Review article

Adsorbents based on montmorillonite for contaminant removal from water: A review

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ABSTRACT

Clay minerals and their modified derivatives have composed a large family of adsorbents which can be used for the adsorption of most of the chemical contaminants from aqueous solution. Among this family of adsorbents, those based on montmorillonite (Mt), a typical 2:1 type clay mineral, have been most extensively studied. This article intends to give a general overview of the microstructure, adsorptive characteristics, and environmental applications of the Mt based adsorbents. A comprehensive survey of the numerous literatures shows that Mt based adsorbents have rather complicated structural and adsorptive characteristics. They may have porous or nonporous structure and contain various functional groups; their interlayer structure may be evidently affected by the incorporation of water molecules in aqueous medium. With the complicated structural characteristics, these adsorbents can be used for a wide variety of contaminants, including hydrophobic organic contaminants, cationic/anionic dyes, heavy metal cations, oxyanions, radioactive nuclides, etc. Accordingly, a wide variety of mechanisms are involved for the uptake of these contaminants, such as surface adsorption, partition, ion exchange, surface precipitation, and structural incorporation. Finally, the approaches for proper disposal/reutilization of the spent adsorbents after contaminant adsorption will be briefly discussed. This review on one hand can help the readers in choosing proper and developing novel clay mineral based adsorbents for target contaminants, and on the other hand can give a proper example to systematically show the various mechanisms for the uptake of contaminants on adsorbents.

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1. Introduction

Adsorption has long been considered as a highly efficient approach for pollution control. Various adsorbents have been developed for the removal of contaminants from wastewater, polluted air and soil. One may say that most (if not all) of the contaminants can find proper adsorbents for their environmental remediation. For example, the adsorbents used for heavy metal cations include resin (Ahmad et al., 2015), metal (oxyhydr)oxide (Garcia-Sanchez et al., 1999; Kumpiene et al., 2008), zeolite (Babel and Kurniawan, 2003), clay minerals (Bhattacharyya and Gupta, 2007, 2008), biosorbents (Bailey et al., 1999), etc. Among the various adsorbents, clay minerals and their derivatives have composed one large family which are in contrast to other adsorbents such as activated carbon, zeolite, and resin in terms of the microstructure, adsorptive characteristics, and environmental applications (Yuan, 2004; Churchman et al., 2006; Yuan et al., 2013; Zhu et al., 2015c). This large family of adsorbents, therefore, are drawing wide concerns nowadays.

Clay minerals are phyllosilicates in which the individual layers are composed of a tetrahedral (T) and an octahedral (O) sheet in either a 1:1 or 2:1 proportion (Brigatti et al., 2013). Due to isomorphous substitution (e.g., Al^{3+} for Si^{4+} in the T sheet and/or Al^{3+} for Mg^{2+} in the O sheet), the layers of many 2:1 type clay minerals (e.g., the smectite group and vermiculite group) carry a permanent negative charge, which is balanced by cationic counterions occupying interlayer space (Brigatti et al., 2013). The counterions can be exchanged by other organic/inorganic cations, making clay minerals efficient adsorbents for cationic contaminants (Arvanitoyannis et al., 1987; Bhattacharyya and Gupta, 2007, 2008; Yagub et al., 2014). On the other hand, when special cations (e.g., organic cations, hydroxymetal cations) were exchanged into the interlayers, the resulting modified clay minerals can be further used as adsorbents for a wide range of contaminants (Churchman et al., 2006; Theng et al., 2008; Yuan et al., 2013). Besides, some other approaches (e.g., acid washing, thermal treatment) have been applied to modify the surface structure and physicochemical properties of clay minerals, which then may enhance the capacity of clay minerals in uptaking specific contaminants as well (Bojemueller et al., 2001; Churchman et al., 2006; Heller-Kallai, 2013; Yuan et al., 2013).

Based on the numerous studies, the synthesis, characterization, and adsorptive characteristics of the adsorbents based on clay minerals have been reviewed in several publications (Xu et al., 1997; Akcay and Akcay, 2004; Ahmaruzzaman, 2008; Ruiz-Hitzky et al., 2010; Srinivasan, 2011; Lee and Tiwari, 2012). For example, Gupta and Bhattacharyya (2011, 2012, 2014) reviewed the adsorption of various heavy metal cations

on kaolinite and montmorillonite based adsorbents; Liu and Zhang (2007) summarized the adsorption of a variety of dyes on clay based adsorbents from aqueous solution; and de Paiva et al. (2008), Theng et al. (2008), Yuan et al. (2013), and Zhu et al. (2015c) reviewed the synthesis, microstructure and adsorptive characteristics of organoclays synthesized by intercalating 'cationic' clay minerals with organic cations. These reviews have shown that montmorillonite (Mt) plays particularly important roles in this family of adsorbents and have been most extensively studied.

Mt is a typical 2:1 type clay mineral with one O sheet being sandwiched between two T sheets (Fig. 1). Mt has an intermediate layer charge density in the range of 0.2 to 0.6 per half unit cell, and the negative charges mainly arise from the isomorphous substitution of Al^{3+} by Mg^{2+} in the O sheet (Brigatti et al., 2013). Therefore, Mt has good cation exchange capacity (CEC) and layer expansion capacity (Brigatti et al., 2013). In terms of being used as adsorbents, Mt and its derivatives have the following merits: (1) Mt is inexpensive, environmentally benign, and rich in reserve (Lagaly, 1995; Gates et al., 2009); (2) Mt itself can be directly used as high efficient adsorbent for various cationic contaminants (Lagaly, 1995; Bailey et al., 1999; Lagaly et al., 2013), and it also can be easily modified (e.g., intercalating with cationic modifiers, thermal treatment, acid washing) to synthesize various adsorbents (Ake et al., 2003; Yuan et al., 2013); (3) the adsorbents based on Mt can be used for a wide variety of contaminants, and the related adsorption mechanisms in general are transferable to their counterparts based on other clay minerals (Alkaram et al., 2009; Yuan et al., 2013); and (4) the adsorbents based on Mt often have better adsorption capacity than their counterparts (Jaynes and Boyd, 1991b; Zhu et al., 2008b; Yuan et al., 2013). As such, the adsorbents based on Mt have drawn most concerns. On the other hand, as most previous reviews focused on a particular type of adsorbents (e.g., organoclays) (Xu et al., 1997; Beall, 2003; Akcay and Akcay, 2004; de Paiva et al., 2008; Nguyen et al., 2013; Zhu et al., 2015c), or particular contaminants (e.g., heavy metal cations, dyes, phenolic compounds) (Bailey et al., 1999; Garcia-Sanchez et al., 1999; Ahmaruzzaman, 2008; Crini, 2006; Lin and Juang, 2009; Malamis and Katsou, 2013; Nafees and Waseem, 2014), a comprehensive overview of the microstructure of all the adsorbents based on Mt and their adsorptive characteristics toward various contaminants is still necessary, particularly the advantages and disadvantages of these adsorbents during environmental applications, which have not been well discussed in previous publications.

This article attempts to give a comprehensive review of the various adsorbents based on Mt At first, a brief introduction of the general mechanisms for uptaking contaminants on solid surface will be given. Then, the preparation and structural characteristics of the adsorbents based on Mt will be briefly introduced, and the adsorptive characteristics of these adsorbents then will discussed in detail, including the advantages and disadvantages of these adsorbents in environmental applications. Finally, the disposal methods of the spent adsorbents after environmental applications will be briefly summarized. This review may help the readers in choosing proper adsorbents for target contaminants and in developing novel adsorbents as well.

2. The mechanisms for uptaking contaminants on adsorbents

So far, the mechanisms for uptaking various contaminants on adsorbents have been well introduced in a large number of publications (Dabrowski, 2001; Toth, 2001; Chiou, 2002; Zagorodni, 2006; O'Day and Vlassopoulos, 2010; Brown and Calas, 2011). This section intends to give a brief introduction of these mechanisms, with the aim of
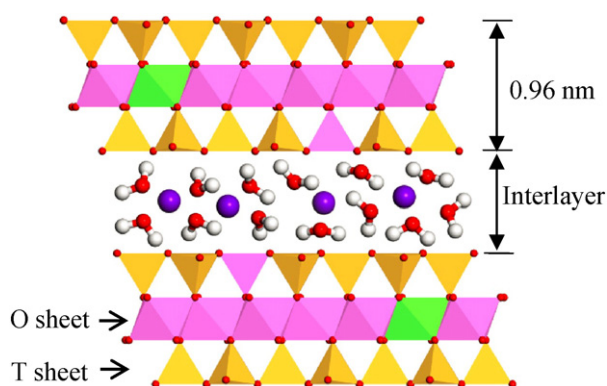

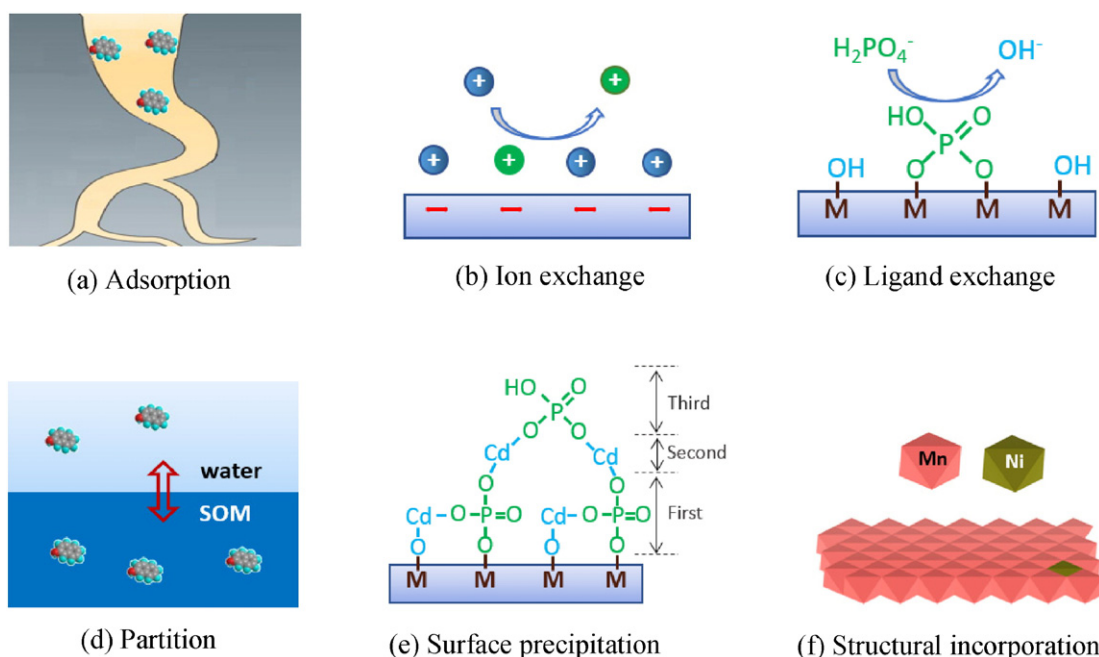**Fig. 1.** Structure of montmorillonite.

Fig. 2. Schematic illustrations showing the main mechanisms for the uptake of contaminants on various adsorbents. (a) Adsorption of HOC on activated carbon; (b) the uptake of cationic contaminants on the negatively-charged sorbents through ion-exchange; (c) the uptake of phosphate on metal (hydr)oxides surface through a ligand exchange process (a typical chemisorption process); (d) the uptake of HOC to SOM through a partition process; (e) co-adsorption of phosphate and Cd^{2+} on metal (hydr)oxides through a surface precipitation process (or multilayer adsorption); and (f) the uptake of heavy metal cation (Ni^{2+}) on birnessite through a structural incorporation process.

helping the readers in understanding the adsorptive characteristics of the adsorbents based on Mt.

According to the terminology used in *Handbook of Clay Science* (Bergaya and Lagaly, 2013), the word 'adsorption' will be used for all the processes involved in uptaking/immobilizing contaminants on adsorbents. The related mechanisms for uptaking contaminants mainly include surface adsorption, partition, surface precipitation, and structural incorporation (Fig. 2) (Chiou, 2002; O'Day and Vlassopoulos, 2010; Yuan et al., 2013; Malamis and Katsou, 2013). 'Surface adsorption' refers to the concentrate of contaminants onto or near the surface or pores of an adsorbent, which includes physical adsorption (driven by London–van der Waals forces) and chemisorption (involving the formation of chemical bonds) (Chiou, 2002; Waychunas et al., 2002). Adsorption of hydrophobic organic contaminants (HOC) onto activated carbon is a typical physical adsorption process (Chiou, 2002; Bandosz, 2006); while adsorption of heavy metal cations and oxyanions on metal (hydr)oxides always involves chemisorption (O'Day and Vlassopoulos, 2010; Li et al., 2010). Besides, the 'ion-exchange' process, referring to the exchange of ionic contaminants with the pre-adsorbed ions on the adsorbents, has been regarded as one type of adsorption process as well in some publications (O'Day and Vlassopoulos, 2010). Electrostatic interaction is the dominant interaction force between the adsorbed ions and the adsorbent, and adsorption of heavy metal cations by Mt is primarily an ion-exchange controlled process (Bhattacharyya and Gupta, 2008). An analog adsorption process to 'ion-exchange' is the 'ligand-exchange', in which the contaminants exchange the ligands on the adsorbents during the adsorption process. However, a ligand can be an ion or a molecule binding to a metal ion on the adsorbent, and this adsorption process always involves a highly specific chemisorption (Zagorodni, 2006). The adsorption of oxyanions on metal (hydr)oxides has been regarded as a typical ligand-exchange process (Xie et al., 2014).

'Partition' refers to the distribution of contaminants between two phases (e.g., organic phase-bulk water, organic phase-air, bulk water-air), which means that the contaminants will penetrate into the entire network of an bulk phase, rather than concentrate onto the surface, of the adsorbents (Chiou et al., 1979, 1981; Chiou, 2002). A typical partition-dominated process is the uptake of HOC by soil organic

matters (SOM), and one can generally observe relatively linear isotherm, non-competitive uptaking of multi-contaminants, and only small exothermic heats (Chiou et al., 1979, 1981; Chiou, 2002; Yuan et al., 2013).

'Surface-precipitation' involves the formation of precipitates on the surface of the adsorbents, which generally needs relatively high concentrations of cations and anions (but still below the formation of precipitates in aqueous solution) (Scheidegger et al., 1996, 1997; Waychunas et al., 2002; Ler and Stanforth, 2003; Grafe et al., 2004). The adsorbents concentrate contaminants on their surface by adsorption/ion-exchange at first, which then is followed by the formation of precipitates because of the over-saturation of cations and anions on the surface (Scheidegger et al., 1997; Li and Stanforth, 2000; Ler and Stanforth, 2003; O'Day and Vlassopoulos, 2010). The formation of surface-precipitates, therefore, requires relatively high surface concentration of cations and anions. A typical adsorption process that involves the surface-precipitation is the co-adsorption of cations (e.g., Cd^{2+}, Zn^{2+}) and oxyanions (e.g., phosphate, arsenate) on the surface of metal (hydr)oxides (Liu et al., 2016; O'Day and Vlassopoulos, 2010).

'Structural incorporation' refers to the incorporating of ions into the solid phase of adsorbents (Nachtegaal et al., 2005; Schlegel and Manceau, 2007; Brown and Calas, 2011), e.g., sequestration of metal cations into the crystal structure of minerals by isomorphous substitution (O'Day and Vlassopoulos, 2010). This adsorption process always follows the surface adsorption process and generally has a low adsorption rate. As the contaminants are incorporated into the bulk phase of the adsorbents, they can be well sequestrated by this type of adsorption (Nachtegaal et al., 2005; O'Day and Vlassopoulos, 2010; Brown and Calas, 2011).

One should notice, however, the categorization of adsorption mechanisms may differ in different literatures. For example, 'ion-exchange' may not be considered as an 'adsorption' process (Chiou, 2002); 'surface-precipitation' may be regarded as one form of 'structural incorporation' (O'Day and Vlassopoulos, 2010). Moreover, in many cases the uptake of contaminants on adsorbents is indeed operated by more than one type of mechanisms. For example, the uptake of heavy metal cations on metal (hydr)oxides always simultaneously involves surface

Table 1
Some Mt based adsorbents and the related adsorption properties.

Sorbents[a]	Synthesis method	Contaminants	adsorption mechanism(s)	Ref
Mt	–	Heavy metal cations, radioactive nuclides, cationic dyes	Cation exchange, specific adsorption, surface precipitates	Aytas et al. (2009), Gupta and Bhattacharyya (2012), Leodopoulos et al. (2015)
AMt	Acid washing	Heavy metal cations, cationic dyes, radioactive nuclides; anionic dyes	Cation exchange, specific adsorption; anion exchange	Banat et al. (2007), Eren and Afsin (2009), Toor et al. (2015)
TMt	Thermal treatment	Heavy metal cations, radioactive nuclides	Cation exchange	Banat et al. (2007), Aytas et al. (2009)
Type I OMt (TMA-Mt)	Loading small organic cations	HOC	Adsorption	Jaynes and Boyd (1990, 1991a)
Type II OMt (HDTMA-Mt)	Loading large cationic surfactants	HOC; anionic dyes, oxyanions	Partition, adsorption; anion exchange	Boyd et al. (1988a,b), Zhu et al. (2011), Khenifi et al. (2007), Xi et al. (2010)
Type III OMt (polymer-Mt)	Loading cationic polymers	Heavy metal cations; anionic dyes, oxyanions; HOC	Specific adsorption; anion exchange; partition, surface adsorption	Boyd et al. (1988b), Zhu et al. (2011), Khenifi et al. (2007), Xi et al. (2010), Churchman (2002)
IMt (hydroxyiron-Mt)	Loading hydroxymetals	Heavy metal cations; oxyanions, F$^-$; oxyanions + heavy metal cations	Cation exchange, specific adsorption, surface precipitation; LIGAND-exchange, anion exchange, surface precipitation; specific adsorption, surface precipitation	Lothenbach et al. (1997, 1998), Matthes et al. (1999), Wu et al. (2009), Kasama et al. (2004), Peak et al. (2006), Saha and Inoue (1998), Borgnino et al. (2010), Zhu et al. (2014c), Ma et al. (2015)
IMt (NZVI-Mt)	Loading NZVI	Heavy metal cations, oxyanions	Adsorption, reduction	Shi et al. (2011, 2013), Wu et al. (2015)
IOMt (hydroxyiron-HDTMA-Mt)	Loading organic and inorganic modifiers	HOC; oxyanions; HOC + oxyanions	Partition, adsorption; ligand exchange, anion exchange; combination of above four mechanisms	Wu et al. (2001), Li et al. (2009), Ren et al. (2014), Zhang et al. (2015), Zhu and Zhu (2007), Zhu et al. (2009c)

[a] The sample in the brackets is the representative of the corresponding Mt based sorbents.

adsorption, surface precipitation, and structural incorporation (O'Day and Vlassopoulos, 2010; Brown and Calas, 2011; Elzinga and Kretzschmar, 2013). As both the 'surface precipitation' and 'structural incorporation' processes should start from the 'adsorption' and/or 'ion-exchange' process, completely differentiate these processes may be difficult under some circumstances (Ler and Stanforth, 2003).

3. The various adsorbents based on Mt

Both original Mt and their modified derivatives can be used as adsorbents (Table 1). (1) Mt has been generally used as adsorbents for cationic contaminants, including heavy metal cations, cationic dyes (Ai et al., 2011; Abollino et al., 2003; Li et al., 2011). (2) Thermal treatment and acid washing of Mt may change its surface properties (e.g., enhancing its specific surface area (SSA)), and thus enhance the adsorption capacity toward various contaminants as well (Bhattacharyya and Gupta, 2007, 2008; Yuan et al., 2013). (3) Various organic modifiers can be loaded on Mt to synthesize organo-Mt complexes (OMt), which have been used as adsorbents for a variety of organic and inorganic contaminants, particularly for HOC (Cowan and White, 1962; Ake et al., 2003; Al-Asheh et al., 2003; Yuan et al., 2013). (4) Inorganic modifiers have been loaded on Mt, and the resulting composites (IMt) have high affinity toward both heavy metal cations and oxyanions (Comets and Kevan, 1993; Cooper et al., 2002; Thakre et al., 2010). (5) To synthesize multifunctional adsorbents, both organic and inorganic modifiers have been used to intercalate Mt. The resulting inorgano–organo-Mt (IOMt) then can simultaneously uptake both organic and inorganic contaminants from water (Zhu and Zhu, 2007; Zhu et al., 2009c; Lee and Tiwari, 2012).

Besides the above mentioned adsorbents, some less studied adsorbents based on Mt can be found in the literatures as well, e.g., adsorbents based on mechanical treatment (grinding, sonication, etc.) of Mt (Maqueda et al., 2013). However, these adsorbents received less attention because of their relatively low efficiency and/or high costs, which therefore will not be specifically introduced in this article. Although Mt based adsorbents have been used for the uptake of contaminants from various mediums, e.g., bulk water, air, organic solvent (Borisover et al., 2008; Ruan et al., 2008; Jarraya et al., 2010), the adsorption from aqueous environment has been most studied, and thus this review will only focus on those studies related to aqueous adsorption.

4. Uptake of contaminants by original Mt

Original Mt has been directly used for the uptake of various cationic contaminants, particularly heavy metal cations and cationic dyes (Ai et al., 2011; Abollino et al., 2003; Grini, 2006; Deng et al., 2010). The cation exchange process has been proposed as the primary mechanism for the uptake of cationic contaminants on Mt (Li et al., 2011; Wang et al., 2011), while other mechanisms have been proposed as well. For example, the terminal –OH groups and the acidic sites (both Brönsted and Lewis type) of Mt have specific interaction with heavy metal cations; at relatively high solution pH heavy metal cations may form surface precipitates (Elzinga and Sparks, 1999; Gupta and Bhattacharyya, 2011, 2012). For the adsorption of organic cations, the hydrophobic moieties of pre-adsorbed organic cations on Mt can have hydrophobic interaction with the counter part of organic cations in bulk water, which can further contribute to the uptake of organic cations from water (Wei et al., 2009; Leodopoulos et al., 2015). As such, the adsorption capacity of many organic cations can be larger than the CEC of Mt (Wei et al., 2009).

To date, the adsorption behaviors of a variety of heavy metal cations on Mt have been studied (Abd-Elfattah and Wada, 1981; Auboiroux et al., 1996, 1998; Bailey et al., 1999; Babel and Kurniawan, 2003; Glatstein and Francisca, 2015; Jackson, 1998;

Kumpiene et al., 2008; Aytas et al., 2009). The adsorption capacity of heavy metal cations generally cannot excess its CEC, or in the order of several to several tens of mg/g (Gupta and Bhattacharyya, 2012). According to Lagaly (1995), the adsorption affinity of heavy metal cations follows the order: $Cu^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+} \sim Mn^{2+}$. This order in general is in consistent with the hydrolysis constants of the metal cations. However, Chen et al. (2015) gave the following sequences: $Pb^{2+-} > Cd^{2+} > Zn^{2+} > Cu^{2+}$. Swift and McLaren (1991) suggested that the factors affecting the selective adsorption of heavy metal cations on Mt are diverse and should not be reduced to a universally applicable rule. Bhattacharyya and Gupta (2008) summarized the literature and came to a similar conclusion: the adsorption capacities of heavy metal cations on Mt varied, depending on the Mt from different sources.

Mt has also been shown to be efficient adsorbents for radionuclides. The adsorptive characteristics of Mt toward various radionuclides, including Cs, Sr, Eu, Th, U, Co, Pu, etc., have been investigated (Dent et al., 1992; Olguin et al., 1997; Ritherdona et al., 2003; Pusch, 2006; Missana et al., 2008). Similar to heavy metal cations, radioactive cations are primarily adsorbed on Mt by a cation exchange process as well, and the adsorption capacity is generally less than the CEC of Mt (Aytas et al., 2009). With the relatively high adsorption capacity and expandable interlayer spaces, Mt has been widely used as engineered barrier system in radioactive waste disposal sites (Boggs et al., 2015).

The uptake of various cationic dyes on Mt has also been extensively studied, including crystal violet, methylene blue, Congo red, malachite green, rhodamine B, etc. (Gürses et al., 2006; Almeida et al., 2009; Nogueira et al., 2009; Kyzas et al., 2013; Leodopoulos et al., 2015). Several reviews summarized the adsorption capacities of a variety of cationic dyes on Mt, which are generally in the range of several tens to several hundreds mg/g (Crini, 2006; Gupta and Suhas, 2009; Leodopoulos et al., 2015). Gupta and Suhas (2009) compared the adsorption capacity of cationic dyes on various low-cost adsorbent, and showed that Mt has similar or even better adsorption capacity in comparison with activated carbon, but much better adsorption capacity than most other adsorbents.

The strong electrostatic interaction between Mt and dye cations, in combination with the relatively hydrophobic properties of dye cations and the intermolecular interactions among dye cations, can always result in rather high adsorption efficiency, particularly when the adsorbed amount of cationic dye is below the CEC of Mt (Rytwo et al., 2000, 2007; Wei et al., 2009; Zhu and Zhu, 2011; Zhu et al., 2014a). Wei et al. (2009) showed that the removal efficiency of crystal violet on Mt can be over 99% when the adsorbed amount of crystal violet was below the CEC of Mt, and the maximum adsorbed amount reached 1.87 times of the CEC of Mt Due to the strong interaction among dye molecules, they can aggregate on Mt and form dye aggregates, leading to unique spectroscopic and photochemical properties (Leodopoulos et al., 2015; Lagaly et al., 2013).

The advantages for applying Mt in the uptake of cationic contaminants are obvious, e.g., low-cost, high efficient, and environmentally benign (Gupta and Suhas, 2009; Gupta and Bhattacharyya, 2012; Yuan et al., 2013). In addition, with expandable interlayer spaces, Mt is suitable for the uptake of large organic cations, and its adsorption capacity toward many cationic dyes can be even larger then commercial activated carbons (Wei et al., 2009). One should notice that the price of Mt is almost one order lower than that of activated carbon (Babel and Kurniawan, 2003).

Because of its high adsorption capacity toward cationic contaminants and swelling ability, Mt can retain contaminants and create a hydraulic seal, and thus has been used as a component of base liners in municipal solid-waste landfills as well as in regulated industrial storage and mining waste-disposal facilities (Bouazza, 2002; Montes-H et al., 2005; Pusch, 2006; Missana et al., 2008; Gates et al., 2009). Recently, the application of Mt as reactive barriers for various containment systems (e.g., nuclear waste, industrial spills and leaks, tailings dams and leachate ponds) has been well reviewed by Gates et al. (2009).

5. Uptake of contaminants by acid-washed and thermal-treated Mt

5.1. Acid-washed Mt

Acid washing of Mt, generally using HCl or H_2SO_4, can eliminate mineral impurities and dissolve Al from the O sheet, which then will SSA of the resulting Mt (AMt) and enhance its adsorption capacity toward many contaminants (Komadel, 2003; Jozefaciuk and Matyka-Sarzynska, 2006; Teng and Lin, 2006; Bhattacharyya and Gupta, 2007, 2008; Banat et al., 2007; Komadel and Madejova, 2013; Toor et al., 2015). For example, Bhattacharyya and Gupta (2007) found that the AMt generally have better adsorption capacity toward heavy metal cations (e.g., Cd^{2+}, Pb^{2+}) than Mt, although the enhancement was not very significant.

In addition to large SSA, an excess of protons can be adsorbed on AMt during the acid activation process, changing its surface charge from negative to positive (Espantaleón et al., 2003). As such, the adsorption capacity toward anionic contaminants (e.g., anionic dyes) can be evidently enhanced (Özcan and Özcan, 2004; Kyzioł-Komosińska et al., 2014; Toor et al., 2015). Özcan and Özcan (2004) found that the adsorption capacity of acid red 57 and acid blue 294 on AMt reached 416.3 and 119.1 mg/g, respectively, according to the Langmuir equation. They attributed this high adsorption capacity to the positive charge on AMt surface.

Several other studies, however, showed that the adsorption capacity of some cationic contaminants on AMt can be smaller than on that on Mt. Eren and Afsin (2009) found that AMt had a weaker adsorption capacity toward crystal violet in comparison with Mt, although the former had a faster adsorption rate. Hajjaji and El Arfaoui (2009) also reported that acid treatment of Mt would lead to decrease in the adsorption of cationic dye methylene blue and heavy metal cations (Zn^{2+}). They ascribed the reduced adsorption to partial collapse of the layered structure of Mt and the formation of amorphous silica after acid treatment.

5.2. Thermal-treated Mt

Thermal treatment of Mt can lead to the dehydration and dehydroxylation, and even the movements of octahedral cations within the octahedral sheet (Emmerich, 2000; Heller-Kallai, 2013). In addition, thermal treatment may also change the textural properties and influence the dispersibility of Mt in water (Chorom and Rengasamy, 1996; Aytas et al., 2009; Heller-Kallai, 2013). These changes were suggested to be able to enhance the adsorption capacity of the resulting sample (TMt) toward cationic contaminants and HOC (Al-Asheh et al., 2003; Banat et al., 2007; Aytas et al., 2009; El Mouzdahir et al., 2010; Maqueda et al., 2013). Aytas et al. (2009) compared the adsorption capacity of UO_2^{2+} on TMt within the temperature range of 100–500 °C. They found the sample heated at 400 °C showed the best adsorption capacity, as higher temperature (500 °C) would break the crystal structure and decrease the adsorption capacity. Maqueda et al. (2013) suggested that Al cations liberated by the thermal treatment were bound to the external surfaces and edges of TMt, which could increase the uptake of diuron.

The combination of acid-treatment and thermal treatment (acid-wash) has been applied to enhance the SSA of Mt, and then enhance its adsorption capacity toward contaminants (El Mouzdahir et al., 2010; Toor and Jin, 2012; Toor et al., 2015). Toor et al. (2015) found that the sample obtained by the combination of acid- and thermal-treatment of Mt has larger SSA (70% increase) and pore size than those obtained by single method treatment, and accordingly it had better adsorption capacity toward Congo-red (25% increase).

Clearly, the microstructure of AMt strongly depends on the factors such as acid concentration, treatment time (Komadel, 2003; Komadel and Madejova, 2013); similarly, the heating temperature and time will affect the microstructure of TMt as well (Komadel, 2003; Aytas et al., 2009; Heller-Kallai, 2013). Therefore, one should carefully choose
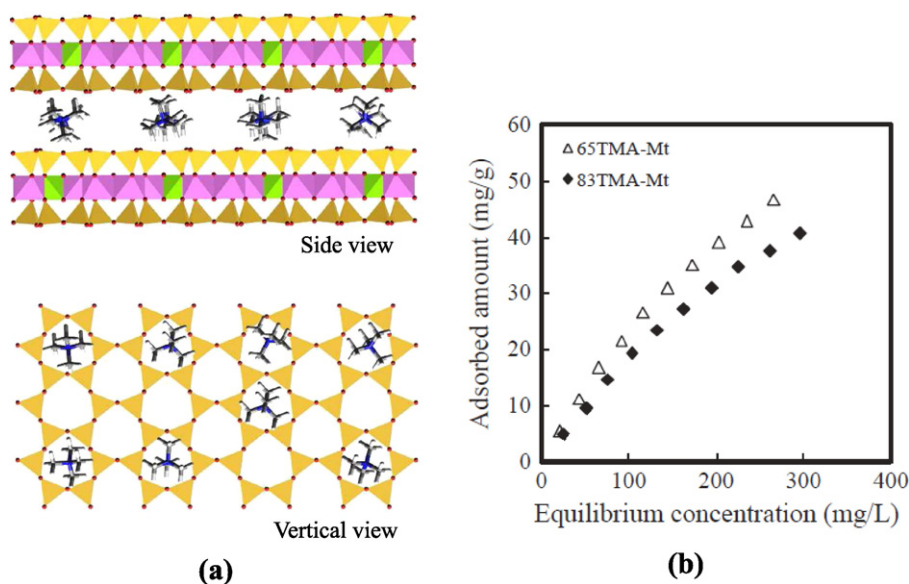
Fig. 3. The structure and adsorptive characteristics of type I OMt. (a) The interlayer structure of TMA-Mt; (b) The nonlinear adsorption isotherms of nitrobenzene on TMA-Mt with different layer charges (the number before TMA denotes the CEC of Mt in cmol/kg).
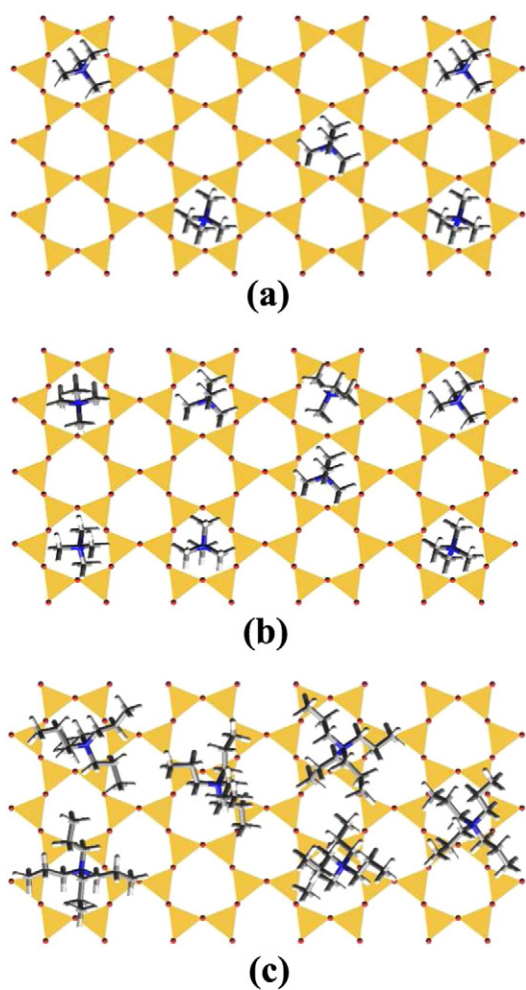Image was reproduced from Zhu et al. (2014c), with the permission of Elsevier.

Fig. 4. Effect of layer charge and molecular size on the available siloxane surfaces on type I OMt. (a) TMA-Mt with low layer charge; (b) TMA-Mt with high layer charge; and (c) tetrapropylammonium-Mt.

these treatment conditions to optimize the adsorption capacity of the resulting adsorbents. In general, the adsorptive characteristics and applications of the two types of adsorbents are similar to those of Mt, with the major difference being that AMt has much better adsorption capacity toward anionic contaminants.

6. Uptake of contaminants by organo-Mt

6.1. Small organic cations modified Mt

Organic modifiers can alter the surface structure and environment of clay minerals, which then can enhance the affinity of the resulting materials (i.e., organoclays) toward organic contaminants, particularly HOC (Cowan and White, 1962; Jaynes and Boyd, 1990, 1991a,; Yariv and Cross, 2002; Lee et al., 2004; Groisman et al., 2004a,b). Generally, OMt can be divided into three types according to their synthesizing methods and molecular structure of the modifiers. Type I are those synthesized with small rigid organic cations (e.g., tetramethylammonium (TMA), crystal violet, methylene blue) (Barrer and McLeod, 1955; Borisover et al., 2001; Rytwo et al., 2000, 2007; Fuller et al., 2007). Type II are those synthesized with organic cations containing at least one long alkyl chains (i.e., cationic surfactants), such as hexadecyltrimethylammonium (HDTMA) (Bartelt-Hunt et al., 2003; Alkaram et al., 2009; Zhu et al., 2007, 2008a). Other less typical OMt, which may be synthesized using special organic modifiers (e.g., nonionic/zwitterionic surfactants, cationic polymers, organosilanes, chelating reagents) (Groisman et al., 2004b; Yue et al., 2007a,b; Solener et al., 2008; Stathi et al., 2007; Guerra et al., 2009; He et al., 2014; Ma et al., 2016), or using more than one type of organic modifiers (e.g., surfactants + polymers, small organic cations + cationic surfactants) (Smith and Galan, 1995; Zhu and Chen, 2000; Wang et al., 2010; Zhu et al., 2010), can be categorized into type III.

For type I OMt, both experimental and molecular modeling studies showed that the small rigid organic cations (e.g., TMA) act as pillars, propping the silicate layers apart (Fig. 3). As such, type I OMt have porous structure, with a relatively SSA (Rutherford et al., 1997; Wang et al., 2004; Zhu et al., 2012b). For example, TMA-Mt typically has a SSA of 100–300 m^2/g, depending on the layer charge of Mt and loading level of TMA (Zhu et al., 2014c). Water saturation generally will not cause layer expansion of type I OMt, as long as the remaining un-
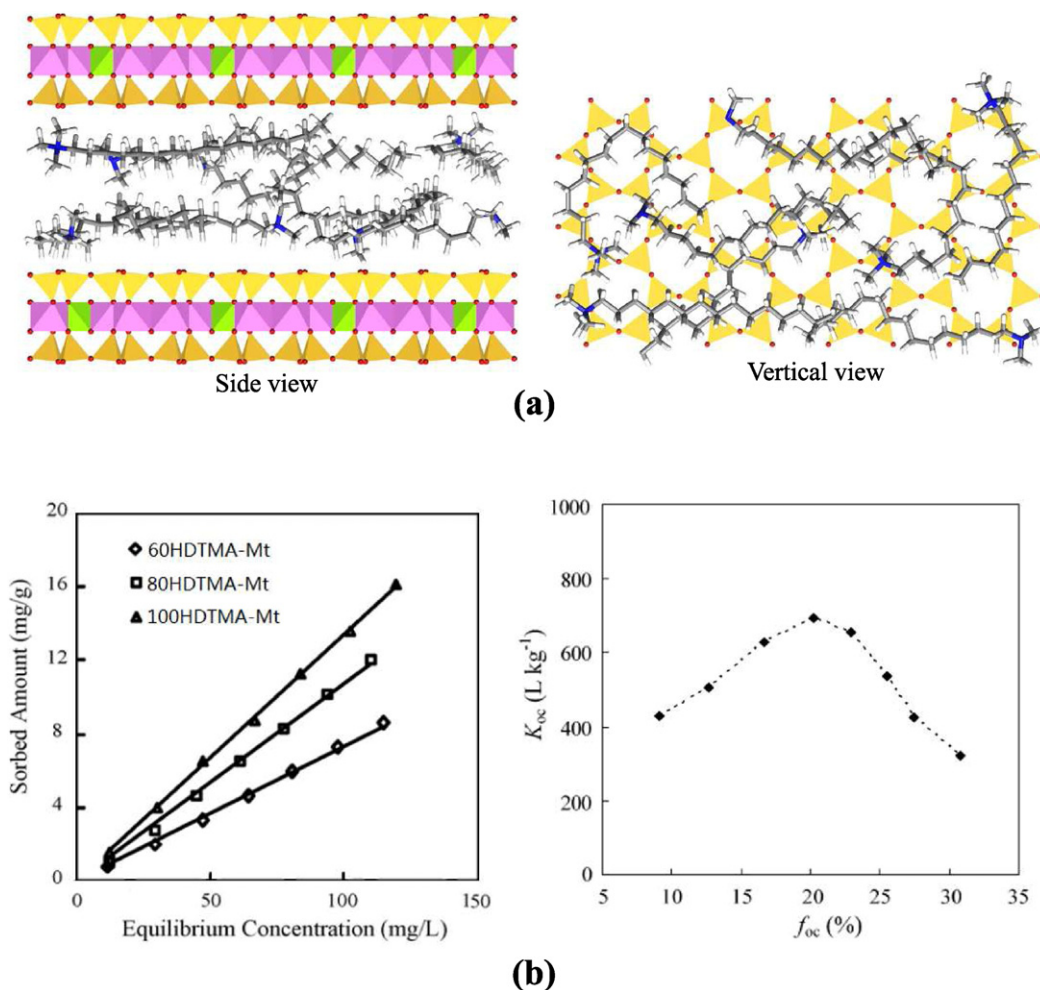
Fig. 5. The structure and adsorptive characteristics of type II OMt. (a) The interlayer structure of HDTMA-Mt; (b) the linear isotherms for the uptake of phenol on HDTMA-Mt (the number before HDTMA denotes its loading level in %CEC), and the correlation between sorption coefficient of phenol and the surfactant loading level (i.e., the organic carbon content of HDTMA-Mt). Images were reproduced from Wang et al. (2010) and Zhu et al. (2007), with the permission of Elsevier.

exchanged inorganic cations are not extensively hydrated (Ruan et al., 2008).

The adsorptive characteristics of type I OMt toward HOC are quite similar to those of traditional porous adsorbents such as activated carbon and porous resin, with surface adsorption being the main mechanism for the uptake of HOC. Accordingly, the adsorption isotherms therefore are always shown to be highly nonlinear over a relatively large concentration range (Jaynes and Boyd, 1990, 1991a; Roberts et al., 2006; Zhu et al., 2012b; Yuan et al., 2013). The adsorption sites can be the hydrophobic siloxane surface of Mt and the intercalated organic cations (Jaynes and Boyd, 1990, 1991a; Stevens et al., 1996; Sheng and Boyd, 1998). As the available (or exposed) siloxane surfaces are reversely related to the amounts of interlayer cations (including both inorganic and organic cations), Mt with lower layer charges generally have larger available siloxane surface, and thus better adsorption capacity (Fig. 4a) (Lee et al., 1990; Ruan et al., 2008; Huang and Zhu, 2011). On the other hand, as the intercalated organic cations also occupy some of the siloxane surface, increasing their molecular size therefore may lead to the decrease of available siloxane surfaces for the uptake of HOC (Fig. 4b) (Smith et al., 1990; Fuller et al., 2007; Zhu et al., 2012b).

The intercalated organic cations may have special interactions with organic contaminants, e.g., π–π interaction and cation–π interaction, which then can further enhance the adsorption capacity of type I OMt (Nir et al., 2000; Zhu et al., 2004; Qu et al., 2008; Kameda et al., 2012). Thanks to the π–π interaction, benzyltrimethylammonium-Mt always

has better adsorption capacity toward aromatic contaminants than TMA-Mt, although TMA has smaller molecular size (Smith et al., 1990). The hydrophobicity of organic cations can affect the adsorption capacity as well; the OMt synthesized using less hydrated organic cations (e.g., trimethylphosphonium) may be better adsorbents than those synthesized using more hydrated cations (e.g., TMA) (Kukkadapu and Boyd, 1995; Lawrence et al., 1998).

Compared with activated carbon, type I OMt in general have weaker adsorption capacity because of their relatively smaller SSA (Marsal et al., 2009). Several methods have been developed to increase the SSA and the adsorption capacity, e.g., reducing the layer charge of Mt (Zhu et al., 2014c; Ruan et al., 2008), using novel approaches to synthesize reduced-charge OMt (Zhu et al., 2014c). However, the obtained SSA is still less than 300 m^2/g in most cases, much smaller than that of activated carbon. As such, a large gap still exists in terms of enhancing the adsorption capacity of type I OMt.

6.2. Cationic surfactant modified Mt

With respect to type II OMt, their interlayer space is commonly being fully occupied by the intercalated cationic surfactants (Fig. 5), and thus they have a low porosity and a small SSA (in the order of several m^2/g) (Rutherford et al., 1997; Wang et al., 2004; Yildiz et al., 2005; Atia, 2008). However, water molecules may cause layer swelling and change the interlayer structure of type II OMt when they are dispersed in aqueous solution (Zhu et al., 2008b). Recent molecular modeling studies

provided detailed insight to the interlayer structure of type II OMt, which clearly showed the presence of both surfactant aggregates and water-dominated zone within the interlayers of HDTMA-Mt. In addition, a large portion of the siloxane surface of Mt was occupied by HDTMA (Zhu et al., 2011; Zhao and Burns, 2012, 2013; Zhou et al., 2014, 2015). With increasing loading level, cationic surfactants will occupy more of the interlayer spaces, forming larger surfactant aggregates and expelling water molecules out of the interlayer; the packing density of these surfactant aggregates will increase accordingly (Zhu et al., 2007, 2008a,b, 2011; Zhou et al., 2015).

Type II OMt shows quite different characteristics for the uptake of HOC in comparison with porous adsorbents, and partition has been regarded as the predominant uptaking mechanism (Boyd et al., 1988a, b; Roberts et al., 2006; Zhu et al., 2007, 2008a,b, 2011). The surfactant aggregates on type II OMt can form nano-sized organic phases, which are the main accommodation place for the uptake of HOC. As such, type II OMt generally has linear isotherms in the uptake of HOC over a relatively wide range of solute concentrations (Boyd et al., 1988a,b; Zhu et al., 2011).

As the interlayer structure of type II OMt can be evidently affected by various factors such as layer charge of Mt (Slade and Gates, 2004; Zhu et al., 2007), molecular structure and loading level of cationic surfactants (Chen et al., 2005; Xi et al., 2007; He et al., 2014; Xu et al., 2014), and interlayer hydration states (Yariv et al., 2011; Borisover et al., 2012;), and their behaviors in uptaking HOC can be affected by these factors as well (Shen, 2004; Chen et al., 2005). Zhu et al. (2007, 2012a) suggested that at relatively low loading level of surfactant (e.g., <0.6 times of the CEC of Mt), the organic phases (formed by surfactants) have too small size to effectively adsorb HOC; at high loading level (e.g., over 1.4 times of the CEC of Mt), the packing density of surfactants will rise to a high level, which then may cause steric hindrance effect for the uptake of HOC. Finally, the presence of charge-balance inorganic ions on type II OMt may decrease their hydrophobicity and thus their capacity in uptaking HOC as well (Bonczek et al., 2002; Xu and Zhu, 2009). As a result, the capacity of type II OMt in uptaking HOC generally increases with surfactant loading at first, and then decreases as the loading exceed a critical level (general in the range of 1.0–1.2 times of the CEC of Mt) (Bonczek et al., 2002; Chen et al., 2005; Zhu et al., 2007). Other studies also showed that increasing Mt layer charge and molecular size of cationic surfactants can enhance the capacity of type II OMt in uptaking HOC as well, as larger organic phases can be formed on them (Smith et al., 1990; Bartelt-Hunt et al., 2003; Shen, 2004; Zhu et al., 2007).

Indeed, the uptake of HOC on type II OMt should not be considered as a classical partition process, because the nano-sized organic phases on type II OMt behave quite differently from bulk organic phases (e.g., oil) in uptaking HOC. That is, their affinity for and accessibility to HOC can be significantly affected by the interlayer structure of type II OMt (Bonczek et al., 2002; Zhu et al., 2007, 2008b, 2012a; Zhou et al., 2015). Zhu et al. (2007, 2008b, 2010) suggested that adjusting the arrangement of interlayer surfactants (using a second intercalant) can be a feasible approach for enhancing their uptaking capacity.

Compared with those traditional adsorbents with porous structure (e.g., activated carbon), type II organoclays in general have weaker capacity in the uptake of HOC (Marsal et al., 2009). However, they have their own advantages in pollution control because of their special structural (e.g., expandable interlayer spaces) and adsorptive characteristics (partition-dominated process for uptaking HOC): (1) they are well suited to treating wastewater containing high concentrations of multiple HOC and clearing up oil spills, as the removal efficiency of contaminants maintains relatively constant in these cases (Alther, 1995; Adebajo et al., 2003; Carmody et al., 2007; Carvalho et al., 2012; Li et al., 2013); (2) they are efficient in the uptake of HOC of large molecular size and/or high hydrophobicity, as these HOC molecules can effectively enter the expanded interlayer spaces (Groisman et al., 2004a; Ramos Vianna et al., 2005; Upson and Burns, 2006; Polubesova et al., 2006); (3) they

are proper liners/barrier materials because of their expandable interlayer spaces, as expansion can increase liner density and hence retard the migration of contaminants to soil and groundwater (Brixie and Boyd, 1994; Smith and Jaffe, 1994; Gullick and Weber, 2001; Lo and Yang, 2001; Polubesova et al., 2002; Smith et al., 2003; Gates et al., 2004); and (4) one can directly utilize the cationic surfactants in wastewater to synthesize type II OMt, by which both the cationic surfactants and HOC can be simultaneously removed (Ma and Zhu, 2007; Khenifi et al., 2009; Zhu et al., 2014a).

In addition to HOC, type II OMt has been used for the uptake of various anionic contaminants as well, which include acidic herbicides and pesticides (El-Nahhal et al., 2001; Anirudhan and Ramachandran, 2006), anionic dyes (Baskaralingam et al., 2006; Khenifi et al., 2007; Jovic-Jovicic et al., 2010), oxyanions (Li, 1999; Atia, 2008; Xi et al., 2010), anionic radioactive nuclide (Bors, 1990; Bors et al., 2000), etc. In general, relatively high loading level of cationic surfactant (e.g., over 1.0 time of the CEC of Mt) is necessary, as in this case a portion of surfactant will be loaded on type II OMt as molecular form containing counterbalance anions, which serve as exchangeable anions in the uptake of anionic contaminants (Hsu et al., 2000; Baskaralingam et al., 2006; Yuan et al., 2013). While for the uptake of organic anions, the hydrophobic interactions between organic anions (e.g., anionic dyes) and surfactant may contribute to the adsorption as well (Zhu and Ma, 2008). One should notice that this kind of application may be limited, as increasing loading level of surfactants will undoubtedly rise the price of the adsorbents. Indeed, the price of type II OMt is mainly determined by the cost of the used cationic surfactants (e.g., Bartelt-Hunt et al., 2003). For example, for the most often studied HDTMA-Mt, the price of the surfactant can be more than thirty times higher than that of Mt in China (~30,000 CNY/t vs. ~800 CNY/t). In addition, desorption of cationic surfactants should also be considered as well, as the molecular form surfactants can be desorbed much more easily as compared with the cationic form.

Finally, type II OMt has been used for the removal of more than one type of contaminants (Andini et al., 2006; Jovic-Jovicic et al., 2010; Huang et al., 2012; Dentel et al., 1998; Oyanedel-Craver et al., 2007; Sheng et al., 1999). The co-adsorption of different types of organic contaminants (e.g., HOC, anionic dyes), or the co-adsorption of both organic and inorganic contaminants (e.g., heavy metal cations), were studied, and the co-adsorption process can be competitive (Andini et al., 2006) or non-competitive (Dentel et al., 1998; Sheng et al., 1999; Jovic-Jovicic et al., 2010). For example, Sheng et al. (1999) used a carboxylic group-bearing carboxydecyltriethylammonium cation to synthesize OMt, which showed non-competitive uptake of Pb^{2+} and chlorobenzene. For the OMt synthesized using the surfactant without special functional groups (e.g., HDTMA), the co-adsorption of HOC and heavy metal cations seemed to be competitive (Andini et al., 2006; Oyanedel-Craver et al., 2007), but the co-adsorption of HOC and anionic dyes was non-competitive (Dentel et al., 1998).

6.3. Other organo-Mt

As a wide variety of organic modifiers were used to synthesize type III OMt, their microstructure and adsorptive characteristics will be quite different accordingly. Similar to the other two types of OMt, the SSA of type III OMt should be reversely related to the molecular size and loading level of the organic modifiers; organic phases may be formed when large organic modifiers were used for the synthesis (Zhu and Chen, 2000; Guimaraes et al., 2009; Wang et al., 2010; Zhu et al., 2010). On the other hand, as some of the organic modifiers contain functional groups, the resulting OMt may have special interactions with contaminants (Cruz-Guzman et al., 2004, 2006; Malferrari et al., 2007; Guerra et al., 2009; Ma et al., 2016).

A wide variety of polymers have been used to synthesize type III OMt, which then have been applied for the uptake of HOC (Breen and
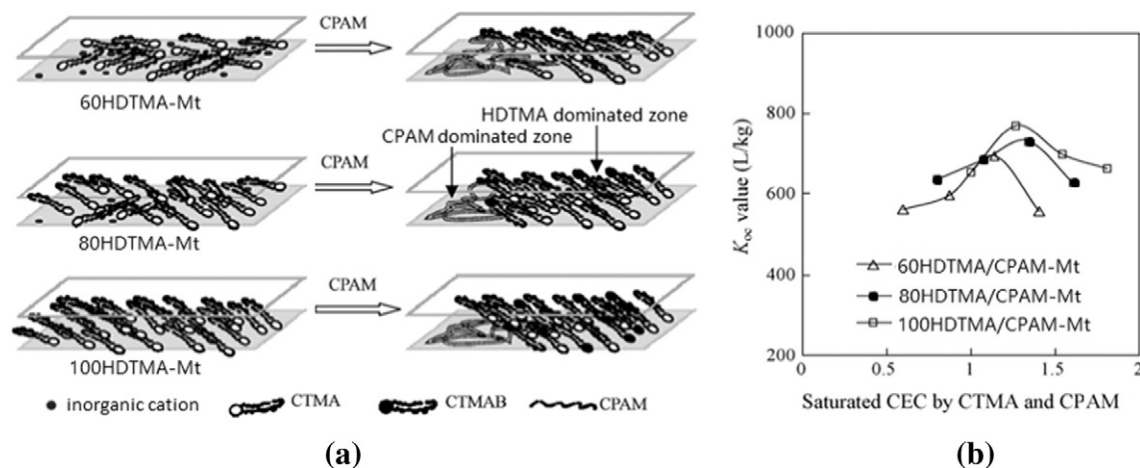
Fig. 6. The structure and adsorptive characteristics of HDTMA/CPAM-Mt. (a) Schematic drawing of the interlayer structure of HDTMA-Mt and HDTMA/CPAM-Mt with different HDTMA loading (the number before HDTMA denotes its loading level in %CEC); (b) the K_{oc} value of phenol on the three serials of HDTMA/CPAM-Mt (fixing HDTMA loading while increasing CPAM loading), as a function of saturated CEC by HDTMA and CPAM.
Images were reproduced from Wang et al. (2010), with the permission of Elsevier.

Watson, 1998; Churchman, 2002; Cao et al., 2009; Unuabonah and Taubert, 2014), anionic dyes (Churchman et al., 2006; Li et al., 2007; Yue et al., 2007a,b; Wang et al., 2008; Kang et al., 2009; Shen et al., 2009), and heavy metal cations (Anirudhan and Ramachandran, 2008; Anirudhan and Suchithra, 2010). Churchman (2002) synthesized four different type III OMt using polydiallyldimethylammonium, poly-amine, polystyrene, and polyacrylamide, respectively. The author found that polystyrene-Mt has the best capacity in the uptake of tol-uene from solution, and the uptaking process may be operated by various mechanisms (e.g., surface adsorption, partition), depending on the polymers used for synthesizing OMt. As cationic polymers contain rather high charge density, the resulting OMt generally con-tain positive patches even though the surface negative charge of Mt has not been sufficiently neutralized yet (Theng, 2012); these posi-tive patches therefore can provide adsorption sites for anionic con-taminants through electrostatic interaction (Churchman et al., 2006; Yue et al., 2007a,b). On the other hand, the specific groups on polymers (e.g., carboxylic group) can have particular interaction affinity toward heavy metal cations, and then OMt may effectively uptake heavy metal cation through both cation exchange and com-plexation reactions (Anirudhan and Suchithra, 2010).

Cationic surfactants have been used to intercalate Mt with other or-ganic modifiers (e.g., cationic polymer, cationic dyes) to synthesize type III OMt. As the arrangement of cationic surfactants within the inter-layers of Mt can be adjusted by the co-intercalated organic cations, the resulting type III OMt then may have better capacity in uptaking HOC than the corresponding type II OMt, with partition generally being the predominant mechanism (Wang et al., 2010; Zhu et al., 2010, 2014a). Zhu et al. (2010) found that OMt synthesized using both polyacrylamide and HDTMA has much better capacity in uptaking HOC than that syn-thesized using HDTMA alone, and the distribution coefficient for nitro-benzene increased more than 30% (Fig. 6).

To enhance the adsorption capacity of heavy metal cations, organic modifiers with particular functional groups (e.g., $-SH$, $-NH_2$, $-COOH$, $-CS_2$) that can specifically interact with heavy metal cations have been used to synthesize type III OMt (Mercier and Detellier, 1995; Manohar et al., 2002; Cruz-Guzman et al., 2006; Malferrari et al., 2007; Stathi et al., 2007; Guimaraes et al., 2009). Stathi et al. (2007) synthesized four OMt using four organic modifiers containing different chelating functionalities ($-NH_2$, $-COOH$, $-SH$, or $-CS_2$), and studied their adsorption capacity toward Pb^{2+}, Cd^{2+} and Zn^{2+}. The results showed that the resulting OMt had much better capacity than original Mt in the uptake of heavy metal cations. In addition, these OMt also showed adsorption selectivity because of the special

chelating functionalities, i.e., $-NH_2$ for Pb, $-SH$ for Pb and Zn, $-COOH$ for Cd, and $-CS_2$ for Pb.

In general, type III OMt have similar characteristics as type II OMt in terms of uptaking HOC, and thus they share similar advantages and dis-advantages. On the other hand, since cationic polymers generally have high charge density, type III OMt can be quite suitable in uptaking an-ionic contaminants. As for the uptake of heavy metal cations, choosing proper organic modifiers (e.g., with special groups and low costs) is of high importance for the synthesis of type III OMt.

7. Uptake of contaminants by inorgano-Mt

7.1. Hydroxymetal modified Mt

Inorganic modifiers (e.g., cations, oxides, nanoparticles) has been loaded on Mt to synthesize various functional materials (i.e., IMt), which can be used as both catalysts and adsorbents (Gil et al., 2008; Tian et al., 2009; Vicente et al., 2013). Among the various inorganic modifiers, hydroxymetal polycations have been most often used to modify Mt, and the adsorptive characteristics of the resulting IMt (Hyd-Mt) toward various contaminants (e.g., heavy metal cations, oxyanions) have been most concerned (Na et al., 2010; Yuan et al., 2013; Vicente et al., 2013). In addition, as Hyd-Mt are ubiquitous geosorbents in soils and sediments and can significantly affect the trans-port and fate of contaminants, their adsorptive characteristics therefore draw much more attentions aside from contaminant removal (Borgnino et al., 2009; Zhu et al., 2014b).

Until now, a variety of hydroxymetal polycations have been used to synthesize Hyd-Mt, e.g., hydroxyaluminum, hydroxyiron, hydroxyzirconium, hydroxytitanium, hydroxygallium, and hydroxychromium (Comets and Kevan, 1993; Matthes et al., 1999; Matthes and Kahr, 2000; Gil et al., 2008; Yuan et al., 2008; Na et al., 2010; Vicente et al., 2013). In addition, many studies also used more than one metals to prepare hydroxymetal cations, e.g., hydroxyaluminum/iron, hydroxyaluminum/zirconium, and hydroxyaluminum/iron/copper, with the purpose of enhancing the physicochemical properties of Hyd-Mt (e.g., SSA, catalytic activity, adsorption capacity) (Gil et al., 2008; Guerra et al., 2008; Tian et al., 2009; Yang et al., 2010; Zhou et al., 2010; Tomul, 2011; Vicente et al., 2013).

The most prominent structural characteristics of Hyd-Mt that relat-ed to the adsorption of contaminants are their large SSA and abundant chemically active surface groups (e.g., $-OH$). For example, the SSA of hydroxyaluminum-Mt is generally in the range of 150–300 m^2/g,
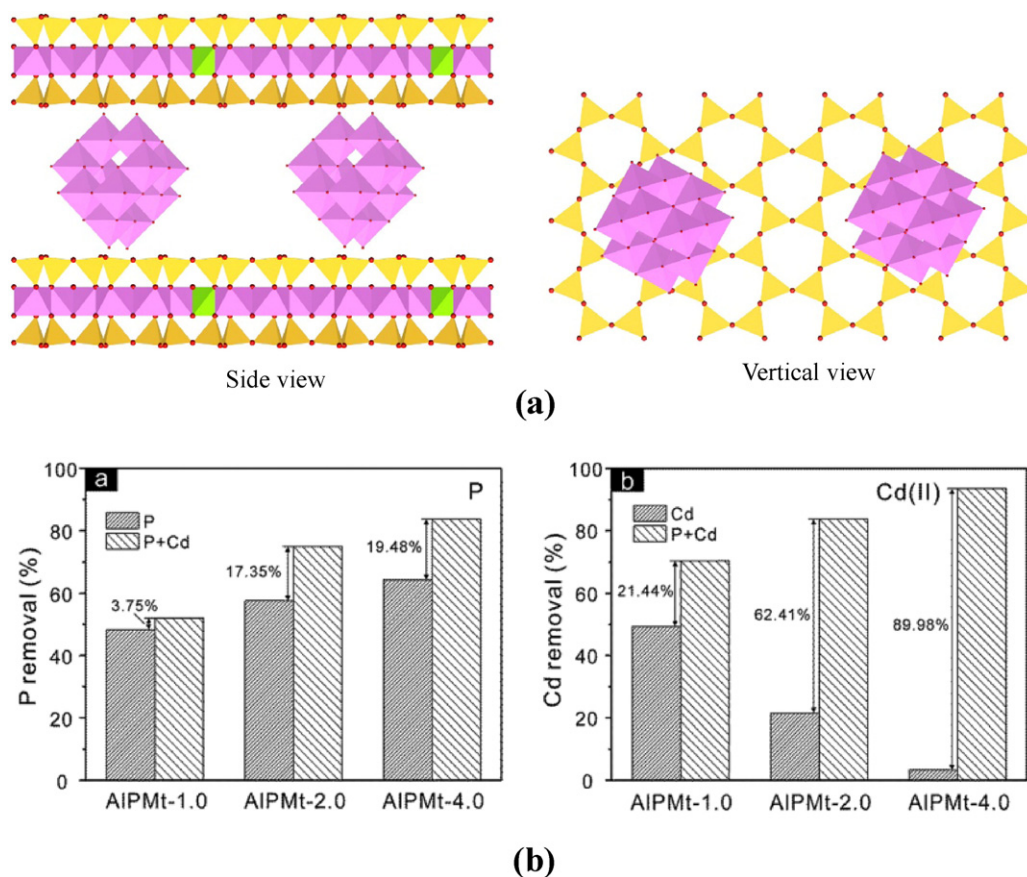
Side view   Vertical view

(a)

(b)

Fig. 7. The structure and adsorptive characteristics of IMt. (a) The interlayer structure of hydroxyaluminum-Mt; (b) comparative adsorption of phosphate (left) and Cd(II) (right) on hydroxyaluminum-Mt in single (P or Cd) and simultaneous (P + Cd) adsorption system ($C_{0, P}$ = 80 mg/L, $C_{0, Cd}$ = 90 mg/L), showing synergistic adsorption on the adsorbent. Images were reproduced from Ma et al. (2015), with permission from The Royal Society of Chemistry.

depending on the factors such as layer charge of Mt and loading level of hydroxyaluminum; increasing loading amount of hydroxyaluminum and layer charge of Mt generally can lead to larger SSA of the resulting hydroxyaluminum-Mt (Fig. 7) (Lenoble et al., 2002; Zhu et al., 2009a; Tian et al., 2009; Catrinescu et al., 2011). In addition, with the intercalation of hydroxymetal, basal spacing of the resulting Hyd-Mt can be enlarged as well (Zhu et al., 2009a). Therefore, the interlayer spaces of Hyd-Mt become more accessible to inorganic contaminants. The porous structure in combination with the abundant –OH group makes Hyd-Mt efficient adsorbents for both cationic and anionic contaminants, and various adsorption mechanisms have been proposed for the adsorption processes (Harsh and Doner, 1984; Keizer and Bruggenwert, 1991; Comets and Kevan, 1993; Cooper et al., 2002; Kasama et al., 2004; Thakre et al., 2010; Bergaoui et al., 1999; Zhou et al., 2010; Zhu et al., 2014b).

So far, the adsorptive characteristics of a variety of heavy metal cations (e.g., Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}) on Hyd-Mt have been examined (Harsh and Doner, 1984; Lothenbach et al., 1997, 1998, 1999; Bergaoui et al., 1999; Matthes et al., 1999; Janssen et al., 2003, 2007; Guo et al., 2011). In general, four different mechanisms have been proposed for the uptake of heavy metal cations on Hyd-Mt, including cation-exchange, chemical adsorption, structural incorporation, and surface precipitation (Lothenbach et al., 1997, 1998, 1999; Matthes et al., 1999; Nachtegaal et al., 2005; Janssen et al., 2007). Hereinto, the commonly recognized uptaking mechanism was the cation-exchange process. That is, heavy metal cations are adsorbed as inner-sphere complexes involving the deprotonated surface hydroxy groups on hydroxymetals and on the edges of Mt, particularly at low adsorption density of heavy metal cations when sufficient surface hydroxy groups are available (Lothenbach et al., 1997, 1998; Saha et al., 2001, 2002;

Wu et al., 2009). However, the adsorbed heavy metal cations may form chemical bonds with the surface deprotonated sites, which then involves a chemical adsorption process (Lothenbach et al., 1997, 1998; Matthes et al., 1999).

Some heavy metals (e.g., Cu^{2+}, Zn^{2+}, Ni^{2+}) have comparable ion size as the metal cations within hydroxymetals (e.g., Al^{3+}, Fe^{3+}), and thus they may become incorporated into the solid phase of hydroxymetals (Lothenbach et al., 1997, 1998, 1999; Nachtegaal et al., 2005). Nachtegaal et al. (2005) demonstrated that Ni^{2+} can be incorporated into the gibbsite-like structure in the interlayer spaces of a hydroxyaluminum-Mt complex. At relatively high heavy metal concentration and high solution pH (i.e., abundant OH^-), heavy metal cations may also form hydroxide precipitates on the surface of Hyd-Mt, even when the concentrations of heavy metal cations and OH^- are still far below the level at which precipitates can be formed in aqueous medium (Matthes et al., 1999; Saha et al., 2001; Janssen et al., 2007).

As various mechanisms are involved in the uptake of heavy metal cations Hyd-Mt, their adsorption capacities therefore can be affected by a diversity of factors as well, such as the microstructure of Hyd-Mt (e.g., type and loading amounts of hydroxymetals, layer charge of Mt, porosity), the physicochemical properties of heavy metal cations (e.g., ion size, valence, hydrolysis constant), and the solution conditions (e.g., solution pH, solute concentration, co-existing ions) (Lothenbach et al., 1997, 1999; Cooper et al., 2002; Nachtegaal et al., 2005; Matthes et al., 1999; Janssen et al., 2007; Guo et al., 2011). Among these factors, solution pH plays particular important role. Increasing solution pH generally can accelerate the deprotonation of hydroxy group and help the formation of surface precipitates, thus leading to significant enhancement of the adsorption capacity (Matthes et al., 1999; Saha et al., 2001; Guerra et al., 2008; Guo et al., 2011). On the other hand, the

interplay of these factors then leads to a rather complex adsorptive characteristics of heavy metal cations on Hyd-Mt. In this case, correlating the structure of Hyd-Mt and their adsorption capacity toward heavy metal cations, or the physicochemical properties of heavy metal cations and their adsorption capacity on Hyd-Mt, can be quite difficult. Saha et al. (2001, 2002) showed that the adsorption capacity of several heavy metals on hydroxyaluminum-Mt was in the order $Pb^{2+} \gg Zn^{2+} \geq Cd^{2+}$. Similar results were also observed by Matthes et al. (1999). However, Lothenbach et al. (1997) showed that Zn^{2+} had better adsorption capacity than Pb^{2+} on hydroxyaluminum-Mt at relatively low pH (<pH 5.5). Keizer and Bruggenwert (1991) also showed that the preference affinity of heavy metal cations for hydroxyaluminum-Mt was in the order $Cu^{2+} > Zn^{2+} > Pb^{2+} > Cd^{2+}$.

Compared with original Mt, Hyd-Mt may have better or weaker capacity in the uptake of heavy metal cations, depending on the factors such as the type of Hyd-Mt and heavy metal cations, solution pH, and solute concentration (Harsh and Doner, 1984; Matthes et al., 1999; Saha et al., 2001; Cooper et al., 2002; Guo et al., 2011). Matthes et al. (1999) found that hydroxyaluminum-Mt had better capacity than original Mt in the adsorption of four heavy metal cations (Zn^{2+}, Pb^{2+}, Cu^{2+}, and Cd^{2+}) only at very low solute concentration (e.g., less than 10 μmol/L for Cd^{2+}); while hydroxyzirconium-Mt showed better adsorption capacity than original Mt over a much wider solute concentration range (e.g., less than 100 μmol/L for Pb^{2+} and Cd^{2+}). Saha et al. (2001, 2002) showed that hydroxyaluminum-Mt and hydroxyaluminosilicate-Mt had better capacity than Mt in the uptake of Cd^{2+} and Zn^{2+} at relatively high solution pH (>pH 5), and better capacity in the uptake of Pb^{2+} in the whole tested pH range (pH 4–8). Since the uptake of heavy metal cations on Mt is primarily a cation-exchange process, the adsorption capacity therefore may not be so much significantly affected by solution conditions as compared to the adsorption on Hyd-Mt.

The adsorptive characteristics of a variety of oxyanions (e.g., phosphate, arsenate, arsenite, chromate, selenite, selenite, and sulfate) on Hyd-Mt have been well concerned as well (He et al., 1999; Matthes et al., 1999; Lenoble et al., 2002; Kasama et al., 2004; Peak et al., 2006; Bergaoui et al., 2010; Yang et al., 2010; Wang et al., 2015). The proposed adsorption mechanisms mainly involve ligand-exchange, ion-exchange, and surface precipitation (Lenoble et al., 2002; Kasama et al., 2004; Bergaoui et al., 2010). A ligand-exchange process involves the exchange of oxyanions with the ligands (e.g., —OH) on hydroxymetals and the edges of Mt As such, oxyanions will be adsorbed as inner-sphere complexes on the surface of dehydroxylated Hyd-Mt, which will be accompanied by the release of OH^-. An evident increase of solution pH, therefore, can be observed during the adsorption process (Kasama et al., 2004; Zhu and Zhu, 2007). However, several studies also regard this kind of adsorption as an anion-exchange process because of the release of OH^- (Kasama et al., 2004; Zhou et al., 2010). The adsorbed oxyanions can form various complexes with Hyd-Mt, depending to the factors such as physicochemical properties of the oxyanions, surface structure of Hyd-Mt (particularly hydroxy density and distribution), solution pH, and the adsorbed density of oxyanions (Borgnino et al., 2010). According to the ATR-FTIR results, Borgnino et al. (2010) suggested that phosphate formed nonprotonated bidentate complex and monoprotonated bidentate complex with hydroxyiron (on hydroxyiron-Mt) at pH 4.5, and nonprotonated bidentate complex and nonprotonated monodentate complex at pH 7.0 and 9.0.

As the polycationic hydroxymetals generally have quite high charges, particularly at acidic solution in which the hydroxy groups on hydroxymetals are likely to be protonated ($-OH_2^+$). In this case, some counter anions (e.g., Cl^-, NO_3^-) may be incorporated on Hyd-Mt as well during the synthesis process. These anions can contribute additional uptake of oxyanions on Hyd-Mt by an anion-exchange mechanism (or electrostatic interactions between oxyanions and Hyd-Mt) (Saha et al., 2004; Peak et al., 2006). According to the X-ray absorption spectroscopy characterization results, Peak et al. (2006) showed that selenite was adsorbed on

hydroxyaluminum-Mt and hydroxyaluminosilicate-Mt as both outer-sphere and inner-sphere complexes, and the outer-sphere complexes were formed by the electrostatic interaction between the adsorbents and selenite.

Finally, oxyanions may be adsorbed on the surface of Hyd-Mt by forming precipitates on the surface of Hyd-Mt with metal cations released from the hydroxymetals (Saha and Inoue, 1998). Saha and Inoue (1998) suggested that the released Al cations from hydroxyaluminum could form precipitates with phosphate on the surface of hydroxyaluminum-Mt. However, Kasama et al. (2004) suggested that this adsorption process should not play an important role for the uptake of phosphate on hydroxyaluminum-Mt.

Similar to the uptake of heavy metal cations, the capacity of Hyd-Mt in uptaking oxyanions can differ significantly as well, depending on the factors such as the microstructure of Hyd-Mt, the physicochemical properties of oxyanions, the solution conditions (e.g., solution pH, solute concentration, concomitant ions) (He et al., 1999; Kasama et al., 2004; Zhu and Zhu, 2007; Tian et al., 2009; Zhou et al., 2010). Among these factors, solution pH plays a particularly significant role. Increasing solution pH can inhibit the ligand exchange process (i.e., inhibit the release of OH^- from Hyd-Mt) and then decrease the adsorption capacity of oxyanions; while on the other hand hydroxymetals may dissolve under too much acidic conditions (e.g., below pH 3). As such, suitable equilibrium solution pH (generally in the range of pH 3–5) can optimize the adsorption capacity of oxyanions on Hyd-Mt (Kasama et al., 2004; Zhu and Zhu, 2007; Tian et al., 2009). For example, pH 5 was suggested to be the proper solution pH for the uptake of phosphate on hydroxyaluminum-Mt (Zhu and Zhu, 2007). Increasing loading amounts of hydroxymetal polycations clearly can provide more adsorption sites for contaminants (Kasama et al., 2004).

Hyd-Mt synthesized using those hydroxymetals containing more than one type of metals may have better adsorption capacity (Tian et al., 2009; Zhou et al., 2010; Shanableh and Elsergany, 2013; Huang et al., 2015). For example, Tian et al. (2009) showed that the hydroxyaluminum/lanthanum-Mt had better capacity (i.e., 1.3 times the value) than hydroxyaluminum-Mt in the uptake of phosphate. Zhou et al. (2010) showed that hydroxyaluminum/zirconium-Mt had better adsorption capacity toward Cr(VI) than both hydroxyaluminum-Mt and hydroxyzirconium-Mt. Probably the decreased crystallinity of the mixed hydroxymetals can provide more adsorption sites for oxyanions. However, silication of hydroxyaluminum-Mt (i.e., hydroxyaluminosilicate-Mt) always leads to a decreased adsorption of oxyanions, as the Si–OH groups are less efficient than metal–OH groups in the uptake of oxyanions (Saha et al., 2004; Peak et al., 2006).

Phosphate, chromate, and arsenate generally have strong interaction with Hyd-Mt, while nitrate, sulfate, chlorate, acetate have relatively weak interaction (Tian et al., 2009; Na et al., 2010; Zhou et al., 2010; Huang et al., 2015). Zhou et al. (2010) found that nitrate, chlorate, and acetate showed no significant effect on the uptake of chromate on hydroxyaluminum/zirconium-Mt, while phosphate, sulfate, and tartrate can evidently inhibit the uptake of chromate. Tian et al. (2009) showed that the inhibiting effect of anions on the uptake of phosphate on Hyd-Mt followed the order: $HCO_3^- > Cl^- > SO_4^{2-} \approx NO_3^-$. Na et al. (2010) showed that sulfate and nitrate could not have evident effect on the uptake of arsenate on hydroxytitanium-Mt, while phosphate could evidently inhibit the adsorption capacity.

Hyd-Mt have been used for the uptake of F^- as well, and the adsorption mechanisms are similar to those of oxyanions (Polubesova et al., 2000; Zhu et al., 2006; Mohapatra et al., 2009; Bia et al., 2012; Wei and Deng, 2013). Zhu et al. (2006) suggested that the uptake of F^- on hydroxyaluminum-Mt could be much better at acidic solution (below pH 4.5), and the adsorption mechanisms involved both ligand exchange (with surface-OH) and coprecipitation (with the released Al^{3+}). Inner-sphere complexes were supposed to form between F^- and Hyd-Mt.

Moreover, Hyd-Mt have been applied for the uptake of organic contaminants as well (He et al., 1999; Hou et al., 2011; Hao et al.,

2014). He et al. (1999) showed that both tartrate and oxalate could be effectively adsorbed on hydroxyaluminum-Mt, but with weaker adsorption capacity as compared with phosphate. Hou et al. (2011) found that hydroxyiron-Mt could more effectively uptake Rhodamine B than the original Mt, with the optimum solution pH of 5. Hao et al. (2014) showed that the capacity of hydroxyaluminum-Mt in the uptake of three dyes was in the order: Basic Green > Basic Fuchsin > Acid Turquoise Blue A.

Interestingly, heavy metal cations and oxyanions can be simultaneously adsorbed on Hyd-Mt (Zhu et al., 2014b; Ma et al., 2015). Zhu et al. (2014c) recently showed that phosphate and Cd^{2+} can be synergistically adsorbed on hydroxyiron-Mt through the formation of ternary complexes between the contaminants and the adsorbents, which on the other hand may be considered as the formation of surface precipitates. Therefore, Hyd-Mt can be particularly used for the treatment of wastewater containing low concentrations of both oxyanions and heavy metal cations. Similar synergetic adsorption results were observed by Ma et al. (2015) in the uptake of Cd(II) and phosphate on hydroxyaluminum-Mt. As such, Hyd-Mt can be suitable adsorbents for wastewater containing both cationic and anionic contaminants.

Calcination of the Hyd-Mt can obtain metal oxides pillared Mt, which then have better chemical stability and have been used as catalysts for various industrial application purposes. The adsorptive characteristics of various contaminants on oxides pillared Mt have been studied as well (Gil et al., 2011; Wang et al., 2015). Generally, their adsorption capacity will decrease as compared with those of Hyd-Mt because of the dehydroxylation, which leads to the decrease of active adsorption sites for both cationic and anionic contaminants (Wang et al., 2015).

7.2. Nanoparticle-loaded Mt

Recently, several studies also loaded nanoparticles on Mt, and the resulting nanocomposites have been used as adsorbents for both heavy metal cations and oxyanions as well (Yuan et al., 2009; Mockovciakova et al., 2010; Zhang et al., 2011; Wu et al., 2015). In these nanocomposites, nanoparticles can disperse on Mt to reduce the aggregation, which then can enhance the efficiency of these nanoparticles in the removal of contaminants (Yuan et al., 2009; Zhang et al., 2013; Wu et al., 2015). Yuan et al. (2009) loaded magnetite nanoparticles (about 15 nm) on Mt by dropping the mixture of Mt and NaOH solution into ferric chloride/ferrous chloride solution, or by directly mixing the magnetite hydrosol with Mt. These nanoparticles existed on the surface or inside the interparticle pores of Mt, and the resulting nanocomposites had similar SSA in comparison with original Mt (about 80 m^2/g). The authors showed that the obtained nanocomposites could effectively uptake Cr(VI) and subsequently reduce it into Cr(III). Mockovciakova et al. (2010) prepared similar iron oxide/Mt nanocomposites for the uptake of Zn^{2+}, Cd^{2+}, and Ni^{2+}, and the authors showed that in the low solute concentration range the magnetic nanocomposites have better adsorption capacity than original Mt.

Fe° on Mt can reduce their aggregation and enhance their chemical stability thanks to the protection effect provided by Mt interlayer spaces. Shi et al. (2011, 2013) loaded Fe° on Mt by reducing the pre-adsorbed ferric iron with borohydride under the protection of N_2. The authors found that after being adsorbed onto the nanocomposites, Cr(VI) could be reduced into Cr(III) and Cu(II) into Cu^0, while Zn(II) was not reduced. Wu et al. (2015) using the similar method synthesized
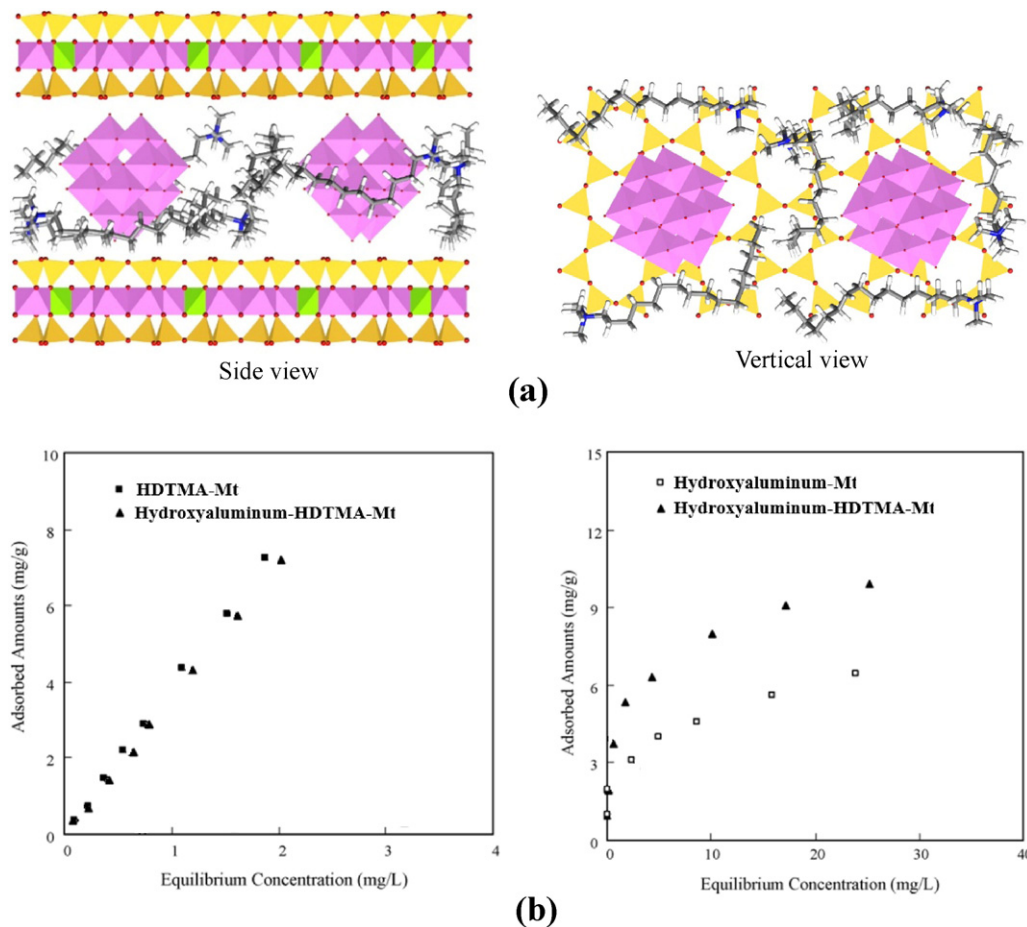

Fig. 8. The structure and adsorptive characteristics of IOMt. (a) The interlayer structure of hydroxyaluminum-HDTMA-Mt; (b) The adsorption isotherms of naphthalene and phosphate on hydroxyaluminum-HDTMA-Mt.
Images were reproduced from Zhu et al. (2009c), with the permission of Elsevier.

a serials of nanocomposites with different loading amounts of Fe°. They found that Fe° were loaded both on the outer surface and into the inter-layer spaces of Mt, leading to an obvious increase of basal spacing. As such, Cr(VI) could access the interlayer spaces of Mt and be reduced into Cr(VI). Zhang et al. (2011) loaded Fe° on Hyd-Mt by adding NaBH$_4$ solution to the mixture of hydroxyaluminum-Mt and FeSO$_4$. The resulting nanocomposites could effectively remove nitrate by a combined adsorption–reduction process, with the reduced products being identified as ammonium and nitrogen. The authors suggested that the uptake of nitrate by hydroxyaluminum-Mt enhanced the mass transfer of nitrate from solution to Fe° surface, which therefore accelerated the reduction rate.

8. Uptake of contaminants by inorgano–organo-Mt

IOMt have been synthesized for the purpose of developing multifunctional adsorbents for both organic and inorganic contaminants (Ma and Zhu, 2006; Zermane et al., 2010; Ma et al., 2014; Hamidouche et al., 2015). Organic and inorganic modifiers can be simultaneously or sequentially loaded on Mt in the synthesis of IOMt (Fig. 8a) (Srinivasan and Fogler, 1990a,b; Zhu et al., 2009a,c; Ren et al., 2014). A large portion of these studies adapted the sequential loading method and synthesized IOMt by modifying Hyd-Mt with surfactant (Srinivasan and Fogler, 1990a,b; Li et al., 2009; Zermane et al., 2010). Ma et al. (2014) found that HDTMA could be loaded on hydroxyaluminum-Mt by hydrophobic interaction and then partially desorbs the pre-loaded hydroxyaluminum. However, Zhu et al. (2009a,c) showed that the loading amount of HDTMA on hydroxyaluminum-Mt was quite small, probably because the interlayer spaces of Mt was 'locked' by the pre-adsorbed hydroxyaluminum. The authors suggested that the simultaneous modification approach might be more effective in loading these modifiers to Mt. Clearly, the final structure of IOMt can be affected by many factors, such as the properties of Mt, the properties and added amounts of modifiers, and the synthesize methods.

Because of the simultaneous presence of organic and inorganic modifiers within the interlayers of Mt, the basal spacing of IOMt will be larger than both the corresponding OMt and IMt, while the SSA of IOMt will be quite small (i.e., close to that of OMt) (Bouras et al., 2001, 2007; Zhu and Zhu, 2007; Hamidouche et al., 2015). Until now, most of the IOMt are synthesized using surfactants and hydroxymetal polycations. In this case, surfactants on IOMt can create organic phases for organic contaminants while hydroxymetals provide chemically active –OH groups for inorganic contaminants (Fig. 8b) (Srinivasan and Fogler, 1990a,b; Ma and Zhu, 2006; Zhu and Zhu, 2007; Zhu et al., 2009c). On the other hand, as both cationic surfactants and hydroxymetals possess positive charges, some anions may be loaded on IOMt as well to balance the charge of these modifiers, which may provide additional adsorption of oxyanions through an anion-exchange process (Zhu and Zhu, 2007; Zhu et al., 2009c).

The capacity of IOMt in the simultaneous uptake of organic and inorganic contaminants has been examined by several studies (Ma and Zhu, 2006; Zhu and Zhu, 2007; Zhu et al., 2009c; Hu et al., 2011). Zhu et al. (2009c) found that the two IOMt (i.e., HDTMA and hydroxyaluminum simultaneously modified Mt and hydroxyaluminum modified HDTMA-Mt) had comparable capacity as HDTMA-Mt in the uptake of naphthalene and much better capacity than hydroxyaluminum-Mt in the uptake of phosphate. They proposed that in addition to ligand-exchange with –OH, the anion-exchange with the counterbalance anions also contributed to the uptake of phosphate. Hu et al. (2011) also showed that the IOMt synthesized using HDTMA modified hydroxyaluminum-Mt had similar capacity as HDTMA-Mt in the uptake of para-nitrochlorobenzene and much better capacity than hydroxyaluminum-Mt in the uptake of Cr(VI). The small SSA did not significantly affect the uptake of phosphate on IOMt, probably because the interlayer spaces of IOMt were expanded by water molecules in solution, which then enabled the access of the interlayers by oxyanions.

In addition, the surface of IOMt may provide some adsorption sites for phosphate as well.

Several studies synthesized IOMt for the purpose of enhancing the capacity in uptaking organic contaminants (Michot and Pinnavaia, 1991; Bouras et al., 2001, 2007; Jiang et al., 2002; Jiang and Zeng, 2003; Al-Asheh et al., 2003; Bouberka et al., 2009; Li et al., 2009; Cheknane et al., 2010), or inorganic contaminants (Zhang et al., 2015). Bouberka et al. (2009) found that IOMt synthesized by modifying hydroxyaluminum-Mt and hydroxychromium-Mt with HDTMA had much better capacity than the corresponding Hyd-Mt in the uptake of acid dye Supranol Yellow4GL. Li et al. (2009) exhibited that HDTMA modified hydroxyaluminum-Mt and hydroxyiron-Mt had better capacity in the uptake of anionic herbicide 2,4-D while weaker capacity in the uptake of nonionic herbicide acetochlor, in comparison with HDTMA-Mt. The authors suggested that in addition to the van der Waals interaction with organic cations, the specific interactions with hydroxymetal polycations also contributed to the uptake of 2,4-D to IOMt, which therefore led to an efficient uptake of 2,4-D. While for the uptake of nonionic acetochlor, the specific interactions with hydroxymetal polycations should be much weaker. Zermane et al. (2010) showed that HDTMA modified hydroxyiron-Mt could simultaneously uptake both basic dye yellow 28 and 4-nitrophenol, and the presence of yellow 28 enhanced the uptake of 4-nitrophenol. Zhang et al. (2015) showed that the octadecyltrimethyl-ammonium and hydroxyiron simultaneously modified Mt had much better capacity in the uptake of Cr(VI) than the corresponding octadecyltrimethylammonium-Mt and hydroxyiron-Mt. Ren et al. (2014) modified HDTMA-Mt with hydroxyiron polycations, but the authors showed the resulting IOMt had weaker capacity in uptaking As(V) and As(III) as compared with hydroxyiron-Mt.

As the presence of inorganic modifiers in the interlayers can enhance the thermal stability of Mt, IOMt has been used as recyclable adsorbents for organic contaminants (Srinivasan and Fogler, 1990a,b; Wu et al., 2001). In this case, the spent can be calcined to remove organic modifiers and contaminants, and the resulting products were further modified with surfactants to synthesize IOMt for further uptake of organic contaminants (Wu et al., 2001).

Some of the intercalated hydroxymetal cations may degrade the adsorbed organic contaminants, and thus IOMt can be used as novel functional materials in the removal of organic contaminants through a combined adsorption-degradation process (Breen and Moronta, 2000; Wallis et al., 2010, 2011). Wallis et al. (2010) modified Fe(III)-Mt using HDTMA to synthesize IOMt, which can effectively uptake organic contaminants (2-naphthol and anthrone) and then degrade them. The authors further proposed that the increased hydrophobicity of IOMt (by the intercalation of surfactants) made the interlayer catalytic sites (provided by Fe(III)) more accessible by organic contaminants; thus the IOMt may be more effective catalysts than IMt.

9. Comparison of the adsorbents

According to the above discussions, each type of Mt based adsorbents can be used for the uptake of more than one type of contaminants; in other words, each type of contaminant always have more than one type of Mt based adsorbents for their removal. Therefore, we should consider the advantages and disadvantages of these adsorbents for the target contaminants and choose proper adsorbents for their removal.

Cationic contaminants (e.g., heavy metal cations, cationic dyes, radioactive nuclides) can be adsorbed by original Mt, AMt, TMt, OMt, and IMt. Mt has the lowest price among them (because no modification was needed for Mt) and also has quite efficient adsorption capacity. AMt, TMt, and IMt may have better adsorption capacity than Mt under optimized conditions, but the enhancement is generally not quite significant. Considering the higher price of the three types of adsorbents, they

are less suitable adsorbents for cationic contaminants as compared with original Mt. Choosing proper organic modifiers (with special functional group) may synthesize OMt with high adsorption capacity toward target heavy metal cations, but the cost can rise as well. As such, Mt should be the first choice for cationic contaminants.

HOC can be adsorbed mainly by OMt and IOMt. IOMt generally has comparable capacity in the uptake of HOC as compared with the counterpart OMt (i.e., similar loading amounts of surfactant). However, IOMt clearly has much higher price as it should be modified by both surfactants and hydroxymetals. In addition, the desorption of surfactants from IOMt should also be much easier, as a large portion of surfactants were loaded on IOMt as molecular form (Zhu and Zhu, 2007; Zhu et al., 2009c). As such, OMt should be the suitable materials for the uptake of most of the HOC from water.

Anionic contaminants (e.g., anionic dyes, oxyanions, F$^-$) can be removed by AMt, OMt, IMt, and IOMt. As the uptake of anionic contaminants on AMt mainly relies on the excess H$^+$ on AMt, the adsorption capacity is commonly not quite high. IOMt may have the best adsorption capacity toward anionic contaminants, but its cost is probably the highest as well (because of the loading of two types of modifiers). OMt and IMt can have efficient adsorption capacity toward organic anions and inorganic anions, respectively, and their costs may be controlled by choosing proper modifiers (e.g., cationic polymers for OMt, hydroxyiron for IMt). In addition, their prices are lower than that of IOMt (less loading amount of modifiers on OMt and IMt). As such, one may suggest that OMt and IMt should be the more suitable for the removal of organic anions and inorganic anions, respectively.

As stated above, some adsorbents can simultaneously uptake more than one type of contaminants. For the wastewater containing both HOC and oxyanions, IOMt seems to the a good choice; IMt can be most suitable for the uptake of both heavy metal cations and oxyanions; Mt can be used for the simultaneous uptake of both organic cations and HOC; some particular OMt can uptake both heavy metal cations and HOC. However, one should notice that besides the price and the adsorption efficiency of the adsorbents, many other factors should also be considered as well to properly choose suitable adsorbents for target wastewater, e.g., the stability and environmental compatibility of the adsorbents, the tolerance to co-existing chemical compounds, the regeneration/disposal of the spent sorption.

10. Disposal and reutilization of the spent adsorbents

Application of adsorbents in pollution control will inevitable produce large amount of spent adsorbents, which need to be properly disposed or reutilized before the adsorbents can be widely used. As such, a number of studies addressed this issue and developed some approaches to deal with the spent adsorbents, which will be briefly overviewed in this section.

As stated above, Mt is probably the most promising adsorbents in this family for the removal of cationic contaminants (e.g., heavy metal cations, radioactive nuclides, cationic dyes), thanks to its low-cost and high-efficiency. One approach for safely disposal of the spent Mt after the uptake of heavy metal cations (e.g., Cd^{2+}, Cu^{2+}) and radioactive nuclides (e.g., Lu^{3+}, La^{3+}, UO$_2^{2+}$) is to in-situ sequestrate the adsorbed contaminants by thermal treatment (Fig. 9) (Munoz-Paez et al., 1995; Ritherdona et al., 2003; Zhu et al., 2015b). That is, heating the spent Mt to a relatively high temperature can cause the collapse of Mt interlayers, which then will close the desorption pathway for the adsorbed contaminants, leading to in-situ sequestration of contaminants within the interlayers of Mt. As such, the sequestration efficiency of the adsorbed contaminants generally increases with heating temperature (Munoz-Paez et al., 1995; He et al., 2001; Ritherdona et al., 2003; Zhu et al., 2015b). For some heavy metal cations with small ionic radius (e.g., Ni^{2+}, Cu^{2+}), they can migrate into Mt layers even at relatively low heating temperature (e.g., less than 300 °C) (He et al., 2001; Komadel et al., 2005; Zhu et al., 2015b).

Cationic dyes can be strongly adsorbed on Mt because of the electrostatic interaction between dyes and Mt and also the relatively hydrophobic characteristics of dyes. Those methods based on the desorption of cationic dyes (e.g., salt washing) therefore could hardly be considered as suitable choice for reutilizing the spent Mt. Recently, Chen et al. (2014) and Zhu et al. (2015a) used Mt as template and directly transformed the adsorbed cationic dyes into carbon monolayer within the interlayers of Mt by thermal treatment of the spent Mt under nitrogen atmosphere. After removing Mt by acid washing, they obtained carbon materials with graphene-like structure. Interestingly, heteroatoms (e.g., N, S) can be doped into the carbon materials as long as the precursor dyes contain heteroatoms (Fig. 10). The resulting graphene-like carbon materials were shown to have comparable catalytic activity in oxygen reduction reactions as other heteroatoms-doped graphene (Zhu et al., 2015a).

Regeneration and reutilization of the spent OMt after the uptake of HOC has been studied by a number of publications, some of those studies can be found in the review by Zhu et al. (2009b). As the adsorbed HOC generally only have relatively weak dispersion-van der Waals interactions with the OMt, they can be easily desorbed from OMt (Sarkar et al., 2012). As such, a variety of physical, chemical, and biological regeneration approaches based on the desorption of HOC have been developed: (I) thermal desorption involves the desorption of organic contaminants (e.g., phenols) from the spent OMt by heating at proper
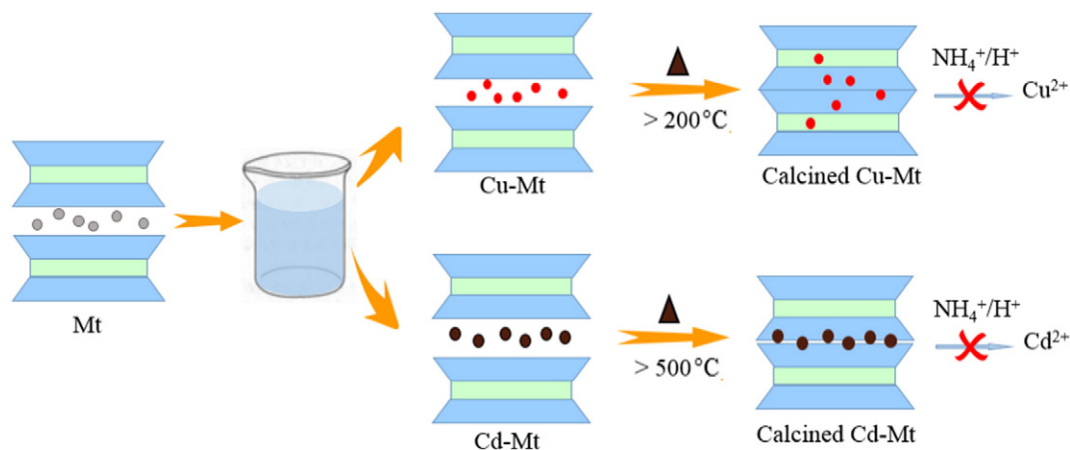

Fig. 9. Sequestrating heavy metal cations on Mt by thermal treatment of the spent Mt. Cu^{2+} has smaller size and can migrate into Mt layers at relatively low heating temperature; while much higher heating temperature is needed to sequestrate Cd^{2+} because of its larger size.
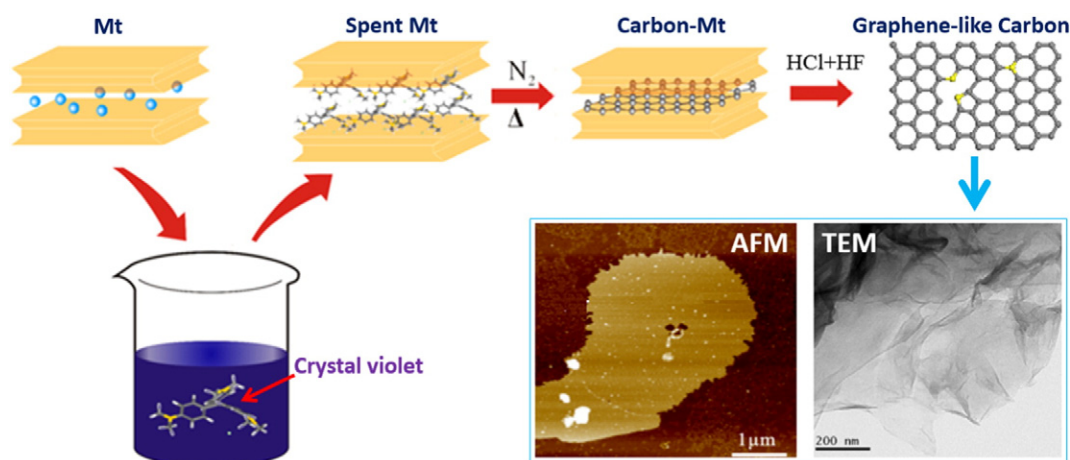Image was reproduced from Zhu et al. (2015b), with permission of Elsevier.

Fig. 10. The spent Mt after the adsorption of crystal violet can be reutilized to synthesize graphene-like carbon materials. Image was reproduced from Zhu et al. (2015a), with permission from The Royal Society of Chemistry.

temperature (e.g., 200 °C) (Lin and Cheng, 2002; Dammak et al., 2015); (II) CO_2 supercritical fluid can effectively extract HOC (e.g., phenols) from the spent OMt (Park and Yeo, 1999, Salgın et al., 2004; Cavalcante et al., 2005); (III) chemical solution such as NaOH can directly desorb organic contaminants (e.g., phenol, tannin) from the spent OMt (Yang et al., 2003; Anirudhan and Ramachandran, 2006); (IV) Catalysts such as TO_2 can be dispersed with the spent OMt in solution, or directly loaded on OMt, to degrade the adsorbed organic contaminants (e.g., chlorophenols) (Ilisz et al., 2002, 2004; Mogyorosi et al., 2002; An et al., 2008; Wallis et al., 2010, 2011); and (V) microbes such as bacteria and yeast have been used to degrade the desorbed HOC from spent OMt (Theng et al., 2001; Singh et al., 2003; Witthuhn et al., 2005, 2006; Scurtu et al., 2008; Sarkar et al., 2012). These approaches generally will not evidently desorb or degrade cationic surfactants on OMt. As such, the microstructure and adsorption capacity of OMt can be preserved. The bioregeneration approach as an in-situ, low-cost, and easy-operating approach is applicable for regenerating the spent OMt from both wastewater treatment and soil remediation, and perhaps has promising applications.

The reutilization of spent Hyd-Mt after the uptake of heavy metal cations or oxyanions have been shown in several publications as well, and washing the spent samples using NaOH solution has been most often used (Tian et al., 2009; Zhou et al., 2010; Shanableh and Elsergany, 2013; Huang et al., 2015). Tian et al. (2009) regenerated the spent hydroxyaluminum/lanthanum-Mt (after the uptake of phosphate) by washing with NaOH solution. The regenerated adsorbents still maintained quite high removal efficiency of phosphate (>91%) after six regeneration cycles.

11. Conclusions

This review comprehensively introduced the Mt based adsorbents, which can be used for the uptake of most of the chemical contaminants from aqueous solution, and a variety of mechanisms are involved for the related adsorption processes. (1) Original Mt can effectively uptake cationic contaminants such as heavy metal cations and cationic dyes through a cation exchange process. (2) AMt and TMt are also mainly used for the uptake of heavy metal cations through a cation exchange process. (3) OMt can have quite different microstructure and adsorptive characteristics depending on the used organic modifiers. They can efficiently uptake HOC through surface adsorption and/or partition; uptake anionic contaminants by anion exchange; uptake heavy metal cations through specific interaction. (4) IMt can effectively uptake cationic and anionic contaminants through ion exchange, adsorption, surface precipitation, and/or structural incorporation. Synergistic uptake of

inorganic cations and anions has been observed on IMt by forming ternary complexes and/or surface precipitation. (5) IOMt as multifunctional adsorbents can uptake HOC by partition/adsorption and anionic contaminants through anion/ligand exchange. They can also remove HOC through an adsorption–degradation combined process.

Various approaches have been developed to properly dispose the spent adsorbents after the adsorption of contaminants. Thermal treatment of the spent adsorbents can sequestrate inorganic contaminants (e.g., heavy metal cations, radioactive nuclides) on Mt, or transform the organic contaminants (e.g., cationic dyes) into graphene-like carbon materials within the interlayer spaces of Mt. Regeneration of the spent adsorbents can be achieved through various physical, chemical, or biological methods.

Nomenclature

AMt	acid-washed montmorillonite
CEC	cation exchange capacity
HDTMA	hexadecyltrimethylammonium
HOC	hydrophobic organic contaminants
Hyd-Mt	hydroxymetal polycation modified montmorillonite
IMt	inorganic modifiers modified montmorillonite
IOMt	inorganic and organic modifiers modified montmorillonite
Mt	montmorillonite
OMt	organo-montmorillonite
SOM	soil organic matter
SSA	specific surface area
TMA	tetramethylammonium
TMt	thermal-treated montmorillonite

Acknowledgments

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