Research progress of novel adsorption processes in water purification: A review

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Abstract

As an effective, efficient, and economic approach for water purification, adsorbents and adsorption processes have been widely studied and applied in different aspects for a long time. In the recent years, a lot of novel adsorption processes have been developed for enhancing the efficiency of removing the organic and inorganic contaminants from water. This article reviews some new adsorbents and advanced adsorption methods that specialize in their compositions, structures, functions, and characteristics used in water treatment. The review emphasizes adsorption/catalytic oxidation process, adsorption/catalytic reduction process, adsorption coupled with redox process, biomimetic sorbent and its sorption behaviors of POPs, and modified adsorbents and their water purification efficiency.

Key words: adsorbents; adsorption; pollutants; water purification

Introduction

Various treatment techniques and processes have been used to remove the pollutants from contaminated water. Among all the approaches proposed, adsorption is one of the most popular methods and is currently considered as an effective, efficient, and economic method for water purification. The adsorbents used include activated carbon (Nouri *et al.*, 2002; Pereira *et al.*, 2003), clay minerals (Celis *et al.*, 2000; Abollino *et al.*, 2003), zeolites (Oliveira *et al.*, 2004), metal oxides (Wu *et al.*, 2004, 2005; Zhang *et al.*, 2007a), agricultural wastes (Robinson *et al.*, 2002), biomass (Loukidou *et al.*, 2003) and polymeric materials (Atia *et al.*, 2003).

Due to its high surface area, porous structure, and special surface reactivity, activated carbon has been the most popular and widely used adsorbent in water purification all over the world (Babel and Kurniawan, 2003). This adsorbent is highly inert and thermally stable, and it can be used over a broad pH range. Although it has great capacity of adsorbing various organic compounds and can be easily modified by chemical treatment to increase its adsorption capacity, activated carbon has several disadvantages. It is expensive and the powdered one is difficult to be separated from aquatic system when it becomes exhausted or the effluent reaches the maximum allowable discharge level. Furthermore, adsorption process just transfers pollutants from one phase to another rather than eliminating them from the environment. The regeneration of exhausted activated carbon by chemical and thermal procedure is also expensive and results in loss of the sorbent. Recently,

numerous approaches have been investigated for the development of cheaper and more effective novel composite adsorbents (Oliveira *et al.*, 2004; Gu *et al.*, 2005; Machado *et al.*, 2006; Zhang *et al.*, 2007b). These composite materials deserve particular attention because they combine the properties and advantages of each of their components. They represent an interesting and attractive alternative as adsorbents and/or catalysts due to their high reactivity and excellent selectivity towards specific pollutant compounds. This article describes the latest development in the above aspects.

1 Adsorption/catalytic oxidation process

Adsorption/catalytic oxidation process can be divided into two categories: in situ and out situ adsorption with catalytic oxidation, according to whether adsorption process and oxidation process occur in the same reactor. Evidently, the photocatalytic degradation of organic pollutants by TiO₂ supported on adsorbents belongs to the former. The adsorption and catalytic oxidation of dyes by magnetic metal oxide composite (Wu *et al.*, 2004) can be identified under the latter described.

1.1 Photocatalytic degradation by TiO₂ supported on adsorbents

Titanium dioxide has been widely used as photocatalytic material for removing toxic chemicals from waters. However, certain limitations exist in using bare TiO₂ in photocatalytic reactors. For example, due to small size (about 4–30 nm) TiO₂ aggregates rapidly in a suspension losing its effective surface area as well as the catalytic

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efficiency (Bhattacharyya *et al.*, 2004). It also shows low adsorption ability for the pollutants due to its non-porous property (Torimoto *et al.*, 1997), especially for the non-polar organic compounds due to its polar surface (Lepore *et al.*, 1996). Thus, in recent years, attempts have been made to immobilize fine TiO_2 on porous adsorbent materials like silica (Lepore *et al.*, 1996; Xu *et al.*, 1999), activated carbon (Torimoto *et al.*, 1997; Yoneyama and Torimoto, 2000), alumina (Anderson and Bard, 1997), clay and zeolites (Sampath *et al.*, 1994; Xu *et al.*, 1997; Bhattacharyya *et al.*, 2004) to produce composite adsorbent/catalyst. The sol-gel route is well established as an excellent method to prepare the TiO_2 -based materials.

TiO_2 supported on adsorbent provides higher specific surface area and facilitates more effective adsorption sites than bare TiO_2 (Anderson and Bard, 1995; Takeda *et al.*, 1997). And the degradation rates of organic pollutants are usually better than that of bare TiO_2 . For example, Bhattacharyya *et al.* (2004) loaded TiO_2 on three different kinds of porous adsorbents, mesoporous (MCM-41), microporous (β -zeolite), and pillared structure (montmorillonite) using sol-gel method, and the photocatalytic efficiency of the supported catalysts was evaluated using an azo-dye, namely, Orange II as model compound in water under different operating conditions. Their results revealed that these three supported composite catalysts were more effective than bare TiO_2 in photodegradation of Orange II. A similar result was obtained by Machado *et al.* (2006b) who dispersed TiO_2 on the surface of high surface area vermiculite to prepare composite adsorbent/catalyst for the decomposition of reactive textile dye, namely, Drimaren Red. Noticeably, the composite with a high specific area can be floating on the water surface. In their opinions, the enhanced decomposition rates are attributed to the increased condensation of organic substrates on the supported catalyst by adsorption and the reduced electron-hole recombination process on the surface.

1.2 Adsorption and catalytic oxidation by magnetic metal oxide composite

Another kind of composite adsorbent/catalyst, which processes high adsorption capacity and catalytic activi-

ty towards organic compounds, is magnetic metal oxide composite and magnetic metal oxide supported adsorbents. Wu and co-workers (Wu *et al.*, 2004, 2005) firstly prepared magnetic metal oxide composite adsorbents (powder CuFe_2O_4 and $\text{MnO-Fe}_2\text{O}_3$) by a simple co-precipitation method from environmental friendly and low cost materials. These adsorbents have a relatively high surface area, a smaller particle size, and porous structure. In particular, the excellent magnetic property of the powders makes them to be easily recovered by magnetic separation technology after adsorption or regeneration, which overcomes the disadvantage of separation difficulty of common powdered adsorbents.

The adsorption performance of the magnetic composites was studied using azo dye, namely, Acid Red B (ARB) as a model compound. The results demonstrated that both the CuFe_2O_4 and $\text{MnO-Fe}_2\text{O}_3$ adsorbents had high adsorption rate and the maximal adsorption capacities for ARB are 86.8 and 105.3 mg/g, respectively. Through systematic thermal degradation experiments and in situ Fourier transform infrared (FTIR), along with by-product analysis by GC-MS, the catalytic combustion process of ARB on CuFe_2O_4 was thoroughly investigated. It was found that the CuFe_2O_4 had high catalytic activity, and it greatly lowered the degradation temperature of ARB. This can be easily seen from Fig.1 (Wu *et al.*, 2004). Similarly, $\text{MnO-Fe}_2\text{O}_3$ also had high catalytic activity, despite being not higher than that of CuFe_2O_4 . The regeneration experimental results suggested that these adsorbents could be used repeatedly over many cycles.

On the other hand, Peng *et al.* (2006) prepared a montmorillonite-Cu(II)/Fe(III) oxides magnetic composite adsorbent using the same method of co-precipitation. In comparison with that of montmorillonite, the specific surface area of the composite increased remarkably. The composite was used to remove humic acid from water and exhibited favorable adsorption capacity. The exhausted montmorillonite-Cu(II)/Fe(III) oxides were regenerated under 300°C and the result confirmed the high catalytic activity of copper ferrite once again.

The magnetic composite adsorbents are good for adsorption of pollutants and their separation from water. But they

Fig. 1 FTIR spectra of Acid Red B (ARB) combustion in the absence of CuFe_2O_4 (a) and $\text{ARB/CuFe}_2\text{O}_4$ combustion (b) at different temperatures (Wu *et al.*, 2004).

also have some shortcomings. For example, only certain kind of pollutants can be adsorbed by them.

Up to now, numerous new composite adsorbents have been developed for water purification by adsorption/catalytic oxidation process. Every one has its own advantage and disadvantage. It seems that these magnetic composite adsorbents that own high catalytic activity and are easily separated from aquatic system are more promising in practical application.

2 Adsorption/catalytic reduction process

Adsorption/catalytic reduction process has been found to be efficiently used in water purification. In the recent years, many kinds of adsorbents with the catalytic reduction function were developed and used in removing nitrate, heavy metals, and organic pollutants from water. Here, we take the modified hydrotalcite-type (HT) adsorbent as an example.

2.1 Hydrotalcite-type (HT) adsorbent and its modification

HT compounds, a class of layered double hydroxides, consist of positively charged metal hydroxide layers separated from each other by anions and water molecules (Cavani *et al.*, 1991). It was found that many kinds of cations, whose ionic radius are not too different from that of Mg^{2+} , may be introduced inside the brucite-like sheet, and thus, HT with various compositions and structure were obtained. This feature resulted in the occurrence of more synthetic HT compounds, which consequently exploited their further application in various scopes. Wherein, the use of HT as a kind of adsorbent in the water treatment was focused by many researchers. As reported, many kinds of ions, such as inorganic anions (Kuzawa *et al.*, 2006; Yoshioka *et al.*, 2007), organic acids (Silverio *et al.*, 2007), and colored organics (Orthman *et al.*, 2007; Bouraada *et al.*, 2007), may enter the interlayer space of HT and consequently be adsorbed. Especially, after calcinations, the reconstruction of the original hydrotalcite with the positive charge layers was obtained. Researches (Sasaki *et al.*, 2006) indicated that Zn-Al hydrotalcite, with the intercalation of water-soluble *p*-sulfonated calix arene (CS4) in the interlayer, showed effective adsorption capacity for benzyl alcohol and *p*-nitrophenol and would be new organic-inorganic hybrid adsorbents for many organic molecules. Additionally, another important application of HT compounds was as a catalyst or catalyst support (Chang *et al.*, 2007; Parida *et al.*, 2007). Because of the electrostatic repulsive force between M^{II} and M^{III} cations

on the brucite-like sheet, higher dispersion of cations may be obtained. This result facilitated the formation of the homogeneous mixtures of oxides with small crystal size after calcinations, which was usually beneficial for catalytic reaction.

2.2 Hydrotalcite-supported Pd-Cu adsorbent for nitrite removal

In recent years, nitrate contamination of water in many parts of the world has become a serious problem. Accordingly, the current technologies used for nitrate removal from water receive an increasing attention. Based on the property of HT, a novel hydrotalcite-supported Pd-Cu material, combining the high adsorption capacity of HT and the reduction property of active metals (Pd-Cu) for nitrate, were developed (Wang Y, 2006; Wang *et al.*, 2007a). In this case, HT was used not only as an adsorbent but also as a catalyst support. The performance of adsorption and chemical catalytic reduction of nitrate may be promoted by each other. In these processes, nitrate ions in water may be adsorbed by HT, which would enhance the concentration of nitrate ions around active sites (Pd-Cu) on HT, and thus, increase the catalytic reduction efficiency of nitrate. Inversely, catalytic reduction of nitrate may refresh the surface of HT, and then promote the continuous adsorption of nitrate on HT.

Table 1 shows the main characteristics of a series of powder-calcined hydrotalcite-supported Pd-Cu materials with the same Pd-Cu loading (about 1 wt.% Pd and 0.25 wt.% Cu) for nitrate adsorption and catalytic reduction from water (Wang *et al.*, 2007b). The results indicated that these materials exhibited high surface area of 183.9–236.6 m^2/g and mesopore structure. The highest was obtained on the material prepared by co-precipitation method, which exhibited more homogeneous dispersion of active metal clusters by the analysis of SEM and TEM (Wang *et al.*, 2006). Active metals of Pd and Cu on the surface of the catalyst presented both oxide and metallic state, in which metallic state was dominant. These characteristics were considered to be beneficial for the catalytic reduction reaction, and thus further evaluation on adsorption and catalytic reduction of nitrate using hydrogen as reducer were conducted.

According to the experimental results, hydrotalcite-supported Pd-Cu materials showed effective adsorption capacity for nitrate removal from water, which followed the order: HT3 (Pd-Cu) > Pd-Cu/HT5 > Pd-Cu/HT3 > Pd-Cu/HT2 > Pd-Cu/HT4. The material obtained by co-precipitation exhibited a higher adsorption capacity for nitrate than that prepared by the co-impregnation

Table 1 Chemical composition and characteristics of different hydrotalcite supported Pd-Cu materials (Wang *et al.*, 2007b)

Sample	Atomic ratio of Mg/Al	Preparation method	BET (m^2/g)	Volume of pores (ml/g)	Average diameter of pores ($\times 10^{-10}$ m)
Pd-Cu/HT2	2	impregnation	184.7	0.250	52.17
Pd-Cu/HT3	3	impregnation	185.3	0.243	52.20
Pd-Cu/HT4	4	impregnation	183.9	0.241	54.23
Pd-Cu/HT5	5	impregnation	195.0	0.228	46.68
HT3 (Pd-Cu)	3	coprecipitation	236.6	0.849	143.60

method. Theoretically, the maximum adsorption amount (q_m) reached 9.44 mg- NO_3^- -N/g for HT3 (Pd-Cu) (Wang *et al.*, 2007b).

As reported in literature (Maia *et al.*, 2007; Laurin *et al.*, 2006), catalytic reduction of nitrate ions obeys a consecutive reaction scheme, in which nitrite appears as an intermediate, whereas nitrogen and ammonia are the final products. Wang *et al.* (2007b) compared the catalytic reduction capacity of hydrotalcite-supported Pd-Cu materials for nitrate using hydrogen as reducer in a batch reactor. After 180 min reaction, the total removal rate for nitrate was 61.9%, 79.4%, 47.0%, 85.4%, and 96.8% for Pd-Cu/HT2, Pd-Cu/HT3, Pd-Cu/HT4, Pd-Cu/HT5 and HT3 (Pd-Cu), respectively. The order of catalytic reduction capacity of these materials agreed well with the result of adsorption. Simultaneously, nitrite and ammonium ions were formed during the catalytic hydrogenation for nitrate. The highest selectivity for N_2 was observed on HT3 (Pd-Cu). It indicated that different ratio of Mg/Al and preparation method resulted in different adsorption and catalytic reduction capacity. Furthermore, the preparation method was a key influencing factor, and the material prepared by co-precipitation method showed the highest adsorption and catalytic reduction capacity, possibly due to different introduction method of active metals (Wang *et al.*, 2007b).

Temperature and co-existed ions in water influence the adsorption and catalytic reduction capacity of hydrotalcite-supported Pd-Cu materials for nitrate (Wang *et al.*, 2007b). Higher reaction temperature promoted the adsorption and catalytic reduction capacity of hydrotalcite-supported Pd-Cu materials and simultaneously debased the accumulation of nitrite and ammonium. Co-existed cations in water with higher valence, and lower crystal ionic radius and solubility constant of hydroxide showed a stronger affinity toward OH^- and consequently increased the concentration of active sites accessible to NO_3^- and NO_2^- . The competitive adsorption of Cl^- , SO_4^{2-} , and HCO_3^- with nitrate on the surface of hydrotalcite-supported Pd-Cu materials suppressed the adsorption and reduction of NO_3^- .

It was speculated that the nitrate removal on these materials, with H_2 provided, was a consecutive and dynamic adsorption and catalytic hydrogenation process, as shown

Fig. 2 A reaction scheme for the catalytic hydrogenation of nitrate on hydrotalcites-supported Pd-Cu catalysts (Wang *et al.*, 2007b)

in Fig.2 (Wang *et al.*, 2007b). First, layer structure may be reconstructed once calcined hydrotalcite was put into nitrate solution. During this process, nitrate ions were adsorbed rapidly between the brucite-like layers and on the external surface by electrostatic force, resulting in high adsorption rate at the initial time. Then, adsorbed nitrate ions were reduced by Pd/Cu active sites to nitrite ions, which were sequentially reduced to N_2 or ammonium. The electroneutrality of the system was maintained by the OH^- anions produced during the reduction process. Whereafter, hydrotalcite-supported Pd-Cu materials may continuously adsorb nitrate ions through ion exchange with OH^- , which was followed by the catalytic hydrogenation process. Therefore, the prepared hydrotalcite-supported Pd-Cu materials may effectively combine the adsorption and catalytic reduction process, and thus exhibit a good potential for nitrate removal from water.

3 Adsorption coupled with redox process

Combining the oxidation and reduction effect in adsorption processes, some redox composite adsorbents have been developed and applied in water purification recently. It is a good example to remove arsenic from drinking water by using novel redox adsorbents.

In natural water, arsenic is primarily present in inorganic forms and exists in two predominant species, namely, arsenate (As(V)) and arsenite (As(III)). As (III) is much more toxic (Ferguson and Gavis, 1972), more soluble, more mobile, and more difficult to dispose than As(V). Various adsorbents including natural and synthetic materials are effective for As(V) (Driehaus *et al.*, 1998) but fail in case of As(III) (Driehaus *et al.*, 1994). To achieve higher arsenic removal, a pretreatment for As(III) oxidation is, therefore, usually involved followed by adsorption of the As(V) formed onto metal oxyhydroxides. However, the pretreatment increased not only running cost but also the complexity of operation. Besides, traditional oxidants such as chlorine, ozone, and hydrogen peroxide are not feasible for a specific oxidation of As(III) because of the side reactions with natural organic matter. So, the development of adsorbent that could simultaneously oxidize arsenite and adsorb the formed arsenate is becoming the focus of research (Chakravarty *et al.*, 2002; Deschamps *et al.*, 2005; Zhang and Itoh, 2006; Zhang *et al.*, 2007b). Many composite adsorbents have been developed, and they can be mainly divided into the following two classes.

3.1 TiO_2 -based composite adsorbents

As mentioned above, titanium dioxide is an excellent photocatalytic material. Using titanium dioxide photocatalyst, the arsenite can be rapidly oxidized to arsenate. The oxidation mechanism of arsenite has been studied by several researchers and most of them believed that hydroxyl radicals are the dominant oxidants for arsenite oxidation (Dutta *et al.*, 2005; Xu *et al.*, 2005a). Moreover, titanium dioxide can also be used as a sorbent for arsenic removal (Bang *et al.*, 2005; Pena *et al.*, 2006). Bang and co-workers (2005) thoroughly investigated the adsorption

performance of nano and granular titanium dioxide towards both arsenate and arsenite. They found that titanium dioxide had a relatively high adsorption capacity. But the arsenite removal by the TiO_2 adsorbent was not effective as that of arsenate. Furthermore, the adsorption mechanism of arsenate and arsenite on the surface of TiO_2 was also explained by using FT-IR spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy and found that both As(V) and As(III) formed bidentate binuclear inner-sphere surface complexes (Pena *et al.*, 2006).

However, the low adsorption capacity and separation problem of TiO_2 powder from aqueous solution usually limit its application in contaminated water. In order to utilize the photocatalytic activity of TiO_2 and the adsorption capacity of iron oxide sufficiently, Zhang and Itoh (2006) prepared a slag-iron oxide- TiO_2 composite adsorbent by loading iron oxide and TiO_2 on municipal solid waste melted slag for arsenite removal. The synthetic composite could rapidly oxidize arsenite to arsenate and simultaneously remove the arsenate from aqueous solution.

3.2 MnO_2 -based composite adsorbents

Manganese dioxide is an effective oxidizing agent of arsenite and is emphasized by some researchers (Oscarson *et al.*, 1981; Stumm and Morgan, 1981). In addition, due to relatively low oxidation potential, MnO_2 is a favorable oxidant for specific oxidation of arsenite. The redox reaction mechanism between manganese dioxide and arsenite has been investigated by some researchers (Scott and Morgan, 1995; Nesbitt *et al.*, 1998; Manning *et al.*, 2002). The works by Moore *et al.* (1990) and Nesbitt *et al.* (1998) demonstrated that the oxidation of As(III) by the synthetic birnessite surface proceeds by a two-step pathway, involving the reduction of Mn(IV) to Mn(III) and then Mn(III) to Mn(II).

Manganese dioxide can also be used as adsorbent for removal arsenic, but its adsorption capacity is commonly low (Lenoble *et al.*, 2004) and this limits its application. To improve the removal efficiency, many composite adsorbents containing MnO_2 have been synthesized. For examples, a manganese dioxide-coated sand (MDCS) adsorbent was prepared (Bajpai and Chaudhuri, 1999) by the oxidation of manganous ion by permanganate in the presence of sand. The MDCS showed a good removal performance for both arsenate and arsenite. Lenoble *et al.* (2004) achieved an R- MnO_2 adsorbent by loading manganese dioxide on a polystyrene resin matrix. The composite adsorbent had a markedly higher arsenic removal capacity than that of

manganese dioxide. Besides, synthetic Fe oxide-coated MnO_2 (Oscarson *et al.*, 1983) has also been studied for the oxidation and sorption of As(III), but its As(III) adsorption capacity was lower than that of pure Fe oxide since MnO_2 was coated by Fe oxide and could hardly oxidize As(III).

On the other hand, two natural Fe-Mn-mineral composite materials whose main components are Fe_2O_3 and MnO_2 have been investigated as adsorbents for As(III) and As(V) removal from water (Chakravarty *et al.*, 2002; Deschamps *et al.*, 2005). Both of them are more effective for As(III) removal than that of As(V). They ascribed the higher As(III) uptake to the oxidation ability of manganese oxides content. However, their adsorption capacities for both As(III) and As(V) are low.

Recently, a novel Fe-Mn binary oxide composite adsorbent has successfully developed from low cost materials using a simultaneous oxidation and co-precipitation method for arsenic removal (Zhang *et al.*, 2007b). This composite combined the oxidation property of manganese dioxide and the adsorption features to As(V) of iron (hydr)oxides which are well-known for their high affinity to arsenate and low cost (Pierce and Moore, 1982; Driehaus *et al.*, 1998; Dixit and Hering, 2003). The composite was well characterized with a variety of techniques. It was found that this adsorbent had a high specific surface area and abundant surface hydroxyls. The test results exhibited that it had a high removal capacity towards both As(V) and As(III) and showed a significantly higher As(III) uptake than As(V). The maximal adsorption capacities for As(V) and As(III) were 0.93 and 1.77 mmol/g, respectively. Fig.3

Fig. 3 Adsorption isotherms for As(III) and As(V) by Fe-Mn adsorbent in a 200 mg/L suspension at $\text{pH } 5.0 \pm 0.1$ at low equilibrium As solution concentrations (Zhang *et al.*, 2007b).

Table 2 Maximum arsenic adsorption capacities of some adsorbent system^a

Adsorbent	Max. As(III) adsorption capacity (mmol/g)	Max. As(V) adsorption capacity (mmol/g)	Reference
Fe-Mn composite	1.77 (pH 5.0)	0.93 (pH5.0)	Present study
MnO_2	0.13	0.1	Lenoble <i>et al.</i> , 2004
Goethite	—	0.53 (pH 3–3.3)	Matis <i>et al.</i> , 1997
$\text{Al}_2\text{O}_3/\text{Fe}(\text{OH})_3$	0.12 (pH 6.6)	0.49 (pH 7.2)	Hlavay <i>et al.</i> , 2005
Fe(III)-loaded sponge	0.24 (pH 9.0)	1.83 (pH 4.5)	Muñoz <i>et al.</i> , 2002
Fe-Mn-mineral material	0.16 (pH 5.5)	0.09 (pH 5.5)	Deschamps <i>et al.</i> , 2005 2005
TiO_2	0.43 (pH 7.0)	0.55 (pH 7.0)	Bang <i>et al.</i> , 2005

^a pH is shown in parentheses.

depicted this clearly (Zhang *et al.*, 2007b). These results are favorable, compared with those obtained using other adsorbents (Table 2). Furthermore, to interpret the result of higher arsenite removal, the mechanism of As(III) removal by the Fe-Mn binary oxide adsorbent was well approved (Zhang *et al.*, 2007c) and can be described as follows. As(III) was firstly transported to the solid-water interface by convection or diffusion from bulk solution. Then As(III) was adsorbed onto the surface by formation of surface complex. The adsorbed As(III) near the Mn atoms was oxidized into As(V) by MnO_2 and the formed As(V) released into the solution with the reductive dissolution of MnO_2 . During this process, fresh active adsorption sites were formed at the solid surface. The As(V) was then transported to the solid-water interface and adsorbed onto the surface of the Fe-Mn adsorbent, occupying empty adsorption sites or replacing the sorptive As(III). The whole process can be briefly represented by reaction equations (1)–(3).

where, $(-\text{S}_{\text{Fe-Mn}})$ represents an adsorption site on the Fe-Mn adsorbent surface. $\text{As(III)}-\text{S}_{\text{Fe-Mn}}$ represents the As(III) surface species and $\text{As(V)}-\text{S}_{\text{Fe-Mn}}$ represents the As(V) surface species. This process proceeded until As(III) or available MnO_2 was depleted.

The formation of fresh adsorption sites at the solid surface during As(III) oxidation was attributed to the higher As(III) uptake.

In a summary, TiO_2 -based composite adsorbents can effectively oxidize arsenite and remove the formed arsenate in water treatment. However, the arsenite removal process still needs UV light to produce oxidants and this makes it not so convenient to operate. On the contrary, MnO_2 -based composite adsorbents, in particular the Fe-Mn binary oxide adsorbent, could effectively oxidize arsenite and adsorb the produced arsenate simultaneously. Therefore, the immobilization and practical application of Fe-Mn composite materials may be a major research avenue in the arsenic removal.

4 Biomimetic sorbent and its sorption behaviors of persistent organic pollutants (POPs) in water

Researches had shown that most hazardous vestigial POPs are especially difficult to be eliminated from water by activated carbon due to the lower concentration of POPs, from nanogram per liter to picogram per liter in water (Wang and Liu, 2001; Zhang *et al.*, 2003). Consequently, it is attractive to develop novel sorbents to remove organic micropollutants from water efficiently.

Even at trace concentrations in water, POPs can accu-

mulate in the lipid of organisms, such as white whales (Andersen *et al.*, 2001), arctic wolves (Mary and Birgit, 1999), South African fur seals (Walter *et al.*, 1999), marketable fish (Ahmed and Aly, 2004), and mussels (Azza *et al.*, 2004; Perihan and Hulya, 2004). Using the concept of bioaccumulation, some researchers prepared biomimetic sorbent to remove POPs from water. Liu *et al.* (2005b) synthesized salmon milt DNA hydrogel beads as selective adsorbent of dioxins. Compared with normal adsorbents such as activated carbon and alumina, this DNA matrix showed a selective adsorptivity for the dioxin derivatives with planar structure such as dibenzo-*p*-dioxin, dibenzofuran, and biphenyl. Some researchers (Xu *et al.*, 2005b; Ke *et al.*, 2006) prepared a new type of composite membrane, triolein embedded-cellulose acetate membrane (TECAM), and used it in the uptake of six organochlorine pesticides. Results indicated that TECAM quickly and efficiently accumulated hydrophobic organochlorine pesticides (OCPs) from water. Semi-permeable membrane devices (SPMD), which are based on the diffusion of hydrophobic substances from water to membrane bags filled with lipophilic phases, are widely used for monitoring organic contaminants in water (Huckins *et al.*, 1990; Lu *et al.*, 2002; Lu and Wang, 2003; Frank, 2005). Recently, a novel composite absorbent, triolein-embedded sorbent, is proposed for selectively removing trace POPs from water (Ru *et al.*, 2007a, 2007b; Huo *et al.*, 2005a, 2005b; Liu *et al.*, 2005a, 2007).

4.1 Design and preparation of triolein-embedded sorbent

The designed structure of triolein-embedded sorbent is shown in Fig. 4. The sorbent either consists of the supporting materials and the surrounding triolein-embedded cellulose acetate membrane or prepares by embedding triolein into cellulose acetate (CA) spheres. Activated carbon and silicon gel granules were chosen as the supporting materials. The reasons for selecting triolein are that triolein has a high accumulation capacity (10^5 – 10^7) for trace concentrations of POPs in water (Chiou, 1985) and it exhibits low membrane solubility and permeability because of its large molecular mass of 885.45 Da (Huckins *et al.*, 1990). A cellulose acetate polymer was chosen for preparing hybrid materials because it can be easily molded into different forms such as membranes, fibers, and spheres. Furthermore, its hydrophilicity improves the

Fig. 4 Designed structure of triolein-embedded sorbent. 1: cellulose acetate membrane; 2: triolein; 3: supporting materials.

accessibility of aqueous solutions to the surface of the film.

Three sorbents were produced which were composed of supporting activated carbon (Ru *et al.*, 2007a, 2007b) or silicon gel granules (Huo *et al.*, 2005a, 2005b) and the surrounding triolein-embedded cellulose acetate membrane, or CA-triolein sphere (Liu *et al.*, 2005a, 2007), respectively. The analysis results of SEM and XPS for the sorbent showed that the triolein was wrapped in the thin CA polymer and constituted a significant fraction of the lipid pool in the sorbent. Fluorescence test showed that triolein was fixed in the cellulose membrane tightly and no triolein had been detected in the water when using the sorbent for the water treatment.

4.2 POPs removal efficiency by triolein-embedded sorbent

Dieldrin, endrin, aldrin, and heptachlor epoxide were chosen as model pollutants to test the sorption efficiency of triolein-embedded sorbent. Results showed that these pollutants could be removed by the CA-triolein adsorbent effectively. When the initial concentration of these selective POPs was 1–10 µg/L, nearly 90% of the POPs was removed after 1 h of sorption by the triolein-embedded sorbents. This suggests that triolein-embedded sorbent may serve as a good sorbent for those selected POPs. Triolein in the sorbent significantly increased the sorption capacity, and lower residual concentrations of POPs were achieved when compared to the use of cellulose acetate adsorbent and granular activated carbon (GAC). Results also indicated that triolein-embedded sorbent appeared to be a promising sorbent with good selectivity for hydrophobic organic compounds, and the adsorption rate and removal efficiency for lipophilic POPs were positively related to their octanol-water partition coefficients ($\log K_{ow}$). In addition, the sorbent also had satisfactory removal rate for lipophilic POPs from aqueous solutions when present in trace amounts.

A fixed-bed column experiment was also conducted to test the potential practical application. Results of the initial column experiments indicated that triolein-embedded sorbent had high removal efficiency for dieldrin when the influent concentration was 1–1.5 µg/L and the empty-bed contact time (EBCT) was 20 min. It did not reach the breakthrough point (0.1 µg/L) at breakthrough empty-bed volumes of 4000.

4.3 Sorption behaviors of POPs on triolein-embedded sorbent

The sorption isotherms of CA sorbent and triolein-embedded sorbent (CA-T), which using activated carbon as supporting material and GAC, were investigated using dieldrin as model pollutant. The results indicated that the experimental data fitted the Freundlich isotherm well in a range of initial concentrations from 1 to 50 µg/L, and the correlation coefficients were between 0.994 and 0.998, which is shown in Fig.5. The magnitude of K_F and n values showed the easiest uptake of dieldrin and the highest equilibrium adsorptive capacity of CA-T.

The sorption of POPs on triolein-embedded sorbents has

Fig. 5 Dieldrin adsorption isotherms at 25°C (Ru *et al.*, 2006).

four steps. Organic pollutants were firstly adsorbed onto the surface of sorbents, then transferred into channels of CA, and finally absorbed into the triolein. If there are supporting materials, the pollutants will be absorbed into the supporting materials.

The above sorption process can be proved by the intra-particle diffusion equation for bio-sorption systems, which is given by Weber and Morris (1963):

$$q_t = k \times t^{0.5} \quad (4)$$

where, q_t is the amount of adsorbent at time t (µg/g) and k is the rate constant (µg/(g·h^{0.5})).

The multilinear plots of q_t vs. $t^{0.5}$ using the absorption results showed the intra-particle diffusion model for CA-triolein sphere sorbent. The order of absorption rate for the POPs follows the order $k_1 > k_2 > k_3$. In addition, the absorption rate for the four selected POPs has positive relation with the $\log K_{ow}$ of the chemicals.

The thermodynamic analysis of dieldrin sorption on triolein-embedded with experimental data of different temperatures was conducted. Thermodynamic parameters, such as change in free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) were calculated from the variation of the thermodynamic equilibrium constant K_0 with the change in temperature. The calculation methods used were discussed in detail by Niwas *et al.* (2000). A positive value of ΔH^0 indicated that the adsorption of dieldrin on CA-triolein sphere was endothermic. Since ΔG^0 were negative and were accompanied by positive ΔS^0 , the reactions were spontaneous with high affinity for dieldrin (Matsui *et al.*, 2003).

The results of the triolein-embedded sorbent showed that it is a promising sorbent for removal of the trace level POPs. These encouraging results will help in future work to address engineering issues for implementing the process on a larger scale.

5 Modified adsorbents and their water purification efficiency

Adsorbent which is modified by physical or chemical method could be recognized as modified adsorbent. Actually, almost all the adsorbents can be modified to

enhance the adsorption capacity and the efficiency in water treatment. Modified adsorbents are, therefore, various, and the number is tremendous. For example, several tens of carbon-based modified adsorbents from granular activated carbon, powdered activated carbon, and carbon nanotube can be found in the literature. Here, we would like to emphasize the magnetic particles modified adsorbents because these adsorbents can be easily prepared and utilized in the water purification. The main aim of developing such adsorbents is to integrate two separate phases for enhanced separation. In brief, these adsorbents may be classified as three categories, according to the difference of the support of magnetic particles.

5.1 Surface modified Fe_3O_4 adsorbent

Magnetite is one of the most common and important magnetic materials. As a magnetic particle, it can be easily integrated with other adsorbents to produce magnetic composite adsorbent for water purification. But commercially available Fe_3O_4 is usually poor in adsorption properties, except for nano-scale one.

To enhance the adsorption capacity of commercial Fe_3O_4 , Wu and Qu (2004) modified it by the precipitate of Fe(III) hydroxide on the surface without affecting its magnetism property. Acid Red B was selected as a model organic compound for adsorption test in the study. The results showed that the specific surface area and the adsorption capacity of modified Fe_3O_4 for Acid Red B significantly increased. Besides, the regeneration of saturated sorbent by oxidation using Fenton's reagent was investigated. They found the modified magnetite could be well regenerated even with a higher adsorption capacity and be used repeatedly.

5.2 Magnetic-particle-modified carbon adsorbent

The powdered activated carbon not only has high adsorption rate and capacity for various organic pollutants but is inexpensive. However, it is difficult to separate it from aquatic phase because of its small size. The traditional filtration method could cause the blockage of filters. Therefore, powdered activated carbon has been traditionally discarded with the process sludge after using it in water treatment (Clifford *et al.*, 1983).

Recently, the synthesis of magnetic carbon adsorbent by integrating magnetic particles with powdered activated carbon has gained increasing attention from a good many of researchers worldwide. A series of activated carbon/magnetic particle composites have been prepared. And several methods such as impregnation (Wang *et al.*,

1994; Gorria *et al.*, 2006), ball milling (Rudge *et al.*, 2000), and chemical co-precipitation (Šafařík *et al.*, 1997; Oliveira *et al.*, 2002) have been developed. Among these methods, chemical co-precipitation is the most promising one because it is simple and no special chemicals and procedures are needed.

The most frequently used magnetic particle is iron oxide, especially magnetite. Researchers (Šafařík *et al.*, 1997; Oliveira *et al.*, 2002) have successfully prepared activated carbon/iron oxide magnetic composites, which could be used to remove a wide range of organic pollutants and be separated by magnetic separation technology conveniently. Gorria *et al.* (2006) synthesized a magnetic activated carbon containing nickel nanoparticles within the porous network. The magnetic composite obtained exhibits a large surface area and a high pore volume. In addition, Peng *et al.* (2005) prepared a carbon nanotube-iron oxides magnetic composite and tested the adsorption of Pb(II) and Cu(II) from water. The findings reveal that the composite adsorbent has high effectiveness for metal ion removal. However, these studies mainly focused on how to make activated carbon magnetic but no regeneration of the spent magnetic composites was involved.

To combine the high adsorption capacity of activated carbon with the magnetic and excellent catalytic properties of powdered CuFe_2O_4 , Zhang *et al.* (2007a) synthesized a novel magnetic CuFe_2O_4 /activated carbon composite adsorbent using a chemical co-precipitation method. The characteristics such magnetization and BET surface area of the obtained adsorbent were determined. The results indicate that the composite was magnetic and the presence of CuFe_2O_4 did not significantly affect the surface area and pore structure of the activated carbon. This can be confirmed by the data listed in Table 3. Besides, the adsorption of azo dye Acid Orange II on the adsorbents was examined by batch tests. Interestingly, no reduction in adsorption capacity was produced by the formation of the composite when used to adsorb Acid Orange II from water, compared with original activated carbon. The adsorption isotherm in Fig.6 can exhibit this result (Zhang *et al.*, 2007a). Furthermore, the decomposition process of Acid Orange II adsorbed on the surface of activated carbon and the composite in an inert atmosphere was studied by the authors using *in situ* FTIR technique. The results indicated that the CuFe_2O_4 particles could effectively catalyze the thermal pyrolysis of Acid Orange II. The results of regeneration tests suggested that the most adsorption capacity of the composite adsorbent was re-established after thermal treatment and it could be used for several recycles.

Table 3 Magnetization, BET surface area and microporosity measurements for the CuFe_2O_4 /activated carbon composites (Zhang *et al.*, 2007)

Composite	CuFe_2O_4 (wt.%)	Specific saturation magnetization (emu/g)	BET surface area (m^2/g)	Micro-pore volume(cm^3/g)
Pure activated carbon	0	0	799	0.229
Composite 1:2	33	0.97	558 (794*)	0.153 (0.223*)
Composite 1:1.5	40	2.30	549 (857*)	0.144 (0.231*)
Composite 1:1	50	5.93	488 (889*)	0.118 (0.223*)
CuFe_2O_4	100	22.5	87	0.013

*expressed on activated carbon mass basis.

Fig. 6 Adsorption isotherm for Acid Orange 7 (AO7) on (a) original activated carbon and (b) the 1:1.5 composite. (50 ml AO7 solution, initial concentrations up to 1200 mg/L, pH 5.2 ± 0.1 ; $25 \pm 1^\circ\text{C}$; 0.100 g adsorbent).

5.3 Magnetic-particles-modified clay mineral adsorbent

As a kind of low-cost and readily available materials, clay minerals have excellent cation exchange properties and are often used to adsorb metallic contaminants in the water treatment. The adsorption capacity of clays results from a relatively high surface area and a net negative charge on their structure. But the smaller particle size of the clays make them difficult to separate from water phase like the powdered activated carbon.

To separate the clay adsorbents conveniently, Oliveira *et al.* (2003, 2004) combined iron oxide with clay minerals and achieved two kinds of magnetic particle modified adsorbents, namely, bentonite-iron oxide and zeolite-iron oxide magnetic adsorbents. The adsorbents obtained both have good magnetic property. The adsorption of metal ions such as Ni^{2+} , Cu^{2+} , and Cd^{2+} by the magnetic composites from aqueous solutions was studied. The results show that they are effective in metal ion removal.

5.4 Magnetic-particle-modified biopolymer adsorbent

Biopolymers such as chitin and alginate are common and readily available materials. In terms of abundance, chitin is the second biopolymer after cellulose in nature. Alginate can be abundantly extracted from various species of brown seaweed.

These polymers and their derivatives have excellent adsorption performance because of the presence of a great number of active functional groups (acetamido, primary amino and/or hydroxyl groups) (Crini, 2005). Besides, they have many advantages including being low-cost, widely available in many countries, renewable, and modifiable. They also have biological and chemical properties such as nontoxicity, biocompatibility, and biodegradability. In spite of these properties and advantages, some problems still exist. They are often used as powder forms, which are difficult to separate from water or may cause a significant pressure drop in the column.

Making these biopolymers magnetic by integrating magnetic particles with them may efficiently solve these problems. Therefore, many magnetic biopolymers have been synthesized and used as adsorbents for removal of contaminants in the recent years. Chang *et al.* (2005a, 2005b, 2006) fabricated a chitosan-bound Fe_3O_4 magnetic

adsorbent by the covalent binding of carboxymethylated chitosan on Fe_3O_4 nanoparticles via carbodiimide activation. The analysis results indicated that the chitosan-bound Fe_3O_4 nanoparticles were monodisperse with a mean diameter of 13.5 nm, and the binding of chitosan did not change the spinel structure of Fe_3O_4 . They also investigated the adsorption of Cu^{2+} , Co^{2+} , and acid dyes of Crocein Orange G (AO12) and Acid Green 25 (AG25) on the magnetic adsorbent from the solution. They found that the adsorption rate was quite fast and the maximal adsorption capacities for Cu^{2+} , Co^{2+} , AO12 and AG25 were 21.5, 27.5, 1883 and 1471 mg/g, respectively. Such fast adsorption rate and adsorption capacity were ascribed to the absence of internal diffusion resistance and the high specific surface area. Ma *et al.* (2007) also prepared the magnetic chitosan adsorbent by a co-precipitation method. This adsorbent was tested for the removal of fluoride from water in batch systems and an adsorption capacity of 20.96–23.98 mg/g was achieved. In addition, they studied the regeneration of the exhausted adsorbent using 0.8%–1% NaOH washing water. Donia *et al.* (2007) synthesized a chemically modified magnetic chitosan adsorbent. The obtained adsorbent was tested for the recovery of Au(III) and Ag(I) from their aqueous solutions using batch and column methods. Uptake values of 3.6 and 2.1 mmol/g were reported for Au(III) and Ag(I), respectively.

A magnetic alginate microcapsule containing an extractant of Cyanex 272 was achieved by Ngomsik and co-workers and was used as adsorbent for the heavy metal nickel(II) removal from water. The results of batch adsorption tests demonstrated that the maximal uptake of Ni^{2+} was 0.52 mmol/g (Ngomsik *et al.*, 2006). Lim and Chen (2007) prepared a calcium-alginate magnetic sorbent using an electrostatic extrusion technique and tested it for removal of copper ions and arsenate. The maximal capacities of arsenate and copper ions are 6.75 and 60.24 mg/g. In order to selectively remove organic compounds from wastewater, alginate beads containing magnetic nanoparticles and activated carbon (AC-MAB) were prepared (Rocher *et al.*, 2007). Two dyes, Methylene Blue (MB) and Methyl Orange (MO), were chosen as models of pollutant for test and found that the magnetic composite had a quite higher adsorption capacity to methylene blue, compared with pure carbon.

In summary, the modification of adsorbent with magnetic particles may represent an important and promising approach to produce magnetic composite which can be easily separated and is attracting more and more attentions from researchers worldwide.

6 Conclusions

To obtain the anticipated function and enhance the efficiency of water purification, adsorbents can be designed and modified in their compositions, structures, surfaces, and preparation methods. These kinds of adsorbents can possess their special physical, chemical, and biological properties and exhibit some peculiar behaviors in the reactions, transformation, and removal of contaminants in water. In fact, the ability and efficiency of the adsorption technologies in water treatment also depend on the characteristics and functions of adsorbents. Therefore, to transfer the species of pollutants for promoting the adsorption rate, we can design and prepare some special composite adsorbents with the redox, catalytic, and adsorptive functions which can carry out the processes of oxidation/reduction and adsorption of pollutants synchronously. In order to eliminate some trace concentration of organic substances in water, we can synthesize some biomimetic sorbents and develop the corresponding technologies for water purification. In addition, according to the water quality modifying some applied adsorbents, such as active carbon, no doubt is a very significant way to enhance the efficiency of water treatment processes.

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