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Biomimetic fat cell (BFC) preparation and for lindane removal from aqueous solution

Song Liyan [a,1], Zhao Youcai [a,*], Wang Guojian [b], Li Bing [a],
Niu Dongjie [a], Chai Xiaoli [a]

[a] *State Key Laboratory of Pollution Control and Resource Reuse, School of Environmental Science and Engineering Tongji University, Shanghai 200092, China*
[b] *Institute of Polymer Materials, School of Material Science and Engineering Tongji University, Shanghai 200092, China*

Abstract

Fat tissue of organism can accumulate hydrophobic chemicals efficiently and the accumulation level has a positive correlation with fat quantity. In this work, based on this characteristic, an innovative agent, that is, biomimetic fat cell (BFC) has been synthesized with interfacial polymerization. BFC has a hydrophobic nucleolus-triolein and hydrophilic membrane-polyamide, through which water, carrying hydrophobic organic contaminants (HOCs), can pass. This process is followed by the accumulation of HOCs. BFC has 97.39% lindane removal ability. This is close to 98.12% lindane removal by powder active carbon (PAC) in aqueous solution and 7 mg/L initial concentration of lindane. BFC can be regenerated easily by organic solvent dialysis in comparison with high temperature or pressure used for PAC regeneration. Lindane removal by BFC may occur through two mechanisms: bioaccumulation by BFC nucleolus-triolein; and adsorption by BFC membrane. Bioaccumulation is the prevailing mechanism.
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1. Introduction

Organic chemicals, especially the hydrophobic organic contaminants (HOCs) in aqueous environment are toxic and hazardous to various organisms. They are very difficult to remove because of their chemical and biological stability and hydrophobic behavior [1,2]. Conventional water treatment processes, such as aerobic process, sedimentation and coagulation appear to remove efficiently only selected materials [3] or the easily degradable ones [4] although the normal water quality index (COD, BOD, SS, etc.) can reach the requirement. Adsorption onto activated carbon has been proved to be one of the most efficient methods for the HOCs removal, but the high cost of activated carbon and regeneration difficulty limits its use [5]. Thus, alternative adsorbents with low cost, such as bagasse fly ash [6–9], bottom ash [10,11], red mud [12,13], carbon columns obtained from fertilizer waste material [14] and so on, have been widely tested for the removal HOCs.

Fat tissue of organism can accumulate hydrophobic chemicals and the accumulation level has a positive correlation with fat quantity [15–18]. The result has been successfully used as a semi-permeable membrane device (SPMD) for monitoring or evaluating HOCs in aqueous solution [19–21].

In this research, based on this bioaccumulation characteristic of fat tissue, an innovative agent, biomimetic fat cell (BFC) with a hydrophobic nucleolus-triolein and hydrophilic membrane structure-polyamide, from which water carrying HOCs can pass causing the accumulation of the HOCs, was synthesized employing interfacial polymerization. The characteristics of BFC were also studied. Aiming at selected HOCs removal by traditional wastewater treatment, the purpose of this new "BFC" synthesis is to develop an agent for wide-spectrum HOCs removal.

Lindane (γ-hexachlorocyclohexane, γ-HCH) [22], which is included in the environmental protection agency's (EPA) list of organic priority pollutants, was selected to evaluate the HOCs

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* Corresponding author. Tel.: +86 21 65982684; fax: +86 21 65980041.
E-mail addresses: 0310050044@smail.tongji.edu.cn (S. Liyan), zhaoyoucai@mail.tongji.edu.cn (Z. Youcai).
[1] Tel.: +86 21 65980609; fax: +86 21 65980041.

removal capacity by BFC, in comparison with powder active carbon (PAC) known for its moderate hydrophobic property (K_{ow}: 7.8E3; BCF: 1.4E4) [23].

2. Materials and methods

2.1. Reagents and chemicals

Terephthaloyldichloride and 1,6-hexanediamine were purchased from Shanghai Guoyao Chemical Co. Ltd. (China) and used as wall forming materials as received. Triolein was purchased from Shanghai Yunjie Chemical Co. Ltd. (China) as nucleolus materials, and Tween-20 was also purchased from this company as emulsifier. Powder activated carbon (300 mole sieve) was obtained from Liyang Carbon Company (China). Lindane (certified analytical standard, $99.8 \pm 0.1\%$) was provided by institute of organic industrial chemistry, Germany.

Trichloromethane, cyclohexane and methanol were of analysis-grade.

2.2. BFC preparation

Triolein, terephthaloyldichloride and Tween-20 were dissolved into a mixing organic solvent (cyclohexane/trichloromethane) to form a clear oil phase. 1,6-Hexanediamine was mixed with distilled water to form the water phase. The oil phase without triolein and the same water phase before was design to prepare BFC prepolymer.

2.3. BFC characterization

Thermal gravimetric analysis, particle size analysis and appearance analysis of BFC were used with Q 600 SDT (America Thermal) system, LS particle size analyzer (Brruker Equinox 55) and S-2360N SEM (Hitachi, Japan), respectively.

2.4. Lindane removal

Lindane removal experiments were employed the typical jar-test procedure [5], using 1-L beakers and magnetic stirring apparatus under room temperature. Accurately weighted BFC and PAC doses (100 ± 0.1 mg) were added into 500 ml aqueous solutions of lindane (lindane initial concentration: 7 mg/L [22]) with 100 rpm stirring rate to keep the BFC and PAC suspended. PAC used here was boiled in 100 °C hot water for 20 min to remove impurity, and cooled by adding water prior to use [24]. 10 ml samples were taken at prescribed time. Liquid–liquid extraction with subsequent GC–ECD determination was used for the analysis of lindane. After filtered through 0.45 μm membrane filters, 10 ml of each sample were added into 50 ml separatory funnel, and 10 ml cyclohexane was added and the samples were extracted for 10 min. After the phase separation, 1 μl of the extract was used for analysis with GC–ECD.

2.5. BFC regeneration

Every 500 ml cyclohexane, 5% HCl and 5% HNO₃ were used to dialyze the used BFC and PAC, respectively. 10 ml samples in cyclohexane dialysis solution were taken at different interval time (0.5, 1.0, 1.5, 2.0, 2.5, 8.0, 12.0, 24.0 h), filtered through 0.45 μm membrane filters and analyzed directly, and liquid–liquid extraction mentioned above was added to samples in 5% HCl and 5% HNO₃ dialysis solution analysis process.

2.6. GC analysis

A Trace GC Ultra gas chromatography equipped with a ⁶³Ni electron capture detector (ECD) and a Restek 7 m × 0.3 mm × 0.25 mm capillary column was used to detect and quantify lindane [25]. Inlet and detector temperature were 250 and 300 °C, respectively. The carrier gas was nitrogen and the temperature program was as follows: initial temperature 50 °C holding 1 min; increased from 50 to 230 °C at 15 °C/min and subsequently held for 2 min; increased from 230 to 300 °C at 10 °C/min subsequently held for 10 min. Split ratio is 50. The retention time of lindane was 7.9 min. For the quantitation, external calibration was carried out. Standard curve of lindane was recorded. The mean recovery of lindane over the examined concentration ranger (0.05–10 mg/L) was 92% with a relative standard deviation of 7.2%. This recovery was not taken into account for the results evaluation.

3. Results and discussion

3.1. BFC preparation

Interface polymerization, which relies on monomer in the oil phase reacting at the oil/water interface with monomer from the aqueous phase, was employed in BFC preparation [26,27]. When the monomer in oil phase contacts the monomer in water phase, the polymer grows simultaneously in the interface between oil/water phases. If some dissolved materials in oil or water phase are inert in this polymer reaction, they will be entrapped into this growing polymer.

According to the purpose of BFC preparation, BFC should have hydrophilic membrane, and polyamide, which has been successfully used in separation membrane preparation [28,29], was selected to build BFC membrane. Here, terephthaloyldichloride was selected as oil phase monomer, and 1,6-hexanediamine as water phase monomer, and the polyamide reaction equation is shown in Fig. 1

Triolein, which is widely found in fat tissue of most organisms, was selected as the nucleolus material for its hydrophobic
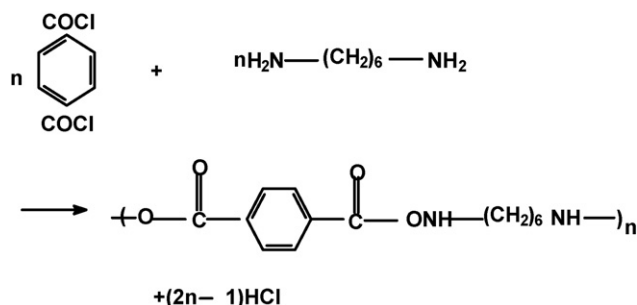

Fig. 1. Chemical reaction equation of BFC.

behavior, and many researches have proved that triolein could accumulate hydrophobic chemicals [30–32]. Triolein quantity could not be more than 30% in this polymerization, because the reaction would not run smoothly when the triolein quantity is above 30%.

Physical property is very important to adsorption effect of adsorbent [26]. Physical property of adsorbent is mainly depended on the influence factors in polymerization process, such as the rate of shear, the phase viscosity, the design of the stirrer and vessel, and the concentration of emulsifier, and so on.

Based on the results of series experiments, the optimization polymerization factors was given from: 0 °C reacting temperature to efficient removal-reaction heat; 2000 rpm stirring rate to keep reaction run smoothly; and 0.5% emulsifier-Tween-20 to make oil phase clear. When the organic phase in a 250 ml separatory funnel was pored into the water phase in a 1-L beaker successively, BFC was formed immediately as solid materials suspending in water. Decompress filtration was used to separate BFC from water. After washing three times with distilled water, BFC was dried at room temperature and stored in a desiccator before used.

3.2. BFC characterization

3.2.1. Thermal gravimetric analysis

Thermal gravimetric analysis of BFC were taken on a Q 600 SDT system under nitrogen at a rate of 10 °C/min from 50 to 700 °C. Fig. 2 shows the derivative thermogravimetric (DTG) of prepolymer for triolein and BFC (15 and 30% triolein contained, respectively). The DTG for two kinds of BFC (15 and 30% triolein contained) showed that BFC nucleolus material–triolein was entrapped by BFC membrane during the polymerization process, as shown by their existing T_{max} (402.3 °C) of triolein for both of them, and this peak height expressed their different quantity of contained triolein. The DTG of prepolymer without T_{max} (402.3 °C) peak of triolein was not entrapped, which matches the composition of oil phase in prepolymer preparation.

3.2.2. Particle size

BFC particle diameter distribution analysis results showed that the particle diameter increased with the contained triolein quantity in BFC preparation. The mean and median particle
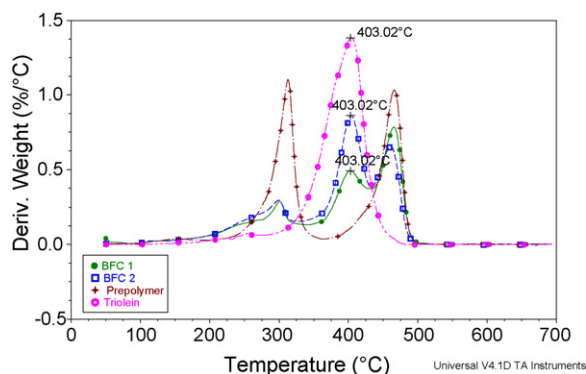
Table 1
Particle diameter of prepolymer, BFC (5, 15 and 30% triolein containing)

Name	Mean diameter (μm)	Median diameter (μm)
BFC prepolymer	0.0976	0.0837
BFC (5% triolein)	0.936	0.732
BFC (15% triolein)	3.104	2.281
BFC (30% triolein)	4.493	4.061

diameters (Table 1) of BFC prepolymer and BFC (5, 15 and 30% triolein contained) were 0.0976, 0.936, 3.104 and 4.493 μm, respectively and 0.0837, 0.732, 2.281 and 4.061 μm, respectively, with 10,000 rpm stirring. It is a supplement proof of the fact that triolein was entrapped within BFC. The BFC could aggregate into particles in millimeters in size, and a 500 rpm stirring could not break the aggregated particles, this situation make BFC engineering using column equipment become possible.

3.2.3. BFC appearance

When the triolein was entrapped by polyamide membrane, the structure of BFC prepolymer and BFC would be different. Compared with the BFC prepolymer, the structure of BFC (15% triolein contained) is regular (Fig. 3) and plump, and the dark area is the triolein contained. Though the surface of BFC is relative smooth, some loci are also produced during the polymerization. The structure of BFC prepolymer (Fig. 4) is irregular, unconsolidated and flocculent. The flocculent structure can possibly bond lindane.

In conclusion, BFC has the hydrophobic nucleolus-triolein and hydrophilic membrane-polyamide membrane, the water carrying the hydrophobic chemicals dissolved in water can pass through the membrane of BFC into the interior, and then the hydrophobic chemicals are accumulated by triolein. Based on the selectively hydrophobic chemicals accumulation function of fat cell, here we call the polymer "biomimetic fat cell".

3.3. Lindane removal

Lindane concentration in aqueous solution is very low, usually in ppb level [5]. Adsorption, for example, activated carbon

Fig. 2. DTG thermograms of prepolymer, triolein, BFC 1 and BFC 2 (triolein contained 15 and 30%, respectively).
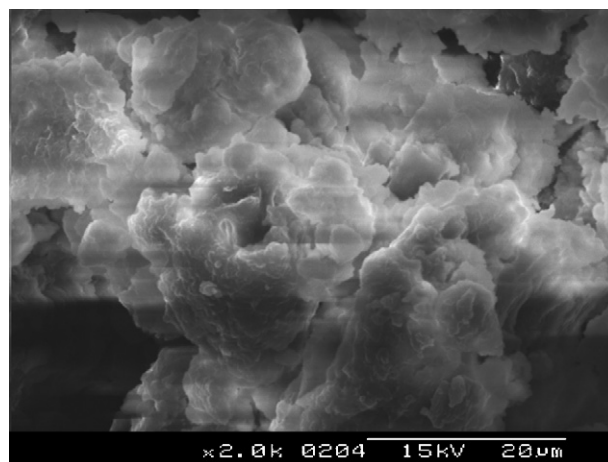

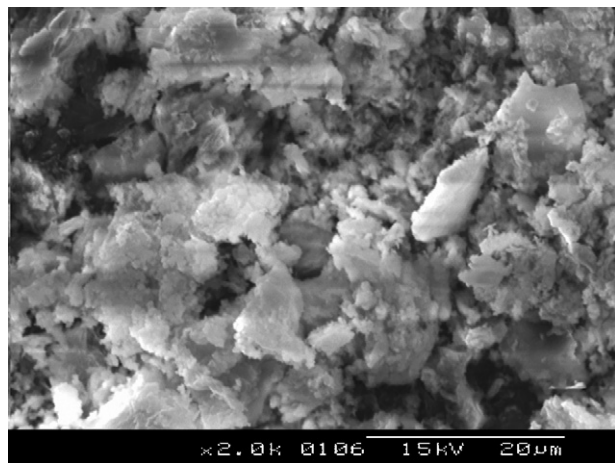Fig. 3. SEM of BFC (15% triolein contained).

Fig. 4. SEM of BFC prepolymer.

[33,34] and bagasse fly ash [6], was efficiently used to remove ppb concentration of lindane from aqueous solution. In this research, lindane was selected to evaluate the HOCs removal capacity of BFC, so here the maximum solution concentration of lindane in aqueous solution (7 mg/L) [22] was selected.

Bioaccumulation can be understood with the principle of "like dissolves like" [33], which means lindane dissolves into triolein with the same hydrophobic property.

After 8 h, the residual lindane in different BFC and PAC experiment is given in Table 2. Clearly, BFC containing with different quantity triolein showed different lindane removal capacity. BFC accumulation capacity of lindane mainly depends on the quantity of triolein similar with fat hydrophobic chemicals bio accumulation relationship with the quantity of fat, but there did not exist the positive correlation between them though it seemed that positive correlation existed in low concentration of triolein (0–15%).

The reason that 30% triolein contained in BFC showed lower lindane removal than that of 15% triolein contained in BFC is because that not all the 30% was entrapped into BFC membrane possible.

Fifteen percent triolein contained in BFC has a 97.39% lindane removal, which is close to 98.12% lindane removal by PAC. Hence, the BFC of 15% triolein contained will be referred to as the best BFC for lindane removal in this study.

Prepolymer also had 15.65% lindane removal. It is possibly because of some adsorption locus formation in the BFC membrane during the polymerization process. Comparing with the 97.39% lindane removal by BFC (15% triolein containing), the mainly lindane (81.74%) should be "accumulated" or "dissolved" by BFC nucleolus-triolein. It means that BFC have two kind hydrophobic chemicals removal mechanism-bioaccumulation and physical adsorption, and bioaccumulation is the main hydrophobic chemicals removal mechanism.

With the large surface area and macro and micro pore structure, the main lindane removal mechanism of active carbon is physical adsorption, this has been reported by some workers [34,35].

3.4. Lindane regeneration

In lindane regeneration, solvent dialysis was used. Obviously, 5% HCl and 5% HNO$_3$ cannot dialyse lindane from BFC and PAC for its hydrophilic property against the hydrophobic property of lindane.

When cyclohexane was used to dialyse lindane, lindane could be easily dissolved into cyclohexane from triolein with the generation of instantaneous dipole between them, which can overcome the instantaneous dipole between triolein and lindane. Lindane residual in BFC and PAC regeneration solution are showed in Table 3. Lindane residual increased in the BFC regeneration solution with the time increasing, and it seemed that 12 h is the appropriately absolute regeneration time. As for PAC, lindane dialysis did not occurred for the physical and chemical stabilities of PAC. In PAC regeneration, usually high temperature and pressure are needed to overcome the stable bond between adsorbed target materials as PAC decomposes these adsorbed materials [36].

With repeated lindane removal experiments, lindane removal efficiency decreased, and lindane removal efficiency by BFC reached the prepolymer when the dialysis was repeated five times (Fig. 5). The reason could be explained by the thermal gravimetric analysis of BFC after five times by cyclohexane dialyze (Fig. 6). T_{max} (402.3 °C) peak of triolein did not exist in the used BFC thermal gravimetric graph after five times cyclohexane dialysis, which means that triolein was also dialysed by cyclohexane step by step.

BFC regeneration mainly depends on the appropriate BFC membrane pore size, which should be between the size of lindane and triolein. When organic solvent is used to dialyse lindane, lindane and triolein both can be dissolved into organic solvent,

Table 2
Lindane removal capacity of different adsorbent

Adsorbents	Lindane removal ratio (%)
Prepolymer	15.65
BFC (5% triolein containing)	60.0
BFC (15% triolein containing)	97.39
BFC (30% triolein containing)	72.03
Powder active carbon	98.12
Contract sample	0

Initial concentration of lindane: 6.9 mg/L.

Table 3
Lindane residual in dialysis solution

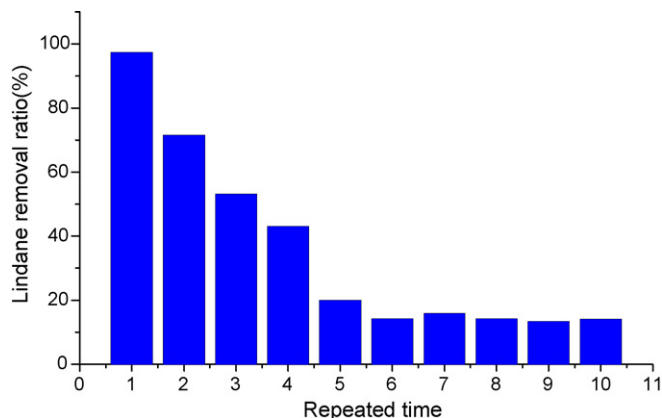| Desorption time (h)	Lindane residual in BFC dialysis solution (mg/L)	Lindane residual in PAC dialysis solution (mg/L)
0.5	0.9	0
1.0	1.3	0
1.5	1.7	0
2.0	1.9	0
2.5	2.8	0
8.0	6.6	0
12	6.7	0
24	6.7	0

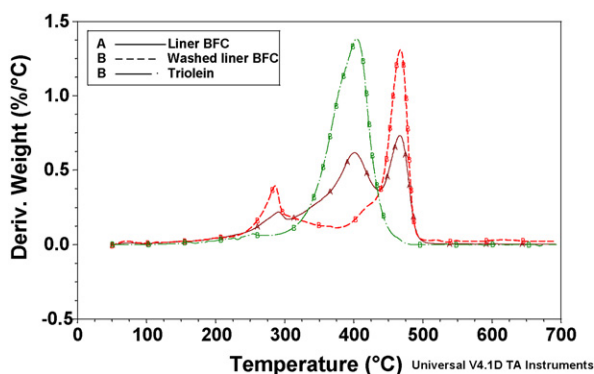Fig. 5. Lindane removal efficiency of regeneration BFC.

Fig. 6. DTG thermograms of L-BFAA after five times dialysis by cyclohexane.

if the BFC membrane pore only permits lindane out of BFC with organic solvent, but stopping triolein, the BFC regeneration will be stable.

4. Conclusion

Low concentration and high toxicity of HOCs in aqueous solution needs innovative control materials or technology to overcome the HOCs selected removal by conventional water treatment technology.

Based on the bioaccumulation of fat tissue, an innovative agent, that is, BFC has been synthesized employing interfacial polymerization. The synthesized BFC has a hydrophobic nucleolus-triolein and hydrophilic membrane structure-polyamide, from which the water carrying the HOCs can pass into the interior, followed by the accumulation of the HOCs. BFC is white solid granular with 3.104 μm mean diameter, and it can be aggregated into relative stable larger particle in millimeters in size for engineering use. As for PAC, it is rather difficult to be applied in a context of a treatment process.

BFC has a good lindane removal capacity close to that of PAC. BFC can be regenerated easily using organic solvent dialysis, while PAC regeneration needs high temperature or high pressure to overcome the stable bond between lindane and PAC or decompose lindane. Furthermore, organic solvent dialysis for BFC regeneration also can recover the target HOCs through distillation, and the organic solvent could be used again. The

BFC synthesis rough materials, such as Terephthaloyldichloride, triolein and 1,6-hexanediamine, can be easily obtained with relative low cost. If the regeneration cost of BFC and PAC was calculated, the BFC showed the cost advantage with close lindane removal capacity.

Lindane removal efficiency of BFC decreased with regeneration time's increasing, so further research will focus on the modification of BFC in order to make BFC regeneration more times. BFC have two kinds HOCs removal mechanisms-bioaccumulation by hydrophobic nucleolus-triolein and physical adsorption by hydrophilic polyamide membrane, and bioaccumulation is the main hydrophobic chemicals removal mechanism.

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