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ScienceDirect
Carbohydrate Polymers 72 (2008) 550–556
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Short communication

Applications of chitosan beads and porous crab shell powder combined with solid-phase microextraction for detection and the removal of colour from textile wastewater

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Received 6 February 2007; received in revised form 21 September 2007; accepted 24 September 2007
Available online 9 October 2007

Abstract

A new method to remove the colour from textile wastewater using porous crab shell and chitosan beads as adsorbents is described. The delivery of colour in the form of dyes onto textile fibers is not an efficient process. As a result, most of the wastewater produced by the textile industry is coloured. Colour pollution in aquatic environments is an escalating problem, despite the fact that there has been substantial research into the modification of the dyeing process to improve the level of affinity/fixation of the dye stuffs onto the substrate. The biotechnology approach to colour removal from textile effluent has been investigated. However, in this report, we present here concerns the use of crab shell and chitosan powder for the reduction of water-soluble dyes present in textile dyeing wastewater. Removal of colour from aqueous solution with crab shell and chitosan powder was studied by means of solid-phase microextraction (SPME) and determined by gas chromatography/mass spectrometry (GC/MS).

Keywords: Colour removal; Textile wastewater; Chitosan; Crab shell; SPME

1. Introduction

Coloured wastewater is a consequence of batch processes both in the dye manufacturing industries and in the dye-consuming industries. Coloured wastewater is particularly associated with those reactive azo dyes that are used for dyeing cellulose fibers. These dyes make up approximately 30% of the total dye market (Pearce, Lloyd, & Guthrie, 2003; Willmott, 1997). Residual colour is a problem with reactive dyes because, in current dyeing processes, as much as 50% of the dye is lost in the wastewater. These losses are due to the relatively low levels of dye-fiber fixation and to the presence of unreactive hydrolysed dye in the dyebath. Azo dyes have been widely used as colourants in a variety of products such as textiles, paper and leather. These chemicals present a potential human health risk as some of them have been shown to be carcinogenic (Cioni, Bartolucci, Pieraccini, Meloni, & Moneti, 1999; Waeker, 1970). It has also been shown that synthetic precursors, intermediates, by-products and degradation products of these dyes may be potential health hazards, owing to both their toxicity and their carcinogenity.

Currently, the major methods of textile wastewater treatment involve physical, chemical and/or using whole bacterial cells process (Abraham et al., 2003; Brass, Ferra, Pinheiro, & Goncalves, 2001; Martins, Queiroz, Silvestre, & Lima, 2002; Pearce et al., 2003; Stolz, 2001). In this work, we report the removal of colour from textile wastewater with chitosan beads and natural porous crab shell powder. In our experiments, the crab shell powder is homemade. Chitosan is produced from *N*-deacetylation of chitin, a major component of crustacean shells and fungal biomass, and is readily available from seafood processing wastes. The chemical structure of chitosan is shown in Fig. 1.

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doi:10.1016/j.carbpol.2007.09.031

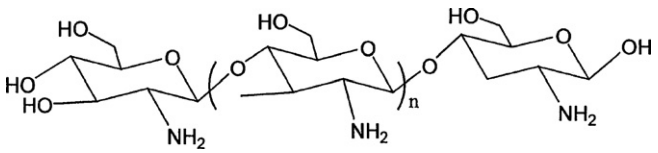

Fig. 1. The chemical structure of chitosan.

To detect these compounds of dyes, we describe here a simple and more rapid method with lower detection limit that allows for the extraction and analysis of these chemicals by using solid-phase microextraction (SPME) technique and a gas chromatograph coupled with a mass spectrometer detector (GC/MS).

2. Experimental

2.1. Materials

All analyses were performed using a gas chromatograph (Hewlett-Packed 6890) equipped with flame ionization detector (FID) and Varian GC/MS system composed of a CP 3800 gas chromatograph coupled with a Saturn 2000 mass spectrometer detector. For solid-phase microextraction, the fibers employed were coated with polydimethylsiloxane (PDMS), 100 μm film thickness, and were purchared from Supelco. All fibers were conditioned in the hot injector part of the gas chromatograph for 0.5 h at 250 °C, according to the instructions provided by the manufacturer.

Chitosan (50/100 mesh, 149–297 μm), which is powder from crab shells, was purchased from kiotek Inc. (Hsinchu, Taiwan). Its degree of deacetylation determined by NMR was 89%, and molecular weight (MW) was 4.57×10^5 Da. The crab shell powder (50/100 mesh) was conditioned under a helium flow (5 mL/min, 200 °C) for 5 h before use. Reaction vials (total capacity 5.0 mL) were purchased from Pierce (Rockford, IL, USA).

The textile wastewater from Taipei County, Taiwan was used in this study. Wastewater sample was sieved to remove coarse particles and debris. A 50 mL textile wastewater was for the batch adsorption experiments. The glassware used in this study was washed with the cleaning solution to remove trace amounts of organics on the surface of vials.

2.2. Experimental conditions

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 80 °C for 1 min, then increased to 250 °C at a rate of 3 °C/min, and then hold 10 min at 250 °C. Helium served as carrier gas. Signal areas were measured with an integrator (Shimadzu C-R6A). Mass spectrometric conditions were: transfer line temperature 270 °C; ion trap temperature 200 °C; electron ionization (70 eV) and the acquired mass range 70–250 Da.

The SPME fiber was immersed in the sample (3 mL) in reaction vial for 30 min during agitation. After extraction, the fiber was thermally desorbed for 4 min into the glass liner of the gas chromatograph injector at 260 °C. Possible carryover was removed by keeping the fiber in the injector for an additional period of time with the injector in the split mode.

The adsorption column was of pyrex glass with a bed length of 10 cm, inside diameter 1.5 cm; the overall length of the column was 22 cm. Chitosan bead (3.15 g) and crab shell powder (8.73 g) were used as adsorbents. Each adsorption column was packed with chitosan or crab shell powder plugged with silanized glass wool and pre-conditioned with distilled water before use.

3. Results and discussion

The physical properties such as adsorption surface area of chitosan adsorbent were examined using a scanning electron microscope (SEM). Fig. 2 shows the result of morphology characterized by SEM. The SEM micrographs of the crab shell powder surface was obtained in previous work (Sye, Chen, & Wu, 2003). The adsorption surface area of crab shell adsorbent measured by the BET sorptometer was 19.5 m^2/g, and total pore volume and pore diameter were 0.12 ml/g and 22.8 nm; and for chitosan were 1.99 m^2/g, 0.005 ml/g and 3.67 nm, respectively. As shown in the physical properties of crab shell, the material of crab shell is composed of relatively large pore size, and show the small number of pores per unit area in comparison to porous polymers available commercially.

We have developed a new SPME analytical method to check for the presence of colour compounds in textile dyeing wastewater. The method is both rapid and simple

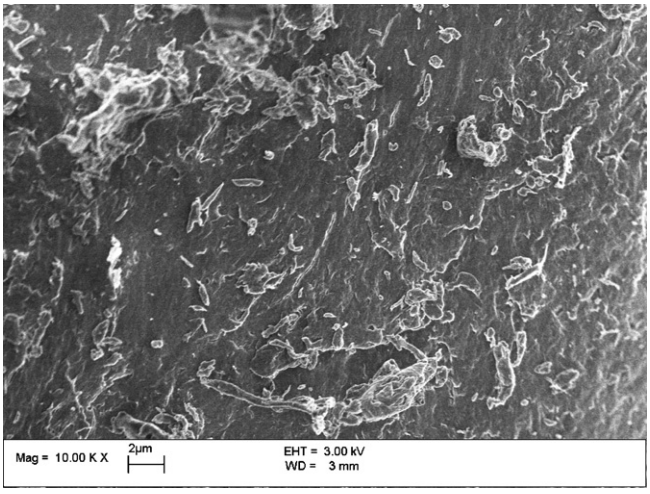

Fig. 2. SEM micrographs of the chitosan surface: 1×10^4 magnified image.

to use, and produces good results. Fig. 3A shows the gas chromatogram of textile wastewater sample by injecting 1 μL to gas chromatograph. Fig. 3B presents another gas chromatogram of the same sample obtained by a PDMS 100 μm fiber under the optimal conditions described above. As can be seen, using a nonpolar stationary phase (poly(phenylmethyldimethyl)siloxane phase), we obtained good chromatographic performance and satisfactory resolution of analytes. In the extraction step, the good results were obtained with PDMS fiber. Comparison of Fig. 3A and B reveals that trace colour compounds are detectable even when enriching very small textile wastewater sample volumes by SPME extraction method. A typical GC/MS chromatogram from SPME extraction of the same textile wastewater sample solutions is presented in Fig. 4. A total number

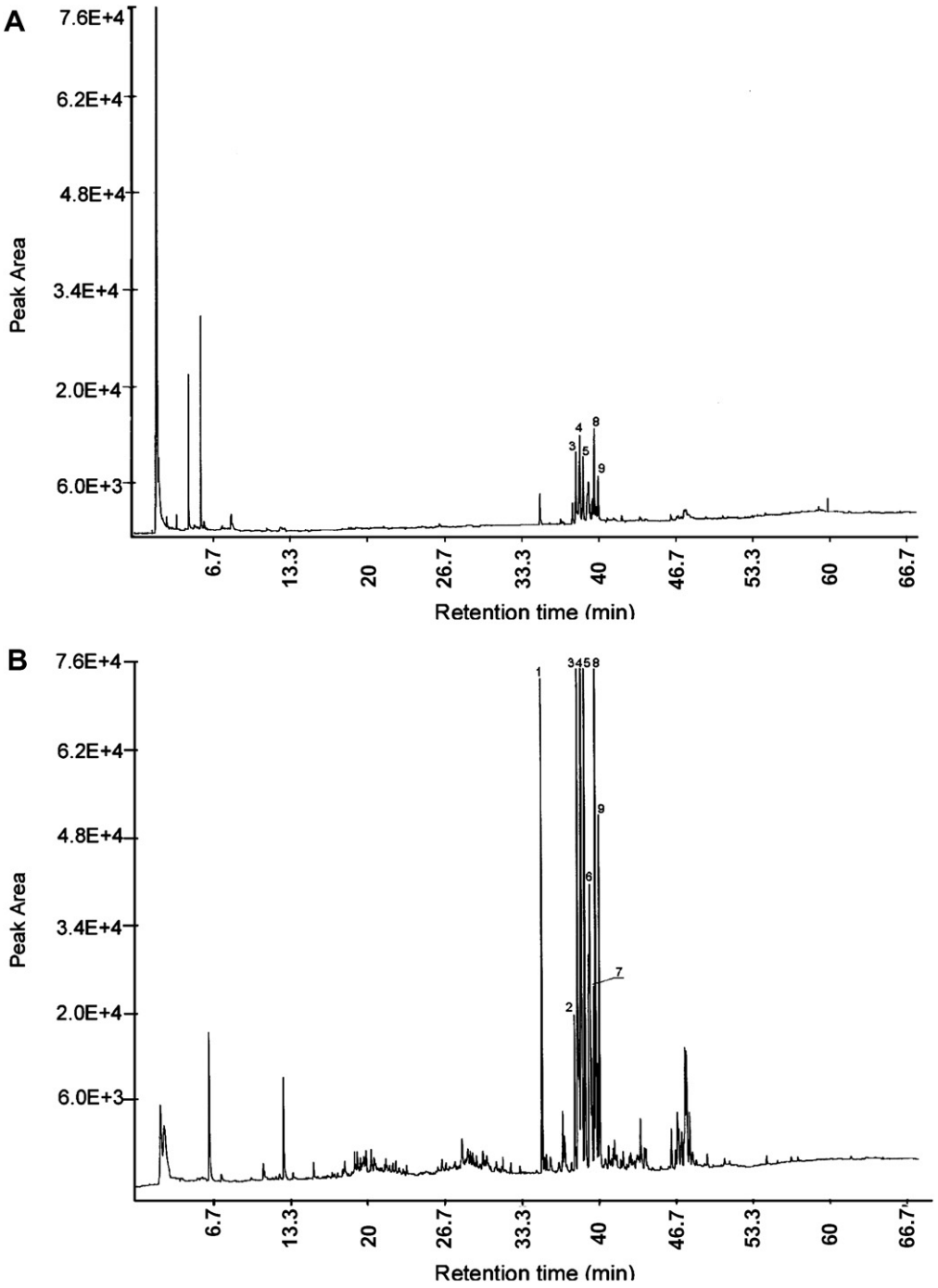

Fig. 3. Gas chromatograms of textile wastewater sample. (A) By direct injection 1 μL; (B) by a 100 μm PDMS fiber under SPME direct immersed extraction mode.

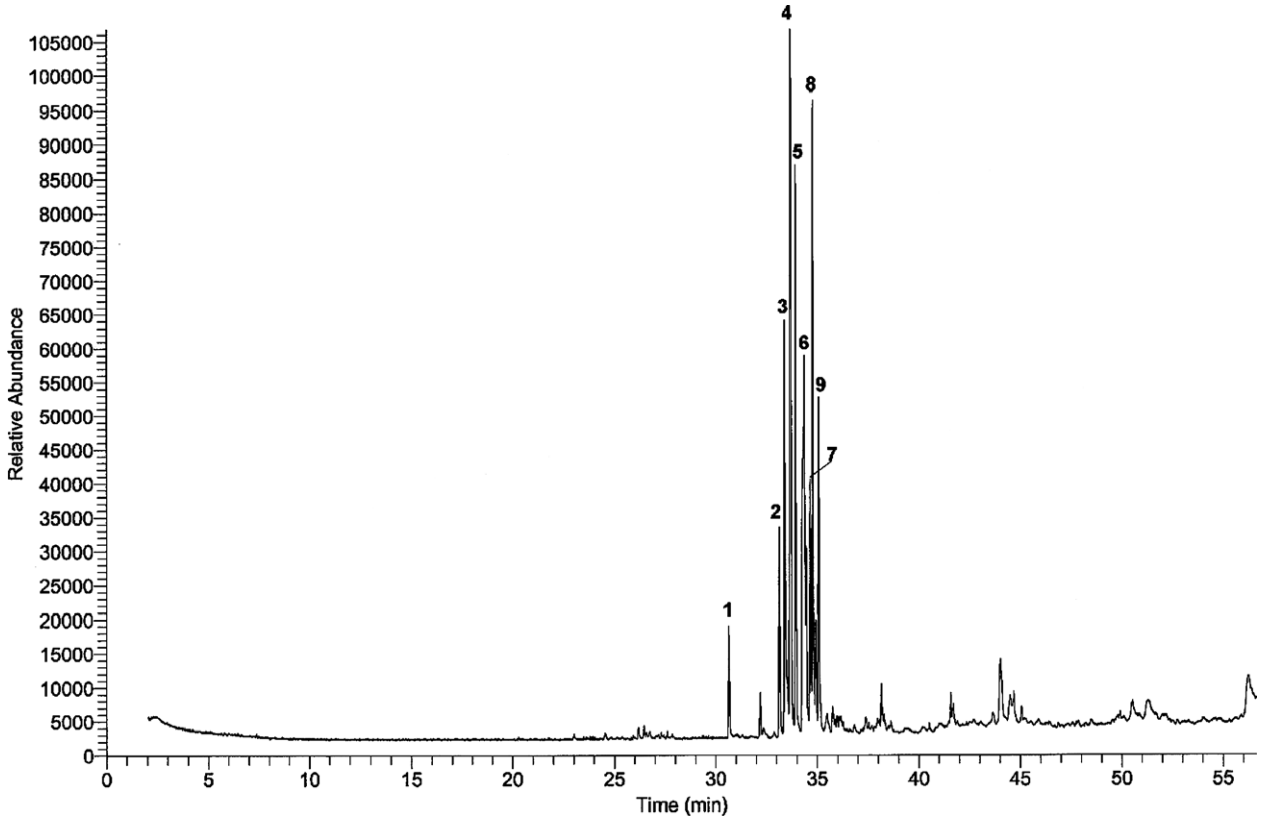

Fig. 4. GC–MS chromatogram of textile wastewater sample extract after SPME. Peaks: (1) 2-[4-(1,1-dimethylethyl)phenoxy]-ethanol; (2) 6,7,8a-tetrahydro-2,3,5,5,8a-pentamethyl-5H-benzo[b]pyran-8-ol; (3) *p*-tert-amyl phenoxy ethanol; (4) 2-hydroxy-5-methoxy-1-indolinecarboxaldehyde; (5) methyl ester 2-hydroxy-3-[(2-hydroxy-4-methoxy-6-propylbenzoyl)oxy]-4-methoxy-6-propyl-benzoic acid; (6) 9-methyl-acridine; (7) brallobarbital; (8) 2′,4′-dimethoxy-3′-methylpropiophenone and (9) 2-[4-(1,1-dimethylethyl)-2-methylphenoxy]-ethanol. Conditions are given in the text.

of nine compounds have been identified, that is, 2-[4-(1,1-dimethylethyl)phenoxy]-ethanol, 6,7,8a-tetrahydro-2,3,5,5,8a-pentamethyl-5H-benzo[b]pyran-8-ol, *p*-tert-amyl phenoxy ethanol, 2-hydroxy-5-methoxy-1-indolinecarboxaldehyde, methyl ester 2-hydroxy-3-[(2-hydroxy-4-methoxy-6-propylbenzoyl)oxy]-4-methoxy-6-propyl-benzoic acid, 9-methyl-acridine, brallobarbital, 2′,4′-dimethoxy-3′-methylpropiophenone and 2-[4-(1,1-dimethylethyl)-2-methylphenoxy]-ethanol. The textile sample positive for 2-hydroxy-5-methoxy-1-indolinecarboxaldehyde (peak 4) and brallobarbital (peak 7) are also displayed in Fig. 5, showing also the comparison between the mass spectrum recorded for the sample and that found in a commercial mass spectral library.

Chitosan, which is a natural coagulant, was an effective coagulant as compared to mineral coagulants such as aluminum sulfate and polyethyleneimine in removing chlorophenols from aqueous solution (Ganjidoust, Tatsumi, Wada, & Kawase, 1996). Chitosan is also often used in the form of flakes or powder in metal adsorption. Process has been made to produce chitosan hydrogel beads so that they can be regenerated after metal adsorption and be 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 or phenols (Muzzarelli, 1977; Sun, Payne, Moas, Chu, & Wallace, 1992). The fact that the crab shell has adsorption properties (Muzzarelli, 1977; Park, Kim, Lee, & Lee, 1998; Peter, 1995) gave rise to an idea that is could be utilized as an adsorbent for trapping and preconcentrating volatile organic compounds (VOCs) in air samples and the sulfur-containing compounds in natural gas (Sye et al., 2003). Crab shell is mainly composed of $CaCO_3$, protein and chitin (poly(β-1,4-*N*-acetyl-D-glucosamine)), and its important types of adsorption mechanisms are electrostatic and dipole interactions; the adsorption mechanisms of chitosan (poly(β-1,4-D-glucosamine)), beside the electrostatic and dipole interactions, the complexation interactions are also important (Li and Bai, 2002). Fig. 6A shows the chromatogram of textile wastewater sample treated by crab shell powder and sequentially extracted from the solution by means of SPME method. The textile wastewater using chitosan powder for the treatment, the chromatogram as shown in Fig. 6B. Comparison

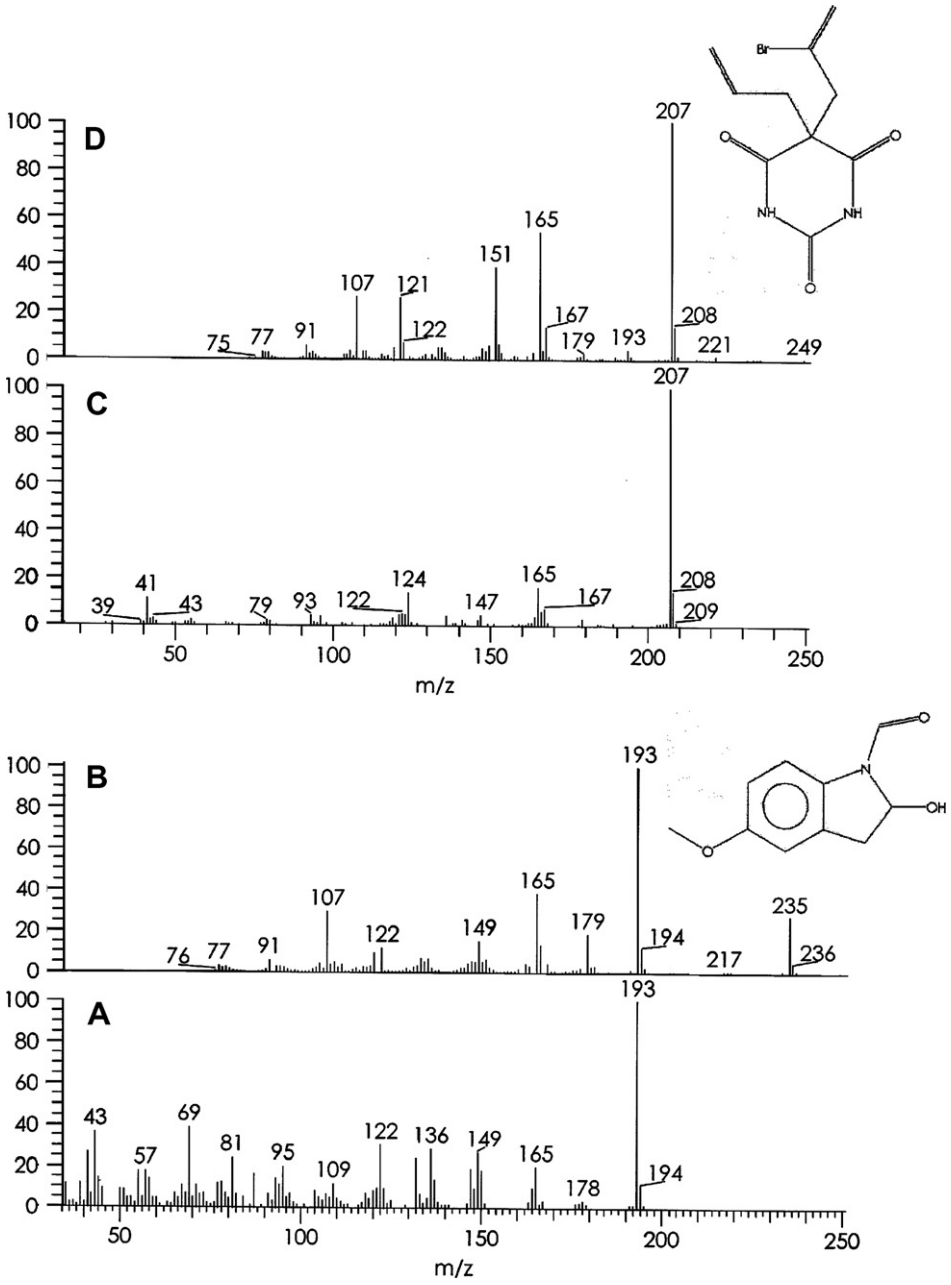

Fig. 5. GC/MS total ion chromatogram of the textile sample, an example of a positive result for the presence of two azo dyes. (A and C) The spectrums for peaks 4 and 7 are displayed; (B and D) as well as the spectral library confirmation for the amine.

of Figs. 6A,B and 3B indicates that the nine compounds in this textile wastewater sample were significantly removed when chitosan powder or crab shell was used. Tables 1 and 2 report the results for our method. As can be seen, the nine compounds are removed by crab shell ranges from 95% to 99%, and by chitosan powder are all 99%. For the adsorption capacity (g dye/g powder) between crab shell and chitosan powder, we use *p*-tert-amyl phenoxy ethanol for adsorption capacity study. The results reveal that the adsorption capacity of crab cell powder is between 1.2×10^{-3} and 1.7×10^{-3} g , and that of chitosan powder is between 2.7×10^{-3} and 4.0×10^{-3} g.

4. Conclusions

The results presented in this report indicate that chitosan beads and crab shell powder can both effectively remove the colour from textile wastewater, and the application of direct solid-phase microextraction (SPME), by using the PDMS fibers, has shown to be a suitable methodology for the determination of the nine compounds in tex-

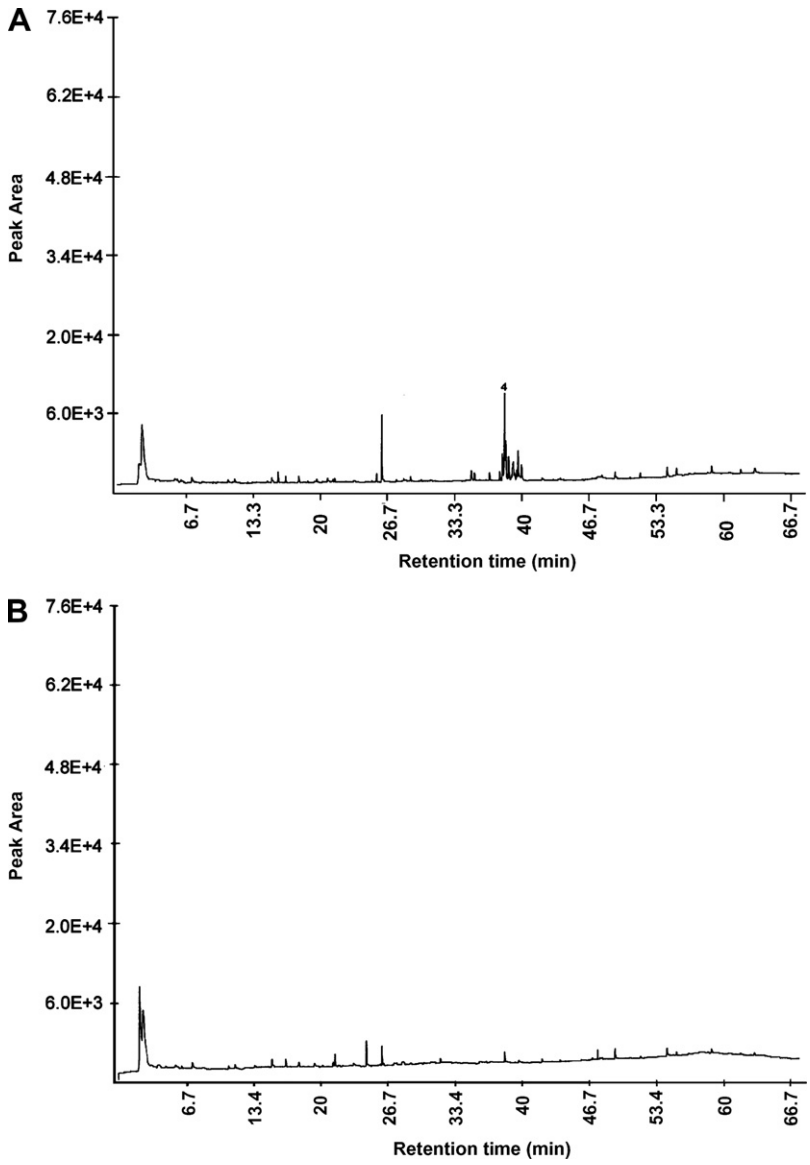

Fig. 6. Gas chromatograms of textile wastewater sample of the SPME extracts of (A) after the treatment by crab shell powder, (B) after the treatment by chitosan.

Table 1
Comparison of average peak area counts ($n = 3$) of direct injection and using SPME of colour from textile wastewater sample

Peak no.	Injection methods	
	Direct	SPME
1	N.D.	62280
2	N.D.	21593
3	8486	76422
4	14976	126726
5	9478	80835
6	N.D.	46781
7	N.D.	23897
8	11515	91666
9	5685	53216

Conditions given in Section 2.

Table 2
Changes in average peak area counts ($n = 3$) of colour from textile wastewater after treatment by porous crab shell and chitosan beads

Peak no.	Adsorbents			
	Crab shell		Chitosan beads	
	Before	After	Before	After
1	62280	N.D.[a]	62280	N.D.
2	21593	N.D.	21593	N.D.
3	76422	N.D.	76422	N.D.
4	126726	6129	126726	N.D.
5	80835	N.D.	80835	N.D.
6	46781	N.D.	46781	N.D.
7	23897	N.D.	23897	N.D.
8	91666	N.D.	91666	N.D.
9	53216	N.D.	53216	N.D.

Conditions given in Section 2.
[a] N.D. means no response or peak area <1000.

tile wastewater. It is a very simple and fast technique and shows good reproducibility.

Acknowledgments

We thank the National Science Council of the Republic of China for financial support of this work. We thank Dr. Shu H. Chien for surface areas test of crab shell and chitosan and Dr. Chun H. Wu for providing the data of degree of deacetylation of chitosan.

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