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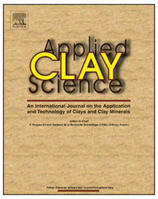

Research paper

Bentonite-decorated calix [4] arene: A new, promising hybrid material for heavy-metal removal

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ABSTRACT

There is global concern about the contamination of ground, river, and tap waters as well as soil contamination with heavy metal ions; these chemical species are known to not degrade and to cause severe health problems if ingested by humans and animals. Such environmental and health concerns necessitate the development of ultrasensitive sensors and high-capacity adsorbents. This study demonstrates for the first time the potential of organophilic bentonite combined with tetra(2-pyridylmethyl)amide calix [4] arene as a high-performance hybrid material for the removal of toxic heavy metals.

After consecutive synthesis steps, the modified bentonites were thoroughly characterized by FT-IR, XRD, UV spectroscopy, and TEM. In particular, the XRD analysis showed strong supporting evidence for intercalation in the clay following each modification step.

The salient feature of the newly prepared hybrid material is its high extraction capacity for Cd(II) and Zn(II) metals, as determined by atomic absorption spectrometry and UV spectrometry. Different preparation methods, with respect to the quantity of the added cationic surfactant, were investigated to determine the optimal conditions for synthesis. The extraction percentage for the as-prepared hybrid material was measured to be as high as 97.4% and 94.2% for Cd(II) and Zn(II), respectively.

1. Introduction

Heavy metals can cause serious environmental problems due to their abundant use and toxicity. Indeed, high amounts of heavy metals are used in many industries, including tanneries, electroplating, pesticides, phosphate fertilizers, mining, and batteries(Halim et al., 2003; Liu et al., 2018). Once introduced into the environment, heavy metal pollution of both surface and ground waters poses a serious threat because of the metal motility and solubility, which can represent serious risks to the environment and human health (Balasubramanian et al., 2009; Chen et al., 2018). Among all heavy metal water pollutants, cadmium and zinc heavy metals have received increased attention because of their hazardous effect on humans. Cadmium may cause kidney damage and renal disorder (Godt et al., 2006), while zinc can cause abnormal pregnancy and retardation of children's growth(Galbeiro et al., 2014). To remove zinc and cadmium from aqueous solutions, several methods and techniques have been proposed(Uddin, 2017); chemical precipitation, evaporation, adsorption, ion exchange, electrochemical treatment, and membrane filtration technologies(Uddin, 2017). Among all these techniques, adsorption is considered as the most efficient and most cost-effective method to remove low metal concentrations(Khan et al., 2014; Rao et al., 2015). Many types of adsorbent materials have been tested for zinc and cadmium ion uptake, such as clay(Hamid et al., 2017; Refaey et al., 2017), carbon nanotubes (Tofighy and Mohammadi, 2012), calixarenes(Sliwa and Deska, 2008), polymers(Liu et al., 2017), and zeolites (Adinehvand et al., 2016).

Bentonite can be used as advantageous absorbent for water treatment(Mo et al., 2017), compared to commercial adsorbents; because of their abundance(Bergaya and Lagaly, 2006; Bouazizi et al., 2016), low cost(Hamid et al., 2017) and high cation exchange capacity(Heller-Kallai, 2006), which is responsible for the hydration and swelling of the absorbent(Sidhoum et al., 2013). The uptake of trace heavy metals by bentonite requires complex adsorption mechanisms involving direct bonding between metal cations and the surface of the clay, surface

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complexation, and ion exchange(Churchman et al., 2006).

In several studies, pretreatment(de Paiva et al., 2008) was necessary to enhance the adsorption of bentonite and to improve the metals uptake(Behera et al., 2016). Such pretreatment facilitates the reaction between clay and calixarene organic macromolecules. Although pretreatment methods can be carried out using a variety of techniques, such as grafting of organosilanes(Jlassi et al., 2013) and diazonium salt treatments(Jlassi et al., 2014), cation exchange is the most commonly implemented method(Slabaugh, 1954).

Calixarenes, which are cyclic oligomers, are especially important in separation chemistry, and they are commonly prepared by oligomerization of phenol and formaldehyde (Baldini et al., 2007). The popularity of these compounds is attributed to their simple and large-scale synthesis, amenability to simple chemical tailoring and modification, excellent capability to form complexes between host and guest molecules(Notestein et al., 2006; Troian-Gautier et al., 2016; Zhang et al., 2016), and multi-center bonding with guest molecules. Furthermore, different types of inorganic and organic molecules can be bound specifically and selectively to calixarenes(Ludwig, 2000; Vögtle and Weber, 2012). In recent years, numerous studies have been conducted using calixarenes and their derivatives as potential extractants of metal ions in liquid–liquid extraction processes and transport via liquid membranes(Ohto, 2010). Functionalization at the level of the phenolic OH by amide functions opens up more interesting applications(Maya et al., 2017). Indeed, (Hamdi et al., 2001) reported a new synthesis route for tetra (2-pyridylmethyl) amide calix [4] arene, and they demonstrated the use of this material for cation complexation(McKervey et al., 1996). Moreover, the compound contains an additional cavity delineated by the attachment of the four pyridine moieties via the amido functions that is capable of complexing cations via the nitrogen atoms.

Despite the progress in the preparation of calixarene molecules and organophilic clays as separate materials, organophilic clay-decorated calix [4] arene heterostructures have not been previously prepared.

In this report, organophilic bentonite-decorated tetra(2-pyridylmethyl)amide calix [4] arene hybrid materials are prepared by simple cation exchange method using the benzyltetradecyl dimethyl ammonium (C14) cationic surfactant to increase the bentonite interlayer space for intercalation of the calixarene organic species. Organophilic bentonite-calixarene hybrids were characterized by FTIR, UV, TEM, and XRD to investigate their surface morphology, chemical composition, and crystalline structure. The extraction performances of the prepared hybrid materials were evaluated using Zn(II) and Cd(II) heavy metals.

Surprisingly, to the best of the authors's knowledge, there is no report describing the preparation of an organophilic bentonite-decorated tetra(2-pyridylmethyl)amide calix [4] arene hybrid material. Such a material is expected to be highly important for many applications, including the removal of Zn(II) and Cd(II) heavy metals.

2. Experimental

2.1. Materials

Tetra(2-pyridylmethyl)amide calix [4] arene was prepared following previous method(Hamdi et al., 2001), the benzyltetradecyl dimethyl ammonium surfactant was purchased from Sigma Aldrich and used without further purification. The organic solvents used were of analytical grade; deionized (DI) water was used for washing and solution preparation.

The raw bentonite was extracted from the Gafsa-Metloui basin, Tunisia, and purified according to standard procedures(Bergaya and Lagaly, 2013). The cationic exchange capacity (CEC) of the used bentonite was 101.86 meq/100 g calcined clay, as determined from the adsorption isotherm of methylene blue (Brindley and Thompson, 1970). The total Brunauer-Emmett-Teller (BET) surface area of the as-used bentonite was estimated to be 736 m^2/g, consisting of external and internal surfaces with BET areas of 113 and 623 m^2/g, respectively (Jlassi et al., 2013).

To prepare organophilic bentonites, the surfactant benzyldodecyl dimethyl ammonium chloride (C14) was used as provided by Sigma Aldrich (purity, 99%). The critical micellar concentration (cmc) obtained from the conductimetry measurements was 2.07×10^{-3} M. The dimensions of C14 in relation to the length of the chemical C—C and C—N bonds as well as the C-C-C and C-N-C angles have been previously determined from crystallographic data (Rodier et al., 1995). These are listed in Table (see SI1) (Othmani-Assmann et al., 2007).

2.2. Synthesis of tetra(2-pyridylmethyl)amide calix [4] arene (calix)

Tetra (2-pyridylmethyl)amide calix [4] arene (calix) was prepared by reacting tetrakis(carboxymethoxy)calix[4]arene with an excess of 2-(aminomethyl)pyridine in a refluxing 1:1 mixture of methanol–toluene for 10 and 8 days(Hamdi et al., 2001). The as prepared calixarene is tetra-functionalized, and its height (H) was calculated from the crystallographic data based on the lengths of the C—C and C—N bonds, the molecular diameter of the pyridine ring, and the C-C-O and C-N-C angles (Fig. 1).

2.3. Preparation of the organophilic bentonite

An aqueous solution of C14 surfactant (0.3, 0.7 and 1 CEC) was added dropwise to an aqueous dispersion of bentonite (1 g dissolved in 100 mL of deionized water). The mixture was stirred for 24 h at room temperature. The resulting dispersion was centrifuged and then washed several times with deionized water to remove any unreacted surfactant molecules. Finally, the resulting product was dried at 70 °C for 48 h.

Hereafter, purified Bent is denoted purified Bent, and the organo-modified bentonites are abbreviated as OxBent (x stands for the CEC fraction).

2.4. Preparation of the organophilic bentonite calixarene

In a typical procedure, BP and BPxCEC samples (approximately 4 g in weight) were dispersed in 50 mL of acetonitrile and mechanically stirred (12 h, room temperature).

Then, calixarene solutions (10^{-3} M, 0.3 CEC) were prepared and added dropwise to the bentonite dispersions using a micropipette. The mixture was kept under mechanical stirring for 5 h, centrifuged (9000 rpm, 45 min), and washed several times with acetonitrile to remove unreacted calixarene molecules. The resulting material was recovered and dried at 40 °C. The supernatants were collected to quantify the amount of reacted calixarene.

In the following sections, the resulting products are denoted OxBent-Calix, where x stands for the fraction of CEC (0.3, 0.7, or 1.0).

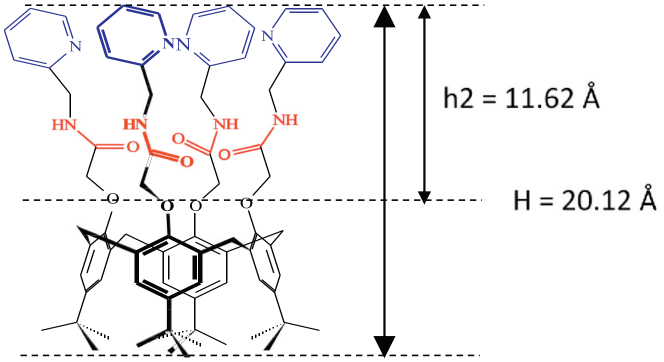

Fig. 1. Structure of tetra(2-pyridylmethyl)amide calix [4] arene (calix) including the calculated height.