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ScienceDirect
Journal of Hazardous Materials 151 (2008) 805–810
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

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

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Received 28 April 2007; received in revised form 12 June 2007; accepted 14 June 2007
Available online 19 June 2007

Abstract

To improve the regeneration ability of biomimetic fat cell (BFC), an innovative agent for hydrophobic organic contaminants (HOCs) removal, BFC was modified through introducing 1, 3, 5-benzenetricarboxyl trichloride with trifunctional group and heterocyclic piperazine in this research. Modified biomimetic fat cell (MBFC) has a good lindane removal capacity close to that of BFC and powder activated carbon (PAC), and the lindane removal is 97.68, 96.65 and 98.36% with 7 mg/L lindane initial concentration, respectively. At the same time, 20 mg/L MBFC or PAC is sufficient for 10 μg/L lindane removal, and in 20–60 mg/L doses range the lindane removal by both MBFC and PAC can reach 99.0%; When the doses is below 10 mg/L, MBFC showed better lindane removal than PAC and MBFC even could reach 96.8% lindane removal in 5 mg/L dose. Lindane removal by MBFC could be held on 95% above in first 6-time reuse. Though the lindane removal by MBFC decreased with the reuse time increasing, MBFC still could remove 80 % lindane after 9 times regeneration. In contract with BFC, MBFC showed obvious advantage on the regeneration. The lindane removal mechanism by MBFC, similar with BFC, includes bioaccumulation by MBFC nucleolus-triolein and adsorption by MBFC membrane, and the bioaccumulation is the main way.
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Keywords: Modified biomimetic fat cell (MBFC); Hydrophobic organic contaminants (HOCs); Lindane removal regeneration

1. Introduction

Adsorption, especially the activated carbon adsorption, has been proved to be one of the most important techniques for hydrophobic organic contaminants (HOCs) removal in aqueous environment, but the high cost of activated carbon and regeneration difficulty limits its use. Thus, alternative adsorbents with low cost, such as bagasse fly ash [1–4], bottom ash [5,6], red mud [7,8], carbon columns obtained from fertilizer waste material [9] and so on, for the removal HOCs have been tried widely. A review about low-cost adsorbents could be found at the chapter "adsorbents for water treatment: low cost alternatives to carbon" of book "Encyclopedia of surface and collide science" [10].

Based on the fact that fat tissue of organism could accumulate hydrophobic chemicals and the accumulation level has the positive correlation with fat quantity [11–14], an innovative agent, i.e., biomimetic fat cell (BFC) has been synthesized employing with interfacial polymerization. BFC has hydrophobic nucleolus-triolein and hydrophilic membrane-polyamide, the water carrying with the HOCs can pass through the polyamide membrane, and then the HOC_S will be accumulated by the triolein. BFC has 97.39% lindane (7 mg/L) removal ability close to 98.12% lindane removal by powder active carbon (PAC) in aqueous solution, but its regeneration is limited for its linear structure [15].

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

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0304-3894/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.jhazmat.2007.06.057

lindane, lindane and triolein both can be dissolved into organic solvent, if the BFC membrane pore only permits lindane out of BFC with organic solvent, but stopping triolein, the BFC regeneration will be accepted.

The characteristics of polymer such as pore size result from how the chains are linked together in space. Symmetrical monomers such as terephthaloyldichloride and 1, 6-hexanediamineas can join together in only one way to form regular linear structure, while unsymmetrical multifunctional monomers such as 1, 3, 5-benzenetricarboxyl trichloride, terephthaloyldichloride could join piperazine together in random to form networked structure. With the increasing of cross-linkage, the pore size will become smaller and the density and rigidity of polymer will also improve [16].

The object of this research is to improve the regeneration ability of BFC through changing BFC membrane from linear structure to networked structure. Lindane was also selected to evaluate the HOCs removal capacity by modified biomimetic fat cell (MBFC) as selected in BFC preparation [15].

2. Materials and methods

2.1. Reagents and chemicals

Terephthaloyldichloride, 1, 6-hexanediamine and piperazine purchased from Shanghai Guoyao Chemical Co. Ltd. (China) and 1, 3, 5-benzenetricarboxyl trichloride provided by Qingdao Shanli Chemical Co. Ltd. (China) were used as wall forming materials. The nucleolus material-triolein and emulsifier-Tween 20 was purchased from Shanghai Yunjie Chemical Co. Ltd. (China). Powder activated carbon (PAC) (300 mol sieve) was obtained from Liyang Carbon Company (China). Lindane (certified analytical standard, 99.8 ± 0.1%) was provided by institute of organic industrial chemistry, Germany.

Trichloromethane and cyclohexane were of analysis-grade.

2.2. MBFC preparation and characterization

1, 3, 5-Benzenetricarboxyl trichloride, triolein and Tween-20 were dissolved into a mixing organic solvent (cyclohexane: trichloromethane, 4:1) to form the oil phase. 1, 6-hexanediamine and piperazine were mixed with distilled water to from the water phase. The oil phase without triolein and the same water phase before were used to prepare MBFC prepolymer.

Thermal gravimetric analysis, particle size analysis, appearance analysis and specific area analysis of MBFC were used with Q 600 SDT system (America Thermal), LS particle size analyzer (Brruker Equinox 55), S-2360N SEM (Hitachi, Japan) and mercury porosimetry Autoscan 60 (Quantachrome, USA) respectively.

2.3. Lindane removal

The procedure for lindane removal experiments here is same as the procedure described in BFC preparation [15]: Accurately weighted MBFC, BFC and active PAC doses (100 ± 0.1 mg) were added into 500 mL aqueous solutions of lindane (lindane initial concentration: 7 mg/L) contained in 1 L beakers with 100 rpm stirring rate to keep the agents suspended under room temperature.

Liquid–liquid extraction with subsequent GC–ECD determination was used for the analysis of lindane [11]. 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. The retention time of lindane was 7.9 min with 50 split ratio. The mean recovery of lindane over the examined concentration range (0.05–10 mg/L) was 92% with a relative standard deviation of 7.2%.

2.4. MBFC regeneration

Five hundred millilitres cyclohexane was used to dialyze the used MBFC. Ten milliliter samples in cyclohexane dialysis solution were sampled at 12.0 h prescribed in BFC preparation [15], filtered through 0.45 μm membrane filter and analyzed directly.

2.5. Trace lindane removal

With the same procedure as 2.3, accurately weighted a series doses (5,10,20,30,40,50,60 ± 0.1 mg) of MBFC and PAC were added into 1 L aqueous solutions of lindane (lindane initial concentration: 10 μg/L). The lindane analysis is also same as 2.3, except no split was used at GC determination, and the corresponding mean recovery of lindane over the examined concentration range (0.05–10 μg/L) was 94.7% with a relative standard deviation of 5.3%.

3. Results and discussion

3.1. MBFC preparation

The linear structure of BFC formed by double functional group, terephthaloyldichloride and 1, 6-hexanediamineas, could accumulate HOCs, but the relative larger pore size could not make BFC regeneration efficiently [15]. Networked polymer could grow smaller pore size with the increasing of cross linkage comparing with linear polymer [16].

Adding with cross-linking agents and introducing multifunction monomer in polymerization are classical methods to change the linear structure to networked structure of polymer [16]. In this BFC synthesis, it is difficult to find a cross-linking agent which only reacts with monomers but inert to reaction phases. Hence, the trifunctional monomer, 1, 3, 5-benzenetricarboxyl trichloride, was employed, the heterocyclic piperazine was also used as water phase's monomer for the improving of rigidity, and the MBFC reaction equation was showed in Fig. 1.

Polymerization factors, such as the rate of shear, the phase viscosity, the design of the stirrer and vessel, and the concentration of triolein and emulsifier, etc, in the series MBFC experiments were employed with the optimization factors of

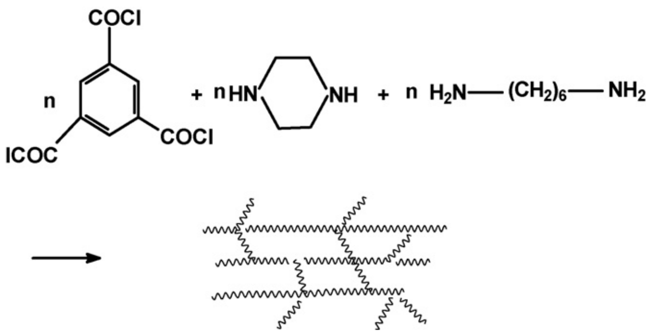

Fig. 1. Chemical reaction equation of MBFC.

BFC preparation, and the relative polymerization factors would be adjusted.

The optimization polymerization for BFC modification was achieved with 0 °C reacting temperature to remove reaction heat, 1500 rpm stirring rate to keep reaction run smoothly and 0.5% emulsifier-Tween 20 to make monomer absolutely dissolve in the oil phase. Organic phase includes 1, 3, 5-benzenetricarboxyl trichloride and terephthaloyldichloride, and water phase is piperazine. When the organic phase in a 250 mL separatory funnel was pored into the water phase in a 1 L beaker successively, MBFC formed immediately as white solid materials suspending in water. Decompress filtration was used to separate MBFC from water. With three times distilled water washed, MBFC dried at room temperature and stored in a desiccator for further use.

3.2. MBFC characterization

3.2.1. Thermal gravimetric analysis

Thermal derivative thermogravimetric (DTG) analysis of MBFC (Fig. 2) by Q 600 SDT system showed that MBFC nucleolus material-triolein was entrapped by MBFC membrane in the polymerization process with a proof of the common existing triolein T_{max} (403.02 °C) in both DTG of MBFC and triolein. Furthermore, the unchanged triolein T_{max} (403.02 °C) peak in the overlapped DTG of MBFC and one time cyclohexane dialyzed MBFC revealed that one time cyclohexane dialyze could not dialysed the triolein (Fig. 2).

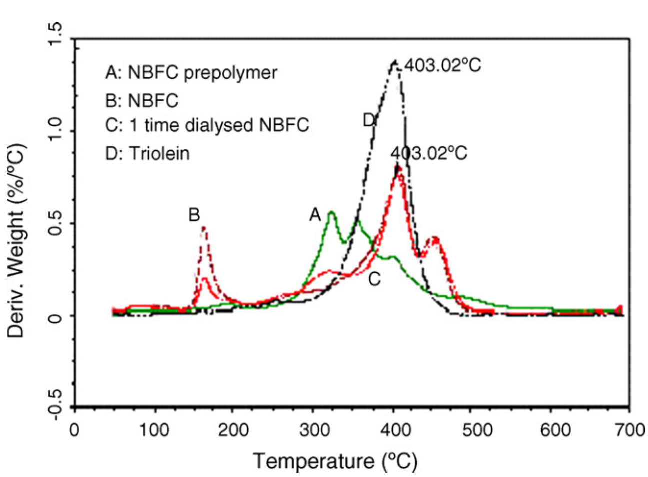

Fig. 2. DTG thermograms of prepolymer of MBFC, triolein, MBFC (containing 15% triolein) and one time cyclohexane dialyzed MBFC.

Table 1
Particle size and specific area summaries of BFC series

BFC series	Mean diameter (μm)	Median diameter (μm)	Specific area (m^2/g)
p-BFC	0.0976	0.0837	21.4621
p-NBFC	1.616	1.353	28.6719
BFC	3.104	2.281	22.3271
NBFC	4.968	3.41	30.2755

p, prepolymer.

3.2.2. Particle size

Particle diameter distribution analysis showed that the mean and median particle diameters of MBFC increased to 4.968 and 3.41 μm from that of 3.104 and 2.281 μm of BFC (Table 1). The particle diameter's growth is because the cross linking degree growth by introduction of the monomers with trifunctional group, and MBFC grew to be relative bigger polymer. Comparing with the mean and median particle diameters of MBFC prepolymer (1.616 and 1.353 μm), the increasing of MBFC particle diameter also indicated that triolein was entrapped into the interior of MBFC.

3.2.3. Appearance

The appearance of BFC and MBFC is different with different structure. Compared with the relative regular BFC's structure (Fig. 3 left part), the structure of MBFC is much more compacted and plump (Fig. 3 right part). The reason is because the increasing of linkage degree.

3.2.4. Specific area

The specific area is one of the most important parameters for adsorption or accumulation. 30.2755 m^2/g specific area of MBFC is larger than 22.3271 m^2/g specific area of BFC (Table 1), and this means that more activated locus could be supplied for lindane reaching.

In a conclusion, the white solid MBFC has the hydrophobic nucleolus-triolein and hydrophilic networked polyamide membrane produced in polymerization. Comparing with BFC, MBFC is bigger, stable and compacted, and the larger specific area might make the HOCs accumulation faster.

3.3. Lindane removal

With 8 h reaction, the residual lindane in the series of MBFC, MBFC prepolymer, BFC and PAC is given in Table 2. MBFC has 97.68% lindane removal, close to 98.36% lindane removal by PAC and 96.65% lindane removal by BFC. Some adsorption locus formation in MBFC or BFC membrane during the polymerization process make the prepolymer of MBFC and BFC also had low lindane removal ability, which are 11.69 and 15.23%, respectively. Comparing with the lindane removal by BFC, BFC prepolymer, MBFC and MBFC prepolymer, the main part of lindane (81.42 and 85.99%) should be

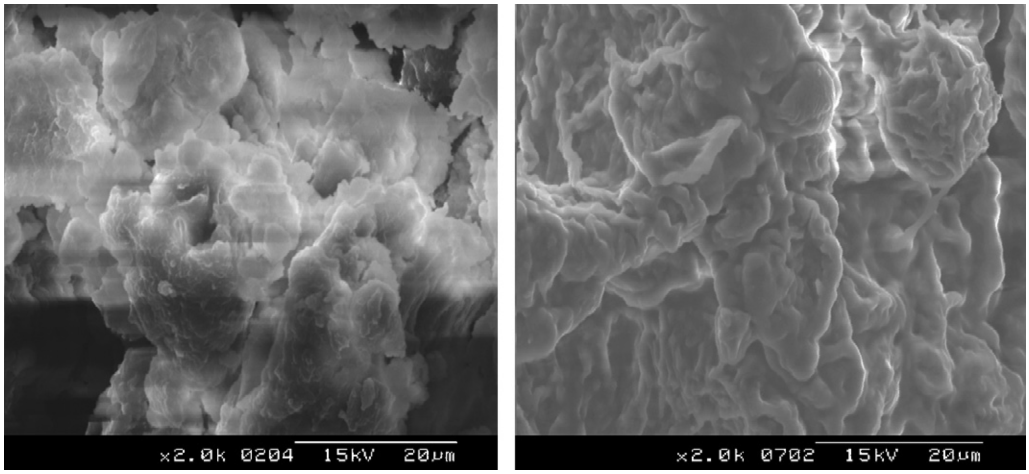

Fig. 3. SEM of MBFC (right) and BFC (left) at 2000× magnifications.

"accumulated" or "dissolved" by BFC and MBFC's nucleolus-triolein [14]. It means that MBFC and BFC both have two kind HOCs' removal mechanisms, which includes bioaccumulation by MBFC nucleolus-triolein and adsorption by BFC membrane and bioaccumulation is the main HOCs' removal mechanism.

3.4. Lindane regeneration

Cyclohexane could be used for MBFC regeneration because that the instantaneous dipole generated between itself and triolein could overcome the instantaneous dipole produced between triolein and lindane.

Lindane removal efficiency by MBFC could be kept on above 95% in the first 6 times reuse and then decreased slow ly. At the 10th reuse, MBFC still could remove 80% lindane.

MBFC and BFC regeneration mainly depends on their appropriate membrane pore size, which should be between the size of lindane and triolein. The existing T_{max} (402.3 °C) peak of triolein in 10 times used MBFC indicated that 10 times used MBFC still has the HOCs removal ability (Fig. 5). Comparing with the T_{max} (402.3 °C) peak of triolein in original MBFC, the T_{max} peak of triolein in 10 times used MBFC decreased, and this is the reason that MBFC regeneration decreases after 6 times used. The MBFC reuse experiment and DTG analysis of MBFC indicated that not all pore size of MBFC was between the size of triolein and lindane, but MBFC has showed obvious regeneration advantage than that of BFC (Fig. 4).

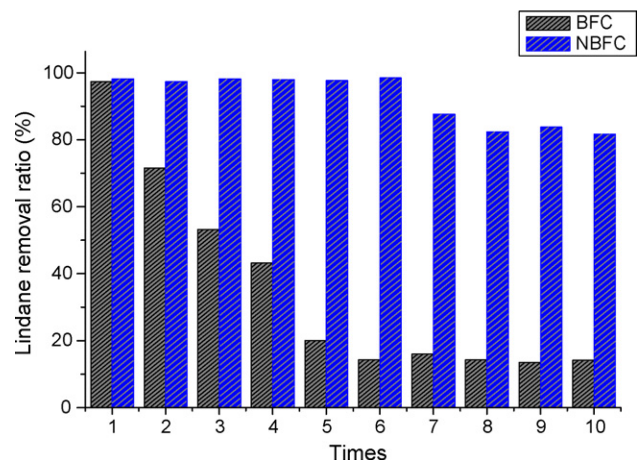

Fig. 4. Lindane removal efficiency of regenerated MBFC and BFC.

Table 2
Lindane removal capacity of different agents

BFC series	Lindane removal ratio (%)
p-BFC	15.23
p-NBFC	11.69
BFC	96.65
NBFC	97.68
PAC	98.36
Control sample	0

p, prepolymer.

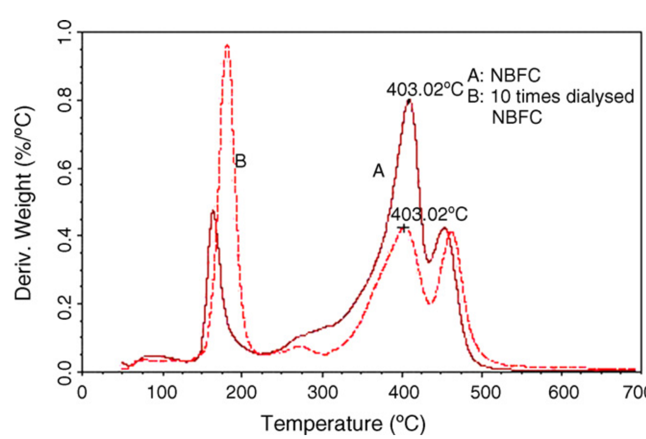

Fig. 5. DTG thermograms of MBFC and MBFC with 10 times dialyzed by cyclohexane.

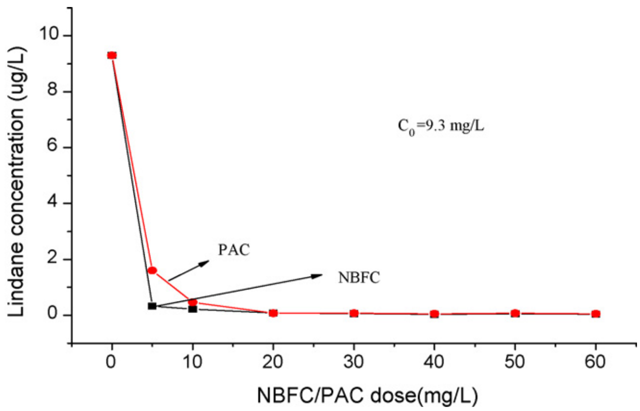

Fig. 6. Effect of MBFC/PAC dose on lindane removal.

3.5. Trace lindane removal

Lindane concentration in aqueous solution usually is pg or ng level, in some river Lindane residual could reach 0.15 μg /L [17], and in some sediment lindane even could reach 0.10–10.37 μg/kg [18]. PAC [17,19] showed better effect on trace lindane removal than conventional wastewater treatment methods [20,11].

The comparison between MBFC and PAC in 10 μg/L lindane removal with 8 h showed MBFC and PAC has the close lindane removal when the dosage of adsorbents is above 20 mg/L (Fig. 6). Lindane removal by MBFC and PAC both increased from 5 mg to 20 mg dosage, and then becomes constant showing that 20 mg/L of MBFC or PAC is sufficient for the optimum removal of lindane. In 5 and 10 mg/L dosage, MBFC showed higher lindane removal than that of PAC, and the relative amount adsorbed is 1.796 and 0.908 μg/mg for MBFC, 1.540 and 0.884 μg/mg for PAC. The relative high lindane removal by MBFC in low dosage could be supported by the fact of hydrophobic chemicals' persistent bioaccumulation by organism [11,21].

4. Conclusions

To improve the regeneration ability of BFC, BFC was modified here through changing its membrane from linear structure to networked structure. The synthesized MBFC is comprised of a hydrophobic nucleolus-triolein and hydrophilic-networked polyamide membrane. MBFC is a white solid granular with 4.968 μm mean diameter larger than 3.104 μm of BFC. The bigger specific area of MBFC, comparing with BFC, might make the HOCs accumulation faster.

MBFC has a good lindane removal capacity close to that of BFC and PAC, and the lindane removal is 97.68, 96.65 and 98.36% with 7 mg/L lindane initial concentration, respectively. mg/L MBFC or PAC is sufficient for 10 μg/L lindane removal, and in the 20–60 mg/L doses range the lindane removal of MBFC and PAC is very close (99%). With the support of HOCs' persistent bioaccumulation by fat issue, the MBFC showed better lindane removal than PAC when the doses is below 10 mg/L and MBFC even could reach 96.8% lindane removal in 5 mg/L dosage.

Both MBFC and BFC could be regenerated easily using cyclohexane dialysis, the target HOCs can recover through distillation from cyclohexane, and cyclohexane could be used again. Lindane removal efficiency of MBFC could be held on above 95% in the first 6 times reuse, and then deceased slowly with the dialysis time increasing, but still had 80% lindane removal capacity when the dialysis time is 10. Comparing with BFC, the MBFC showed great advantage on the regeneration.

MBFC 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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