Organo/LDH nanocomposite as an adsorbent of polycyclic aromatic hydrocarbons in water and soil-water systems

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are considered as priority pollutants because of their high risk to human health. In this paper, we addressed the issue of using hydrotalcite-based nanocomposites as adsorbents of six low molecular weight PAHs (acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene) to reduce their negative effects on the environment. A nanocomposite (HT-DDS) was prepared by intercalating the organic anion dodecylsulfate (DDS) in a Mg-Al hydrotalcite (HT), and then characterized using several analytical techniques. A Mediterranean soil was selected for being a high-risk scenario of groundwater contamination by leaching of pollutants. The nanocomposite displayed enhanced affinity for the PAHs in water as compared to carbonate-hydrotalcite ($HTCO_3$) and its calcined product (HT500), and showed a high irreversibility of the adsorption process (hysteresis coefficient, $H < 0.15$). The results revealed an increase of the pollutants retention in the soil by the addition of the nanocomposite that depended on the nanocomposite application rate and also on the hydrophobicity of each PAH. Accordingly, the use of HT-DDS as an amendment or barrier in contaminated soil is proposed for reducing the mobility of PAHs and, consequently, the adverse effect derived from rapid transport losses of the pollutants to the adjoining environmental compartments.

Key words: adsorption; contaminated soils; hydrotalcite; nanocomposite; polycyclic aromatic hydrocarbons.

1. Introduction

The nature of Mediterranean soils is strongly influenced by climate conditions, characterized by long periods of drought, together with short, strong, and irregular rainfalls. These characteristics contribute to the creation of natural systems sensitive to degradation, entailing a situation of high risk for chemical pollution of various kinds.

A representative group of organic pollutants are the polycyclic aromatic hydrocarbons (PAHs), whose study is prioritized by their great ubiquity, potential bioaccumulation, carcinogenicity, and resistance to biodegradation [1,2]. PAHs are often found in contaminated soils as a mixture of low (2-4 aromatic rings) and high (5 or more aromatic rings) molecular weight compounds, generally owning hydrophobic characteristics and low solubility in water. Nevertheless, low molecular weight PAHs are less hydrophobic and more water soluble than high molecular weight PAHs, and hence can display greater mobility in soils and increased risk of pollution of adjacent aquatic ecosystems. In this work, six PAH compounds (acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene) have been selected primarily by their low molecular weight, higher solubility and lower hydrophobicity compared with other chemicals of the same nature.

There is growing interest in the study and development of new adsorbents applicable to the remediation of soils as immobilizers and insulating contaminants therein [3,4]. Water contamination by transport of pollutants from the adjacent environmental compartments would involve the application of treatments for decontamination that are usually complicated, lengthy, expensive, and often not feasible. The research of new adsorbents is a strategy to remediate the contamination of water produced by the increase of the anthropogenic activities [5-8]. In addition, application of environmentally friendly adsorbents into natural systems is particularly important to entail minimal environmental impact.

Layered double hydroxides (LDHs) are minerals that can be easily synthesized in the laboratory. They consist of positively charged brucite-type layers of mixed divalent (M^{II}) and trivalent (M^{III}) metal hydroxide, $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}$, where the positive charge is balanced by exchangeable hydrated anions located in the interlamellar domain ($A_{x/n}^{n-} \cdot mH_2O$) [5,9]. LDHs,

also referred to as anionic clays, are considered as very useful materials in diverse fields of application, due to the ease of synthesis, peculiar properties derived from their structure, and wide combination range of the components of both layers and interlayers [6,10].

According to their behavior as anion exchangers and their "memory effect" (i.e. recovering of the original layered structure by rehydration of the LDH calcined product), LDHs have good properties as adsorbents for anionic organic pollutants [11-14]. However, the original inorganic composition of these materials gives them a hydrophilic nature. As a result, they usually have a low affinity for non-ionic organic compounds. The intercalation of organic anions in LDHs changes the nature of the surface to hydrophobic, improving the adsorption ability to non-ionic organic compounds. Consequently, these organo/LDHs have applications in a wide range of organic pollution control fields [6,7,15-18].

To date, literature on the potential usefulness of organo/LDHs as adsorbents of PAHs from aqueous solution is scarce. Recently, Chuang et al. [19] demonstrated that a Mg/Al (2:1) LDH intercalated with dodecylsulfate (DDS) anions and the bio-surfactant rhamnolipid displayed good adsorbent properties for naphthalene in aqueous solution. However, to our knowledge, there is no published information about the use of LDH-DDS nanocomposites as adsorbents of other PAHs from water or as soil amendments to enhance the PAH retention process in soil.

The aim of this work was to prepare and characterize an organo/LDH nanocomposite, consisting of Mg/Al (3:1) LDH or hydrotalcite intercalated with DDS anions. Once synthesized, the most novel aspect of this work lied in the assessment of the removal of six PAHs (acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene) from water using the nanocomposite, as well as to determine the effect of its application to a typical Mediterranean soil in the process of retention of such pollutants, as a strategy to reduce their mobility in the soil and decrease their spread through the different environmental compartments.

2. Materials and methods

2.1. PAHs, organic anion and soil

The six PAHs used in this study were supplied by Sigma-Aldrich in powder form and with a purity ranging between 96% and > 99% depending on the compound. Table 1 summarizes the molecular structure and some of the most relevant physicochemical properties of these chemicals [20-22].

The organic anion dodecylsulfate (DDS) used for the preparation of the organo/LDH nanohybrid was purchased as soluble sodium salt from Sigma-Aldrich (Spain), with a purity > 99%. All the chemicals were used as received without further purification.

The soil used in the experiments was a sandy clay loam soil from Coria del Rio (Seville, Spain) and contained no background concentration of the PAHs chosen, as determined by soxhlet extraction for 8 h with dichloromethane [23]. The Mediterranean soil was sampled (0–20 cm), air-dried, sieved (2 mm), and stored at 4ºC until used. Soil texture (25% clay, 8% silt, and 67% sand) was determined by sedimentation. The organic carbon content was 0.52% and the pH was 7.2 in a 1:2 (w:w) soil:deionized water mixture.

2.2. Preparation and characterization of the organo/LDH

Organo/LDH $[Mg_3Al(OH)_8][CH_3(CH_2)_{10}CH_2SO_4]\cdot nH_2O$ was obtained by the coprecipitation method in a N_2 atmosphere and CO_2-free water. An aqueous solution (100 mL) containing 0.06 mol of $Mg(NO_3)_2\cdot 6H_2O$ and 0.02 mol of $Al(NO_3)_3\cdot 9H_2O$ (Mg/Al ratio = 3) was added dropwise to an alkaline solution (500 mL) containing 0.16 mol of NaOH and 0.05 mol of sodium dodecylsulfate. The suspension thus obtained was hydrothermally treated at 80 °C for 24 h, and the precipitate washed with CO_2-free distilled water, and dried at 60 °C. The sample was figured as HT-DDS.

For comparison purposes, an inorganic hydrotalcite $[Mg_3Al(OH)_8]_2CO_3\cdot nH_2O$ ($HTCO_3$) was prepared by the coprecipitation method [24], adding dropwise an aqueous solution (100 mL) containing 0.75 mol of $Mg(NO_3)_2\cdot 6H_2O$ and 0.25 mol of $Al(NO_3)_3\cdot 9H_2O$ to an alkaline solution (500 mL) containing 2 mol of NaOH and 0.375 mol of Na_2CO_3. The suspension was subjected

to the same process described above. Afterward, an aliquot of the sample was calcined at 500 ºC to obtain magnesium aluminum oxide $Mg_3AlO_{4.5}$ (HT500).

HT-DDS and $HTCO_3$ were characterized by different physicochemical techniques. Elemental chemical analysis of Mg and Al was conducted using atomic absorption spectrometry on a Perkin Elmer AA-3100 instrument, after dissolving the samples in a 10% HCl solution. Elemental C, N and S analyses were conducted in a Perkin Elmer 240C analyzer.

Powder X-ray diffraction (PXRD) diagrams were collected at room temperature under air conditions, on a Siemens D-5000 instrument with CuK_α radiation (λ = 1.54050 Å) and quartz as an external standard. The Fourier-transform infrared (FT-IR) spectra were obtained with a Perkin Elmer Spectrum One spectrophotometer using the KBr disk technique. One hundred scans were averaged to improve the signal-to-noise ratio, at a nominal resolution of 2 cm^{-1}.

The hydration water content was obtained from thermogravimetric (TG) curves recorded on a Setaram Setsys Evolution 16/18 apparatus. The analyses were carried out flowing air from Air Liquide (Spain) and using a heating rate of 5 °C/min.

2.3. Adsorption-desorption isotherms

The procedure used to study the adsorption of PAHs on HT-DDS, $HTCO_3$ and HT500 was the batch equilibration technique at 20 ± 2 ºC, thus obtaining the corresponding adsorption-desorption isotherms. Duplicate 10 mg adsorbent samples were equilibrated under end-over-end shaking at 52 rpm for 24 h with 10 mL of an aqueous solution containing a mixture of the six PAHs, with individual initial PAH concentrations (C_i) ranging between 0.05 and 0.65 µmol L^{-1}. Previously, it was determined that equilibrium was reached in < 24 h and that no measurable degradation occurred during this period. Initial PAH solutions without adsorbent were also shaken for 24 h and served as controls to account for losses of the PAHs due to processes different from adsorption to the solid (volatilization, adsorption to glassware, etc.). After equilibration, the suspensions were centrifuged (9000 × g, 15 min) and 4 mL of the supernatant solution were removed. The PAHs were determined by high performance liquid

chromatography (HPLC) as described below, calculating the amount of PAH adsorbed (C_s) from the difference between the initial (C_i) and equilibrium (C_e) solution concentrations:

$$C_s = [(C_i - C_e) / m] \cdot V \qquad (1)$$

where C_s (μmol kg^{-1}) is the amount of PAH adsorbed at the equilibrium concentration C_e (μmol L^{-1}), m is the adsorbent mass (kg) and V is the solution volume (L).

Desorption was performed immediately after adsorption from the highest equilibrium point of the adsorption isotherm. The 4 mL of supernatant removed, and used for the adsorption analysis, were replaced with 4 mL of distilled water. After shaking for 24 h at 20 ± 2 ºC, the suspensions were centrifuged, and the equilibrium concentrations of the PAHs in the supernatant were determined by HPLC. This desorption procedure was conducted three times. Adsorption–desorption data were fit to the logarithmic form of the Freundlich equation: $\log C_s = \log K_f + N_f \log C_e$, where K_f ($\mu mol^{1-Nf} L^{Nf} kg^{-1}$) and N_f (unitless) are the empirical Freundlich constants. Hysteresis coefficients, H, were calculated according to $H = N_{f\text{-}des} / N_f$, where N_f and $N_{f\text{-}des}$ are the Freundlich slopes of the adsorption and desorption isotherms, respectively [25].

2.4. PAHs adsorption by unamended and organo/LDH-amended soil

Triplicate samples (100 mg) of soil were amended with HT-DDS at different rates (0%, 4% and 10%) in order to evaluate its effect on PAHs adsorption compared with unamended soil samples. The mixture was homogenized and 10 mL of an aqueous solution containing the six PAHs selected at C_i = 50 μg L^{-1} each was added. PAHs adsorption was measured using the batch equilibration procedure by stirring the samples for 24 h at 20 ± 2 ºC, after which they were centrifuged at 4000 rpm for 20 min and the amount of PAHs in the supernatant was analyzed by HPLC. Quantification of the adsorbed PAHs was achieved from the difference between the initial concentration (C_i) and the equilibrium solution concentration (C_e), and was expressed as a percentage of the initial concentration (C_i).

2.5. Organo/LDH as an immobilizer amendment in a PAH-contaminated soil

The effect of HT-DDS as an amendment to reduce the mobility of PAHs in a previously contaminated soil was studied by means of a desorption experiment in which 100 mg of soil was spiked with 100 mg kg^{-1} of each PAH, previously dissolved in acetone. The organic solvent was allowed to evaporate afterward for 24 h at room temperature. Then, two different amounts of HT-DDS (4% and 10% w/w) were added to the soil and the mixture was homogenized. Ten mL of distilled water was added to 100 mg of unamended or HT-DDS-amended contaminated soil, shaken at 52 rpm for 24 h at 20 ± 2 ºC, centrifuged and analyzed for PAHs content of the supernatant by HPLC. The desorption of PAHs from unamended and HT-DDS-amended soil was compared.

2.6. PAHs analysis

Analysis of the PAHs was carried out by HPLC. Chemicals were separated on a Water PAH C-18, S-5 µm, 250 mm x 4.6 mm column, with 50:50 acetonitrile/water to 100% acetonitrile linear gradient, run over 18 min at a flow rate of 1.5 mL min^{-1}. The gradient was produced by a Waters 1525 Binary HPLC Pump. A 20 µL injection volume of PAHs was analyzed by HPLC using a UV detector (Waters 2996 diode-array detector) at 254 nm and a fluorescence detector (Waters 2475 Multi λ fluorescent detector) operating simultaneously in series. All data were processed and stored using the program Empower System designed by Water. External calibration curves with standard solutions of PAHs between 0.1-100 µg L^{-1} were used in the calculations.

3. Results and discussion

3.1. Characterization of organo/LDH nanohybrid adsorbent

Table 2 shows the elemental analysis results for Mg, Al, C and S for $HTCO_3$ and HT-DDS, as well as some molar ratios. Chemical compositions indicated that the solids prepared had a Mg/Al ratio of 3.0:1.0, which was the same as in the starting Mg/Al nitrate solution. The

elemental analysis revealed no detectable amount of N in the samples, indicating lack of NO_3^- ions in the interlayer.

The empirical formula of the $HTCO_3$ sample was derived from its chemical composition. On the basis of the lack of N in the samples, CO_3^{2-} was assumed to be the intercalated anion, whereas the water content was obtained from the mass lost in the corresponding TG-curves (not shown). For HT-DDS, the S/Al molar ratio (S/Al = 1.28), allows to determine the organic anion content, which is higher than that required to compensate the layer charge (S/Al = 1). This phenomenon has also been observed by other authors for Mg-Al hydrotalcites [18,26], and indicates that a number of DDS anions should be associated with sodium ions (or hydrogen ions) to balance the charge. You et al. [18] reported that the excess of surfactant intercalated could be due to non-polar interactions with the hydrophobic alkyl groups of exchanged DDS anions. In fact, the high affinity between DDS and the LDH surface has been confirmed in a previous study on the effect of DDS adsorption on the surface charge characteristics of LDH, where DDS was found to change the positive electrokinetic (ζ) potential values of a Mg-Al-Cl LDH to negative values even at low amounts of adsorbed DDS [27].

The PXRD patterns obtained for $HTCO_3$, HT-DDS, and HT500 are shown in Fig. 1 and are similar to those previously reported for similar samples [28-30]. The diffractograms of $HTCO_3$ and HT-DDS samples correspond to those typical of hydrotalcite-like compounds with a well-ordered layered structure . The PXRD pattern of $HTCO_3$, with the basal spacing of d_{003} = 7.8 Å, is characteristic for carbonate as interlayer anion. Several orders of basal (*00l*) reflections were identified in the diffractogram of HT-DDS between 25.9 and 3.8 Å, and as expected, they were shifted to higher d_{00l} values (d_{003} = 25.9 Å) compared to $HTCO_3$, consistent with the successful perpendicular intercalation of the surfactant in an all-trans conformation of the alkyl chains regarding to the brucite-type layer [26]. On the other hand, the diffractogram shown in Fig. 1C corresponds to $HTCO_3$ calcined at 500°C (HT500), with the diffraction peaks characteristic of an Al and Mg mixed oxide [31].

Figure 2 shows the FT-IR spectra of $HTCO_3$ and HT-DDS, as well as the spectrum of the dodecylsulfate sodium salt (Fig. 2B), which was recorded as a reference. As expected, the

infrared spectra of $HTCO_3$ (Fig. 2A) and HT-DDS (Fig. 2C) show the characteristic absorption bands according to the hydrotalcite structure and composition. Besides a broad band centered at 3500 cm^{-1} due to the stretching mode $\nu_{O\text{-}H}$ of hydration water molecules and OH−groups of the brucite-like layers, we observed a weak peak at 1640 cm^{-1} corresponding to the H_2O water bending mode ($\delta_{O\text{-}H}$) of the interlayer water molecules. The bands in the range of 500-800 cm^{-1} can be assigned to metal-oxygen lattice vibration, suggesting the formation of Mg-Al hydroxide layers.

For $HTCO_3$, the band at 1370 cm^{-1} confirms the presence of intercalated CO_3^{2-} (ν_{CO_3}) [5]. The presence of DDS anions in the organo/LDH (HT-DDS) is evidenced by the triplet observed in the 2850-2965 cm^{-1} region, due to the C-H stretching vibration ν_{CH_3} bands (2958, 2919 and 2851 cm^{-1}), and the C-H bending vibration band $\delta_{C\text{-}H}$ at 1469 cm^{-1}. In addition, bands due to antisymmetric (doublet at 1246 and 1224 cm^{-1}) and symmetric (1066 cm^{-1}) sulfate S=O stretching vibration ($\nu_{S=O}$) were also observed [15,26].

3.2. Adsorption-desorption isotherms

Figure 3 shows the adsorption isotherms of the six PAHs on HT-DDS. The PAHs adsorption on the inorganic samples $HTCO_3$ and HT500 was very low (data not included), as has been observed for other non-polar organic compounds [16]. The adsorption parameters of the PAHs on HT-DDS were obtained by fitting the adsorption isotherms to the Freundlich model, and the parameters are summarized in Table 3. Determination of Freundlich constants was not possible in cases where adsorption was close to 100% (phenanthrene, fluoranthene, and pyrene) or in cases of very low adsorption ($HTCO_3$ and HT500). Adsorption isotherms, along with K_f values, showed the greater affinity of the PAHs for HT-DDS than for $HTCO_3$ and its calcined product (HT500), which could be attributed to hydrophobic interactions between the PAHs and the alkyl chains of the DDS anions. This result is very similar to that previously reported for the adsorption of the herbicides carbetamide, metamitron and terbuthylazine by the same adsorbents [16,32]. This behavior confirmed that the transformation of the nanocomposite surface nature

from hydrophilic to hydrophobic increases its affinity for hydrophobic compounds, such as PAHs, by adsolubilization mechanisms [16,19].

The adsorption of the PAHs by HT-DDS increased with the molecular weight of the compound, reaching up to 100% for fluoranthene and pyrene at all concentrations tested. Isotherms and N_f values, close to unity, indicated linear or C-type adsorption according to the classification of Giles et al. [33]. This type of isotherms characterize systems with a minimum competition between the solute and the solvent for adsorption sites of the adsorbent, reflecting a constant partition mechanism, in this case through hydrophobic-type interactions into the bulk state of the interlayer organic phase [34]. Moreover, C-type isotherms are very common for the adsorption of very hydrophobic organic compounds, whose concentration is limited by their low water solubility.

Desorption curves showed very high hysteresis in most cases, revealing a great irreversibility of the adsorption process. This agrees with the low values of H coefficient ($N_{f\text{-des}}$ / $N_{f\text{-ads}}$) found in those cases where its calculation was possible. Otherwise, these results also confirmed the very high affinity of the PAHs to HT-DDS, where once adsorbed, water is not able to reach the adsorption sites where PAHs remain retained [35]. This may be interesting from the point of view of the applicability of these nanomaterials as adsorbents of PAHs as a water decontamination strategy.

3.3. PAHs adsorption by unamended and HTDDS-amended soil samples

Since HT-DDS displayed good adsorbent properties for the PAHs, we studied its application as an amendment to increase the adsorption capacity of a typical Mediterranean soil. The soil was chosen because of its physicochemical characteristics, with a coarse texture and low organic matter content resulting in a high-risk leaching potential for chemicals like the PAHs studied. Figure 4 shows the results of the PAHs adsorption to the Mediterranean soil, unamended and amended with different amounts of HT-DDS (4% and 10% w/w). Adsorption of non-polar organic compounds strongly depends on the organic carbon (OC) content in soil or sediment [36,37]. In this case, the soil presents a low capacity of adsorption for the lower

molecular weight PAHs, probably due to its low organic matter content. Adsorption increased with the hydrophobicity of the PAHs and their molecular weight (from acenaphthene: ~ 13%, to pyrene: ~ 60 %, Table 1), with a very good correlation between log K_{ow} and log K_d (Fig. 5), which suggests the dominance of nonspecific interactions (van der Waals forces) in the adsorption mechanism of these compounds [38].

The application of HT-DDS to the soil increased its adsorption properties for the six PAHs. The increase in adsorption was particularly high for the more hydrophilic PAHs as a result of the low affinity of these PAHs for the unamended soil (Fig. 4). It is noticeable that the increase in adsorption depended on the amount of organo/LDH added. However, the differences found in the PAH adsorption after increasing the amount of nanocomposite added to the soil, from 4% to 10%, was not so important. This could be due to the high affinity of the nanocomposite for the PAHs and the high amount of amendment used. Consequently, the percentage of amendment is a parameter that must be optimized from the point of view of the adsorption efficiency.

In order to compare the effectiveness of HT-DDS in adsorbing the PAHs in the presence of soil, the experimentally measured adsorption constants, $K_{d\text{-meas}}$, for PAHs on the amended soil were compared with the expected values, $K_{d\text{-}calc}$ (Table 4). The expected values were calculated assuming linear and independent adsorption behavior of both systems, soil and HT-DDS, using the following equation:

$$K_{d\text{-}calc} = \theta_{soil}\, K_{d\text{-}soil} + \theta_{HT\text{-}DDS}\, K_{d\text{-}HTDDS} \qquad (2)$$

where $K_{d\text{-}soil}$ and $K_{d\text{-}HTDDS}$ are the distribution coefficients for PAHs adsorption on soil and HT-DDS, respectively, and θ_{soil} and $\theta_{HT\text{-}DDS}$ are the respective mass fractions of soil and HT-DDS in the mixture [39-41].

The results show that the adsorption of PAHs by the soil increased after its amendment with HT-DDS, being the values of the experimental adsorption coefficients for the mixtures close to those expected (Table 4). Unlike previous findings with organoclays for adsorbing polar non-ionic pesticides [39], the presence of soil components resulted in little competition for

adsorption sites and the nanocomposite maintained the performance in adsorbing PAHs. It should be noted that acenaphthene did not meet the prerequisite of linearity (N_f= 1) required to use Eq. 2 (Table 3), whereas for fluoranthene and pyrene the calculation of K_d values was not possible because of the complete adsorption of both PAHs by the nanocomposite.

In order to compare the effectiveness of the organic C of soil and HTDDS in adsorbing the PAHs, the K_d values at Ci = 50 µg L^{-1} were normalized to the organic C content of the different samples. As shown in Table 3, C-normalized K_d constants, $K_{d\text{-}oc}$, for HTDDS became at least ten times higher than that of the soil (Table 4). This result indicates enhanced interaction of PAHs with HTDDS compared to the soil, with regard to their organic C contents, and higher efficiency of HT-DDS as an adsorbent of PAHs.

3.4. Effect of HTDDS addition on PAHs desorption from a previously contaminated soil

Figure 6 shows the amount of PAH desorbed from the polluted soil, either unamended or amended with HT-DDS at two different rates (4% and 10% w/w). The amount of PAH desorbed from the amended soil was referenced to the amount of PAH desorbed from the unamended soil. The addition of HT-DDS to the soil improved the immobilization of the PAHs, with a decrease in the amount of PAH desorbed from the soil ranging from 70 to 95% under the experimental conditions tested. For unamended soil, the concentrations of desorbed PAHs ranged between ca. 800 µg L^{-1} (acenaphthene) and 60 µg L^{-1} (anthracene). For HTDDS-amended soil, the concentrations of desorbed PAHs were in all cases less than 50 µg L^{-1}. They ranged between 48 µg L^{-1} (acenaphthene) and ca. 7 µg L^{-1} (pyrene) for soil amended with HTDDS at 4%, and between ca. 40 µg L^{-1} (acenaphthene) and 3 µg L^{-1} (pyrene) for soil amended with HTDDS at 10%.

The increase in PAHs retention depended on the amount of HT-DDS added, although increasing the amendment rate from 4% to 10% resulted in little improvement in PAH immobilization. Therefore, the amendment rate is a parameter that should be optimized, since further addition of HT-DDS does not necessarily involve a significant improvement in the soil capability to immobilize the PAHs.

The results show that the addition of HT-DDS, used as an adsorbent material, could be a strategy for immobilizing hydrophobic organic compounds such as PAHs. Organo/LDH materials could be used as amendments or barriers emplaced in soils polluted with non-ionic organic compounds to reduce their mobility and, therefore, to prevent the pollution of environmental compartments adjacent to that zone, even enabling the natural degradation of these compounds in situ.

4. Conclusions

Our results show that the successfully synthesized organo/LDH (HT-DDS) presents higher affinity for the adsorption of hydrophobic compounds such as the six PAHs selected (acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene) compared with inorganic hydrotalcite ($HTCO_3$) and its calcined product (HT500), with a great irreversibility of the adsorption process. These results are consistent with the hypothesis that the transformation of the nature of the hydrotalcite surface from hydrophilic to hydrophobic increases its affinity for very hydrophobic organic compounds. On the other hand, our experiments testing the HTDDS nanocomposite as an immobilizer or barrier for PAHs in soil show that the amount of PAH adsorbed in HTDDS-amended soil depends on the amount of HTDDS applied, as well as on the nature of the PAH. The adsorption of PAHs in HTDDS-amended soil increases as expected according to an independent adsorption behavior of both systems: soil-water and HTDDS-water. Significant correlations were found between logarithmic values of K_{ow} and K_d, suggesting nonspecific interactions in the adsorption mechanism of the PAHs. By normalizing adsorption coefficient K_d to the organic C content, HTDDS revealed more efficient properties as an adsorbent compared to the soil. Therefore, the nanocomposite HTDDS can also be used as an amendment or barrier of contaminated soils as a strategy to enhance the soil retention capacity of PAHs and to decrease their mobility.

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Legends to the figures

Fig. 1. PXRD patterns for the samples A) $HTCO_3$, B) HT-DDS and C) HT500. (* diffraction peaks due to the Al sample holder).

Fig. 2. FT-IR spectra of A) $HTCO_3$, B) DDS and C) HT-DDS.

Fig. 3. PAHs adsorption (solid symbol) – desorption (open symbol) isotherms on HT-DDS.

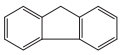
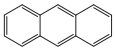
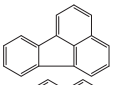
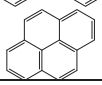
Fig. 4. PAH adsorption by unamended and HT-DDS-amended soil (4% or 10%) at an initial PAH concentration of 50 μg L^{-1}.

Fig. 5. Relationship between log K_{ow} and Log K_d in unamended soil at an initial concentration of 50 μg L^{-1} of each PAH.

Fig. 6. Percentage of PAH desorbed from the organo/LDH-amended soil (4 or 10% w/w), referenced to the amount desorbed from unamended soil.

Table 1

Molecular structure and physicochemical properties of the PAHs.

Molecule	Molecular structure	MW (g mol^{-1})	Water solubility [a] (mg L^{-1})	log K_{ow}
Acenaphthene		154.2	3.93	3.92 [b]
Fluorene		166.2	1.98	4.18 [b]
Phenanthrene		178.0	1.29	4.57 [b, c]
Anthracene		178.0	0.07	4.54 [b]
Fluoranthene		202.0	0.26	5.22 [b]
Pyrene		202.0	0.14	5.18 [c]

[a] Solubility in water (25ºC), [20].

[b] From reference [21]

[c] From reference [22].

Table 2

Chemical composition of adsorbents and proposed formulae.

Sample	Weight (%)				Atomic ratio			Proposed Formulae
	Mg	Al	C	S	S/Al	C/Al	Mg/Al	
$HTCO_3$	23.8	8.8	2.3	-	-	1.30	3.04	$Mg_{3.0}Al(OH)_8\ (CO_3)_{0.5} \cdot 2.8\ H_2O$
HT-DDS	10.8	4.0	29.6	6.1	1.28	16.70	3.00	$[Mg_{3.0}Al(OH)_8\ (DDS)_{1.00} \cdot 2.6\ H_2O]\ (NaDDS)_{0.28}$

Table 3

Freundlich model parameters for PAH adsorption on HT-DDS, hysteresis coefficient (H) and organic C-normalized K_d values ($K_{d\text{-}oc}$; L g^{-1}).

Adsorbent	Molecule	K_f	N_f	R^2	H	$K_{d\text{-}oc}$ [b]
HT-DDS	Acenaphthene	3.96 (2.05 - 7.66) [a]	0.76 ± 0.12	0.98	0.13	40
	Fluorene	18.20 (14.64- 22.70)	0.99 ± 0.04	0.99	0.10	62
	Phenanthrene	-	-	-	-	194
	Anthracene	70.41 (55.41 - 89.46)	0.99 ± 0.03	0.99	0.01	239
	Fluoranthene	-	-	-	-	-
	Pyrene	-	-	-	-	-

[a] Standard error.

[b] $K_{d\text{-}oc}$ at C_i = 50 µg L^{-1}.

Table 4

Measured and calculated distribution coefficients K_d (L g^{-1}) for PAHs adsorption on unamended and organo/LDH-amended soil, and the organic C-normalized K_d values ($K_{d\text{-}oc}$; L g^{-1}).

PAH	Treatment	$K_{d\text{-}meas}$	$K_{d\text{-}calc}$	$K_{d\text{-}oc}$
Acenaphthene	Unamended	< 0.1		2.9
	HT-DDS 4%	0.8 ± 0.3	0.5	
	HT-DDS 10%	1.0 ± 0.0	1.2	
Fluorene	Unamended	< 0.1		3.8
	HT-DDS 4%	1.0 ± 0.4	0.8	
	HT-DDS 10%	1.7 ± 0.2	1.9	
Phenanthrene	Unamended	< 0.1		7.6
	HT-DDS 4%	2.7 ± 0.6	2.3	
	HT-DDS 10%	5.3 ± 0.6	5.7	
Anthracene	Unamended	< 0.1		10.5
	HT-DDS 4%	3.2 ± 0.7	2.9	
	HT-DDS 10%	6.1 ± 0.1	7.1	
Fluoranthene	Unamended	0.13 ± 0.05		24.4
	HT-DDS 4%	-	-	-
	HT-DDS 10%	-	-	-
Pyrene	Unamended	0.15 ± 0.05		29.4
	HT-DDS 4%	-	-	-
	HT-DDS 10%	-	-	-

Figure 1

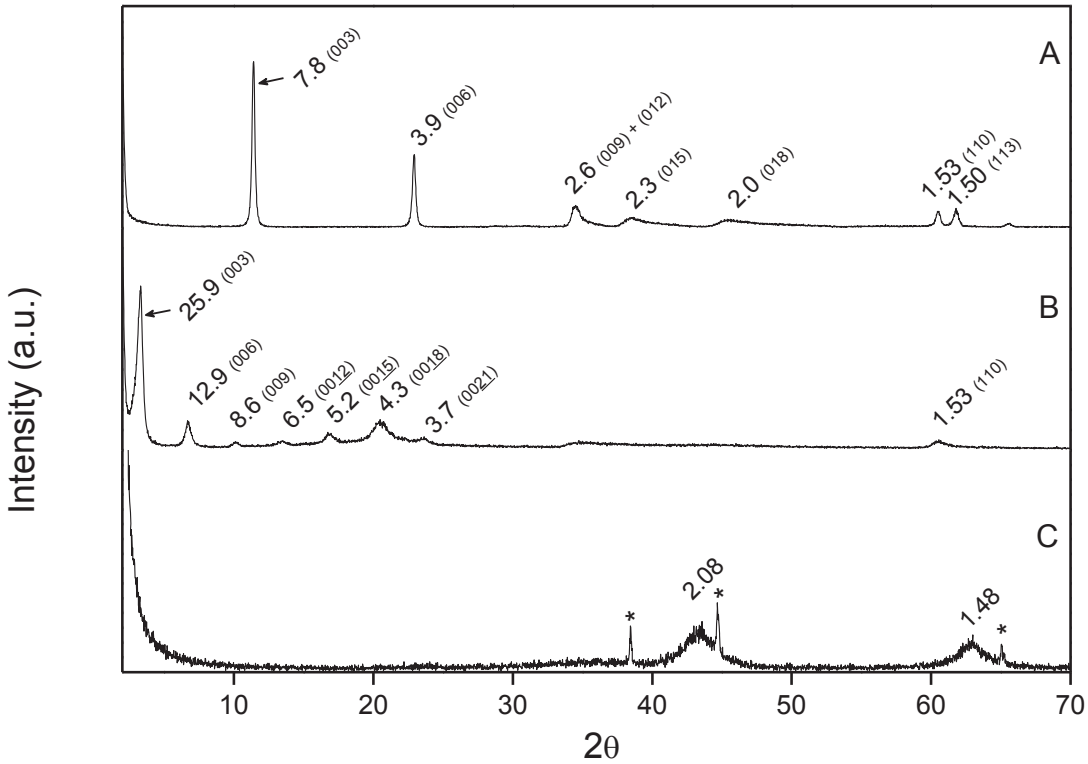


Figure 1. PXRD patterns for the samples A) $HTCO_3$, B) HT-DDS and C) HT500. (* diffraction peaks due to the Al sample holder)

Figure 2

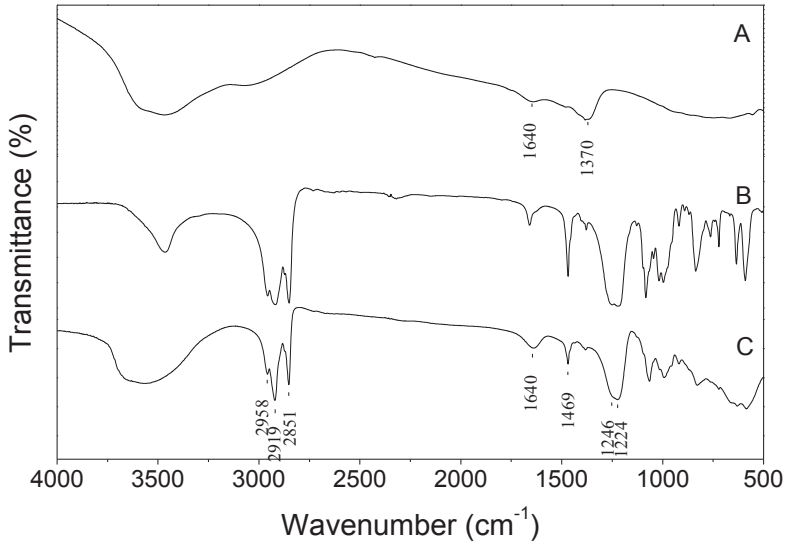


Figure 2. FT-IR spectra of A) $HTCO_3$, B) DDS and C) HT-DDS.

Figure 3

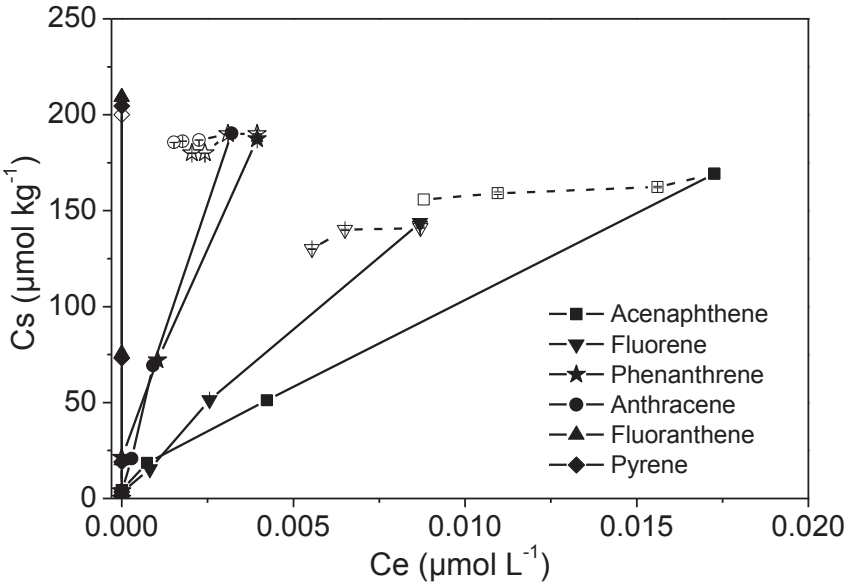


Figure 3. PAHs adsorption (solid symbol) – desorption (open symbol) isotherms on HT-DDS.

Figure 4

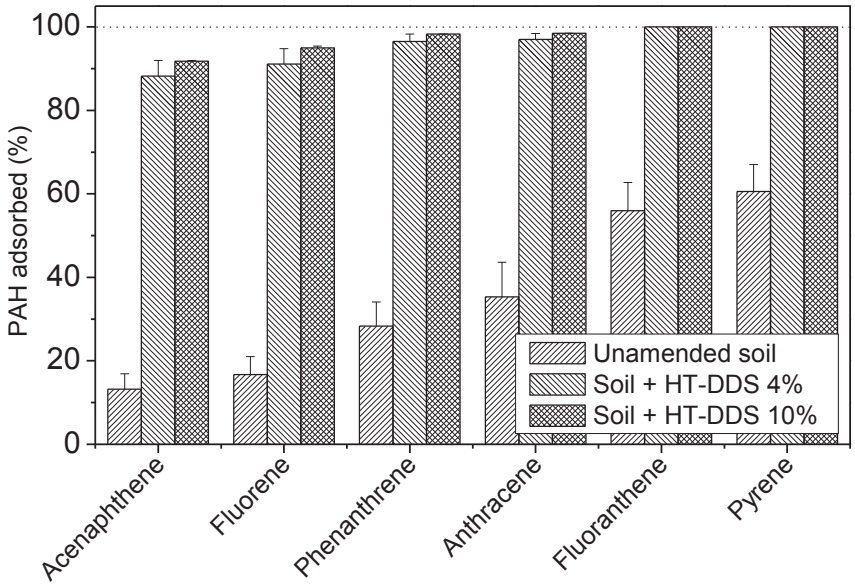


Figure 4. PAH adsorption by unamended and HT-DDS-amended soil (4% or 10%) at an initial PAH concentration of 50 μg L^{-1}.

Figure 5

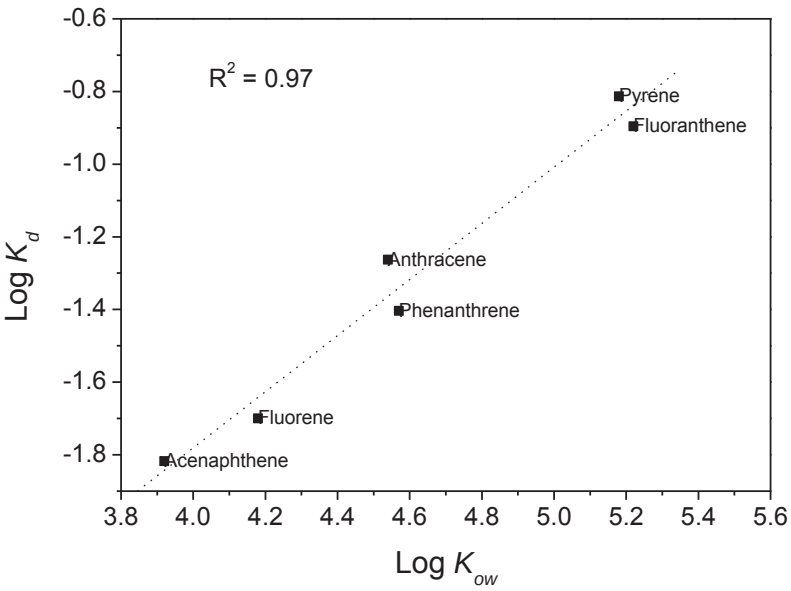
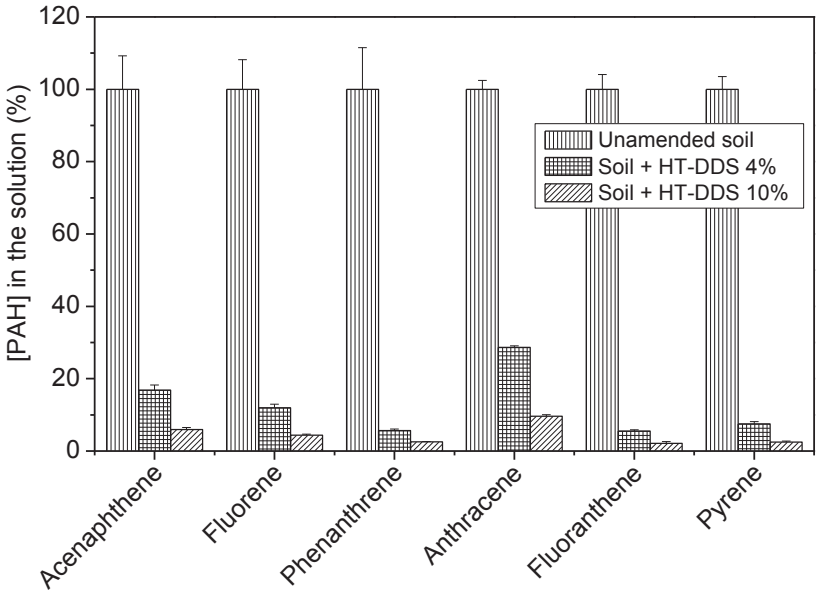


Figure 5. Relationship between log K_{ow} and Log K_d in unamended soil at an initial concentration of 50 μg L^{-1} of each PAH.

Figure 6



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