



## Sorption of phenanthrene by dissolved organic matter and its complex with aluminum oxide nanoparticles

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*Size of aluminum oxides significantly affects sorption of polymerin and phenanthrene.*

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### ABSTRACT

Intent of this study was to explore the potential application of polymerin, the polymeric, dissolved organic matter fraction from olive oil wastewaters, in technologies aimed at remediating hydrophobic organic compounds (HOCs) point-source pollution. Phenanthrene binding with polymerin was investigated. Moreover, the effect of addition of micro and nanoscale aluminum oxides ( $\text{Al}_2\text{O}_3$ ) was studied, as well as sorption of polymerin on the oxides. Phenanthrene binding capacity by polymerin was notably higher than the sorption capacities for both types of  $\text{Al}_2\text{O}_3$  particles. Polymerin sorption on nanoparticles was nearly 100 times higher than microparticles. In a three-phase system, using microparticles, higher phenanthrene sorption was found by adding into water polymerin, oxides and phenanthrene simultaneously. In contrast, using nanoparticles, a considerable enhancement of phenanthrene sorption was shown by adding phenanthrene to a pre-formed and dried polymerin–oxide complex. These findings support the application of polymerin, especially associated with  $\text{Al}_2\text{O}_3$  nanoparticles, in remediation of water contaminated with HOCs. This work highlights the significant role of nanoparticles.

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### 1. Introduction

The necessity to develop new technologies aimed at mitigating the risk deriving from soil and water pollution is constantly increasing. Accidental releases, illegal operations or not-appropriate disposal of wastes from industries and farms are the main causes of point sources of soil and water pollution by several kinds of compounds, from pesticides to hydrophobic organic chemicals (HOCs). One tool for the reduction of point-source contamination is the use of biobeds. These systems can be represented by a column with layers of straws, peat moss and top soil, being able to adsorb and degrade pollutants from water, and they were introduced by Torstensson and Castillo (1997) and then improved by numerous researchers (Spliid et al., 2006; Coppola et al., 2007; Fait et al., 2007). At this aim, it is important to find new and cheap sorbents to better develop this technique. Several studies propose the use of natural organic materials or wastes as biosorbent (Rodriguez-Cruz et al., 2007; Wang et al., 2006, 2007) due to the high sorption capacity of organic matter (Kang and Xing, 2005; Gunasekara and Xing, 2003).

Olive oil mill wastewater (OMW) is a vegetable biomass waste produced in large amounts, especially in Mediterranean countries, which are the main producers of olive oil worldwide. Its disposal represents a significant problem for these countries because OMW is a potential pollutant due to its high COD and BOD values (Arienzo and Capasso, 2000), and also because it is produced in large quantity in a very short period of 1 year. However, OMW may also be regarded as a source of useful products. In this light, we recovered the mineral-organic fraction, named polymerin, showing polyelectrolyte and humic acid-like properties (Capasso et al., 2002). High binding capacity of metals and ionic and ionisable pesticides by polymerin was observed (Sannino et al., 2006, 2008; Capasso et al., 2004). Moreover, sorption of heavy metals on the polymerin complexed with ferrihydrite (Sannino et al., 2006; Capasso et al., 2004) was recently studied because of its significant capacity to adsorb ions. The obtained results showed an effective enhancement of the sorption capacity of the complex in comparison with either polymerin or ferrihydrite used individually.

Polymerin is a cheap sorbent of potential economic interest and, at the same time, its use could minimize the OMW disposal problem. Some studies considering the binding of polar compounds with polymerin were carried out, but its interaction with HOCs is unknown. For this study, we choose phenanthrene as a representative HOC. Moreover, in this work we selected different-sized

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aluminum oxides to interact with polymerin and phenanthrene in order to investigate the sorption capacity variation. This mineral possesses a positively charged surface and due to the hydration layer it is not an effective sorbent for HOCs. By coating the oxides with a negatively charged organic matter, it is possible to change their hydrophilic surface into hydrophobic, which have a great affinity for HOCs. Several studies suggest the application of aluminum oxides (Al<sub>2</sub>O<sub>3</sub>) coated with anionic surfactants in wastewater treatment techniques (Park and Jaffè, 1993; Valsaraj et al., 1998). Polymerin could represent an advantageous alternative to the use of surfactants. The use of polymerin instead of synthetic surfactants may be convenient because it derives from a cost free material and its recovery is very simple and not expensive (methanol used for precipitation can be totally recovered and recycled).

Moreover, since polymerin by itself is soluble in water, it cannot be readily used in biobeds, which need solid materials. Thus, by coating Al<sub>2</sub>O<sub>3</sub> with polymerin we may obtain a new solid sorbent for a biobed system. Therefore, the main objective of this work was to investigate the behavior of phenanthrene in water in the presence of polymerin and in a polymerin–oxide–water three-phase system. Moreover, possible application of these sorption systems as a bio-filter for remediation of pollution point sources is discussed.

## 2. Materials and methods

### 2.1. Sorbates and sorbents

An aliquot of OMW (2004) from a pressure processing system located in Monteroduni (Italy) was processed in order to obtain the complex polymeric mixture. Polymerin was characterized according to the procedure previously reported by Capasso et al. (2002). Microscale aluminum oxide was purchased from J.T. Baker Chemical Co. (New Jersey) and nanoscale aluminum oxide from Hongchen Material Sci. & Tech. Co., China. Ring-UL-14C labeled and unlabelled phenanthrene (Phen) was purchased from Sigma–Aldrich Chemical Co.

Sorbents and sorbates were used without any further treatment. Specific surface area of the particles was determined by H<sub>2</sub>O sorption at 20% relative humidity using the method by Quirk (1955). Point of zero charge (PZC) of both aluminum oxides was measured using a Zetasizer (Malvern Instruments). Microscale particle size was analyzed by static light scattering (Coulter LS230). XRD of randomly oriented samples were recorded with a Rigaku Geigerflex D/Max IIIC diffractometer using iron-filtered CoK $\alpha$  radiation generated at 40 kV and 30 mA, at a scan speed of 2°/min. The XRD intensities of the mineralogical entities were enhanced by summing eight times the signal. Chemical composition and physical properties of sorbents and sorbates are listed in Table 1.

**Table 1**  
Properties and chemical composition of sorbents and sorbate

Mineral sorbents	Al <sub>2</sub> O <sub>3</sub> microparticles	Al <sub>2</sub> O <sub>3</sub> nanoparticles
Surface area (m <sup>2</sup> g <sup>-1</sup> )	32	228
Point of zero charge, PZC	7.3	8.5
Mean particle size (μm)	110	0.06 <sup>a</sup>
Organic sorbent	Polymerin	
Chemical composition (% w:w)		
Polysaccharide	43.07	
Protein	22.4	
Melanin	29.76	
Metals	4.77	
Carbon	41.49	
Range of molecular weight (Da)	First peak: 3500–10 000 Second peak: 45 000	
Organic pollutant	Phenanthrene	
Molecular weight	178	
Aqueous solubility	1.29 mg L <sup>-1</sup>	
Octanol–water partition constant, log K <sub>ow</sub>	4.57	

<sup>a</sup> Provided by the supplier.

### 2.2. Sorption experiments

#### 2.2.1. Adsorption of phenanthrene on aluminum oxides

Adsorption isotherms on both micro and nanoparticles were obtained by a batch equilibration technique. No electrolyte buffer was used. The experiments were carried out at native pH, ranging from 6.0 to 6.4. Solid-to-solution ratios were adjusted to reach 30–80% solute uptake by sorbents. Due to its low water solubility, Phen stock solution was prepared in methanol at high concentrations. <sup>14</sup>C labeled and unlabelled Phen were mixed to give an initial concentration ranging from 10 to 1000 μg L<sup>-1</sup> in water. These solutions were added to 15 mL screw cap vials containing 500 mg or 20 mg of Al<sub>2</sub>O<sub>3</sub> microparticles or nanoparticles, respectively, until a minimum headspace was achieved. Methanol concentrations were kept below 0.1% of the total solution volume. Vials were immediately sealed with aluminum foil-lined Teflon screw caps and then mixed on a shaker for 3 days at 23 ± 1 °C. After mixing, the vials were centrifuged at 3000 rpm for 30 min, and 1 mL of supernatant was removed and added to 7 mL Scintiverse cocktail (Fisher Scientific Co., Pittsburgh) for liquid scintillation counting (LSC) (Beckman LS 6500, CA). Adsorbed Phen on Al<sub>2</sub>O<sub>3</sub> was determined by mass balance, because of the negligible mass loss of solute.

#### 2.2.2. Adsorption of polymerin on aluminum oxides

Adsorption of polymerin on Al<sub>2</sub>O<sub>3</sub> was carried out by diluting a 5000 mg L<sup>-1</sup> (2000 mg OCL<sup>-1</sup>) stock solution of polymerin, in a range from 10 to 400 mg OCL<sup>-1</sup>, in 15 mL screw cap vials containing 500 or 20 mg of micro and nanoparticles, respectively. The experiments were conducted in distilled water at pH 6.0–6.4. After 3 days of equilibration, vials were centrifuged and supernatants were analyzed by an Agilent (Palo Alto, CA) 8453 UV–visible spectrometer set at 254, 465 and 665 nm. To determine the organic matter concentration 254 nm was chosen, since it is characteristic of natural substances such as humic acids, aromatic compounds, tannins and lignin. In order to calculate E<sub>4</sub>/E<sub>6</sub> ratio 465 and 665 nm were chosen, deriving from the absorbance ratio between 465 nm and 665 nm. The detection limit was 0.2 mg OCL<sup>-1</sup>. Uptake of polymerin by particles was obtained by mass balance. Sorptive losses of polymerin by the vials were excluded by the comparison with blanks. Samples of polymerin in water without Al<sub>2</sub>O<sub>3</sub> were run in the same tubes and the final concentration was compared with the initial one.

#### 2.2.3. Binding of phenanthrene by polymerin

Binding isotherms of Phen by polymerin were obtained by a batch equilibration technique using dialysis bags as described by Pan et al. (2007). The dialysis bags were made of regenerated cellulose with molecular weight cut-off (MWCO) of 3500 Da (Spectra/Por 3, Spectrum Laboratories, CA). During polymerin preparation, the bulk solution was dialyzed using 3500 Da MWCO dialysis membrane. This procedure assured to avoid sorbent loss during the sorption experiments. Polymerin solution (40 mg OCL<sup>-1</sup>) was added inside a 10 cm length dialysis bag and an increasing concentration of Phen in the same range used for adsorption on the Al<sub>2</sub>O<sub>3</sub> particles was added outside the bag in a 15 mL screw cap vial. The solution pH was not adjusted (5.7). After 3-day shaking in dark, 1 mL solution from both inside and outside the bag was collected and analyzed by LSC. Uptake of solute by polymerin was calculated by the difference between inside and outside amounts of Phen (Pan et al., 2007, 2008).

#### 2.2.4. Three-phase sorption

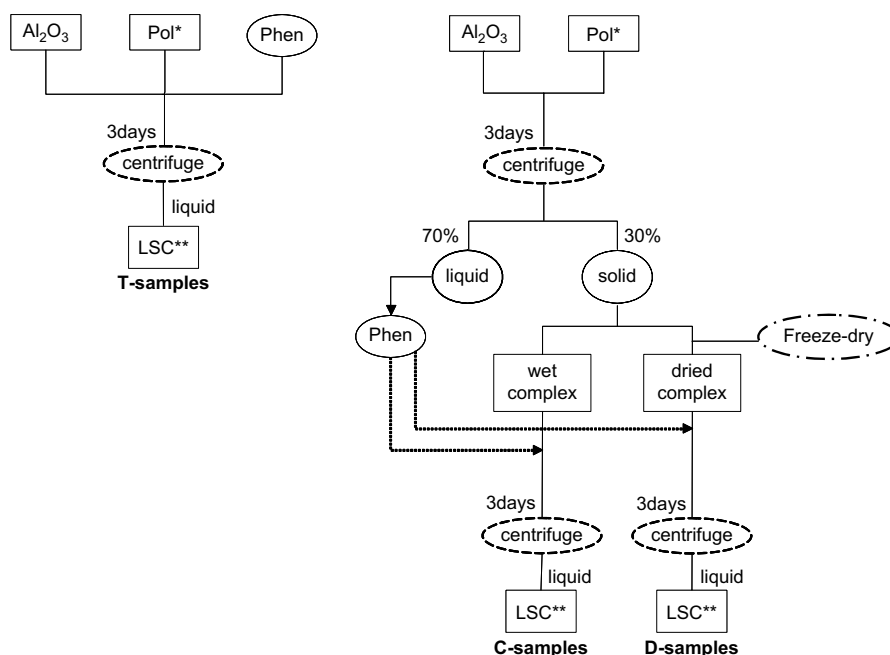
Three-phase sorption experiments were carried out in two different ways by: (i) keeping constant Phen concentration and varying polymerin concentration and (ii) using a fixed amount of polymerin and different concentrations of Phen. In the first case, increasing concentrations of polymerin, ranging from 0 to 600 mg OCL<sup>-1</sup>, were added to 500 or 20 mg of micro or nanoscale Al<sub>2</sub>O<sub>3</sub> particles, respectively, together with 1000 μg L<sup>-1</sup> of Phen using a batch equilibration method. In the second case, samples were divided into three different batches prepared as schematically reported in Fig. 1. Three-phase samples (T-samples) were prepared by adding particles, polymerin and Phen simultaneously; after 3 days samples were centrifuged and the supernatant was analyzed by LSC. Complex samples (C-samples) were prepared by shaking particles and polymerin for 3 days in order to create the complex. Then, the samples were centrifuged and 70% of supernatant was collected and used to prepare Phen stock solution to add to the samples. After 3 days the samples were centrifuged and the supernatant was analyzed by LSC. Dried samples (D-samples) were prepared following the same protocol used for C-samples, but, before adding Phen solution, the complex (30% remaining in the vials) was freeze-dried (Fig. 1). Phen stock solution was prepared in the polymerin solution remaining after adsorption on the particles in order to keep a constant concentration of polymerin in the system in all of the different batches. Moreover, polymerin solution remaining after adsorption on both micro and nanoparticles was collected and sorption isotherms of Phen were obtained using the dialysis bags method as described above. All the experiments were conducted in duplicate.

#### 2.2.5. Sorption isotherms models

According to the type of interaction occurring between sorbent and sorbate, we used different models to fit the data, such as the logarithmic form of Freundlich equation, Langmuir equation and a linear model.

The linearized form of the Freundlich equation is:

$$\log S = \log K_F + N \log C_e \quad (1)$$



**Fig. 1.** Flow chart of the experimental design used to study phenanthrene behavior in a three-phase system. \*Pol is the abbreviation of polymerin. \*\*LSC is the abbreviation of Liquid Scintillation Counter. *Liquid* represents polymerin solution remaining after adsorption on particles. *Solid* represents the polymerin-particles complex.

where  $S$  is the solid-phase concentration of Phen ( $\mu\text{g kg}^{-1}$ ) and  $C_e$  represents the aqueous-phase concentration of Phen ( $\mu\text{g L}^{-1}$ ).  $K_F$  [ $(\mu\text{g kg}^{-1})/(\mu\text{g L}^{-1})^N$ ] and  $N$  (dimensionless) are the Freundlich sorption parameters.

Langmuir equation was employed to fit polymerin sorption on mineral particles:

$$S = S_m K C_e / (1 + K C_e) \quad (2)$$

where  $S$  is the amount of polymerin sorbed on particles ( $\text{mg OC kg}^{-1}$ ),  $K$  is the Langmuir constant related to the binding energy,  $S_m$  is the maximum amount of polymerin sorbed ( $\text{mg OC kg}^{-1}$ ) and  $C_e$  is the equilibrium concentration of polymerin ( $\text{mg OCL}^{-1}$ ).

The single point sorption coefficient was used widely for comparisons in the literature due to isotherm nonlinearity (Wang et al., 2006). Therefore, the single point  $K_d$  was calculated based on Freundlich equation at a given concentration ( $C_i$ ):

$$K_d = S/C_i = K_F \times C_i^{n-1} \quad (3)$$

#### 2.2.6. Mathematical corrections used in $K_d$ calculation for three-phase systems

In a three-phase system Phen can be adsorbed by three different sorbents: (i) particles, (ii) polymerin, and (iii) polymerin-particle complex. In the solid phase, it is possible to find exposed particles and the complex; liquid phase consists of un-adsorbed polymerin and water. Freundlich parameters for all the three-phase isotherms are shown in Table 1. For each batch,  $K_d^*$  (apparent  $K_d$ ) was calculated as:

$$K_d^* = S/C_e = K_F \times C_e^{n-1} \quad (4)$$

Successively, it was adjusted in the denominator by subtraction of Phen bound with polymerin ( $C_b$ ) from aqueous Phen, obtaining  $K_d1$ .  $C_b$  was calculated by fitting with a linear equation deriving from the isotherm performed between Phen and polymerin solution remained after adsorption on particles. Being linear,  $C_{\text{free}}$  is proportionally related to  $C_e$  (aqueous-phase concentration) with the ratio of  $\alpha$ . Thus,

$$C_e = \alpha \times C_{\text{free}} \quad (5)$$

$$C_{\text{free}} = C_e / \alpha \quad (6)$$

$$K_d1 = S/C_{\text{free}} = K_F \times C_{\text{free}}^{n-1} \quad (7)$$

This correction was necessary to calculate the real amount of Phen distributed between solid particles and water. An additional correction was done in the numerator of  $K_d1$  by subtraction of adsorbed Phen on free particles from the solid phase, obtaining  $K_d2$ .  $S_{\text{particles}}$  was derived from Phen  $K_d$  calculated for both micro and nanoparticles.

$$S_{\text{particles}} = K_d \times C_{\text{free}} \quad (8)$$

$$S_{\text{complex}} = S - S_{\text{particles}} = S - K_F \times C_{\text{free}}^n \quad (9)$$

$$K_d2 = S_{\text{complex}}/C_{\text{free}} \quad (10)$$

This subtracted value was representative of the maximum contribution given by particles, even if they were engaged in complex formation, therefore it would be overestimated.

### 2.3. Spectroscopic analysis

The ratio of absorbance of polymerin at 465 and 665 nm ( $E_4$  to  $E_6$  ratio) was determined from aqueous solution remaining after adsorption on micro and nanoparticles. We collected and analyzed each supernatant from polymerin-particles sorption experiments. The same solutions were also analyzed by Fourier Transform Infrared Spectroscopy (FT-IR) using a Perkin-Elmer spectrometer (Spectrum One) equipped with a Universal ATR Sampling accessory (Zirconium selenide crystal, Kang and Xing, 2007).

## 3. Results and discussion

### 3.1. $\text{Al}_2\text{O}_3$ particle size considerably affected polymerin sorption

Sorption isotherms of polymerin by micro and nanoparticles of  $\text{Al}_2\text{O}_3$  are shown in Fig. 2a. Freundlich and Langmuir parameters for the sorption studies are listed in Table 2. By comparing  $R^2$  from both Freundlich and Langmuir equations, polymerin sorption on the particles follows a Langmuir-type trend ( $R^2 \geq 0.99$ ). In addition, the error analysis using  $(C_{b(\text{observed})} - C_{b(\text{expected})})/C_{b(\text{observed})}$  vs.  $C_e$  showed a bell-shaped error distribution for the regression using Freundlich model, but this type of error distribution is not observed for the regression using Langmuir model. Therefore, the regression results using Langmuir model were used for further discussion. The sorption capacity ( $S_m$ ) of nanoparticles was almost two orders of magnitude higher than that of microparticles ( $S_m = 203800$  and  $2970 \text{ mg OC kg}^{-1}$ , respectively). Moreover, nanoparticle Langmuir adsorption constant ( $K$ ) was higher than microparticle's constant. According to XRD analysis (data not showed), microparticles

**Table 2**  
Parameters of Freundlich and Langmuir sorption isotherms fitting for bi-phase and three-phase systems

Freundlich parameters			Langmuir parameters			
Sorbents	Sorbates	log K <sub>f</sub>	N	R <sup>2</sup>	S <sub>m</sub>	K
Al-Micro	Pol	2.043 ± 0.025	0.63 <sup>h</sup> ± 0.02	0.969	2970 ± 80	0.02
Al-Nano	Pol	4.424 ± 0.029	0.43 <sup>h</sup> ± 0.02	0.941	203 800 ± 5300	0.08
Al-Micro	Phen	0.431 ± 0.039	1.06 ± 0.02	0.997		
Al-Nano	Phen	1.590 ± 0.024	1.04 ± 0.01	0.999		
Pol <sup>d</sup>	Phen	3.642 ± 0.090	0.88 <sup>h</sup> ± 0.05	0.967	2640	3194
Pol-Al-Micro T <sup>e</sup>	Phen	1.453 ± 0.018	0.98 ± 0.01	0.999		
Pol-Al-Micro C <sup>f</sup>	Phen	1.370 ± 0.021	0.97 ± 0.01	0.998		
Pol-Al-Micro D <sup>g</sup>	Phen	1.365 ± 0.018	0.97 ± 0.01	0.999		
Pol-Al-Nano T <sup>e</sup>	Phen	3.019 ± 0.032	0.96 ± 0.02	0.995		
Pol-Al-Nano C <sup>f</sup>	Phen	3.051 ± 0.021	0.93 <sup>h</sup> ± 0.01	0.997		
Pol-Al-Nano D <sup>g</sup>	Phen	3.270 ± 0.011	0.98 ± 0.01	0.999		
				R <sup>2</sup>		
				0.990		
				0.994		
				K <sub>d1</sub> <sup>a</sup> (L/Kg)		
				C <sub>e</sub> = 0.1C <sub>s</sub>		
				3.5		
				50.3		
				14.6		
				18.8 (Koc = 2106)		
				19.0 (Koc = 2204)		
				11.6		
				11.6		
				299		
				331		
				391		
				660		
				K <sub>d2</sub> <sup>c</sup> (L/Kg)		
				C <sub>e</sub> = 0.1C <sub>s</sub>		
				20.2 (Koc = 2609)		
				14.9		
				15.2		
				478 (Koc = 1951)		
				479		
				1030		
				C <sub>e</sub> = 0.01C <sub>s</sub>		
				617.0 (Koc = 2184)		
				1080 (Koc = 4734)		
				C <sub>e</sub> = 0.01C <sub>s</sub>		
				391		
				660		
				570		

<sup>a</sup> The apparent K<sub>d</sub> in a three-phase system.

<sup>b</sup> The corrected K<sub>d</sub> by subtraction of C<sub>b</sub> from the solution.

<sup>c</sup> The corrected K<sub>d</sub> by subtraction of the amount of Phen sorbed on free particles.

<sup>d</sup> The abbreviation of polymerin.

<sup>e</sup> The sample obtained by mixing Phen, Pol and Al<sub>2</sub>O<sub>3</sub> simultaneously.

<sup>f</sup> The sample obtained by forming the complex first and then adding Phen in the solution.

<sup>g</sup> The sample obtained by freeze-drying the pre-formed complex and then adding Phen.

<sup>h</sup> Nonlinear sorption.

showed a well-crystallized structure, while nanoparticles seems in a relatively less crystalline form. Since elemental composition was identical, the first reasonable explanation for such a large difference was initially related to the surface area. In fact, nanoparticle surface area was considerably higher than microparticle (228 and 32 m<sup>2</sup> g<sup>-1</sup>, respectively, Table 1). But, even if surface area significantly influenced the sorption, it was not enough to explain the two orders of magnitude enhancement. Nano-to-micro surface area ratio was only seven (228/32). Another investigated parameter was zeta potential. Microparticle's PZC was lower than nanoparticles (7.30 and 8.50, respectively), hence micro-Al<sub>2</sub>O<sub>3</sub> might have a lower charge density at our experiment pHs. In fact, PZC indicates the pH in which the sum of the charges present on a material is equal to zero, or, to be more precise, the particle's surface is neutral. Below this pH point, positive charges start to prevail over negative ones, making the surface positive. The farther from the PZC, the higher number of positive charges, the higher charge density. This factor may influence polymerin sorption due to the electrostatic attraction. However, sorption experiments were conducted at pH 6.0–6.4 and, due to their high PZC, both kinds of particles were significantly positively charged. Therefore, an additional factor must have influenced polymerin sorption on different-sized Al<sub>2</sub>O<sub>3</sub> particles. Polysaccharide, melanin and proteins are the main components of polymerin (Capasso et al., 2002), which is rich in hydroxyl and carboxyl groups and phenol rings. Polymerin also contains paraffinic carbon moiety (i.e., long aliphatic CH<sub>2</sub> chains) as indicated by the absorption band at 2930 cm<sup>-1</sup> (Kang and Xing, 2005) in the FT-IR spectra (Fig. 3) and reported by Capasso et al. (2002). Reaching a microparticle, polymerin could find a wide surface to interact with. Each macromolecule may bind a microparticle using multiple functional groups from the same unit, spreading itself on the surface, assuming a *flat configuration* (Fig. 4a). With regard to nanoparticles, each polymerin macromolecule may find a limited area on the highly charged surface. Polymerin macromolecules may have only one or few anchor points on the surface, but they must extend out their branches radially from the central focus of the particle toward the solution because they do not have enough space on the surface. Since the charge density is high, several macromolecules are attracted by the mineral surface, forming a *radiant configuration* (Fig. 4b). Moreover, after the first layer, other macromolecules can be adsorbed via both polar and hydrophobic interactions. This *radiant configuration*, along the contribution from the higher surface area and zeta potential, can explain such a large variation of sorption capacity between different sizes of Al<sub>2</sub>O<sub>3</sub>.

### 3.2. Fractionation of polymerin adsorbed by Al<sub>2</sub>O<sub>3</sub> microparticles

Polymerin behavior on Al<sub>2</sub>O<sub>3</sub> particles was analyzed by FT-IR spectroscopy of the complexes. Spectrum A in Fig. 3 represents the difference between polymerin-microparticles complex and pure microparticles, showing the fraction of polymerin adsorbed on microparticles oxides. Only few bands were significant, probably because of the low amount of adsorbed polymerin. The only significant bands of this spectrum were those observed at 3290, 3160, 1590, 1395 and 667 cm<sup>-1</sup>. In particular, the band at 3298 may be attributed to the stretching of phenolic OH, and is correlated with the band at 1394 cm<sup>-1</sup> correspondent to the bending of the phenolic group. The band at 3160 cm<sup>-1</sup> was attributed to the stretching of aromatic C–H, that at 1590 to the stretching of aromatic C=C, correlated with the band at 667 cm<sup>-1</sup> due to the out-of-plane C–H aromatic bending. Therefore, all these bands were correlated with each other, strongly indicating the phenolic nature of the fraction of polymerin adsorbed on microparticles, i.e., the melaninic portion. The adsorption of the aromatic fraction on microparticles was also supported by the UV–vis analysis of the supernatants derived after adsorption of polymerin on particles, as shown in Fig. 5. The E<sub>4</sub>/E<sub>6</sub>

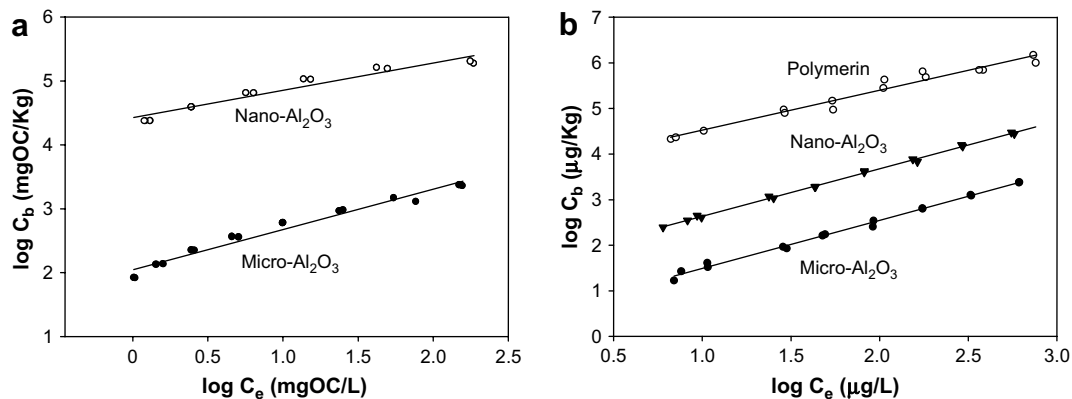


Fig. 2. Sorption isotherms of polymerin by micro and nanoparticles of aluminum oxides (a) and sorption isotherms of Phen by polymerin, micro- $\text{Al}_2\text{O}_3$  and nano- $\text{Al}_2\text{O}_3$  (b).

ratio is a parameter related to the condensation degree of the aromatic C network of dissolved organic matter. At low polymerin concentration,  $E_4/E_6$  ratio of the polymerin solution remaining after adsorption on microparticles was higher than that of original polymerin. With increasing polymerin concentration,  $E_4/E_6$  ratio decreased until the same value of original polymerin was achieved. At this point, the high polymerin concentration in solution did no longer permit to discriminate the differences. The higher  $E_4/E_6$  ratio was an evidence of fractionation occurring during adsorption. Based on the notion that higher ratio may be related to lower condensation degree for the same organic matrix (Stevenson, 1994), this set of data showed that polymerin remaining after adsorption on  $\text{Al}_2\text{O}_3$  microparticles contained less condensed components relative to the original polymerin. Therefore, FT-IR and UV-vis data showed that  $\text{Al}_2\text{O}_3$  microparticles preferably adsorbed the aromatic (melaninic) component of polymerin.

As regard to nanoparticles, FT-IR and UV-vis data did not show fractionation of polymerin. In fact, spectrum B (Fig. 3), related to the fraction of polymerin adsorbed on nanoparticles, may be almost overlapped to the spectrum of polymerin (spectrum C). All of the characteristic bands of polymerin were reported in both of them. In particular, the region between  $3553$  and  $3316$   $\text{cm}^{-1}$ , assigned to alcoholic groups, appeared sharper in spectrum B, stating the presence of OH fixed by H-bonding. Moreover, a sharp and medium band at  $2926$   $\text{cm}^{-1}$  (CH and methylester  $\text{CH}_3$  groups), four weak albeit correlated bands at  $1725$  and  $1289$   $\text{cm}^{-1}$ , and  $1439$  and  $1362$   $\text{cm}^{-1}$  (CO and CO- $\text{CH}_3$  methylester groups, and symmetric and asymmetric bending of the methylester  $\text{CH}_3$  groups, respectively), an absorption at  $1638$   $\text{cm}^{-1}$  (aromatic C=C stretching and CO peptide group), and a very strong absorption at  $1075$   $\text{cm}^{-1}$  (C-OH bonding of the polysaccharide component) were observed. The absence of fractionation of polymerin on nanoparticles was also confirmed by UV-vis data (Fig. 5).  $E_4/E_6$  ratio of polymerin solution remaining after adsorption on nanoparticles was similar to the original polymerin in the whole concentration range. This behavior was an additional evidence of nanoparticles high sorption capacity. Nanoparticles were able to adsorb polymerin components (including paraffinic carbons) indistinctly, without making any significant selection.

### 3.3. Sorption of phenanthrene on each single sorbent

Sorption isotherms of Phen on aluminum oxides and binding isotherms of Phen with polymerin are shown in Fig. 2b. Both micro and nanoparticles had an approximately linear sorption, with their  $N$  values being 1.06 and 1.04, respectively (Table 2). Nanoparticles had a sorption capacity much higher than microparticles, with a  $K_d$  value almost 15 times greater than microparticle's  $K_d$ . Phen binding

with polymerin fits the Freundlich equation. Polymerin binding capacity was more than two orders of magnitude higher than nanoparticles' sorption capacity. The binding mechanism of Phen by polymerin may be mainly due to  $\pi$ - $\pi$  interaction between the catechol-melaninic core of polymerin and the aromatic rings of the pollutant. Moreover, CH- $\pi$  interaction with the aliphatic chains may occur, as well as induced dipole-dipole interaction. Phen  $\log K_{oc}$  of polymerin (3.5) was lower than  $\log K_{oc}$  of lignin (4.38) and humic acid (4.31) (Wang et al., 2007; Pan et al., 2007), but higher than cellulose coefficient (2.57) (Wang et al., 2007). This result was reasonable, with polymerin polarity ( $O/C = 0.908$ ) lower than cellulose ( $O/C = 0.942$ ) but greatly higher than lignin and humic acids ( $O/C = 0.326$  and  $0.575$ , respectively). As regard to mineral particles, Phen sorption may be due to a partitioning process between

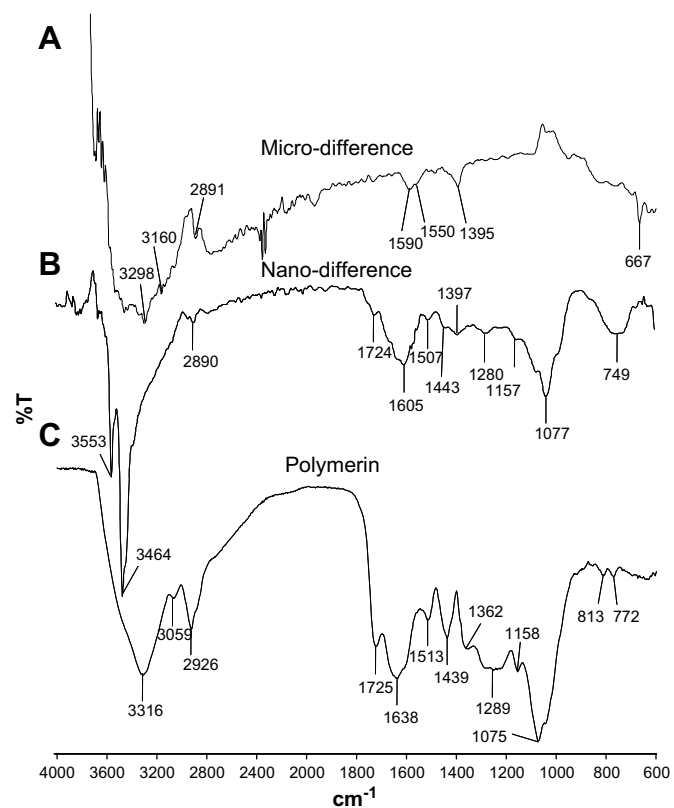
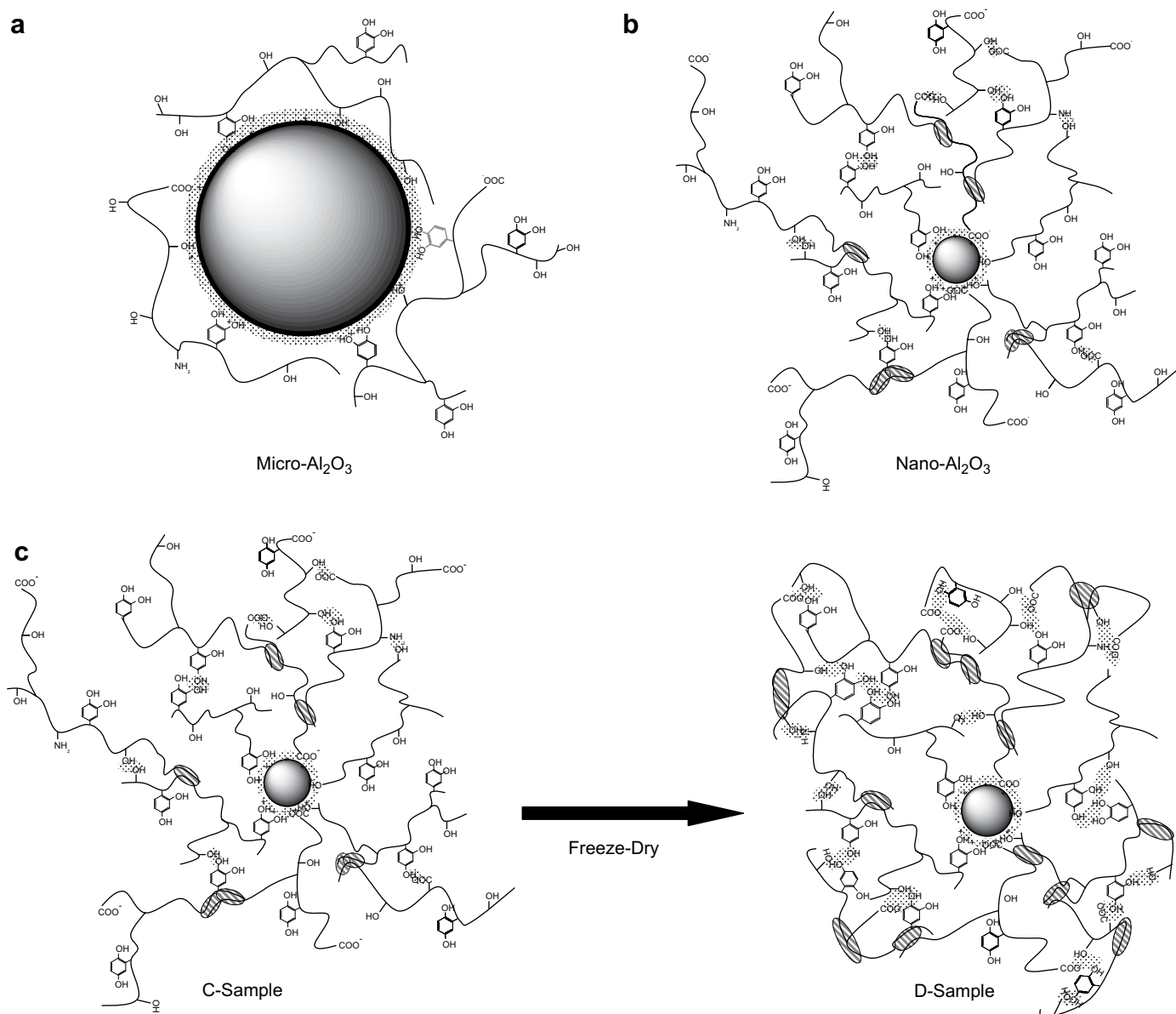


Fig. 3. Differential FT-IR spectra between polymerin-microparticles complex and microparticles oxides (A), between polymerin-nanoparticles complex and nanoparticles oxides (B) and spectrum of original polymerin (Polymerin, C).



**Fig. 4.** Schematic illustration of the hypothetical interaction between polymerin and aluminum oxides. The first panel (a) represents the *flat configuration* of polymerin on micro- $\text{Al}_2\text{O}_3$ ; the second panel (b) represents the *radiant configuration* of polymerin on nano- $\text{Al}_2\text{O}_3$ . Panel (c) shows the conformational change of polymerin chains occurring after the drying treatment on nanoparticles of aluminum oxides. The curve lines represent polysaccharide and paraffinic carbon chains, light grey circles show polar interactions (e.g., H-bonding), hatched areas indicate hydrophobic interactions (domains). This is an illustrative representation not drawn to scale.

the disorganized bulk aqueous solution and the *vicinal water* immediately adjacent to the solid surface, more organized and oriented (Schwarzenbach et al., 2003).

#### 3.4. Effect of polymerin concentration on apparent sorption coefficient ( $K_d$ ) of particles

Phen sorption on particles in the presence of increasing concentration of polymerin was studied by keeping a constant Phen concentration and the quantity of aluminum oxides. Apparent  $K_d$  of Phen was highly enhanced by increasing added polymerin (Fig. 6a and b). The high initial enhancement was related with the increasing of organic carbon complexed on the particles. In reality, both aqueous and solid polymerin concentrations increased; therefore Phen sorption on solid particles was affected by the balance between these two phases. The increase of the sorption in the beginning of the curve showed the complex as the dominant

sorbent. Many studies (Xiao et al., 2004; Gregory et al., 2005) reported that the higher SOM in a soil–water system, the higher PAHs (Polycyclic Aromatic Hydrocarbons) sorption. Once polymerin reached the saturation point on the nanoparticles, the apparent  $K_d$  started to slightly decrease by increasing polymerin concentration (Fig. 6b). That is easily explainable by comparing  $K_d$  and  $K_{OC}$  of Phen on the particles alone and polymerin, respectively. Polymerin–particles complex showed higher Phen sorption than the oxides alone, and the sorption intensified by increasing the organic percentage of the complex. Once the complex is saturated and no more polymerin can be adsorbed, the organic fraction in solution competes on the complex for Phen sorption. This behavior was only evident for nanoparticles. Microparticles showed a constantly increasing trend, probably because these particles did not reach a polymerin saturation point in the examined polymerin concentration range. In fact, by considering the last polymerin equilibrium concentration (Fig. 6a and 6b) for both micro and

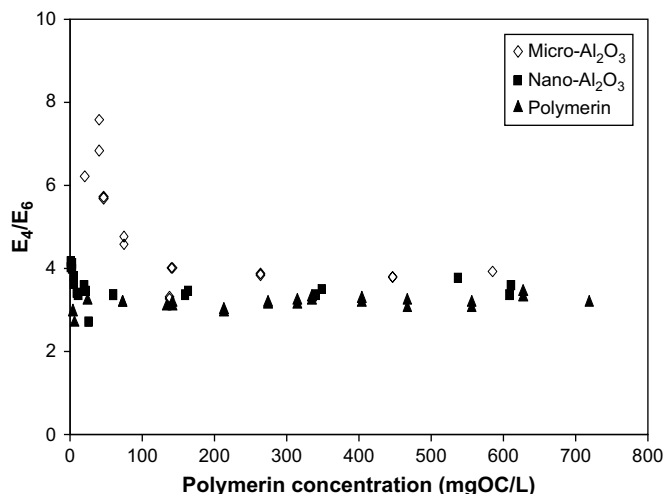


Fig. 5.  $E_4/E_6$  ratio of original polymerin and polymerin solution remaining after the interaction with micro and nanoparticles of aluminum oxides.

nanoparticles (450 and 600 mg OC L<sup>-1</sup>, respectively), the adsorbed amount, calculated by using Langmuir parameters, is 2670 and 199 600 mg OC kg<sup>-1</sup>, respectively. The amount of polymerin adsorbed on microparticles was significantly different from the maximum sorption capacity ( $S_m = 2970 \pm 80$ ). Thus, polymerin did not saturate micro-Al<sub>2</sub>O<sub>3</sub>, differently from what occurred for nanoparticles ( $S_m = 203\,800 \pm 5300$ ).

### 3.5. Sorption sequence influenced microparticles behavior

Phen sorption in a three-phase system was studied by keeping a constant polymerin concentration and varying Phen amount. Moreover, the effect of sorption sequence and the influence of the sorbent physical state were investigated by following the experimental design shown in Fig. 1. Microparticles showed a sorption coefficient following an order: T-samples (20.2) > C-samples (15.0)  $\approx$  D-samples (15.2), with a T-samples'  $K_d$  value 34% higher than the others (Table 2). All the isotherms presented a slightly nonlinear shape with  $N$  values around 0.97. The effect of sorption sequence significantly influenced Phen behavior in a three-phase system. A higher sorption coefficient was registered when Phen and polymerin were added simultaneously into the system (Fig. 7a). This was a clear evidence of the competition occurring between Phen and polymerin for the sorption sites on the particles. In T-samples, all the particles sorption sites were available for both sorbates (Phen and polymerin), but in C- and D-samples oxides were coated by polymerin, hence the only available sorption sites

for Phen were on polymerin-particles complex or on un-adsorbed polymerin in solution.

By summing the isotherm resulted from both microparticles alone and C- or D-samples, the obtained curve could overlap to the T-samples curve (Fig. 8). This mathematical calculation demonstrated the contribution of both particles and complex in a three-phase system (T-samples). After complex formation, oxides contribution to sorption of Phen was negligible. Huang and Weber (1997) reported that minerals do not play a significant role in PAHs sorption in soil/sediment–water system. Kile et al. (1995) suggested the occurring of a strong suppression by water of solute adsorption on polar mineral surfaces. Moreover, sorption of HOCs from aqueous solutions by soil and sediments is dominated by soil organic matter. By analyzing our results, in addition to the above reasons we can contend that minerals contribution to sorption of PAHs in a complex system is also insignificant because their surface sites are preferentially covered by organic matter and/or water.

### 3.6. The drying treatment increased the sorption of phenanthrene by nanoparticles

Nanoparticles showed a sorption coefficient following an order different from microparticles: D-samples (1030)  $\gg$  T-samples (478)  $\approx$  C-samples (480–570), with a D-samples'  $K_d$  value being two times higher than the others. T- and D-samples presented a linear sorption, while C-samples isotherm was nonlinear, with an  $N$  value of 0.93 (Table 2).

The addition of Phen and polymerin simultaneously or in two successive times was not crucial for Phen sorption in a nanoparticles three-phase system (Fig. 7b). T- and C-samples showed similar  $K_d$  values. This result means that polymerin affinity for nanoparticles was much stronger than Phen affinity. Critical point for Phen sorption was the physical state of the complex. Dried samples showed a  $K_d$  value twice higher than the other systems. Since there was no difference between wet and dry complexes in terms of polymerin adsorption on the particles (data not shown), this result can be explained according to the *radiant configuration*, as suggested in Fig. 4c. In C-samples, polymerin chains extended their branches in solution, exposing hydrophilic domains and leaving the lipophilic ones relatively inside. During the freeze-dry process, water molecules gradually left from the complex changing the chain configuration. Water molecules on the surface left faster than the ones inside the complex. Therefore, hydrophilic groups of polymerin would rearrange to contact with the water molecules inside. This rearrangement led polymerin branches to fold, exposing a relatively lipophilic surface and creating hydrophilic domains relatively inside the matrix (D-samples, Fig. 4c). Effect of drying on the increase in hydrophobicity of the surfaces of soil particles was

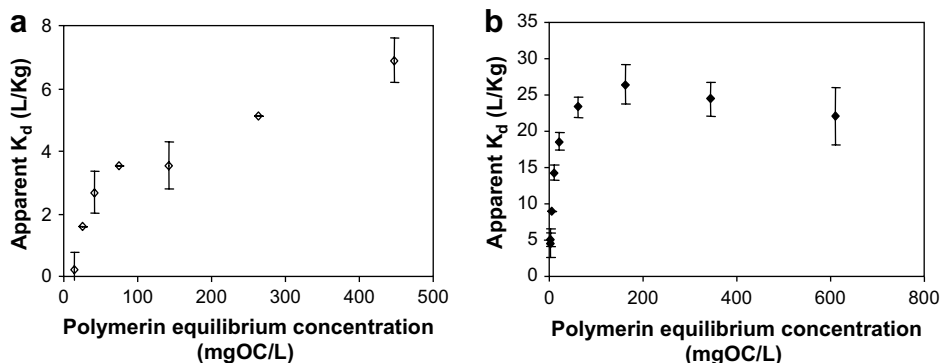


Fig. 6. Variation of the apparent sorption coefficient ( $K_d$ ) in a three-phase system using a fixed concentration of phenanthrene and increasing polymerin amount in solution with Al<sub>2</sub>O<sub>3</sub> microparticles (a) and nanoparticles (b).

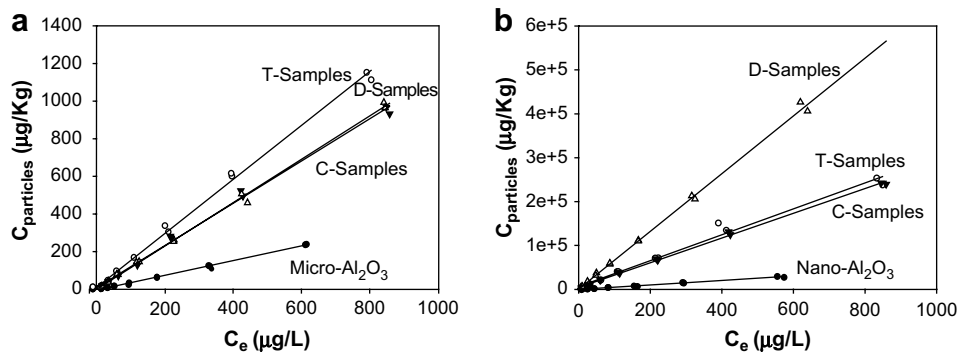


Fig. 7. Sorption isotherms of phenanthrene in a three-phase system using  $\text{Al}_2\text{O}_3$  microparticles (a) and nanoparticles (b) in different experimental conditions (see Fig. 1).

recently described by Klitzke and Lang (2007). Moreover, this drying process created additional lipophilic sites relative to the C-samples, increasing the affinity for Phen. Furthermore, sorption linearity for D-samples was slightly higher than for C-samples, indicating that the increase of hydrophobic regions led to an increase of a more partitioning process. Dried nanoparticles–polymerin complex showed a  $K_{oc}$  of Phen of 4730, even higher than uncomplexed polymerin (3190), demonstrating that the former sorbent was more lipophilic than the latter one. Another important result was that a dried nanoparticles complex showed a sorption coefficient nearly 70 times higher than a dried microparticles complex (Table 2), making the former more eligible than the latter for the application as bio-filter in water treatment and emphasizing the important role of nanoparticles.

#### 4. Potential application of the $\text{Al}_2\text{O}_3$ /polymerin system in water remediation

PAHs contamination is a real problem. The main anthropogenic sources are the wide and intensive industrial areas. PAHs in the air are in gaseous form or adsorbed on particulates, which tends to fall down on soil, surface water and plants with the rain. Plants and fruits can also receive PAHs through direct deposition from the air (Bakker et al., 2000), then, once on the skin of the fruits, these pollutants can enter the food chain. The presence of PAHs in fruits, vegetables and

their transformation products cultivated in allotments close to industrial areas (Wennrich et al., 2002; Rodríguez-Acuña et al., 2008; Moret et al., 2007) has been widely demonstrated. Therefore, other than accidental releases, the water coming from the washing of the fruits before processing them is another typical example of PAHs point-source polluted water. The cleaning up of washing waters deriving from agricultural plants located close to industrial areas may be done using  $\text{Al}_2\text{O}_3$  nanoparticles complexed with polymerin as a bio-filter. A number of reactors in series, equipped with an agitator system, may contain the sorbent. A porous septum between adjacent reactors may avoid the sorbent passage. A flow of wastewater may be merged into the system and react with the complex. After the sorption saturation,  $\text{Al}_2\text{O}_3$ /polymerin system may be recycled by incinerating the organic fraction, being this a low cost material. The mineral fraction may be recovered and reused for further applications. Moreover, showing good sorption capacity for pesticides (Sannino et al., 2008), polymerin may be used as a component of a biobed in farms for cleaning up water coming from washing process of either the pesticides spraying equipments or PAHs contaminated fruits. After the treatment, water passed through the biobed may be reused for irrigation (Fogg, 2007). In addition, the use of polymerin, even having less sorption capacity of phenanthrene relative to the highly used activated carbons, would be convenient due to the simplicity and low expenditure of energy of the recovering procedure.

#### 5. Conclusion

Polymerin sorption on  $\text{Al}_2\text{O}_3$  significantly depended on particles size. The higher surface area and zeta potential of nanoparticles compared to microparticles partially increased polymerin sorption. However, a different configuration of polymerin molecules on the particle surface might be the effective cause of a large enhancement of the sorption on nanoparticles. UV-visible and FT-IR analyses demonstrated polymerin fractionation by  $\text{Al}_2\text{O}_3$  microparticles, which preferentially adsorbed the melaninic fraction of polymerin. In a three-phase system with a varying amount of polymerin, Phen sorption directly depended on the carbon content of the complex. Using a fixed polymerin concentration, Phen sorption on microparticles was affected by the sorption sequence. The highest sorption was registered by adding Phen and polymerin simultaneously on the  $\text{Al}_2\text{O}_3$  particles. Nanoparticles behavior was not influenced by the sorption sequence, but by the physical state of the complex. The drying treatment considerably enhanced Phen sorption. These findings support the application of polymerin, especially associated with  $\text{Al}_2\text{O}_3$  nanoparticles in a dry complex, for removing HOCs from point-source polluted water. Polymerin represents a cheap sorbent and its use could minimize OMW disposal problem. Thus, use of

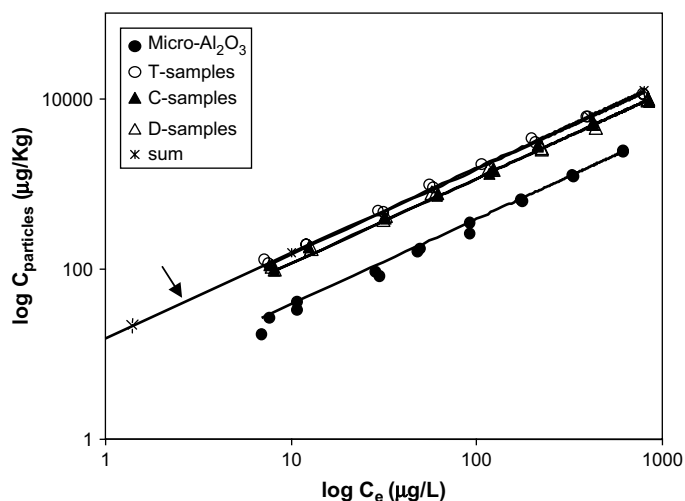


Fig. 8. Sum of the isotherms of phenanthrene on aluminum microparticles alone and C- (or D-) samples. The line, pointed with an arrow, overlaps the isotherm of T-samples.



polymerin along with Al<sub>2</sub>O<sub>3</sub> nanoparticles in water treatment could give both economic and ecologic advantages.

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