Evaluation of new surfactant expanded zirconium and titanium phosphates for polycyclic aromatic hydrocarbons extraction from waters

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Abstract

A newly synthesized family of materials prepared with surfactant as organic template were tested for the extraction of polycyclic aromatic hydrocarbons (PAHs) from water, using pyrene (Pyr) and benzo[a]pyrene (B[a]P) as PAHs representatives. Particular attention was paid to the evaluation of the recovery factors with dichloromethane as eluent in order to estimate their potential as adsorbing solid phases for PAH remediation or analysis. Eleven lamellar MCM-50 type materials incorporating n-alkyl- (n = 12, 16, 18) trimethylammonium bromide molecules with different concentrations and chain lengths and two hexagonal MCM-41 type materials incorporating octadecyl-trimethyl ammonium bromide were tested. Best results were obtained by preparing lamellar MCM-50 zirconium and titanium phosphates in the presence of n-dodecyl-trimethylammonium at a relative molar concentration (surfactant/phosphate) of 1.

Keywords: Solid sorbent; Zirconium; Titanium; Phosphate; Polycyclic aromatic hydrocarbons; Surfactant template

1. Introduction

Public interest in environmental quality, and particularly in the problem of soil and groundwater contamination, has increased dramatically in the European Union over the recent years (Boenke et al., 2002). Actually, in reason of their high toxic, carcinogenic and mutagenic potential, it is admitted that the emission of polycyclic aromatic hydrocarbons (PAHs) from human activities endangers the quality of environment (IARC, 1983).

The researches actually conducted for the remediation of PAH contaminated soils and waters are dealing with the development of a great variety of techniques. One of these is the so called surfactant flushing (EPA, 1995; Ming et al., 2000; Grasso et al., 2001) which is used for cleaning up PAHs contaminated groundwater. This technique has been employed by the petroleum industry to enhance oil recovery (Ling et al., 1987). Others include in situ bioremediation (EPA, 1992; Guerin, 2002). Commercial humic acid which has also been successfully used for the recovery of diesel fuel in a model aquifer (Van Stempvoort et al., 2002) offers
several advantages over other extracting compounds, such as lower cost, lower toxicity, and greater persistence (surfactants may be readily biodegraded, some of them are toxic). In addition, extensive researches have been conducted using various binding materials to extract PAHs from contaminated waters. The most extensively used is granular activated carbon (Rivera-Utrilla and Sanchez-Polo, 2003) which revealed also to be very effective for the extraction of pesticides (Badriyha et al., 2003) and halogenated compounds (Bembnowska et al., 2003). However, it was observed that its capacity decreases in the presence of natural organic matter (Hopman et al., 1994).

On line with these researches for new sorbents, there is actually a renew of interest for developing new materials based on modified clay mineral or presenting similar structural properties. Sorbing barriers based on cationic exchange consisting of sand or clay minerals coated with a cationic surfactant (organoclays) have been evaluated by measuring PAH sorption onto sand coated with cetylpyridinium chloride (Moon et al., 2003) or onto modified clay (Ake et al., 2003; Wu et al., 2003). A similar approach was also evaluated for the sorption of pesticides (Ake et al., 2003). However, the sorption property of these clay materials presents some limitation in reason of their low cationic exchange capacity (CEC) which does not allow the incorporation of a large amount of surfactant in interlayer spaces. A representative example is montmorillonite clay whose CEC is about 85 meq 100 g\(^{-1}\).

Other types of materials, like hydrogen metal (IV) phosphates, which also have a layer structure, present larger CEC and appear more promising. This is the case of hydrogen zirconium phosphate (ZrP) whose CEC value amounts 663 meq 100 g\(^{-1}\), close to eight folds the capacity of montmorillonite clay and thus, similarly to clay materials, can incorporate surfactant molecules into their interlayer spaces by cationic exchange but in much larger amount. A direct pathway for their preparation, is the synthesis of zirconium phosphate in the presence of surfactant molecules which act as templates for forming organo-inorganic structures. This leads to three possible geometrical arrangements (Beck et al., 1992): hexagonal (MCM-41), cubic (MCM-48) or lamellar (MCM-50). By this way, a well marked hydrophobic character can be given to these phosphate materials and it could be of interest to test them as potential materials for the retention of nonpolar organic molecules such as PAHs.

In this work we have evaluated the efficiency of newly synthesized templated forms (Jimenez-Jimenez et al., 1997, 1998a,b) of zirconium and titanium phosphates associated with a surfactant for the extraction and recovery of PAHs from contaminated waters. As test compounds, pyrene and benzo[a]pyrene were chosen as prototypical PAHs.

2. Materials and methods

2.1. Materials

Dodecyl-trimethylammonium bromide (DTAB), hexadecyl trimethylammonium bromide (HTAB), octadecyl-trimethylammonium bromide (OTAB), zirconium tetra-n-propoxide, titanium tetra-n-isopropoxide used for the synthesis as well as benzo[a]pyrene (BaP) and pyrene (Pyr) were purchased from Aldrich (Milwaukee, WI, USA).

All the solvents: methanol (MeOH), dichloromethane (DCM), tetrahydrofurane (THF) and dioxane (Dx) were of HPLC grade. Deionized water (18.2 M\(\Omega\)cm) was prepared with a Milli Q/Milli-Q2 system (Millipore, Bedford, MA). PAH standard solutions (1000 \(\mu\)g ml\(^{-1}\)) were prepared by dilution in acetonitrile and the PAH working solutions in water (1 \(\mu\)g ml\(^{-1}\)) were prepared daily by addition of an appropriate small volume of the standard solution in water in such a way that, in all cases, their content in acetonitrile does not exceed 0.1%. Solid phase extraction C\(_{18}\) cartridge (Supelclean\textsuperscript{TM} ENVI-18, 6 ml) were obtained from Supelco (Sigma-Aldrich Chimie, France) and taken as reference for the evaluation of the extracting and recovery efficiency of the synthesized materials. Extraction tubes, all identical, were filled with the same weight (1 g) of either commercial or synthesized solid sorbents.

2.2. Synthesis of sorbent material

Two types of zirconium or titanium hydrogen phosphates incorporating surfactant molecules with respectively a laminar (L) and a three-dimensional hexagonal (T) structure were synthesized. A detailed description of their synthesis and characterization were previously published (Jones et al., 1997; Jimenez-Jimenez et al., 1997, 1998a,b).

Briefly, for the laminar materials, the synthesis was carried out first by dissolving DTAB (C\(_{12}\)), HTAB (C\(_{16}\)) or OTAB (C\(_{18}\)) in 1-propanol at different concentrations. Under vigorous stirring, H\(_3\)PO\(_4\) (85%) and zirconium tetra-n-propoxide were subsequently added at phosphate/Zr molar ratio = 2.

Surfactant molar ratios (\(S =\) surfactant/phosphate) added were 0.25, 0.5, 1.0 and 1.5 for the different materials. After 1 day under stirring at room temperature, white solids were obtained. They were washed in ethanol and dried at 60 °C. The materials obtained are labelled (S)L-ZrP \(C_n\), where S is the initially prepared surfactant molar ratio defined above, L refers to the laminar structure and \(C_n\) \((n = 12, 16\) and 18\) indicates the chain length of the organic surfactant.

For three-dimensional materials (T symbol) of MCM-41 structure, two compounds in combination
with only HTAB as surfactant at a molar ratio S of 1.5 were synthesized: (1.5)T-ZrP C_{16} and (1.5)T-TiP C_{16}. Their synthesis was performed in a similar way as the above materials, excepted that titanium tetra-n-isopropoxide was used instead of zirconium tetra-n-propoxide and that conditions for obtaining MCM-41 structure require that water instead of 1-propanol was chosen as solvent.

2.3. Main structural characteristics of the synthesized materials

In Table 1 are indicated some relevant data concerning the structure and the composition of the synthesized materials. In Fig. 1a and b is schematised the arrangement of the surfactant molecules in the inorganic laminar and hexagonal molecular frame, respectively.

The most stable allotropic lamellar form of zirconium hydrogen phosphate is the \( \alpha \)-form (Fig. 1a). In the inorganic layer, zirconium (IV) atoms are located in a plane and octahedrally coordinated with six oxygen atoms which in turn are bonded with phosphorous (V) atoms tetrahedrally coordinated. The PO_4^{3-} tetrahedrons share three oxygens with three different zirconium (IV) atoms, while the fourth oxygen atom is placed outside of the layer and bonded to a proton (H\(^+\)). This proton, can be exchanged with other cationic species and this explains the acidity and cationic exchange properties of this material. When this proton is exchanged with voluminous species, the separation between inorganic

Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>( d_{001}(\text{Å}) )^a</th>
<th>Surfactant/P</th>
<th>% Organic matter</th>
<th>% H_2O</th>
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<tbody>
<tr>
<td>(0.25)L-ZrPC_{12}</td>
<td>33</td>
<td>0.08</td>
<td>9.5</td>
<td>7.5</td>
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<td>0.15</td>
<td>15.5</td>
<td>6.0</td>
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<tr>
<td>(1.50)L-ZrPC_{12}</td>
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<td>0.18</td>
<td>15.8</td>
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<tr>
<td>(0.25)L-ZrPC_{16}</td>
<td>36</td>
<td>0.08</td>
<td>10.1</td>
<td>8.9</td>
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<td>(0.50)L-ZrPC_{16}</td>
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<td>0.13</td>
<td>15.3</td>
<td>4.8</td>
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<tr>
<td>(1.00)L-ZrPC_{16}</td>
<td>36</td>
<td>0.21</td>
<td>24.2</td>
<td>4.0</td>
</tr>
<tr>
<td>(0.25)L-ZrPC_{18}</td>
<td>38</td>
<td>0.08</td>
<td>10.6</td>
<td>8.4</td>
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<tr>
<td>(0.50)L-ZrPC_{18}</td>
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<td>0.12</td>
<td>16.0</td>
<td>4.7</td>
</tr>
<tr>
<td>(1.00)L-ZrPC_{18}</td>
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<td>0.20</td>
<td>25.4</td>
<td>3.8</td>
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<tr>
<td>(1.50)L-TiPC_{12}</td>
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<td>0.19</td>
<td>24.8</td>
<td>3.5</td>
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<td>(1.50)T-ZrPC_{16}</td>
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<td>0.22</td>
<td>17.3</td>
<td>10.2</td>
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<tr>
<td>(1.50)T-TiPC_{16}</td>
<td>41</td>
<td>0.22</td>
<td>17.3</td>
<td>8.7</td>
</tr>
</tbody>
</table>

\(^a d_{001}\) for T-ZrP and T-TiP.
layers is increased, and the $d_{001}$ reflection is shifted from 7.6 Å to higher value depending on the guest size. This is the case with surfactant cationic species such as DTA, HTA and OTA used in this work.

The two other synthesized materials, (1.5)T-ZrP C$_{16}$ and (1.5)T-TiP C$_{16}$, present a three-dimensional structure of MCM-41 type (hexagonal). In these cases, surfactant cylindrical micelles are arranged in hexagonal arrays (Fig. 1b) separated by walls made of the inorganic array which serve as cement of the structure.

2.4. Preparation of solid phase extraction tubes and analysis

The preparation of the solid phase extraction tubes were as follow: the same weight (1 g) of synthesized material was packed into an empty commercial extraction tube. Conditioning was performed according to manufacturer recommendation for the Supelco Superclean™ ENVI-18 commercial SPE-C18 phase, with 5 ml of methanol followed by 5 ml of pure water. The extraction tubes were connected to a Visiprep™ SPE Vacuum Manifold system purchased from Supelco. 50 ml of PAH solution in water (1 µg ml$^{-1}$) was passed through the tubes with a constant flow rate of 5 ml min$^{-1}$. DCM, MeOH, THF and DCM/MeOH (1/1 vol) were tested as eluting solvents.

All fluorometric measurements were performed with a Hitachi F-4500 spectrofluorometer equipped with a 150 W xenon lamp and a PMT R-3788 operating at 950 V. The instrument is interfaced to a microcomputer for operation and spectra processing.

The slit-widths were adjusted at 2.5 nm for both excitation and emission and the scan speed set at 60 nm min$^{-1}$. The fluorescence synchronous spectra were corrected for variation with wavelength of the lamp intensity and photomultiplier sensitivity. The corrected synchronous spectra (sample and blank) were recorded in the excitation range 240 and 400 nm with an offset: $\Delta \lambda_j = \lambda_{em} - \lambda_{ex} = 37$ nm for both Pyr and B[a]P.

The water solubility’s of BaP and Pyr at 25 °C are respectively around 3.0 and 132 ng ml$^{-1}$ (Shiu and Ma, 2000). In order to be able to measure the fluorescence intensity with enough precision it was necessary to prepare test solutions at concentration as high as 1 µg ml$^{-1}$. To increase the PAH solubilities, 10% of isopropanol were added to the water solutions. It was already observed that this has no noticeable effect on the sorption property of the solid sorbent but improves the recovery factor of PAHs solute (Urbe and Ruana, 1997).

Fluorescence intensity measurements were made with a 1 cm fused silica cell. In the experimental conditions used, the absorbance at the wavelength of excitation was less than 0.1 absorbance unit i.e. in a range where a linear relationship between fluorescence intensity and concentration can be applied with enough precision.

Powder X-ray diffraction pattern (XRD) were recorded using Siemens D501 diffractometer using Cu K$\alpha$_1 radiation and a graphite monochromator. IR spectra were recorded at room temperature with a Perkin–Elmer 883 infrared spectrophotometer (Norwalk, CT), using KBr pellet method.

To avoid loss of the analytes on the container walls, all water solutions were prepared in stainless steel vessel.

3. Results and discussion

In the majority of cases, no or only minute traces of analyte were found by fluorometry in the water solution after it percolated through the SPE cartridge. It is then concluded that most of the phases we synthesized are good solid sorbents for PAHs and could be promising phases for the solid phase extraction of PAHs.

However for the application of these phases for PAH analysis or in view of their recycling in water remediation process, it is important that the adsorbed PAHs can be quantitatively eluted with an usual organic solvent. So, particular attention was paid to the measurements of the recovery factors which for a better evaluation were compared to that obtained with the commercial phase using the same experimental procedure.

3.1. Choice of the eluting solvent

ENVI-18 extraction tubes from Supelco were loaded with 50 ml of a benzo[a]pyrene solution in water (1 µg ml$^{-1}$) and used according to the procedure described above. For elution, five solvents: dichloromethane (DCM), methanol (MeOH), tetrahydrofuran (THF) and a DCM/MeOH mixture (1/1 vol) were tested. Their respective efficiency were evaluated simply by comparing the fluorescence intensity of the permeate. Dichloromethane (DCM) and the DCM/MeOH mixture (1/1 vol) revealed to be the best eluting solvents (Fig. 2). All the measurements discussed in the following have been made using pure DCM for eluting the PAH retained onto the tested sorbing materials. The goal was just to evaluate the potentiality of new type of sorbent by comparison with a commercial and commonly used one. Referring to literature, dichloromethane is likely to be one of the most appropriate eluting solvent and the choice of an other solvent which would also appear suitable but will not probably lead to very different relative results (Song et al., 2002; Pleil et al., 2004).

The volume of eluting solvent was also optimised. As shown in Fig. 3, a volume of 5 ml appears to be sufficient to obtain more than 90% of the maximum concentration of B[a]P which could be recovered from the sorbent. Further addition of solvent hardly leads to the desorption of an extra amount of the adsorbed analytes. A similar observation was made with pyrene.
The recovery factors for BaP and Pyr were estimated by comparing their fluorescence intensity in DCM, at a concentration identical to that in the working water solution (1 μg ml⁻¹), with the fluorescence intensity of the organic permeate solution corrected for the volume ratio: water loading/eluting solvent (50 ml/5 ml). For this estimate, the solvent effect on the PAH fluorescence parameters (absorption coefficients, fluorescence quantum yields) was neglected.

The results are shown in Fig. 4. In the case of Pyr, a recovery factor larger than 94% was obtained with the commercial SPE-C₁₈ phase while a low recovery factor was obtained for BaP (vide infra).

### 3.2. Synthesized phase recovery factors

The same procedure as that used with the commercial phase was applied with the synthesized phases. With pyrene, only three of them lead to similar or even better results than the commercial SPE-C₁₈ phase: (1.0)L-ZrP C₁₂, (1.5)L-ZrP C₁₂ and (1.5)L-TiP C₁₂ (Table 2).

As with the commercial SPE-C₁₈ phase, not so good results were obtained for BaP. Obviously in that case, BaP dissolution is not complete and aggregates or crystallites are present in the water solution in spite of the presence of isopropanol. Because, on one hand, as reported above, practically no more BaP is recovered upon further addition of organic solvent (Fig. 2), and on the second hand, no BaP is detected in the permeate solution, it is concluded that BaP associated forms are strongly retained in the ENVI-18 cartridge either in the solid phase itself or on the cartridge wall. In Fig. 4, however, it can be noticed that the recovery factor for BaP varies relatively in the same way from one phase to another than that of pyrene, but in the following only results obtained with pyrene will be discussed.

An important point for the understanding of the phase retention mechanism is the observation that upon

![Fig. 2. Evaluation of the efficiency of different organic solvents for the elution of B[a]P adsorbed on Supelco SPE ENVI-18 cartridge from an aqueous solution: dichloromethane (DCM), methanol (MeOH), tetrahydrofuran (THF), dioxane (Dx), dichloromethane:methanol (DCM:MeOH, 1/1 vol).](image1)

![Fig. 3. Evaluation of the efficiency of DCM to elute B[a]P and Pyr from the commercial SPE C₁₈ phase in function of the organic solvent volume passed through the extraction cartridge.](image2)

![Fig. 4. Recovery factors (%) estimated for BaP and Pyr with the different synthesized template materials as compared with those measured with the commercial SPE C₁₈ phase.](image3)

<table>
<thead>
<tr>
<th>Material</th>
<th>Pyrene R %</th>
<th>Benzo[a]pyrene R %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPE-C₁₈ Cartridge</td>
<td>94.1</td>
<td>36.8</td>
</tr>
<tr>
<td>(0.25)L-ZrP C₁₂</td>
<td>67.5</td>
<td>30.5</td>
</tr>
<tr>
<td>(0.50)L-ZrP C₁₂</td>
<td>83.4</td>
<td>34.6</td>
</tr>
<tr>
<td>(1.00)L-ZrP C₁₂</td>
<td>97.1</td>
<td>58.6</td>
</tr>
<tr>
<td>(1.50)L-ZrP C₁₂</td>
<td>97.3</td>
<td>37.6</td>
</tr>
<tr>
<td>(0.25)L-ZrP C₁₆</td>
<td>40.8</td>
<td>36.2</td>
</tr>
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<td>(0.50)L-ZrP C₁₆</td>
<td>47.5</td>
<td>40.2</td>
</tr>
<tr>
<td>(1.00)L-ZrP C₁₆</td>
<td>51.2</td>
<td>52.5</td>
</tr>
<tr>
<td>(0.25)L-ZrP C₁₈</td>
<td>33.3</td>
<td>19.90</td>
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<td>(0.50)L-ZrP C₁₈</td>
<td>34.1</td>
<td>37.7</td>
</tr>
<tr>
<td>(1.00)L-ZrP C₁₈</td>
<td>36.8</td>
<td>51.6</td>
</tr>
<tr>
<td>(1.50)L-TiP C₁₂</td>
<td>92.5</td>
<td>30.4</td>
</tr>
<tr>
<td>(1.50)T-ZrPC₁₂</td>
<td>74.2</td>
<td>30.1</td>
</tr>
<tr>
<td>(1.50)T-TiP C₁₆</td>
<td>71.8</td>
<td>29.8</td>
</tr>
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</table>
increasing the chain length or the relative concentration of the surfactant (surfactant/phosphate ratio), opposite variation of the recovery factor is observed. As a prerequisite hypothesis we may assume that lower recovery factor implies that the adsorbed molecules are more strongly retained by the solid phase and/or that they are less accessible to the organic solvent molecules.

Upon increasing the surfactant chain length, the decrease of the recovery factor may be interpreted by an increase of the molecular interaction linking the guest molecules to the hydrophobic chain of the surfactant. As a result, the molecules are more retained by the hydrophobic chain and even eventually penetrate more deeply in the interlayer space. This latter effect may be also favoured by the slight increase of the interlayer distance, $d_{001}$, observed upon increasing the surfactant chain length (Table 1). It follows that in that conditions, the guest elution by the organic solvent is expected to be less efficient.

Contrary to what is observed upon increasing the surfactant chain length, the increase in the relative surfactant concentration (S) from 0.25 to 1.5, is accompanied by an increase of the elution efficiency of the organic solvent. From XRD measurement (Table 1), it is observed that for the same surfactant chain length, the increase of the surfactant concentration does not lead to a noticeable increase of the interlayer distance. This implies that the packing density of the surfactant molecules must be larger and that the adsorbed molecules can penetrate less deeply or are less retained in the interlayer space. Moreover, increasing the surfactant concentration may also induce irregular (disordered) arrangement of the alkyl chains. All these factors may contribute to reduce the interaction energy with the PAH molecules and thus to facilitate the elution of the PAH guest by the organic solvent.

These results indicate that increasing the chain length or the surfactant concentration has different effect on the inorganic layer space, yields to different molecular organisation of the surfactant and consequently implies that different molecular interaction with the PAH guest molecules are operative.

In the case of lamellar ZrPC$_{12}$ material there is a surfactant concentration limit as evidenced by the fact that a recovery factor close to 100% is obtained with (1.0)L-ZrP C$_{12}$. Accordingly, no substantial improvement of the recovery factor can be expected by increasing the surfactant concentration. Similarly, no improvement can be also expected by decreasing the chain length. Indeed a quite similar recovery factor was obtained with the (1.5)L-ZrP C$_{12}$ phase, so, among all the new sorbent materials incorporating surfactant molecules we synthesized, (1.0)L-ZrP C$_{12}$, prepared with C$_{12}$ surfactant chain length and a surfactant/phosphate ratio of 1.0 appears as the most promising sorbent to be used.

As indicated in Table 1, the materials we synthesized appear to contain about 4–10% of water. Although the role played by the water molecules is not clear, it is known that the water molecules may contribute to the swelling of lamellar material (Daryn and Thomas, 2002). Water molecules are thought to be located close to the inorganic layer into the interlayer space. Their presence are indicative of potential “empty” space which could be suitable for the accommodation of PAH guest molecules and thus may indirectly contribute to the PAH retention.

As shown by comparing (1.5)L-ZrP C$_{12}$ with (1.5)L-TiP C$_{12}$ or (1.5)T-ZrP C$_{16}$ with (1.5)T-TiP C$_{16}$ (Fig. 4), the exchange of zirconium by titanium does not modify substantially the recovery factors in spite of their different acidity. However a larger number of different materials must be compared to know whether for the same structural conditions, this parameter may have an influence on their PAHs retention property.

The two phases with hexagonal structures we synthesized, (1.5)T-ZrP C$_{16}$ and (1.5)T-TiP C$_{16}$ respectively, lead to quite similar recovery factors of about 71–74%. As compared to the recovery factor (51%) obtained for the lamellar (1.0)L-ZrP C$_{16}$ material their values are substantially larger. This result can be interpreted as being due to the more rigid structure of the inorganic array which impedes the swelling and therefore does not favour a deep penetration of the organic molecules guests in the surfactant layer thus facilitating their elution by the organic solvent.

4. Conclusions

All the newly synthesized material, we tested here, made from hydrogen phosphates of zirconium or titanium and incorporating surfactant molecules as templating organic structure, reveal to be good sorbent material for extracting pyrene and benzo[a]pyrene from water. However only three of them are presenting comparable efficiency as commercial SPE-C$_{18}$ phase for recovering between 92% and 97% of pyrene using dichloromethane as organic solvent. They all have MCM-50 lamellar structure and are associated with dodecyl-trimethylammonium as the surfactant at an optimum relative molar concentration (surfactant/phosphate) determined to be in the range 1.0–1.5.

In our experimental conditions, bad recovery factors were obtained for B[a]P both for the commercial SPE-C$_{18}$ phase and the synthesized phosphate material. This result may be reflect the fact that further optimisation of our extraction protocol is still needed (other solvents, flow rate) but presently this was beyond the scope of this paper.

It may be noticed however that with respect to the commercial SPE-C$_{18}$ phase, alike for pyrene, a notice-
ably better recovery factor for B[α]P was obtained with the (1.0)L-ZrP C_{12} material (Fig. 4). Thus this latter compound reveals to be of interest as an example of new type of material for PAHs extraction both in reason of its good adsorbing property but also in reason of the possibility it offers to recover adsorbed PAHs with a good yield which may allow to use it for remediation or analysis purposes.

Other important aspect of the synthesized material presented in this work is the economical aspects. In Table 3, is shown the different estimated cost in euros (€) of them, which can be optimised by recovery of the surfactant used in excess. In this case the cost is similar for the different materials synthesized for each surfactant as is noted in the second column. In comparison with the commercial SPE-C_{18}, a pack of 30 tubes of 1 g/ tube is 11.5€. So, economically this material is comparable whenever the excess of surfactants used in the synthesis are recovered.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cost €/100 g</th>
<th>Cost €/100 g^a</th>
</tr>
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<tbody>
<tr>
<td>0.25L-ZrPC_{12}</td>
<td>91.46</td>
<td>91.4</td>
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<td>0.50L-ZrPC_{12}</td>
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<td>1.50L-TiPC_{18}</td>
<td>46.37</td>
<td>24.4</td>
</tr>
</tbody>
</table>

^a Recovering the surfactant used in excess.

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References


