Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Efficient Extraction of Fuel Oil Hydrocarbons from Concrete

Ganna Baglayeva[a]; Inna E. Popova[a]; Evguenii I. Kozliak[a]
[a] Department of Chemistry, University of North Dakota, Grand Forks, ND

To cite this Article Baglayeva, Ganna , Popova, Inna E. and Kozliak, Evguenii I.(2011) 'Efficient Extraction of Fuel Oil Hydrocarbons from Concrete', Separation Science and Technology, 46: 2, 254 — 264
To link to this Article: DOI: 10.1080/01496395.2010.509078
URL: http://dx.doi.org/10.1080/01496395.2010.509078

Separation Science and Technology, 46: 254–264, 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.509078

Taylor & Francis
Taylor & Francis Group

Efficient Extraction of Fuel Oil Hydrocarbons from Concrete

Ganna Baglayeva, Inna E. Popova, and Evguenii I. Kozliak
Department of Chemistry, University of North Dakota, Grand Forks, ND

A strategy is presented for the efficient extraction of hydrocarbons from concrete to enable their monitoring. Both polar and non-polar solvents were examined with the application of several techniques: cold solvent extraction with shaking, Soxhlet, and ultrasound-assisted extraction. The impacts of sample aging and inundation with water on the extraction efficiency were investigated to elucidate the nature of analyte-matrix interactions. Organic matrix-destructive solvents that partially disintegrate concrete (ethyl acetate, methanol, and acetonitrile) were most efficient for all considered scenarios, yielding recoveries in a range of 95-100% upon a two-step, four-day, cold solvent extraction or 24-h Soxhlet extraction even for highly contaminated and aged samples.

Keywords concrete; fuel oil; hydrocarbons; solvent extraction

INTRODUCTION

Concrete, a major construction material, can be contaminated with hydrocarbons during their production (e.g., oil drilling), storage, transportation, and spillage (1,2). Concrete is a composite material made of mortar, cement paste, calcium silicate hydrate, calcium hydroxide, free and bound water and aggregates, such as sand, gravel, crushed stones, and/or coarse rocks (3). Due to its inherent heterogeneity, the concrete pore microstructure covers several orders of magnitude in size, ranging from nanometers (calcium silicate hydrate) to centimeters (the size of a typical coarse aggregate) (4,5). The high porosity of concrete allows for free movement and retention of water and other substances, e.g., hydrocarbons (2,4).

Once in contact with concrete, liquid hydrocarbons diffuse into the bulk of this building material within hours with a significant penetration depth (6). The worst-case scenario for chemical contamination in residential buildings occurs when heating fuel oil mixes with water (e.g., during catastrophic floods) and then would be entrained in concrete. In this case, the hydrocarbons become not only entrapped within the pores of concrete but also sealed by water, thus hindering (yet not preventing) their natural removal via evaporation (6). The resulting slow release of hydrocarbons into indoor air can negatively affect the indoor environment and human health. In addition to this sealing effect of water, long-term contamination may lead to developing strong matrix-contaminant interactions (so-called "aging" effect) thus further aggravating this problem by creating a hydrocarbon fraction whose release into the indoor air is even further delayed.

To address the problem of hydrocarbon removal from the bulk of concrete, several methods have been reported, based on a continuous surface reaction causing a contaminant concentration gradient toward the surface. Such methods include bioremediation (application of a suitable bacterial strain on the surface of contaminated concrete) (6), photoremediation (irradiation with UV light, with and without a photocatalyst, TiO_2, applied on the concrete surface) (7) and sorption using a suitable absorbent/adsorbent (2). However, the assessment of the efficiency of these treatments requires the prior development of reliable and efficient extraction protocols based on the use of most suitable extraction solvents.

The choice of extraction solvents depends heavily on hydrocarbon-solvent, water-solvent, and concrete matrix-solvent interactions. Particularly under water-submerged conditions, the interactions of the solvent, solute, and matrix with water can take place. Hydrocarbons become entrapped within the concrete pores, which may complicate the analyte removal from the matrix.

Typical solvents recommended by the US Environmental Protection Agency (EPA) for the extraction of polycyclic aromatic hydrocarbons from solid matrices are acetone, methylene chloride, and hexane as well as their mixtures. A multi-stage extraction process using a complex mixture of solvents was proposed by EPA as Microscale Solvent Extraction Method 3570 (8) for recovering volatile, semivolatile, and nonvolatile organic compounds from such solids as soils, sludges, and wastes. However, EPA does not specify the type of solvent to use with a particular analyte or matrix because neither of them is optimal for all analyte groups.

An alternate approach to solvent extraction is partial concrete disintegration, such as acid etching with hydrochloric acid (ASTM D 4260) (9). This treatment may cause

---

Received 10 February 2010; accepted 14 July 2010.

Address correspondence to Dr. Evguenii I. Kozliak, Department of Chemistry, University of North Dakota, Abbott Hall Room 236, 151 Cornell St. Stop 9024, Grand Forks, ND 58202-9024, USA. E-mail: ekozliak@chem.und.edu

an increase of the matrix pore size. As a result, the analyte fraction otherwise non-accessible to non-destructive solvents can be accessed, thus yielding a more efficient extraction.

The aim of this study was to develop an efficient extraction protocol for fuel oil hydrocarbons while using a systematic approach to the solvent and method selection. Specific objectives of the current study were:

1. optimization of the solvent system (including a search for efficient organic matrix-destructive solvents) for removal of *n*-hexadecane, as a representative fuel oil hydrocarbon, from water inundated long-term contaminated concrete via cold solvent extraction;
2. comparison of the extraction efficiencies for optimized solvent system among cold solvent, Soxhlet and/or ultrasound-assisted extractions;
3. application of the most efficient solvent / technique to standard heating fuel oil #2, a "real-world" hydrocarbon sample.

EXPERIMENTAL

Reagents

Radiolabeled *n*-hexadecane-1-^{14}C was purchased from Sigma-Aldrich (St. Louis, MO, USA). The prepared stock solution (obtained by dilution with the non-labeled *n*-hexadecane) had a scintillation counting rate of $3.4 \cdot 10^4$ DPM/μL (15.3 nCi/μL). Fuel Oil #2 was obtained locally (Vilandre Inc., Grand Forks, ND, USA). All other chemicals used were, at least, of reagent grade and were obtained from either Sigma-Aldrich (St. Louis, MO, USA) or Fisher Scientific (Fair Lawn, NJ, USA).

Concrete Samples

Low straight 3,000-psi concrete was obtained locally (Concrete, Inc., Grand Forks, ND, USA). Similar size (3.5 ± 0.5 g) pieces of concrete were chipped off from a single concrete tile. Aliquots of 20.0 µL (unless indicated otherwise) of neat *n*-hexadecane-1-^{14}C were applied evenly on concrete samples resulting in a *n*-hexadecane concentration of 4.4 ± 0.6 mg/g. Sample aging was conducted under ambient and water-submerged conditions as described below.

Ambient Conditions

Upon a contaminant application, samples were set on a bench at room temperature for 5 min for contaminant absorption into the sample. Following this procedure, the contaminated samples were wrapped in aluminum foil and stored under a fume hood at ~22°C and ambient air humidity (55–66%) for 1 day (24 h, freshly contaminated samples), or 10 days (aged samples), unless otherwise specified. The 10-day aging time was selected as representative for the evaluation of other parameters.

Water-Submerged Conditions

Following the "aging" period of 1 or 10 days, the contaminated concrete pieces were submerged into a beaker containing a sterile aqueous medium (3.8 g/L of sodium chloride in distilled water). The beaker was covered with aluminum foil and the samples were stored for 3 h under a fume hood, as specified for ambient conditions.

Extraction Protocols

To increase the surface area for contaminant extraction, contaminated concrete samples were crushed into powder/crumbs using a hammer prior to the extraction procedure.

Cold Solvent Extraction

Crushed samples were placed in 22-mL vials with screw-top solid PTFE lined caps and fully submerged into 10.0 mL of a selected solvent. Samples were agitated on a rotary shaker at 100 rpm and room temperature. The 4-day (i.e., 96 ± 1 h) extraction time was used, unless indicated otherwise. In case of a two-step extraction either two different solvents were used sequentially or the same solvent was applied twice (to assure efficient and reproducible results). In both cases, after 4 days of extraction the first solvent was decanted; then, the second solvent was added to the same concrete sample for additional 4-day shaking. Both solvent fractions were analyzed separately to determine the extraction efficiencies of each step.

Soxhlet Extraction

The Soxhlet extraction protocol applied in this study was based on EPA Method 3540C (10). To remove moisture, samples were homogenized with anhydrous Na_2SO_4 (1:1, w:w) and placed into 25×90 cellulose extraction thimbles (Whatman Int., Maidstone, UK). Each extraction was carried out using 100 mL of a solvent (or a mixture of two different solvents) for 24 h (as recommended by EPA Method 3540C) (10) unless indicated otherwise. The extraction rate was 6–10 cycles per hour. The resulting extract was concentrated by rotary evaporation to 15–20 mL prior to the analysis.

Ultrasound-Assisted Extraction

Samples were placed in 22-mL vials with screw top solid caps and PTFE liners and extracted with 20 mL of a solvent under ultrasound using an Ultrasound Generator (Branson 2510, Branson Ultrasonics Corp., Danbury, CT, USA) for 4–24 h.

Liquid Scintillation Counting (LSC) Analysis

Analyses of *n*-hexadecane extracts for the extraction method development were carried out on a LS 6500 multi-purpose scintillation counter (Beckman Coulter, Inc., Fullerton, CA, USA), using the ^{14}C-labeled analyte. 1.0-mL extract aliquots were added into standard scintillation plastic vials (20 mL) with 5.0 mL of the biodegradable Econo-safe scintillation counting cocktail (Research Products International, Mt. Prospect, IL, USA). For HCl extracts, the whole extracts were used in select experiments to avoid artifacts due to the analyte's low solubility in water. The counting time was 5 min and the procedure was repeated four times for each sample yielding a substantially smaller variance than the sample-to-sample variance. Samples with high chemiluminescence levels were set on a counter for 60 min before counting; this procedure was sufficient for the elimination of any time-dependent signals.

The readings were taken in DPM (disintegrations per minute) being proportional to the analyte concentration. The radioactivity measured in the extracts was verified by performing control experiments, in which concrete samples were spiked with the allotted analyte amounts and then extracted and analyzed immediately. Radioactivity monitored in this manner was indeed proportional to the concentration of the chemical of interest, regardless of the solvent selection.

Gas Chromatographic Analysis with Mass Spectrometry Detection (GC-MS)

Analyses of fuel oil extracts were carried out on an HP 5890 Series II gas chromatograph (Hewlett-Packard Co., Avondale, PA, USA) equipped with a HP 5972 Series single quadrupole mass selective detector (Hewlett-Packard Co., Avondale, PA, USA). A 30 m long DB-5 MS capillary column (0.25 mm ID, 0.25 μm film thickness) with 10 m duraguard column was used (J&W Scientific, Folsom, CA, USA). Zero grade helium was used as a carrier gas with a constant flow rate of 1.0 mL/min. The injector and detector temperatures were 300 and 280°C respectively. The sample was injected in a split mode with a split ratio 20:1. The column oven temperature program was as follows: 40°C, held for 5 min, then at a rate of 20°C/min increased to 320°C, with a final hold of 5 min. The total run time was 24 min. The ionization mode was positive EI, with an electron's energy of 70 eV. After a solvent delay of 8 min, full scan spectra were acquired with a m/z range of 40–600 Da. Extracted ion chromatograms (EIC) of m/z 85.1 representing hexyl ion were used for quantification of saturated hydrocarbons. The extraction efficiency was calculated with respect to blanks, i.e., when samples were spiked with the allotted fuel oil amounts in the appropriate solvents.

Statistical Treatment of Data

All experiments were performed at least in triplicate and the results were represented as (mean value ±confidence interval) with a 95% confidence level. Before calculating the mean value, all data were subject to the *Q*-test for elimination of outliers.

RESULTS AND DISCUSSION

Solvent Selection and Non-Destructive Solvent Extraction of *n*-Hexadecane from Freshly Contaminated Concrete

A variety of solvents based on their polarity, molecular size, and ability to disintegrate the concrete matrix (called henceforth matrix-destructive and non-destructive solvents) as well as their combinations were tested for the extraction of *n*-hexadecane from concrete (Table 1). The extraction efficiency was expected to depend on the solute-solvent, the water-solvent, the concrete matrix-solute, and the concrete matrix-solvent interactions. In order to achieve quantitative recoveries of *n*-hexadecane from concrete samples, potential extraction solvents were pre-screened.

For freshly-contaminated ambient samples (aged for only one day to assure consistency), where the interactions between the solute and matrix are minimized and water is not involved, all the organic selected solvents listed in Table 1 yielded nearly quantitative (>90%) extraction efficiency (not shown). However, when these solvents were tested using one-day aged water-submerged concrete samples, the difference in extraction efficiency became apparent (Table 2, the leftmost set of data labeled as such). This difference may be explained based on the following qualitative and semi-quantitative considerations.

n-Hexadecane is a hydrophobic non-polar organic compound; therefore it can be removed from ambient concrete with a solvent exhibiting similar properties, e.g., alkanes. By contrast, in water-submerged samples the solvent's diffusion path toward the analyte may be blocked by water. This complication may necessitate the use of polar solvents as for the hydrocarbon extraction from wood reported earlier (11). In terms of solvent-matrix and solvent-water interactions, polar solvents that have a higher affinity to concrete due to hydrogen bonding (Table 1) may readily break the interactions between the pore surface and water (to release the analyte trapped in micropores) and then transport the released solute toward the surface.

On a numerical scale, the solute-solvent and water-solvent interactions can be expressed via the logarithm of octanol-water partition coefficient (log *P*). The values of this and other pertinent solvent parameters are shown in Table 1. The concrete-solvent interactions can be quantified in terms of so-called hydrogen bonding basicity, $\sum \beta_2^{\mathrm{H}}$ (12). As far as the water-submerged samples are concerned, the solvent must be of a similar hydrogen-bonding basicity to water, in order to be able to penetrate into concrete pores filled with capillary water. Furthermore, the size of solvent molecules (measured as either the molar volume,

TABLE 1
Pertinent parameters of the extraction solvents used in this study

Solvent	MW[a]	D[b], g/mL	V_m[c], mL/mol	d_m[d], nm	Log P[e],	$(\sum \beta_2^H)$[f]
Acetone	58.08	0.791	73.43	0.62	−0.24	0.49
Acetonitrile	41.05	0.786	52.23	0.55	−0.34	0.32
Benzene	78.11	0.874	89.37	0.66	2.13	0.14
Dichloromethane	84.93	1.325	64.10	0.59	1.25	0.05
Dimethyl sulfoxide	78.13	1.100	71.03	0.61	−1.35	0.78
Ethyl acetate	88.11	0.902	97.68	0.68	0.73	0.45
HCl	36.46	1.200	30.38	0.46	0.25	NA[g]
n-Hexane	86.18	0.672	128.24	0.74	4.00	0.00
Methanol	32.04	0.791	40.51	0.50	−0.74	0.47
n-Pentane	72.15	0.626	115.26	0.72	3.45	0.00
2-Propanol	60.10	0.785	76.56	0.62	0.05	0.56
Water	18.02	0.996	18.09	0.39	NA[g]	0.35

[a] MW–molecular weight, taken from reference 19.
[b] D–density, taken from reference 19.
[c] V_m–molar volume, $V_m = MW/D$.
[d] d_m–molecular diameter, $d_m = 2(3V_m/4\pi N)^{1/3}$taken from reference 13.
[e] log P–logarithm of the octanol-water partitioning coefficient, taken from reference 19.
[f] $\sum \beta_2^H$–hydrogen-bonding basicity, $\sum \beta_2^H = (\log K_B^H + 1.1)/4.636$, taken from reference 12.
[g] NA–not applicable.

TABLE 2a
Cold solvent extraction efficiencies for *n*- hexadecane (4.4 mg/g of concrete) from freshly-contaminated and aged concrete samples using non-destructive solvents[d]

	Water-submerged samples						Ambient samples		
	Freshly-contaminated samples			Aged samples			Aged samples		
Extraction solvent	1st solvent	2nd solvent	Total	1st solvent	2nd solvent	Total	1st solvent	2nd solvent	Total
Acetone[e]	ND[b]	ND[b]	ND[b]	40 ± 3[c]	NA[a]	40 ± 3	79 ± 3 [c]	2 ± 3	81 ± 3
Acetone followed by *n*-pentane	ND[b]	ND[b]	ND[b]	40 ± 3 [c]	5 ± 1	45 ± 3	79 ± 3 [c]	8 ± 1	87 ± 3
Acetone + *n*-pentane (1:1 v/v)	ND[b]	ND[b]	ND[b]	51 ± 1	NA[a]	51 ± 1	ND[b]	ND[b]	ND[b]
Benzene	ND[b]	ND[b]	ND[b]	33 ± 7	NA[a]	33 ± 7	ND[b]	ND[b]	ND[b]
Benzene + *n*-pentane (1:1 v/v)	ND[b]	ND[b]	ND[b]	28 ± 1	NA[a]	28 ± 1	ND[b]	ND[b]	ND[b]
Dichloromethane	ND[b]	ND[b]	ND[b]	29 ± 2	NA[a]	29 ± 2	ND[b]	ND[b]	ND[b]
Dimethyl sulfoxide	ND[b]	ND[b]	ND[b]	28 ± 1	NA[a]	28 ± 1	ND[b]	ND[b]	ND[b]
n-Hexane[e]	74 ± 2 [c]	7 ± 5	81 ± 5	58 ± 4	5 ± 4	63 ± 4	ND[b]	ND[b]	ND[b]
n-Hexane followed by methanol	74 ± 2 [c]	24 ± 6	98 ± 6	ND[b]	ND[b]	ND[b]	ND[b]	ND[b]	ND[b]
n-Hexane followed by *n*-pentane	74 ± 2 [c]	19 ± 4	93 ± 4	ND[b]	ND[b]	ND[b]	ND[b]	ND[b]	ND[b]
n-Pentane[e]	102 ± 8	NA[a]	102 ± 8	52 ± 2 [c]	NA[a]	52 ± 2	97 ± 7	1 ± 1	98 ± 7
n-Pentane followed by 2-propanol	ND[b]	ND[b]	ND[b]	52 ± 2 [c]	3 ± 1	55 ± 2	ND[b]	ND[b]	ND[b]
2-Propanol[e]	96 ± 7	NA[a]	96 ± 7	78 ± 22 [c]	1 ± 1	79 ± 22	88 ± 6 [c]	7 ± 7	95 ± 9
2-Propanol followed by *n*-pentane	ND[b]	ND[b]	ND[b]	78 ± 22 [c]	5 ± 1	83 ± 22	88 ± 6 [c]	4 ± 2	89 ± 4
2-Propanol +*n*-pentane (1:1 v/v)	ND[b]	ND[b]	ND[b]	58 ± 1	NA[a]	58 ± 1	ND[b]	ND[b]	ND[b]

V_m, or equivalent molecular diameter, d_m (13)) may play a significant role in assuring efficient extraction because the solvent penetration into concrete pores should be easier for small molecules than for large molecules. In case of the water-submerged samples, when concrete capillaries are filled with water, the solvent's molecular diameter must be close to that of water. Thus, the solvent can readily replace water and continue penetrating into the matrix.

Based on these criteria, 2-propanol was selected as a representative polar non-destructive solvent, along with acetone and dimethyl sulfoxide used in select experiments. In addition, these criteria were met by the organic destruction solvents as described in the next section.

By contrast, as predicted, hydrophobic *n*-hexane due to weak solvent-matrix interactions was less efficient in this process. For instance, *n*-hexane, as a single solvent, recovered only 74 ± 2% of *n*-hexadecane (Table 2a). Yet, upon a two-step extraction using a more efficient solvent in the second step, i.e., with *n*-hexane followed by either a polar (methanol) or non-polar (*n*-pentane) solvent, more than 90% extraction efficiency was achieved.

However, *n*-pentane, another hydrophobic solvent, yielded a much greater recovery than its nearest homologue, *n*-hexane (Table 2a). *n*-Pentane exhibits a higher solubility in water (log $P = 3.45$ vs. 4.00 of that of *n*-hexane (12)) and smaller molecular size than other liquid alkanes (Table 1). In addition, it is most volatile among any alkanes that are liquid at room temperature; this implies high mobility of its molecules. These features appear to affect, primarily, the analyte's accessibility by extraction solvents. These observations corroborate our previously reported data on *n*-hexadecane extraction from another construction material, wood (11).

The examination of *n*-hexadecane recovery from one-day aged water-submerged concrete did not allow us to study possible matrix-analyte interactions (see the section on extraction of *n*-hexadecane from 10-day aged ambient concrete); however, its results pointed out the importance of solvent-matrix and solvent-water interactions, suggesting the use of polar over non-polar solvents.

Extraction of *n*-hexadecane from One-Day Aged Concrete with Matrix-Destructive Solvents

Based on the American Concrete Institute (ACI) recommendation (14), the first destructive solvent tested was HCl. However, when 0.5 M HCl was applied to disintegrate concrete samples, only 5 ± 2% of *n*-hexadecane was recovered (Table 2b). The increase of acid concentration from 0.5 to 2.0 M did not improve the extraction efficiency. This recovery was much lower than that of a more polar

TABLE 2b

Cold solvent extraction efficiencies for *n*-hexadecane (4.4 mg/g of concrete) from freshly-contaminated and aged concrete samples[d] using matrix-destructive solvents

	Water-submerged samples						Ambient samples		
	Freshly-contaminated samples			Aged samples			Aged samples		
Extraction solvent	1st solvent	2nd solvent	Total	1st solvent	2nd solvent	Total	1st solvent	2nd solvent	Total
Methanol[e]	109 ± 10	NA[a]	109 ± 10	88 ± 11	3 ± 3	91 ± 11	90 ± 15	3 ± 3	93 ± 15
Ethyl acetate[e]	106 ± 11	NA[a]	106 ± 11	82 ± 6[c]	18 ± 2	100 ± 6	88 ± 11	10 ± 6	98 ± 13
Ethyl acetate followed by 2-propanol	ND[b]	ND[b]	ND[b]	82 ± 6[c]	6 ± 2	88 ± 6	ND[b]	ND[b]	ND[b]
Acetonitrile[e]	101 ± 4	NA[a]	101 ± 4	84 ± 6[c]	11 ± 3	95 ± 7	92 ± 12	3 ± 3	95 ± 12
Acetonitrile followed by methanol	ND[b]	ND[b]	ND[b]	84 ± 6[c]	8 ± 4	92 ± 7	ND[b]	ND[b]	ND[b]
HCl followed by *n*-pentane	5 ± 2	11 ± 2	16 ± 3	3 ± 1[c]	9 ± 8	12 ± 8	3 ± 1	8 ± 1	11 ± 2
HCl followed by 2-propanol	5 ± 2	53 ± 5	58 ± 5	3 ± 1[c]	20 ± 8	23 ± 8	ND[b]	ND[b]	ND[b]

[a] NA–not applicable. Extraction was performed with a single solvent.

[b] ND–not determined.

[c] Average value for all experiments using this extraction solvent as the first extraction solvent (n = 6, for *n*-hexane n = 9).

[d] Data are presented as mean value ± standard deviation (n = 3, $P = 0.05$). Extraction time was four days for each solvent. Freshly-contaminated samples were contaminated with *n*-hexadecane (4.4 mg/g of concrete) and then stored for 1 day under ambient temperature, pressure, and humidity. Aged samples, upon *n*-hexadecane application (4.4 mg/g of concrete) were stored for 10 days. Water-submerged samples were prepared by submerging concrete samples into water for 3hours after "aging". Ambient samples were analyzed right after the "aging" period.

[e] In case of a two-step extraction the same solvent was applied twice.

analyte, 2,4-dinitrotoluene, observed in our earlier study with a similar HCl extraction (15). This difference was apparently due to the low *n*-hexadecane solubility in water.

However, contrary to expectations, even subsequent extractions of the dust-like substance remaining after the acid digestion with polar (methanol) and non-polar (*n*-pentane) non-aqueous solvents did not lead to near-quantitative recoveries (only 58 ± 5% and 16 ± 3%, respectively). This observation suggested that even though HCl could disintegrate the bulk of concrete, it did not break up its fine structure. Thus, the remaining small particles of concrete still contained *n*-hexadecane trapped inside its micropores. On the other hand, the addition of an aqueous medium (HCl solution) enhanced the aqueous barriers that separated the trapped *n*-hexadecane and extraction solvents, thus sealing off the analyte and making it less accessible for the subsequent extraction with other solvents.

Based on these results, the search for suitable extraction solvents was re-focused toward organic solvents to assure the analyte transport out of the matrix. A visually noticeable gradual decomposition of the concrete matrix (leading to a collapse) was observed upon its contact with ethyl acetate. A possible reason for this destruction is a partial alkaline hydrolysis of ethyl acetate inside the concrete pores, which yields ethanol and acetate ion as reaction products. As a result, the bound water (which accounts for up to 15–20% of the total concrete mass (16)) plus alkali may be consumed thereby causing the concrete disintegration.

Two more organic solvents, acetonitrile and methanol, showed some minor matrix destructive effects, resulting in the formation of turbid suspensions upon their contact with concrete (yet, the bulk structure appeared to be unchanged upon a visual inspection). While acetonitrile could be hydrolyzed, similar to ethyl acetate, the reasons for partial concrete disintegration with methanol are less clear. Perhaps, methanol can partially replace the chemically bound water in hydrates, thus compromising the concrete's structural stability.

It remained to be seen whether this partial loss of concrete integrity would result in any increase of hydrocarbon extraction efficiency. These three solvents (to be called organic matrix-destructive solvents henceforth), along with HCl, were selected for *n*-hexadecane extraction from aged concrete samples in addition to several representative non-destructive solvents selected as described in the previous section.

Effect of Sample Aging on *n*-hexadecane Extraction Efficiency

Sample aging proved to be one of the most significant complications for quantitative extraction of hydrocarbons from solid matrices, such as concrete. For instance, *n*-hexadecane could be extracted almost completely with 2-propanol within the first few hours, up to 1 day, after the concrete contamination. However, for more aged samples, the extraction recovery with the same solvent declined to less than 60% (Fig. 1). Yet, after seven days of aging, extraction efficiencies became near-constant. Based on this information, ten-day aging was selected as a representative time period reflecting significant contribution of analyte-matrix interactions, while one-day aged samples considered in two previous sections served as controls (Fig. 1).

Extraction Time

To determine the optimum extraction time, time profiles for *n*-hexadecane extraction were examined for 10-day aged water-submerged concrete samples as one of the worst-case scenarios for quantitative recovery. Under such conditions, all possible interactions between the solute, solvent, and matrix were in attendance with additional obstacles due to the presence of water.

The maximum possible recoveries with non-destructive solvents (*n*-pentane, acetone, and *n*-hexane) were achieved only after 3–4 days of extraction, whereas the use of organic destructive solvents (acetonitrile, methanol, and ethyl acetate) resulted in a faster achievement of high recoveries (70–80% in 5 h and 95% in one day, not shown). This difference was expected because the extraction time with non-destructive solvents would include the solvent diffusion toward the entrapped analyte through the network of matrix pores, followed by the diffusion of *n*-hexadecane toward the surface. By contrast, extraction with matrix-destructive solvents is fully or mostly controlled by their chemical reaction with concrete, which may be considerably faster than diffusion.

To assure an accurate comparison, the four-day extraction period was selected for any tested solvent under any

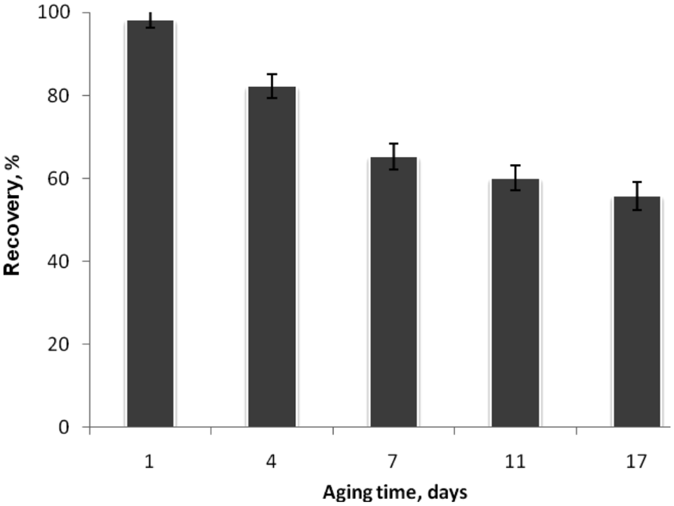

FIG. 1. Extraction efficiencies of *n*-hexadecane (4.4 mg/g) from aged ambient concrete by 2-propanol as a function of aging time.

applied conditions. The observed independence of extraction efficiency from extraction time within 1–4 days warranted the use of thermodynamic rather than kinetic considerations for an explanation of the observed trends.

Extraction of *n*-hexadecane from 10-day Aged Ambient Concrete

The sample aging studies were first conducted with ambient concrete, to separate the influence of matrix-analyte (namely, aging) and matrix-water interactions (to be considered in the next section). The values of *n*-hexadecane extraction efficiency from ambient concrete with various solvents are presented in Table 2 (the rightmost set of data labeled as such). Among the non-destructive solvents used (Table 2a), the highest analyte recovery in a single-step extraction (97 ± 7%) was achieved with *n*-pentane. Single-step extractions with more polar solvents (acetone, 2-propanol) yielded somewhat lower recoveries (79 ± 3% and 88 ± 6%, respectively).

In contrast with high efficiency of a one-step extraction of ambient samples with *n*-pentane, a two-step procedure, when *n*-pentane was used as a second solvent after an extraction with a polar solvent (e.g., 2-propanol or acetone), only additional 4 ± 2% of *n*-hexadecane could be extracted (i.e., virtually, statistical zero). The repeated application of the same solvent did not improve the *n*-hexadecane recovery from aged ambient concrete samples.

Presumably, as a result of aging in ambient concrete, hydrocarbons are merely physically entrapped within the matrix micropores, without developing significant specific matrix-analyte interactions upon aging. As a result, low molecular weight hydrocarbons would serve as efficient extraction solvents due to strong solvent-solute interactions without any need for prior polar solvent treatment discussed in the next section for water-submerged samples. Aging *per se*, i.e., in ambient concrete samples, does not appear to alter the analyte extraction efficiency.

Application of the EPA-recommended leaching procedure (using HCl as a matrix-destructive solvent) to ambient concrete yielded merely 3 ± 1% of *n*-hexadecane recovery, similar to freshly contaminated water-submerged samples considered earlier in this study. A subsequent extraction of the remaining dust-like substance with *n*-pentane improved the recovery only slightly (11%, Table 2b). This observation indicates that the matrix modification by filling concrete pores with water (or with another polar solvent as in the case of prior extraction with 2-propanol or acetone) may alter the analyte accessibility and, thus, the optimum extraction strategy.

Thus, when an aqueous acid enters concrete samples, additional obstacles appear to be created between *n*-hexadecane (trapped inside the water-sealed pores) and the extraction solvent, thus equalizing the ambient concrete to that submerged in water. By contrast, organic destructive solvents, e.g., methanol, ethyl acetate, or acetonitrile, yielded near-quantitative analyte recoveries, although the achievement of this high efficiency required a two-step extraction (Table 2b). Apparently, prolonged hydrocarbon diffusion into concrete pores in aged samples required more time and a greater concentration gradient for the analyte transport toward the surface from poorly accessible sites by polar solvents, which is achieved upon the second extraction with a fresh solvent.

Extraction of *n*-hexadecane from 10-day Aged Water-Submerged Concrete Samples

The values and trends obtained for *n*-hexadecane extraction from aged water-submerged samples (Table 2, the middle set of data) turned out to be significantly different when compared to both aged ambient and freshly-contaminated water-submerged samples (Table 2, the other two data sets). This observation indicates that aging effects may reflect different processes in ambient and water-submerged samples (i.e., altering analyte-matrix interactions), so they need to be considered separately. Since the difference between the ambient and water-submerged concrete was addressed in the previous section, the focus henceforth will be on the aging effects in this matrix modified by water.

For all non-destructive solvents tested, the *n*-hexadecane recoveries from aged water-submerged concrete were substantially lower than for similar freshly contaminated samples (Table 2a). Also, unlike freshly contaminated samples, no clear correlation was observed between the analyte recovery and either the polarity or molecular size of the non-destructive solvents tested. Polar acetone, 2-propanol, and dimethyl sulfoxide, as well as non-polar or low-polarity *n*-pentane, *n*-hexane, benzene, and dichloromethane, all proved to be almost equally inefficient for the removal of *n*-hexadecane from aged water-submerged concrete (as opposed to freshly contaminated concrete under similar conditions). Analyte recoveries using the above-mentioned solvents as well as their combinations did not exceed 83% even for two-step extractions (2-propanol followed by *n*-pentane).

By contrast, matrix-destructive organic solvents, namely, methanol and, particularly, acetonitrile and ethyl acetate, yielded near-complete *n*-hexadecane recoveries upon two-step extractions of aged water-submerged samples approaching the near-quantitative values obtained for freshly contaminated samples (Table 2b, the middle and leftmost sets of data, respectively). It is worth mentioning that in our previous work acetonitrile was also successfully applied for the extraction of a different contaminant, 2,4-dinitrotoluene, from water-submerged concrete (15). This observation further stresses the critical importance of physical entrapment (matrix interactions with water) as an apparent limiting factor for the extraction of any chemicals from concrete. Destructive solvents, except for aqueous HCl for extremely hydrophobic *n*-hexadecane, appear to increase drastically the analyte accessibility compared to non-destructive solvents.

As for methanol, the small size of its molecules appears to provide an additional advantage for extraction. In comparison, the application of an alcohol of a larger molecular size, 2-propanol, with 0.62 nm in effective molecular size vs. 0.50 nm of methanol, cf. Table 1, resulted only in a 78 ± 22% *n*-hexadecane recovery. However, as can be seen from Table 2, the application of methanol, as well as of 2-propanol, yields poor reproducibility compared to the other organic concrete-destructive solvents used in this study (several additional experiments, compared to other solvents, had to be performed to verify the obtained value).

Thus, significant differentiation was observed among the extraction solvents when they were applied to aged water-submerged samples, apparently, due to the difference in water-solvent interactions. In addition, the use of polar organic matrix-destructive solvents was proved to be essential to break the matrix-analyte interactions created by excess water inundating the concrete pores (presumably, due to a physical hydrocarbon entrapment).

Extraction of *n*-hexadecane from a 10-day Aged Water-Submerged Concrete: Dependence on the Applied Analyte Concentration

The extraction recoveries were found to be significantly affected by the variation of *n*-hexadecane amounts applied on a concrete surface (Fig. 2). When the analyte amount was increased from 4.4 mg analyte/g concrete to 22.1 mg/g, reduced recoveries were obtained upon extraction with the same solvents. This effect was particularly pronounced in the case of acetonitrile (84 ± 6% *vs.* 45 ± 4%) and 2-propanol (78 ± 22% vs. 53 ± 5%).

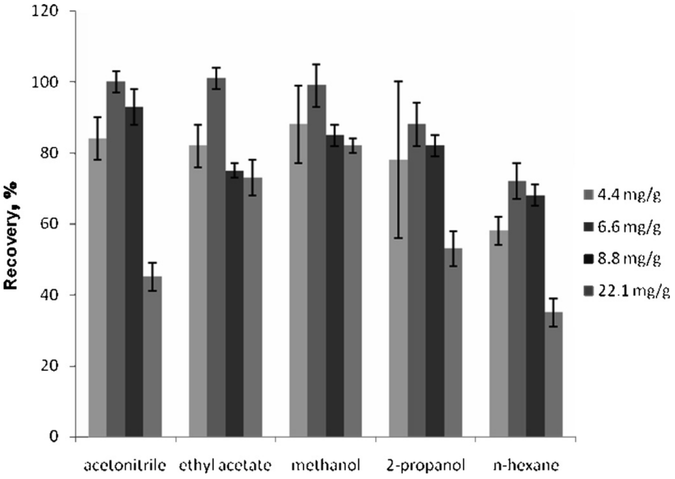

FIG. 2. *n*-Hexadecane extraction efficiencies (upon one-step cold solvent extractions) from 10-day aged water-submerged concrete as a function of *n*-hexadecane concentration. Data are presented as mean value ±standard deviation (n = 3, $P = 0.05$).

Similar to the data presented in the previous section, the observed concentration profiles can be explained in terms of the analyte availability. Low and moderate amounts of *n*-hexadecane fill only the near-surface fraction of concrete, which is characterized by higher capillary porosity and larger pores (4). Thus, the analyte may be readily accessible to extraction solvents. The application of high analyte concentrations may cause its further penetration into the bulk of concrete pores under capillary pressure, including smaller and more disconnected pores (similar to aging effects if no strong analyte adsorption is assumed). Thus, a considerable fraction of *n*-hexadecane may become less accessible to extraction solvents, even to those partially destructing concrete. This explanation is supported by an observation that the analyte extraction with presumably more mobile methanol (having the smallest molecular size of the tested solvents (12), Table 1) does not change significantly upon the variation of the *n*-hexadecane amount.

In case of lower than 4.4 mg/g concentrations of *n*-hexadecane, e.g., 1.1 mg/g, more than 50% of the contaminant was recovered in the aqueous medium (used for the imitation of water-inundation according to our standard procedure) and only 15–30% were extracted from concrete samples themselves (not shown). The observation of this artifact confirms our hypothesis that *n*-hexadecane applied in low concentrations stays near the surface of the concrete matrix, where the analyte-matrix and analyte-water interactions do not play a significant role.

A two-step extraction with organic matrix-destructive solvents was found to be essential for a near-quantitative extraction of high analyte concentrations (i.e., 22.1 mg/g). While the first extraction step was not efficient, the second application of the same solvent yielded a 92 ± 3% recovery in case of methanol, 84 ± 5% and 76 ± 4% for ethyl acetate and acetonitrile, respectively (Table 3).

Soxhlet and Ultrasound-Assisted Extraction of *n*-hexadecane from 10-day Aged Water-Submerged Concrete

In an attempt to further improve the extraction recovery of *n*-hexadecane from 10-day aged water-submerged concrete while speeding up the procedure, Soxhlet and ultrasound-assisted extractions with acetone, acetonitrile, ethyl acetate, *n*-hexane, methanol, *n*-pentane, and 2-propanol were performed. Both of these methods were selected as recommended by EPA for the removal of semi-volatile and non-volatile organics from solid matrices (10,17). Extraction efficiencies were compared to those of cold extraction at similar extraction times (12–24 hours for ultrasound-assisted and 24 hours for Soxhlet extractions). The recoveries obtained upon the application of ultrasound-assisted

TABLE 3

Comparison of cold solvent and Soxhlet extraction efficiencies from water-submerged aged concrete as functions of applied *n*-hexadecane concentration, extraction time, and number of extraction steps[c]

	n-Hexadecane concentration						
	4.4 mg/g				22.1 mg/g		
	Cold solvent extraction			Soxhlet extraction	Cold solvent extraction		Soxhlet extraction
Extraction solvent	24 hours	4 days one step	4 days two step	24 hours	4 days one step	4 days two step	24 hours
Acetone	12 ± 4	40 ± 3	ND[b]	26 ± 3	ND[b]	ND[b]	ND[b]
Acetonitrile	84 ± 12	84 ± 6	95 ± 7	109 ± 4	45 ± 4	76 ± 4	99 ± 2
Ethyl acetate	82 ± 11	82 ± 6	100 ± 6	102 ± 6	73 ± 5	84 ± 5	106 ± 7
n-Hexane	ND[b]	58 ± 4	63 ± 4	ND[b]	35 ± 4	65 ± 17	78 ± 4
Methanol	86 ± 10	88 ± 11	91 ± 11	86 ± 6	82 ± 2	92 ± 3	97 ± 3
n-Pentane	9 ± 1	52 ± 2	NA[a]	20 ± 3	ND[b]	ND[b]	ND[b]
2-Propanol	19 ± 5	78 ± 22	79 ± 22	32 ± 6	53 ± 5	70 ± 17	90 ± 5

[a] NA–not applicable. Extraction was performed with a single solvent.

[b] ND–not determined.

[c] Data are presented as mean value ±standard deviation ($n = 3$, $P = 0.05$). Concrete samples were incubated with *n*-hexadecane for 10 days followed by submerging into water for 3 h.

extraction were similar to those obtained using cold solvent shaking extraction of similar duration (not shown). This observation corroborates our hypothesis of relatively low importance of matrix-analyte interactions between the hydrocarbons and concrete. Also, low recoveries were obtained using higher-temperature (Soxhlet) extractions for non-destructive solvents, namely acetone, *n*-pentane, and 2-propanol (Table 3). By contrast, for matrix-destructive organic solvents, the Soxhlet extraction proved to be more efficient than the ambient-temperature shaking extraction. This observation further supports the hypothesis assuming that the physical entrapment of *n*-hexadecane

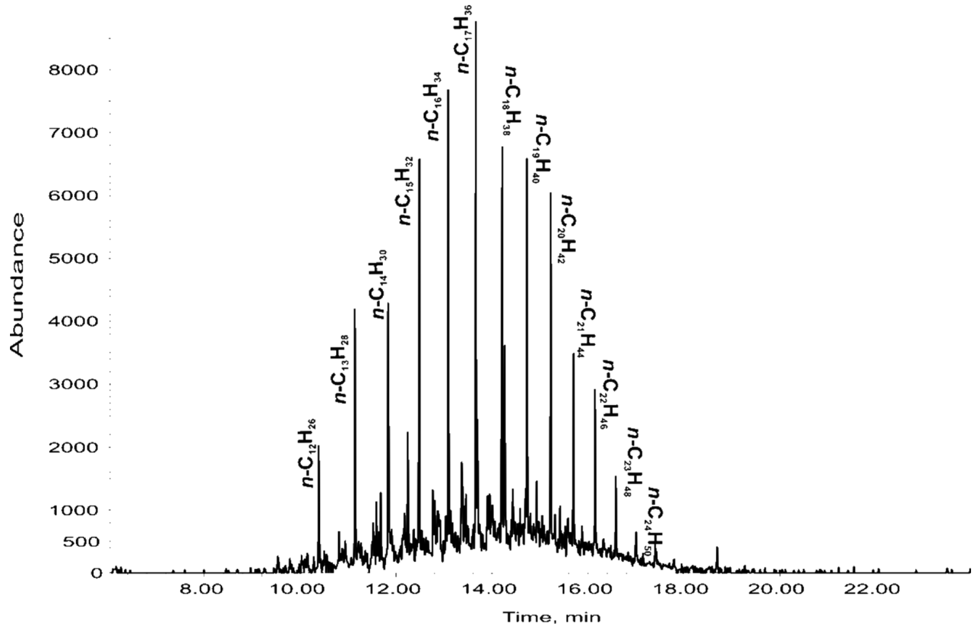

FIG. 3. Extracted ion chromatogram (EIC) of m/z 85.1, representing hexyl ion of saturated hydrocarbons, obtained under extraction of fuel oil #2 from 10-day aged water-submerged concrete via Soxhlet extraction for 24 hours with methanol.

rather than specific interactions with the matrix influences the extraction efficiency.

A comparison of cold solvent and Soxhlet extractions was further extended to a high analyte concentration (22.1 mg/g). The use of Soxhlet extraction provided a significant improvement in comparison to cold shaking extraction for both non-destructive and matrix-destructive solvents (Table 3). The Soxhlet extraction performed in one step for 24 hours yielded near-100% recoveries for acetonitrile, ethyl acetate, and methanol, 90 ± 5% for 2-propanol, and 78 ± 4% for *n*-hexane (Table 3). Note that the matrix-destructive organic solvents, once again, proved to be more efficient than the non-destructive solvents.

A greater Soxhlet extraction efficiency also corroborates our earlier observation that efficient cold solvent extraction required a two-step procedure. Soxhlet extraction is equivalent to a multistep procedure also conducted at an elevated temperature. Both factors contribute to greater analyte mobility within the matrix, thus accelerating its movement toward the extraction solvent. Upon the extension of Soxhlet extraction time up to 48 h, extraction recoveries remained similar to those of 24 h (not shown).

Extraction of Fuel Oil #2 from 10-day Aged Water-Submerged Concrete

The selected polar and non-polar solvents were then tested for the extraction of fuel oil #2 from 10-day aged water-submerged concrete samples via Soxhlet extraction. A sample GC-MS chromatogram is shown in Fig. 3; only the straight-chain hydrocarbons exhibiting pronounced peaks were addressed. The extraction efficiencies varied depending on the hydrocarbon size. Namely, *n*-nonane and *n*-decane were not recovered at all; *n*-undecane was recovered under 40%; *n*-dodecane recoveries did not exceed 50%; whereas longer-chain hydrocarbons (up to C_{24}) were quantitatively extracted. The low recoveries of hydrocarbons less than C_{13} in size can be explained by their evaporation, according to the results of our remediation studies reported earlier (18). The highest recoveries for n-$C_{13}H_{28}$–n-$C_{24}H_{50}$ hydrocarbons were obtained upon the application of polar solvents, both matrix-destructive and non-destructive (Fig. 4). The non-polar solvents tested (*n*-pentane and *n*-hexane) exhibited lower extraction efficiencies thus corroborating the trends observed for *n*-hexadecane extraction.

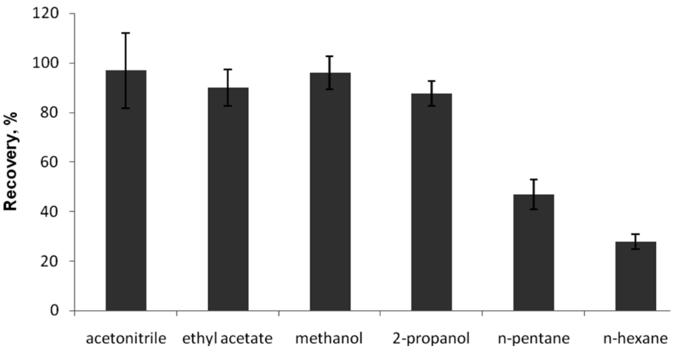

FIG. 4. Extraction efficiencies of fuel oil #2 (n-$C_{13}H_{28}$–n-$C_{24}H_{50}$ hydrocarbons) from 10-day aged water-submerged concrete samples. Extraction was performed using a 24-hour Soxhlet extraction; the data were analyzed using GC-MS. Data are presented as mean value ±standard deviation ($n = 3$, $P = 0.05$).

CONCLUSIONS

The hydrocarbon extraction protocols developed in this study provide near-quantitative recoveries even for aged and/or water-inundated samples and thus can be used as an analytical tool for monitoring the removal of the contaminants. Two-step 4-day cold-shaking extraction with organic concrete-destructive solvents appears to be essential to overcome the problems created by aging and application of larger analyte amounts under water-submerged conditions. The alternate 24-h Soxhlet extraction with the same matrix-destructive solvents is more precise and less dependent on the analyte amount, so it may be recommended as the method of choice. The current study also sheds light on hydrocarbon sorption/entrapment mechanisms inside the pores of building materials, which may be used for developing remediation strategies and models.

ACKNOWLEDGEMENTS

Funding for this work was provided by the USDA Forest Products Laboratory (FPL) via cooperative agreements #04-JV-11111120-070 and 05-JV-11111120-102. The authors are grateful to Dr. A. Kubátová for providing access to her equipment and fruitful discussion of the manuscript and to S. Nelson for technical help.

REFERENCES

1. Wilson, S.A.; Langdon, N.J.; Walden, P.J. (2001) The effects of hydrocarbon contamination on concrete strength. *Proc. Inst. Civ. Eng. Geotech. Eng.*, 149: 189–193.
2. Kozliak, E.I.; Seames, W.S.; Baglayeva, G.V.; Nelson, S.L.; Renner, J.N.; Jalan, N.N.; Paca, J. (2009) Novel Approaches to the Remediation of Building Materials (Wood and Concrete) Contaminated with Chemicals. In: *Soil Remediation*, Aachen, L.; Eichmann, P., eds.; Nova Science Publishers: Hauppauge, NY.
3. Mehta, P.K. (1986) *Concrete: Structure, Properties, and Materials*; Prentice-Hall.
4. Garboczi, E.J. (1995) Microstructure and Transport Properties of Concrete. In: *Performance Criteria for Concrete Durability*, Kropp, J.; Hilsdorf, H.K.E., Eds.; and F.N. Spon: London.
5. Kumar, R.; Bhattacharjee, B. (2003) Porosity, pore size distribution and in situ strength of concrete. *Cem. Concr. Res.*, 33: 155–164.
6. Beklemishev, M.K.; Kozliak, E.I. (2003) Bioremediation of concrete contaminated with *n*-hexadecane and naphthalene. *Acta Biotechnol.*, 23: 197–210.
7. Popova, I.E.; Kozliak, E.I. (2008) Photo-assisted removal of fuel oil hydrocarbons from wood and concrete. *J. Environ. Sci. Health. Part A Toxic/Hazard. Subst. Environ. Eng.*, 43: 1132–1143.

8. EPA Method 3570 (2002) *Microscale Solvent Extraction (MSE)*; U.S. Environmental Protection Agency.
9. ASTM Standard D4260–05 (2005) *Standard Practice for Liquid and Gelled Acid Etching of Concrete*; ASTM International: West Conshohocken, PA.
10. EPA Method 3540C (1996) *Soxhlet Extraction*; U.S. Environmental Protection Agency.
11. Popova, I.E.; Kozliak, E.I. (2008) Efficient extraction of fuel oil hydrocarbons from wood. *Sep. Sci. Technol.*, 43: 778–793.
12. Abraham, M.H. (1993) Scales of solute hydrogen-bonding: Their construction and application to physicochemical and biochemical processes. *Chem. Soc. Rev.*, 22: 73–83.
13. Van Der Bruggen, B.; Schaep, J.; Wilms, D.; Vandecasteele, C. (1999) Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. *J. Membr. Sci.*, 156: 29–41.
14. Xiong, G.; Cui, Y.; Chen, L.; Jiang, H. (2004) Influence of hydrochloric acid etching on bond strength between concrete substrate and repair materials. *Cem. Concr. Compos.*, 26: 41–45.
15. Phutane, S.R.; Renner, J.N.; Nelson, S.L.; Shames, W.S.; Páca, J.; Sundstrom, T.J.; Kozliak, E.I. (2007) Removal of 2,4-dinitrotoluene from concrete using bioremediation, agar extraction, and photocatalysis. *Folia Microbiol.*, 52: 253–260.
16. Scanlon, J.M. (1987) Concrete durability. In: *Katharine and Bryant Mather International Conference*, Am. Concr. Inst. SP, p. 1069.
17. EPA Method 3550B (1996) *Ultrasonic Extraction*; U.S. Environmental Protection Agency.
18. Popova, I.E.; Beklemishev, M.K.; Kozliak, E.I. (2005) Bioremediation of hydrocarbons from contaminated wood: A proof-of-concept study. *Eng. Life Sci.*, 5: 223–233.
19. Lide, D.R. (Ed.) *CRC Handbook of Chemistry and Physics*; CRC Press (an imprint of Taylor & Francis Group): Boca Raton, FL, 2009–2010.