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Biomimetic Adsorbents: Enrichment of Trace Amounts of Organic Contaminants (TAOCs) in Aqueous Solution

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1. Introduction

The purification of the wastewater containing trace amounts of organic contaminants (TAOCs) is a very challenging subject in the field of environmental engineering. Although the concentration of TAOCs in wastewater is extremely low (in the range of mg/L-ng/L), the mutagenic and carcinogenic effects of TAOCs (e.g. PCBs, PAHs, PCDDS, EDCs, etc.) are non-negligible. Traditional technologies, such as biological degradation, chemical oxidation/reduction and coagulation, are less effective for this kind of wastewater both technically and economically owning to the low concentration of the contaminants. The adsorption technique has been found to be not only effective, but also practical in application for this kind of wastewater due to the high enrichment capacity of the adsorbents towards the contaminants. By the enrichment of adsorbents, the subsequent decomposition and detoxification of the contaminants become possible using other biological and chemical methods. Therefore, development of the adsorbents with high enrichment capacity to TAOCs is highly necessary.

It is well known that TAOCs in natural water body can be greatly enriched by the aquatic oragnism such as fish and shellfish, namely bioaccumulation. This is a very interesting phenomenon because it motivates the idea of developing biomimetic adsorbents originated from aquatic animals for removing TAOCs. The tissues of aquatic animals which enrich the maximum amount of organic contaminants are found in brain which mostly consists of lipid. This suggests that materials of biological lipid possess an excellent adsorption capacity towards TAOCs. TAOCs normally exhibit low water solubility but high compatibility with organic matters, as evidenced from a high logK_{ow} value (octanol – water partition coefficient). Hence, TAOCs can be enriched in the lipid through an interaction like the "solid phase extraction". The binding force between the solids and TAOCs is neither the covalent binding nor the electrostatic force, but a kind of hydrophobic bond. This type of adsorption does not have an obvious selectivity for the functional groups located at the molecules of TAOCs. Indeed, the molecular hydrophobility plays an important role in the adsorption process. In order to achieve an efficient enrichment, we need to find out the suitable biomimetic adsorbent which has a high organic compatibility towards TAOCs. In our previous studies (Zhang et al., 2010b), a biomimetic adsorbent prepared by poly-3-hydroxybutyrate (PHB) exhibited high enrichment ability for trace amounts of chlorobenzene and *o*-chloronitrobenzene at a low level of specific surface area (8.5 m^2/g), confirming the assumption of the adsorption mechanism.

This chapter provides a review of this new type of adsorbents and their application in the removal of various organic pollutants. The fundamental processes involved in the technique are elaborated with a discussion of some recent novel concepts in biomimetic adsorbents. The preparation and characterization of biomimetic adsorbents and the evaluation of their adsorption capacity are subsequently described.

2. Organic micro pollutant and control technology

2.1 Organic micro pollutant

1. Source and generation mechanism

Organic micro pollutants have a wide range of wastewater sources produced from chemical, pharmaceutical and pesticide industries. Most of these pollutants are petroleum pollutants, phenols, ketones and hydrocarbon, etc. Although their solubility is very low, they can be stable in water for decades (Díaz-Cruz and Barceló, 2008).

As a representative of the industrial production, chemical industry is an important source of TAOCs. Many types of trace non-degradable organic compounds remaining in the tail water are discharged into the natural water. For example, polycyclic aromatic hydrocarbons (PAHs) are common pollutants, mainly from coal-based chemical production, garbage incineration and sudden oil leakage (Khim et al., 2001). In addition, naphthalenedisulfonates are widely-used chemical intermediates in the production and are detected both in industrial wastewater and domestic sewage (Díaz-Cruz and Barceló, 2008). TAOCs can not only be detected in industry wastewater but also in municipal wastewater, which main sources are chemical commodities such as cosmetic, cleaner and drug. Alkylphenol ethoxylates (APEOs), as a kind of common household and industrial cleanser as well as, and one of the main components of plastic products and prophylactic, can often be detected in the natural waters. APEOs and their degradation products have also become the common organic pollutants in water (Kolpin et al., 2002). Corcia et al. pointed out that APEOs could be partially decomposed in water treatment process, since approximately 40% of APEOs were discharged to water body as intermediate products (Corcia et al.2000).

As herbicides, insecticide and phytocide are widely used in modern agriculture, the pesticide residues are found to spread into the river, ground water and ocean with the rainfall. Postle et al. (2004) randomly tested chlorine acetanilide phytocide and its metabolites' from of 336 well in Wisconsin, America. They found that 38±5.0% of the wells were detected of these herbicides and the average concentrations of acetochlor ESA and alachlor OA are 0.15 ± 0.082 μg/L and 1.8 ± 0.60 μg/L, respectively. The widely use of organochlorine pesticides in the last century causes an extensive ubiquitous distribution of them in the natural environment. For example, 7.06 mg/kg DDT was detected in the Antimora rostrata (found at 200 m depth of the Atlantic) fish liver and DDT concentration in the same order was detected in Atlantic cod (found in the shallow water of Canada Atlantic coast) (Barber et al., 1979).

In addition to the above direct sources of organic pollutants, TAOCs also can be produced during disinfection of drinking water as disinfection by-products (DBPs). The disinfection by chlorine which was initiated in the early of 20th century has such advantages as low cost and high efficiency. However, chlorine can react with the natural organics in water, leading to the formation of DBPs during the disinfection. Since the first discovery of trihalomethanes (THMs) by Rook at 1974, many studies on the generation mechanism and toxicity of DBPs have been conducted (Richardson et. al, 2002). The production of DBPs has an intimate connection with concentrations of bromide, iodide and natural organic matter (NOM) in water. Furthermore, the pH value of water affect the generated type of DBPs (Richardson et. al., 2002). In order to prevent the formation of THMs and haloacetic acids (HAAs), new disinfectants such as ozone, chlorine dioxide and chloramine have been used to instead chlorine. However, some new problems appeared. When using ozone as the disinfectant, bromate (a strong carcinogen) forms in spite of significant reduction of the formation of THMs and HAAs. (Richardson et al., 2002). Therefore, how to effectively reduce DBPs is a long-term consideration during the wastewater treatment.

2. Solution property

The wastewater containing organic micro pollutants is very different with common organic wastewater. The total organic matter content is much less than common organic wastewater which likes the lean phase solution. Such features of organic micro pollutants affect their conversion in the environment and the selection of the treatment technologies. Moreover, TAOCs are normally featured with high hydrophobility. For some organics such as dioxin, it is very difficult to test their solubility in water and is even difficult to be measured by experiments (Yang et al., 2006) ,but only calculated by theory methods. TAOCs also are normally lipophilic. When an organic solid is present in wastewater, the pollutants predominantly exist in the solid phase rather than in the water phase. Typically, the fat of aquatics (e.g., fish) usually has a high concentration of TAOCs. It is widely , although organics are hydrophobic and lipophilic, hydrophobility and lipophilia are conspicuous for TAOCs with complex molecular structures. The treatment technology for wastewater containing TAOCs should be adjusted according to their great change in solution. Therefore, it is worthy of consideration and investigation on how to treat such kind of wastewater efficiently.

3. Typical pollutants

There are a variety of typical organic micro pollutants, such as persistent organic pollutants (POPs), environmental endocrine disputing chemicals (EDCs), and DBPs.

POPs are a group of organic substances, which are toxic, persistent, bioaccumulative and prone to long-scale migration (Lohmann et al., 2007). POPs mainly include halogenated aromatic compounds (polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and-furans (PCDD/Fs)), polybromodiphenyl ethers (PBDEs) and organochlorine insecticide (such as dichlorodiphenyltrichlorothane (DDT) and its metabolites). Most of POPs are hydrophobic, lipophilic, and easily to bioaccumulate at he top of the food chain. There is a large number of literature concerning POPs hazard on organism (Armitage and Gobas, 2007; Lohmann and Muir, 2010; Gioia et al., 2007; Kellyn et al., 2005). POPs are generally carcinogenic, environmental hormonal and immune system nocuous. Currently, the harm of POPs to human body is still under investigation. The hazard mechanism of POPs will be revealed by the further study.

EDCs present in environment can disrupt the procreation for human and animals, the metabolism and growth of embryo or children and the function of nerves (Kandarakis et al., 2009). PCBs, organo-chlorine pesticide, unpersistent pesticide, phthalate, bisphenol A, nonyl phenols, brominated flame retardant and some other new pollutants are all included in the category of EDCs. Natural or artificial-synthesized estrogens, male hormone, cortisol and organotin are widely detectable in the drainage basins. Previous studies have shown that, not only the procreation problem and abnormal rate of embryo, but also the deterioration of male sperm and testosterone are related to EDCs. Besides, it may lead to spermary cancer and thyroid cancer. Thus the harmful effect of EDCs on male health becomes a concerned environmental problem.

DBPs are mainly generated from reaction of disinfectant and natural organic pollutants or man-made pollutants (e.g., bromine and iodine) (Hebert et al., 2010). Most of the pathology studies concern with the two main kinds of DBPs: THMs and HAAs. Because chlorine disinfection increases the risk of urinary bladder and colon cancer, World Health Organization (WHO) and some developed countries have made strict criteria to limit the discharge of DBPs to minimize the harm to human beings.

4. Effect on drinking water safety

For human beings, TAOCs have the greastest threat on the drinking water safety. These TAOCs dissolve in drinking water during water migration. Many countries have established a lot of strict criterions to control the content of TAOCs. U.S. EPA made a list of 120 kinds of priority pollutants in water quality standard, 115 belonging to among them are TAOCs. However, drinking water in many countries are still facing tremendous risks due to the high transitivity and stability of TAOCs. By analyzing the micro pollutants in the sediment of Seine in France, Carpentier et al. (2002) found that, the concentrations of PCB and PAHs reached moderate level of pollution. Götz et al. (1996) analyzed 145 kinds of pollutants in water of Elbe in Hamburg and found that the concentrations of 1,2-dichloroethane, 1,4-dichlorobenzene, hexachlorobenzene (HCB) and nitrobenzene were greater than those depicted in the water criteria of Germany. The improper disposal of hospital sewage containing large amounts of disinfectant, drugs and organic solvents also cause the potential threat to drinking water safety (Laber et al., 1999). In developing countries, septic tanks are generally used for storing hospital sewage, which increases the risk of the pollution to groundwater. Emmanuel et al. (2009) evaluated the pollution risk of the hospital sewage collection device (as shown in Fig.1) by monitoring COD, chloroform, dichloromethane, dibromochloromethane, dichlorobromomethane and tribromomethane. Results showed that the concentrations of organic pollutants in groundwater of the hospitals using these devices were greater than those in others. This implies a high security risk of directly drinking water.

2.2 Biological enrichment

In the polluted natural water, aquatic animals' adipose tissues act as the "natural sorbent" due to the high hydrophobic characteristic of TAOCs. The relationship of TAOCs migration behavior and aquatic animals enrichment (See Fig.2) indicates that, aquatic animals are the important site were micro pollutants are enriched during the food chain transmission.

PCBs are important species of POPs, and have been widely studied on enrichment behaviors with respect to many kinds of aquatic animals. Magnusson et. al. (2006) studied accumulation of 29 nonplanar and 11 coplanar congeners of PCBs in 9 seabed mollusks and found that the accumulation of PCBs in different aquatic animals didn't have linear correlation with concentrations of pollutants, but strongly dependent on the specific kind, figure and longevity of animals. Ribeiro et al. (2008) studied the residual concentration of PCBs in eel living in Nature Camargue Reserve and found that 10 out of the 70 detected PCBs were dioxin-like PCBs. PCBs had a high concentration that was up to 29.6 pg/g (dry weight) with 22% and 29% of PCBs consisted in liver and fat of eels, respectively, which suggested that it has potential risk for eating these eels. Pierce et al. (2008) studied PCBs concentrations in the fat of living dolphins in coast of Western Europe and their effect on

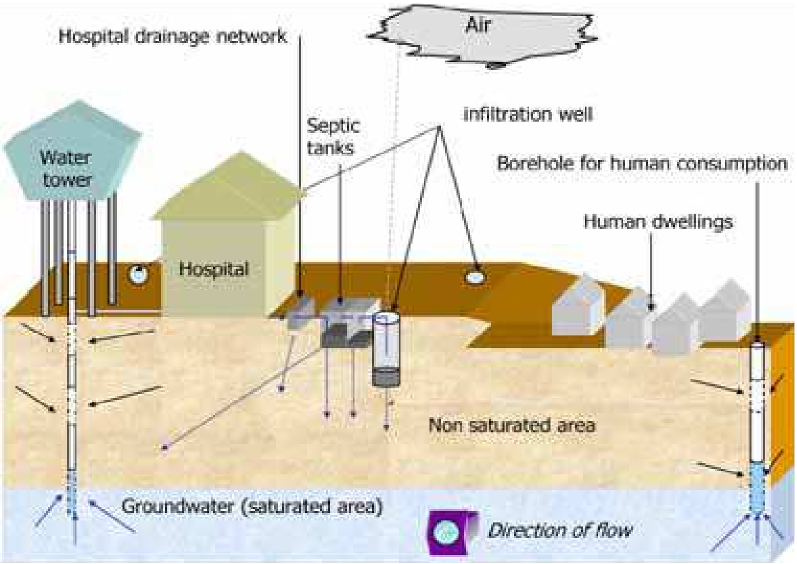


Fig. 1. Graphic representation of the scenario studied. (Emmanuel et al., 2009)

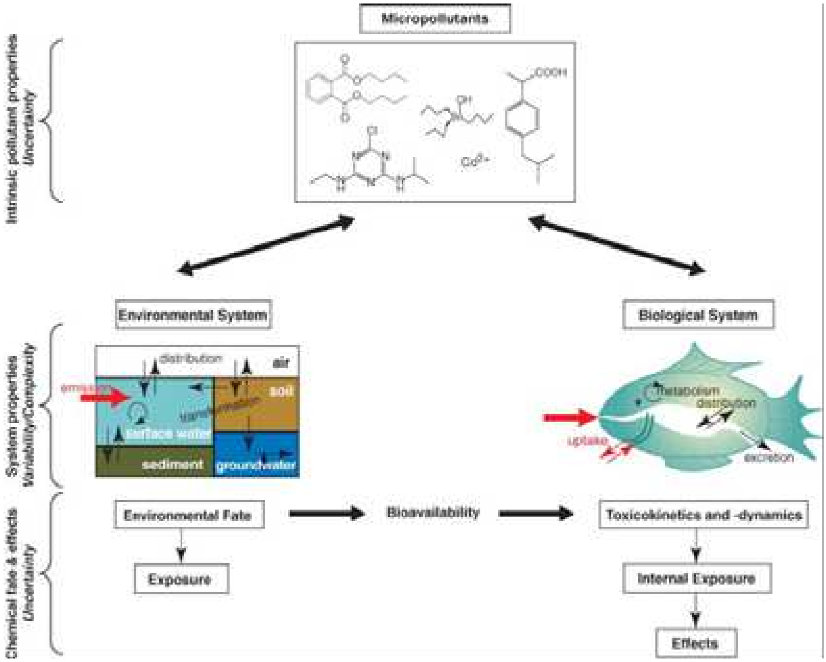


Fig. 2. Consistent exposure and effect assessment is possible if processes in the environmental system and in the organisms (biological system) are treated with the same modeling structure and tools. (Schwarzenbach et al., 2006)

reproduction and death of dolphins. PCBs concentrations were found to exceed the safe level in fat of every Atlantic dolphins and porpoises analyzed. Concentrations of PCBs in porpoises died of disease or parasitic were be higher than that of normal porpoises.

Many previous studies (Ikemoto et al., 2008; Voutsas et al., 2002; Liu et al., 2007) indicated that contents of many micro pollutants in aquatic animals were much greater than normal, and that these micro pollutants were considered to affect the metabolism. It can be concluded from micro pollutants enrichment behavors of aquatic animals. Concentrations of pollutants in animals are not only much greater than that of normal environment, but also greater than that adsorbed by other substrates. In nature, many organisms have extraordinary abilities, such as high hydrophobility self-cleaning lotus leaves, and adhesive forces of lizards. These all can be considered as bionic behaviour and are being under investigation. The super enrichment ability for aquatic animals to absorb organic pollutants is not a natural phenomenon but appears after exposure to the increasing pollutants in water. Nevertheless, that is also a hint for organic pollutants control: novel absorbents imitated from the super absorbing behaviors of aquatic animals will provide a new approach for pollutant treatment.

2.3 Control technology

1. Adsorption technology

Adsorption technology plays an important role in the wastewater treatment process. In recent years, adsorption technology has been developed rapidly and concentrated on the protection and recycling of water resource. For TAOCs, carbonaceous adsorbents are the most used materials due to their abundant micropore structure and hydrophobic surface. There are various kinds of carbonaceous adsorbents such as activated carbon, activated carbon fiber, carbon nanotube. Zhang et al. (2010) studied the adsorption of three TAOCs by four types of carbonaceous adsorbents [a granular activated carbon (HD4000), an activated carbon fiber (ACF10), two single-wall carbon nanotubes (SWNT, SWNT-HT), and a multiwalled carbon nanotube (MWNT)] with different structural characteristics but similar surface polarities. Isotherm results demonstrated that the molecular sieving and micropore effects played an important role in the adsorption of TAOCs onto carbonaceous porous adsorbents. ACF10 and HD4000 with greater microporous volumes exhibited higher adsorption affinities to low molecular-weight TAOCs than SWNT and MWNT with greater mesopore and macropore volumes. The adsorption behavior of organic pollutants onto activated carbons has been widely studied. The amount of adsorption not only depends on the properties of pollutants (hydrophobility, polarity, aromaticity, etc, but also has a strong relation with the surface properties of activated carbon (Ridder et al., 2010). Furthermore, the particle size of activated carbon has an important effect on the removal ability, especially in the practical use. Crowin et al. (2010) investigated the effect of particle size on the reduction of granular activated carbon (GAC) adsorption capacity for trace organic contaminants by dissolving organic matter and demonstrating the lower adsorption capacity per mass of adsorbent in relation to the larger GAC particles. On the preparation of activated carbons, many novel methods have been developed in order to optimize the surface properties for better performance regarding pollutant removal and their regeneration. Ji et al. (2009) synthesized a microporous carbon with very high specific surface area and narrow pore size distribution using Y zeolite as a template. The synthesized - microporous carbon showed extraordinarily high adsorption affinity (comparable or higher than activated carbons and carbon nanotubes) for phenol, 1,3-

dichlorobenzene, and 1,3-dinitrobenzene, and very fast adsorption/desorption kinetics. These adsorption properties were attributed to the large hydrophobic surface area and the regular-shaped, open and interconnected three-dimensional pore structure of the synthesized microporous carbon. In the case of practical treatment, the effect of NOM on adsorption is important. Yu et al. (2009) investigated preloading effects of NOM on adsorption capacity and kinetics under conditions and concentrations relevant to drinking water treatment. The isotherms demonstrated that all compounds were significantly negatively impacted by NOM fouling.

Although activated carbon has a good adsorption capacity for organic pollutant, the expensive price and relatively weak affinities for trace amount pollutants limit its wide application. Many studies have been conducted to search the substitutes of activated carbon including agricultural wastes, natural and modified clays, organic polymer, etc. Nowadays, these new adsorbents can not readily replace activated carbon but the development of adsorbents with greater cost performance for TAOCs adsorption has become a new trend.

2. Membrane technology

Membrane technology has gained interest in the last decades in water purification applications. In addition to their use for desalination of seawater and brackish water, the technologies such as nanofiltration and reverse osmosis membrane offer good removal efficiencies (Verliefde et al., 2009). The treatment efficiency of membrane is related to the molecular size directly but not the molecular weight. The non-polar molecule has better removal efficiency than polar molecules. Agenson et al. (2003) compared the removal of DBPs, EDCs, and plastics additives by nanofiltration and reverse osmosis at low pressure (100-300 kPa). Their results indicated that reverse osmosis exhibited better removal capability to VOCs than nanofiltration membrane which removal rate was 20% only. By the multiple linear regression, they predicted that larger molecular size and higher hydrophobility favored the removal. In the treatment of membrane, the control factors include diffusion, adsorption, partition and desorption (Ducom et al., 1999; Chellam et al., 2001; Nghiem et al., 2004; Lee et al., 2001). Due to the close relationship between the removal rate and the physicochemical properties of pollutants, some pollutants can not be treated well (Bellona et al., 2004). Especially, for the large-scale production such as drinking water purification, the poor performance for TAOCs will bring about a series of problems (Verliefde et al., 2009). Moreover, the high cost of membrane and its regeneration restrict its large scale application.

3. Membrane bioreactor (MBR)

MBR is considered as the next-generation technology of wastewater treatment, which is expected to replace the traditional activated sludge process. MBR possesses such advantages as small footprints and a superior effluent quality (Wever et al., 2007). Wever et al. (2007) compared MBR and conventional activated sludge systems (CAS) for micro pollutant degradation in laboratory-scale experiments with synthetic and real domestic wastewater. MBR treatment can significantly enhance the removal of the micro pollutants, and reduce the lag phases for degradation, implying that they may respond quicker to variable influent concentrations. Nghiem et al. (2009) conducted laboratory-scale experiments to investigate the removal mechanisms of MBR system for trace organic contaminants. Results indicated that removal efficiency of specific trace organic contaminants strongly depended on their physicochemical properties. Approximately 90% of bisphenol A was removed, while, the removal efficiency of sulfamethoxazole was only about 50% under the same condition.. Both biodegradation and adsorption to the sludge were thought to be responsible for the removal of bisphenol A, which is a relatively hydrophobic organic compound. In contrast, the latter mechanism was absent for sulfamethoxazole as this compound is rather hydrophilic. Chu et al. (2010) investigated the feasibility of treating micro polluted surface water for drinking water production with a bio-diatomite dynamic membrane reactor (BDDMR) at a laboratory-scale-discontinuous-flow mode. Results indicated that the BDDMR was effective in removing trihalomethanes' formation potential (THMFP) at a hydraulic retention time (HRT) of 3.5 h due to its high concentrations of mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS).

4. Other technologies

Because of the great difficulty in treating TAOCs, single technology can not meet the purification purpose. Thus the combination of different technologies is employed. Reungoat et al. (2010) assessed the removal of organic micro pollutants and the concurrent reduction of their biological activity in a full-scale reclamation plant treating secondary effluent. The treatment consists of 6 stages: denitrification, pre-ozonation, coagulation/flocculation/ dissolved air flotation and filtration (DAFF), main ozonation, activated carbon filtration and final ozonation for disinfection. The process is shown in Fig. 3. Results showed that, among the 54 micro pollutants quantified in the influent water, 50 were removed to below their limit for quantification (0.01 μg/L)which represents that more than 90% of pollutants were removed. The key processes responsible for the plant's performances were the coagulation/flocculation/DAFF, main ozonation and activated carbon filtration. Hollender et al. (2009) studied the removal efficiency for 220 micro pollutants from a municipal wastewater treatment plant (WWTP) upgraded with post-ozonation followed by sand filtration. During post-ozonation, compounds with activated aromatic moieties, amine functions, or double bonds such as sulfamethoxazole, diclofenac, or carbamazepine with second-order rate constants for the reaction with ozone>10^4 M^{-1} s^{-1} at pH 7 (fast reacting) were eliminated to concentrations below the detection limit for an ozone dose of 0.47 g O_3/g dissolved organic carbon (DOC). Compounds more resistant to oxidation by ozone such as atenolol and benzotriazole were increasingly eliminated with increasing ozone doses, resulting in >85% removal for a medium ozone dose (~0.6 g O_3/g DOC). Only a few micro pollutants such as some X-ray contrast media and triazine herbicides with second-order rate constants <10^2 M^{-1} s^{-1}(slowly reacting) persisted to a large extent. With a medium ozonedose, only 11 of micro pollutants 55 detected in the secondary effluent were found at >100 ng/L. The energy requirement for the additional post-ozonation step was about 0.035 kWh m^{-3}, which corresponded to 12% of a typical medium-sized nutrient removal plant (5 g DOC/m^3).

In comparison with the ordinary municipal sewage and industrial wastewater, organic micro polluted wastewater has the characteristics of low load and poor nutrient. Thus, some energy-effective eco-treatment technologies have been adopted. Among them, the constructed wetland is one of a representative technology. An engineered constructed wetland, fed with wastewater effluent, was investigated with respect to the control of organic micro pollutants (Park et al., 2009). The levels of 30 different micro pollutants, including pharmaceuticals, endocrine disruptors and personal care products, were measured using solid phase extraction, followed by liquid chromatography/tandem mass spectrometer. Only 9 out of the 30 chemicals exhibited relatively high concentrations in the effluent samples. Furthermore, analyses of the removal efficiencies and two characteristic parameters (log*K*ow and p*K*a) showed no evidence supporting hydrophobic and electrostatic interactions for the control of micro pollutants.

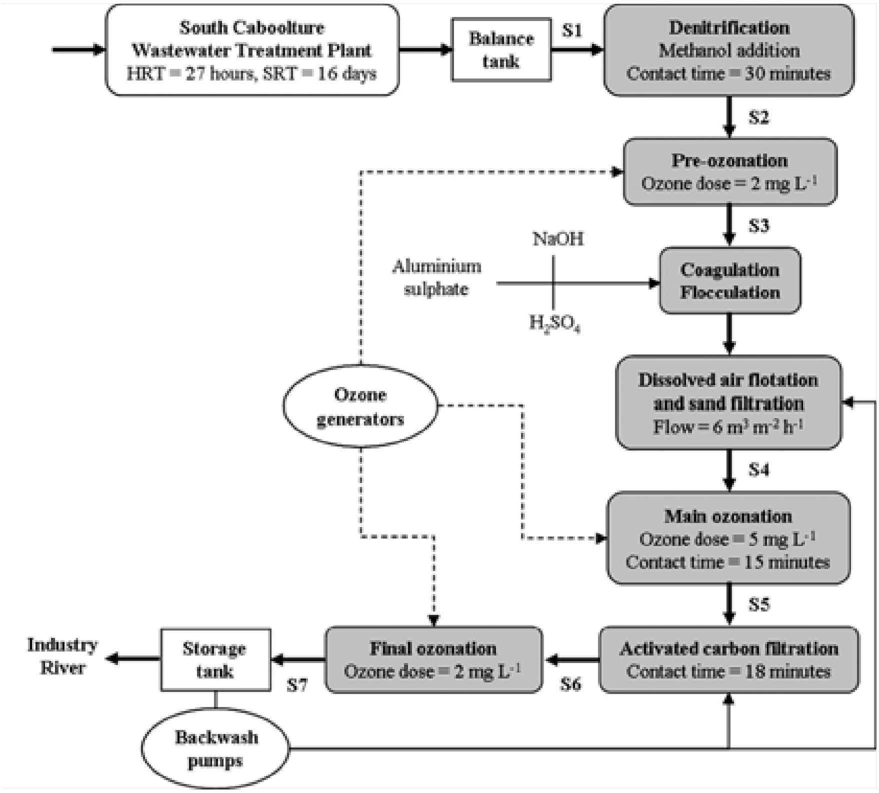


Fig. 3. South Caboolture Water Reclamation Plant. S1 to S7: sampling locations. HRT: hydraulic retention time. SRT: sludge retention time. (Reungoat et al., 2010)

3. Biomimetic adsorbent

3.1 Definition of biomimetic adsorbent

The study of biomimetic phenomena has a long history. Plenty of knowledge through imitating nature is available. For example, the pot experiments showed that the peanut (*Arachis hypogaea*), soybean (*Glycine max*) and sesame (*Sesamum indicum*) had great bioaccumulativity for DDT. The order of DDT concentration in each grain was: peanut > sesame > soybean, which indicated that the concentration of DDT had a positive correlation with the oil contents of grains (Wei et al., 2006). More generally, the water plant with large rich fat skin can adsorb lipophilic OCPs (Ockenden et al., 1998). The concentration of PCBs in blubber of neonate *Delphinapterus* leucas, *Orcinus orca*, adult *Delphinapterus leucas* and *Balaena mystice* was 17563, 78000, 59000 and 354 ng/g, respectively, which was 1-3 orders of magnitude higher than that in other tissues (Liu et al., 2008). Also, the concentration of DDT in blubber was 1-2 orders of magnitude higher than that in other tissues, and was 2230, 98600, 56000 and 377 ng/g, respectively (Liu et al., 2008). The measured concentrations of PCBs and DDT in different organs were in the ascending order: blubber, liver, kidney, brain and muscle (Liu et al., 2008). BCF_{lipid} (bioconcentration factor based on lipid content) of 13

OCPs in 18 fish species from Qiantang River in China ranged from 1000 to 251189, and the bioaccumulation capacity of fish organ was high when the lipid content of organ was high (Zhou et al., 2007). The methods of POPs entering organism body contained breathing in from air, inhaling by skin and feeding food. The POPs eliminating processes included 4 methods. The first one was breathing out, but the discharged amount of method was very small and can be ignored. The second one was discharge by dejecta. Breathing in from air, inhaling by skin and feeding food are the main ways of POPs entering organism body. The third one was metabolism. Youth biology can metabolize POPs in some extent, but the metabolic function may become slow with the increasing age. The fourth one was transference. For example, POPs in fat of mammals can be transferred to milk. The absorption rate is much higher than the elimination rate, so that some special pollutants transfer to and accumulate in lipid and protein tissues of plants and animals. The process that people simulate these natural phenomena to prepare adsorbent to remove pollutants is biomimetic adsorption, and therefore the adsorbent is denoted as biomimetic adsorbent.

Triolein has a high accumulation ability for trace POPs in water (Chiou, 1985). People design and prepare biomimetic adsorbents through imitating the cell structure and using the accumulation ability of lipid for POPs. The biomimetic fat cell (BFC) was synthesized with a hydrophobic nucleolus-triolein and hydrophilic membrane-polyamide (Song et al., 2007). CA-triolein was prepared by embedding triolein in the cellulose acetate (CA) spheres (Liu et al., 2007). Zhang et al. (2010b) found that the lipophilic poly-3-hydroxybutyrate (PHB) produced by many microorganisms contains the same functional groups of the lipid. They prepared PHBBMA with PHB to enrich the trace chlorobenzene and *o*-nitrochlorobenzene from water and found that all these biomimetic adsorbents had a good enrichment effect for low-concentration POPs.

The adsorption materials prepared by the molecular imprinting technology represent another kind of biomimetic adsorbents. According to the principle of the interaction force or template structure between two kinds of molecule or group, a selective adsorbent was prepared with a template of adsorbate or analogue. For example, imprinting polymer prepared with dibenzothiophene sulphone (DBTS) as the template can separate organosulfur compound such as dibenzothiophene (DBT) and benzothiophene (BT) from the mixture (Castro et al., 2001). Researchers also used mimetic antibody and enzyme as the template to prepare adsorption materials which adsorbed special pollutants according to the interaction between antibody and antigen, and the interaction between enzyme and substrate (Cormack and Mosbach, 1999).

As can be seen from the above materials, the whole or part of some plants and animals in nature can enrich specific substances. Their characters, such as the structure, group interaction and principle of enrichment, are simulated to design and prepare adsorbents. This biomimetic adsorbent can quickly and effectively realize the adsorption/enrichment function of organisms in nature.

3.2 Adsorption principles of biomimetic adsorbent

The adsorption principle of biomimetic adsorbent is the same or similar as the enrichment mechanism of organisms. The enrichment process is a balance process of adsorption, absorption, metabolism and storage. For example, the processes of algae enriching trace element include physical adsorption, biosorption, surface deposition, active transport and passive diffusion. Biosorption and active transport are the main ways of bioconcentration, accounting for 80% and 20% of the total enrichment amount, respectively. Biosorption is a process that organisms adsorb metal ions, non-metallic compounds and solid particles from the solution by complexation and ion exchange. The complexation is the combination of metal ions and the negative function groups of biological ligands. For example, the strong complexation is favorable between carboxyl, sulfonic, thiol, amino, hydroxyl, etc. and different metal ions, such as Cu^{2+}, Al^{3+} (Li et al., 1998). Some metal ions are adsorbed by algae, while other ions are released. The charge number of released ions such as Ca^{2+}, Mg^{2+}, H^+ is approximately equal to that of adsorbed ions, making the biosorption as an ion exchange process. For most algaes, carboxyl and sulfonic are the main groups involved in the ion exchange process, as alginate and sulphate polysaccharide have a significant ion exchange capacity (Li et al., 1998). Active transport is an intracellular active absorption process related to metabolism, which need energy and some specific enzyme. This is a unique way of enriching trace elements by live organisms. The process, however, is very complicated and associated with the algae fat, sugar, protein, inorganic salt, etc. Irgolic et al. (1971) showed that arsenic are actively involved in the lipid metabolism in some algaes. It can replace the phosphorus atom or nitrogen atom in phosphatidylethanolamine (PE) and phosphatidylcholine (PC) to enter phospholipid biosynthesis process and form some arsenic fats, such as arsenic-phosphatidylethanolamine (As-PE) and arsenic-phosphatidylcholine (As-PC). Arsenic in algaes is also involved in glucose metabolism, resulting in the formation of arsenic sugar. Edmonds and Francesconi (1983), Pillips and Depledg (1985) considered that arsenic sugar was transformed from S-adenosylmethionine, and the latter thought the translation occurred in the process of As-PC synthesis by the As-PE. According to the mechanism of the formation of selenoprotein, selenium can be combined with lipid, polysaccharide and protein in the algae. Selenate and sulfate have the same assimilation pathway in the algal. Selenite enteres the algae and replaces the sulphur atom in cysteine (Cys) and methionine (Met) to form selenocysteine ([Se]Cys) and selenomethionine ([Se]Met). The process allowed toxic selenate transfer to a large number of non-toxic selenium compounds.

Biomimetic adsorption is inspired from nature system. The mechanisms of BFC, CA-triolein absorbent and PHBBMA are their dissolution for adsorbates. Triolein-embedded sorbent consists of the supporting materials and the surrounding triolein-embedded cellulose eacetate membrane by embedding triolein into CA spheres. Triolein has a high dissolution capacity for trace lipophilic pollutants in water. A cellulose acetate polymer can be easily molded into different forms such as membranes, fibers and spheres, and its hydrophilicity improves the accessibility of aqueous solutions to the surface of the film. PHB is analogous to the lipid with strong affinity for organic pollutants, so PHBBMA has excellent compatibility with lipophilic chemicals. At the same time, the porous structure of PHBBMA can be regarded as an uptake process of fish. For biomimetic adsorbents, the role forces include strong affinity between adsorbent and adsorbate, hydrophobic force, van der Waals force and principle of "like dissolves like". In the nature system, lipophilic chemicals are always accumulated in the lipid of organism because the pollutants are absorbed by organisms through skin, gill, and feeding, while they are difficult to depurate by metabolism. Therefore, TAOCs are found in almost all plants, animals and human, especially in lipid organs. This phenomenon can inspire people to prepare biomimetic adsorbents to eliminate the pollutants. An important adsorption mechanism of imprinting adsorbent is the strict chimeric structures between adsorbent and adsorbate.

3.3 Evaluation of biomimetic adsorption

The principle of biomimetic adsorption is different from that of traditional adsorption. The traditional adsorption only happens on the interface of adsorbent and water. The surface area, namely active site, plays most important role in such adsorption. The biomimetic adsorption, however, occurs not only on the interface but also in the inner of adsorbent, because pollutants can be dissolved in the lipid phase. The adsorption isotherms like Langmuir, Freundliuch are useful for predicting the interface adsorption processes, but may not be suitable to interpret the biomimetic adsorption processes.

Adsorption quantity and adsorption rate are two important parameters for evaluating the efficiency of adsorption. The adsorption amount highly depends on the surface area, pore size distribution and properties of surface groups. In nature, the bioconcentration of pollutants that includes surface infiltration and food intake, is also influenced by environment, metabolism and growth of aquatic organisms. The discharge of pollutants from animal bodies.

The models of bioconcentration of pollutants in aquatic animals include steady-state model, two-compartment model and biodynamic model. The steady-state model is based on the balance between biology and water. The biology grows for long time in water, so that many processes approximately reach balance. However, concentrations of some heavy metals are difficult to reach a steady state. Therefore, the steady-state model cannot be applicable for this case. The bioconcentration of heavy metals can be depicted by the mass transfer model. According to conservation of mass, bioaccumulation and metabolism of heavy metals are expressed as:

Enrichment rate of substances in individual = individual input rate - output rate + net generation (conversion) rate

Heavy metals cannot be formed and transformed by life activities, giving rise to the simplified model of the bioaccumulation of heavy metals:

Enrichment = input - output

As a consequence, the interaction process of biology and water can be described by two-compartment model (Croisetiere, 2005). Assuming the accumulation of pollutants in vivo is approximated as two-phase distribution process of pollutants between biology and water, the enrichment and discharge processes can be described by the first-order dynamics (Kahle et al., 2002). Compared with the steady-state model, the two-compartment model afford the calculation of the dynamics parameters of heavy metals at the theory equilibrium before reaching the balance. The biodynamic model includes the absorption process of heavy metals from water and food, the discharge process of heavy metals from organisms, and the dilution due to organisms growing (Luoma et al., 2005). This model includes comprehensive consideration, but the parameter measurement is complex and the practical application is inconvenient.

Biomimetic adsorbent is designed based on the enrichment process of pollutants. The process is similar to that related to the two-compartment model. In order to evaluate the accumulation ability of biomimetic adsorbent, we propose a concept of enrichment factor (EF) which is a dimensionless ratio of the concentrations of adsorbate on biomimetic adsorbent and those in the solution at equilibrium:

$$\mathrm{EF} = \frac{q_{\mathrm{e}}\rho}{c_{\mathrm{e}}}$$

where q_e (mg/g) and c_e (mg/L) are the concentrations of adsorbate on biomimetic adsorbent and in the solution at equilibrium, respectively. ρ, solution density, is about 1000 g/L.

Although biomimetic adsorbents have been well developed, there is a lack of effective evaluation method as conventional adsorption isotherms and adsorption kinetics are widely applied to describe this adsorption process. The principle of POPs adsorbed on biomimetic adsorbent is "like dissolves like", and POPs concentrations are usually very low. This urges to develop the new evaluation method for biomimetic adsorption.

4. Application of biomimetic adsorbent

4.1 Preparation and application of biomimetic adsorbent

Polyhydroxyalkanoates (PHAs) are biodegradable polyesters as carbon and energy sources, which are sorted in microorganisms in the form of granules. Zhang et al. (2010a; 2010b) successfully prepared a new biomimetic adsorbent with high porosity named as PHBBMA using PHB, a representative compound of PHAs, produced from microorganism degrading pollutants. As shown in Fig. 4, a modified double emulsion solvent evaporation technique was used for preparing this adsorbent.

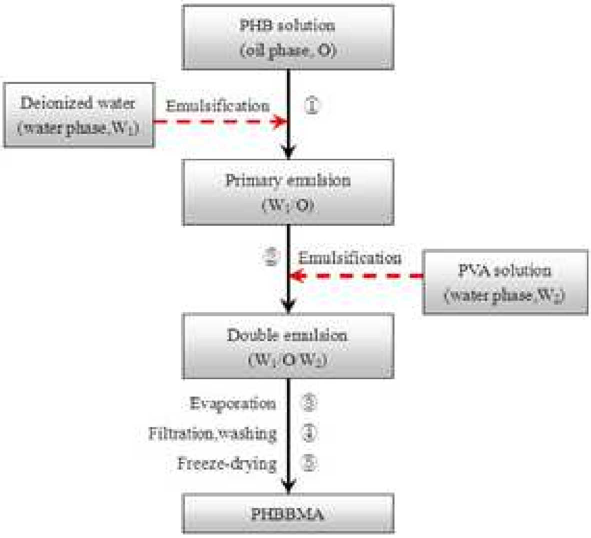


Fig. 4. Diagram of PHBBMA preparation. 1, 2, 3, 4, and 5 express the operation order. (Zhang et al., 2010a)

The textural and surface characteristics of PHBBMA were shown in Fig.5. The results indicated that PHBBMA was composed of spherical particles with rough surface and micropores. The diameter of the particles was 100–200 µm. The BET surface area, total pore volume, and average pore diameter were 8.45 m^2/g, 0.0105 cm^3/g, and 4.9 nm, respectively. PHBBMA has a wide pore distribution with diameter ranging from 2 to 90 nm. Few particles were collapsed because the thin PHB walls broke up at the pressure when the big cavities were produced by big water particles (W1). PHBBMA particle size and pore diameter were affected by many factors including the concentrations of oil phase and extra-water

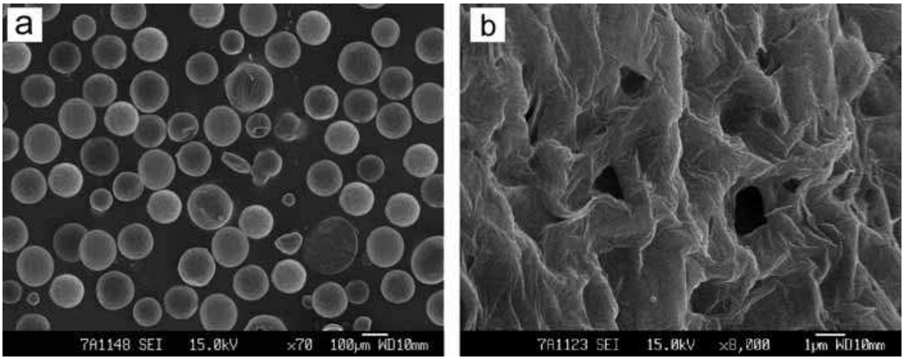


Fig. 5. Scanning electron micrographs of PHBBMA .(a) whole particles (×70) and (b) surface of particle (×8000). (Zhang et al., 2010b)

phase (W_2), the volume ratio of W_1 and oil phase, the volume ratio of oil phase and W_2, and the stirring speed.

Among the organochlorine compounds (OClCs), chlorobenzene (CB) is structurally similar to *o*-nitrochlorobenzene (*o*-NCB). It is always released to the environment during manufacturing and application processes as a carrier, a solvent and/or an intermediate (Adebusoye et al., 2007). In addition, CB and *o*-NCB with low concentrations are easily enriched in lipid in organisms owing to their strong hydrophobic and lipophilic properties. Zhang et al. (zhang (b) et al., 2010) evaluates the adsorption capacity of PHBBMA using CB and *o*-NCB as target compounds in their extreme low concentration.

Adsorption isotherms of CB and *o*-NCB on PHBBMA under different temperature are shown in Fig.6. It was clear that the adsorption amount of CB was always greater than that of *o*-NCB under the same conditions. This is because that the adsorption amount has a positive correlation with the affinity between PHBBMA and the compounds. CB had stronger affinity than *o*-NCB due to the absence of a hydrophilic group (-NO_2). Furthermore, the adsorption capacity decreased when the temperature increased for both CB and *o*-NCB. The acting force between the PHBBMA and CB or *o*-NCB is van der Waals Force and hydrophobic force, suggesting that the process of PHBBMA adsorption is a physical adsorption.

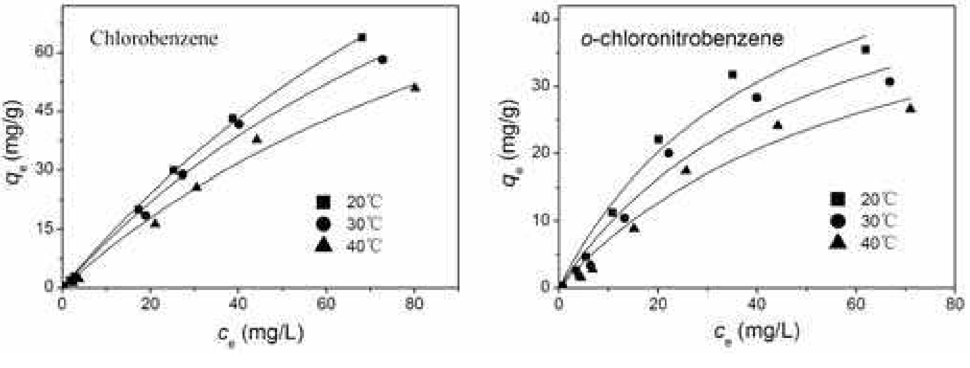


Fig. 6. Langmuir adsorption isotherms for CB and *o*-NCB onto PHBBMA. (Zhang et al., 2010b)

EF was employed as a criterion for the evaluation of the adsorption ability for different pollutants. The EF of PHBBMA for CB and *o*-NCB was calculated by equilibrium data from experiments and Sips model fitting curves. Fig. 7 presents the variety of EF as a function of different equilibrium concentrations. For both CB and *o*-NCB, EF showed a pattern that increased at first and then decreased with the increasing equilibrium concentrations. It can be interpreted by the fact that there are enough available active adsorption sites at the surface of PHBBMA in the case of low equilibrium concentrations. The value of q_e increased faster than c_e, indicating that EF increased with the increase of c_e. In the case of high concentrations, however, adsorbent was gradually saturated, resulting in a slow increase in q_e and a decrease in EF with the increase of c_e. The change of EF versus temperature for CB and *o*-NCB had the same trends, i.e. $EF_{20°C}$ (EF at 20°C) > $EF_{30°C}$ > $EF_{40°C}$ because the increasing temperature significantly increases aqueous solubility, although it causes a decrease in K_{ow} (Finizio et al., 2001). High K_{ow} and low aqueous solubility imply strong lipophilic and hydrophobic properties, causing the easy adsorption of compounds for PHBBMA.

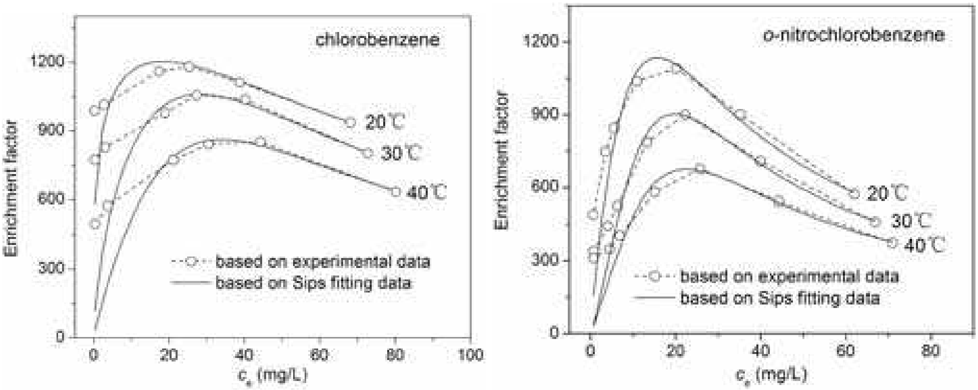


Fig. 7. EF variety of PHBBMA for CB and *o*-NCB with equilibrium concentrations at different temperatures. (Zhang et al., 2010b)

4.2 Preparation and application of lipoid adsorbent

Triolein is one of the most important lipid components and the main materials for soap preparation. According to the principle of similarity and intermiscibility, triolein has a strong absorbability for trace level of hydrophobic organic pollutants. Previous studies (Liu et al., 2007; Liu et al., 2009; Huo et al., 2005; Ru et al., 2007; Qu, 2008) showed the preparation of a biomimetic adsorbent by embedding triolein into cellulose acetate (CA) spheres. The section structure is shown in Fig. 8. Triolein was wrapped entirely into CA spheres through optimizing the preparation method, and thus it can not be expelled during the adsorption process. The hydrophilicity of (CA polymer improved the accessibility of trace organic pollutants to the surface of the adsorbent. In addition, the formation of mesh structures of CA (Fig. 9) provided enough channels for organic pollutant molecular transfer through CA. This design weakens the diffusion and the mass transfer obstacle between the lipid phase and the water phase by providing a hydrophilic and porous film at the top surface of the obtained biomimetic adsorbent.

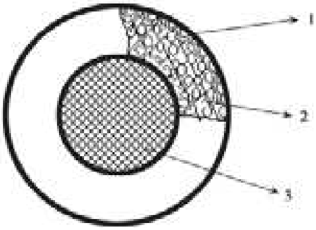
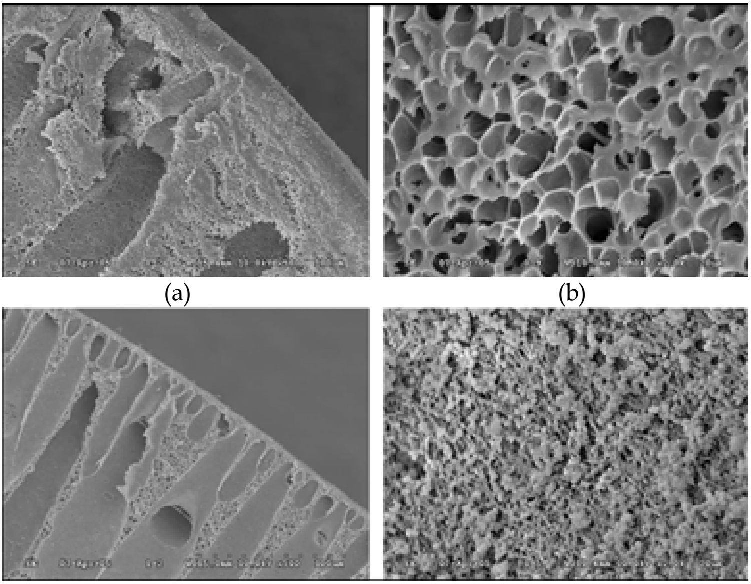


Fig. 8. Designed structure of triolein-embedded sorbent. (1) cellulose acetate membrane, (2) triolein and (3) supporting materials. (Qu, 2008)


(a) (b)

(c) (d)

Fig. 9. SEM micrographs of cross-sections of CA and CA-triolein adsorbents. (a) CA adsorbent (×500), (b) CA adsorbent (×2000), (c) CA-triolein adsorbent containing 2.0% (w/w) triolein (×500), and (d) CA-triolein adsorbent containing 2.0% (w/w) triolein (×2000). (Liu et al., 2007)

Liu et al. (2007) investigated the adsorption efficiency for selected POPs (e.g. aldrin, dieldrin, endrin and heptachlor epoxide) by this biomimetic adsorbent. The comparison of CA-triolein and granular activated carbon (GAC) for dieldrin removal was also performed. Results showed that the adsorption capacity of CA-triolein was larger than that of GAC, although GAC had high removal rate in the first 4 h of adsorption. Adsorption isotherms of the selected POPs exhibited linear isotherms, which indicated that the POPs were mainly adsorbed onto CA-triolein by a partition mechanism. Partitioning of organic compounds between water and triolein may be similar to that between organic solvent and water. The partition coefficient of POPs was closely related to their hydrophobicity. The higher the hydrophobicity of POPs was, the larger the adsorption amount was. Furthermore, the reusability of the biomimetic absorbent was tested. Although the CA-triolein was regenerated five times, the removal efficiencies were almost unchanged.

Due to the particular adsorbed amount and bioaffinity, layer by later (LBL)-assembled hydrogel films have been applied in the research of sustained release of medicines and genetic science. Ding et al. (2009) loaded alginate sodium (ALG) and chitosan to weakly cross-link melamine formaldehyde (MF) colloidal particles, preparing a kind of saccate biomimetic adsorbent. 2,4-dichlorophenol and salicylic acid were adsorbed by this adsorbent. Fig. 10 shows the SEM pictures the adsobents before and after adsorption. The gap between two shells was filled after adsorption. This phenomenon indicated that the organic componds entered into the internal of bursa. The cliff of bursa was gradually uplifted with the increase of adsorption, making the adsorbent like a balloon filled with gas. Fig. 11 shows that the adsorption isotherms of DCP and SA cpmpiled with the Langmuir equation.

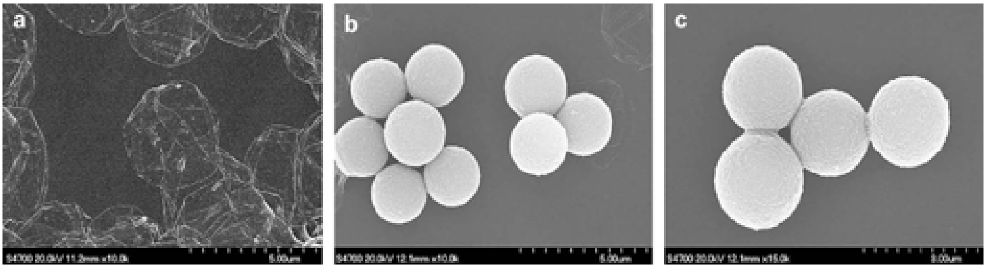


Fig. 10. SEM images of the (ALG/CHI)5 hollow shells (a) and shells upon incubating the preformed shells in various organic solutions in pure water medium: (b) DCP; (c) SA. Scale bars are 5 mm for a, 5 mm for b and 3 mm for c. (Ding et al., 2009)

There are a lot of materials that can serve as the biomimetic adsorbents are in nature. If these materials are successfully used to manufacture the commercial adsorption materials, they will have such a distinct advantage as high performance-to-price ratio. Baruch-Teblum (2010) used the α-cyclodextrin as the basic material and adopted the method of miniemulsion polymerization to produce a series of controlled-size nanoparticles under the link of isophorone diisocyanate (Fig.12). In the molecular structure of cyclodextrin, there was hydrophobic channels (as shown in Fig.13), which could adsorb organic pollutants especially for the pollutants with benzene ring in the interface of water-nanoparticle. Toluene and phenol were tested as the model pollutants to evaluate adsorption capacity. Results indicated that the nanoparticles exibited good adsorption. Compared with inorganic adsorbents, biomass materials can be made into different shapes such as granule, powder and membrane depending on the used conditions needed.

In addition to the nature polymer, super hydrophobic and lipophilic adsorption materials were synthesized in the laboratory. Although some materials did not have large specific surface area, their adsorption capacities were much higher than the porous materials, showing unique advantages of biomass adsorbents in adsorption principles and mechanism. Zhang et al. (2009) produced a super hydrophobic polydivinylbenzene with high specific surface area and pore volume, controllable pore size distribution, super hydrophobicity and super lipotropy. The adsorption capacity for organic pollutants was compared with activated carbon and Amberlite XAD-4 resin, as illustrated in Fig 14. It could found that the adsorption capacity of polydivinylbenzene was much higher than that of activated carbon and Amberlite XAD-4 resin, suggesting good potential for applications.

Activated carbon is dominant in the field of adsorption materials. However, activated carbon can not meet the requirement of purification of wastewater containing TAOCs. Biomimetic adsorption materials are now reported frequently owing to their higher adsorption capacity than activated carbon. With the development of bionics and material science, the biomimetic adsorbents can see more applications to remove TAOCs on a large scale.

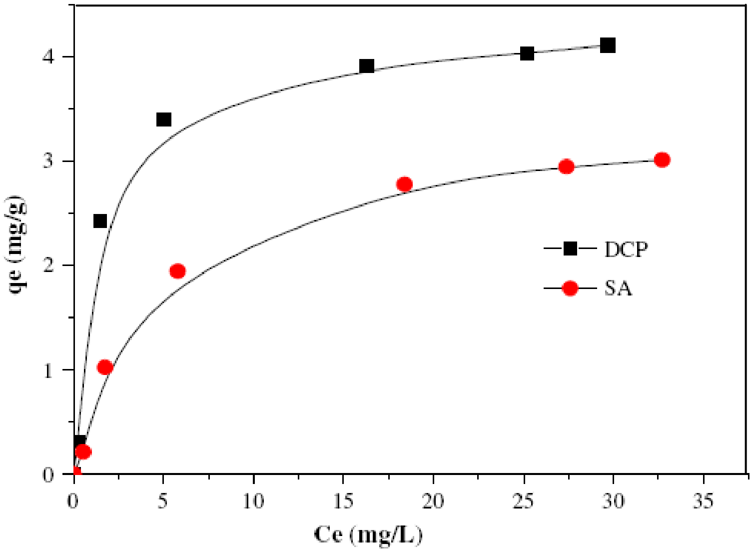


Fig. 11. Loading isotherms of DCP and SA into ALG/CHI shells: experimental equilibrium uptakes and the Langmuir model fitting (pH 7; 25°C). (Ding et al., 2009)

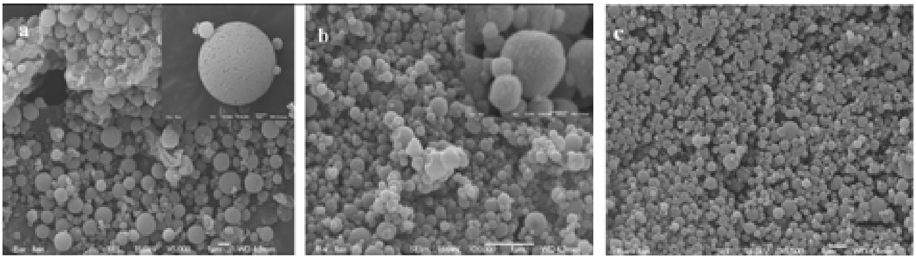


Fig. 12. HR-SEM images of (a) sample A, (b) sample B, and (c) sample D. (Baruch-Teblum et al., 2010)

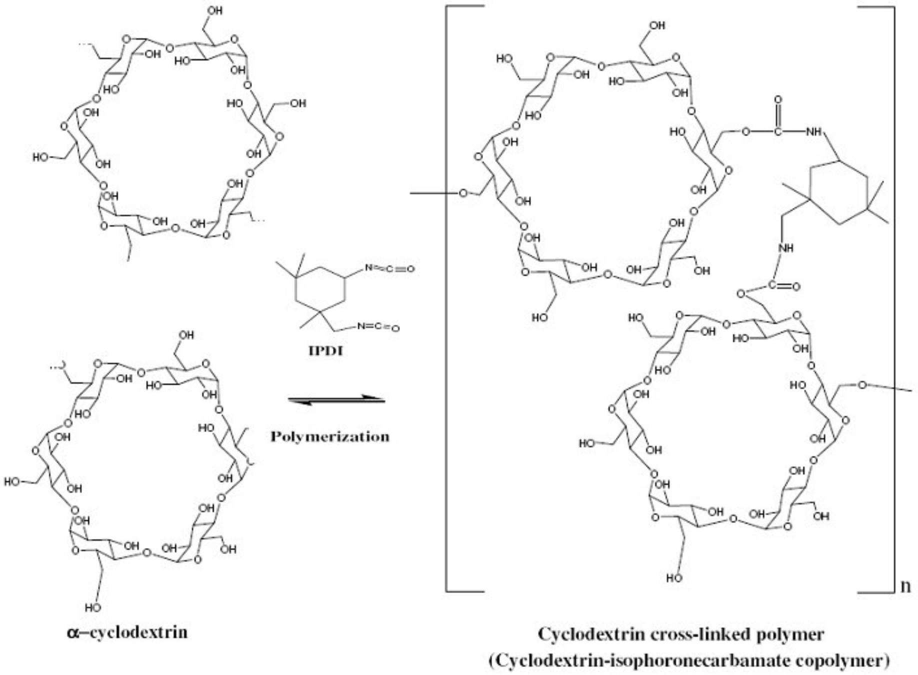


Fig. 13. Copolymerization of cyclodextrine–isophoronecarbamate copolymer. (Baruch-Teblum et al., 2010)

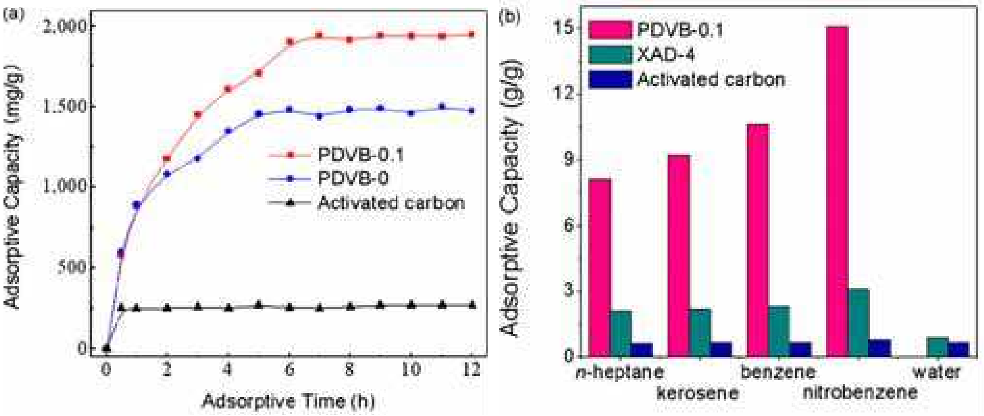


Fig. 14. Dependence of adsorptive capacity for benzene on adsorption time over various samples. (b) Saturated adsorptive capacity of probing molecules in liquid phase over various samples. (Zhang et al., 2009)

5. Biomimetic adsorption and advanced treatment

Although pollutants can be effectively separated from the aqueous phase by adsorbents, an improper treatment of saturated adsorbent will result in secondary pollution. Biological treatment is one of the most common technique for wastewater treatment, as evidenced from the fact that 65% of wastewater all over the world is treated by biological process (the percentage is up to 95% particularly for the municipal sewage). However, biodegradation is affected by two factors: the solubility and concentration of pollutants. Organic compounds with higher solubility are more easy to be degraded by biomass than those with lower solubility. This is why PCB compounds with high chlorine content and with lower solubility are more difficultly to be degraded than those with low chlorine content. Furthermore, if the concentration of pollutant is too low, there will be a lack of nutrients needed for the biomass and the enzyme will not work efficiently. In general, the low concentration of contaminants can not make full use of the degradation ability and satisfy the growth requires of microorganisms. In contrast, the microorganism will be toxic damaged if the concentration of pollutant is too high. In the low concentration range, the degradation rate is linearly enhanced with the increase of contaminants concentration until the maximal concentration value is reached. Therefore, the coupling of adsorption and microbiological degradation for the treatment of POPs will break the balance constantly, thus the contaminants will be removed constantly by the new dynamic process.

Vogt et al. (2004) reported that chlorobenzene can be adsorbed by granular active carbon from ground water and then degraded by biomass. The adsorptive capacity of chlorobenzene on granular active carbon is up to 450 mg/g and permineralization of chlorobenzene was achieved through biomass. The amount of the lipophilic POPs on active carbon and bentonite is limited, but can be significantly improved by addition of PHBBMA and other lipoid adsorbents. The treatment efficiency of refractory wastewater is not satisfactory by the way of biological technique owing to two issues. On the one hand, many pollutants (e.g. POPs) are foreign substances for environment, thus the microorganism is lack of corresponding enzyme system to produce degrading enzyme. On the other hand, the amount of functional microorganism in sludge is not enough to degrade the pollutants. The first issue can be resolved by long-time acclimation because this allows the formation of proper enzyme secreted from microorganism to degrade POPs. To overcome the second problem, polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE) technique can be explored to isolate functional microorganisms bacteria in sludge, and therefore higher efficiency will be obtained by the introduction of functional microbial into the biological treatment system. The conception of PHBBMA, a kind of biomimetic adsorbent, combines the adsorption technology for TAOCs and immobilized cell technology of microorgnism, which use PHAs as the main material and cyclodextrin, tween, polyving alcohol as the excipient. This adsorbent is the immobilized cell support with adsorption capacity, which can embed single or hybrid functional bacteria. TAOCs can be enriched on the surface of PHBBMA, which not only impulses the process of microbial degradation, but also improves the adaptability and resistance of functional bacteria. Furthermore, it is also easy to separate biomass from the aqueous solution. With the pre-enrichment of biomimetic adsorbents for POPs, followed by the enhanced biodegradation of functional bacteria, TAOCs can be detoxificated rapidly and thoroughly. This coupling technology, namely biomimetic adsorption-functional microbial degradation technology, is proved to be a possible practical technology.

Moreover, the combination of adsorption and chemical degradation such as adsorption-catalytic wet oxidation/reduction process and, adsorption-catalytic supercritical water oxidation/reduction may be effective in removing various contaminants with different concentrations. During the control of industrial wastewater, the advanced oxidation/ reduction often served for the pretreatment process, advanced treatment and emergency of highly toxic and non-biodegradable pollutants. It includes photocatalytic oxidation, wet (supercritical) oxidation, Fenton oxidation, hydrogenation reduction and metal reduction, etc. Photocatalytic oxidation that utilizes the power of ultraviolet or visible light and semiconductor catalyst can produce ·OH radical, which possesses high oxidation capacity for degrading of many organic pollutants. Wet oxidation, especially the condition of supercritical water, can mineralize organic compounds to CO_2 and H_2O with in a very short time (~5 min), which is an efficient advanced technology in treating the wastewater containing concentrated, toxic and non-biodegradable contaminants. Fenton technique is based on the reaction of Fe^{2+} and H_2O_2, which can produce ·OH radical to oxidize the organic pollutants. In contrary, advanced reduction technology is able to remove the functional groups such as halogene and nitryl by the reductive substance, which can significantly decrease the toxicity of the organic pollutants. Based on the above principles, to prepare the composite materials combined with biomimetic adsorbents and catalysts, and coupled with the mentioned advanced oxidation or reduction processes is capable of achieving the transform and degradation of the TAOCs. Furthermore, the adsorbents can be regenerated automatically without special treatment, thus a development route of biomimetic adsorbents which integrates multi-coupling technologies needs to be constructed.

6. Acknowledgements

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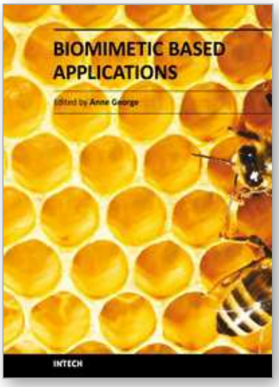

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The interaction between cells, tissues and biomaterial surfaces are the highlights of the book "Biomimetic Based Applications". In this regard the effect of nanostructures and nanotopographies and their effect on the development of a new generation of biomaterials including advanced multifunctional scaffolds for tissue engineering are discussed. The 2 volumes contain articles that cover a wide spectrum of subject matter such as different aspects of the development of scaffolds and coatings with enhanced performance and bioactivity, including investigations of material surface-cell interactions.

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