# Adsorption of phenanthrene by stevensite and sepiolite

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ABSTRACT: Polycyclic aromatic hydrocarbons are increasingly widespread pollutants introduced into the environment *via* oil spillage and incomplete anthropogenic combustion of fossil fuels. In this work, the capacity of stevensite and sepiolite to adsorb phenanthrene (PHE) has been evaluated experimentally by batch testing. Both clay minerals are distributed widely in the Madrid Basin, are of low cost and can be applied with minimal environmental impact. In the context of few previous studies, adsorption isotherms have been developed to understand the adsorption mechanisms and were fitted to the Freundlich and linear models with virtually the same results. Although stevensite showed greater adsorption capacity than sepiolite, the isotherms were constructed for equilibrium concentrations up to 0.8–1.0 mg/L due to the low solubility of PHE in water. When compared to other adsorbents the ability of stevensite to retain PAHs should be examined further in order to add and complement novel functions in reactive barriers.

KEYWORDS: organic pollutants, phenanthrene, sepiolite, stevensite, adsorption isotherms.

The presence in the environment of organic pollutants is a concern. Due to their potential carcinogenic and recalcitrant effects, both the US Environmental Protection Agency (EPA, 1980) and European Community Water Framework Directive (EU, 2000) have included polycyclic aromatic hydrocarbons (PAHs) in the list of priority pollutants. The PAHs are generated during incomplete combustion of fossil fuels and find their way into the soil and water *via* atmospheric fallout, urban run-off, municipal effluents, industrial effluents and oil spillage (Changchaivong & Khaodhiar, 2009). Phenanthrene (PHE), containing three fused benzene rings, is one of the most widespread PAHs and is often used as a model compound to study the fate of PAHs in contaminated soils (Jia *et al.,* 2012). The dispersion and migration of PAHs through water and sediments depends on their interactions with the soil components. Adsorption to the surfaces of soil components is governed by the structural properties of soil particles, *e.g.* the presence of interlayers in clay minerals, large specific surface area (SSA), surface conformation, density location of electric charge and type of exchangeable cations (Zhang *et al.,* 2011). Clays and clay minerals are considered some of the most reactive components of soil (Huang *et al.,* 2012). These are nanostructured materials or nanoparticles (NPs) capable of retaining organic compounds from aqueous phases and sediments (Brigatti *et al.,* 2006). Application of clay minerals for non-polar ionic compounds (NOPCs) control involves cation saturation with organic or inorganic modification. Clay minerals are naturally hydrophilic, *e.g.* smectite surfaces are modified with suitable organic molecules (Lee & Tiwari, 2012). Exchange reactions with large organic cations enhance the surface hydrophobicity of clay materials, thereby

enhancing sorption capacity towards PAHs mainly by van der Walls forces and hydrogen bonding (Lee *et al.*, 1990; Lagaly *et al.*, 2006). In addition, cation-modified clay minerals may adsorb larger amounts of NOPCs such as PHE (Jia *et al.,* 2015). These modified clay materials have shown great potential as sorbents of PAHs. Nevertheless, in terms of retention of NPOCs, few studies have focused on natural sepiolite (Cobas *et al.,* 2014) and to the authors' knowledge, no previous such studies on stevensite exist, even though this mineral was studied previously for trapping of ionic organic compounds and metals (Benhammou *et al.*, 2005a, 2005b; Khalid *et al.*, 2011). Stevensite and sepiolite are Mg-rich clay minerals with small cation exchange capacities (CEC) and potential surface area for non-ionic interactions (Lee *et al.*, 2004; Liu *et al.*, 2009). Stevensite and sepiolite are also attractive materials because they are widespread, generally easily mined and relatively inexpensive. Their large specific surface area (SSA) and volume of small pores enable them to adsorb significant amounts of PAHs, properties which make attractive for environmental protection purposes (Churchman *et al.*, 2006).

At present, there is debate about the mechanism governing the interaction between clay minerals and PAHs (McBride, 1994) and therefore, about the best model to use to describe this interaction. Useful tools for understanding adsorbate-adsorbent interaction are adsorption isotherms. Hence, batch assays were run in order to determine the appropriate isotherm. Previous studies reported that the Freundlich model provided the strongest correlation between sepiolite and PHE interaction (Cobas *et al.*, 2014). Regarding smectites, several works have reported a best fit for the Freundlich model, involving physical attraction (Huang *et al.,* 1996; Zhang *et al.,* 2011). On the other hand, Changchaivong & Khaodhiar (2009) found that the main adsorption mechanism is partitioning which is explained by a linear model. Permeable reactive barriers represent a well established technology studied mostly for removal of inorganic compounds such as metals ions or nitrates. However, the interaction with NPOCs is in the early stages of development and few laboratory or field examples are available for this type of pollutant remediation. The aims of the present study were to: (1) quantify the PHE adsorption capacity of stevensite and sepiolite; and (2) to approach the main adsorption mechanisms and investigate how the structural differences influence the behaviour of the selected materials within the context of clay minerals and other adsorptive materials.

The results of the present work suggest stevensite as material with potential for use in permeable reactive barriers due to its versatile capacity to retain polar and non-polar polluting compounds. In addition, these materials are of low cost and have minimal environmental impact (Suárez & García-Romero, 2012) compared to materials currently used, *e.g.* active carbon or artificially processed, cation-modified clay minerals.

## MATERIALS AND METHODS

### Phenanthrene

Phenanthrene, with a purity of 98%, was obtained from Aldrich Chemical Company. A primary methanol stock solution was prepared by dissolving an appropriate amount of solute in methanol and storing it in the dark at 4°C. The use of methanol shortens the preparation time for PHE solutions and increases their stability for extended periods (Hundal *et al.*, 2001), while, simultaneously, the final low methanol concentration achieved in batch assays (<1%) does not modify the PHE sorption properties of the sorbents (Weber & Huang, 1996; Changchaivong & Khaodhiar, 2009).

### Clay minerals

Stevensite and sepiolite materials were supplied by Tolsa SA (Spain) under the commercial names of MINCLEAR N100® (stevensite) and PANSIL® (sepiolite). Both clay minerals are quarried from the deposits of the Madrid Basin. MINCLEAR N100® contains at least 90 wt.% stevensite while PANSIL® has a minimum of 90 wt.% sepiolite.

The clay minerals were characterized by X-ray diffraction (XRD) and by transmission electron microscopy (TEM) (Fig. 1a,b). The XRD patterns were recorded using a θ/2θ X-PERT Panalytical® instrument with an X-CELERATOR detector and Cu-*K*α monochromatic radiation. The TEM images were obtained using a JEOL 200FX microscope. Millimetre chip samples were indurated with LR-White Resin, then mounted and prepared as thin sections and transferred to a TEM copper ring sample support (following Warr & Nieto, 1998). The samples were thinned using ion-beam equipment prior to examination.

The MINCLEAR N100® contains illite impurities, dolomite, feldspar and quartz. Nevertheless, according to the MINCLEAR N100® specifications, the stevensite content is large because *hk*0 asymmetric reflections dominate the pattern profile. Basal spacing Bragg reflections (00*l*) are very broad and are poorly developed.

The analyses confirmed the dominance of nanometre-sized particles. In sepiolite samples a typical
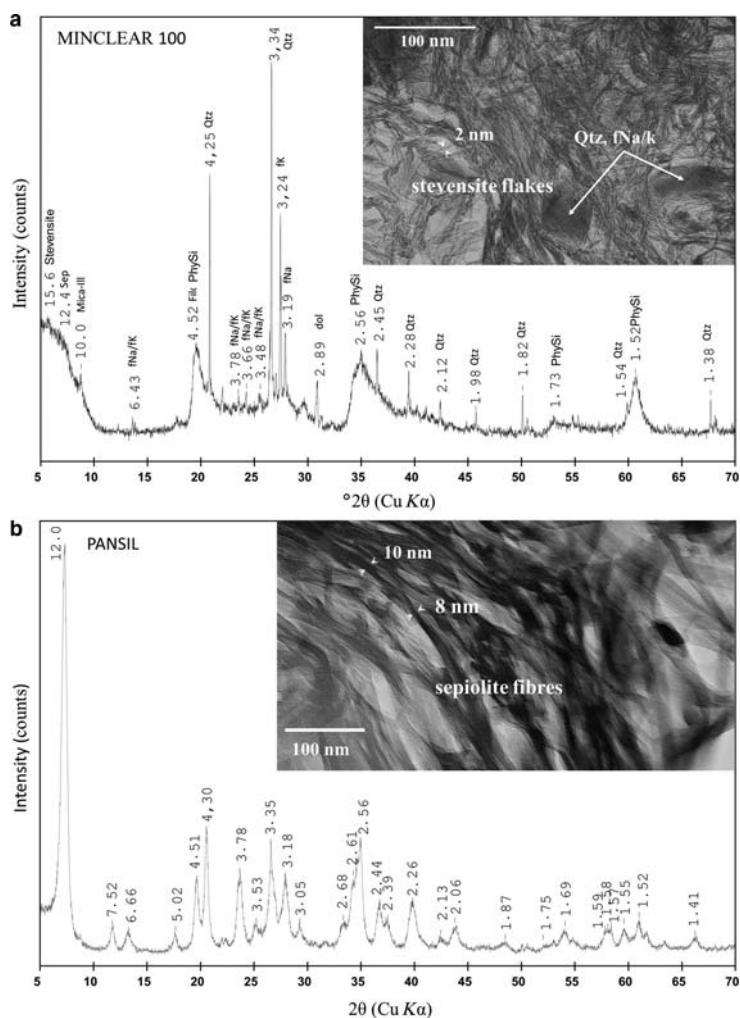
FIG. 1. XRD patterns and TEM images of the clay minerals: (a) stevensite; (b) sepiolite. Sep: sepiolite, Ill: illite; fNa/fK: sodium and potassium feldspars; PhySi: Phyllosilicates; dol: dolomite; Qtz: quartz.

fibrous morphology was observed (8–10 nm width and 1–10 μm maximum length, Fig. 1b). The fibres are grouped into parallel bundles, yielding an open porosity. Stevensite occurs as aggregates with a laminar structure and with flakes <2 nm thick (two structural sheets; Fig. 1a). Characterization of the material was complemented by SSA measurements *via* $N_2$ adsorption using the BET method (Brunauer *et al.*, 1938, in Webb & Orr, 1997) using a Gemini V porosimeter (Micromeritics®). The samples have large external SSA ($221 \pm 2$ m$^2$/g for MINCLEAR N100® samples and $293 \pm 4$ m$^2$/g for PANSIL samples). These SSA values are consistent with those of

Cuevas *et al.* (1993) for stevensite (250–280 m$^2$/g) and of Suárez & Romero (2012) for sepiolite (308 m$^2$/g), on materials obtained from the same quarries.

The sorption capacity of clay minerals was tested in batch experiments. Sorption-rate and equilibrium experiments were conducted at $25 \pm 3$°C, in Erlenmeyer flasks (trademark SIMAX®), at a clay/water ratio of 1:125 (w:w). Initially, 0.3 g of clay minerals was suspended in 0.1 M NaNO$_3$ of background electrolyte solution for ionic strength control. Subsequently, the pH conditions were adjusted at $6.0 \pm 1.0$. Finally, the required amount of stock solution was added to prepare 0.3 mg/L to 3.6 mg/l (supersaturated) PHE solutions.

In order to avoid PHE loss, the flask reactors were sealed with aluminium foil. In addition, blanks test without clay minerals were also prepared to account for loss of PHE by means other than sorption by the clays. The samples were equilibrated on a reciprocating shaker (P. Selecta® Fuse) for 2 h at 120 rpm in order to ensure homogenous mixing. After equilibration, the samples and controls were centrifuged for 10 min at 4500 rpm and the PHE concentrations in the supernatants were analysed by UV-spectrophotometry using a Milton Roy Spectronic® instrument at 254 nm (Manoli & Samara 1999; Jia *et al.*, 2012). The clay minerals deposited on the flask reactors during centrifugation were recovered, dried and stored for further studies.

*Data analysis*

The amount of PHE adsorbed onto the adsorbent was calculated using the following equation:

$$q_e = C\frac{C_{o-}C_e}{m}V \qquad (1)$$

where $q_e$ is the amount (mg) of PHE adsorbed per g of clay mineral (solid phase concentration). $C_o$ and $C_e$ are the initial and final equilibrium concentrations, respectively (mg/L), $V$ is the volume of the solution (L), and $m$ is the mass of clay mineral used (g).

The data for the sorption of PHE by clay minerals were fitted to two sorption isotherm models: (i) the linear model:

$$q_e = K_D C_e V \qquad (2)$$

and (ii) the Freundlich model:

$$q_e = K_F C_e^n \qquad (3)$$

where $C_e$ is the equilibrium solution concentration (mg/L) of PHE. $K_D$ (equation 2) is the linear distribution coefficient and $K_F$ is the Freundlich coefficient. Both parameters provide the amount of PHE adsorbed per unit mass of sorbent [(mg/g)/(mg/mL)$^n$] (sorption capacity). The Freundlich exponent, n, is an empirical constant representing site-energy heterogeneity. The Freundlich model (equation 3) reflects heterogeneous sorption sites with a distribution of sorption energies.

To compare several types of sorbent materials, a modified Freundlich model was used due to the limitations of the Freundlich equation (Bowman & Sans, 1985). The Freundlich coefficient, $K_F$, is of limited use because of its inconsistent units. The dimensions of $K_F$ can be rendered independent of n by modifying the Freundlich model and using the concept of reduced concentration. Carmo *et al.* (2000) discussed in detail the derivation of the Freundlich model. Briefly, $C_e$ is substituted for $C_r$ (reduced concentration) in equation 3:

$$q_e = K_F' C_r^n \qquad (4)$$

where $C_r$ (dimensionless) is the ratio of $C_e$ to the supercooled liquid-state solubility of PHE (5.902 μg/mL at 25°C). $K_F'$ is the modified Freundlich coefficient and provides an index of sorption capacity. The values of $K_F'$ can be used to compare directly the sorption characteristics of heterogeneous sorbents using equivalent Freundlich coefficients.

The sorbents used for comparison were K-hectorite (Hundal *et al.,* 2001), purchased from the Source Clays Repository of The Clay Minerals Society (Chantilly, Virginia, USA) and Ca-smectite, (Zhang *et al.,* 2011), obtained from Beijing Ruizhx Tech Co., Ltd, China. These smectites were fractionated by sedimentation to collect the <2 μm fractions, which were saturated with $K^+$ and $Ca^{2+}$, respectively, using chloride salts. After saturation, excess salts were removed by washing and the clays were freeze dried. Non-porous alumina ($α$-$Al_2O_3$) and silica gel were also used for comparison (Huang *et al.,* 1996). $α$-$Al_2O_3$ with a particle diameter of ~1 μm was provided by Alfa Inc and silica gel in porous beads of 63–300 μm diameter was provided by Davisil, Aldrich. All adsorption experimental data were fitted to mathematical adsorption models using *ORIGIN PRO® 8* software.

## RESULTS

*Stevensite and sepiolite adsorption isotherms*

The equilibrium adsorption isotherms were evaluated by plotting the solid-phase concentration ($q_e$) against the liquid-phase concentration ($C_e$). The Freundlich and the linear model showed virtually the same fit for PHE adsorption on clay minerals (Table 1). Both clays exhibited affinity for PHE, with stevensite showing greater sorption rates; the Freundlich parameters $K_F$ and n are greater in stevensite than in sepiolite, as is the $K_D$ value of the linear model. The PHE uptake increased concomitantly with PHE equilibrium concentration (Fig. 2a,b). For aqueous equilibrium concentration of PHE >~1 mg/L (Fig. 2a) it was not possible to attribute adsorption of PHE to precipitation or volatilization (de Maagd *et al.*, 1998; Sawamura, 2000).

TABLE 1. Parameters of the Freundlich and linear models for sepiolite and stevensite obtained after adjustment.

|  |  | Sepiolite | Stevensite |
|---|---|---|---|
| Freundlich model | $K_F$ | $0.59 \pm 0.04$ | $1.87 \pm 0.04$ |
| $q_e = k_F\, C_e{}^n$ | $n$ | $0.79 \pm 0.06$ | $0.99 \pm 0.03$ |
|  | $R^2$ | 0.92 | 0.95 |
|  | RMSE | 0.04 | 0.11 |
| Linear model | $K_D$ | $0.56 \pm 0.03$ | $1.86 \pm 0.05$ |
| $q_e = k_D\, C_e$ | $R^2$ | 0.89 | 0.95 |
|  | RMSE | 0.04 | 0.10 |

$K_F$: Freundlich coefficient. n: Freundlich exponent. $R^2$: Coefficient of determination. RMSE: root mean square error. $K_D$: Partition coefficient.

## Comparison with heterogeneous sorbent materials

Based on the isotherms obtained from the different materials examined in this study, the smectite minerals showed the greatest PHE sorption capacity (Fig. 3). The best $K'_F$ parameters were obtained using Ca-smectite, from Beijing, followed by stevensite from the Madrid Basin and K-hectorite from Wyoming (Table 2). In contrast, the lowest sorption capacity rates were provided by natural sepiolite, silica gel and alumina ($\alpha$-Al$_2$O$_3$).

# DISCUSSION

## Main adsorption mechanism

The experimental results for stevensite and sepiolite, showed good fits to the Freundlich and linear models as compared to the Langmuir model (data not shown). The Freundlich model assumes that sorption occurs on heterogeneous surfaces or surfaces supporting sites with varying sorption affinities for adsorbate molecules. The Freundlich model is based on a physical adsorption mechanism, without molecule-sorbent association after interaction (Cobas *et al.*, 2014), while the linear model describes constant partitioning between the solid and aqueous phase (Rutherford *et al.*, 1992). The linear model (also named C-curve) is characterized by an initial slope that remains independent of adsorptive concentration until the maximum possible adsorption is achieved. This kind of isotherm can be produced by a proportional increase in the amount of the adsorbing surface as the surface excess increases (Sposito, 2008). The adjustment of isotherm results suggests an acceptable good fit for both models, but the limited aqueous solubility of PHE did not allow us to follow the isotherm bending upwards to greater concentrations and thus to decide which model predominates.

The choice of the two mechanisms explains best the behaviour of highly hydrophobic compounds such as PHE on clay minerals. Molecular modelling has shown that the degree of adsorption of PHE on montmorillonite is not significant in the presence of water (Meleshyn & Tunega, 2011). In addition, linear adsorption isotherms indicated partition as the main adsorption mechanism (Changchaivong & Khaodhiar, 2009). In this respect, the repulsion strength between water molecules and PHE would cause molecular displacement towards the hydrophobic sites, thereby increasing entropy and favouring a more stable energy state (Piatt *et al.*, 1996). Other studies have shown, however, that the Freundlich model described better the PHE adsorption on clays (Huang *et al.*, 1996, Zhang *et al.*, 2011). The ability of water to accommodate the hydrophobic compounds is very dependent on molecular size (McBride, 1994; de Maagd *et al.*, 1998; Churchman *et al.*, 2006; Lee & Tiwari, 2012; Lagaly *et al.*, 2013). The present work showed a good fit for both models (Table 1), suggesting that both models may interpret the results.

The PHE was adsorbed preferentially to stevensite rather than sepiolite as the Freundlich and linear model parameters $K_F$, n and $K_D$ are significantly greater for stevensite (Table 1; Fig. 2a,b). The reason for the different behaviours of stevensite and sepiolite might be due to their structural and textural differences. The interlayer thickness of smectites may range from 0.2–0.4 nm in the dry state, to several nm in wet conditions, separating coherently stacked layers (quasicrystals, Hundal *et al.*, 2001; Fig. 4a), thus providing good accessibility to planar PHE molecules in the interlayer micropore surfaces. In contrast, sepiolite has fibrous morphology due to the periodic inversion of Si tetrahedra, forming channels. The dimensions of the channels are ~0.4 nm × 1.08 nm (Fig. 4b) (Helmy & de Bussetti, 2008; Suárez & Romero, 2012; Tang *et al.*, 2012) whereas the size of the PHE molecule is 1 nm in aqueous solution (Huang *et al.*, 1996). Thus, accommodation of the PHE molecule in the sepiolite channels might be hampered because of size. Although the organic compounds could be replaced readily by water molecules, van der Walls forces (π-π interactions with the siloxane surface, significant in large NPOC molecules of low solubility; Lagaly *et al.*, 2013), may result in hydrophobic bonding. Another critical
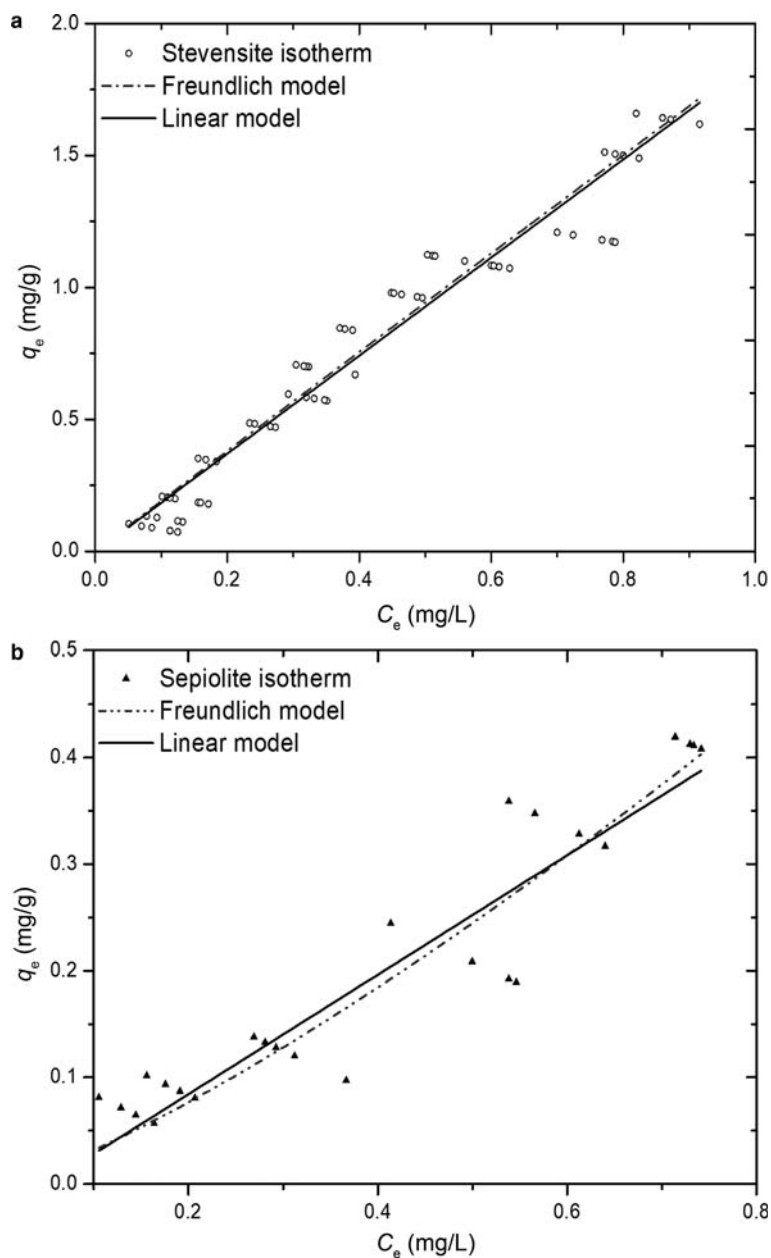
FIG. 2. Adsorption isotherms of: (a) stevensite, and (b) sepiolite. The solid lines represent the fit of the sorption data to the linear model (equation 2) while the dashed-dotted line represents the fit to the Freundlich model (equation 3) using the analysis module of *OriginPro®* 8 software.

parameter is the SSA. In the case of sepiolite, SSA is external, but in expandable colloids such as stevensite, the BET method underestimates the total particle surface. Indeed, the $N_2$ gas used in BET measurements penetrates to a small proportion of the interlayer space, which is precisely where 80% of the total surface area is located (Bohn *et al.*, 1993). Hence, because the materials tested have comparable external SSA,
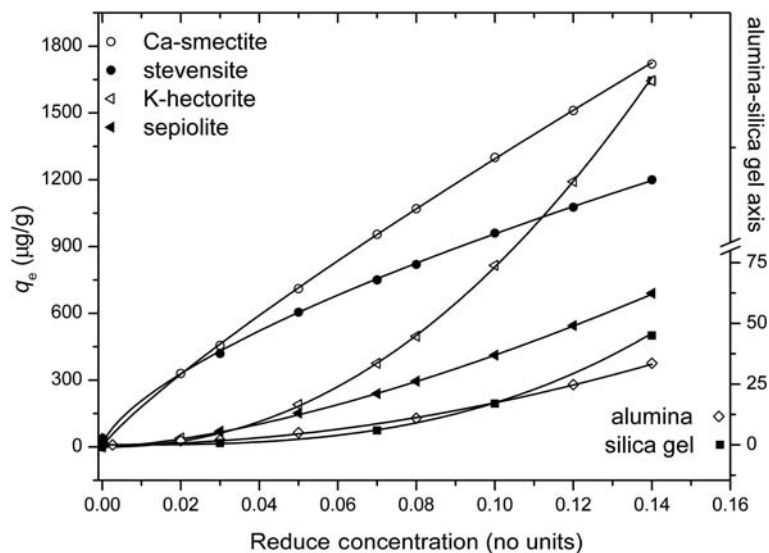
FIG. 3. Adsorption isotherms of PHE for the various materials. Lines show the fit to the modified Freundlich model (equation 4) for the sorption data using the non-linear regression curve module from the *OriginPro®* 8 software. The left vertical axis refers to the Ca-smectite, stevenstite, K-hectorite and sepiolite whereas the vertical axis to the right refers to α-Al$_2$O$_3$ and silica gel.

stevensite would have larger planar surface sites available for adsorption than sepiolite.

### Comparison with heterogeneously sorbing materials – modification of the Freundlich equation

The results obtained using the modified Freundlich equation are in agreement with previous work. The affinity of K-saturated smectites for some NOPCs may be similar and even exceed the affinity of soil organic matter (Yuan *et al.,* 2013). Similarly, the uptake of NOPCs by swelling clay minerals such as smectites is enhanced when the saturating cations are weakly

TABLE 2. Modified Freundlich coefficient ($K_F'$) obtained from selected materials.

| Adsorbent materials | $K_F'$ (µg/g) |
|---|---|
| α-Al$_2$O$_3$ | $24.40 \pm 0.01$ |
| Silica gel | $543 \pm 49$ |
| Stevensite | $26878 \pm 1796$ |
| Ca-smectite | $2044.01 \pm 0.08$ |
| K-hectorite | $9282 \pm 680$ |
| Sepiolite | $108.45 \pm 0.12$ |

hydrated and provide larger areas for adsorption. The comparison based on the modified Freundlich equation suggests that stevensite might have sorption capacities similar to those of Ca-smectite and K-hectorite. In any case, the greatest adsorption capacity of the smectites (Table 2; Fig. 3) might be due to the presence of hydrophobic sites with strong affinity for non-polar compounds attributed to the presence of laminar siloxane groups in the basal planes (Cruz-Guzmán, 2007). The hydrophobicity of the smectite surface is influenced mainly by the type of layer and location of the charge, tetrahedral or octahedral (Laird, 1999). Moreover, in aqueous solutions, clay platelets form a fine network of quasicrystals with a large number of micropores to retain PHE. The PHE adsorption capacity increases in the cation-modified minerals when the zeta potential of these minerals approaches zero (Zhang *et al.*, 2011). Likewise the adsorption increases as the layer charge of the clay mineral decreases (Sheng *et al.*, 2002). The association of NOPCs and clay minerals may also be enhanced by van der Walls interactions between the compounds and the basal siloxane surface of clay minerals. Similarly, Qu *et al.* (2011) suggested that the adsorption to montmorillonite is affected by *n*–π electron donor–acceptor interactions between the compound and the siloxane oxygens (*n*-donors) of the clay mineral.
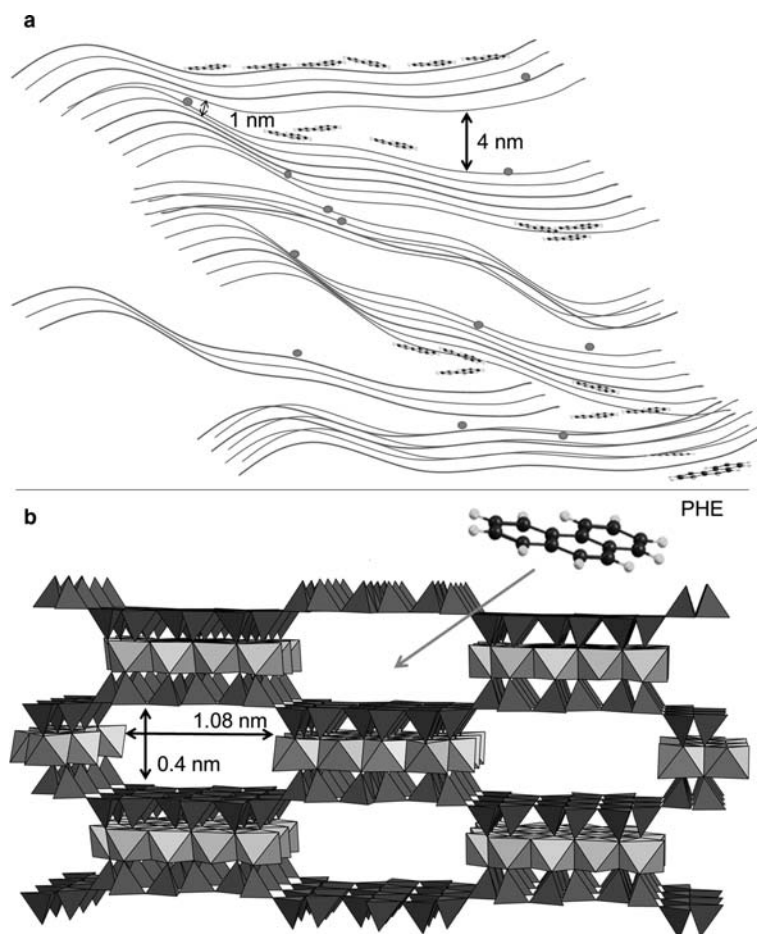
F𝗂𝗀. 4. Structural and textural constraints considered in the adsorption of PHE. (a) Accommodation of PHE between planar surfaces of the quasicrystals formed by the smectite stacked layers. Black circles are exchangeable cation positions dispersed due to the small CEC value (after Hundal *et al.*, 2001). (b) Structure of sepiolite and channel dimensions.

However, in the present study, although stevensite was not modified with any cation so as to enhance its potential interactions with hydrophobic compounds, it showed a large adsorption capacity also. The stevensite is attractive in comparison with modified clay minerals because it is widespread, easily mined, and relatively inexpensive. In addition, stevensite is a naturally occurring material, non-toxic, and the results of the present study suggest considerable capacity in controlling PHE. Besides, stevensite displays colloidal behaviour and swelling capacity, probably because it has very low cation exchange capacity generated by a deficiency of octahedral cations rather than isomorphic substitutions (Cuevas *et al.*, 2003; De Santiago *et al.*, 2000). Moreover, stevensite has nm-sized particles

with very small thickness and large external specific surface area, as suggested by TEM and SSA analyses.

Compared to the remaining materials, the smooth and external planar surfaces of the smectite quasicrystals favoured PHE adsorption. Indeed, the rough or cylindrical surface of silica gel or alumina seems less effective for adsorption (Huang *et al.,* 1996). Despite the fact that all of these materials have average pore diameters greater than the molecular length of PHE, these pores are much less efficient for PHE sorption.

## CONCLUSIONS

The present study has provided promising results in support of the use of stevensite (smectite group) as a

component in a reactive permeable barrier for retention of non-polar organic pollutants. The smectites modified with inorganic cations retained large amounts of PHE, a hazardous organic pollutant. Natural stevensite has certain advantages over other sorbents such as availability in significant amounts, e.g. from the Madrid Basin (Cuevas *et al.*, 2003), and its relatively small cost. The adsorption isotherms were fitted with the Freundlich model and were compared with similar adsorbents including sepiolite. Because hydrophobic interactions and accommodation in external planar surfaces of quasicrystals are probably the dominant mechanisms of PHE adsorption by stevensite, sepiolite offered fewer sites for adsorption.

The exact adsorption capacity of clay minerals should be established using complementary analytical measurements and experiments such as column assays with higher PHE concentrations, using solvents that avoid PHE loss in order to achieve complete isotherms up to higher PHE concentrations. In addition, in further experiments, the clay minerals recovered from the centrifugation stage (deposited on the flasks reactors) will be characterized and the regeneration of the sorbents will be tested.

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