Chemical Engineering Journal 254 (2014) 559–570

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# The role of operational parameters on the uptake of mercury by dithiocarbamate functionalized particles

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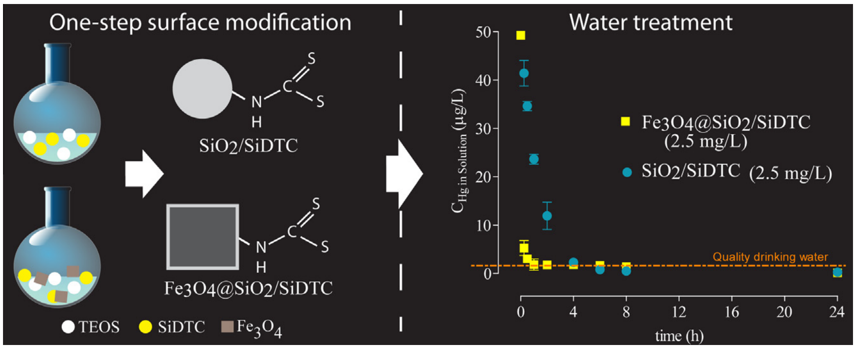
## HIGHLIGHTS

- One-step method for the surface modification of magnetite and silica sorbents.
- Efficient and fast uptake of Hg by both dithiocarbamate functionalized sorbents.
- Hg levels in solution ~100-folds lower than the guideline value for drinking water.
- The degree of sorbents functionalization only affected the kinetics of the process.
- Confirmation of the strong affinity of dithiocarbamate functional groups toward Hg.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 2 April 2014
Received in revised form 30 May 2014
Accepted 3 June 2014
Available online 12 June 2014

*Keywords:*
Mercury sorption
Dithiocarbamate functionalization
Silica
Magnetite
Water treatment

## ABSTRACT

Sorbents based on silica and silica coated magnetite particles have been functionalized with dithiocarbamate groups, aiming at the uptake of mercury. The uptake capacity of the synthesized materials were evaluated systematically for variable operational parameters including degree of functionalization, sorption time, sorbent dose, and initial Hg(II) concentration. Removal efficiencies of 99.6–99.9% were achieved in 8–24 h, regardless the sorbent dose, type of substrate and degree of functionalization. All sorbents were able to decrease an initial Hg(II) concentration of 50 µg/L to values circa 100 times lower than the guideline value for drinking water quality (1 µg/L), with the additional advantage of magnetic separation by application of an external magnetic field, in the case of the silica coated magnetite. The high capacity of these materials for Hg(II) uptake from water is attributed to their functionalization due to the strong complexation of the mercury ions and dithiocarbamate groups. The modelling of the kinetic and the equilibrium results was well described by common kinetic and equilibrium equations.

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## 1. Introduction

Considerable attention has been given to the amount of non-essential metals found in the environment resulting from human activities. While the levels of metals found naturally in rocks, soils, air and waters usually are not cause for great concern, anthropogenic activities such as industry, agriculture and medicine, are often the principal source of pollution throughout the environment.

In order to remove non-essential metals from waters, numerous methods have been used including evaporation, precipitation, ion

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http://dx.doi.org/10.1016/j.cej.2014.06.008
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exchange, adsorption, membrane filtration and electrochemical technologies [1]. Among these techniques, adsorption has been one of the most effective and simplest approaches developed for removal purposes [2–5]. The efficiency of the adsorption process is mostly affected by the properties of the adsorbent, namely the type of interactions occurring between the adsorbate and the sorbent's surfaces. Therefore, the development of new adsorbents with high adsorption capacity, fast adsorption–desorption kinetics and easy separation from solution is particularly important.

Recently, the application of nanoparticles in water treatment technology has attracted growing interest, namely because these materials possess some advantages over their bulk counterparts, such as a high specific surface area and ability for surface chemical functionalization. In particular, iron oxide nanoparticles have been reported as very promising sorbents because several pollutants can be adsorbed and removed from solution by application of an external magnetic field [6,7]. Additionally, these particles can be coated with silica shells, which confer chemical robustness and new possibilities of surface modification with a variety of chemical groups. Examples of these approaches include the use of $Fe_3O_4$ nanoparticles for treating wastewaters contaminated with Ni(II), Cu(II), Cd(II) and Cr(VI) [8], while Zhang et al. [9] reported that thiol groups grafted on the surfaces of $Fe_3O_4$ nanoparticles act as binding ligand for Hg ions and humic acids coated $Fe_3O_4$ nanoparticles were found to effectively sorb Hg(II), Pb(II), Cd(II) and Cu(II) from water [10].

Mercury (Hg) is a non-essential metal classified as a priority substance by several organizations such as the Agency for Toxic Substances and Disease Registry [11] and the European Union [12]. Mercury has high toxicity, persistent character in the environment and biota, with bioaccumulation and bioamplification effects along food chain. Mercury is toxic in all forms and in all compartments of the biosphere, but it is in the hydrosphere that this metal gives rise to greater concern because it is easily converted into methylmercury, a neurotoxin extremely toxic. For all these reasons the removal of Hg from water is crucial.

Mercury is classified as a soft acid and as such shows strong affinity for soft Lewis base groups [13], including S donor groups. This principle has been exploited to produce functionalized silica's whose surfaces have chemical moieties with high affinity for mercury [14,15]. Our interest in this kind of sorbents led us to develop dithiocarbamate functionalized core/shell magnetite/silica particles with high sorption capacity for Hg(II) [16,17]. Very recently, we have reported a new strategy for the surface modification of magnetite particles that resulted into magnetic sorbents with silica shells enriched in dithiocarbamate groups [18].

Here, we report a new and systematic study where we: (i) explored the degree of functionalization of dithiocarbamate groups on silica and silica coated magnetite sorbents, in order to evaluate the importance of dithiocarbamate groups for an effective Hg(II) uptake and (ii) studied the role of important operational parameters such as sorbent dose, initial Hg concentration, equilibration time, and pH in order to understand and optimize the sorption process.

## 2. Materials and methods

### 2.1. Chemicals

Chemicals used in this work were obtained from commercial suppliers and used without further purification. Tetraethyl orthosilicate: ($Si(OC_2H_5)_4$: TEOS, >99%) was purchased from Sigma–Aldrich (Sintra, Portugal), sodium hydroxide (NaOH) (>98%) was purchased from VWR Prolabo (Carnaxide, Portugal), ethanol ($CH_3CH_2OH$) (>99%) obtained from Panreac (Odivelas, Portugal) and ammonia solution (25% $NH_3$) obtained from Riedel-de-Häen (Sintra, Portugal). The certified standard solution of mercury nitrate (1000 ± 2 mg/L) was purchased from Merck (Carnaxide, Portugal). The siloxydithiocarbamate precursor (SiDTC) was synthesized as reported in the literature [18].

### 2.2. Preparation of the sorbents

Two types of sorbent materials have been used in this study: silica and silica coated magnetite substrates, with different amounts of dithiocarbamate moieties. These materials were prepared according with the procedure described by Tavares et al. [18]

Briefly, silica particles ($SiO_2$/SiDTC) were generated and modified with dithiocarbamate groups by hydrolytic condensation of tetraethyl orthosilicate (TEOS) in the presence of a siloxydithiocarbamate precursor (SiDTC). Three samples with different moieties of dithiocarbamate groups were prepared, using a mixture of TEOS:SiDTC at molar ratios 3:1, 1:1 and 1:3, that will be designated hereafter by $SiO_2$/SiDTC-1, $SiO_2$/SiDTC-2 and $SiO_2$/SiDTC-3, respectively. $SiO_2$ particles were also prepared in the absence of SiDTC.

The synthesis of magnetic particles ($Fe_3O_4$@$SiO_2$/SiDTC) included two distinct steps. Firstly the synthesis of the magnetic core (magnetite, $Fe_3O_4$) by hydrolysis of $FeSO_4 \cdot 7H_2O$ and then its encapsulation and grafting of dithiocarbamate group in amorphous silica shells by alkaline hydrolysis of TEOS in the presence of the siloxydithiocarbamate ligand (SiDTC) [18]. As in the case of silica particles, the same mixtures of TEOS:SiDTC were used during the functionalization of the magnetic materials at molar ratios 3:1, 1:1 and 1:3, that will be designated hereafter by $Fe_3O_4$@$SiO_2$/SiDTC-1, $Fe_3O_4$@$SiO_2$/SiDTC-2 and $Fe_3O_4$@$SiO_2$/SiDTC-3, respectively. $Fe_3O_4$@$SiO_2$ particles without functionalization were also prepared according with the procedure described by Girginova et al. [16].

### 2.3. Characterization of the sorbents

The morphology of the particles was confirmed by transmission electron microscopy (TEM) using a Hitachi H-9000 TEM microscope operating at 300 kV. A drop of sample dispersed in ethanol on a carbon-coated copper grid was air-dried. Scanning electron microscopy (SEM) was performed using a Hitachi SU-70 instrument operated at an accelerating voltage of 15 kV. SEM samples were prepared by evaporating diluted ethanolic suspensions of the samples over a double-side carbon tape. Brunauer–Emmett–Teller (BET) surface areas of the particles were determined by $N_2$ adsorption/desorption on a Gemini V2.0 Micromeritics instrument. Fourier Transform Infrared (FT-IR) spectra of the $SiO_2$/SiDTC and $Fe_3O_4$@$SiO_2$/SiDTC were recorded using a spectrometer Mattson 7000 at 4 $cm^{-1}$ resolution, using a horizontal attenuated total reflectance (ATR) cell. Elemental analysis for carbon, nitrogen, hydrogen and sulfur was obtained on an Eager 300. The $^{29}Si$ magic-angle spinning (MAS) nuclear magnetic resonance (NMR), $^{29}Si$ cross-polarization (CP) MAS NMR and $^{13}C$ CP/MAS NMR spectra were recorded using a Bruker Avance III 400 MHz (9.4 T) spectrometer at 79.49 and 100.61 MHz, respectively. Chemical shifts have been quoted in ppm from tetramethylsilane (TMS).

### 2.4. Sorption experiments

The ability of $SiO_2$/SiDTC and $Fe_3O_4$@$SiO_2$/SiDTC particles to uptake Hg(II) from water was evaluated by contacting an accurately known mass of these particles with an aqueous solution containing Hg(II), for variable periods of time. All sorption experiments were conducted at batch isothermal conditions (21 ± 1 °C), and in the case of the silica particles, the trials were carried out in 2 L volumetric flasks, under magnetic stirring, while for magnetic particles, they were carried out in a 1 L glass batch

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