Journal of Colloid and Interface Science 386 (2012) 381–391

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Transition metal modified and partially calcined inorganic–organic pillared clays for the adsorption of salicylic acid, clofibric acid, carbamazepine, and caffeine from water

Wilman A. Cabrera-Lafaurie [a], Félix R. Román [b], Arturo J. Hernández-Maldonado [a,*]

[a] *Department of Chemical Engineering, University of Puerto Rico-Mayagüez Campus, Mayagüez, Puerto Rico 00681-9000, Puerto Rico*
[b] *Department of Chemistry, University of Puerto Rico-Mayagüez Campus, Mayagüez, Puerto Rico 00681-9000, Puerto Rico*

ARTICLE INFO

Article history:
Received 29 May 2012
Accepted 11 July 2012
Available online 23 July 2012

Keywords:
Pillared clays
Inorganic–organic clays
Partial calcination
Transition metal
Complexation
Adsorption
PPCP
Caffeine

ABSTRACT

Pharmaceutical and Personal Care Products (PPCPs) are considered emerging contaminants, and their efficient removal from water is going to be a challenging endeavor. Microporous adsorbent materials, including pillared clays, could offer a potential solution if tailored properly. Although pillared clays have been employed previously for the removal of organics, the effective removal of PPCPs will only be possible if their surface and textural properties are manipulated from the bottom-up. This work presents the use of modified inorganic–organic pillared clays (IOCs) for the adsorption of salicylic acid, clofibric acid, carbamazepine, and caffeine. The IOCs have been modified with Co^{2+}, Cu^{2+}, or Ni^{2+} to induce complexation-like adsorbate–adsorbent interactions at ambient conditions, in an attempt to provide an efficient and yet reversible driving force in the sub-ppm concentration range. Furthermore, the IOCs were partially calcined to increase effective surface area by an order of magnitude while preserving some hydrophobicity. In general, the Ni^{2+} IOCs exhibited the greatest interaction with salicylic and clofibric acids, respectively, while the Co^{2+} adsorbents excelled at adsorbing caffeine at low concentrations. All of the metal-modified IOCs showed comparable adsorption capacities for the case of carbamazepine, probably due to the lack of availability of particular functional groups in this adsorbate.

1. Introduction

During the last decade, the fate and possible effects of Pharmaceuticals and Personal Care Products (PPCPs) entering the environment has gained considerable attention [1–11]. Interestingly, the problem was first exposed in the US during the late 1970s when Hignite and Azarnoff studied the presence of salicylic acid and clofibric acid in a municipal sewage treatment plant in Missouri, US [12]. It was not until the 1990s, however, that additional reports became available thanks to the advancement of detection analytical chemistry techniques [13–15]. These have continued to evolve as evidenced by recent reports in the US, Europe, and Asia, which have identified several other PPCPs and their metabolites in a number of water sources [16–22]. For example, contaminants detected in wastewater influent and effluent included carbamazepine, clofibric acid, diclofenac and caffeine, with contamination levels of 463, 772, 50, and 5650 ng L^{-1}, respectively [22]. Moreover, it has been reported that the level of concentration being observed today for some PPCPs may have potential adverse effects, specifically in infants and people with enzyme deficiencies [23].

Despite considerable efforts made during the last decade to advance water treatment processes, the routines employed in treatment plants to date (e.g., flocculation, coagulation, disinfection, and conventional activated sludge) are not suitable for the efficient removal of these emerging contaminants [24–30]. Advanced oxidation processes (AOPs) and ozonation have been reported to be effective in the removal of PPCPs on various aqueous systems [31,32]. However, treatment of some pharmaceuticals in aqueous media by AOPs could also result in energy intensive processes because of the extremely high conversions required [32,33]. There are also reports indicating some residual activity after treatment by ozonation or photocatalysis processes that may result in other potential risks to the environment [34,35].

Recent initiatives to address the removal of PPCPs with minimal energy input or unwanted side products include adsorption processes [36–43]. Until recently, much of the effort made to advance water treatment adsorption processes has been focused on the removal of metals and other contaminants from water [44,45]. Traditional systems that aim at the removal of organic contaminants from water, including some pharmaceuticals, still revolve around the use of activated carbons [36,46–49]. However, it is known that

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* Corresponding author. Fax: +1 787 834 3655.
E-mail address: arturoj.hernandez@upr.edu (A.J. Hernández-Maldonado).

0021-9797/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2012.07.037

their capacity and selectivity greatly decrease due to competition from the many species involved in the water matrix. Their thermal regeneration also requires a significant amount of energy, which may lead indirectly to environmental risks greater than those brought by the sole presence of trace PPCPs. On the other hand, naturally occurring and modified clays such as bentonite have shown promising results for the removal of organic compounds from water systems due to their swelling properties and high surface areas [50–52]. By introducing inorganic polyoxocation and cationic surfactant molecules into the interlamellar space, the properties of the bentonites could be enhanced considerably [53,54]. Processes involving inorganic–organic clays (IOCs) have shown high affinity toward hydrophobic organic compounds (HOCs) and could simultaneously remove HOCs and oxy-anionic contaminants from water [55–59]. In terms of regeneration, there are several reports in the literature that show that organo-clays that are spent after adsorption of organics from water can be successfully and feasibly regenerated using alkaline washing [57,60,61] or supercritical CO_2 extraction [61,62]. Notwithstanding the IOCs adsorption properties, their framework still offers opportunities for further tailoring in an attempt to produce novel adsorbents, particularly for the removal of PPCPs.

Hernandez-Maldonado and co-workers have already reported on the positive effect that inclusion of transition metals onto the surface of non-pillared IOCs, and even onto mesoporous silicas, has on the adsorption of some PPCPs [37,41,63]. Transition metals are known to undergo complexation with compounds containing aromatic groups based on an electron donation and back donation process. This has been observed during studies related to the interaction of transition metals and drugs and aimed at synthesizing stable new drug complexes in solution [64–66]. Since the processes are dominated by weak-chemical interactions, formation of such complexes onto the surface of an adsorbent could provide the basis for the removal of aromatic-like PPCPs while still permitting regeneration via accessible engineering means [67]. Although results obtained for the adsorption of some PPCPs onto non-pillared transition metal containing IOCs proved that it is possible to tailor the uptake amounts based on the nature of the transition metal [41], the adsorbents did not exhibit appropriate textural properties and adsorption capacities. Therefore, the aim of this paper is to present the synthesis and a comprehensive evaluation of pillared IOCs modified with transition metals for the adsorption of a particular set of PPCPs that showcases different physico-chemical properties and a high rate of occurrence in surface waters. Moreover, the transition-metal modified IOCs were partially calcined to elucidate the effect of increasing surface area while preserving hydrophobicity.

2. Experimental

2.1. Materials

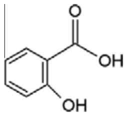
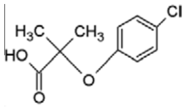
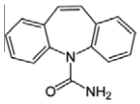
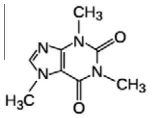
The NaK-Bentonite used in the present study was purchased from Sigma–Aldrich. The chemical composition (wt.%) was the following: 52.44% SiO_2, 20.01% Al_2O_3, 8.25% Fe_2O_3, 10.86% Na_2O, 5.90% MgO, 1.80% CaO, and 0.74% K_2O. The NaK-Bentonite was pre-treated with a Na_2CO_3 solution (0.5 M) for 24 h and washed thoroughly with copious amounts of deionized water. An estimated cation exchange capacity of 100 mmol/100 g was used throughout our calculations since it is the typical value reported in the literature for bentonites with similar composition [68]. For reference, the material that resulted from this modification will be known as NaBt.

The chemicals used for the modifications described below were obtained from Sigma–Aldrich. These were 1-hexadecylpyridinium bromide (98.0% purity), aluminum chloride ($AlCl_3$, ⩾99.9%), sodium carbonate (Na_2CO_3, ⩾99.0%), copper (II) nitrate ($Cu(NO_3)_2$, ⩾99.99%), cobalt (II) nitrate ($Co(NO_3)_2$, ⩾98%), and nickel sulfate hexahydrate ($Ni(SO_4)_2$. $6H_2O$, ⩾99%). Chemicals used for the adsorption experiments were caffeine (⩾99%), salicylic acid (acetylsalicylic acid, >99%), clofibric acid (2-(4-chlorophenoxy)-2-methyl propionic acid, 97%), and carbamazepine. A summary of the relevant properties and uses of these PPCPs is presented in Table 1. The water used during the syntheses and adsorption tests was distilled and later deionized to a resistivity of less than 18 mΩ cm.

2.2. Preparation of Al-pillared and modified clays

An aluminum-pillared bentonite clay (Al-NaBt) was prepared using an aluminum chloride solution and following recipes

Table 1
Relevant properties of selected PPCPs.

PPCP	pK_a	log K_{ow}	Natural pH	Max. Occurrence Wastewater (ppb)	Common use
 Salicylic acid	2.97[69]	2.24	4.28	0.07[30]	Medical; cosmetic; food preservative
 Clofibric acid	2.57[69]	2.5[70]	3.18	0.258[71]	Metabolite of lipid regulators clofibrate, etofibrate, theofibrate, antiphlogistic
 Carbamazepine	13.9[72]	2.3–2.5[73]	6.23	0.3[30] 0.37[30]	Antiepileptic
 Caffeine	0.6[74]	−0.07[75]	6.55	5.7[76]	Stimulant