Preparation and characterization of a lipoid adsorption material and its atrazine removal performance

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Abstract

A novel adsorbent named lipoid adsorption material (LAM), with a hydrophobic nucleolus (triolein) and a hydrophilic membrane structure (polyamide), was synthesized to remove hydrophobic organic chemicals (HOCs) from solution. Triolein, a type of lipoid, was entrapped by the polyamide membrane through an interfacial polymerization reaction. The method of preparation and the structure of the LAM were investigated and subsequent experiments were conducted to determine the characteristics of atrazine (a type of HOC) removal from wastewater using LAM as the adsorbent. The results showed that LAM had a regular structure compared with the prepolymer, where compact particles were linked with each other and openings were present in the structure of the LAM in which the fat drops formed from triolein were entrapped. In contrast to the atrazine adsorption behavior of powdered activated carbon (PAC), LAM showed a persistent adsorption capacity for atrazine when initial concentrations of 0.57, 1.12, 8.31 and 19.01 mg/L were present, and the equilibrium time was 12 hr. Using an 8 mg/L initial concentration of atrazine as an indicator of HOCs in aqueous solution, experiments on the adsorption capacity of the LAM showed 69.3% removal within 6–12 hr contact time, which was close to the 75.5% removal of atrazine by PAC. Results indicated that LAM has two atrazine removal mechanisms, namely the bioaccumulation of atrazine by the nucleous material and physical adsorption to the LAM membrane. Bioaccumulation was the main removal mechanism.

Key words: lipoid adsorption material; atrazine; powdered activated carbon

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Introduction

Some organic chemicals, such as hydrophobic organic contaminants (HOCs), can be toxic to living organisms in the aqueous environment. HOCs are very difficult to remove from water because of their chemical and biological stability and hydrophobic behavior (Covaci et al., 2002; Galassi et al., 2002). Adsorption onto activated carbon has been shown to be one of the most important techniques for HOC removal from water. However, the high cost of activated carbon materials and their regeneration presents difficulties that limit the application of activated carbon for HOC removal. Recently, low cost alternatives to activated carbon, such as bagasse fly ash (Gupta and Ali, 2001, 2004a; Gupta et al., 2002; Gupta and Sharma, 2003), red mud (Gupta et al., 2005; Jain et al., 2003) and bottom ash (Gupta et al., 2004b, 2004c) have been investigated to determine their capacity to remove HOCs from solution. New agents are also being developed, such as a biomimetic fat cell (BFC) for removal of lindane from aqueous solution (Song et al., 2007, 2008, 2009) and a composite adsorbent for dieldrin removal (Ru et al., 2007).

Previous researchers have shown that the fatty tissue of organisms can accumulate hydrophobic chemicals and that the level of accumulation has a positive correlation with the quantity of fat (Burgaz et al., 1994; Alexander et al., 2000; Kareen et al., 2001; Costabeber and Emanuelli, 2003). Based on this bioaccumulation as a function of the quantity of fat tissue, an innovative lipoid adsorption material (LAM), with a hydrophobic nucleolus (triolein) and hydrophilic membrane structure (polyamide), was synthesized in this research using an interfacial polymerization reaction. A similar material, BFC, was synthesized in previous studies (Song et al., 2007, 2008), however, lindane was chosen to be the only target pollutant. More HOCs should be studied to completely characterize the adsorption performance of this innovative adsorbent.

In this research, atrazine (2-chloro-4-ethylamine-6-siopropylamino-s-triazine) was selected to evaluate the HOC removal capacity of the synthesized LAM. Atrazine is a selective triiazine herbicide used to control weeds in various crops and in non-agricultural areas (Castro et al., 2009). Atrazine is the world’s most commonly applied
herbicide, used globally in agriculture and forestry with 70,000–90,000 tons applied annually (Ta et al., 2006). Atrazine is classified as a potential human carcinogen by the US EPA (Belluck et al., 1991). Atrazine is also a significant source of groundwater contamination because of its resistance to microbial degradation, slow hydrolysis, low vapor pressure, and moderate aqueous solubility.

1 Materials and methods

1.1 Reagents and chemicals

For the preparation of LAM, terephthaloyldichloride, 1,6-hexanediamine, triolein and 4′-aminoacetophenone were purchased from Shanghai Guoyao Chemical Co., Ltd. (China). Tween-20 was purchased from Shanghai Jierun Chemical Co., Ltd. (China). Sodium hydroxide, hydrochloric acid, pyridine, cyclohexane and methanol were purchased from Tianjin Basifu Chemical Co., Ltd. (China). All chemicals were of analytical grade.

Atrazine was purchased from Jiema Chemical Co. Ltd. (China). Powdered activated carbon (PAC) (300 mole sieve) was obtained from Chemical plant of Tianjin (China), which produces material with a specific surface area of 500–1000 m$^2$/g. The PAC was boiled in distilled water for 2 hr to remove impurities and subsequently dried for 24 hr at a temperature of 105°C.

1.2 LAM preparation

An interface polymerization reaction was employed for the preparation of LAM (Goran et al., 2005). To begin, triolein, terephthaloyldichloride and tween-20 were dissolved into quantitative cyclohexane to form the oil phase of the reaction. 1,6-Hexanediamine and sodium hydroxide were then mixed with distilled water to form the water phase. The water phase was slowly added to the oil phase drop by drop to control the interfacial polymerization speed. The oil phase without triolein and the same water phase were used to prepare the LAM prepolymer. The synthesized material was thoroughly rinsed with deionized water then dried for 24 hr at a temperature of 105°C.

1.3 LAM characterization

Thermal gravimetric analysis was used to characterize the LAM produced using the STA 449C system (Netzsch, Germany). Particle size analysis was carried out with a Mastersizer SLS particle size analyzer (Malvern, England). Appearance was examined using an S-570 scanning electron microscope (SEM) (Hitachi, Japan). Specific area and pore size were analyzed using an ASAP2020 specific surface area and pore size analyzer (Micromeritics Inc., USA).

1.4 Adsorption equilibrium

Atrazine was selected as a model chemical to represent HOCs. Preliminary kinetic tests were carried out to determine the equilibrium time and adsorption capacity. It was assumed that equilibrium was attained when no further changes in the atrazine concentration were observed after a 24 hr contact time.

The adsorption of atrazine from aqueous solution by the LAM (with 3% triolein content) and by PAC were compared in the experiment. The effect of the initial concentration of atrazine was investigated by mixing LAM or PAC (30 mg respectively) with 150 mL volumes of atrazine solution of four different initial concentrations (0.57, 1.12, 8.31 and 19.01 mg/L). The suspensions were agitated using a mechanical shaker at 150 r/min and at a temperature of 30°C for 24 hr. Liquid samples were taken throughout the reaction period until equilibrium was achieved.

1.5 Atrazine removal

The adsorption of atrazine from aqueous solution by the LAM prepolymer, LAM with 3% triolein content and PAC were compared. LAM and PAC (30 mg) were added to conical flasks with 150 mL aqueous solutions with an initial concentration of 8 mg/L atrazine. Flasks were shaken at room temperature for 24 hr. Liquid samples were taken throughout the reaction period until equilibrium was achieved.

1.6 Atrazine analytical procedure

To determine the concentration of atrazine, samples were removed by liquid-liquid extraction (LLE) and subsequently analyzed using a UV-spectrophotometry (7825N, SPSIC, China) to determine the residual concentrations of atrazine.

Each water sample (5 mL) was extracted by LLE with 10 mL of cyclohexane in a separating funnel for three times. The extracts were dried in a vacuum at –50°C for 24 hr, then 2 mL distilled water and 0.2 mL of pyridine solution (9% (V/V) of concentrated hydrochloric acid, 55% (V/V) of pyridine and 36% (V/V) of distilled water) were added into the dried samples before the mixture was boiled at 105°C for 15 min. After the samples were cooled to room temperature, 1 mL of 2 mol/L NaOH solution and 2 mL of 4-aminoacetophenone were added to produce a color reaction. After a 5 min reaction, distilled water was added to give a 10 mL volume. The reaction system was observed by spectrophotometry at 464 nm. The detection limit for the method was 0.16–1.6 mg/L atrazine. Recovery of the atrazine varied from 97%–103%, which demonstrated that favorable recoveries and good repeatability were obtained in the analytical process.

2 Results and discussion

2.1 Lipoid adsorption material LAM preparation

Two types of adsorbent were synthesized, one without biomimetic fat (prepolymer) and the other one with biomimetic fat (polyamide polymer, or LAM).

According to the purpose of LAM preparation, LAM should have a hydrophilic membrane. In these experiments, polyamide was selected to build the hydrophilic membrane. Triolein, which is widely found in the fatty membrane. Triolein, which is widely found in the fatty
lus material. An interface polymerization reaction was employed to form an absorbent with a hydrophobic nucleolus (triolein) and hydrophilic membrane structure (polyamide). Based on the results of a series of production trials, the optimum conditions to achieve polymerization were found to occur at room temperature with a ratio of oil phase to water phase equal to 1:1, and at a stirring rate of 1500 r/min to ensure the reaction proceeded smoothly.

Under these optimal reaction conditions, LAM was formed immediately as a light yellow solid powder with good flexibility and ability to bear hydraulic shear, as shown in Fig. 1. The synthesized LAM was thoroughly rinsed with deionized water and dried for 24 hr at 105°C and stored in a desiccator until use.

2.2 LAM characterization

2.2.1 Appearance

SEM was used to investigate the appearance of both LAM with 3% trioilein and its prepolymer. Figure 2a and b shows the appearance of the prepolymer at 500 and 2000 times magnification, respectively. It can be seen that the structure of the prepolymer was much less dense compared with LAM (Fig. 2c and d). The particle size of prepolymer was non-uniform and most of the particles were smaller than 100 μm. Obvious openings were present due to the very loose arrangement of the particles. Figure 2c and d shows the appearance of the LAM at 500 and 2000 times magnification. With a stable membrane of polyamide, LAM shows a regular structure compared with that of the prepolymer, as compact particles were linked with each other. Openings were present in the structure of the LAM in which the fat drops formed from trioilein were entrapped.

Increases in the trioilein content (from 3% to 5% and 10%) resulted in the formation of larger fat drops, which affected the uniformity of the LAM structure (photo not
shown. The SEM photographs for the LAM with 3% triolein showed a relatively regular spherical structure and openings. Based on this, the optimum triolein content in the LAM used in this research was considered to be 3%.

2.2.2 Thermal gravimetric analysis and particle size

Thermal gravimetric (TG) analysis results for triolein, LAM and its prepolymer are shown in Fig. 3. The TG analysis results for the four kinds of LAM (LAM with 1%, 3%, 5% and 10% triolein content, respectively) showed that the $T_{\text{max}}$ (the temperature at maximum rate of degradation) of triolein (470°C) was evident for all materials, and the peak height reflected their different triolein contents. This indicated that the LAM nucleolus material, triolein, was entrapped by LAM membrane during the polymerization process. The $T_{\text{max}}$ (470°C) peak was absent from the TG analysis of the prepolymer, indicating that triolein was not entrapped.

Particle size distribution analysis results are shown in Table 1. The results showed that the mean and median particle diameters of LAM increased with the increases in triolein content during LAM preparation. The mean diameters of LAM prepolymer and LAM with 1%, 3% and 5% triolein content were 52.24, 59.17 and 66.83 μm, respectively. The median particle diameters of these materials were 18.25, 44.02 and 50.01 μm, respectively. This shows that triolein was entrapped within LAM, and that the increasing concentration of triolein increased the pore size of the poly membrane, consequently increasing the particle size during the aggregation of LAM. Song et al. (2007) synthesized BFC at 0°C and a 2000 r/min stirring rate, which resulted in a much smaller mean and median particle diameter.

2.2.3 Specific area and pore size analysis

The specific area is one of the most important parameters for adsorption performance. Larger specific area means more activated locus could be supplied during the adsorption of HOCs, leading to a faster HOC accumulation. The specific area and the average pore size of the prepolymer and the LAM with 3% triolein content were analyzed in our experiment, and the results are shown in Table 2.

The higher specific area, specific pore capacity and average pore size of LAM with 3% triolein compared to the LAM prepolymer provides strong evidence that more HOCs may be adsorbed by the LAM with 3% triolein content.

2.3 Atrazine adsorption equilibrium

The adsorption equilibrium processes of atrazine on LAM with 3% triolein content and PAC at 30°C, with four different initial atrazine concentrations are presented in Fig. 4. Results showed that, for PAC, the adsorption equilibrium could be achieved in 2 hr when the initial concentration of atrazine varied from 0.57 mg/L up to 19.01 mg/L. However, LAM shows a persistent adsorption capacity for atrazine, and the equilibrium time was 12 hr. The equilibrium adsorption capacity of the tested adsorbents are listed in Table 3. Both of the absorbents show an increase in the adsorption of atrazine per unit weight with increasing initial concentration, however, when the initial concentration of atrazine was 19.01 mg/L, the difference in the adsorption capacity of LAM and PAC became more significant than those with lower initial atrazine concentration. The results suggested that LAM may present a good

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Table 1. Particle size distribution analysis

<table>
<thead>
<tr>
<th>Name</th>
<th>Mean diameter (μm)</th>
<th>Median diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prepolymer</td>
<td>52.24</td>
<td>18.58 (12–15)</td>
</tr>
<tr>
<td>LAM (3% triolein)</td>
<td>59.17</td>
<td>44.02</td>
</tr>
<tr>
<td>LAM (5% triolein)</td>
<td>66.83</td>
<td>50.01</td>
</tr>
</tbody>
</table>

Table 2. Pore characteristics and specific area of prepolymer and LAM (3% triolein content)

<table>
<thead>
<tr>
<th>Name</th>
<th>Specific area (m²/g)</th>
<th>Average pore size (nm)</th>
<th>Specific pore capacity (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prepolymer</td>
<td>4.92</td>
<td>23.08</td>
<td>0.0010</td>
</tr>
<tr>
<td>LAM (3% triolein)</td>
<td>20.27</td>
<td>47.18</td>
<td>0.0489</td>
</tr>
</tbody>
</table>

Table 3. Adsorption capacity in relation to the initial atrazine concentration of LAM (3% triolein content) and PAC

<table>
<thead>
<tr>
<th>Initial atrazine concentration (mg/L)</th>
<th>LAM adsorption capacity (μg/mg)</th>
<th>PAC adsorption capacity (μg/mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.57</td>
<td>2.192</td>
<td>2.166</td>
</tr>
<tr>
<td>1.12</td>
<td>4.358</td>
<td>4.822</td>
</tr>
<tr>
<td>8.31</td>
<td>27.705</td>
<td>32.35</td>
</tr>
<tr>
<td>19.01</td>
<td>55.924</td>
<td>78.86</td>
</tr>
</tbody>
</table>
2.4 Atrazine removal

The atrazine removal capacity of the prepolymer, LAM with 3% triolein and PAC, is shown in Fig. 5. After being shaken for 24 hr, 69.3% of atrazine was removed from solution using the LAM with 3% triolein content, which equates to 27.7 mg atrazine per gram of LAM. The maximum absorbent rate occurred after 6–12 hr. The atrazine removal of prepolymer was 23.7% after 24 hr, probably due to the formation of adsorption locations in the LAM membrane during the polymerization process.

Based on this, the atrazine removal by LAM with 3% triolein content was caused by both the physical adsorption of the LAM membrane and by the bioaccumulation of the LAM nucleous-trolein. The PAC removed 75.5% of the atrazine from solution, which is equivalent to 31.7 mg atrazine per gram PAC. This was probably due to the large surface area of PAC and the nature of the macro and micro pore structure. Previous reports have shown that the main atrazine removal mechanism of PAC is physical adsorption (Zadaka et al., 2009). Similar comparison research was carried out on BFC, PAC and granular activated carbon (GAC) for HOCs removal from pretreated landfill leachate (Song et al., 2009), the result showed that BFC can remove more HOCs than PAC and GAC. A triolein-embedded activated carbon composite adsorbent (CA-T) was prepared and applied for the adsorption and removal of dieldrin from aqueous systems (Ru et al., 2007), and the performance was compared to that of GAC. The result indicated that CA-T was advantageous over pure GAC in dieldrin removal in trace amount. The results of both this research and relative studies suggest that these new triolein entrapped adsorbents are promising material for removing lipophilic pollutant.

A higher lindane removal by BFCs was reported by Song et al. (2007, 2008), who indicated that more than 96% of lindane could be removed from water by a BFC and a modified BFC with an initial lindane concentration of 7 mg/L. There are three reasons for this difference in results. Firstly, the synthesized BFC used in the research by Song et al. had a higher triolein content. A BFC with 15% triolein content was indicated to perform most effectively for lindane removal. Secondly, the BFC synthesized by Song et al. had much smaller mean and median particle diameter and larger specific area than the BFCs in the current study due to a higher stirring speed during production than that used in the current study. Thirdly, atrazine has a higher water solubility than lindane. According to the principle of “like dissolves like”, lindane may have dissolved more effectively than atrazine into the nucleolus of the BFC in that study.

3 Conclusions

Based on the bioaccumulation of HOCs within fatty tissue in previous research, an innovative absorbent, LAM, was synthesized by interfacial polymerization. The synthesized LAM had a hydrophobic nucleolus (triolein) and hydrophilic membrane structure (polyamide), through which water carrying HOCs could pass while the HOCs accumulated in the nucleolus. The synthesized LAM in this research was a light yellow powder with a mean diameter of 59.17 μm and specific area of 20.27 m²/g (with a 3% triolein content). The synthesized LAM showed an effective atrazine removal capacity which was close to that of PAC. An atrazine removal capacity of 69.3% was achieved by LAM with 3% triolein content. Atrazine...
removal was attributed to both physical adsorption to the LAM membrane and bioaccumulation of atrazine by the LAM nucleolus.

Acknowledgments

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References


