



Research paper

The effect of montmorillonite clay in alginate gel beads for polychlorinated biphenyl adsorption: Isothermal and kinetic studies

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ABSTRACT

Beads of alginate montmorillonite have been used as sorbent for polychlorinated biphenyls from aqueous solutions.

The structure and the differences between the different beads were established by IR spectroscopy (FT-IR). The adsorption at 25 °C has been studied in a batch system, following its kinetics and assessing adsorbent dose, initial PCB concentrations, and pH effects. The results show that increasing the initial concentration of the PCBs and the adsorption time favored the adsorption. Adsorption isotherm data were modeled using Chapman, Freundlich and Langmuir adsorption isotherms and the appropriate parameters were calculated.

Adsorption of trichlorobiphenyls on alginate–montmorillonite beads followed a Freundlich isotherm type model, while adsorption of tetra-, penta-, and hexachlorobiphenyls displayed a sigmoid-shaped (S-type) isotherm fitting the Chapman sigmoidal equation with the highest non-linear R^2 values among the three tested models. By comparing the percentage adsorptions using the same number of beads (same volumes), best removals were obtained by using alginate montmorillonite beads.

Kinetic models were investigated to determine the mechanism of adsorption showing a best fit for the pseudo-second order model (R^2 from 0.998 to 0.982).

Moreover, to underline the effect of montmorillonite in alginate gel beads, we have compared the isothermal adsorption curves between alginate montmorillonite and alginate beads.

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1. Introduction

The industrial growth and population increase have resulted in the release of different pollutants in the environment and the treatment of effluents has become a challenging topic in environmental sciences. Hydrophobic organic compounds (HOCs) consist of wide classes of persistent contaminants in environmental matrices, particularly in water (Pace and Barreca, 2013) soils (Orecchio, 2010a, 2010b; Van Jaarsveld et al., 1997) and sediments (Barreca et al., 2014a; Orecchio et al., 2010).

Polychlorinated biphenyls (PCBs), an example of HOCs, are a class of compounds containing from one to ten chlorine atoms bound to a biphenyl molecule (Frame et al., 1996).

The low aqueous solubility of this class of contaminants is a fundamental feature that is directly related to their equilibrium concentration in the aqueous phase, which controls the toxicity (Giesy and Kannan, 1998), sorption, bioaccumulation and biodegradation (Sinkkonen and Paasivirta, 2000). In fact, several PCB congeners are resistant to degradation, which allows them to persist in the environment for long times

and become widespread via atmospheric and water transport mechanisms (Meneses et al., 2002; Stevens et al., 2001).

The PCB determination in environmental samples may be carried out by traditional methods (Method 1668C U.S. Environmental Protection Agency, April 2010) or using innovative and environmentally friendly techniques (Barreca et al., 2013).

PCBs were used for industrial purposes from the 1930s until the late 1970s. In Europe, although their industrial production ended in the late 1970s, PCBs' presence in the environment is still significant due to inconsiderate disposal activities or leakage from industrial facilities and their removal from aqueous matrices is a topic of great environmental interest.

The use of clay such as montmorillonite for PCB removal from water solutions has been widely discussed in the past (Delle Site, 2001), but because of physical properties such as low water permeability, the montmorillonite use for decontaminations is still under investigation (Brigante et al., 2013).

Efforts are therefore still needed in order to produce low cost adsorbents that are versatile e.g. having high adsorption capacity of inorganic and/or organic pollutants.

Due to their economic feasibility, adsorption–regeneration properties and mechanical strength, polymeric adsorbents have been recently used

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as an alternative to conventional materials such as activated carbon. Several studies report the use of chitosan in the form of flakes, powder or with hydrogel beads or clay-based composites for inorganic and organic pollutant adsorption (Bleiman and Mishael, 2010; Celis et al., 2012; Chatterjee et al., 2010; Chia Yang and Hsiung Hon, 2009; Yamani et al., 2012; Zhu et al., 2010).

Chitosan, a poly(D-glucosamine), is obtained from chitin by deacetylating its acetamide groups with a strong alkaline solution. Chitin is a natural polymer extracted from crustacean shells, such as prawns, crabs, shrimps, as well as insects and fungal biomass. Chitosan has already been described as a suitable natural polymer for the removal of phenolic compounds, through chelation involving the amino and hydroxyl groups in the glucosamine unit (Inoue et al., 1996; Juang and Ju, 1998; Rhee et al., 1998). Sodium alginate, a natural polymer extracted from seaweed, has been used in environmental decontamination, including the removal of organic compounds from water. For example, alginate filled with montmorillonite was used for the removal of nitrophenol and as a pesticide adsorbent (Barreca et al., 2014b; Ely et al., 2009; Fernández-Pérez et al., 1999; Gerstl et al., 1998). Sodium alginate exhibits a sol–gel transition when subjected to cation exchange, e.g. when a calcium ion replaces two sodium cations. This material is biocompatible, economical and can be easily prepared by encapsulation (Kittinaovarat et al., 2010).

Alginate beads are common and well-known support materials in biosciences applications (Bayramoglu et al., 2002) and are now used in the environmental field (Aguzzi et al., 2007; Silva et al., 2008).

Aluminosilicates (natural or modified) have been tested since more than 40 years ago in the removal of toxic metals or organic pollutants (Bailey et al., 1968; Griffin and Shimp, 1976; Montarges et al., 1998) from aqueous solutions due to favorable surface properties, availability, and environmental and economical considerations. Most of these materials are not suitable for extensive process utilization due to the lack of a spherical or uniform shape. Consequently, encapsulation of these materials in a polymeric matrix, such as calcium alginate, can be envisaged as an alternative technique to resolve these issues (Jing et al., 2013).

Hybrid hydrogels, which are water-swollen materials that maintain a distinct three-dimensional structure and are composed of polymeric and inorganic components, have gained great attention as effective adsorbents due to their high water retention and low cost.

Clays supported on calcium alginate beads have been reported to improve the mechanical and thermal stabilities of the beads and to simplify the separation procedures compared to the use of natural clays (Cavallaro et al., 2013).

In this report we present adsorption studies for PCBs at different chlorination grades onto alginate and alginate–montmorillonite beads highlighting the effect of montmorillonite on the adsorption mechanisms. Moreover, kinetic studies were carried out considering the amount of PCBs adsorbed by the biopolymer beads, in order to assess the mechanisms responsible for analyte adsorption.

2. Materials and methods

2.1. Chemicals

Dichloromethane, hexane, hydrochloric acid, sodium hydroxide, and sodium chloride were purchased from Carlo Erba (GC pure grade). Sodium alginate was purchased from Fluka and used without further purification. K10 montmorillonite clay (nitrogen (external) specific surface area = 274 m² g⁻¹, cation exchange capacity = 1.19 Meq g⁻¹) was purchased from Sigma-Aldrich.

The work solutions were prepared by drying and re-dilution from stock internal standard solutions of PCB mixture (1 mg L⁻¹) (Chemical Research WELEPA-1668IS). In detail, the components of PCB mixture are reported in Table 1.

For PCB analysis, stock standard solution containing a mixture of analytes was purchased from Chemical Research.

Stock internal standard solutions of PCBs (a mixture of PCB28, PCB52, PCB95, PCB101, PCB99, PCB81, PCB110, PCB77, PCB151, PCB149, PCB123, PCB118, PCB114, PCB146, PCB153, PCB105) were prepared (100 µg L⁻¹) in hexane from commercial standard nonane solutions (1 mg L⁻¹) (Chemical Research WELEPA-1668IS) by drying and re-dilution.

Stock congener solutions of PCBs were prepared at different concentrations in hexane from commercial standard isooctane solutions (10 mg L⁻¹) (Chemical Research O2S130111-01) by drying and re-dilution. Both stock internal and commercial standard solutions were stored in a refrigerator (4 °C).

2.2. Preparation of alginate and alginate–montmorillonite beads

Alginate beads were prepared according to the procedure reported in literature (Silva et al., 2008).

In turn, alginate montmorillonite beads were prepared by adapting the ionic gelation method (Bee et al., 2011; Guibal et al., 2010; Vincent et al., 2008).

K10 montmorillonite (8 g) was dispersed in 50 mL of Milli-Q water under continuous stirring. A 2% (w/v) Na-alginate suspension was prepared by dissolving 1 g of sodium alginate in Milli-Q water (50 mL). The alginate suspension (50 mL) was added to the suspension of montmorillonite and the mixture was stirred for 2 h. Once the mixture appeared homogeneous, it was forced through a micropipette tip by a peristaltic pump and the resulting gel droplets were collected in a beaker containing 150 mL of a stirred solution of 0.1 M CaCl₂.

Bead formation is driven by the interaction of calcium ions with the G-block regions of the polymer (Badwan et al., 1985) that complexes the calcium ions like egg box system (Rendevski and Andonovski, 2005; Roger et al., 2006).

After 8 h, the beads were filtered, washed with Milli-Q water (4 × 100 mL).

2.3. Adsorption studies

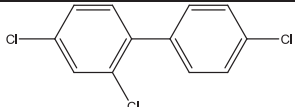
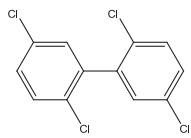
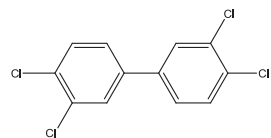
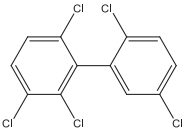
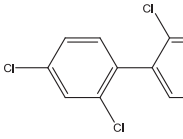
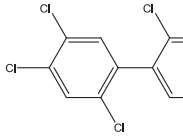
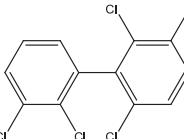
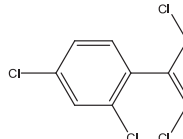
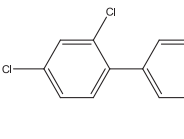
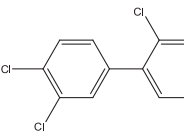
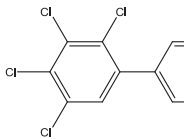
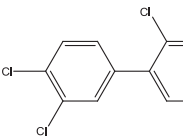
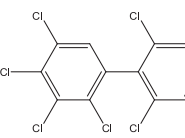
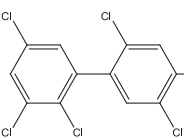
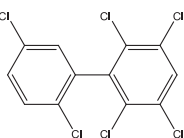
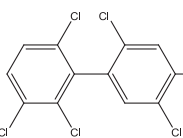
Sorption kinetic and isotherm experiments were conducted in batch mode without pH adjustment (initial pH = final pH = 5.5) by shaking different amounts of alginate composite beads with 10 mL of solution containing different concentrations of PCBs in mixture (16 single components). Moreover, to compare the adsorption data, adsorption studies were carried out also using alginate beads without montmorillonite. In detail, given the low PCB solubility, solutions with PCB concentrations ranging from 2 to 15 µg L⁻¹ were prepared by placing different volumes of a 1 mg L⁻¹ PCB hexane solution in a beaker containing 0.087 g of NaCl and removing the hexane by heating at 40 °C for 30 min. After hexane evaporation, 10 mL of Milli-Q water was added to each sample together with the alginate montmorillonite beads. It should be noted that, if considered as single components, PCB 5 Cl phase would separate from the aqueous phase at concentrations above 9.8 ppb. The same would occur to PCB 6 Cl at concentrations higher than 3 ppb. However, in the presence of other more soluble PCBs (PCB 3 Cl and PCB 4 Cl) the solubility of PCB 5 Cl and PCB 6 Cl should increase. Indeed, we did not observe any precipitations/phase separations at the highest concentration values (15 ppb of each compound).

A series of batch experiments were conducted to study the effect of parameters influencing the adsorption, such as pH, contact time, amount of adsorbent and initial concentration of adsorbate. All experiments were performed at room temperature (25 ± 1 °C) and in 0.15 M NaCl solution.

Preliminary tests showed that 6 h of equilibration time was sufficient to obtain an equilibrium condition between adsorbent and adsorbate.

At the end of the adsorption process, the beads were easily separated by filtration and the residual amount of PCBs in solution was extracted by liquid–liquid extraction using dichloromethane, according to the

Table 1
Structure and IUPAC name of single PCB in the mixture.

 <p>PCB 28 (2,4,4'-Trichlorobiphenyl)</p>				
 <p>PCB 52 (2,2',5,5'-Tetrachlorobiphenyl)</p>		 <p>PCB 77 (3,3',4,4'-Tetrachlorobiphenyl)</p>		
 <p>PCB 95 (2,2',3,5',6-Pentachlorobiphenyl)</p>	 <p>PCB 99 (2,2',4,4',5-Pentachlorobiphenyl)</p>	 <p>PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl)</p>	 <p>PCB 84 (2,2',3,3',6-Pentachlorobiphenyl)</p>	 <p>PCB 110 (2,3,3',4',6-Pentachlorobiphenyl)</p>
 <p>PCB 123 (2,3',4,4',5'-Pentachlorobiphenyl)</p>	 <p>PCB 118 (2,3',4,4',5-Pentachlorobiphenyl)</p>	 <p>PCB 114 (2,3,4,4',5-Pentachlorobiphenyl)</p>	 <p>PCB 105 (2,3,3',4,4'-Pentachlorobiphenyl)</p>	
 <p>PCB 143 (2,2',3,4,5,6'-Hexachlorobiphenyl)</p>	 <p>PCB 146 (2,2',3,4',5,5'-Hexachlorobiphenyl)</p>	 <p>PCB 151 (2,2',3,5,5',6-Hexachlorobiphenyl)</p>	 <p>PCB 149 (2,2',3,4',5,6-Hexachlorobiphenyl)</p>	

literature methods (Method 1668C U.S. Environmental Protection Agency, April 2010). The organic extract was dried and diluted with a solution containing an internal standard.

The residual concentration of each single PCB in solution was determined by GC–MS analysis performed using a Shimadzu GC–MS 2000 QP Plus gas-chromatograph equipped with a SLB-5ms (30 m × 0.25 mm I.D., 0.25 μm film thickness) fused-silica capillary column from Supelco SLB-5ms, lot. 41579-03A. Ultra pure (99.999%) helium was used as carrier gas and the flow rate was maintained at 1.7 mL min⁻¹. 1 μL of each concentrated solution was injected using the Shimadzu Auto Injector AOC-20I, in splitless mode with a 0.61 min split delay. The injector was maintained at 250 °C and the detector at 270 °C. The GC temperature ramp increased: from 60 °C (1 min) to 170 °C (1 min) at a 30° min⁻¹ heating rate, from 170 °C to 300 °C at a 5° min⁻¹ rate and then from 300 °C to 330 °C (5 min) at 20° min⁻¹ rate.

The calibration was performed weekly. The data were acquired operating in single-ion monitoring (SIM) mode. Identification of the components of the standard mixture was carried out by comparing retention times for each component in the mixture with those of the

corresponding pure compounds analyzed under the same experimental conditions. Identification was confirmed by comparing the corresponding MS spectra.

The sorption capacity of the beads was determined by material mass balance of the initial and equilibrium concentrations of the solution. Adsorption on the glassware was found to be negligible and was determined by running several blank experiments. Each experiment was repeated three times and mean values were considered for the fitting process.

The adsorbed PCB amount for mass unit of adsorbent at equilibrium is reported in Eq. (1):

$$q_e = ((C_o - C_e) / m) V \quad (1)$$

where q_e (μg g⁻¹) is the amount of PCB adsorbed at equilibrium, C_o and C_e are the initial and equilibrium concentrations of PCB solutions (μg L⁻¹), V is the volume (liters) of the solution and m is the mass of the adsorbent used (grams).

3. Results and discussion

3.1. Bead characterization

The formation of hybrid beads, such as reported in literature, could be driven by polar interactions between the uncharged siloxane moieties of the clay and the hydroxyl groups of the alginate biopolymer (Cavallaro et al., 2013). Compared to normal alginate beads, the introduction of montmorillonite into alginate capsules was accompanied

by a significant change in color of the beads, from uncolored to white, easily detectable by the naked eye.

Fig. 1 shows the FT-IR spectra of calcium alginate beads (Fig. 1, top), montmorillonite (Fig. 1, middle) and alginate montmorillonite beads (Fig. 1, bottom).

The spectrum of Ca-alginate montmorillonite beads is a spectrum mix of alginate and montmorillonite. Differences between alginate montmorillonite beads and alginate beads are detectable at: 3631 cm^{-1} corresponding to OH stretching mode in molecular water and Si–OH; 1044 ,

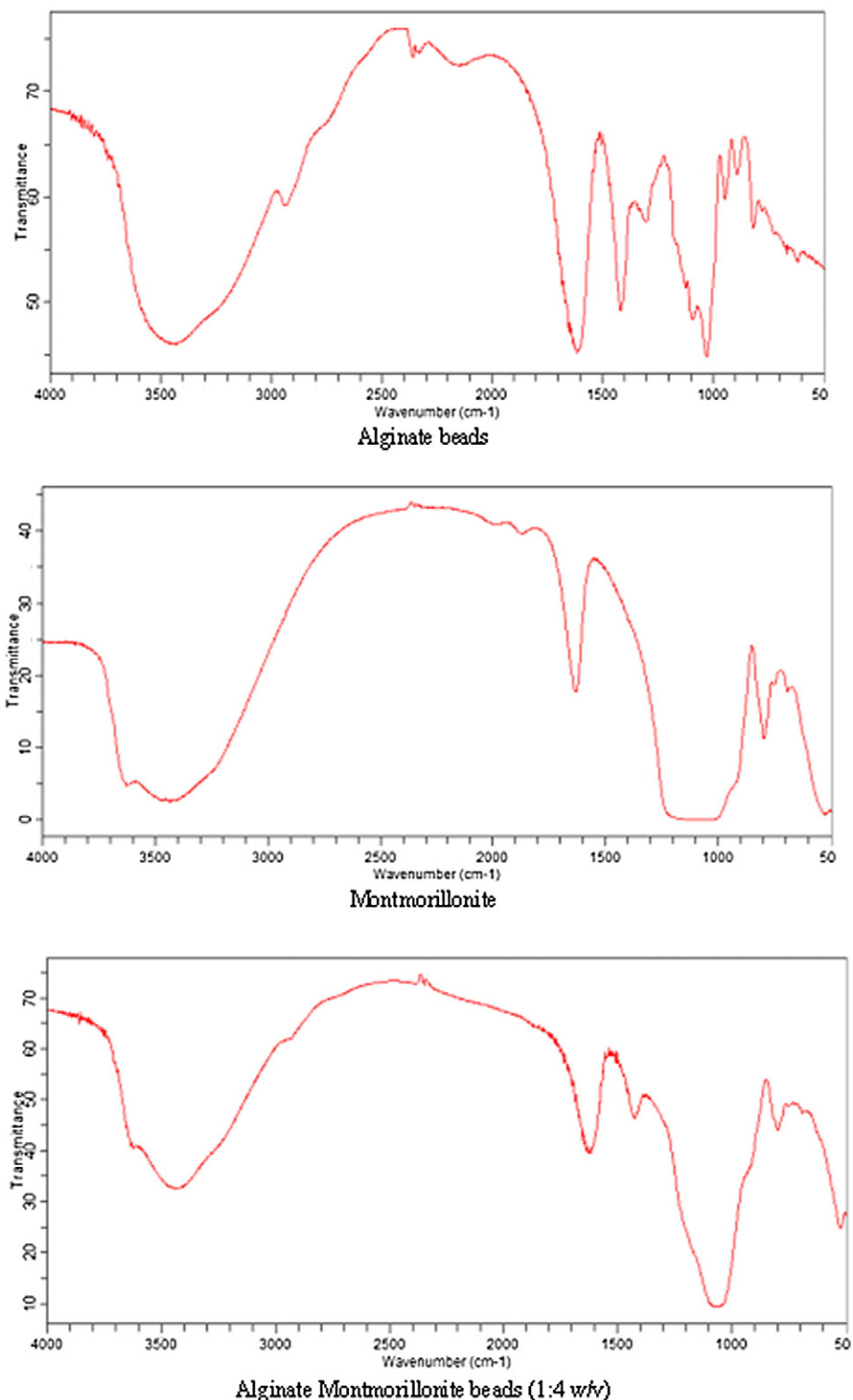


Fig. 1. FTIR spectra of alginate beads (top), montmorillonite (middle) and alginate montmorillonite beads (1:4 w/v) (bottom).

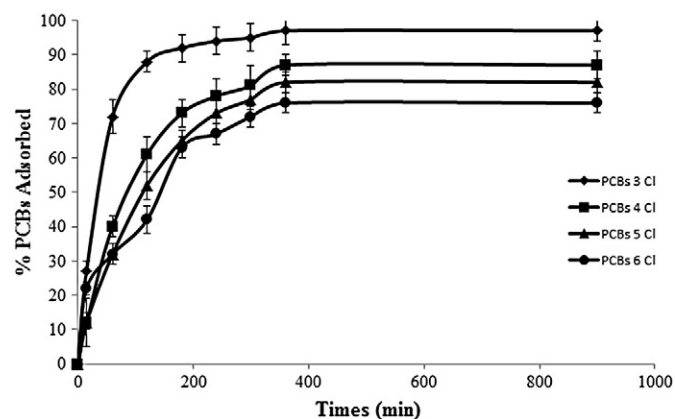


Fig. 2. Kinetic data for adsorption of PCBs by alginate montmorillonite beads. Each PCB solution ($10 \mu\text{g L}^{-1}$) was contacted with 100 mg alginate montmorillonite beads in aqueous solution at 25°C and pH 5.5.

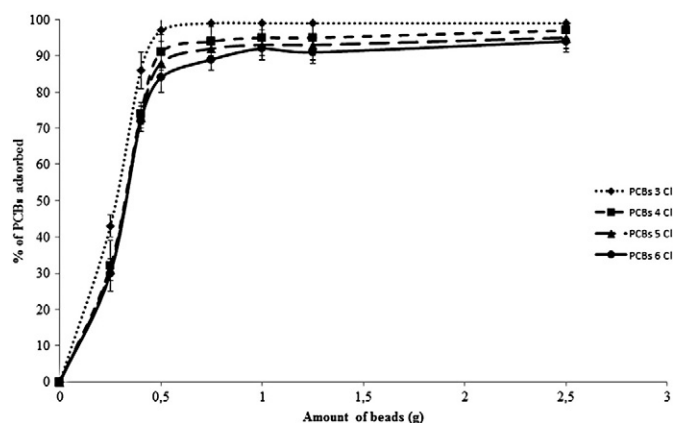


Fig. 3. The adsorbent dose effect on the adsorption of PCB mixture in alginate montmorillonite gel beads (initial PCB concentration $10 \mu\text{g L}^{-1}$).

623 and 523 cm^{-1} corresponding to Si–O stretching in $[\text{SiO}]_4^-$ tetrahedral; 916 cm^{-1} corresponding to Al–Al–OH bending vibration; and 798 cm^{-1} corresponding to Si–O in SiO_2 .

Differences between alginate montmorillonite beads and montmorillonite are detectable at: 2900 cm^{-1} corresponding to C–H stretching and 1623 and 1428 cm^{-1} corresponding to carboxylate antisymmetric/symmetric.

3.2. Effect of pH

Generally, the pH has an important effect on the adsorption of target compound by affecting the existing form of compound and the charge type and density on the sorbent's surface. To investigate the effect of pH on the adsorption of target compounds, either 0.1 M NaOH or 0.1 M HCl was added to the solutions containing PCBs.

PCBs exist as neutral molecules under ordinary conditions, which may cause their adsorption to be unaffected by charges on the surface of the sorbents.

The interaction between Ca alginate beads or montmorillonite clay and PCBs can be considered mainly as non-polar, and the forces responsible on the adsorption are physical van der Waals forces. This behavior provides potential for recovery of the adsorbate as well as regeneration of adsorbent by affecting simple nondestructive methods such as solvent washing.

The variation of pH in solutions containing the contaminants did not produce appreciable differences in the adsorption capacity of PCB using alginate montmorillonite beads. In fact, PCB adsorption remained constant in the range pH = 2.0–8.3 (data not shown).

This behavior is in agreement with literature data involving the adsorption of hydrophobic compounds by functionalized alginate beads (Zhang et al., 2010).

3.3. Adsorption kinetic study

The adsorption of PCB mixture was monitored from 1 to 16 h. The percentage of adsorption gradually increased during the first 6 h of

contact and remained constant after this time as observed for other organic pollutants in biomaterial beads (Chen et al., 2007).

The relationships between contact times and PCBs in solution adsorption are shown in Fig. 2.

These results could be explained considering that adsorption sites are more numerous and available at the beginning of the experiment.

Kinetic models can be used to determine the mechanism of adsorption and the efficiency of the adsorbents for the removal of pollutants. In this study, the adsorption data of PCBs by alginate–montmorillonite were fitted through two kinetic models including pseudo-first-order and pseudo-second-order. The pseudo-first order kinetic (Trivedi et al., 1973) is shown in Eq. (2).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of PCBs adsorbed on the alginate–montmorillonite beads, at equilibrium and at time (t), respectively. k_1 (1 h^{-1}) is the pseudo-first order rate constant. k_1 and q_e were determined from the slope and intercept of the linear plot of $\ln(q_e - q_t)$ vs t , respectively.

The experimental data were also analyzed by pseudo-second order model (Ho and McKay, 1999). This adsorption kinetic is shown by the equation where q_e and q_t have the same definition as those of pseudo-first order model. The pseudo-second order kinetic is shown in Eq. (3).

k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the pseudo-second order rate constant. k_2 and q_e can be determined from the intercept and slope of t/q_t versus t .

$$t/q_t = 1 / (k_2 q_e^2) + t/q_t \quad (3)$$

Table 2 shows the parameters for different kinetic models.

The higher linear correlation coefficient of the pseudo-second order model shows that this kinetic model fitted the data better than other kinetic models described earlier. Moreover, the q_e , calculated ($\mu\text{g g}^{-1}$) using this kinetic model, is reasonably similar to experimental q_e ($\mu\text{g g}^{-1}$) obtained from experimental data. The pseudo-second order kinetic parameters are presented in Table 1.

Table 2
Kinetic adsorption parameters of PCBs ($10 \mu\text{g L}^{-1}$) on alginate montmorillonite beads in aqueous solution at 25°C and pH 5.5.

C_0 ($5 \mu\text{g L}^{-1}$)	Pseudo-first order			Pseudo-second order			Experimental q_e ($\mu\text{g g}^{-1}$)
	K_1 (min^{-1})	q_e ($\mu\text{g g}^{-1}$)	R^2	K_2 ($\text{g mg}^{-1} \text{ min}^{-1}$)	q_e ($\mu\text{g g}^{-1}$)	R^2	
PCB 3 Cl	0.0147	1.53	0.988	0.0210	2.28	0.998	2.20
PCB 4 Cl	0.0131	2.10	0.992	0.0220	2.10	0.993	2.16
PCB 5 Cl	0.0117	2.45	0.899	0.0055	2.10	0.988	1.91
PCB 6 Cl	0.0106	2.24	0.968	0.0100	1.85	0.982	1.85

Table 3Fitted model of sorption isotherms of PCBs (from 2 to 15 $\mu\text{g L}^{-1}$) at different chlorination grades in alginate montmorillonite beads.

Analyte	Langmuir			Freundlich				Chapman		
	q_m ($\mu\text{g g}^{-1}$)	K	R^2	q_m ($\mu\text{g g}^{-1}$)	K	1/n	R^2	q_m ($\mu\text{g g}^{-1}$)	K	R^2
PCB 3 Cl	4.74	225.70	0.860	–	5.26	0.211	0.953	–	–	–
PCB 4 Cl	7.04	0.85	0.824	–	2.93	0.694	0.761	5.17	3.62	0.939
PCB 5 Cl	11.24	0.28	0.885	–	2.40	0.700	0.856	5.30	2.35	0.985
PCB 6 Cl	12.39	0.18	0.939	–	1.87	0.924	0.920	5.19	1.10	0.975

The pseudo-second order rate constant values, k_2 ranged from 0.0055 to 0.0220 $\text{g } \mu\text{g}^{-1} \text{ min}^{-1}$.

3.4. Effect of adsorbent dose

Effect of adsorbent dose was investigated by monitoring the amount of pollutant adsorbed from alginate–montmorillonite beads as a function of mass. The experiments were carried out increasing the mass of beads from 0.25 g to 2.5 g in the experiments keeping constant the volume (10 mL) and concentrations of PCB mixture (from 3 to 6 chlorination grade) in solutions (10 $\mu\text{g L}^{-1}$).

From Fig. 3, it is evident that PCB percentage removal increases rapidly with the mass of alginate–montmorillonite beads, due to the greater availability of binding sites of the sorbent.

Starting from penta-chlorinated PCBs, the adsorption reaches its maximum by using 2.5 g of alginate beads. Moreover, the percentage of removal varies with the chlorination degree.

Comparing adsorption results for PCBs of different chlorination grades, the sorbent showed a higher adsorption capacity for PCBs at low chlorination grade.

The adsorption of PCBs could not be correlated to physical parameters such as solubility and octanol–water partition coefficients. This behavior can be ascribed at different interaction types between PCBs at different chlorination grades and alginate montmorillonite beads. Moreover, Calace et al. (2002) observed the same trend in adsorption of other organic pollutants such as phenols on paper mill sludge.

3.5. Adsorption isotherms for PCB mixture in alginate–montmorillonite beads

An adsorption isotherm describes the relationship between the amount of pollutant that is adsorbed on the beads and the concentration of dissolved pollutant in the solution at equilibrium. Several models have been published (Foo and Hameed, 2010) to describe experimental data of adsorption isotherms.

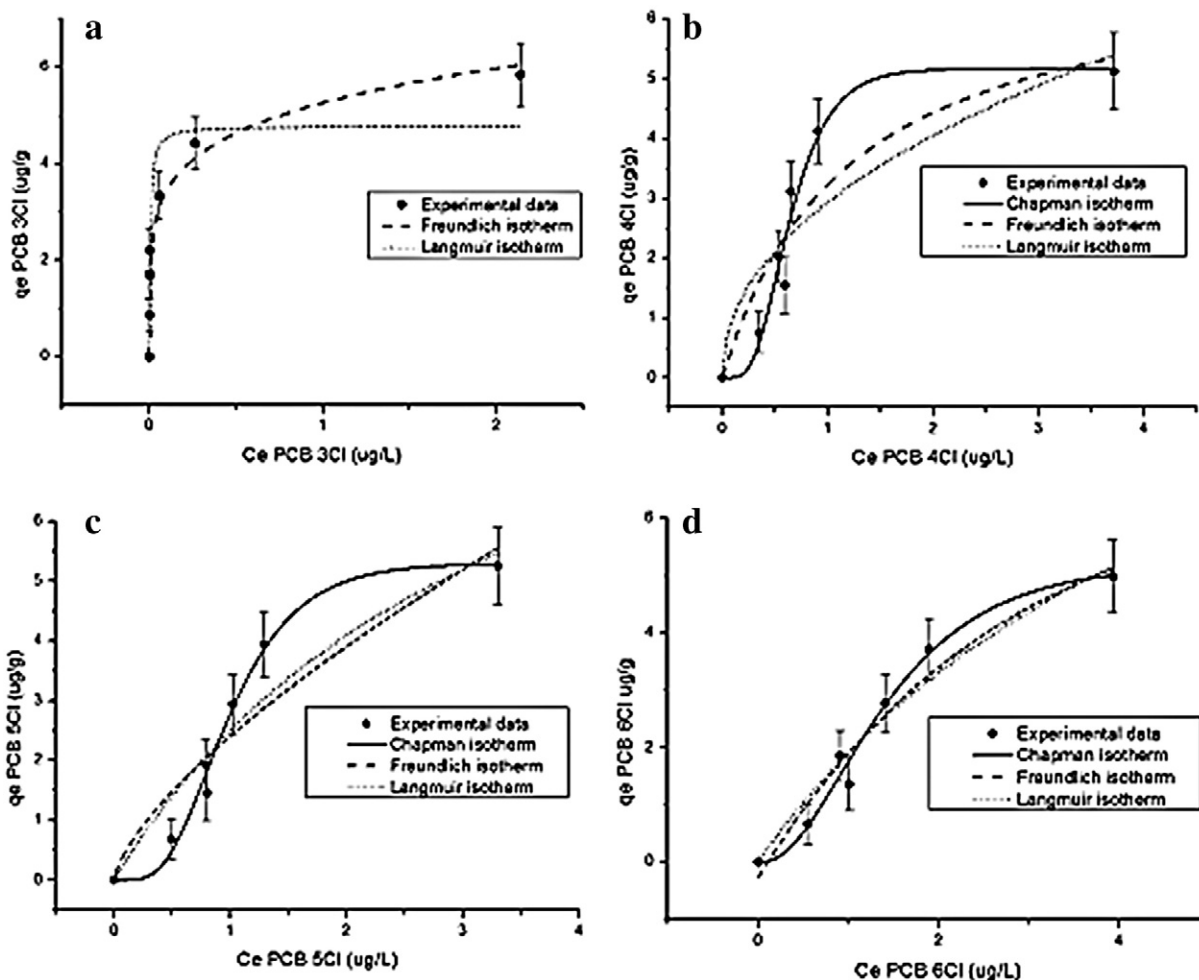


Fig. 4. Experimental isotherms for PCB adsorption on alginate montmorillonite beads. a) Tri-chlorinated PCB; b) tetra-chlorinated PCB; c) penta-chlorinated; d) hexa-chlorinated PCB.

Table 4
Fitted model of sorption isotherms of PCBs (from 2 to 15 $\mu\text{g L}^{-1}$) at different chlorination grades in alginate beads.

Analyte	Langmuir			Freundlich				Chapman		
	q_m ($\mu\text{g g}^{-1}$)	K	R^2	q_m ($\mu\text{g g}^{-1}$)	K	1/n	R^2	q_m ($\mu\text{g g}^{-1}$)	K	R^2
PCB 3 Cl	332.56	0.29	0.991	–	83.71	0.762	0.989	–	–	–
PCB 4 Cl	69.97	0.36	0.976	–	18.10	0.662	0.985	–	–	–
PCB 5 Cl	54.95	0.44	0.986	–	16.25	0.604	0.997	–	–	–
PCB 6 Cl	44.94	0.40	0.977	–	12.78	0.565	0.992	–	–	–

Langmuir, Freundlich and Chapman isotherm adsorption models were applied to analyze the relationship between the amounts of different PCBs adsorbed on the alginate–montmorillonite beads.

The Langmuir isotherm predicts the maximum monolayer adsorption capacity of the adsorbent. The expression of the Langmuir equation is reported in Eq. (4) (Langmuir, 1918):

$$q_e = (q_m K_L C_e) / (1 + K_L C_e) \quad (4)$$

where C_e (mg L^{-1}) is the adsorbate concentration at equilibrium time, q_e (mg g^{-1}) is the adsorption capacity of the adsorbent at equilibrium, K_L (L mg^{-1}) is the Langmuir constant and q_m (mg g^{-1}) is the maximum monolayer adsorption capacity (Ho and McKay, 1999). q_m and K_L are obtained from the intercept and slope of linear plot of $C_e q_e^{-1}$ versus C_e , respectively and are shown in Table 3.

The Freundlich isotherm model is usually employed for multilayer adsorption on a heterogeneous adsorbent surface (Koyuncu et al.,

2011). The non-linear expression of the Freundlich model is reported in Eq. (5):

$$q_e = K_F C_e^{(1/n)} \quad (5)$$

K_F is the Freundlich constant related to the sorbent capacity of alginate–montmorillonite beads and n is an empirical parameter representing the heterogeneity of site energies.

The Chapman isotherm model is based on the assumption of cooperative interactions between adsorbate molecules.

The expression of the Chapman sigmoidal equation is reported in Eq. (6):

$$q_e = q_m (1 - e^{-K C_e})^c \quad (6)$$

The value of q_m in the Chapman equation is related to the sorption capacity of sorbent. The constant terms of the Chapman equation (q_m , K and

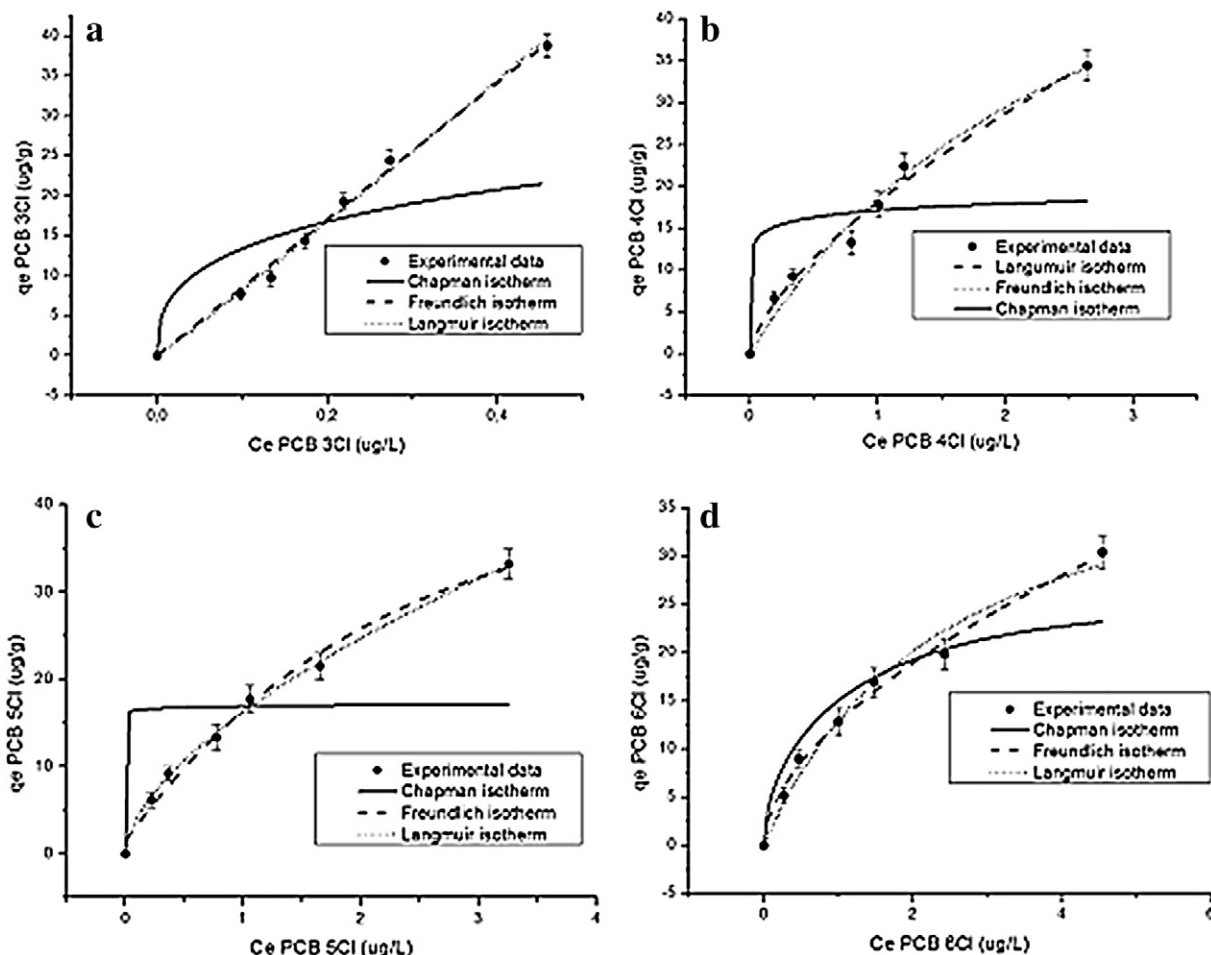


Fig. 5. Experimental isotherms for PCB adsorption on alginate beads. a) Tri-chlorinated PCB; b) tetra-chlorinated PCB; c) penta-chlorinated; d) hexa-chlorinated PCB.

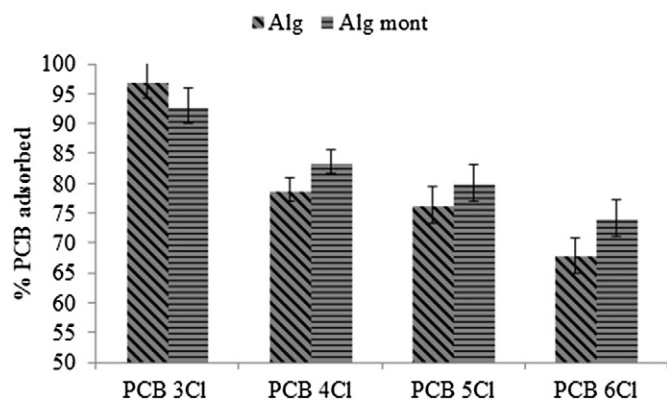


Fig. 6. Percentage of PCBs at different chlorination grades (from 3 to 6) adsorbed on alginate montmorillonite beads and alginate beads.

c) are listed with conventional constant terms of the Langmuir and Freundlich isotherm models along with their correlation coefficients (R^2) in Table 3.

q_m and K_F values obtained from the Langmuir and Freundlich isotherm models, respectively, could not give the proper information about its real maximum sorption capacity because both isotherm models were not found suitable for explaining the isotherm data due to low R^2 value of non-linear curve fitting (Fig. 4).

The results reported in Fig. 4 showed that all the PCBs, except for the trichlorinated biphenyls, displayed a sigmoid-shaped isotherm (or S-type isotherm) according to the Giles classification (Hinz, 2001). This trend could be ascribed to the different polarities of PCB classes.

Each isotherm showed small sorption at low concentrations of PCBs in the solution and the sorption increased with the solute concentration, indicating that solute–solute attractive forces are playing a role in the adsorption process. Thus, the Chapman sigmoidal equation appeared to have the best fit with the highest non-linear R^2 values for 4 Cl PCB (0.939), 5 Cl PCB (0.985), and 6 Cl PCB (0.975).

In Table 4 and Fig. 5 are reported the parameters for isothermal studies of PCBs adsorption by alginate beads alone. From Fig. 5 it is possible to verify that the isothermal curves for PCB adsorption in alginate beads are significantly different from those of alginate montmorillonite beads. The effect of montmorillonite addition on the adsorption capacity of alginate gel beads can be explained by considering a cooperative adsorption phenomenon (Hinz, 2001). In fact, the adsorption of non-polar organic compounds is a typical case of isothermal S-type. In particular, non-polar organic compounds have low affinity for clay but as soon as a clay surface is covered by these compounds, other organic molecules are adsorbed more easily (Pignatello, 2000). A similar behavior was observed for surfactants in naphthalene sorption by chitosan hydrogel beads (Lee et al., 2010).

Finally, to emphasize the effect of montmorillonite as filler in alginate beads, studies on the adsorption percentages for PCB mixture at low PCB concentrations ($2 \mu\text{g L}^{-1}$) as function of number of beads (10 beads, same volume of beads) were conducted and the results are reported in Fig. 6.

Data showed that adsorption differences are measurable (10%) for the adsorption of PCBs containing at least four chlorine atoms. The best removal efficiency was obtained by employing hybrid alginate montmorillonite beads.

4. Conclusions

We presented an economical and environmentally friendly system, based on hybrid beads consisting of alginate/montmorillonite components, for the PCB removal from aqueous media. Beads were used for sorption of PCB mixture at different chlorination grades. For PCBs containing more than three chlorine atoms, the adsorption isotherm can be well described by Chapman equation. The kinetic investigation

of PCB solution adsorption in alginate montmorillonite beads has shown that kinetic mechanism of adsorption best fits with a pseudo second order mechanism. By taking advantage of cooperative adsorption processes, hybrid alginate/montmorillonite beads could be a valid alternative for organic pollutant removal in wastewater treatment.

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References

- Aguzzi, C., Cerezo, P., Viseras, C., Caramella, C., 2007. Use of clays as drug delivery systems: possibilities and limitations. *Appl. Clay Sci.* 36, 22–36.
- Badwan, A., Abumaloo, A., Sallam, A., Abukalaf, A., Jawan, O., 1985. A sustained release drug delivery system using calcium alginate beads. *Drug Dev. Ind. Pharm.* 11, 239–248.
- Bailey, G.W., White, J.L., Rothberg, T., 1968. Adsorption of organic herbicides by montmorillonite: role of pH and chemical character of adsorbate. *Soil Sci. Soc. Am. Proc.* 32, 222–234.
- Barreca, S., Orecchio, S., Pace, A., 2013. Photochemical sample treatment for extracts clean up in PCB analysis from sediments. *Talanta* 103, 349–354.
- Barreca, S., Mazzola, A., Orecchio, S., Tuzzolino, N., 2014a. PAHs and PCBs in sediments from Sicilian coastal area (Scoglitti) using automated Soxhlet, GC–MS and principal component. *J. Polycycl. Aromat. Compd.* <http://dx.doi.org/10.1080/10406638.2014.886078>.
- Barreca, S., Velez Colmenares, J.J., Pace, A., Orecchio, S., Pulgarin, C., 2014b. Neutral solar photo-Fenton degradation of 4-nitrophenol on iron-enriched hybrid montmorillonite–alginate beads (Fe-MABs). *J. Photochem. Photobiol. A Chem.* <http://dx.doi.org/10.1016/j.jphotochem.2014.02.008>.
- Bayramoglu, G., Denizli, A., Bektas, S., Arica, M.Y., 2002. Entrapment of *Lentinus sajor-caju* into Ca–alginate gel beads for removal of Cd(II) ions from aqueous solution: preparation and biosorption kinetics analysis. *Microchemical J.* 72, 63–76.
- Bee, A., Talbot, D., Abramson, S., Dupuis, V., 2011. Magnetic alginate beads for Pb(II) ions removal from wastewater. *J. Colloid Interface Sci.* 362, 486–492.
- Bleiman, N., Mishael, Y.G., 2010. Selenium removal from drinking water by adsorption to chitosan–clay composites and oxides: batch and column tests. *J. Hazard. Mater.* 183, 590–595.
- Brigante, M., Zanini, G., Avena, M., 2013. Effects of montmorillonite on the chemical degradation kinetics of metsulfuron methyl in aqueous media. <http://dx.doi.org/10.1016/j.jclay.2013.03.018>.
- Calace, N., Nardi, E., Petronio, B.M., Pietroletti, M., 2002. Adsorption of phenols by paper mill sludge. *Environ. Pollut.* 118, 315–319.
- Cavallaro, G., Gianguzza, A., Lazzara, G., Milioto, S., Piazzese, D., 2013. Alginate gel beads filled with halloysite nanotubes. *Appl. Clay Sci.* 72, 132–137.
- Celis, R., Adelino, M.A., Herminos, M.C., Cornejo, J., 2012. Montmorillonite–chitosan bionanocomposites as adsorbents of the herbicide clopyralid in aqueous solution and soil/water suspensions. *J. Hazard. Mater.* 209–210, 67–76.
- Chatterjee, S., Lee, M.W., Woo, S.H., 2010. Adsorption of Congo Red by chitosan hydrogel beads impregnated with carbon nanotubes. *Bioresour. Technol.* 101, 1800–1806.
- Chen, C.Y., Chang Chen, C., Chien Chung, Y., 2007. Removal of phthalate esters by cyclodextrin-linked chitosan bead. *Bioresour. Technol.* 98, 2578–2583.
- Chia Yang, H., Hsiung Hon, M., 2009. The effect of the molecular weight of chitosan nanoparticles and its application on drug delivery. *Microchemical J.* 87–91.
- Delle Site, A., 2001. Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. *J. Phys. Chem.* 187–439.
- Ely, A., Baudu, M., Beasley, J.P., Kankou, M.O.S.A.O., 2009. Copper and nitrophenol pollutants removal by Na–montmorillonite/alginate microcapsules. *J. Hazard. Mater.* 171, 405–409.
- Fernández-Pérez, M., Villafranca-Sánchez, M., González-Pradas, E., Flores-Céspedes, F., 1999. Controlled release of diuron from an alginate–bentonite formulation: water release kinetics and soil mobility study. *J. Agric. Food Chem.* 47, 791–798.
- Foo, K.Y., Hameed, B.H., 2010. Insights into the modeling of adsorption isotherm systems. *Chem. Eng. J.* 156, 2–10.
- Frame, G.M., Wagner, R.E., Carnahan, J.C., Brown, J.F., May, R.J., Smullen, L.A., Bedard, D.L., 1996. Comprehensive, quantitative, congener-specific analyses of eight aroclors and complete PCB congener assignments on DB 1 capillary GC columns. *Chemosphere* 33, 603–623.
- Gerstl, Z., Nasser, A., Mingelgrin, U., 1998. Controlled release of pesticides into water from clay–polymer formulations. *J. Agric. Food Chem.* 46, 3803–3809.
- Giesy, J.P., Kannan, K., 1998. Dioxin-like and non-dioxin-like toxic effects of polychlorinated biphenyls (PCBs): implications for risk assessment. *Crit. Rev. Toxicol.* 28, 511–569.
- Griffin, R.A., Shimp, N.F., 1976. Effect of pH on exchange-adsorption or precipitation of lead from landfill leachates by clay minerals. *Environ. Sci. Technol.* 10, 1256–1261.
- Guibal, E., Pinol, A.F., Ruiz, M., Vincent, T., Jouannin, C., Sastre, A.M., 2010. Immobilization of Cyphos ionic liquid in alginate capsules for Cd(II) sorption. *Sep. Sci. Technol.* 45, 1935–1949.
- Hinz, C., 2001. Description of sorption data with isotherm equations. *Geoderma* 99, 225–243.

- Ho, Y., McKay, G., 1999. Pseudo-second order model for sorption processes. *Process Biochem.* 34, 451–465.
- Inoue, K., Yoahizuka, K., Baba, Y., 1996. Adsorption of metal ions on chitosan and its derivatives. In: Abe, M., Suzuki, T. (Eds.), *New Development in Ion Exchange*. Kodansha, Tokyo.
- Jing, G., Wang, L., Yu, H., Amer, W.A., Zhang, L., 2013. Recent progress on study of hybrid hydrogels for water treatment. *Colloids Surf. A Physicochem. Eng. Asp.* 416, 86–94.
- Juang, R.S., Ju, C.Y., 1998. Kinetics of sorption of Cu(II)-ethylenediaminetetraacetic acid chelated anions on cross-linked polyaminated chitosan beads. *Ind. Eng. Chem. Res.* 37, 386.
- Kittinaovarat, S., Kansomwan, P., Jiratumnukul, N., 2010. Chitosan/modified montmorillonite beads and adsorption Reactive Red 120. *Appl. Clay Sci.* 48, 87–91.
- Koyuncu, H., Yildiz, N., Salgin, U., Koroglu, F., 2011. Adsorption of o-, m- and p-nitrophenols onto organically modified bentonites. *J. Hazard. Mater.* 185, 1332–1339.
- Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* 40, 1361–1403.
- Lee, S., Chatterjee, D.S., Lee, M.W., Woo, S.H., 2010. Enhanced molar sorption ratio for naphthalene through the impregnation of surfactant into chitosan hydrogel beads. *Bioresour. Technol.* 101, 4315–4321.
- Meneses, M., Scumacher, M., Domingo, J.L., 2002. A design of two simple models to predict PCDD/F concentrations in vegetation and soils. *Chemosphere* 46, 1393–1402. Method 1668C U.S. Environmental Protection Agency, April 2010.
- Montarges, E., Moreau, A., Michot, L.J., 1998. Removing of organic toxicants from water by Al₃-pluronic modified clay. *Appl. Clay Sci.* 13, 165–185.
- Orecchio, S., 2010a. Assessment of polycyclic aromatic hydrocarbons (PAHs) in soil of a Natural Reserve (Isola delle Femmine) (Italy) located in front of a plant for the production of cement. *J. Hazard. Mater.* 3, 358–368.
- Orecchio, S., 2010b. Contamination from polycyclic aromatic hydrocarbons (PAHs) in the soil of a botanic garden localized next to a former manufacturing gas plant in Palermo (Italy). *J. Hazard. Mater.* 180, 590–601.
- Orecchio, S., Cannata, S., Culotta, L., 2010. How building an underwater pipeline connecting Libya to Sicilian coast is affecting environment: polycyclic aromatic hydrocarbons (PAHs) in sediments; monitoring the evolution of the shore approach area of the Gulf of Gela (Italy). *J. Hazard. Mater.* 181, 647–658.
- Pace, A., Barreca, S., 2013. Environmental organic photochemistry: advances and perspectives. *Curr. Org. Chem.* 17, 3032–3041.
- Pignatello, J.J., 2000. The measurement and interpretation of sorption and desorption rates for organic compounds in soil media. *Adv. Agron.* 69, 1–73.
- Rendevski, S.J., Andonovski, A.N., 2005. Reaggregation of sodium alginate microgel structures after shear-induced deaggregation at filtering. *Polym. Bull.* 54, 93–100.
- Rhee, J.S., Jung, M.W., Paeng, K.J., 1998. Evaluation of chitin and chitosan as a sorbent for the preconcentration of phenol and chlorophenols in water. *Anal. Sci.* 14, 1089–1092.
- Roger, S., Talbot, D., Bee, A., 2006. Preparation and effect of Ca²⁺ ions on water solubility, particle release and swelling properties of magnetic alginate films. *J. Magn. Magn. Mater.* 305, 221–227.
- Silva, R.M.P., Manso, J.P.H., Rodrigues, J.R.C., Lagoa, R.J.L., 2008. A comparative study of alginate beads and an ion-exchange resin for the removal of heavy metals from a metal plating effluent. *J. Environ. Sci. Health A* 43, 1311–1317.
- Sinkkonen, S., Paasivirta, J., 2000. Degradation half-life times of PCDDs, PCDFs and PCBs for environmental fate modeling. *Chemosphere* 40, 943–949.
- Stevens, J., Green, N.J.L., Jones, K.C., 2001. Survey of PCDD/Fs and non-ortho PCBs in UK sewage sludges. *Chemosphere* 44, 1455–1462.
- Trivedi, H., Patel, V., Patel, R., 1973. Adsorption of cellulose triacetate on calcium silicate. *Eur. Polym. J.* 9, 525–531.
- Van Jaarsveld, J.A., Van Pul, W.A.J., De Leeuw, F.A.A.M., 1997. Modelling transport and deposition of persistent organic pollutants in the European region. *Atmos. Environ.* 31, 1011–1024.
- Vincent, T., Parodi, A., Guibal, E., 2008. Pt recovery using Cyphos 1L-101 immobilized in biopolymer capsules. *Sep. Purif. Technol.* 62, 470–479.
- Yamani, J.S., Miller, S.M., Spaulding, M.L., Zimmerman, J.B., 2012. Enhanced arsenic removal using mixed metal oxide impregnated chitosan beads. *Water Res.* 46, 4427–4434.
- Zhang, S., Niu, H., Cai, Y., Shi, Y., 2010. Barium alginate caged Fe₃O₄ C18 magnetic nanoparticles for the pre-concentration of polycyclic aromatic hydrocarbons and phthalate esters from environmental water samples. *Anal. Chim. Acta.* 665, 167–175.
- Zhu, H.Y., Jiang, R., Xiao, L., Zeng, G.M., 2010. Preparation, characterization, adsorption kinetics and thermodynamics of novel magnetic chitosan enwrapping nanosized γ -Fe₂O₃ and multiwalled carbon nanotubes with enhanced adsorption properties for methyl orange. *Bioresour. Technol.* 101, 5063–5069.