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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 $m^2 g^{-1}$, 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, PC146, 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 $CaCl_2$.

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

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