



Research paper

Synthesis and characterisation of surfactant enhanced Mg–Al hydroxalcalite-like compounds as potential 2-chlorophenol scavengers



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ABSTRACT

Magnesium aluminium hydroxycarbonate hydroxalcalites (denoted as MgAl–CO₃–HTs) with different Mg/Al molar ratios (4, 3 and 2) were synthesised by the co-precipitation method under low supersaturation conditions, and then treated with sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS) surfactants to produce the nanocomposites – organo-hydroxalcalites; dodecylsulfate-hydroxalcalites (DS-HTs) and dodecylbenzenesulfonate-hydroxalcalites (DBS-HTs) through calcination–reconstruction method. Powder X-ray diffraction (PXRD) and infrared spectroscopy analysis of intercalated samples showed that dodecylsulfate and dodecylbenzenesulfonate guests were successfully intercalated into the parent hydroxalcalites, with the PXRD revealing that the species could assume varying configurations within the interlayer gallery regions of this clay based materials, displaying monolayer and bilayer orientations.

The uptake ability of the resulting DS-hydroxalcalites and DBS-hydroxalcalites for the adsorption of phenolic compounds from aqueous solution was investigated. The results showed that, the adsorption process can be described by pseudo-second order kinetics, while the capacity of 2-chlorophenol uptake is dependent on the Mg^{II}:Al^{III} ratio within the interlamellar of the organo-hydroxalcalite, the anion present (with DBS modified samples showing higher adsorption capacities) and the pH at which adsorption was carried out.

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1. Introduction

2-Chlorophenol is a familiar pollutant in effluents generated from textile, timber, coal, pesticide, petroleum, petrochemicals, pharmaceuticals and plastic industries. United States Environmental Protection Agency regards it as one of the priority contaminants in wastewater due to its toxic and harmful effect to humans and lower organisms even at low concentrations. The allowable limit has therefore been set at 0.04 mg/dm³ in drinking water (USEPA, 1992 and Copeland, 1993). 2-Chlorophenol is a hazardous pollutant because of the potential toxicity posed to human health. Vital organs like the kidney, liver, eyes, skin and the central nervous system are commonly affected, ultimately causing death. Consequently, the removal of this compound is an environmental issue that needs to be addressed.

Researchers have directed efforts towards developing technologies that are composed of environmentally friendly scavengers that lower their concentration in water and wastewater and render this pollutant inactive. There are several treatment methods for phenolic wastewater, but some researchers identified two major treatment categories, which are destructive oxidation and recuperative processes (Dutta and Robins,

1994; Dutta et al., 1998). The latter of these involves adsorption. Adsorption is one of the most popular and most effective methods for removal of organic compounds from water and process effluents/wastewater (Seki and Yurdakoc, 2005; Liao et al., 2006). In recent years, new materials that are environmentally friendly and efficient, (natural and synthetic) are being developed as adsorbents to adequately remove organic pollutants like phenol and chlorophenols from soil and aquifers. Activated carbon has recorded considerable success as adsorbent in treatment of wastewater or as clean-up for drinking water due to its ability to uptake organic molecules, as a result of its high surface area, micro-porous structure and special reactivity (Hernández et al., 2007). However, its use is limited by its high cost, intra-particle resistance in adsorption processes and difficulty of recovery (Najim et al., 1990; Pibazari et al., 1992). Due to this drawback, other adsorbents ranging from various agricultural by-products to clay minerals, zeolite and others have been examined (Robinson et al., 2002; Ghosh and Bhattacharyya, 2002; Batzia and Sidiras, 2007).

Hydroxalcalites, which are valuable layered clay materials, have received interest on account of their ease of synthesis, adjustability of interlamellar structure and ability to act as host materials through the incorporation of guest species, to generate novel solids with desirable physical and chemical properties. They have found use as adsorbent for phenolic compounds. The general formula of hydroxalcalite is [M^{II}_{1-x}M^{III}_x(OH)₂]^{b+}[A_{b/n}]ⁿ⁻·mH₂O], where the M^{II} can be Mg²⁺,

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Zn^{2+} , Cu^{2+} etc; $M^{III} = Al^{3+}$, Cr^{3+} , Fe^{3+} etc; $A^{n-} = CO_3^{2-}$, Cl^- , SO_4^{2-} or NO_3^- while x can vary between 0.20 and 0.33 (Cavani et al., 1991). The structure can be described as being based on a brucite which consists of Mg^{2+} ions coordinated octahedrally by hydroxyl groups with the octahedral units sharing edges to form charged neutral sheets (Kovanda et al., 1999; Pavan et al., 2000). Isomorphous replacement of some of the Mg^{2+} with trivalent M^{3+} cations, creates a positive charge on the layers requiring the presence of charge balancing anions (to maintain electrical neutrality) within the interlayer gallery region (Trifiro and Vaccari, 1996; Braterman et al., 2004). The layered structure is held together by both ionic and hydrogen bonding (Reichle, 1986). A unique property of impressive anionic exchange capacity, similar to their lamellar permits the replacement of the original hydrotalcite anions with the ones in the aqueous solution (Meyn et al., 1990).

In previous studies into the use of hydrotalcites as adsorbents for phenolic compounds researchers have focussed on materials with the alkylsulfate anions in the interlayer such as the dodecylsulfate anion, and have shown that these can successfully uptake compounds such as trichlorophenol and trinitrophenol from aqueous solutions (Ulibarri et al., 1995; Chuang et al., 2008). In these previous studies, the focus was on a single HT compound with fixed $M^{II}:M^{III}$ ratio in the brucite-like layer, which regulates the concentration of anion that can be intercalated within the interlayer region.

This study focused on synthesising and examining the adsorption capability of hydrotalcites with varying $Mg^{II}:Al^{III}$ molar ratios, as this can allow tuning of both the potential accessible adsorption sites within the structure as well as the balance of hydrophobic-hydrophilic interactions. The intercalation of both alkylsulfate (dodecylsulfate) and alkylaromatic sulfonate (dodecylbenzenesulfonate) guest anions, to observe if the ability for aromatic interactions has any additional effect on adsorption capacity, and the effect of altering the pH at which adsorption is carried out has been investigated. A description of the synthesis and modification of the hydrotalcite materials and their characterisation by X-ray diffraction (XRD), X-ray Fluorescence (XRF), Fourier transform infrared (FT-IR), thermal analysis and their efficiency in the uptake of 2-chlorophenol (2-CP) from aqueous solution is presented in this study.

2. Experimental

2.1. Reagents

All reagents used in this study are of analytical grade. $Mg(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich, Japan, 99% purity) $Al(NO_3)_3 \cdot 9H_2O$, Na_2CO_3 (Sigma-Aldrich, Germany, 98% purity), and NaOH were supplied by Fisher Scientific, UK. Sodium dodecylsulfate and sodium dodecylbenzenesulfonate (98.5%, Sigma-Aldrich).

2.2. Synthesis of series of hydrotalcite-like compounds (HTLcs)

A co-precipitation method was utilised to synthesise HTLcs containing carbonate anions with Mg and Al in the layers at different $Mg^{II}:Al^{III}$ ratios (2, 3 and 4) under low supersaturation (Reichle, 1986; Carretero, 2002; Aguzzi et al., 2007). A mixed solution of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$, in the appropriate stoichiometry to give $Mg^{II}:Al^{III}$ ratios of 2, 3 and 4, such that the total molar cation concentration prepared was 0.8 mol dm^{-3} . A second solution comprising of NaOH (0.726 mol) and Na_2CO_3 (0.212 mol) was also prepared, and these two solutions were added together slowly and simultaneously under vigorous stirring at room temperature, maintaining the pH value (between 12 and 13) of the mixture. The mixture was aged at 110°C for 18 h. The products formed were filtered, washed thoroughly with deionised water, and dried at 60°C for 24 h. The obtained white solid sample was denoted as Mg_nAl-CO_3 HTLcs ($n = 2, 3, 4$).

2.3. Synthesis of organo-hydrotalcite compounds

The synthesised HT was first calcined at a ramp rate of $5^\circ\text{C}/\text{min}$ to 500°C (temperature predetermined from variable temperature XRD and TGA) to convert the HT into oxide form which was named calcined Mg_nAl_{500} . 1 g of each oxide precursor was dispersed in 50 cm^3 of 0.5 mol dm^{-3} sodium dodecylsulfate (SDS) or 0.2 mol dm^{-3} sodium dodecylbenzenesulfonate (SDBS) solutions. The mixtures were equilibrated for 24 h with continuous stirring at ambient conditions under flowing nitrogen gas. The resulting suspensions were centrifuged, washed several times with deionised water and dried at 50°C and stored in sealed containers. The organo-hydrotalcite materials obtained were denoted as Mg_nAl-CO_3-DS and Mg_nAl-CO_3-DBS .

2.4. Characterisation of parent and modified hydrotalcite like compounds (organo-hydrotalcite-like compounds)

Powder x-ray diffraction data was obtained using a Bruker D8 ADVANCE X-ray diffractometer equipped with a Lynx-Eye PSD detector. Data was collected at room temperature in 2Theta transmission geometry with $Cu K\alpha_1$ radiation ($\lambda_{CuK\alpha_1} = 1.54056 \text{ \AA}$) using a step size of $0.02^\circ 2\theta$ and step time of 8 s per step. The samples (as unoriented powders) were collected in the 2θ range from 5° to 70° . A D5005 Siemen diffractometer with $CuK\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) also operating at 40 kV and 30 mA under reflection mode was used for the derived organo-hydrotalcite-like compounds, because of the large d -values expected and low angles to which it was necessary to record the XRD data.

The atomic ratios ($Mg^{II}:Al^{III}$) were measured using X-ray fluorescence spectrometry (Bruker S8 TIGER wavelength dispersive X-ray fluorescence spectrometer) with high intensity rhodium X-ray tube, employing the fused beads method for the major oxides which involved dissolving 1.0 g of sample in 10 g of flux (di-lithium tetraborate).

IR data was collected on a Varian 660 FT-IR spectrometer (36 scan accumulation, 4 cm^{-1} resolution) to identify the anions in the interlayer of the various synthesised hydrotalcites in the range of $700\text{--}4000 \text{ cm}^{-1}$, using the attenuated total reflection (ATR) method. The samples were prepared for FT-IR by grinding dried sample to powder. Approximately 1.0 mg powder was placed on the sample holder to make good contact with the surface of the diamond crystal, and the IR beam directed on it.

2.5. Sorption experiments

Batch adsorption experiments were carried out to study the effect of contact time and pH on the adsorption of 2-chlorophenol (2-CP) on the organo-hydrotalcites. Adsorption studies were carried out using 200 cm^3 of each 2-CP solution and 0.10 g of the adsorbent, at varying pH of 6–10 stirred at 120 rpm at room temperature (25°C). The adsorption reaction was carried out at different time intervals between 5 min to 24 h. At the end of each experiment, the content of each tube was filtered through a $0.2 \mu\text{m}$ syringe filter membrane, after which the concentration of residual 2-CP in the filtrate was measured using UV–vis spectrophotometer analysis. Each adsorption isotherm was determined in duplicate using two independent samples. The adsorbed quantities were then determined from the difference between the initial and final concentrations. The adsorption capacity/kinetics of the different organo-hydrotalcites were evaluated. The 2-CP adsorption capacity (mmol g^{-1}) was obtained from the equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where C_0 = the initial 2-chlorophenol concentration (mmol dm^{-3}) and m is the mass (g) of organo-hydrotalcites. C_t is the concentration (mmol dm^{-3}) of 2-CP at time t , while V is equivalent to the volume (dm^3) of aqueous 2-CP solution and q_t is the adsorption capacity in (mmol g^{-1}) at time t . The calibration curve showed a linear variation.

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