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review article

Engineered Clay Minerals for Future Industries: Food Packaging and Environmental Remediation

미래산업에 적용가능한 점토 화합물: 식품포장 및 환경개선

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ABSTRACT : Clays, which are abundant in nature and eco-friendly, have been utilized throughout human history due to their characteristic physicochemical properties. Recently, a variety of clays such as montmorillonite, kaolinite, sepiolite and layered double hydroxide with or without chemical modification have been extensively studied for potential application in industries. Clays that possess a large specific surface area, high aspect ratio, nanometer sized layer thickness and controllable surface charge could be utilized as polymer fillers after appropriate chemical modifications. These modified clays can improve mechanical and gas barrier properties of polymer materials but also provide sustained antibacterial activity to polymer films. Furthermore, engineered clays can be utilized as scavengers for chemical or biological pollutants in water or soil, because they have desirable adsorption properties and chemical specificity. In this review, we are going to introduce recent researches on engineered clays for potential applications in future industries such as food packaging and environmental remediation.

Key words : Clay, Chemical modification, Industrial application, Food packaging, Environment remediation

요약 : 점토광물은 자연에서 쉽게 얻을 수 있고, 환경친화적이며 다양한 물리화학적 특성을 갖고 있어 인류 역사상 여러 분야에 활용되어 왔다. 최근에는 몬모릴로나이트, 카올리나이트, 세피올라이트, 금속이중층수산화물과 같은 점토 화합물에 화학적 개질을 도입하여 산업분야에 활용하고자 하는 연구가 활발히 진행되고 있다. 넓은 비표면적과 높은 측면비율, 나노수준의 입자 두께, 그리고 조절가능한 표면전하를 갖는 점토화합물에 화학적 개질을 적용하면, 고분자의 기계적 성질과 기체차단성을 개선하고, 고분자 필름에 지속적 항균성을 부여하는 충전제로 사용할 수 있다. 또한, 개질된 점토화합물은 높은 흡착능과 화학적 선택성을 지니므로, 수질이나 토양을 오염시키는 화학적, 생물학적 오염원을 효과적으로 제거하는 물질로도 활용 가능하다. 본 논평에서는 이러한 점토화합물들이 미래의 주요산업군인 식품포장재 및 환경개선 분야에 활용될 가능성에 대해 최근 연구 결과를 소개하고자 한다.

주요어 : 점토, 화학적 개질, 산업응용, 식품포장, 환경개선

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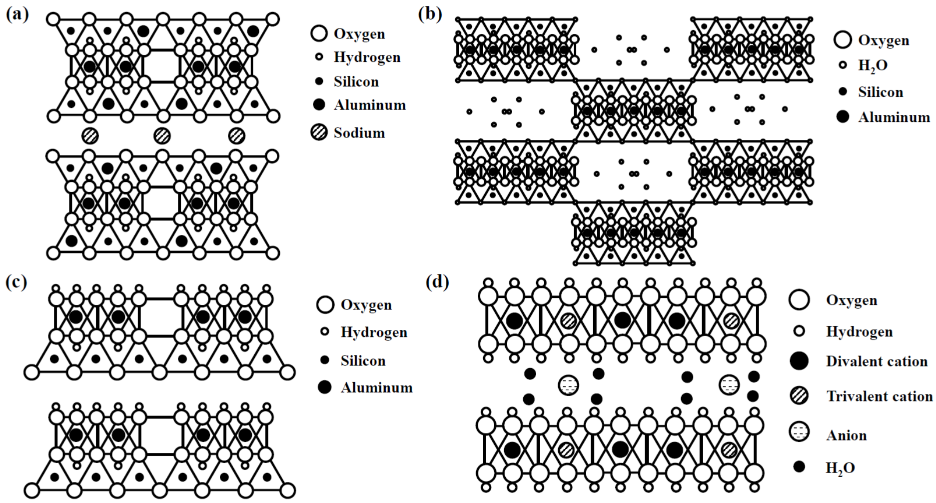


Fig. 1. Schemes of clays; (a) montmorillonite, (b) sepiolite, (c) kaolinite and (d) layered double hydroxide.

Introduction

Clays are generally defined as fine-grained, firm earthy materials (e.g., sand and soils) that have particle size less than 2 mm (Guggenheim and Martin, 1995). In human history, clays have been widely utilized as curative and protective agents as well as materials for pottery and bricks (Carretero, 2002; Veniale *et al*., 2004; Shepard, 1956; Hewamanna *et al*., 2001). Recently, the utility of clays has been expanded to include industrial applications such as catalytic support, adsorbent, cosmetics, etc (Yadav and Kirthivasan, 1995; Silva *et al*., 2013; Yoneyama *et al*., 1991; Park *et al*., 2013). In order to achieve optimum performance in industrial applications, well-defined structures and the incorporation of functional moieties are essential for clays. In this context, phyllosilicates and anionic clays - often referred to as layered double hydroxide have attracted attentions (Wang and O'Hare, 2012; Choy *et al*., 2007; Oh *et al*., 2009).

Montmorillonite ($(Na, Ca)_{0.33}(Al, Mg)_2(Si_4O_{10})$) and vermiculite ($(Mg, Fe^{2+}, Fe^{3+})_3[(Al, Si)_4O_{10}](OH)_2 \cdot 4H_2O$) are representative 2 : 1 (ratio of tetrahedral sheets versus octahedral sheets) phyllosilicates; AlO_6 or MgO_6 octahedral sheet is sandwiched between two SiO_4 tetrahedral sheets (Fig. 1a)(Park *et al*., 2016). They are interesting in industrial point of view due to their 2-dimensional stacking structure, high specific surface area, nanometer sized layer thickness, high aspect ratio, and cationic exchangeable layers (Villanueva *et al*., 2010; He *et al*., 2010). Sepiolite ($Si_{12}O_{30}Mg_8(OH)_4(H_2O)_4 \cdot 8H_2O$) is also a 2 : 1 phyllosilicate, but is different from the aforementioned clays in terms of its morphology; Sepiolite consists of discontinuous layers that are aligned parallel to the fiber direction to develop alternating cavities and has three linked pyronxene-like single chains (Fig. 1b)(Alcântara *et al*., 2016; Yang *et al*., 2016). Kaolinite ($Al_2Si_2O_5(OH)_4$), which is one of the most widely distributed clays, is a 1 : 1 (ratio of tetrahedral sheets versus octahedral sheets) phyllosilicate and has a 2-dimensional structure without a layer charge (Fig. 1c) (Ammala *et al*., 2007; Yang *et al*., 2016). Layered double hydroxide (LDH) has a brucite-like structure, and some of its divalent cations are replaced by trivalent ones to generate a positive layer charge (Fig. 1d). Different from phyllosilicates, which are usually obtained from nature, LDHs can be synthesized to have specific compositions. The general formula of LDH is $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$ (M(II) : divalent metal cation, M(III) : trivalent metal

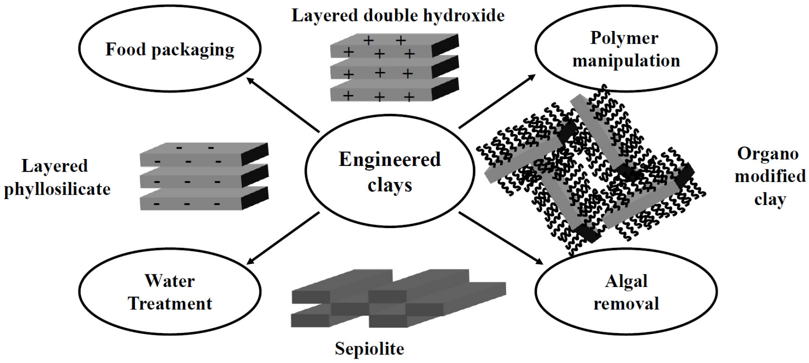


Fig. 2. Schematic diagrams of several clays and their potential applications in industrial fields.

cation, A^{n-} : anionic species; 0.16 < x < 0.75 in general; n and m are integers) - and its particle size can be controlled from tens of nanometers to a few micrometers (Vaccari, 1998).

The above mentioned clays are currently considered as attractive candidates for applications in future industries. As shown in Fig. 2, different types of clays and engineered clays have potential in a variety of industrial fields such as polymer manipulation, food packaging, water treatment, algal removal, etc. For example, the stiffness and strength of clays can be used to improve the mechanical properties of polymers when added as fillers. Additionally, their high aspect ratio hinders the penetration of gas molecules in food packaging films and their large specific surface area and modified organic moieties provide specific adsorption properties against toxic chemical pollutants and harmful microorganisms. The natural abundance, high accessibility and easy modification of clays also serve to reinforce their applicability in industry.

In this review, we discuss recent researches that has investigated clays for use in future industries such as food packaging and environmental remediation. According to International Mineralogical Association (IMA) symbols and the usual nomenclature, the clays discussed in this review are abbreviated as follows: montmorillonite (Mnt), kaolinite (Kln), sepiolite (Sep), vermiculite (Vrm), palygorskite (Plg), halloysite (Ht) and layered double hydroxide (LDH).

Clays in the Food Packaging Industry

Clay minerals are often utilized as fillers in food packaging polymer to enhance the physicochemical properties (e.g., the mechanical strength and gas permeation rate) and to provide smart functionality like sustained antibacterial activity (Villanueva *et al*., 2010; Tyan *et al*., 1999; Costa *et al*., 2012).

Supposing that clay nanosheets with high mechanical durability are well distributed throughout within a polymer matrix, the mechanical properties of polymer films could be improved. Since the invention of the clay-nylon6 composite for enhanced mechanical strength by Toyota Co. Ltd., Japan (Okada *et al*., 1988), clays have been used in the field of food packaging for a similar purpose. Villanueva *et al*. in Spain reported that the mechanical strength (elastic modulus) of polyethylene films was enhanced when the presence of organo-Mnt (Cloisite® 20A) and organo-Kln (NanoBioter® D14) were included as fillers (Villanueva *et al*., 2010). Clays were also tested in biodegradable packaging materials such as starch and non-starch polysaccharides. In spite of their eco-friendliness, their low mechanical strength and susceptibility to moisture absorption are major disadvantages of biodegradable polymers in practical applications. It has been reported that talc can enhance both the stiffness and Young's modulus of corn starch based films;

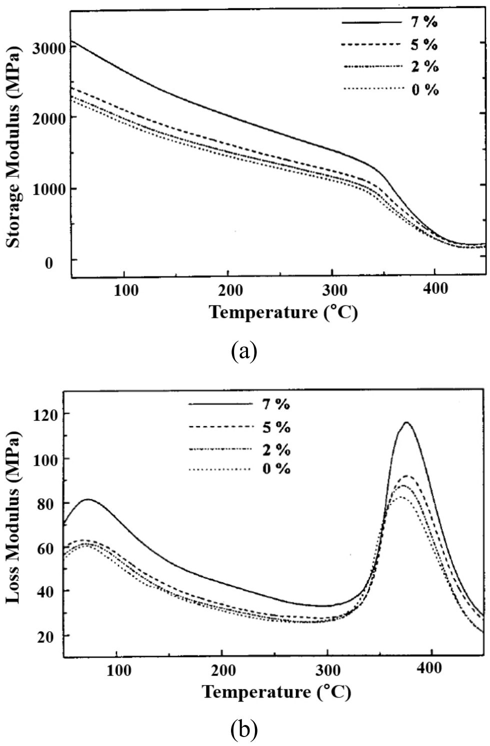
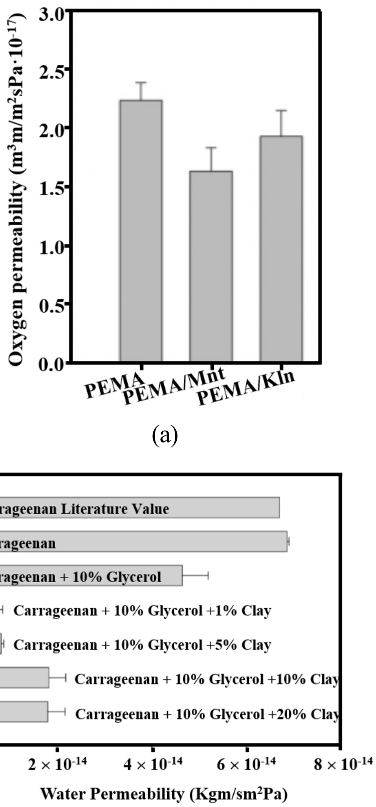


Fig. 3. Temperature-dependent (a) storage modulus and (b) loss modulus of pyromellitic dianhydride-4,4’-oxydianiline film with different organo-Mnt contents. Reproduced and modified with permission from (Tyan *et al*., 1999), H. L. Tyan *et al*., *Chem. Mater.* 11 1942 (1999). Copyright 1999, American Chemical Society.

incorporating 3% of talc raised the film stiffness by 15% and incorporating 5% of talc increased Young’s modulus by 81% (López *et al*., 2015). Alcântara *et al*. incorporated fibrous clays, such as Sep and Plg, into various polysaccharide based films including sodium alginate, xanthan gum, carboxylmethylcellulose, hydroxypropylmethylcellulose, and pectin. They reported that clay additions of up to 50% dramatically enhanced both the tensile strength and tensile modulus of polymer films (Alcântara *et al*., 2016). Tyan *et al*. studied the mechanical strength of composite films made of pyromellitic dianhydride-4,4’-oxydianiline which was incorporated with organically modified Mnt as nanocomposite form (Tyan *et al*., 1999). As shown in Fig. 3, the both storage and loss modulus of the films were enhanced by increasing the content of organo-Mnt (in the temperature range between 50 and 450℃); the difference in modulus was more distinct at lower temperatures (50-300℃) than it was at higher temperatures (300-450℃). It was striking that the storage modulus of nanocomposite film containing 7% organo-Mnt at 50℃ was 3080 MPa, which was 38% higher than the film without clay. Although many papers have demonstrated that adding of clay into a polymer enhances the mechanical strength of the resultant film, some research groups (including Tang *et al.* and Chen *et al.*) have also reported that there is an upper limit to the clay content to improve mechanical strength of polymer films (Tang and Alavi, 2012; Chen and Evans, 2005). At very high concentration, clay particles cannot be homogeneously distributed in the polymer matrix. Instead, clay forms agglomerates, which can negatively influence the overall mechanical properties. Thus, the clay content and blending methods should be carefully determined to obtain optimum mechanical properties of polymer films.

In food packaging for long term circulation, oxygen and water moieties inside the packaging should be maintained below an appropriate level, or they can oxidize and spoil the food. Clay particles, due to their 2-dimensional sheet like morphology, have been considered to provide tortuous pathways to gas moiety, resulting in playing a role of gas barrier. This strategy has been verified in the laboratory and has been partially commercialized. According to Villanueva *et al*., polyethylene-grafted-maleic anhydride (PEMA) film showed improved oxygen barrier properties in the presence of organically modified Mnt (Cloisite® 20A) or Kln (NanoBioter®D14) (Villanueva *et al*., 2010). PEMA films with 5% of organo-Mnt showed a 27.3% increase in their oxygen barrier properties as compared to unmodified PEMA. The oxygen permeability of neat PEMA was $2.23'10^{-17}$ m^3m/m^2sPa, while that of PEMA with Mnt was $1.62'10^{-17}$ m^3m/m^2sPa (Fig. 4a). It was interesting that the Kln did not show a dramatic



(a)

(b)

Fig. 4. (a) Oxygen permeability of polyethylene-grafted-maleic anhydride (PEMA) with and without organo-clay components of montmorillonite (Mnt) and kaolinite (Kln). The composite films are referred to as PEMA/MMT and PEMA/K for films containing MMT and K, respectively. Reproduced and modified with permission from (Villanueva *et al.*, 2010), M. P. Villanueva *et al.*, *J. Appl. Polym. Sci.* 115 1325 (2010). Copyright 2010, John Wiley and Sons. (b) Water permeability for films of carrageenan and their nanocomposites. Reproduced and modified with permission from (Sanchez-Garcia et al., 2010), M. D. Sanchez-Garcia *et al.*, *J. Agric. Food Chem.* 58 6884 (2010). Copyright 2010, American Chemical Society.

decrease in the oxygen permeability as compared to Mnt. The authors explained that the aspect ratio of Mnt in compounded resin was higher than Kln due to variations in the particle distribution homogeneity depending on the clay type. Mnt layers were more exfoliated in films than Kln, which was confirmed by X-ray diffraction and transmission electron microscopy, resulting in higher distribution homogeneity of Mnt. Thus, the tortuous pathway provided by Mnt was more effective than Kln in PEMA films. Similar oxygen barrier properties for clay particles in polyethylene films were reported by Busolo *et al.* (Busolo and Lagaron, 2012). They prepared nanocomposite films consisting of high density polyethylene (HDPE) and 10% iron modified Kln. The oxygen permeability of the neat HDPE film was determined to be 6.46 ± 0.45’10^{-17} m^3 × m/m^2 × s × Pa, while the nanocomposite film showed a 28% increase in the barrier properties, with an oxygen permeability value of 4.65 ± 0.33’10^{-17} m^3 × m/m^2 × s × Pa. In this study, both the tortuous pathways provided by Kln sheets and the oxygen trapping ability of iron were considered to be effective in blocking oxygen permeation. In addition to improving the oxygen barrier properties, including clay particles in a polymer matrix was reported to effectively block water vapor permeation. Sanchez-Garcia *et al*. verified the water barrier abilities of clay in polymer films (Sanchez-Garcia *et al*., 2010). They utilized carrageenan films for this purpose. Carrageenan alone, carrageenan with 10% glycerol as a dispersant, and nanocomposite films of carrageenan (with 10% glycerol) and mica (1, 5, 10 and 20%, respectively) were prepared using a solution-casting method. The water permeability of the carrageenan film was determined to be 6.86 ± 0.041’10^{-14} Kg × m/s × m^2 × Pa with 1% mica, this value was reduced to 0.65 ± 0.19’10^{-14} Kg × m/s × m^2 × Pa (Fig. 4b). The presence of 1% mica reduced the water permeability by ~86%. Unexpectedly, increasing the mica content to 5, 10 and 20% resulted in less effective barrier capabilities compared to using 1% mica. As discussed above, high content of clay might induce particle agglomeration in the polymer matrix, resulting in preferential pathways for gas rather than tortuous one.

Enhancing the freshness of food is an important mission in current smart packaging. In most cases, the main reason behind the decreasing freshness of food is contamination by microorganisms. The presence of bacteria, such as *bacillus subtilis* and *Escherichia coli (E. coli)*, in food processing often lead to the decomposition of food resulting in not only economic damage but also serious food poisoning for the consumers who intake those foods. Thus, finding methods to imbue food packaging films with sustained antibacterial properties is an important problem that must be solved. The widely accepted concept used to accomplish this goal is to incorporate antibacterial moieties into the polymer matrix of food packaging films. However, due to the low stability and uncontrolled release, simple introduction of antibacterial moieties into these films does not guarantee sustainable antibacterial properties. In attempts to overcome these drawbacks, clay minerals have been utilized in the food packaging field. Campos-Requena *et al*. carried out research on antibacterial low density polyethylene (LDPE) films by adding essential oil components (carvacrol and thymol) as antibacterial agents and dimethyldialkyl-Mnt as filler. They reported that dimethyldialkyl-Mnt retarded the release of essential oil by 15% compared with LDPE films without clay. The clay-essential oil-LDPE film had high antibacterial activity on *Botrytis cinerea* inoculated strawberries with an IC50 value (i.e., the concentration at which 50% of proliferation is inhibited) of 13.23 mg/g. They tested both LDPE film with and without the clay-essential oil composite for strawberry storage and found that the strawberries retained their freshness for up to 5 days (Campos-Requena *et al*., 2015). Similarly, Tornuk *et al*. reported that a linear low density polyethylene (LLDPE) film containing a composite of essential oil (carvacrol, eugenol or thymol) and clay (Mnt or Ht) showed antibacterial activity on *E. coli*. (Tornuk *et al*., 2015). Carvacrol-Mnt, carvacrol-Ht, eugenol-Mnt, eugenol-Ht, thymol-Mnt and thymol-Ht combinations in LLDPE films showed 17, 19, 20, 38%, and 33% bacterial inhibition, respectively, in terms of the log CUF/g unit.

Instead of natural essential oils, inorganic antibacterial agent like Ag^+ can be utilized in packaging film along with clays. Costa *et al*. added Ag^+ intercalated Mnt to alginate to coat carrots (Costa *et al*., 2012). In this research, alginate films showed sustained antibacterial effects for up to 50 days and the shelf life of food was extended from 3.6 to 70 days in the presence of Ag^+-Mnt. There has also been an example of using an organo-clay itself was utilized as an active antibacterial component. In this paper, dimethyldialkyl-Mnt was added to chitosan film. The organo-clay played a dual role as filler and antibacterial agent; as a result, the film showed enhanced mechanical strength and oxygen barrier properties as well as ~53% of antibacterial activity on *E. coli.* (Giannakas *et al*., 2016).

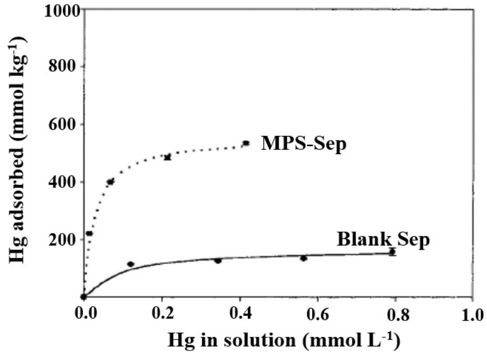
Clays in Environmental Remediation

Clays has been studied as environmental remediation agents because they can remove various source of pollution (Ismadji *et al*., 2015). Phyllosilicates, LDHs, and their organo-modified forms have shown excellent adsorption properties toward chemical pollutants of various types (e.g., cations, anions, hydrocarbons, etc.) as well as to biological pollutants like harmful algae.

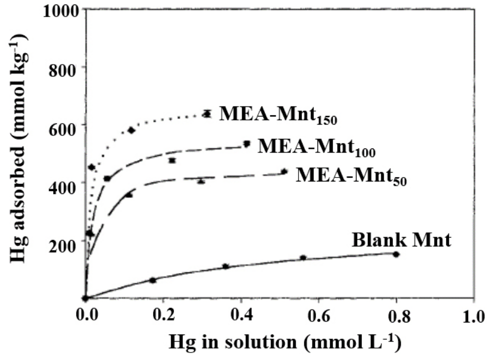
Krishna *et al*. prepared hexadecyltrimethylammonium (HDTMA) modified Kln to develop scavenger for chromate which is a toxic by-product in electroplating and tannery industries (Krishna *et al*., 2001). They reported that HDTMA-Kln adsorbed chromate at an efficiency of 30 mmol/kg at pH < 1; raw Kln did not show significant chromate removal. Although the adsorption amount was not very high, it was noteworthy that the organo modification enhanced the adsorption efficiency of clay. Froehner *et al*. utilized HDTMA modified Vrm to remove phenol from aqueous media. The phenol removal efficacy of HDTMA-Vrm was determined to be 4 times higher than neat Vrm (Froehner *et al*., 2009).

Another environmental pollution in aqueous media is eutrophication which is often caused by the discharge of phosphate containing industrial effluents. As is well-known, eutrophication negatively influences aquatic eco-systems and can lead to phytoplankton blooms, hypoxia, and the death of aquatic animals. Many scientists and engineers have attempted to develop scavengers to reduce the eutrophication of aqueous media; clay has been suggested as an alternative adsorbent. Khitous *et al.* suggested LDH ($Mg_2Al(OH)_6(NO_3)$) as a potential phosphate scavenger (Khitous *et al.*, 2016). According to their study, an aqueous suspension of LDH (2 g/L) removed almost 100% of phosphate from the diluted wastewater (100 mg/L phosphate). This high phosphate removal efficacy was attributed to the high anionic exchange capability (~2.87 meq/g) (Nyambo *et al.*, 2008) which is mediated by an anionic exchange reaction between $H_2PO_4^-$ or HPO_4^{2-} and interlayer nitrate. In order to investigate the effect of LDH's metal composition on phosphate removal, Jiang *et al.* synthesized six kinds of LDHs with different compositions such as CaAl-, CaFe-, MgAl-, MgFe-, MgCaAl- and MgCaFe-LDH along with interlayer nitrate (Jiang and Ashekuzaman, 2015). The phosphate removal efficacies in 10 mg/L phosphate solutions were 99.1, 99.2, 17.9, 14.3, 85.9% and 68.1% for CaAl-, CaFe-, MgAl-, MgFe-, MgCaAl- and MgCaFe-LDH (300 mg/L suspensions), respectively. They revealed that Ca-containing LDHs were excellent in phosphate removal, while the presence of magnesium content seemed to reduce the removal efficacy. Calcium in the LDH framework is thought to act as a phosphate scavenger by forming calcium phosphate precipitates, which are more thermodynamically stable than magnesium phosphates (Ashekuzzaman and Jiang, 2014).

Clays were also studied for the environmental remediation of soil. Soil pollution is caused by pesticides in agriculture or by heavy metal contamination. Endosulfan is a widely used pesticide that is highly persistent in soil and toxic to human. Park *et al.* studied the endosulfan removal efficacy of CaFe- and MgFe-LDH in soil (Park *et al.*, 2004). Both LDHs showed endosulfan decomposition ratios of ~50% in 2 ppm of endosulfan solution, suggesting the potential application of LDHs in solid remediation. Polubesova *et al.* developed a benzyldimethylhexadecylammounium (BDMHDA) micelle-Mnt complex to remove tetracyclin (TC) and sulfonamide (SA); these chemicals are often found in effluents of the pharmaceutical industry and remain undecomposed in soil for at least 40 days. They re-



(a)



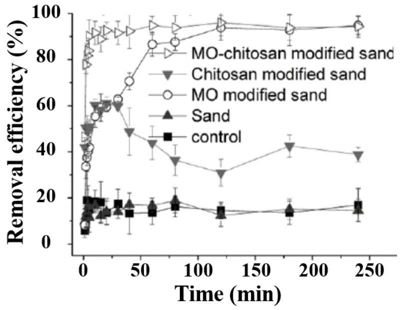
(b)

Fig. 5. Hg^{2+} adsorption isotherms (pH 3) on (a) functionalized Sep (MPS-Sep) and (b) functionalized Mnt (MEA-Mnt) Mnt_{50}, Mnt_{100} and Mnt_{150} indicate that the loading percentage of alkylammonium in Mnt was 50, 100% and 150% respectively, in terms of the cation exchange capacity of Mnt. Reproduced and modified with permission from (Celis *et al.*, 2000), R. Celis *et al.*, *Environ. Sci. Technol.* 34 4593 (2000). Copyright 2000, American Chemical Society.

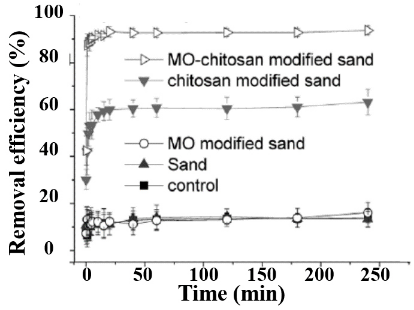
ported that 1% suspension of the micelle-Mnt complex removed almost 100% of TC and SA, which were present at concentrations of 5-50 mg/L (Polubesova *et al*., 2006). Phosphatic clay, which is the major by-product of phosphate strip mining, was used to adsorb heavy metals in soil by Singh *et al.* (Singh *et al*., 2006). They showed that Pb^{2+} (50 mg/L) was completely removed by 3.3 g/L of a phosphatic clay suspension above pH 4. Celis *et al*. reported that heavy metal removal was possible with 2-mercaptoethylammonium (MEA) intercalated Mnt and 3-[trimethoxy-silyl]-1-propanethiol (MPS) grafted Sep. As shown in Fig. 5, functionalized clays showed enhanced Hg^{2+} adsorption efficacies in the Hg^{2+} concentration range of 0-0.5 mmol/L. Specifically, MPS-Sep showed ~3.4 times higher Hg removal than Sep itself (Fig. 5a). Additionally, MEA-Mnt exhibited 2.7-4.1 times higher efficacy than neat Mnt. The Hg^{2+} removal efficacy of MEA-Mnt was determined to be dependent on the MEA content in Mnt (Fig. 5b). The improved Hg^{2+} scavenging ability was attributed to the chelate formation between Hg^{2+} and thiol groups in the functionalized clays (Celis *et al*., 2000).

Organo-clay can also be applied for the elimination of spilt oil. Carmody *et al*. prepared Mnt intercalated with cationic surfactant such as octadecyltrimethylammonium (ODTMA) or dodecyldimethylammonium (DDDMA) (Carmody *et al*., 2007). The long hydrocarbon chains in these surfactants are thought to provide the clay surface with an affinity for hydrocarbon affinity. Both organo-clays, ODTMA-Mnt and DDDMA-Mnt showed 1.2 and 5.2 g-hydrocarbon/g-clay, respectively, for diesel oil; these values are much higher than that of commercial zeolite (0.6 g-hydrocarbon/g-zeolite).

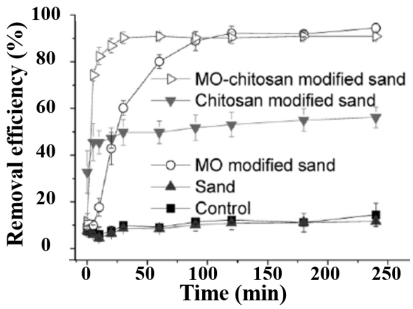
As mentioned above, eutrophication in lakes, rivers and seas can cause the sudden growth of harmful algae, so-called algal bloom, which threatens aquatic life, human health, the fishing industry, local tourism, and water quality in lakes, rivers, reservoirs and marine coastal environments (Sun *et al*., 2004; Anderson, 2009; Trainer and Baden, 1999). Currently, in many countries, yellow loess and clay are utilized to flocculate and remove algae (Pei *et al*., 2014). In order to increase the flocculation and removal efficacy of algae, various kinds of clays have been tested after appropriate modification. Li *et al.*



(a) (A.C. cells/sea water)



(b) (C.S. cells/sea water)



(c) (M.A. cells/fresh water)

Fig. 6. Flocculation kinetics of yellow sand modified with *Moringa oleifera* (MO) and chitosan for the *Amphidinium carterae* cells, *Chlorella sp.* cells and *Microcystis aeruginosa* cells. Reproduced and modified with permission from (Li et al., 2013), L. Li *et al*., *Environ. Sci. Technol.* 47 4555 (2013). Copyright 2013, American Chemical Society.

evaluated the algal removal efficacy of clays (yellow sand) by utilizing natural extracts from *Moringa oliedifera* (MO) and chitosan as flocculants (Li and Pan, 2013). Fig. 6 shows the flocculation kinetics of sand alone, MO-sand, chitosan-sand and MO-chitosan-sand composites against various types of algae such as *Amphidinium carterae* (A.C), *Chlorella sp.* (C.S) and *Microsystis aeruginosa* (M.A). The algal removal efficacy of MO-chitosan-sand was more than 70% within 20 mins for all varieties of algae, while the sand alone exhibited a negligible removal effect. Both chitosan and MO moieties in the sand were proven to be effective in increasing the algal removal efficacy. Furthermore, the combinatorial modification of sand with MO and chitosan synergistically improved the algal removal efficacy. Yu *et al*. studied the algal removal efficacy of phosphatic clay and cationic-polymer treated Kln (CPK) (Yu *et al*., 2004). They reported that phosphatic clay (0.6 g/L) removed 60% of *Aureococcus anophagefferens* (7'10^6 cells/mL) in deionized water and 70% of *Aureococcus anophagefferens* (7'10^6 cells/mL) in seawater. The removal efficacy of CPK (0.6 g/L) was only 40% for *Aureococcus anophagefferens* (7'10^6 cells/mL) in deionized water; however, this efficacy increased up to 100% in seawater.

Conclusion

Hitherto, we briefly summarized recent researches on clays for food packaging and environmental remediation. In food packaging field, clays have been utilized to enhance mechanical property of film, to reduce oxygen and water penetration through polymer matrix, and to provide sustained antibacterial activity to packaging films. For environmental remediation, organically modified clays have shown efficiency in removing metal or chemical pollutant and even harmful algae from soil or aqueous media. Based on those researches, we could expect that clays or engineered clays could open a new era in future industries including smart food packaging films, eco-friendly water or soil treatment system, and so on.

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