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Fluorinated hypercrosslinked polymers as sorbent of lipophilic compounds in wastewater

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ABSTRACT

Fluorinated hypercrosslinked polymer bearing phenyl and fluorinated phenyl moieties has been tested as a sorbent for the solid-phase extraction (SPE) of lipophilic compounds from water samples. Three different polymeric matrices were synthesized by employing Pentafluorostyrene and Styrene as functional monomers, and the specific surface area of the resulting materials was evaluated. Naphol, naphthene and xanthenes were chosen as model compounds simulating Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, the most toxic classes of pollutants from incineration of waste. © 2009 Trade Science Inc. - INDIA

KEYWORDS

Hypercrosslinked polymers;
Solid Phase Extraction;
Fluorinated Polymers;
Waste Water.

INTRODUCTION

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are commonly regarded as one of the most toxic classes of pollutants from incineration of waste^[1,2]. The sources and mechanisms behind their emissions have been intensively studied since they were first detected in flue gases and fly ash in 1977^[3]. Today, emissions of PCDD/Fs are often minimized by adsorption on several materials (polymers, activated carbon)^[4].

The activated carbon adsorption method is widely used for dioxin removal from municipal and other waste incinerators; however, highly effective adsorbents with selectivity for lipophilic compounds such as PCDD/Fs should be necessary^[5].

The activated carbon is typically injected in the flue

gas upstream of a fabric filter, and sometimes a subsequent wet scrubber is employed. At several such incineration plants, elevated dioxin emissions have been found after the wet scrubber even though inlet scrubber concentrations were low. This phenomenon of elevated PCDD/F concentrations after wet scrubbers can be explained by the so called memory effect^[6]. The memory effect occurs when PCDD/Fs are absorbed into plastic materials in a scrubber during periods with high inlet concentrations and then they are slowly desorbed when the inlet concentrations become lower^[7]. High scrubber inlet concentrations may occur during operation periods with elevated formations upstream of the scrubber, such as start up periods or combustion disturbances^[8,9].

In this work we report preliminary results of chromatographic retention of lipophilic compounds, present in wastewater by polymeric networks consisting of styrenic units.

EXPERIMENTAL

Materials

Divinylbenzene (DVB) (technical grade, mixture of meta and para isomers, 55%), 2,3,4,5,6-Pentafluorostyrene (PFS), Styrene (STY) and 2,2'-azobis(isobutyronitrile) (AIBN>98%), naphthol, naphthene, xanthenes, were obtained from Aldrich. All solvents were reagent grade or HPLC-grade and used without further purification and they were provided by Fluka Chemie.

Synthesis of hypercrosslinked polymers

All polymers in this study were prepared according to the following protocol: technical grade divinylbenzene was washed free of inhibitor with KOH solution, washed with water, and dried. A 2.5 g sample of a mixture of the appropriate monomers, 4.5 mL of dichloromethane, and 1 mol % (relative to double bonds) of the radical initiator AIBN were mixed in a test tube and the mixture was degassed by repeated freezing, evacuating, and thawing. The tube was sealed under vacuum and heated in a water bath at 65 °C for 24 h. The resultant bulk rigid polymer was removed from the tube, grounded into powder, washed with methanol and sieved through a 63 nm stainless steel sieve. The sieved materials were collected and the very fine powders, suspended in the supernatant solution (acetone), were discarded to obtain an average particle size of 35 μm ^[10]. The formulations used for the preparation of the different matrices are shown in TABLE 1.

TABLE 1 : Polymerization feeds composition and specific surface area of synthesized resin

Polymers	PFS/STY/DVB (mmol)	Specific surface area (m^2/g)
P-1	1.0/2.0/24.0	280
P-2	2.0/1.0/24.0	320
P-3	3.0/--/24.0	380

Characterization of polymers

Pore volumes and pore size distributions were determined by mercury porosimetry using a Poresizer 9310 from Micromeritics (Norcross, GA, USA). Specific surface areas were determined by nitrogen adsorption/desorption with a DeSorb 2300A from Micromeritics.

Preparation of SPE columns

The 500 mg amount of dry particles was packed into a 6.0 ml polypropylene SPE column. The column was attached with a stop cock and a reservoir at the bottom end and the top end, respectively. The polymer was rinsed with methanol and then with water^[11].

SPE procedure

In each experiment, distilled water (20 L, $n=3$) was prepared in a stainless tank. Before extraction, 6 ng of lipophilic compounds (naphthol, naphthene, xanthene) in methanol was added as a sampling standard of water (final concentration 7 μM). The samples were shaken and allowed to equilibrate for half a day before extraction.

A dry SPE column was conditioned with 10 ml of water followed by loading of 5 ml of standard solutions. After column drying, 5 ml of dichloromethane/ acetic acid 9/1 (elution mixture) to perform the complete extraction of compounds.

HPLC analysis

The liquid chromatography consisted of a Jasco BIP-I pump and Jasco UVDEC-100-V detector set at 254 nm. A 250 \times 4 mm C-18 Hibar[®] column, particle size 10 μm (Merck, Darmstadt, Germany) was employed. The mobile phase was Methanol and the flow rate was 0.5 ml/min.

RESULTS AND DISCUSSION

Synthesis of hypercrosslinked polymers

The aromatic π electron system of PCDD/Fs was targeted through non covalent interactions. On the basis of this consideration, several aromatic comonomers, capable of forming π - π interactions with these lipophilic compounds, were employed for the synthesis of absorbing resins. To increase the retention of lipophilic compounds using polymeric sorbents, two influential parameters, specific surface area and hydrophobicity, can be conveniently tuned.

In this work, three different polymeric hypercrosslinked materials for the retention of lipophilic compounds were synthesized. The electron-deficient PFS and the STY were used in these initial experiments. In our protocol (TABLE 1), different PFS and/or STY amounts were used as functional monomers able to in-

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teract with the lipophilic compounds and DVB as crosslinker. DVB was used to maintain the same polymerizable group. Three kinds of resins, using different molecular ratios among functional monomers, were synthesized. As reported in TABLE 1, P-1 was prepared using a mixture of PFS and STY (1:2). Different molar ratios of PFS/STY were used for the other two matrices: for P-2 2:1 while, in order to maximise the binding sites into the matrix, only PFS was used for P-3. After the grinding, sieving and suspending processes, the obtained materials were characterized by a dimensional size in the range of 35 μm .

Hypercrosslinked polymers as traps of lipophilic compounds

The polymeric matrices were characterized by measurements of specific surface area, and it was found the P-3 was the polymer with the highest value, while the presence of styrene in the polymerization feed carried out to materials with lower porosity properties.

In order to study the affinity of these matrices for lipophilic compounds, SPE cartridges were packed with the P-1, P2 and P3 respectively and the performance of these cartridges for several lipophilic compounds was evaluated.

Naphtol, naphthene and xanthenes were employed as model compounds for the preparation of spiked waters simulating waste samples.

As reported in TABLE 2, all the synthesized polymeric networks are able to retain a great amount of the analytes, and this capacity enhances when the surface areas increases: the P-3 sample, indeed, was able to absorb the higher amount of all the tested compounds.

TABLE 2 : Amount of bound analytes by synthesized polymers. Values are expressed as mg analytes per g polymers. each experiment was performed in triplicate and data expressed as means \pm S.D.

Polymers	Naphtol	Naphthene	Xanthenes
P-1	13 \pm 0.7	12 \pm 0.6	18 \pm 0.7
P-2	15 \pm 0.6	13 \pm 0.9	23 \pm 0.9
P-3	19 \pm 0.8	17 \pm 0.7	25 \pm 0.8

An important parameter to be considered in the application of polymers as sorbents for SPE protocols is their capability to do not change their absorption prop-

erties after repeated uses. In our conditions, the amount of bound compounds by P-1, P-2 and P-3 does not change after five cycles.

CONCLUSIONS

In this study the applicability of new hydrophobic hypercrosslinked resin to extract lipophilic compounds was evaluated.

The polymeric matrices were employed as sorbent in SPE protocol and three model compound (naphtol, naphthene and xanthenes) were employed in the preparation of model samples to be analysed by our polymeric materials.

All the synthesized polymers were found to be able to bind high amount of the tested compounds, and the amount of bound analytes increases when the specific surface area value of the sorbents is higher.

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REFERENCES

- [1] L.-C.Wang, W.-J.Lee, W.-S.Lee, Guo-Ping, Chang-Chien, P.-J.Tsai; *Sci.Total Environ.*, **302**, 185 (2003).
- [2] A.Buekens, E.Cornelis, H.Huang, T.Dewettinck; *Chemosphere*, **40**, 1021 (2000).
- [3] K.Olie, P.L.Vermeulen, O.Hutzinger; *Chemosphere*, **6**, 455 (1977).
- [4] C.-J.Löthgren, B.van Bavel; *Chemosphere*, **61**, 405 (2005).
- [5] M.Wevers, R.De Fré; *Organohalogen Compd.*, **36**, 343 (1998).
- [6] M.B.Chang, J.J.Lin; *Chemosphere*, **45**, 1151 (2001).
- [7] C.-J.Löthgren, S.Andersson; *Chemosphere*, **73**, S101 (2008).
- [8] M.Blumenstock, R.Zimmermann, K.-W.Schramm, A.Kettrup; *Chemosphere*, **40**, 987 (2000).
- [9] H.C.Gass, K.Lüder, M.Wilken; *Organohalogen Compounds*, **56**, 193 (2002).
- [10] F.Puoci, M.Curcio, G.Cirillo, F.Iemma, U.G.Spizzirri, N.Picci; *Food Chem.*, **106**, 836 (2008).
- [11] F.Puoci, G.Cirillo, M.Curcio, F.Iemma, U.G.Spizzirri, N.Picci; *Anal.Chim.Acta*, **593**, 164 (2007).