



Hybrid nanoadsorbents for the magnetically assisted removal of metoprolol from water

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HIGHLIGHTS

- Synthesis of Fe₃O₄ nanoparticles coated with κ-carrageenan hybrid siliceous shells.
- Magnetic hybrids for the uptake of metoprolol tartrate from water.
- The adsorption capacity enhanced 300% compared with the best sorbent in literature.
- Easy separation of sorbents from water under a magnetic gradient.

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ABSTRACT

Metoprolol (MTP) is known as one of the most frequently detected beta blockers in surface waters, with potentially harmful impact on environment and human health due to its widespread use and resistance to hydrolysis. The removal of MTP in wastewater treatment plants is still very low due to fairly ineffective conventional water treatment procedures and, therefore, more efficient treatments are needed. To tackle this challenge, novel biosorbents composed of magnetite nanoparticles functionalized by κ-carrageenan hybrid siliceous shells (Fe₃O₄@SiO₂/SiCRG) were successfully prepared and tested in magnetically assisted removal of metoprolol tartrate from aqueous solutions. The MTP adsorption by the produced core-shell composite structures was thoroughly assessed and modeling of the equilibrium data was best fit with Langmuir and Toth models. The maximum observed MTP adsorption capacity of the magnetic hybrids amounted to 447 mg/g, thus representing an enhancement of 300% compared to most efficient MTP sorbents reported so far. The results of FTIR analysis indicate that the adsorption mechanism is mostly based on electrostatic interactions between sulfonate groups of κ-carrageenan and protonated amine groups of metoprolol. The obtained Fe₃O₄@SiO₂/SiCRG composite particles show a great potential for removing MTP from water, stemming from their high inherent absorption capacity and convenient magnetic separation.

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1. Introduction

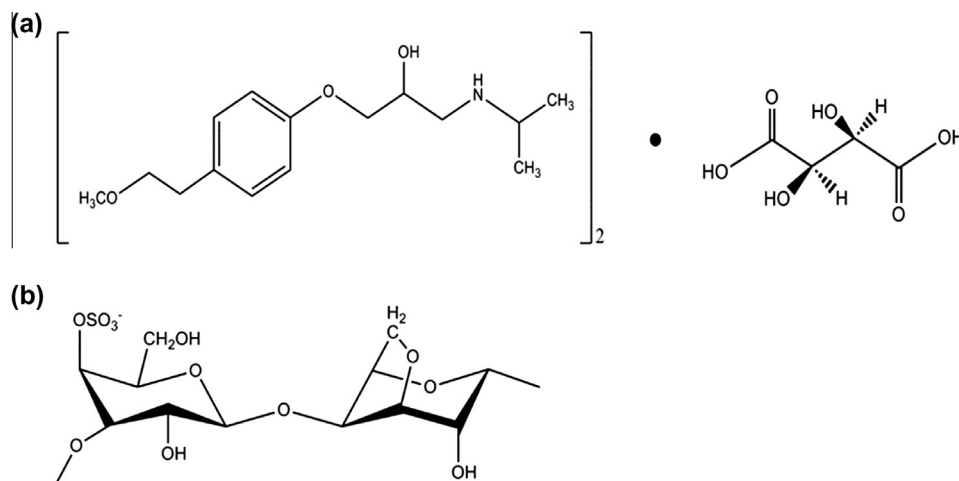
Emerging chemical pollutants (ECPs) encompass a wide range of man-made chemicals used worldwide, such as pesticides, antibiotics and other pharmaceuticals, which are not covered by standard monitoring and regulatory programs and which impact on environment and human health is still poorly understood. The detection of significant concentrations of ECPs in water sources has alerted the scientific community for the need of urgent environmental remediation solutions [1,2]. For certain ECPs, conventional water treatment procedures are not effective. For example, beta-blockers are the most resistant to the treatment in wastewa-

ter treatment plants, with low removal rate (30–40%) [3]. Among beta-blockers, metoprolol (MTP) (Scheme 1) has been widely used to treat angina, hypertension, arrhythmia, infarction, hyperthyroidism and other related diseases [4]. MTP is one of the most frequently detected beta blocker in surface waters and shows highly resistance to hydrolysis [3]. Although ecotoxicity data are not fully available, beta-blockers can adversely affect aquatic organisms, even at low concentrations [5]. Moreover poisoning with beta-blockers results in cardiovascular and neurological effects [6]. Due to its potential impact on environment and human health, MTP must be removed from treated water before discharge or reuse.

Several processes have been proposed for the elimination and degradation of MTP from water, including advanced oxidation processes [7,8], photocatalytic treatment [9–11] and adsorption

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Scheme 1. Chemical structure of (a) metoprolol tartrate and (b) disaccharide unit of κ-carrageenan.

[12–14]. Compared to other methods, adsorption is an attractive process in view of its simplicity of implementation and low cost. However, the efficiency of this process strongly depends, among other factors, on the affinity between the sorbent's surface and the pollutant. Furthermore, the separation of the system sorbent/pollutant from the medium might be also a critical aspect. Thus, the development of sorbents with high affinity to MTP that can be quickly and easily separated from water is highly desirable. This can be achieved using magnetic nanoparticles with functionalized surfaces that confer high affinity towards pollutant molecules and whose magnetic features enable fast magnetic separation from solution. Hence, we have developed a series of sorbents comprising surface modified magnetic particles for the uptake of water pollutants such as metal ions [15–18] and organic dyes [19]. More recently, we have extended this approach to obtain nanoadsorbents of bio-hybrid siliceous materials, containing κ-carrageenan covalently grafted to the surfaces [20]. This biopolymer is an anionic sulfated linear polysaccharide extracted from red seaweeds (Scheme 1) which is widely used as gelling agent in food and cosmetic industry [21]. Although scarcely investigated for sorption applications, κ-carrageenan has shown to be effective in the capture of a number of pollutants from water, namely organic dyes [22,23] and more recently the beta-blocker metoprolol [14]. Besides providing functional groups with affinity towards these pollutants, κ-carrageenan is biodegradable and naturally available, thus being a very attractive source for the development of eco-friendly and low-cost adsorbents for water decontamination processes.

This work reports a novel strategy for the surface modification of magnetite nanoparticles with κ-carrageenan hybrid siliceous shells and explores the application of the resulting materials as magnetic sorbents for the uptake of metoprolol from aqueous solutions.

2. Experimental

2.1. Chemicals

Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (>99%) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) (>99%) were obtained from Panreac. Tetraethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS, >99%), potassium nitrate (KNO_3) (>99%) and 3-(triethoxysilyl)propyl isocyanate ($(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NCO}$, ICPTES, 95%) were purchased from Sigma–Aldrich. Milli-Q water was obtained from the Synergy equipment from Millipore with a 0.22 μm filter. Ammonia solution (25% NH_3) was purchased

from Riedel-de-Haën and potassium hydroxide (KOH) (>86%) was purchased from Pronolab. N, N-Dimethylformamide ($\text{HCON}(\text{CH}_3)_2$) was obtained from Carlo Erba Reagents. Methanol (CH_3OH) (>99%) was purchased from VWR and κ-Carrageenan (300.000 g/mol) was obtained from Fluka Chemie. Metoprolol tartrate ($(\text{C}_{15}\text{H}_{25}\text{NO}_3)_2 \cdot \text{C}_4\text{H}_6\text{O}_6$, >98%) was purchased from Alfa Aesar.

2.2. Preparation of magnetic carrageenan-silica hybrid nanoparticles

The synthesis of magnetic hybrid nanoparticles ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SiCRG}$) included two distinct steps. Firstly, the synthesis of the magnetic core (magnetite – Fe_3O_4) by alkaline hydrolysis of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ under a N_2 stream [24] and then its encapsulation in amorphous silica shells by alkaline hydrolysis of TEOS in the presence of a precursor (SiCRG) comprising the biopolymer κ-carrageenan chemically modified with alkoxyisilyl groups. Briefly, the precursor SiCRG was generated by reaction between the polysaccharide κ-carrageenan and the silane coupling agent ICPTES, as previously reported by us [20]. For the encapsulation, a suspension of Fe_3O_4 nanoparticles (40 mg) in 38 mL of ethanol was prepared and kept immersed in an ice bath, under sonication (horn Sonics, Vibracell) at room temperature. After 15 min, the ammonia (2.4 mL) and a mixture of TEOS (0.406 mL) and SiCRG precursor (0.4 g) were slowly added to the solution which was left for 2 h immersed in an ice bath, under sonication. The resulting particles were collected magnetically using a NdFeB magnet, and washed thoroughly with ethanol. Then, the particles were left to dry by solvent evaporation. For comparative purposes, Fe_3O_4 nanoparticles coated with amorphous silica shells ($\text{Fe}_3\text{O}_4/\text{SiO}_2$) have also been prepared by a similar method. The coating was performed in absence of the precursor SiCRG, using TEOS (0.1 mL) as the only source of Si.

2.3. Preparation of non-magnetic carrageenan-silica hybrid nanoparticles

Non-magnetic hybrid particles were prepared as previously reported by us [20]. The SiCRG precursor (0.6 g) and TEOS (0.372 mL) were mixed in an Erlenmeyer flask containing deionized water (0.9 mL), ethanol (8.5 mL) and ammonia solution (0.15 mL), under constant stirring (250–300 rpm). The reaction was performed over 24 h, at room temperature. The resulting compound was washed five times with deionized water and one time with dry ethanol, followed by centrifugation. Finally, the solvents were evaporated and the hybrid $\text{SiO}_2/\text{SiCRG}$ particles were obtained.

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