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Influence of a cationic surfactant on adsorption of p-nitrophenol by a magsorbent based on magnetic alginate beads

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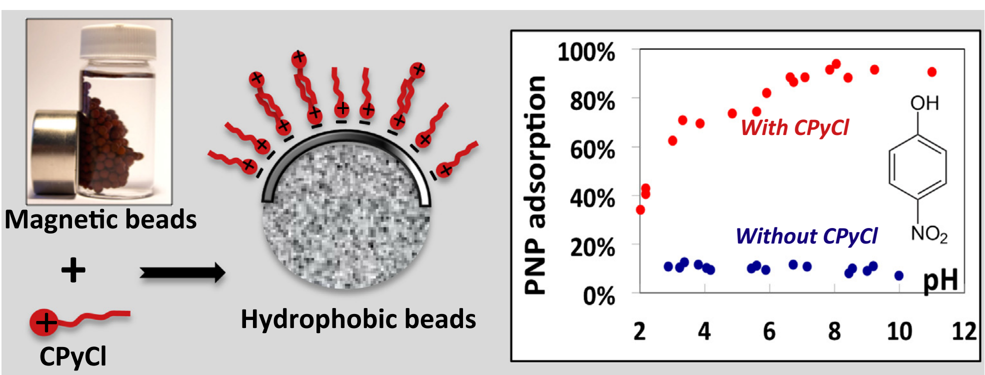
GRAPHICAL ABSTRACT



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ABSTRACT

The paper focuses on the removal of p-nitrophenol by an adsorption process. A magnetic adsorbent was synthesized by encapsulation of magnetic functionalized nanoparticles using alginate as a green biopolymer matrix. A cationic surfactant, cetylpyridinium chloride (CPyCl), was used to confer a hydrophobic character to the magnetic beads and thus to promote their adsorption efficiency. The effect of different parameters such as initial concentrations of both PNP and CPyCl, contact time and solution pH value on the adsorption of PNP in the presence of CPyCl was investigated. It should be noted that combination of magnetic and adsorption properties in a same material is an interesting challenge which could overcome the recovery problems of pollutant-loaded adsorbent.

Abbreviations: PNP, p-nitrophenol; CPyCl, cetylpyridinium chloride.

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Adsolubilisation
p-Nitrophenol

1. Introduction

Sustainable water supply has become a real challenge. Indeed, in today's world, many chemical compounds resulting from human activity are found in water and among them, some act as endocrine disruptors. In order to improve the quality of water, and especially water for human consumption, various processes are developed. Among them, adsorption is widely used for being of low-cost, easy to handle and efficient for the removal of pollutants. Today, activated carbon (AC) is one of the most efficient adsorbents used in industrial processes of water purification due to its high porosity and very large surface area. Despite its efficiency, its use is limited by process engineering difficulties due to its high regeneration cost and loss of materials during its recovery.

To overcome these limitations, cost-effective and environmental friendly materials such as natural biopolymers have been extensively studied to remove pollutants from water by an adsorption process [1–9]. Moreover, due to the encapsulation ability of these biopolymers, advanced materials could be developed to perform adsorption process with subsequent separation. In this framework, the entrapment of magnetic nanoparticles in biopolymer matrix has received considerable attention in recent years. Indeed, the use of magnetic adsorbents (called here magsorbents) is a promising way due to their easy and fast removal from water through the application of an external field [10–12]. Several efficient magnetic adsorbents have been reported in the literature but most of them are especially effective in the removal of cationic or anionic pollutants [13–18]. The difficulty increases for removing of weakly ionisable or non-ionic organic pollutants. The use of a surfactant, which confers a hydrophobic character to the adsorbent, could be an efficient approach for the removal of such pollutants [19–27]. If the effects of surfactants on the sorption of organic compounds have been extensively studied for the extraction and preconcentration of various organic pollutants, few studies report the removal of hydrophobic compounds by magnetic adsorbents modified with a surfactant [28–30] and even less by magnetic biogels. The purpose of this study was thus to provide a material that has both magnetic properties and efficiency in the removal of weakly ionisable organic compounds by using a surfactant; cetylpyridinium chloride (CPyCl) was selected as a representative cationic surfactant and alginate beads with encapsulated magnetic nanoparticles were used as magsorbent. The effect of the pH solution, time contact and initial concentrations of both surfactant CPyCl and pollutant p-nitrophenol (PNP) on adsorption by hydrophobically modified alginate beads was investigated and an adsorption mechanism was proposed. Regeneration experiments were also carried out. PNP was chosen because it is widely used in industries such as high-temperature coal conversion, petroleum refining, and resins and plastics manufacturing.

2. Experimental

2.1. Materials

Alginate is a natural linear polysaccharide extracted from seaweeds. It is constituted from β-d-mannuronate (M) and α-l-guluronate (G) units arranged in blocks rich in G units (G-block) or M units (M-block) separated by blocks of alternating G and M units (MG-block) [31]. In addition, alginate is one of the main encapsulating compounds used in pharmaceutical compositions. The weight average molar weight (M_w) and the number average molar weight (M_n) of the used sodium alginate, obtained by gel permeation chromatography, are respectively equal to 2.07×10^5 and 1.08×10^5 g/mol, leading to a polydispersity index (I_P) equal to 1.91. The amount of carboxylate functions of alginate (p*K*a = 3.4–4.2 [1,32]) was obtained from the dosage of their sodium counter ions ($[Na]_{alg}$) by atomic absorption spectrometry with a Perkin–Elmer Analyst 100 apparatus. It is equal to 4.2 ± 0.1 mmol/g_{alg}.

P-nitrophenol ($C_6H_5NO_3$ noted PNP) is a weak acid (p*K*a ≈ 7.2 [33,34]) with a molecular weight equal to 139.11 g/mol. In aqueous solution, the molecular form of PNP appears colourless whereas its phenolic salt is bright yellow.

Cetylpyridinium chloride ($C_{21}H_{38}ClN{\cdot}H_2O$ noted CPyCl) is a quaternary ammonium surfactant with a pyridine group; its molecular weight is equal to 358 g/mol. The critical micelle concentration (CMC), as determined by surface tension measurements at 25 °C by [22] is equal to 0.83 mmol/L.

Calcium solutions were prepared by dissolving a known quantity of $CaCl_2$, $2H_2O$ in distilled water.

The magnetic nanoparticles and magnetic alginate beads (called MagAlgbeads) used in this work were the same as that previously used in [35]. Briefly, magnetic material was a ferrofluid composed of maghemite (γ-Fe_2O_3) nanoparticles synthesized according to the Massart's method [36,37] and coated by citrate ions. Citrate is the basic form of citric acid, a triacid with p*K*a values equal to 2.79, 4.30, 5.65) [38]. The stability of the ferrofluid is due to the ionisation of adsorbed citrate ions that are deprotonated at the pH value of the ferrofluid (pH ≈ 7.5); the particles are then anionic ones with sodium counterions due to the carboxylate functions of adsorbed citrate. This magnetic material is a polydisperse system of rocklike nanoparticles, which can be described as spheres. Their mean diameter (d_0) and polydispersity index (σ) obtained by a two-parameter fit of the magnetisation curve are equal to 7.2 nm and 0.35 respectively [39]. The iron concentration of the ferrofluid, obtained by atomic absorption spectrometry, is equal to 1.33 mol/L (106.4 $g_{maghemite}$/L).

The magnetic alginate beads were prepared by dropping an alginate/ferrofluid mixture ($m_{alginate}/m_{maghemite} = 0.5$) into a $CaCl_2$ solution and stored in deionized water. Beads appear brown due to the ferrofluid encapsulation (maghemite content = 64±2% w/w dry beads) and roughly spherical with a millimetric size (diameter = 3.3 ± 0.2 mm) (Fig. 1). The moisture content is equal to 94.6 ± 0.1%. Beads present magnetic properties; all beads are attracted when tested with a magnet. After the crosslinking process in the calcium bath, the counterions of the carboxylate functions coming from both alginate and citrate coating of the nanoparticles are calcium ions. Therefore, the number of negative sites of the beads (noted *N*) was deduced from Ca content obtained by atomic absorption spectrometry (N = 1.5 ± 0.1 mmol/g of dried beads). All products were purchased from Fluka and used without purification.

2.2. Adsorption experiments

Batch adsorption experiments were carried out at room temperature (≈20 °C). An appropriate mass of wet MagAlgbeads (noted m_b) was suspended into the cationic surfactant solution at a given initial concentration noted $C_{0,CPyCl}$. PNP solution was added into the mixture, its initial concentration is noted $C_{0,PNP}$. Initial concentrations were expressed in mmol/L or in mmol/g of dried beads.