike those of raw clays, to obtain desired new properties (Seftel et al., 2008; Lei et al., 2021).

Regarding the applications, the use of ecofriendly clay–CS–organic bionanocomposites in food packaging has been expanding due to its biocompatibility and antioxidant properties, which prolong product shelf life (Souza et al., 2018). Recently, a brand-new review explored a few additional particles in clay–CS nanohybrids and highlighted the significance of a third organic element for food packaging (Qu and Luo, 2021). Moreover, organic biomolecules as biopolymers can enhance mechanical properties in food packaging applications (Huang et al., 2020).

Furthermore, applications of biopolymers, such as biomedical and adsorption are extensively reported (Ribeiro et al., 2014; Arabyarmohammadi et al., 2018; Jafari et al., 2021). In the past two years, agrochemical applications in clay–CS–organic BNCs have also emerged (El Assimi et al., 2020; Elsherbiny et al., 2022). Moreover, the product formats vary significantly, e.g., in fibers, films, hydrogels, and spheres (Fig. 2b). There are several methods for clay–CS–organic bionanocomposite constructions that are similar to clay–CS nanohybrids; however, the prime methods are solvent casting, freeze thawing, gamma irradiation, extrusion, ultrasound, and electrospinning (Table 1) (Park et al., 2009; Wang et al., 2014; Wang et al., 2018a; Lei et al., 2021).

Clay–CS BNCs are produced, preferably with biopolymers, and can be classified into two types: those originating from living organisms (e.g., cellulose and starch) - natural biopolymers, and those originating from synthetic processes; however, with biological properties, including biodegradation and biocompatibility - synthetic biopolymers (George et al., 2020; Ilyas and Sapuan, 2020; Sadasivuni et al., 2020). However,

Table 1
Some methodologies that can be used to synthesis clay–CS–organic bionanocomposites.

Synthesis method	CS–clay/organic	Application	Outcomes	Format	Ref.
Solvent casting	Mt/PVA	Food packaging	Improved antibacterial properties	Film	El Bourakadi et al., 2019
	Mt/PLA	–	Increased thermal stability	Film	Wu and Wu, 2006
	Mt/PCL	Biomedical	Enhanced protection against infections	Film	Huang et al., 2019
	OrgMt/corn oil	Food packaging	Improved barrier properties	Film	Giannakas et al., 2017
	Hal/PVA	Biomedical	Hemocompatibility material	Film	Kouser et al., 2020
	Mt/Rosemary Oil (REO)	Food packaging	Increased the surface hydrophobicity and the swelling degree, and decreased the water solubility	Film	Souza et al., 2018
	Mt/PVA	Adsorption	Enhanced antibiofouling property	Film	Sangeetha et al., 2019
	Pal-Glycyrrhizic acid	Biomedical	Improved antibacterial activity and hemocompatibility	Film	Zhang et al., 2022
Electrospinning	Mt/PVA	Adsorption	Enhanced mechanical properties	Fiber	Koosha et al., 2015
	OCT Mt/PVA	Adsorption	Improved uptake capacity	Fiber	Hosseini et al., 2021
	Hal/PVA	Adsorption	Enhanced removal of Cd (II) and Pb (II) ions	Fiber	HMTShirazi et al., 2022
Freeze thawing	Mt/PVA	Biomedical	Excellent antibacterial activity	Hydrogel	Noori et al., 2018
Gamma Irradiation	Lap/PVP	Biomedical	Increased gel fraction	Hydrogel	Oliveira et al., 2014
Ultrasound	Mt/gPAM	Biomedical	Improved rupture energy	Hydrogel	Su et al., 2017
Extrusion	Na+/Mt/starch/bamboo	Food packaging	Improved water vapor barrier	Film	Llanos et al., 2021

clay–CS BNCs also use nonbiodegradable polymers, such as polyacrylamide (PAM) and polyethylene terephthalate (PET). Hence, the OMs will be discussed in more detail in next sections.

2.1. Clay–CS-natural biopolymers

In the last five years, there has been a larger producing of natural biopolymers-CS-clay BNCs. Natural biopolymers have advantages over synthetic ones, such as improved bioactivity, less toxicity, and enhanced cellular response when associated with other cells. However, they also have some limitations, such as poor processability, the possibility of contamination by pathogens, poor or limited properties, such as elasticity, ductility, and low shelf life (Rehman and ur Rehman, 2019; Salehi et al., 2020; Azmana et al., 2021; Reddy et al., 2021). In this regard, several studies with clay–CS-natural biopolymers will be discussed below.

2.1.1. Cellulose

Cellulose is a common material used to develop BNCs with clay–CS for various applications, including paper fabrication and biomedical devices (Cavallaro et al., 2014; Lai et al., 2016). Cellulose is the most abundant natural biopolymer present in the world and can be molded into different shapes, such as hydrogels, spheres, and films (He et al., 2018; Nascimento et al., 2018). In ternary compositions, cellulose can improve barrier, mechanical properties, and thermal stability (Enescu et al., 2019). However, carboxymethylcellulose (CMC) has recently started to gain prominence.

CMC is an anionic hydrophilic biopolymer that is handled due to its gel-forming ability with CS (Javanbakht and Shaabani, 2019; Tang et al., 2021). The interaction can provide benefits, including efficient molecule adsorption and better recycling use, as reported in a study with doxycycline (Fig. 3a) (Wang et al., 2020b; Tang et al., 2021). For example, Bozoğlan et al. (2021) used a quaternary composition of two natural biopolymers (carboxymethylcellulose and scleroglucan) along

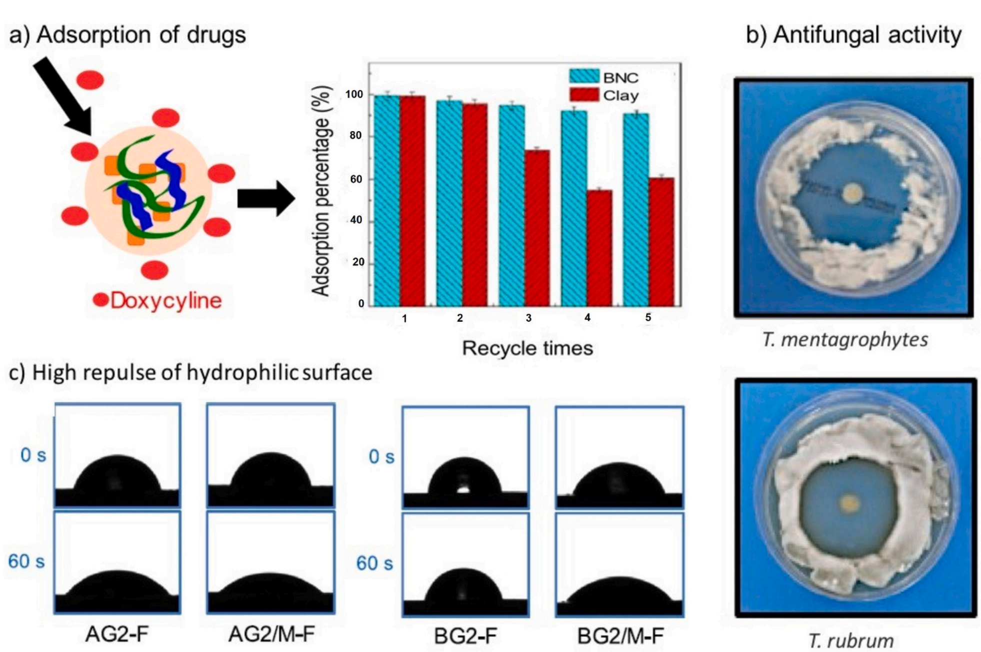

Fig. 3. Examples of cellulose-based BNC properties. (a) Schematic adsorption and graphic recycling performance showing the difference of clay and a CS/CMC/Mt. Adapted and reproduced with permission from Ref. (Tang et al., 2021). Copyright (2021) Elsevier. (b) Antifungal activity formed by OXI-loaded antifungal thermo-sensitive quaternary clay hydrogels against *T. mentagrophytes* and *T. Rubrum*. Adapted and reproduced with permission from Ref. (Bozoğlan et al., 2021). Copyright (2021) Elsevier. (c) High repulse of hydrophilic surface primarily from glycerol in CS (AG2-F) and CS:CMC (BG2-F) compared to the compositions with clay (AG2/M-F and BG2/M-F) by contact angle measurement. Adapted and reproduced with permission from Ref. (Chen et al., 2021a). Copyright (2021) Elsevier.

with CS and montmorillonite to form hydrogels for carrying oxiconazole nitrate, a treating nail fungicide (Bozoğlan et al., 2021). Scleroglucan is a covalent polysaccharide extracellularly secreted by filamentous fungi of the *genus Sclerotium* and is suitable to form hydrogels (Lapasin et al., 2017). Therefore, as represented in Fig. 3b, the area display images indicated a high antifungal activity provided by these BNC hydrogels. On the other hand, the increase of Mt lowered drug release ability; nonetheless, according to the authors, the gelation of these bionanocomposites transformed them into efficient agents for nail fungus treatment (Bozoğlan et al., 2021).

In another biomedical application, Chen et al. (2021a) reported the use of plasticizers (1-ethyl-3-methylimidazolium acetate ([C2 mim][OAc]) and glycerol) in films formed by CMC/CS/Mt. The authors reported an increase in tensile strength, molecular relaxation, and hydrophilicity of BNC films due to the presence of clay. Furthermore, when CS was mixed with ([C2] [OAc mu]) (plasticizer), the contact angle was the same provided by CS/Mt and it occurred because of its strong ability to form hydrogen bonds between the plasticizer and CS. Also, the compositions without clay reduced the hydrophilic surface, as indicated by the contact angle (Fig. 3c). At last, Tağaç et al., 2021 constructed a Mt/CS/CMC/DIL (benzylimidazolium based dicationic ionic liquid) BNC for extracting organochlorine pesticides.

Another emerging suitable organic polymer to use in clay–CS BNCs is nanocellulose, a nanoscale cellulose material that improves the biocompatibility and recyclability of bionanocomposites (Sharma et al., 2020). One example is nanofiber cellulose (CNF), which can be considered an excellent raw material for confining aerogels due to the numerous hydroxyl groups (giving a flexible property) (Rong et al., 2021). Cellulose nanocrystal (CNC) is the other most prevalent nanocellulose derivative. For instance, CNC–CS–Sep changed the crystallinity of the BNC due to clay and CNC morphology (Chen et al., 2021b).

2.1.2. Pectin

Pectin (PEC) is an anionic polysaccharide commercially obtained through acidic aqueous extraction processes from apple and citric fruits (Srivastava and Malviya, 2011), and can mainly be used in clay–CS nanohybrids for drug delivery systems (Ribeiro et al., 2014; Cheikh et al., 2019). However, PEC can be also used as an adsorbent, as reported by Da Costa et al. (2016), who created PEC/CS/montmorillonite hydrogels with different clay–polymer ratios; the authors observed a 1000% increase in the swelling. Moreover, it is possible to configure PEC layers in a pH-responsive nanocarrier; this layer-by-layer construction can be observed primarily because PEC has a negative polarity, and CS becomes electrically positive in an acidic medium. Therefore, electrostatic interactions among the biopolymers and halloysite nanotubes are easily noticed (Fig. 4a1). Moreover, *in vitro* kinetic release profiles (Fig. 4a2) corroborate with the responsiveness application of BNCs (Jamshidzadeh et al., 2020; Rebitski et al., 2020).

2.1.3. Starch

Starch is a natural biopolymer obtained from various natural sources. CS–starch have a strong interaction due to their hydrophilic characters. In BNCs, films with a ternary composition (starch/CS/halloysite) nanotubes were prepared using the solution casting method as proposed by Devi and Dutta (2019). The bionanocomposites were characterized, and the authors verified an improvement in the water absorption capacity. Also, the material exhibited hydrophilic character and a low bacterial permeability. Thus, the authors suggested this BNC for dressing application (Devi and Dutta, 2019). Starch is also used for packing applications due to its antifungal and antimicrobial activity, which can increase food shelf life. Moreover, studies have shown soil protection against microbial activity caused by starch/CS/clay BNCs (Perotti et al., 2017; Jha, 2021; Ferreira et al., 2021).

2.1.4. Other natural biopolymers

Alginate is a linear hydrophilic, biocompatible, mucoadhesive, inexpensive, and anionic polysaccharide that can be used as a platform for controlling drug delivery systems. For instance, BNCs with clay–CS–alginate were reported in the 5-Fluoracil (5-FU) administration (Azhar and Olad, 2014). On the other hand, biopolymers like lignin were reported to be effective for absorbing heavy metals, such as Cu^{2+} in a BNC with LDH/CS (Castillo et al., 2018). Gelatin (a collagen derivative) was employed in clay–CS BNCs in food packing applications due to its outstanding processability (Moosavi and Zerafat, 2021). Also, a cyanobacterium (*Spirulina algae)* was recently reported as an extraordinary organic molecule for food packaging with clay–CS, improving the essential barrier properties, such as oxygen transmission rate (Ramji and Vishnuvarthanan, 2021). Another polymer derivative from algae is

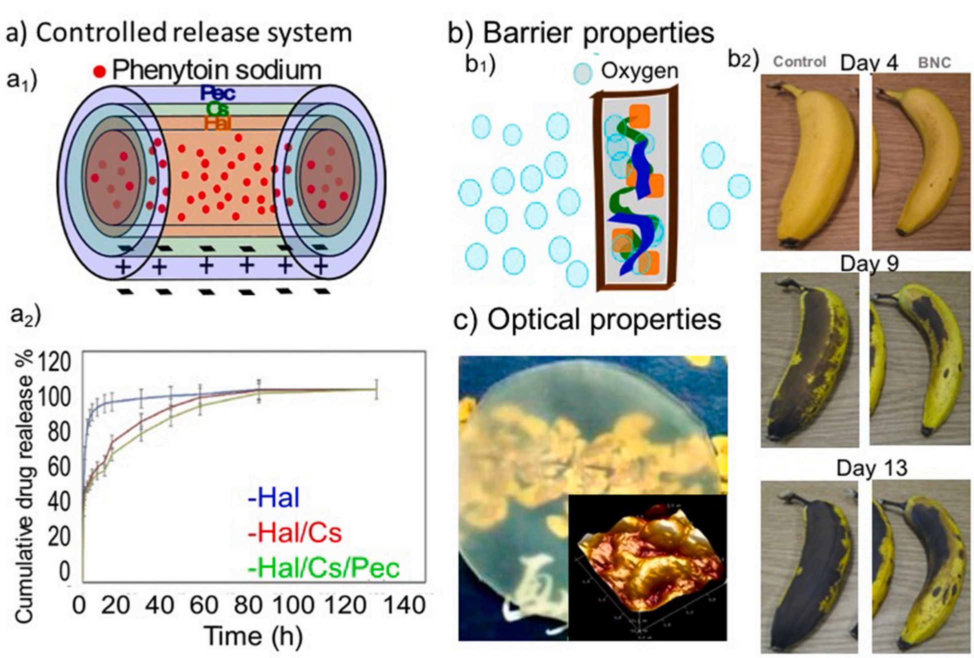

Fig. 4. Examples of natural biopolymers BNC and their applications. (a1) Hal/CS/Pec structure representation and (a2) Hal/CS/Pec release kinetic profiles at stimulated intestinal fluid. Adapted and reproduced with permission from Ref. (Jamshidzadeh et al., 2020). Copyright (2020) Elsevier. (b1) Schematic barrier properties of carrageenan/CS/clay, and (b2) a time lapse of bananas coated with and without BNC structure. Adapted and reproduced with permission from Ref. (Laufer et al., 2013). Copyright (2013) Elsevier. (c) Photograph and AFM of a transparent quaternized hemicellulose/Mt/CS film. Adapted and reproduced with permission from Ref. (Chen et al., 2016). Copyright (2016) American Chemical Society.

carrageenan, which also has excellent barrier properties (Fig. 4b1) in BNC with CS–Mt, protecting food against oxidation (Fig. 4b2) (Laufer et al., 2013).

Hemicellulose is a natural biopolymer provided by lignocellulosic feedstock and includes xyloglucans, and xylans (Lima et al., 2021). In BNC, a composition was notified by Ali et al., 2019, the authors grafted xylan to a quaternized CS and mixed it with Mt (as nanofiller) in order to obtain scaffolds for bone tissue engineering. Another xylan-g-quaternized CS–Mt was reported by Cai et al., 2019, which observed higher retention of the BNC compared to xylan. Modified hemicellulose/xylans are also verified with clay–CS BNCs. For example, films of quaternized hemicellulose–CS–Mt were produced by Chen et al., 2016 and presented higher tensile strength and good transparency. Also, the authors analyzed the films by Atomic Force Microscopy (AFM) (Fig. 4c). Another BNC film reported was Hal/carboxymethyl xylan/CS/*Origanum vulgare* essential oil, where it was reported a higher tensile strength because of the Hal addition (Yousefi et al., 2020).

2.2. Clay–CS-synthetic biopolymers

Synthetic biopolymers provide remarkable antibacterial activity and biodegradability to clay–CS BNCs (Zhang et al., 2017). Several synthetic biopolymers have mechanical and physicochemical characteristics similar to biological tissues. However, one of the disadvantage of synthetic biopolymers is the lack of cell adhesion in specific locations. As an alternative, a semisynthetic biopolymer, such as CS, may help in this bioadhesion. Otherwise, some biopolymers can strongly interact with CS, improving their properties such as drug-carrying, thermal stability, water capturing, and bactericidal activity (Wang et al., 2020a; Parida et al., 2011; Reddy et al., 2021). Therefore, the leading synthetic biopolymers investigated in the formation of bionanocomposites with clay–CS will be highlighted in the next section.

2.2.1. Poly(vinyl alcohol)

Poly(vinyl alcohol) (PVA) is a nontoxic, semicrystalline polymer with excellent thermal and chemical properties. PVA has excellent biocompatibility as well as high water permeability and can form gels in various solvents (Parida et al., 2011; Park et al., 2009; Khazaei et al., 2021). Moreover, its biodegradability, antimicrobial activity, and ability to interact with CS through hydrogen bonding (increasing mechanical resistance) make PVA the most observed polymer in clay–CS–organic BNCs (Koosha and Hamedi, 2019; El Bourakadi et al., 2019; Hu et al., 2020; Huang et al., 2012). Electrospinning can be used to create PVA/CS/Mt nanofibers, where PVA was reported as an excellent thermal stabilizer; however, their tensile strength was negatively affected (Park et al., 2009). Also, PVA/CS/Mt. formulations can be employed to controlled release of drugs (Fig. 5a), as well as antibacterial activity (Fig. 5b) (Reddy et al., 2016). Moreover, PVA/CS/clay BNC improves mechanical properties of hydrogels (Parida et al., 2011; Reddy et al., 2016; Noori et al., 2015). Furthermore, it was observed a plasticity increasing caused by PVA in nanocomposites with CS/Mt. However, it did not enhance antimicrobial action against some bacteria like *Escherichia coli* (Giannakas et al., 2016).

Wang et al. (2018a) prepared Mt/CS nanofilms with PVA/poly

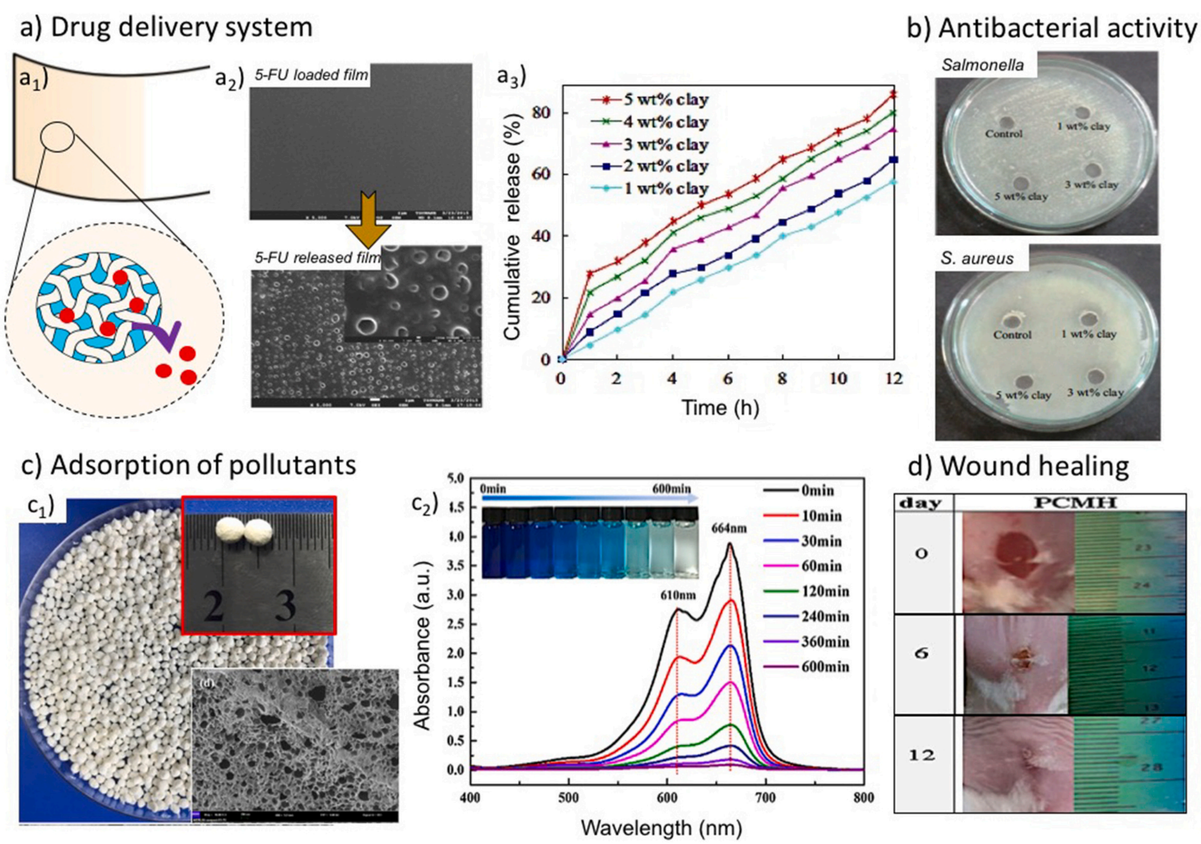

Fig. 5. Examples of PVA-CS-Clay systems and their application. (a_1) Schematic representation of the chitosan/PVA/Na^{+}/Mt nanocomposites film, (a_2) SEM images of the film before and after 5-FU release, (a_3) 5-Fluoracil release profile, and (b) antibacterial activity against *Salmonella* and *Staphylococcus aureus*. Adapted and reproduced with permission from Ref. (Reddy et al., 2016). Copyright (2016) American Chemical Society. (c_1) Hydrogels beads (Mt/PVA/CS) and SEM after freeze-drying from adsorption of pollutants, and (c_2) UV–vis absorbance spectra of methylene blue dye solution at pH = 10. Adapted and reproduced with permission from Ref. (Wang et al., 2018b). Copyright (2018) Elsevier. (d) Wound healing process within 12 days of PVA/CS/Mt/Honey BNCs. Adapted and reproduced with permission from Ref. (Noori et al., 2018). Copyright (2018) John Wiley & Sons. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(ethylene oxide) as a matrix and observed enhanced thermal stability and mechanical properties of the material as well as excellent oxygen and suitable moisture barriers. In another study, Wang et al. (2018b), designed PVA/Sodium Alginate/CS/Mt hydrogels (Fig. 5c1) using a freeze-drying method to remove methylene blue (MB) in alkali medium conditions (Fig. 5c2). Additionally, PVA in a BNC can increase the curative property (Fig. 5d) (Noori et al., 2018), and thermo-mechanical properties of materials (Kouser et al., 2022).

2.2.2. Poly(ethylene glycol)

Poly(ethylene glycol) (PEG) is another nontoxic and degradable biopolymer (Rekik et al., 2019). PEG has immunogenicity and biocompatibility properties. However, there are not many reports on clay–CS BNCs with PEG, and the leading studies are focused on constructing microcompounds exhibiting nanoproperties with nanoclays (Anirudhan and Parvathy, 2018). PEG can be employed to form hydrogels capable of delivering bioactive components due to their responsiveness to external stimuli (Mohamed et al., 2017). In this context, capsules with PEG in clays:chitosan BNCs are observed as bioactive delivery system as alternatives to combat infections (Fig. 6a) (Abd Elsalam et al., 2020). Also, El Assimi et al. (2020) developed sustainable granules that can release fertilizer in soil over longer time periods (Fig. 6b).

2.2.3. Other synthetic biopolymers

Poly (lactic acid) (PLA) is employed in BNCs with clay–CS to improve degradation and enhance antimicrobial properties. Furthermore, this polymer has excellent processability, renewable features, and biocompatible properties (Rihayat et al., 2018; Islam and Islam, 2021; Kamaludin et al., 2021a). Park et al. (2012) prepared PLA films with CS and Mt to improve the barrier properties of the materials, and reported an increase in water and oxygen barrier due to the PLA. Also, Kamaludin et al. (2021a) studied how PLA influenced nanotubes formed by halloysite/CS. The material fabricated was melted and compressed, and the authors reported an enhance in the surface adhesion, thermal stability, tensile strength, elongation break, as well as a uniform dispersion of the Hal nanotubes in the PLA/CS matrix (Kamaludin et al., 2021b).

Polycaprolactone (PCL) is a biodegradable aliphatic polyester prepared by opening the ε-caprolactone ring in the presence of alkoxide metals (Mazumder et al., 2019). BNCs of PCL/CS/Clays are mainly focused on dressing application in order to improve thermal and mechanical properties of materials (Abdolmohammadi et al., 2011). For instance, Sahoo et al. (2010) developed a polymer blend of PCL/CS (20/80) with an organoclay (closite 30B) in various proportions (1%, 2.5%, and 5%) for doxycycline release, and studied the release *in vitro* profiles and swelling behaviors of these materials.

Synthetic hydrophilic copolymers, such as polyvinylpyrrolidone (PVP) can be also combined with chitosan to enhance biocompatibility and biodegradability. PVP also forms hydrogen bonds with the hydroxyls/amine groups of chitosan (Saeedi Garakani et al., 2020; Sizílio et al., 2018). For instance, Zhang et al. (2020) employed two types of clays from palygorskite with PVP/CS. The structure, mechanical, thermal properties were studied and the authors concluded better tensile strength from the BNC films due to improved clay dispersion in the blend.

Poly(acrylic acid) (PAA) is another biopolymer observed in nanoformulations with chitosan and clays, primarily as impurities adsorbent. For instance, PAA compounds BNCs were used for removing heavy metals due to their carboxylic functional group binding capability (Yu et al., 2019). Also, Wang et al. (2008) designed a bionanocomposite (Mt/CS-g-PAA) to remove methylene blue in aqueous media and observed an increase in the maximum adsorption capacity of the

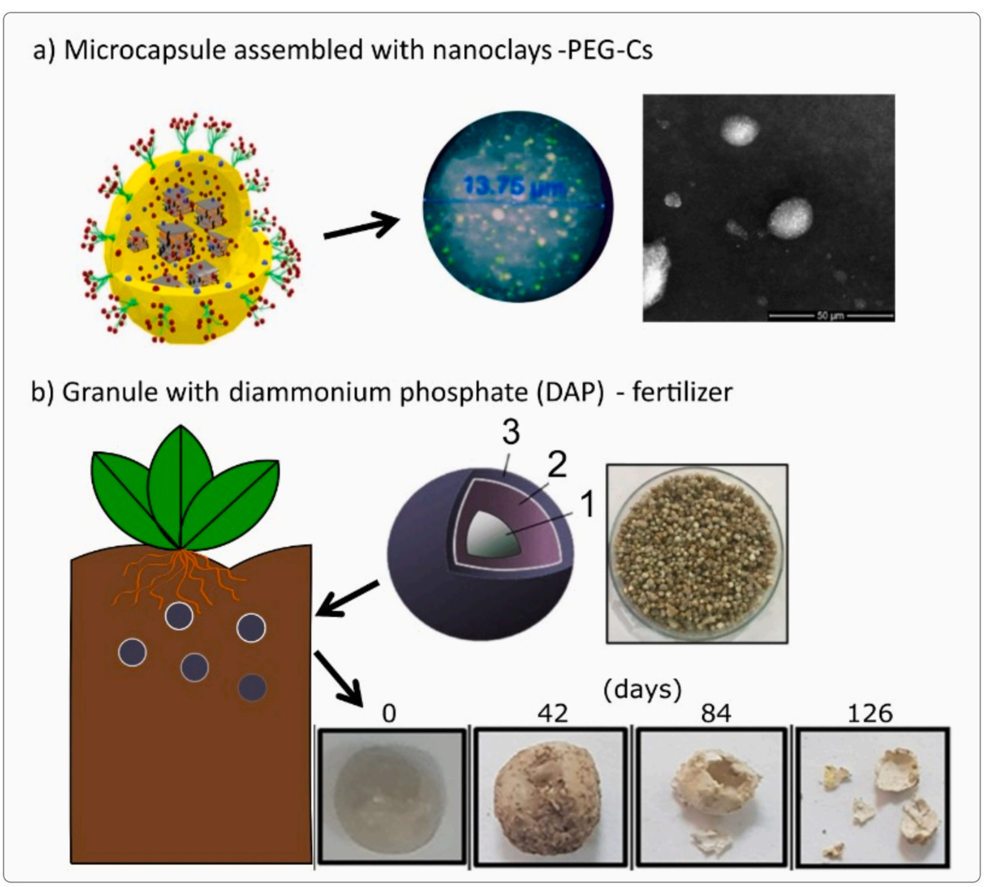

Fig. 6. (a) Nano-in-micro multifunctional platform constituted by nanoclay/PEG/CS/Ag NPs to deliver Ibuprofen using scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX) for characterization. Adapted and reproduced with permission from Ref. (Abd Elsalam et al., 2020). Copyright (2020) Elsevier. (b) Schematic structure of a fertilizer granule constituting diammonium phosphate (DAP), PEG/CS/Mt, and paraffin wax along with their granule time-lapse images. Reproduced with permission from Ref. (El Assimi et al., 2020). Copyright (2020) Elsevier.

material. Furthermore, the reuse capacity of this BNC was reported (Wang et al., 2008). Finally, Poly (lactic-*co*-glycolic acid) (PLGA) is a copolymer used in constructing of BNCs with CS-clay (Fig. 7) as a dressing for burn injuries (Yu et al., 2019; Sadeghi and Yarahmadi, 2011; Hu et al., 2020; Mukhopadhyay et al., 2020; Dan et al., 2021; Mohebali and Abdouss, 2020).

2.3. Clay–CS-nondegradable polymers

Few nondegradable synthetic polymers construct bionanocomposites with clay–CS; e.g., the use of poly(methylmethacrylate) (PMMA) by Khalek et al. (2012). In this study, the authors graphitized PMMA in CS via γ-irradiation polymerization and mixed it with Bent to form a bionanocomposite capable of adsorbing higher mercury ions (Hg^{2+}) concentration. Also, Daraei et al. (2013) reported a polar/nonpolar (clay/poly(vinylidene fluoride) interaction decreasing clay's dispersion in films made from CS/cloisite 15-A-cloiste 30B/poly(vinylidene fluoride). Additionally, Ferfera-Harrar et al. (2014) developed hydrogels of CS-g-PAM/Mt as superabsorbents and observed antibacterial activity in acidic media.

On the other hand, a ternary composition with two types of polyphenylenediamine (pPDA and oPDA)/CS/Mt were published by Ramya et al. (2017), where the authors studied BNCs' optical properties and reported the first nonlinear optical studies of these bionanocomposites. Another nonbiodegradable synthetic polymer was reported by Essabti et al. (2018); in this study, PET was used with CS and vermiculite for food packaging and the authors analyzed an improving in oxygen barrier with the addition of OM and clay. Polybenzoxazine (PBO)/CS/Na^+/Mt aerogels were reported by Alhwaige et al. (2020); they observed an increase in degradation temperature with the addition of clay. Moreover, they indicated high stability in various pH and outstanding water uptake. Köken et al. (2021) notified a BNC nanofiber constituted by CS-*graft*-polyacrylonitrile/sepiolite (CS-g-PAN/Sep) with great water adsorption and thermal resistance properties. Additionally, Minisy et al. (2021) reported a polyaniline PANI/Cs/Mt (Fig. 8a1) bionanocomposite as an ecological adsorbent for methylene blue (Fig. 8a2). Also, BNCs were produced to carry vanillin (Van) and cinnamaldehyde (Cinn) antioxidants by Elsherbiny et al., 2022, their respective pesticide release profiles and antifungal activity against *Fusarium oxysporum* were reported (Fig. 8b).

2.4. Clay–CS-nonpolymeric organic materials

Nonpolymeric OMs are minor compounds made of carbon and hydrogen and are also managed in clay–CS BNCs. For instance, Naguib et al. (2015) used graphitization to link CS to an OM and 4-vinyl pyridine to form a bionanocomposition prepared by CS-g-4VP/Mt. Another example of OM is glycerol (a plasticizer); the presence of glycerol improves CS intercalation in Mt and enhances its mechanical properties (Lavorgna et al., 2010; Kusmono Abdurrahim, 2019; Roy and Rhim, 2021). However, another plasticizer known as oleic acid has also been studied in BNCs with clay–CS (Vlacha et al., 2016). Essential oils and derivatives are also used in these BNCs due to their antioxidant properties since they help with food protection and increase shelf life (Abdollahi et al., 2014; Souza et al., 2018; Pires et al., 2018; Butnaru et al., 2019; Souza et al., 2019; Cui et al., 2021). Furthermore, tea polyphenol (TP)/CS/Hal nanotubes BNCs can be three-dimensionally printed and successfully replace traditional film processing (Wang et al., 2021b).

Otherwise, laccases (Lacs) are blue multicopper enzymes from fungus able to oxidize phenolic and non-phenolic molecules. In BNC, Lacs are known to degrade pesticides/wastes as reported to Kadam et al., 2018, where was investigated Hal nanotubes modified with Fe_3O_4-CS-Lacs for degradation of direct red 80 (DR80); or in Tharmavaram et al., 2021, where laccase-cooper-CS-halloysite nanotubes were used for the degradation of chlorpyrifos (an organophosphate pesticide). All these examples show nonpolymeric OM's diversity and promising potential future in BNCs.

3. Toxicological aspects of clay–CS–organic bionanocomposites

Although several bionanocomposites have been developed in the last years, few toxicity studies were carried out for clays-CS-organic molecules. Hence, it is unknown how the mixture of three (and in some cases, four) nanomaterials can impact the environment and human health since they can interact with cells and may cause toxicity to different organisms (Augustine et al., 2020; Santiago et al., 2020; Ranjan et al., 2021). In this regard, cytotoxicity assays in cells, such as 3-(4,5-Dimethylthiazol-2-yl)-2,5-Diphenyltetrazolium Bromide (MTT) and neutral red (NR), have been the most explored by researchers to comprehend the toxicity of clay hybrid materials, followed by genotoxicity studies (Dusinska et al., 2013; Brandelli, 2018; Kumar et al., 2018). However, it is still a challenge to standardize protocols analysis to these materials since they have different properties and behaviors. Table 2 shows some cytotoxic assays for BNCs constituted by clays-CS-OMs.

By the way, this review does not bring ecotoxicological tests due to the lack of studies in this area. However, there are some ecotoxicological protocols used for nanomaterials that can guide the clay-CS-organics BNCs, such as Organization for Economic Cooperation and Development (OECD) 201, 207, 208, 222, 305 and 315 (Handy et al., 2012; Hjorth et al., 2017; Boros and Ostafe, 2020). Moreover, the lack of a validated government regulation reinforces the need for adequate ecotoxicological/toxicological tests for bionanocomposites (Kulkarni, 2021).

4. Challenges and future perspectives

Clay–CS–OMs BNCs have been investigated for different applications such as adsorption contaminants, drug delivery systems, wound healing, food packaging, among others. Particularly, natural biopolymers are becoming vital to the future of these nanohybrids and will be a trend in the next few years.

However, understanding the impacts of hybrid nanoclays is still a challenge for researchers, mainly due to the lack of ecotoxicity testing protocols and regulatory frameworks. Similar issues are described in nano-enabledmaterials for agriculture (Grillo et al., 2021). Therefore a

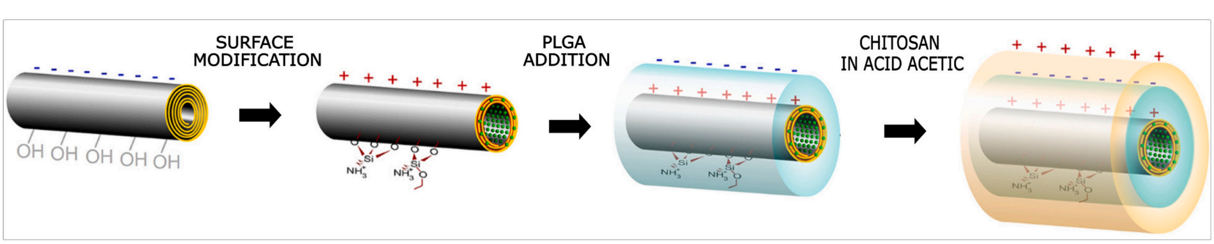

Fig. 7. Synthetic biopolymer poly(lactic-*co*-glycolic acid) with Hal nanotubes/CS for dressing applications. Adapted and reproduced with permission from Ref. (Mohebali and Abdouss, 2020). Copyright (2020) Elsevier.

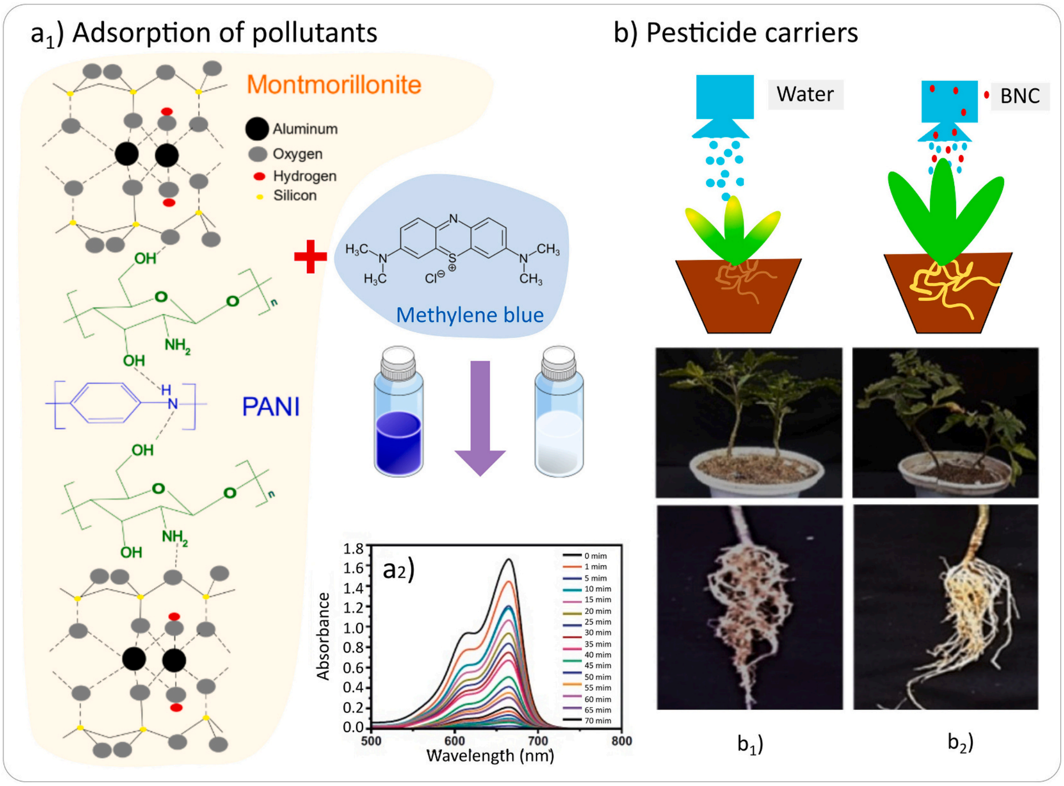

Fig. 8. PANI/CS/Mt Bionanocomposites: (a1) Structural interaction and (a2) UV–Vis spectra demonstrating the adsorption of methylene blue. Adapted and reproduced with permission from Ref. (Minisy et al., 2021). Copyright (2021) Elsevier. (b) Tomato growth after 40 days of treatment under greenhouse conditions: b_1 = water, and b_2 = PANI/CS/Mt/Van. Adapted and reproduced with permission from Ref. (Elsherbiny et al., 2022). Copyright (2022) Elsevier. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Toxicological studies of BNCs constituted by clays:chitosan-OMs.

Cell lines	Type of BNC	Outcomes	Ref.
Human fibroblast cells (A-431)	Mt/CS/PVA	No adverse cytotoxic was detected	Koosha et al., 2015
Fibroblast cells	Bentonite/CS/Gelatin	Samples had more than 90% of cell viability	Nozari et al., 2021
Human osteoblast cells (L929)	Mt/CS/PVA	3D scaffolds were not toxic to these cells	Zolghadri et al., 2019
Human osteoblast cells (L929)	Kaolin/CS/PVA	BNCs had higher cell viability than PVA/CS sample	Salehi et al., 2020
Hypotriploid human cells (MG-63)	Mt/Xylan-g-quaternized CS	Mt enhanced the cell viability	Ali et al., 2019
Peripheral blood mononuclear cells (PBMC)	Mt/CS/PVA/honey	All samples exhibited cell viability of more than 75%	Noori et al., 2018
Human epithelial colorectal adenocarcinoma cells (Caco-2)	3-aminopropyl functionalized magnesium phyllosilicate/glycol CS/Eudragit®S100	No cytotoxicity was found	Lee et al., 2020
Mouse fibroblast cells (NIH3T3)	Modified Hal nanotubes/CS/PVP/PVA	Hal enhanced cell viability	Kouser et al., 2022

sustainable way to produce nanomaterials may be using green synthesis methodologies and biopolymers/OM with intelligent properties (e.g., fabrication of a hybrid delivery system that can be removed from the environment in case of contamination (Forini et al., 2020)), as well as linking the development of materials with safe-by-design principles.

In summary, this review illustrates the interactions among clay–CS with various OMs, highlighting their synthesis method, characterizations, and toxicological aspects. It also demonstrates the significance of these nanohybrids as powerful tools in many areas, providing an excellent opportunity for further studies on the development of new clay bionanocomposites.

Author contributions

P.H.C.L. and A.T.A.: writing, review, and editing the manuscript. S. M.L.S., M.R.M., and F.A.A.: editing and review the manuscript. R.G.: conceptualization, writing, review, editing, and supervision the manuscript. All authors have equally contributed to revising and reading the manuscript and have approved the submitted version.

Declaration of Competing Interest

The authors declare no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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