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Soil washing using cyclodextrins and their recovery by application of electrochemical technology

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ABSTRACT

In this study, the capacity of decontaminated polluted soils, by using the sequence washing with cyclodextrin-electrochemical treatment was evaluated. The initial step of the process involved contacting polluted soil with cyclodextrin to enhance recovery of phenanthrene from soil. The total phenanthrene removal in a washing column with aqueous solutions of 1% hydroxypropyl-β-cyclodextrin attained a value of almost 70% after 6 days. The second step of this operational strategy concerned regeneration of the washing solution via electrochemical phenanthrene degradation. The phenanthrene was almost totally degraded in 1 day and the extracting ability of this treated solution was confirmed. By application of this combined technology, it is possible to recycle the washing solution reducing the consumption of cyclodextrin solutions. Consequently, it has provided an effective and economic treatment of PAHs polluted soil.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are pollutants produced via natural and anthropogenic sources, generated during the incomplete combustion of solid and liquid fuels or derived from industrial activities. Many PAHs can have detrimental effects on both the flora and fauna of affected habitats through uptake and accumulation in food chains, and in some instances, pose serious health problems and/or genetic defects in humans. Therefore, it is important to prevent the transport of these pollutants into the environment by the remediation of source zones where high concentrations of PAHs exist [1].

PAHs are hydrophobic compounds and their persistence in the environment is mainly due to their low water solubility. In addition, environmental factors, such as soil type and structure, pH, temperature and the association with co-pollutants, such as other hydrocarbons and heavy metals, can prolong their time in the environment [2]. Toxic PAHs are persistent and difficult to remove from low permeability clayey soils because these contaminants have a low aqueous solubility and a tendency to strongly bind with clay minerals and organic matter present in these soils [3]. Furthermore, some heavier PAHs (with more than three rings) are difficult to be biodegraded and it is usual to use an organic solvent to dissolve PAHs or use surfactants to increase the solubility of PAHs.

The removal of these contaminants presents a challenge to scientists and engineers. Currently, soil washing techniques are mostly using co-solvents (methanol, ethanol) or surfactants to achieve sufficient solubilization of hydrophobic compounds. But this can be a regulatory concern as those molecules can represent a health or environment hazard. Attempts to increase the solubility of recalcitrant organic contaminants have been made using complexing agents which encapsulate poorly water soluble contaminants and thus may enhance their removal from polluted site. Cyclodextrins appear as a promising complexing agent to enhance organic compounds solubility, while minimizing environmental impact [4]. Cyclodextrins are cyclic oligosaccharides of glucopyranose units with a lipophilic cavity in the centre. They are produced by the action of a group of enzymes called cyclodextrin glycosyltransferases on starch. The natural product consists of a mixture of various cyclodextrins, mainly α-cyclodextrin, β-cyclodextrin and γ-cyclodextrin, which consist of six, seven, and eight glucopyranose units, respectively. Cyclodextrins are capable of forming inclusion complexes with contaminants by taking up a whole contaminant molecule, or some part of it, into the cavity. Cyclodextrins offer some advantages over organic solvents like their non-toxic nature and biodegradability [5]. However, the use of cyclodextrins increases the operating costs of the washing process. In order to avoid this limitation, technologies for recovering and reusing cyclodextrins must be developed.

Several researches have designed alternative methods to recover the extracting agent used in the washing process. Ahn et al. [6] propose that selective adsorption of a hazardous hydrophobic

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organic compound (HOC) by activated carbon is an effective process for the recovery of surfactants after a soil washing process. Moreover, Tao and Marshall [7] evaluated the efficiency of surfactant washing for the removal of PAH compounds that had been accumulated in a sample of soil over many years. Once mobilised, the contaminants were readily detoxified at line in a slightly hydrogen-rich atmosphere of supercritical carbon dioxide. These techniques helped to recycle the surfactant and to remove and detoxify the PAH contaminants from the soil, thus reducing the economic process cost. On the other hand, biotechnology process is used to recovery the extracting agent. Thus, Navarro et al. [8] have studied the biodegradability of PAHs from both model solutions and DNA soil washing effluents by using a pure culture of *Sphingomonas* sp. During PAH degradation, the DNA structure for PAH intercalation remained stable; this permitted its reutilisation for further extractions.

In this study phenanthrene, which is an uncharged organic compound that consists of three aromatic rings, was selected as a representative PAHs. It has environmental properties such as aqueous solubility, K_{ow}, and vapor pressure that are similar to other PAH [9,10]. Although higher molecular weight and more carcinogenic PAHs, such as benzo (*a*) pyrene, may have higher K_{ow} values and lower aqueous solubilities, it was hypothesized that since the parent structures are similar, phenanthrene would be an adequate representative compound that would give a general indication of PAH behaviour.

This study focuses on the development of a system for effective soil washing. This consists in a whole process that includes two steps: first, phenanthrene is removed from the polluted soil by washing process in a packed-bed column with a solution of a cyclodextrin. Secondly, this solution is electrochemically treated in order to degrade the phenanthrene and, consequently, the cyclodextrin can be recovered to be reused in another washing process.

2. Materials and methods

2.1. Materials

Contaminant. The phenanthrene used to contaminate the soil was >97% pure and purchased from Sigma–Aldrich.

Cyclodextrin. Hydroxypropyl-β-cyclodextrin (HPCD) and methyl-β-cyclodextrin (MCD) solutions used in the washing process were supplied by Sigma–Aldrich. All cyclodextrins were used without further purification.

Soil. The studied soil is located in a mine at Touro (Spain) from which road material is extracted. This soil consists mainly of amphibolites, chalcopyrite, limonite, garnets, and iron and copper sulphides. Samples of the top 30 cm were taken by using an Eijkelkamp sampler and were pooled in the field. The pooled samples were transported to the laboratory in polyethylene bags. Soil characteristics are summarised by Vega et al. [11].

2.2. Soil preparation

The soil was polluted with a phenanthrene solution completely dissolved in hexane. This mixture is usually expected to have an initial concentration around 500 mg kg^{-1} of dry soil (456 mg phenanthrene kg^{-1} of dry soil), which is the typical PAH concentration found near source zones of contaminated sites [12]. The resultant mixture was placed in a ventilation hood for 9 days to allow the complete evaporation of the solvent [13]. A sample was taken to measure the exact concentration of phenanthrene, as some of the contaminant may volatilise along with the hexane.

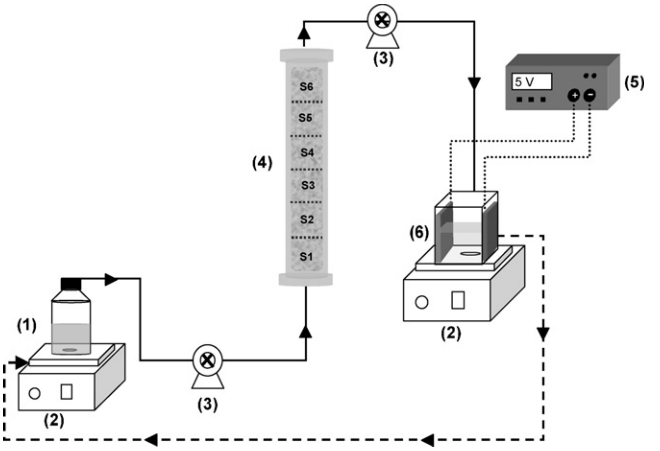

Fig. 1. Experimental set-up: (1) HPCD solution, (2) magnetic stirrers, (3) pumps, (4) packed-bed soil column, (5) electric power supply, (6) Plexiglas electrochemical cell with graphite electrodes.

2.3. Experimental set-ups

Initially, batch extraction experiments were carried out in order to evaluate the ability of the two types of cyclodextrins. Once it has been determined the most appropriate cyclodextrin, the washing process was developed at bench-scale. As shown in Fig. 1, a two-phase soil remediation technology was proposed. The first step is the soil washing in packed-bed column. In the second step, the washing solution that circulated through the soil was collected and treated in an electrochemical cell to achieve phenanthrene degradation and cyclodextrin recycled. Finally, several tests were carried out in shake flasks in order to determine the removal efficiency of the recovered cyclodextrin solution.

Batch extractions. 2.5 g of dry polluted soil was placed in 250 ml Erlenmeyer flasks which were filled with 50 mL of (0.1–4%) cyclodextrin solutions. Control experiments without cyclodextrin solution were also carried out. The Erlenmeyer flasks were maintained in an orbital shaker (Gallenkamp) at 150 rpm and 25 °C. After 24 h, the flasks were centrifuged; supernatant was decanted to determine phenanthrene concentration.

Soil washing in column. 112 g of dry polluted soil was placed in a column (Fig. 1) with a diameter of 3.2 cm and a height of 10 cm. Two chambers were sited, respectively, at the entrance and the exit of the packed-bed column. The bottom entrance chamber of the column was filled with glass beads in order to enhance uniform flow distribution of the washing solution into the column. These compartments were isolated from soil bed by paper filters and porous stones. The washing solution was circulated by means of a peristaltic pump supplying a continuous flow of 0.25 mL min^{-1} of aqueous solution for 6 days. Samples of the washing solutions were removed from the exit chamber to determine phenanthrene concentration.

Electrochemical treatment. The electrochemical treatment was carried out in a cubic Plexiglass cell, with a working volume of 0.4 L, by using graphite electrodes with an immersed area of 52 cm^2 and an electrode gap of 8 cm [14]. A constant potential difference (5 V) was applied with a power supply (HP model 3662), and the process was monitored with a multimeter (Fluke 175). A schematic illustration of the experimental set-up is shown in Fig. 1. Samples of reaction mixtures were taken from the electrochemical cell periodically in order to be analysed for pH and phenanthrene concentration.

Soil washing in shake flask with recycled cyclodextrin. The washing process was carried out in 250 ml Erlenmeyer flasks which were filled with 2.5 g of dry polluted soil and 50 mL of solution

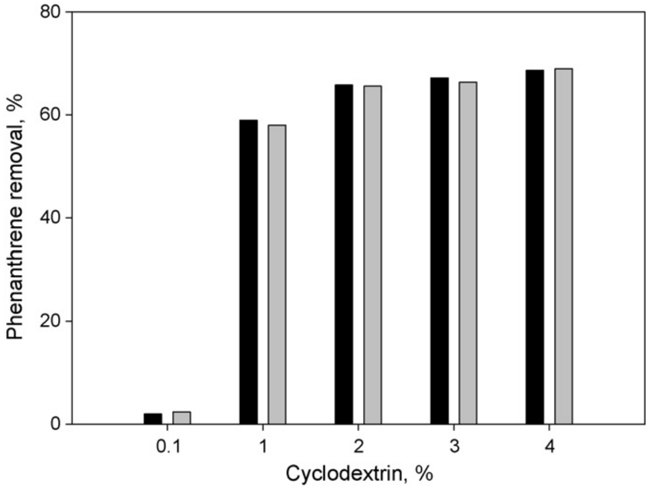

Fig. 2. Phenanthrene removal by shake flask washing with solutions of HPCD (black) and MCD (grey).

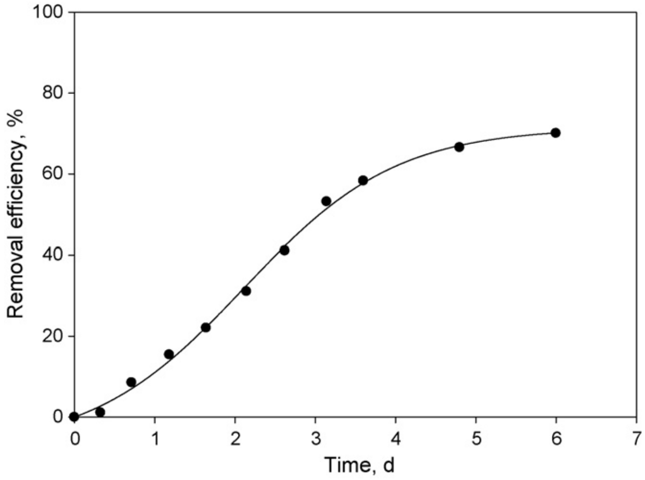

Fig. 3. Profile of phenanthrene removal efficiency in the washing packed-bed soil column with a HPCD solution (1%).

collected in the electrochemical treatment. Control experiments with/without cyclodextrin were also carried out. The Erlenmeyer flasks were maintained in an orbital shaker (Gallenkamp) at 150 rpm and 25 °C. After 24 h, the flasks were centrifuged; supernatant was decanted to determine phenanthrene concentration.

2.4. Methodology and analytical determinations

In this study, all experiments were carried out in duplicate. At the end of each experiment, samples were taken from solutions as well as from the soil for chemical analysis. These were analysed in triplicate, with a standard deviation lower than 15%. The results shown in all figures correspond to mean values.

Phenanthrene extraction. Phenanthrene was extracted from the soil samples by using a Soxhlet apparatus. Dry soil (5 g) was thoroughly mixed with 5 g of Na_2SO_4 and placed into a Whatman cellulose extraction thimble. The extraction solution used was 100 ml of a 1:1 mixture of hexane and acetone. After 24 h at 5 cycles h^{-1}, phenanthrene concentration was assayed by HPLC. The Soxhlet procedure is outlined in USEPA Test Method 3540C [15].

Phenanthrene concentration. This concentration was determined by HPLC (Agilent 1100) equipped with a XDB-C8 reverse-phase column (150 mm × 4.6 mm i.d., 5 μm). Prior to injection, the samples were filtered through a 0.45 μm Teflon filter. The injection volume was set at 5 μL, and the isocratic eluent (70:30 acetonitrile/water) was pumped at a rate of 1 mL min^{-1} for 10 min. Detection was performed with a diode array detector covering from 200 to 400 nm. The temperature in the column was maintained at 20 °C.

3. Results and discussion

3.1. Batch extractions

Desorption from artificially contaminated soils is needed to understand the limitations of cyclodextrin-assisted remediation at high-scale. Initially, batch extraction experiments were carried out to evaluate the ability of two types of cyclodextrins, hydroxypropyl-β-cyclodextrin (HPCD) and methyl-β-cyclodextrin (MCD), to extract phenanthrene from a model contaminated soil. Desorption was evaluated increasing the cyclodextrin concentration up to 4%.

As can be seen in Fig. 2, the removals of both cyclodextrins were similar. The use of the studied cyclodextrins as a solubility enhancement agent was effective for phenanthrene extraction. The higher levels of phenanthrene desorption were around 70% when the employed cyclodextrin concentration was higher than 1%. These two cyclodextrins have close performances and the choice between them should be greatly determined by their respective costs. For this reason, cyclodextrin HPCD at 1% was selected to subsequent experiments.

Although there are few data in the literature about the possible utilization of these compounds as extracting agent, the results obtained are in agreement with previous papers. Viglianti et al. [16,17] investigated the effectiveness of cyclodextrin solutions (β-cyclodextrin (BCD), hydroxypropyl-β-cyclodextrin (HPCD) and methyl-β-cyclodextrin (MCD)) to remove PAH occurring in industrially aged contaminated soil. They determined that PAHs extraction enhancement factor compared to water was about 200.

Oleszczuk [18] tested the application of the non-exhaustive extraction technique with HPCD for the evaluation of the content of potentially bioavailable PAH fraction as well as the evaluation of changes in the content of this fraction during composting of municipal sewage sludges. The fraction extracted with HPCD ranged from 63.5 to 83.1% depending on the sludge and changed the values of the bioavailable fraction.

3.2. Soil remediation by washing with HPCD in column

The main purpose of this study was to develop a competitive and effective combined process in which the pollutant can be removed from soil and cyclodextrin can be recovered to be reused in the next washing process (Fig. 1). Therefore, it was decided to artificially contaminate real soil with a known PAH contaminant (phenanthrene) at a known concentration in order to avoid concerns about the source, type, and concentration of the contaminant, as well as differences due to aged contamination.

Fig. 3 shows the removal efficiency of the washing process versus time. In this case, the term removal efficiency is used to express phenanthrene removal performance of column units with respect to its initial concentration. It can be observed that the phenanthrene removal was fitted by the logistic model and the concentration of phenanthrene is gradually reduced up to a maximum value (around 70%). Considering the flow rate of the washing solution, in 6 days, the ratio soil/washing solution (0.055 g soil per mL of solution) was similar to that attained at shake flask scale. These results confirm the good correlation between the experiments at shake flask and column scales.

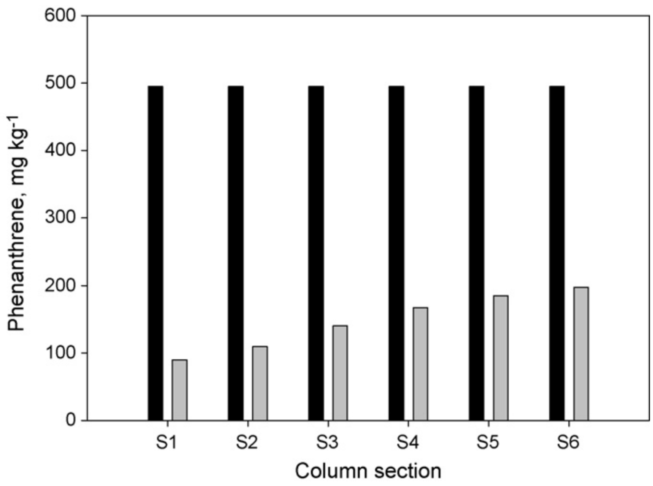

Fig. 4. Phenanthrene concentration retained along the column soil height. Black and grey bars represent initial and final phenanthrene concentration in the soil, respectively.

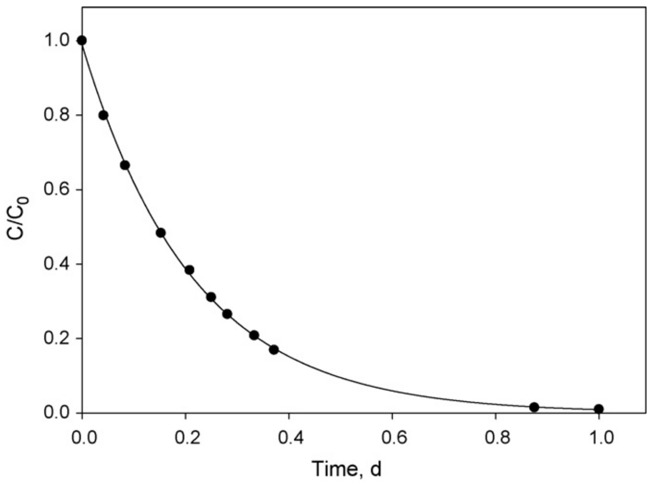

Fig. 5. Normalised phenanthrene concentration profile versus treatment time of electrochemical treatment of HPCD washing outlet solution. Data (●) were fitted to a first-order kinetic equation (line).

Navarro et al. [19] determined a similar behaviour. In their study, the potential of aqueous deoxyribonucleic acid (DNA) solution for washing or flushing PAH-contaminated soil was established. They employed a spiked soil sample containing 102 mg kg^{-1} phenanthrene. Extractions close to 78% was attained with 5% DNA at a 1:50 soil/extractant ratio.

At the end of our experiment, the soil sample was divided into six sections from the bottom column (see Fig. 1) and each one was analysed for phenanthrene concentration. As shown in Fig. 4, the phenanthrene retention in the soil is higher in the upper sections. By mixture of all sections the phenanthrene retained in the soil was around 29% that close the molar balance of the pollutant in soil and washing solution.

3.3. Recovery of HPCD by electrochemical treatment and its reuse in washing process

Due to the high cost of cyclodextrin, there is an obvious need to examine the possibility to recycle the washing solution as well as to verify the efficiency of this solution in another washing process. For this reason, the exhausted washing solution, enriched in phenanthrene, must be treated in order to destroy the pollutant. Recently, electrochemical technology is receiving more and more attention, for its success in degradation process without the production of a secondary pollutant and due to its convenience and simplicity. To our knowledge, no study has been conducted to investigate the degradation of PAHs in the presence of cyclodextrin by electrochemical treatment in order to allow the recycling of the solution in another washing process. In the electrochemical treatment the electric current induces redox reactions upon the electrodes surface resulting in the destruction of the organic compound [20,21]. The oxidation mechanisms involved in this technology have also been characterised. They include direct electrooxidation, hydroxyl radical-mediated oxidation, and oxidation mediated by oxidants generated during the treatment of the salts contained in the waste [22].

In order to achieve high level of efficiency in the overall process of the electrochemical treatment, several factors must be taken into consideration such as the voltage drop and the electric current intensity. In previous work this variables have been optimized [23]. The experiments were conducted at 25 °C and at a constant potential difference of 5 V. In Fig. 5, the profile of phenanthrene degradation in cubic cell has been showed. The pH value inside the electrochemical cell was of around three during the treatment. The total degradation of phenanthrene was achieved after 1 day of treatment.

The phenanthrene concentration shows an exponential profile with the time. Thus, in this first-order electrochemical reaction the rate is proportional to the phenanthrene concentration. The next Eq. (1) fits this behavior:

$$\frac{C}{C_0} = e^{-4.6826t} \quad (r^2 = 0.999) \tag{1}$$

where C and C_0: phenanthrene concentration along the time and initial, respectively; t: time (d) and r^2: statistical correlation parameter.

After the total elimination of phenanthrene, several experiments were carried out in order to determine the removal capacity of the solution after electrochemical treatment in shake flask. It was determined that the level of phenanthrene removal attained with the reused solution was 3% lesser than the value obtained with new HPCD solution. It is clear that selective removal of pollutants from the washing solution is a potentially effective technology for reusing cyclodextrin in another soil washing process.

The evaluation of all stages demonstrates that the sequential process developed in this study (washing and electrochemical treatment) is an ideal approach in order to reduce the economic process cost.

4. Conclusions

In view of the results obtained, it can be concluded that cyclodextrin has a great potential for PAHs extraction. The combination of the sequence washing with cyclodextrin followed by the electrochemical treatment for the recycling of the cyclodextrin permit high removal of PAHs from contaminated soil reducing the economic process cost.

The results suggest that the innovative technology developed in this study for remediation of environments contaminated with PAHs is suitable, low cost and lacking in operational problems. This system has potential application for the “clean-up” of PAHs contaminated soil and the subsequent treatment of residual liquids. Moreover, it is demonstrated that the electrochemical treatment is a versatile complementary alternative with a high potential to replace or improve existing processes.

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References

[1] M.T. Alcántara, J. Gómez, M. Pazos, M.A. Sanromán, PAHs soil decontamination in two steps: desorption and electrochemical treatment, J. Hazard. Mater. 166 (2009) 462–468.

[2] S.M. Bamforth, I. Singleton, Bioremediation of polycyclic aromatic hydrocarbons: current knowledge and future directions, J. Chem. Technol. Biot. 80 (2005) 723–736.

[3] R.G. Luthy, G.R. Aiken, M.L. Brusseau, S.D. Cunningham, P.M. Gschwend, P.M. Pignatello, M. Reinhard, S.J. Traina, W.J. Weber, J.C. Westall, Sequestration of hydrophobic organic contaminants by geosorbents, Environ. Sci. Technol. 31 (1997) 3341–3347.

[4] J.D. Stokes, A. Wilkinson, B.J. Reid, K.C. Jones, K.T. Semple, Prediction of polycyclic aromatic hydrocarbon biodegradation in contaminated soils using an aqueous hydroxypropyl-beta-cyclodextrin extraction technique, Environ. Toxicol. Chem. 24 (2005) 1325–1330.

[5] F.J. Rivas, Polycyclic aromatic hydrocarbons sorbed on soils: a short review of chemical oxidation based treatments, J. Hazard. Mater. 138 (2006) 234–251.

[6] C.K. Ahn, Y.M. Kim, S.H. Woo, J.M. Park, Soil washing using various nonionic surfactants and their recovery by selective adsorption with activated carbon, J. Hazard. Mater. 154 (2008) 153–160.

[7] Y. Tao, W.D. Marshall, Optimizing a washing procedure to mobilize polycyclic aromatic hydrocarbons (PAHs) from a field-contaminated soil, Ind. Eng. Chem. Res. 46 (2007) 4626–4632.

[8] R.R. Navarro, Y. Iimura, H. Ichikawa, K. Tatsumi, Treatment of PAHs in contaminated soil by extraction with aqueous DNA followed by biodegradation with a pure culture of *Sphingomonas* sp., Chemosphere 73 (2008) 1414–1419.

[9] D.W. Connell, Basic Concepts of Environmental Chemistry, Lewis Publishers, New York, 1997.

[10] R.E. Saichek, K.R. Reddy, Evaluation of surfactants/cosolvents for desorption/solubilization of phenanthrene in clayey soils, Int. J. Environ. Stud. 61 (2004) 587–604.

[11] F.A. Vega, E.F. Covelo, M.L. Andrade, Competitive sorption and desorption of heavy metals in mine soils: influence of mine soil characteristics, J. Colloid. Interf. Sci. 298 (2006) 582–592.

[12] USEPA, A Resource for MGP Site Characterization and Remediation, EPA/542-R-00-005, Washington DC, 2000.

[13] R.E. Saichek, K.R. Reddy, Effect of pH control at the anode for the electrokinetic removal of phenanthrene from kaolin soil, Chemosphere 51 (2003) 273–287.

[14] C. Cameselle, M. Pazos, A. Sanroman, Selection of an electrolyte to enhance the electrochemical decolourisation of Indigo. Optimization and scale-up, Chemosphere 60 (2005) 1080–1086.

[15] USEPA, Test Methods for Evaluating Solid Waste, vol. 1A: Laboratory Manual, Physical/Chemical Methods, SW-846, third ed., Office of Solid Waste and Emergency Response, Washington DC, 1986.

[16] C. Viglianti, K. Hanna, C. De Brauer, P. Germain, Removal of polycyclic aromatic hydrocarbons from aged contaminated soil using cyclodextrins: experimental study, Environ. Pollut. 140 (2006) 427–435.

[17] C. Viglianti, K. Hanna, C. De Brauer, P. Germain, Use of cyclodextrins as an environmentally friendly extracting agent in organic aged-contaminated soil remediation, J. Incl. Phenom. Macrocycl. Chem. 56 (2006) 275–280.

[18] P. Oleszczuk, Application of hydroxypropyl[β]cyclodextrin to evaluation of polycyclic aromatic hydrocarbon losses during sewage sludges composting, J. Environ. Sci. Health Part A 43 (2008) 10–17.

[19] R.R. Navarro, H. Ichikawa, Y. Iimura, K. Tatsumi, Removal of polycyclic aromatic hydrocarbons from contaminated soil by aqueous DNA solution, Environ. Sci. Technol. 41 (2007) 4240–4245.

[20] M.A. Sanromán, M. Pazos, M.T. Ricart, C. Cameselle, Electrochemical decolourisation of structurally different dyes, Chemosphere 57 (2004) 233–239.

[21] M.T. Alcántara, J. Gómez, M. Pazos, M.A. Sanromán, Combined treatment of PAHs contaminated soils using the sequence extraction with surfactant-electrochemical degradation, Chemosphere 70 (2008) 1438–1444.

[22] P. Cañizares, C. Sáez, J. Lobato, R. Paz, M.A. Rodrigo, Effect of the operating conditions on the oxidation mechanism in conductive-diamond electrolyses, J. Electrochem. Soc. 154 (2007) E37–E44.

[23] J. Gómez, M.T. Alcántara, M. Pazos, M.A. Sanromán, A two-stage process using electrokinetic remediation and electrochemical degradation for treating benzo[a]pyrene spiked kaolin, Chemosphere 74 (2009) 1516–1521.