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Applications of chitosan beads and porous crab shell powder for the removal of 17 organochlorine pesticides (OCPs) in water solution

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ABSTRACT

A new method for the treatment and elimination of 17 organochlorine pesticides (OCPs) in water solution using porous crab shell and chitosan beads as adsorbents is described. The OCPs have been used worldwide as an agricultural insecticide, and shown to contaminate in both biological and environmental samples. In this report, we investigate the use of crab shell and chitosan powder for the reduction of water-soluble organochlorine pesticides present in water. Removal of OCPs was studied by means of solid-phase microextraction (SPME) method. Two commercially available SPME fibers, 100 μm PDMS and 65 μm PDMS/DVB, were compared in the SPME extraction of OCPs, where the 65 μm PDMS/DVB exhibited better performance. The experimental results indicate that chitosan beads and crab shell powder can both effectively remove the 17 OCPs from water solution with sum of their concentrations ranging from 2.0 to 2.8 ng mL^{-1}.

1. Introduction

Worldwide production and use of organochlorine compounds (OCs) since the 1950s have resulted in their widespread occurrence in the environment. Their chemical properties such as lipophilicity and persistency can lead to bioaccumulation and biomagnifications in the fatty tissues of biological specimens, and within the food chain brought on a high degree of contamination in high tropic organisms (Hoekstra et al., 2003; Kucklic & Baker, 1998; Tanabe, Tanaka, & Tatsukawa, 1984). Bioaccumulation of these compounds has been related to serious toxic threats. During the past several decades, organochlorine pesticides (OCPs) were produced with impurity and were used in large quantities in various countries. These persistent organic pollutants are usually discharged into the environment through waterways and also accumulated in sediment and aquatic organisms (Hong, Chen, Xu, Wang, & Zhang, 1999; Jing, Li, Feng, Wang, & Zhang, 1992; Yang, Shen, Fu, & Min, 1997). They may eventually accumulate in human bodies via food chain concentration.

Monitoring the trace levels of organochlorine pesticides in water is important for human health protection and environmental control. So far, the most important techniques for the analysis of OCPs are liquid–liquid extraction (LLE), solid-phase extraction (SPE) and SPME. LLE, through classical and once widely used, is now seldom used because a large volume of hazardous organic solvent has to be used during the process. For SPE, one inherent disadvantage is the low percentage of injection (Qiu & Cai, 2010). In this study, we conduct a comparative study between headspace solid-phase microextraction (HS-SPME) and direct immersion solid-phase microextraction (DI-SPME).

Chitosan is a natural coagulant, and its coagulative action is very effective as compared to the mineral coagulants such as aluminum sulfate, polyethyleneimine and polyacrylamide in removing chlorophenols from aqueous solution (Ganjidoust, Tatsumi, Wada, & Kawase, 1996). The removal of colours from textile waste water produced by the textile industry using chitosan beads has been reported (Sye, Lu, Tai, & Wang, 2008). Chitosan has also been used in the form of flakes or powder in the adsorption of metals. Process has been made to produce chitosan/PVA (poly(vinyl alcohol)) hydrogen beads so that they can be regenerated after metal adsorption and reused in subsequent adsorption operations (Li & Bai, 2002). Porous crab shell powder is widespread in nature and has been utilized for the treatment of waste water, such as removal of heavy metals, phenols or colour (Muzzarelli, 1977; Sun, Payne, Moas, Chu, & Wallace, 1992; Sye et al., 2008). The fact that the crab shell has adsorption properties (Muzzarelli, 1977; Park, Kim, Lee, & Lee, 1998; Peter, 1995), suggesting an idea that it could be utilized as an adsorbent for trapping and pre-concentrating volatile organic compounds (VOCs) in air samples and the sulfur containing compounds in natural gas (Sye, Chen, & Wu, 2003). Crab shell is mainly composed of $CaCO_3$, protein and chitin (poly(β-1,4-N-acetyl-D-glucosamine)), and the important types of adsorption mechanisms are electrostatic and dipole interactions. The adsorption mechanisms of chitosan (poly(β-1,4-D-glucosamine)), beside

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the electrostatic and dipole interactions, the complexation interactions are also important (Li & Bai, 2002). Many of other natural sorbents, including agricultural waste materials and by-products of cellulosic origin, can remove more metals via ion-exchange mechanism rather than by adsorption (Ho & Wang, 2008).

Currently, the principal methods for the selective removal of OCPs residues involve physical (Aslan & Türkman, 2004; Ru et al., 2007; Sprynskyy, Ligor, & Buszewski, 2008) and/or bacterial cells processes (Awasthi, Singh, Jain, & Khangarot, 2003; Lee et al., 2003). In this paper, we present the concept of using chitosan beads and porous crab shell powder for the treatment and elimination of 17 OCPs in water samples. The analytical method is based on SPME and followed by GC-electron-capture detection (ECD) to determine OCPs in waters. In our experiment, the crab shell powder is home made, and chitosan was purchased from chemical company.

To detect and treat these OCPs, we describe here a simple and more rapid method for the extraction and analysis of these compounds using HS-SPME and DI-SPME techniques and a gas chromatograph coupled with a ^{63}Ni ECD.

2. Experimental

2.1. Reagents and materials

Chitosan (50/100 mesh, 297–149 μm) from crustaceans, with a molecular weight of 4.57×10^5 Da and a degree of deacetylation above 89%, was purchased from Kiotek, Inc. (Hsinchu, Taiwan). Crab shell was obtained from the supermarket, and the crab shell powder is home made with the size of crab shell particles of 50–100 mesh (297–149 μm).

The crab shell powder (50/100 mesh) was conditioned under a helium flow (5 mL/min, 200 °C) for 5 h before use. Volumetric flask (total capacity 22 mL) was purchased from Yih Yu, Inc. (Taipei, Taiwan). Ultra pure water was prepared using a Milli-Q water purification system from Millipore (Bedford, MA, USA).

For solid-phase microextraction, the commercially available SPME fibers, 100 μm PDMS and 65 μm PDMS/DVB were purchased from Supelco (Bellefonte, PA, USA). All fibers were conditioned in the hot injector part of the gas chromatograph for 30 min at 250 °C, according to the instructions provided by the manufacturer.

2.2. Standard solutions

An analytical standard solution of OCPs mixture, containing α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, aldrin, heptachlor epoxide isomer B, α-endosulfan, 4,4′-DDE, dieldrin, endrin, β-endosulfan, 4,4′-DDD, endrin aldehyde, endosulfan sulfate, 4,4′-DDT, endrin ketone and methoxychlor, was purchased from Supelco (Bellefonte, PA, USA). The stock solution was prepared by diluting 1 μL original standard solution mixture (2000 ng/μL) to a 0.4 ng/μL with acetone in a 5 mL reaction vial and stored at −5 °C. Fresh working solutions were prepared by a proper dilution of the stock solution with Milli-Q water following the requirement of the experiments.

2.3. Headspace and direct immersion SPME

Headspace (HS) and direct immersion (DI) SPME techniques were evaluated for analyzing the target organochlorine pesticides in water solution. HS-SPME is used generally for analyzing volatile compounds, whereas DI-SPME is for semivolatile compounds. The analysis of trace levels of OCPs in water solution can normally be carried out using HS-SPME and DI-SPME techniques. On one hand, HS-SPME method can avoid interferences from native compounds contained in the samples, where those compounds would normally be adsorbed on the fiber in DI-SPME mode. On the other hand, DI-SPME is simpler and can potentially offer higher sensitivity when semivolatile and non-volatile compounds are sampled by SPME methods. In our experiments, we propose to use HS-SPME mode for analyzing OCPs in water solution. Aliquots of 5 μL (or 7 μL) of the standard stock solution and 17 mL Milli-Q water were transferred into a 22 mL glass vial and closed with PTFE-coated septum and then the vial was immersed in a temperature-controlled water bath, the heating temperature was set to 72 °C during the sampling process. Sampling was pierced via the septum with the holder needle to allow the SPME fiber to be placed just 5 mm over the surface of the solution. The SPME equilibrium was achieved by stirring the sample for 30 min, during which analytes were adsorbed on the stationary phase of the fiber. After extraction, the fiber was removed from the vial and immediately transferred into the GC injection port at 250 °C, until desorption was completed (4 min). After HS-SPME sampling, the same samples were also extracted by DI-SPME. The holder needle was inserted through the septum and the fiber was directly immersed in the same sample solution for 30 min under magnetic stirring at room temperature (23 °C). The magnetic stirring can facilitate the mass transport of the analytes between the water sample and the fiber. The other extraction steps were the same as those in HS-SPME.

For HS-SPME and DI-SPME, two types of coating fibers were evaluated: 100 μm polydimethylsiloxane (PDMS) and 65 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB). Performances of SPME were also evaluated by calculating the total peak areas obtained for OCPs on eight (8) consecutive extractions of the same solution sample.

2.4. Gas chromatography analysis

A gas chromatograph (Hewlett-packed 6890) equipped with an electron capture detector ^{63}Ni was used for the analysis of organochlorine pesticides. Analyses were performed using a 30 m × 0.32 mm I.D. DB-5 capillary column (0.25 μm film thickness; J&W Scientific, Inc., Folson, CA). The column was held at 100 °C for 1 min, and raised to 265 °C at a rate of 3 °C/min, and then hold for 5 min at 265 °C. Nitrogen (99.999% purity) was used as carrier gas at a constant flow of 1 mL/min. The temperature of the detector was set to 300 °C with nitrogen as makeup gas at a flow rate of 60 mL/min.

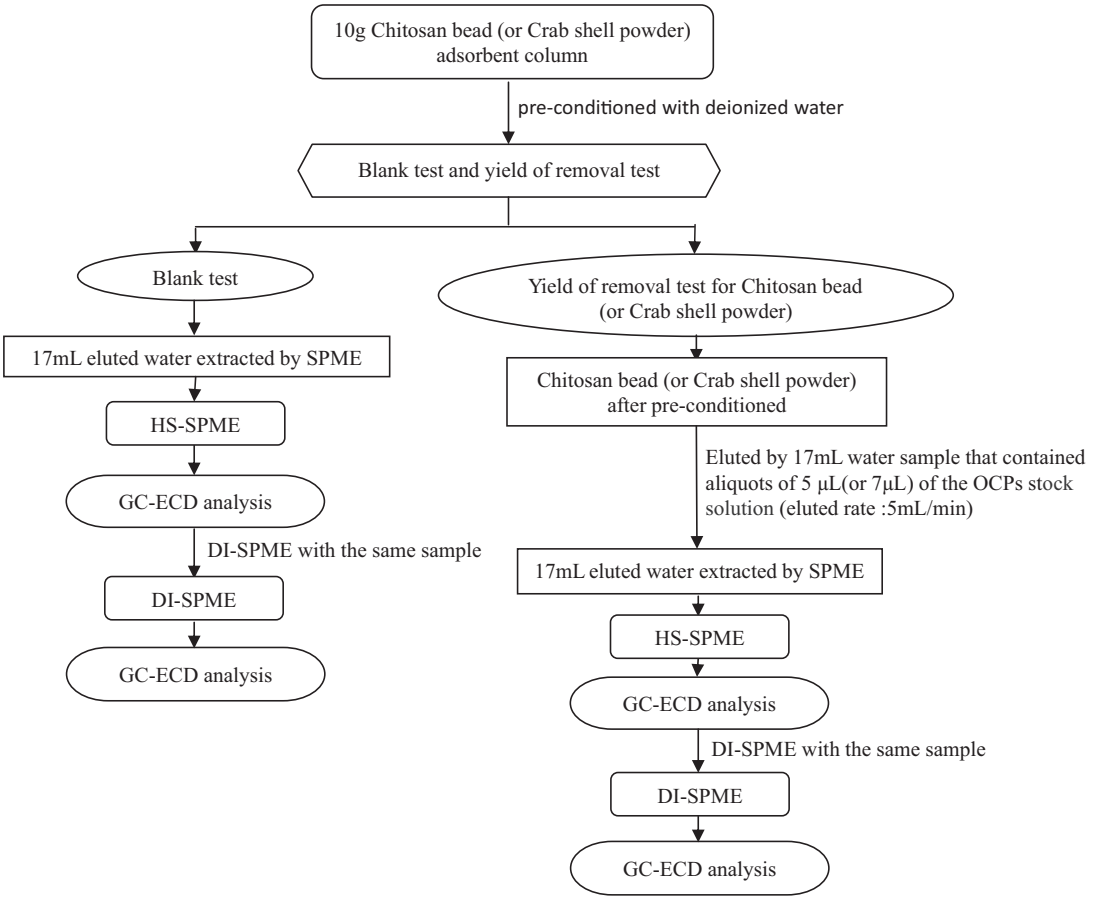
2.5. Adsorption of organochlorine pesticides (OCPs) on chitosan beads and porous crab shell

In this part of study, the chitosan beads and crab shell powders were used as adsorbents for the adsorption of OCPs from water solution. Sorption tests were performed in vertical fixed bed columns filled with 10 g chitosan beads at the size of 1.5 cm × 11 cm (diameter × height) and 1.5 cm × 3.5 cm for 10 g crab shell powders, where the overall length of the column was 20 cm. After the columns were washed with 500 ml Milli-Q water, 17 mL of water spiked with 5 μL of 0.4 ng/μL standard stock solution of OCPs was passed through the columns at a 5 mL/min average flow rate until 17 mL of solution was obtained. Finally, the collected water solution was extracted by headspace and direct immersion SPME. For another sample, aliquots of 7 μL of the standard stock solution of OCPs were conducted with the same procedures described above. Sample processing procedure for removing OCPs from water solution is illustrated in Scheme 1.

3. Results and discussion

3.1. Surface morphology of adsorbents

The surface morphology of adsorbents was examined using scanning electron microscope (SEM). The SEM micrographs of the



Scheme 1. Sample processing procedure for the removal of OCPs from water solution.

chitosan bead and the crab shell powder surface were reported in our previous work (Sye et al., 2003; Sye et al., 2008). From the surface images, they were illuminated that chitosan bead and crab shell powder had a rough surface.

The adsorption surface area of crab shell adsorbent measured by BET sorptometer was 19.5 m^2/g, and total pore volume and pore diameter were 0.12 mL/g and 22.8 nm, respectively; and those for chitosan were 1.99 m^2/g, 0.005 mL/g and 3.67 nm, respectively; were also in agreement with our previous work (Sye et al., 2008). Park et al. (1998) mentioned that pores served as the adsorption site and crab shell composed of relatively large pore size and the small number of pores per unit area in comparison with the porous polymers available commercially. The observations indicated that crab shell adsorbent displays a good adsorptivity for the large airborne compounds.

3.2. Separation of organochlorine pesticide compounds

Fig. 1 shows a gas chromatogram of the separation of α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, aldrin, heptachlor epoxide isomer B, α-endosulfan, 4,4′-DDE, dieldrin, endrin, β-endosulfan, 4,4′-DDD, endrin aldehyde, endosulfan sulfate, 4,4′-DDT, endrin ketone and methoxychlor by injecting 0.8 μL standard stock solution of organochlorine pesticide compounds to GC-ECD. The results show that the resolution of OPCs separation is satisfactory.

3.3. Performance of solid phase microextraction

Two SPME fiber coatings, 100 μm PDMS and 65 μm PDMS/DVB, were evaluated to select the most appropriate system. Fortified aqueous samples (17 mL Milli-Q water spiked with 5 μL standard stock OCPs solution) were extracted by headspace and direct immersion SPME. For each fiber coating, the evaluations were done by calculating the total peak areas obtained for OCPs on eight times (8) consecutive extractions with HS-SPME and DI-SPME. The extraction time for each run was 30 min. The samples were mag-

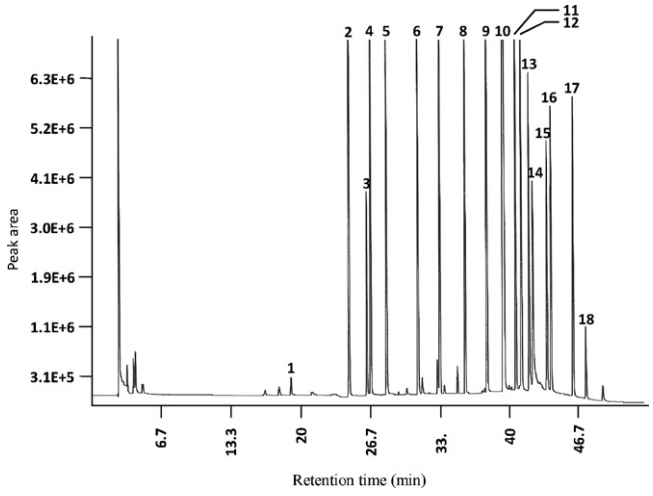


Fig. 1. Typical GC-ECD chromatogram of standard mixture of 18 OCPs (DB-5 column). Peak: 1 = α-HCH; 2 = β-HCH; 3 = γ-HCH; 4 = δ-HCH; 5 = heptachlor; 6 = aldrin; 7 = heptachlor epoxide isomer B; 8 = α-endosulfan; 9 = 4,4′-DDE; 10 = dieldrin; 11 = endrin; 12 = β-endosulfan; 13 = 4,4′-DDD; 14 = endrin aldehyde; 15 = endosulfan sulfate; 16 = 4,4′-DDT; 17 = endrin ketone; 18 = methoxychlor.

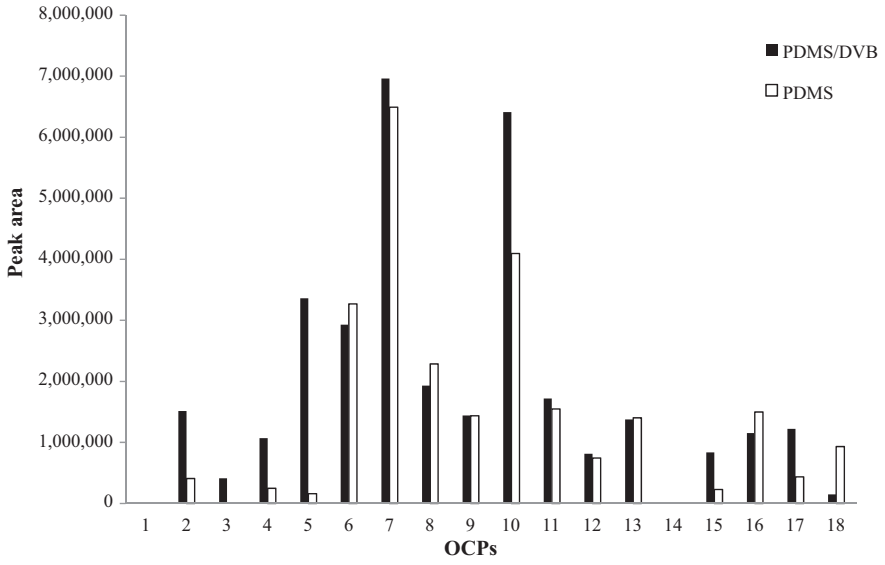


Fig. 2. Comparison of the extraction quantities for the 18 OCPs using 100 μm PDMS and 65 μm PDMS/DVB fiber coatings with HS-SPME and DI-SPME on eight (8) consecutive extractions. Pesticides numbering is the same as in Fig. 1. SPME methods were given in the text.

netically stirred during the extraction process. Areas (sum of all eight (8) consecutive extractions) obtained for each pesticide with different fibers are shown in Fig. 2. The results show that the 65 μm PDMS–DVB fiber coating gave the higher peak areas in the absorption of the analytes as compared to those of the 100 μm PDMS coating. The effectiveness of PDMS–DVB fiber is probably due to the presence of two adsorbents as compared to other compositions, and was selected for further experiments. Fig. 3 shows the gas chromatogram of the OCPs sample, containing 7 μL standard stock solutions in 17 mL water samples. The organochlorine pesticide compounds were extracted by HS-SPME and DI-SPME coated with PDMS–DVB fiber. The peak areas obtained for each pesticide between HS-SPME and DI-SPME are compared in Fig. 4, representing the sum of the data on all eight (8) consecutive extractions of 7 μL standard stock solution in 17 mL water solution.

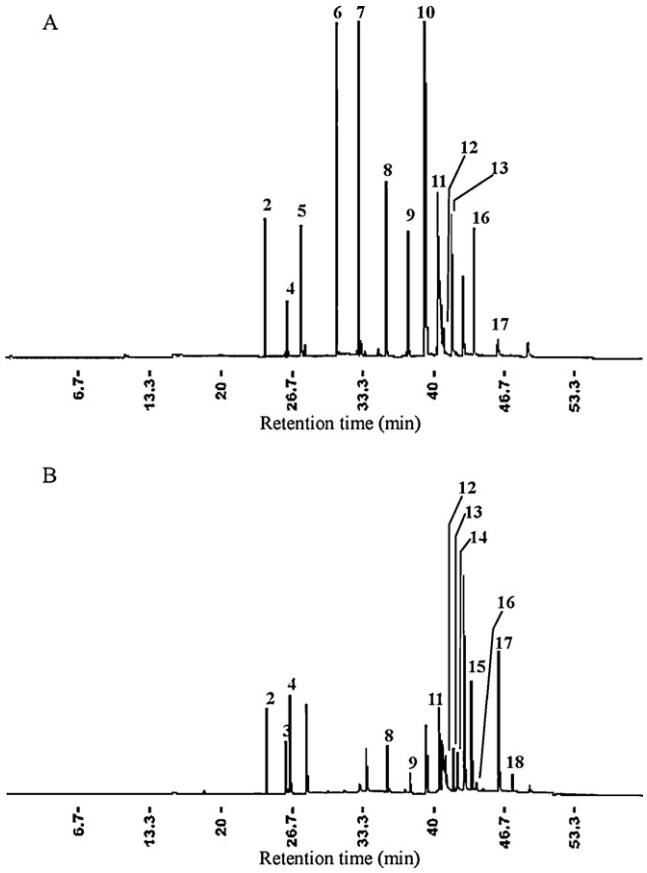


Fig. 3. GC-ECD chromatograms of a OCPs standard mixture sample that extracted by (A) HS-SPME and (B) DI-SPME. Both DI-SPME and HS-SPME were performed for 30 min, at room temperature and 72 °C, respectively. Pesticides numbering is the same as in Fig. 1.

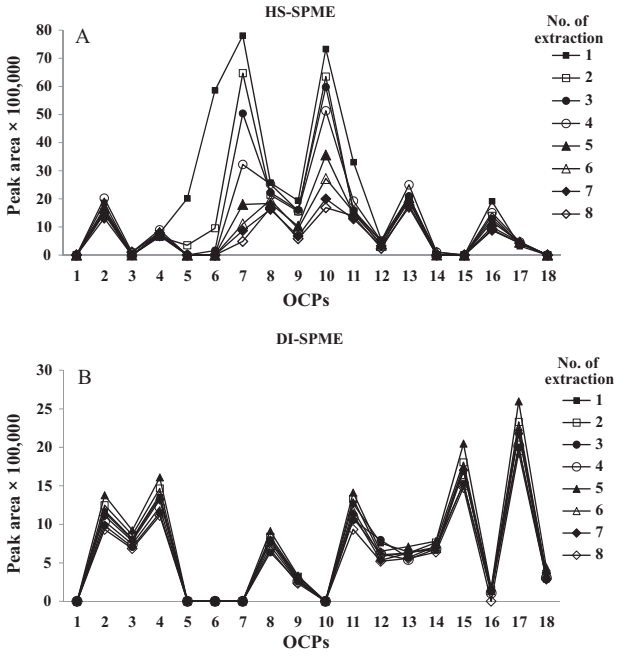


Fig. 4. Comparison of extraction efficiency of 7 μL OCPs standard sample by eight (8) consecutive extractions between HS-SPME and DI-SPME. Concentration of each analyte, 0.4 ng/μL. Both DI-SPME and HS-SPME were performed for 30 min, at room temperature and 72 °C, respectively. Pesticides numbering is the same as in Fig. 1.

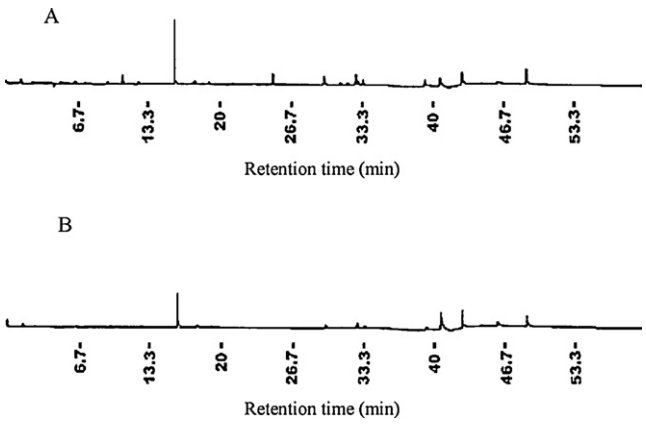


Fig. 5. GC-ECD chromatograms of OCPs water sample after the treatment by crab shell powder obtained by (A) HS-SPME and (B) DI-SPME.

3.4. Removal of OCPs using chitosan beads and porous crab shell

Adsorption of OCPs onto chitosan beads and porous crab shell was monitored chromatographically by the procedure described above. Adsorption results were converted into peak area data of gas chromatography analysis. Fig. 5 shows the chromatogram of OCPs water sample treated by crab shell powder and sequentially extracted from the solution by means of HS-SPME and DI-SPME. Fig. 5 indicates that the OCPs in water solution can be effectively removed when crab shell powder was used. Tables 1 and 2 report the results for our method. As can be seen, the 17 OCPs were significantly removed by chitosan beads and porous crab shell, and their percentages of removal were >99%. As shown in Tables 1 and 2, the peak area for each pesticide (2.0 ng and 2.8 ng) was obtained by the totaling of all eight (8) consecutive extractions with HS-SPME and DI-SPME, respectively. We use 4,4′-DDE to study the adsorption capacity (μg OCP/g powder) between crab shell and chitosan powder. The results indicate that the adsorption capacity of chitosan beads is between 6.7 and 10 μg, and that of crab shell powder is between 0.1 and 0.15 μg. In our previous report (Sye et al., 2008), we used p-tert-amyl phenoxy ethanol (dye) for adsorption capacity study. The adsorption capacity of crab cell powder was determined to be 1.2–1.7 mg, and that of chitosan bead was 2.7–4.0 mg. These results indicated that the adsorption capacity of chitosan beads is better than that of crab shell powder, probably due to the adsorption mechanisms of chitosan (poly(β-1,4-D-glucosamine)), beside the electrostatic and dipole interactions, the complexation interaction may play an important role in the enhancement of adsorptivity.

Ru et al. (2007) have used triolein-embedded composite adsorbent for the selective removal of 4 OCPs, such as dieldrin, endrin, aldrin and heptachlor epoxide from aqueous solution. In this study, we employ chitosan beads and porous crab shell powder that can simultaneously remove the 17 OCPs from water solution.

Table 1
Changes in peak area counts of OCPs (2.0 ng each pesticide) from water solution before and after treatment by porous crab shell and chitosan beads.

	Adsorbents			
	Crab shell		Chitosan beads	
	Before	After	Before	After
α-HCH	N.D.	N.D.[a]	N.D.	N.D.
β-HCH	13,534,127	N.D.	13,534,127	N.D.
γ-HCH	3,977,172	N.D.	3,977,172	N.D.
δ-HCH	10,139,926	N.D.	10,139,926	N.D.
Heptachlor	3,961,555	N.D.	3,961,555	N.D.
Aldrin	3,432,740	N.D.	3,432,740	N.D.
Heptachlor epoxide	20,493,846	N.D.	20,493,846	N.D.
α-Endosulfan	15,130,349	N.D.	15,130,349	N.D.
4,4′-DDE	8,504,635	N.D.	8,504,635	N.D.
Dieldrin	28,417,740	N.D.	28,417,740	N.D.
Endrin	15,694,116	N.D.	15,694,116	N.D.
β-Endosulfan	6,689,142	N.D.	6,689,142	N.D.
4,4′-DDD	11,949,667	N.D.	11,949,667	N.D.
Endrin aldehyde	209,319	N.D.	209,319	N.D.
Endosulfan sulfate	8,207,944	N.D.	8,207,944	N.D.
4,4′-DDT	7,631,604	N.D.	7,631,604	N.D.
Endrin ketone	11,669,194	N.D.	11,669,194	N.D.
Methoxychlor	1,346,026	N.D.	1,346,026	N.D.

Conditions given in Section 2.
[a] N.D. means no response or peak area <100,000.

Table 2
Changes in peak area counts of OCPs (2.8 ng each pesticide) from water solution before and after treatment by porous crab shell and chitosan beads.

	Adsorbents			
	Crab shell		Chitosan beads	
	Before	After	Before	After
α-HCH	N.D.	N.D.[a]	N.D.	N.D.
β-HCH	22,007,225	N.D.	22,007,225	N.D.
γ-HCH	6,626,832	N.D.	6,626,832	N.D.
δ-HCH	16,657,573	N.D.	16,657,573	N.D.
Heptachlor	2,363,111	N.D.	2,363,111	N.D.
Aldrin	6,976,412	N.D.	6,976,412	N.D.
Heptachlor epoxide	26,797,470	N.D.	26,797,470	173,820
α-Endosulfan	22,712,250	N.D.	22,712,250	N.D.
4,4′-DDE	12,168,203	N.D.	12,168,203	N.D.
Dieldrin	34,750,073	N.D.	34,750,073	N.D.
Endrin	23,449,522	N.D.	23,449,522	N.D.
β-Endosulfan	8,384,560	N.D.	8,384,560	N.D.
4,4′-DDD	20,990,560	N.D.	20,990,560	N.D.
Endrin aldehyde	5,854,440	N.D.	5,854,440	N.D.
Endosulfan sulfate	13,538,100	N.D.	13,538,100	N.D.
4,4′-DDT	11,059,568	N.D.	11,059,568	N.D.
Endrin ketone	20,875,806	N.D.	20,875,806	N.D.
Methoxychlor	2,684,539	N.D.	2,684,539	N.D.

Conditions given in Section 2.
[a] N.D. means no response or peak area <100,000.

4. Conclusion

The present study has shown that chitosan beads and crab shell powder can both be effectively used to treat and remove the 17 organochlorine pesticides (OCPs) in water samples. The adsorption mechanisms of crab shell and chitosan, beside the electrostatic and dipole interactions, the complexation interactions are also important. According to the study of surface morphology of these two adsorbents, they display a rough surface and pores that can serve as the adsorption site for pesticides. A rapid and simple multi-residue method based on the HS-SPME and DI-SPME techniques has been developed using PDMS–DVB fibers for determining 17 organochlorine pesticides in water. Performances of SPME were also evaluated by calculating the total peak areas obtained for OCPs on eight (8) consecutive extractions of the same solution sample. In this work, the results indicate that the SPME–GC-ECD method developed was suitable for the qualitative and semi-quantitative analysis of organochlorine pesticides in water solution.

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