



## Review

## Regeneration of spent organoclays after the sorption of organic pollutants: A review

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## ABSTRACT

Clay minerals modified with organic ions, also known as organoclays, have found applications in a wide range of organic pollution control fields because of their excellent sorption capacity towards organic pollutants. Regeneration of the spent organoclays after the sorption of organic pollutants is of great importance during their application in pollution control. In this review, the reported methods for the regeneration of the spent organoclays are summarized, including biological degradation, photo-assisted oxidation, chemical extraction/desorption, supercritical extraction, thermal desorption, et al. The characteristics and applications of these methods are briefly described. It shows that most of these methods have been developed for regenerating spent organoclays from wastewater treatment. The biological regeneration method, as an in situ, low cost and easy-operating method, is applicable for regenerating spent organoclays not only from wastewater treatment, but also from soil and groundwater remediation.

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## 1. Introduction

The layered expandable clay minerals (e.g., smectite, hydro-talcite) always possess charges on their layer sheet, and these charges will be compensated by counter inorganic ions. Because of the strong hydration of these inorganic ions, the interlayer spaces of the clay minerals are hydrophilic in nature. As a result, the natural clay minerals show rather weak affinity to most of the hydrophobic organic compounds (HOCs), and they are seldom used as sorbents for HOCs (Yariv and Cross, 2001).

Under suitable conditions, the inorganic ions on clay minerals can be replaced by organic ions, and then the interlayer spaces become hydrophobic (Lee et al., 1999; Wang et al., 2004; Volzone et al., 2006; Frost et al., 2008). As a result, the sorption capacity of the modified clay minerals (i.e., organoclays) towards HOCs can be significantly improved, and the organoclays have found applications in a wide range of organic pollution control fields (Volzone et al., 2006; Frost et al., 2008; Laha et al., 2009). Organoclays can be efficient sorbent for removal of organic pollutants from water (Zhou et al., 2007a,b; Huang et al., 2007; Zhu and Zhu, 2007; Lin and Juang, 2009) and air (Zhu and Su, 2002; Tian et al., 2004; Volzone et al., 2006; Park et al., 2008), and they are also used as landfill liner and sorptive barrier to prevent down-gradient

pollution of groundwater and aquifer from organic pollutants (Lo, 2001; Lo and Yang, 2001; Brixie and Boyd, 1994).

Sorptive mechanisms of organoclays towards HOCs have been extensively studied in the past decades, and various methods for improving their sorption capacities are proposed accordingly (Sheng et al., 1996; Shen, 2004; Zhu et al., 2007, 2008a,b). For the organoclays modified with organic cations containing long alkyl chains, it is believed that HOCs molecules are incorporated into the alkyl chain formed organic phases (Sheng et al., 1996; Shen, 2004; Zhu et al., 2007). Accordingly, it is suggested that regulating the arrangement model of the alkyl chains of the ions can optimize the sorption capacity of the organoclays (Zhu et al., 2007, 2008a). If the organoclays are synthesized with small organic cations, the HOCs molecules are believed to be primarily adsorbed on the hydrophobic siloxane surface of the organoclays (Shen, 2004; Bartelt-Hunt et al., 2003). Thereby, increasing the exposed siloxane surface can improve the sorption capacity of this class of organoclays (Shen, 2004; Zhu et al., 2008b).

To reduce the pollution control costs, researchers have also developed some novel processes for the application of organoclays in pollution control (Shen, 2002; Ma and Zhu, 2007; Scurtu et al., 2008). Among these processes, the one-step treatment process is of particular interesting (Shen, 2002; Ma and Zhu, 2007). In this process, the synthesis of organoclays and the application of organoclays in pollution control are combined in one step. As thus, the wastewater treatment processes are simplified and the pollution control costs can be greatly reduced (Shen, 2002; Ma and Zhu, 2007).

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Despite of the great achievements for propelling the application of organoclays in pollution control, there remains one problem should be properly resolved. Just like other sorbents (e.g., activated carbon), organoclays will eventually become saturated during the sorption of organic pollutants, and the spent organoclays have to be regenerated and recycled (Yang et al., 2003). In the past decades, researchers have developed different methods for the regeneration of the spent organoclays, including biological degradation (Benzing, 1993; Guerin and Boyd, 1997; Witthuhn et al., 2005a,b, 2006), photo-assisted oxidation (An et al., 2008; Ilisz et al., 2002, 2004; Xiong et al., 2005a,b), chemical extraction/desorption (Anirudhan and Ramachandran, 2006; Bouraada et al., 2008), supercritical extraction (Cavalcante et al., 2005; Coelho et al., 2001; Coelho and Pawliszyn, 2004), thermal desorption (Lin and Cheng, 2002; Peters et al., 1991), et al. This review is to present a brief description of the characteristics and applications of these regeneration methods. In addition, several recycle methods other than direct regeneration are also reviewed. This review may provide some information for the researchers in selecting suitable or developing novel regeneration methods for spent organoclays.

## 2. The methods for organoclay regeneration

### 2.1. Biological degradation method

In the biological degradation method, microbes such as bacteria and yeast are used to degrade the sorbed organic pollutants, and then the spent sorbents can be regenerated. It has been employed for the regeneration of various spent sorbents after the sorption of organic compounds, e.g., activated carbon (Aktaş and Çeçen, 2007), biosorbents (Figueiredo et al., 2005). It has also been applied for the regeneration of spent organoclays, and the investigation results show that the regeneration efficiency strongly depends on the factors such as the type of microbes, molecular structure of organic pollutants and structural characteristics of organoclays (Benzing, 1993; Yang et al., 2003; Witthuhn et al., 2005a,b, 2006).

In most cases, the sorbed organic pollutants on organoclays are unavailable for degradation by microbes, and they should first be desorbed (Hermosín et al., 2006; Bruna et al., 2008; Celis et al., 2002a,b). However, several researches also found that some microbes can directly degrade the sorbed organic pollutants. Boyd and his co-workers (Crocher et al., 1995; Guerin and Boyd, 1997) show that *Pseudomonas putida* has direct access to a portion of the organoclays (hexadecyltrimethylammonium modified montmorillonite) sorbed naphthalene. Thereby, this bacterium can degrade naphthalene more quickly and efficiently than *Alcaligenes* sp. does, which cannot directly degrade the sorbed naphthalene. More than 40% of naphthalene can be mineralized by *P. putida* within hours, while no more than 15% can be mineralized by *Alcaligenes* sp. in the same time course. But still less than 45% of the naphthalene can be mineralized by the two bacteria even after 60 h regeneration.

The complete desorption and degradation of organic pollutants from spent organoclays has been achieved in other researches using bacteria as degrader. Witthuhn et al. (2005a,b, 2006) found that the desorption of 2,4-dichlorophenol and chlorobenzene from dioctadecyldimethylammonium modified montmorillonite is rather quick and complete, and the desorption process is not rate-limiting. As thus, 2,4-dichlorophenol and chlorobenzene can be completely degraded by *Ralstonia eutropha* JMP 134-1 and *Rhodococcus* B528 respectively in the range of hours.

Yeast has some advantage over bacteria in the degradation of organic pollutants, e.g., strong tolerance to high solute concentration, easy to be separated from water (Yang et al., 2003). The yeast *Pityrosporum* sp. has been used for the regeneration of spent organoclays (hexadecyltrimethylammonium modified montmorillonite)

by Yang et al. (2003). The results show that the sorbed phenol can be completely desorbed and degraded as the incubation time is long enough (>90 h), and the degradation rate depends on the loading level of the cationic surfactant hexadecyltrimethylammonium. That is, as hexadecyltrimethylammonium loading level increases from 0.3 CEC (cation exchange capacity) to 0.7 CEC, the incubation time for complete degradation of phenol increases from about 90 h to 140 h. This is because the later has much stronger sorption capacity towards phenol (Yang et al., 2003). Their results also show that the sorption capacities of the regenerated organoclays can be retained even after four times of regeneration.

Since it does not need any additional agents and can be operated in situ, the biodegradation method can be used for the regeneration of spent organoclays from various application fields. This method is particularly suitable for in situ regeneration of spent organoclays from the soil and groundwater pollution control fields (Witthuhn et al., 2005a,b, 2006; Crocher et al., 1995; Guerin and Boyd, 1997). It is suggested that coupling organic pollutant immobilization on organoclays with in situ biodegradation can provide a comprehensive soil and groundwater restoration technology. In such case, organoclays will create a so-called reactive barrier, on which the organic pollutants can be sorbed and degraded in parallel. This can cause a permanent regeneration of the absorbent, and breakthrough of the contaminants caused by the exhausted sorption capacity of the sorbents can thus be prevented (Crocher et al., 1995; Guerin and Boyd, 1997).

It should be noted that cationic surfactants in solution will always have high toxicity to microbes (Nye et al., 1994; Crocher et al., 1995; Guerin and Boyd, 1997). This may significantly decrease the activity of microbes, and thus influence the regeneration efficiency of the spent organoclays. Thereby, desorption of cationic surfactants from spent organoclays should be extremely small. With this respect, the loaded amounts of cationic surfactants on organoclays are always controlled under the clays' CEC. In other words, the bioregeneration method is unsuitable for the organoclays with surfactant loading level larger than the clays' CEC.

### 2.2. Photo-assisted oxidation method

Photocatalytic oxidation and photosensitized oxidation, as advanced oxidation processes, can generate very reactive free radicals for the degradation of organic pollutants (Hoffmann et al., 1995; Xiong et al., 2005a,b). Under suitable conditions, these photo-assisted degradation techniques can quickly degrade organic pollutants to an extremely low concentration level; thus the photo-assisted degradation technique has been employed for the regeneration of spent organoclays in some researches (An et al., 2008; Ilisz et al., 2002, 2004; Xiong et al., 2005a,b).

The photo-assisted regeneration methods in these researches can be divided into two types. In the first type, the photocatalysts or photosensitizers are added to the suspension containing spent organoclays (Mogyorósi et al., 2002; Ilisz et al., 2002, 2004). With this respect, the sorbed organic pollutants are firstly desorbed to the solution and then are degraded under photo irradiation. As the process of desorption and degradation continues, the organoclays can be regenerated. In the second type, the photocatalysts or photosensitizers are incorporated into the interlayers of organoclays, and the resulting novel organoclays possess the capability to effectively sorb organic pollutants and degrade them on the organoclays (An et al., 2008; Xiong et al., 2005a,b).

The most widely used photocatalyst for the regeneration of spent organoclays is TiO<sub>2</sub>. Dombi and his colleagues (Mogyorósi et al., 2002; Ilisz et al., 2002, 2004) have done excellent work for the regeneration of spent organoclays using TiO<sub>2</sub> (they also call it

a combination of adsorption and destruction treatment process). Their results show that the wavelength and intensity of UV have great influence on the degradation efficiency of the sorbed organic pollutants (2-chlorophenol), and thus the regeneration efficiency of the spent organoclays (hexadecylpyridinium montmorillonite). With shorter-wavelength (>254 nm) UV irradiation, about 99% of the sorbed 2-chlorophenol can be degraded within 160 min in the TiO<sub>2</sub> suspension, but destruction of the organoclays has also been observed. With longer-wavelength (>310 nm) UV irradiation, the organic pollutants will take much longer time (7 h) to reach 99% degradation, and no destruction of organoclays has been observed. With this respect, the organoclays are regenerated well and can be used for further sorption of organic pollutants.

TiO<sub>2</sub> has also been incorporated in the interlayers of the clay minerals together with cationic surfactants in some researches. *Ilisz et al. (2004)* show that the resulting novel organoclays (hexadecylpyridinium and TiO<sub>2</sub> modified montmorillonite) can degrade 2-chlorophenol as effectively as the system combining organoclays and TiO<sub>2</sub> suspension does, but the destruction of the organoclays has been observed in the former case. *An et al. (2008)* use this type of novel organoclays (hexadecyltrimethylammonium and TiO<sub>2</sub> modified montmorillonite) for the removal of decabromodiphenyl ether from water. They find that the organic pollutant can be completely removed within 180 min of UV irradiation at 365 nm.

The widely used photosensitizer for the regeneration of spent organoclays is the metal phthalocyanine (*Xiong et al., 2005a,b; Xiong and Xu, 2007; Sun et al., 2008*). The advantage of the photosensitized oxidation using metal phthalocyanine over photocatalytic oxidation using TiO<sub>2</sub> is that the former can be activated under visible light (e.g.,  $\lambda > 450$  nm). Xu and his co-workers (*Xiong et al., 2005a,b, 2007; Sun et al., 2008*) have incorporated metal phthalocyanine to the interlayers of ionic surfactant modified clay minerals to make the organoclays regenerable. The resulting novel organoclays have been used for the removal of phenols (*Xiong et al., 2005a,b; Xiong and Xu, 2007*) and organic sulfides (*Sun et al., 2008*) from water. In this case, the sorbed organic pollutants on organoclays can be directly degraded by the singlet oxygen generated in situ, and thus the organoclays can be regenerated accompanying with the sorption process. The repeated experiments show that the organoclays are relatively stable and can be repeatedly used for sorption and degradation of organic pollutants.

Since light is critical for the activation of photocatalysts or photosensitizers to produce reactive free radicals for the degradation of organic pollutants, the photo-assisted regeneration method is unsuitable for in situ regeneration of spent organoclays from soil and groundwater remediation.

### 2.3. Chemical extraction/desorption method

The organic solvents (e.g., acetone) can strongly solvate the organic compounds. Thereby, the organic solvents have been used to extract the sorbed organic pollutants from organoclays, and then regenerate the spent organoclays (*Bouraada et al., 2008*). *Bouraada et al. (2008)* show that acetone has high extraction efficiency of basic dye (safranin) from anionic surfactant (Sodium dodecyl sulfate or sodium dodecyl benzene sulfonate) modified hydrotalcite without any change of the structure. The remained acetone on organoclays is removed by drying at 40 °C overnight, and the sorption capacity of the regenerated organoclays can also be retained. After two times of regeneration, the sorbents still have the removal efficiency towards safranin above 85%, which is the same as that using the original organoclays.

NaOH solution can efficiently desorb tannin (*Anirudhan and Ramachandran, 2006*) and phenol (*Yang et al., 2003*) from organoclays, and the desorption efficiencies are reported to reach 99.7% and 89.3%, respectively. This is because these ionic sorbates have different structural forms (molecular or ionic form) as solution pH changes, and the sorption capacities of both tannin and phenol on organoclays are weak in high pH value range. For example, *Anirudhan and Ramachandran (2006)* show that the sorption efficiency of tannin on hexadecyltrimethylammonium modified bentonite can reach 99% at pH 4, as compared to about 40% at pH 8.

It should be noted that in the chemical desorption method, both sorption capacity of the regenerated organoclays and desorption efficiency of the sorbates will decrease gradually as the regeneration cycle continues. *Yang et al. (2003)* find that in the fourth cycles, the sorption efficiency of phenol on the regenerated organoclay decreases from 99.7% to 88%, and the desorption efficiency decreases from 95.7% to 87.3%.

### 2.4. Supercritical extraction method

Supercritical fluid shows excellent extraction efficiency towards organic compounds from solid matrixes, and it has been used for the extraction of organic pollutants from various spent sorbents (*Coelho et al., 2001; Coelho and Pawliszyn, 2004; Salgın et al., 2004; Cavalcante et al., 2005*). The supercritical extraction technique has been applied to the extraction of organic pollutants, such as phenols (*Park and Yeo, 1999*), ethyl acetate (*Coelho et al., 2001; Coelho and Pawliszyn, 2004; Cavalcante et al., 2005*) and salicylic acid (*Salgın et al., 2004*), from the spent organoclays, and then the spent organoclays can be regenerated. It shows that the factors as density and viscosity of the supercritical liquid are the determinants for the extraction of sorbed organic pollutants (*Park and Yeo, 1999*). Under optimal conditions, *Park and Yeo (1999)* report that the extraction efficiencies of phenols from spent organoclays can be up to 90%, and *Cavalcante et al. (2005)* also report a 84% extraction efficiency for ethyl acetate.

The extraction efficiency of organic pollutants may be further improved in the presence of cosolvent. *Salgın et al. (2004)* show that the maximum extraction percentage of salicylic acid from organoclays is about 76% by using CO<sub>2</sub> supercritical fluid without the addition of cosolvent. However, with the addition of 10 vol% of ethanol as cosolvent, the extraction efficiency can reach 98%, and the spent organoclays can be well regenerated.

In the supercritical extraction method, the activity of ionic surfactant can remain intact during the extraction of sorbates, and the organoclays exhibit undiminished sorption capacity towards phenols after several regeneration cycles (*Coelho et al., 2001; Coelho and Pawliszyn, 2004*). In addition, it is possible to recycle of the extracted organic compounds. But this method also has its limitation. For example, the cost is high and the operation condition is rather complex.

### 2.5. Thermal desorption regeneration

In the thermal desorption method, the spent organoclays are heated to a relatively high temperature range to desorb the organic pollutants from organoclays, and then the spent organoclays can be regenerated (*Peters et al., 1991; Lin and Cheng, 2002*). Thereby, this regeneration method is primary used for the regeneration of spent organoclays after their sorption of volatile organic compounds (VOCs) and semivolatiles organic compounds (SVOCs).

*Lin and Cheng (2002)* use the thermal desorption method for regenerate organoclays after the sorption of phenol and m-chlorophenol. The air dried spent organoclays are put in a quartz

cylinder and then heated to above 100 °C for 2 h under N<sub>2</sub> protection. Results show that with increasing temperature from 100 to 300 °C, the sorption capacities of the regenerated organoclays are shown to first increase and reach a peak approximately around 200–250 °C. Further increase of temperature results in a decrease of sorption capacities of the regenerated organoclays. This has been ascribed to the decomposition of sorbates and ionic surfactants on clay interlayers. They suggest that 200 °C is the optimal temperature for the regeneration, and most of the organoclays show only slight decrease of sorption capacities toward phenol and m-chlorophenol after five sorption–regeneration cycles under this temperature.

### 3. Methods for recycling the spent organoclays

Besides the direct regeneration of the spent organoclays, several methods for recycling the spent organoclays are also developed. In these methods, the structures of the spent organoclays are destroyed, but the resulting materials can be used to sorb organic pollutants directly or after further modification (Michot and Pinnavaia, 1991; Zhu et al., 1997; Wu et al., 2001).

Zhu et al. (1997) heat the spent organoclays to a high temperature range between 200 and 500 °C under the protection of nitrogen gas, and then the spent organoclays are carbonized. The resulting materials can further efficiently remove naphthol and naphthylamine from water, and the removal efficiencies can reach 90.5% and 94.2%, respectively.

Michot and Pinnavaia (1991) and Wu et al. (2001) develop a class of novel organoclays by incorporating both surfactant and hydroxyl-metal into the interlayers of clay minerals. The organic moiety is to form sorption domains for organic pollutants, while the inorganic moiety is to form pillars upon heating, which can keep the layered and porous structure of the clay minerals. With this respect, the spent organoclays can be heated to remove the sorbates and surfactants, while the layered structure of the clay minerals is retained. This enables the heated clay mineral load with organic agents again, and the resulting organoclays can also efficiently remove organic pollutants from water. The process of sorption–heating–loading can be cycled again and again.

The spent organoclays have also used as starting materials for synthesizing porous clay heterostructures (PCHs) by Zhu et al. (2005). In their work, the spent organoclays (hexadecyltrimethylammonium modified montmorillonite) after sorption of *p*-nitrophenol are mixed with tetraethylorthosilicate and dodecylamine to react for 4 h at 50 °C, and then calcined at 550 °C for 6 h. The BET surface area of the resulting PCHs is 661.5 m<sup>2</sup>/g, which is comparable to that of PCHs synthesized from organoclays (690.4 m<sup>2</sup>/g). It also shows that the PCHs have excellent sorption capacity towards VOCs.

Since the spent organoclays still remain some of the characteristics of original organoclays, they should also have application potential in a wide range of fields. Thereby, in addition to the direct regeneration, more methods can be developed for recycling the spent organoclays.

### 4. Conclusions

Regeneration of the spent organoclays is of great importance for the application of organoclays in organic pollution control, and various regeneration methods are developed in the previous researches. In most of these methods, either chemical agents (e.g., extraction agents, oxidation agents) or auxiliary (e.g., light, heat) have to be added during the regeneration process, which renders the regeneration process effective and/or rapid, but the costs will be relatively high. While in the bioregeneration method, the microbes

can grow without the addition of any chemical agents or auxiliary, which can significantly reduce the regeneration costs. In addition, the bioregeneration method can be operated in situ. Thereby, this method has particular advantage over other methods for the in situ regeneration of spent organoclays from soil and groundwater remediation. However, the processing time is always long in the bioregeneration method. Thereby, the developed regeneration/recycling methods have their own advantages and limitations, and we should choose suitable method according to the characteristics of these methods and source of the spent organoclays.

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