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Adsorption of a cationic surfactant by a magsorbent based on magnetic alginate beads

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ABSTRACT

Adsorption of cetylpyridinium chloride (CPC), a cationic surfactant, by magnetic alginate beads (MagAlgbeads) was investigated. The magnetic adsorbent (called magsorbent) was prepared by encapsulation of magnetic functionalized nanoparticles in an alginate gel. The influence on CPC adsorption of several parameters such as contact time, pH and initial surfactant concentration was studied. The equilibrium isotherm shows that adsorption occurs through both electrostatic interactions with charge neutralization of the carboxylate groups of the beads and hydrophobic interactions inducing the formation of surfactant aggregates in the beads. The dosage of calcium ions released in the solution turns out to be a useful tool for understanding the adsorption mechanisms. Adsorption is accompanied by a shrinking of the beads that corresponds to a 45% reduction of the volume. Adsorption kinetic experiments show that equilibrium time is strongly dependent on the surfactant concentration, which monitors the nature of the interactions. On the other hand, since the pH affects the ionization state of adsorption sites, adsorption depends on the pH solution, maximum adsorption being obtained in a large pH range (3.2–12) in agreement with the pK_a value of alginate (pK_a = 3.4–4.2). Finally, due to the formation of micelle-like surfactants aggregates in the magnetic alginate beads, they could be used as a new efficient magsorbent for hydrophobic pollutants.

1. Introduction

Surfactants are widely used in various domestic and industrial fields. They are present in a large variety of processes and products such as soaps, detergents, disinfectants, pharmaceuticals biocides, emulsifiers, wetting agents, processing additives, hair conditioning, cosmetics and personal care products. Thereby, surfactants are present in many effluents. Due to their surface-active nature, surfactants have toxic effects on some organisms and need to be removed from water to avoid environmental damages and problems of public health [1]. Numerous methods are developed for the removal of pollutants from water and wastewater; their combination is often needed for a better efficiency. Among them, adsorption is considered as one of the most effective processes. In recent years, the search of adsorbents based on natural polymers has intensified [2–6]. Due to their low costs and environmental friendly properties, they can offer an alternative to conventional adsorbents such as activated carbon, which is the most common adsorbent used for water treatment, but factors such as its high regeneration cost and its dispersion make the engineering process difficult and restrict its use. Nevertheless, it is difficult to separate the pollutants-loaded adsorbents from the water; to overcome this problem, magnetic separation has received considerable attention in recent years [7–13]. Indeed, the fast and cost-effective separation of magnetic composites from a medium through the use of a magnetic field gradient obtained with a magnet or an electromagnet is a promising method, which could be also used in various areas of biosciences and biotechnologies [14,15]. In particular, in combination with other classical processes of water treatment, magnetic process could facilitate the decontamination of water if efficient adsorbents are used.

Alginate, which is a natural linear polysaccharide extracted from seaweeds is a good candidate to formulate green adsorbents.

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Indeed, it is bio-compatible, biodegradable, easily produced and cost effective. It is made up from β-d-mannuronate (M) and α-l-guluronate (G) units arranged in blocks of G units (G-blocks) or M units (M-blocks), separated by blocks of alternating G and M units [16]. With a carboxylate function per unit, alginate is a negative polyelectrolyte making it a suitable agent to remove cationic surfactants. This idea is supported by the fact that polyelectrolyte and surfactant can form stable complexes, driven by both electrostatic and hydrophobic strong interactions [17–19].

Alginate has also been extensively studied for its ability to form gels in the presence of divalent cations. It is one of the main encapsulating compounds which is widely used in pharmaceutical compositions. This property makes alginate a suitable matrix to easily encapsulate magnetic nanoparticles for manufacturing magnetic green adsorbents (called magsorbents, general term we use to name our different magnetic adsorbents). Magnetic nanoparticles are also efficient adsorbents but due to the human health and safety risks associated with nanotechnology, their encapsulation into a biopolymer matrix could be a solution to prevent their risks.

The aim of this work was to probe magnetic alginate beads (called MagAlgbeads) as an adsorbent for cationic surfactants. The use of this material as an alternative adsorbent was dictated by two considerations: it is based on natural products, and it can be easily recovered by magnetic separation. Another interest of magnetic alginate beads is the facility to prepare them by a simple extrusion method allowing developments on an industrial scale. In addition, one of the advantages to use this system for the water treatment also derives from the particular properties of the adsorbed surfactant. At low concentrations, surfactant molecules exist in the monomeric state in aqueous solution. When their concentration increases to reach the critical micelle concentration (cmc), they begin to self-associate to form micelles. In a gel network, micelle-like aggregates could be formed inside the polymer matrix even before the cmc [20]. These aggregates may confer to the magnetic alginate/cationic surfactant system the property to adsorb hydrophobic pollutants unadsorbed by alginate alone. Cetylpyridinium chloride (CPC) was chosen as a cationic model surfactant. The influence on adsorption of several parameters such as contact time, pH and initial CPC concentration was studied.

2. Materials and methods

2.1. Chemicals

Sodium alginate powder was purchased from Fluka. The weight average molar weight (M_w) and the number average molar weight (M_n), obtained by gel permeation chromatography (GPC), 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 binding sites of alginate are due to their carboxylate functions ($pK_a = 3.4–4.2$) [21,22]. The sodium content of alginate ($[Na]_{alg}$), equal to 4.2 ± 0.1 mmol/g_{alg}, is directly related to the number of carboxylate functions. It was obtained by atomic absorption spectrometry with a Perkin–Elmer Analyst 100 apparatus.

Cetylpyridinium chloride ($C_{21}H_{38}ClN{\cdot}H_2O$ noted CPC) was purchased from Fluka. The critical micelle concentration (cmc), as determined by surface tension measurements at 25 °C by [23] is equal to 8.3×10^{-4} mol/L; the authors showed that cmc drops to 2.4×10^{-4} mol/L in the presence of 0.01 mol/L NaC1. The concentration of CPC in the samples was determined, after adequate dilution, by UV spectroscopy at 259 nm using an UV–Visible UVIKON XL (Secoman) spectrophotometer. We first performed a calibration curve to determine the molar extinction coefficient at 259 nm ($\varepsilon = 4271$ cm^{-1}mol^{-1}).

Calcium solutions were prepared by dissolving a known quantity of $CaCl_2$, $2H_2O$ (Carlo Erba Reagenti) in distilled water.

2.2. Ferrofluid

The magnetic material was a ferrofluid composed of maghemite (γ-Fe_2O_3) nanoparticles coated by citrate ions and dispersed in an aqueous solution. Nanoparticles were synthesized according to a method described in previous papers [24,25]. Briefly, magnetite (Fe_3O_4) particles were synthesized by coprecipitation of a stoichiometric mixture of ferrous and ferric chlorides in an ammonium hydroxide solution. The magnetic precipitate so obtained was acidified by nitric acid and oxidized in maghemite (γ-Fe_2O_3) at 90 °C with iron (III) nitrate. The maghemite nanoparticles were then washed with acetone and ether before being dispersed into water (acid ferrofluid). To obtain a magnetic dispersion stable at the neutral pH of an alginate solution, a surface treatment was needed. Trisodium citrate was thus added to the acid ferrofluid (33.6 g per mol of iron). The mixture was stirred for 30 min at 80 °C. After washing and dispersion in water, a stable ferrofluid was obtained with a pH value close to 7.5 (Fig. 1a).

The iron concentration of the ferrofluid ($[Fe]_{FF}$) determined by atomic absorption spectrometry is equal to 1.33 mol/L. Before analysis, magnetic particles were carried up to ebullition in concentrate HCl until the total dissolution of the particles in Fe(III) ions. The morphology of the particles was determined by transmission electron microscopy (JEOL 100 CX). Micrographs show a polydisperse system of rocklike nanoparticles which can be described as spheres (Fig 1b). X-ray diffraction of the powdered ferrofluid was performed with a Rigaku Ultima IV diffractometer using Cu Kα radiation ($\lambda = 1.54056$ Å). The diffraction pattern (Fig. 2) shows the peaks that correspond to the maghemite structure (JCPDS 39-1346). The X-ray diameter of the nanoparticles deduced from the Scherrer equation was equal to 6.4 nm. The size of the nanoparticles was also determined from magnetic measurements using a commercial Quantum Design SQUID MPMS magnetometer (Fig. 2). The mean diameter of the particles (d_0) and the polydispersity index (σ) were obtained by a two-parameter fit of the magnetization curve ($d_0 = 7.2$ nm and $\sigma = 0.35$) [26]. Magnetic measurements also allow calculating the iron concentration of the ferrofluid; it is equal to 1.39 mol/L, which is in agreement with the value previously obtained by atomic absorption spectrometry.

The stability of the aqueous dispersion of magnetic nanoparticles is due to the ionization of adsorbed citrate ions. A surface complexation involving, on average, one or two carboxylate functions of the adsorbed citrate is considered [27]; electrostatic repulsions are then achieved by the unbound carboxylate functions. At the pH value of the ferrofluid (pH = 7.5), the three carboxylate functions of the citrate ions are unprotonated ($pK_a = 2.79$, 4.30, 5.65)[28]; the particles are then anionic ones with sodium counterions. The amount of sodium counterions ($[Na]_{FF}$), obtained by atomic absorption spectrometry is equal to 0.61 mmol/$g_{maghemite}$. The ionic strength of the dispersion due to unadsorbed trisodium citrate is equal to 0.56 mol/L.

2.3. MagAlgbeads synthesis

The preparation of magnetic alginate beads was performed according to the protocol described previously [9]. Briefly, a solution containing 3.0 g of sodium alginate in 150 mL of distilled water was added to 56.4 mL of ferrofluid ($[Fe]_{FF} = 1.33$ mol/L) under stirring. The mixture was completed with distilled water to obtain the final volume of 300 mL. The mixture alginate/ferrofluid was then introduced into a plastic syringe equipped with a needle (inner diameter = 1.1 mm). The beads were formed by dropping this mixture using a Kd Scientific 410 push–pull syringe pump