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Environmental applications of inorganic–organic clays for recalcitrant organic pollutants removal: Bisphenol A

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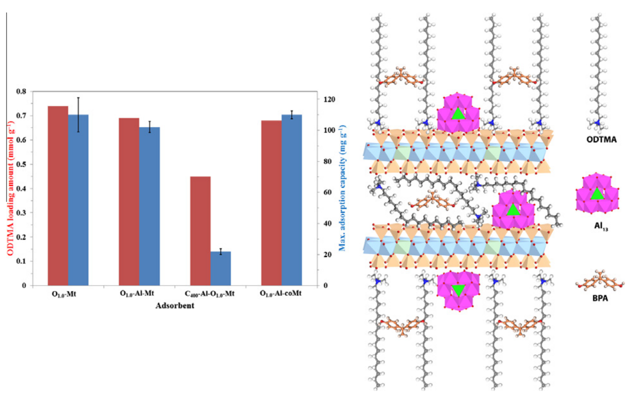
HIGHLIGHTS

- Inorganic-organic clays were characterised using FTIR and BET methods.
- Optimum adsorption conditions for bisphenol-A from water were investigated.
- Maximum bisphenol-A adsorption capacity into inorganic-organic clay is 109.89 mg g^{-1}.
- Bisphenol-A adsorption is related to the loaded surfactant amount.
- Hydrophobic interactions are responsible for bisphenol-A adsorption.

GRAPHICAL ABSTRACT



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ABSTRACT

Bisphenol-A (BPA) adsorption onto inorganic–organic clays (IOCs) was investigated. For this purpose, IOCs synthesised using octadecyltrimethylammonium bromide (ODTMA, organic modifier) and hydroxy aluminium (Al_{13}, inorganic modifier) were used. Three intercalation methods were employed with varying ODTMA concentration in the synthesis of IOCs. Molecular interactions of clay surfaces with ODTMA and Al_{13} and their arrangements within the interlayers were determined using Fourier transform infrared spectroscopy (FTIR). Surface area and porous structure of IOCs were determined by applying Brunauer, Emmett, and Teller (BET) method to N_2 adsorption–desorption isotherms. Surface area decreased upon ODTMA intercalation while it increased with Al_{13} pillaring. As a result, BET specific surface area of IOCs was considerably higher than those of organoclays. Initial concentration of BPA, contact time and adsorbent dose significantly affected BPA adsorption into IOCs. Pseudo-second order kinetics model is the best fit for BPA adsorption into IOCs. Both Langmuir and Freundlich adsorption isotherms were applicable for BPA adsorption ($R^2 > 0.91$) for IOCs. Langmuir maximum adsorption capacity for IOCs was as high as 109.89 mg g^{-1} and it was closely related to the loaded ODTMA amount into the clay. Hydrophobic interactions between long alkyl chains of ODTMA and BPA are responsible for BPA adsorption into IOCs.

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1. Introduction

Recently, there is a great public and environmental concern towards endocrine disrupting chemicals (EDC) because they cause adverse health effects on humans, animals and their descendants effecting growth development, reproduction, and behaviour. Bisphenol-A (BPA) is the most frequently detected EDC in wastewaters [1–3]. It is an organic compound with two phenolic groups (Fig. 1) which is produced in large quantities worldwide for use primarily in the production of polycarbonate plastics and epoxy resins [4]. Polycarbonate plastics are used in some food and drink containers and the resins are used as lacquers to coat metal products such as food cans, bottle tops, and water supply pipes. Other uses include flame retardants, unsaturated polyester resins and polyacrylate, polyetherimide and polysulphone resins [5,6]. BPA is released into the environment mainly through industrial and municipal waste waters contaminating surface waters, underground waters and drinking waters [7,8].

BPA mimics the structure and the function of the hormone estradiol with the ability to bind and activate the same estrogen receptor as the natural hormone at very low concentrations [1,5]. BPA is a recalcitrant water contaminant which cannot be readily removed from the water due to complex aromatic molecular structure and low biodegradability. Therefore, it is detected in the effluents of waste water treatment plants [9,10]. Some of the reported methods for removing BPA from water are adsorption [10–14], biodegradation [15–18], photodegradation [19] chemical oxidation [20] nanofiltration [21–23] and ozonation [24].

Among these methods, adsorption is the easiest and fastest method for the removal of BPA from aqueous solution with no production of harmful secondary products [25]. While activated carbon is a widely used adsorbent for the removal of organic contaminants including BPA in wastewater treatment systems [26–30], naturally abundant clay minerals (e.g.: montmorillonite) are inexpensive precursors for adsorbents with unique properties such as high cation exchange capacity, surface area, micro- and meso-porosity and swelling properties [31]. Surface properties of the clays can be changed from hydrophilic to hydrophobic by replacing the exchangeable interlayer cations with organic cationic surfactants. Organoclays have been tested for BPA adsorption from aqueous solution recently and were found to be effective [10,12].

Clay minerals such as montmorillonite modified by intercalating both inorganic and organic modifiers such as metal hydroxy polycations and organic cationic surfactants are known as inorganic–organic clays (IOCs) [32]. Quaternary alkyl ammonium cations and hydroxy aluminium cation ($[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ or Al_{13}) are the most commonly used organic and inorganic modifiers in synthesis of IOCs. IOCs have the properties of both organoclays and pillared clays including hydrophobicity/organophilic properties, high interlayer distances, thermal stability and porosity [33,34]. According to the literature, IOCs have the ability to simultaneously adsorb wide range of organic and inorganic contaminants and previously reported adsorption studies of IOCs are summarised in Table 1.

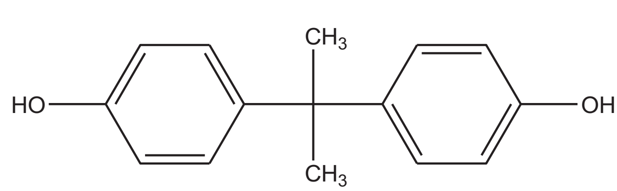

Fig. 1. The chemical structure of BPA ($C_{15}H_{16}O_2$; molecular weight 228.29 g mol^{-1}) IUPAC name: 4,4′-(propane-2,2-diyl)diphenol; Solubility in Water: 120–300 mg L^{-1} (21.5 °C); Acid dissociation constant (p*K*a): 9.6–10.2.

In particular, IOCs are effective adsorbents for the removal of phenol and its chloro and nitro derivatives which are among the most common water pollutants in all types of wastewaters (Table 1). Similarly, IOCs are assumed to be effective adsorbents to remove hydrophobic BPA from water. Although, the adsorption of organic pollutants from water using octadecyltrimethylammonium bromide (ODTMA) modified organoclays have been mentioned in the literature [35–37], more studies are required to investigate the adsorption properties of IOCs synthesised using ODTMA as the organic modifier and Al_{13} as the inorganic modifier.

Therefore, the aims of this study are to investigate optimum adsorption conditions, kinetics and adsorption mechanism of BPA adsorption into IOCs. To fulfil these aims, IOCs synthesised using three different methods with different surfactant concentrations were used. ODTMA and Al_{13} were used as the organic cationic surfactant and metal hydroxy polycation, respectively. IOCs synthesis and characterisation using various techniques including thin film X-ray diffraction (XRD), thermogravimetric analysis (TGA), laser ablation inductively coupled mass spectroscopy (LA-ICP-MS), total organic carbon analysis (TOC) and X-ray fluorescence spectroscopy (XRF) are described in a previously published paper by Rathnayake et al. [54].

In the current study, IOCs were further characterised using Fourier transform infrared spectroscopy (FTIR) and Burnauer, Emmett, and Teller (BET) methodology. The molecular arrangements of intercalated surfactant and Al_{13} pillars and their interactions with the clay structure were investigated using FTIR spectroscopic technique. The effect of intercalation method and surfactant concentration used in the synthesis process on the surface parameters and pore structure of IOCs was determined using the BET method. Adsorption characteristics of BPA into IOCs were investigated through a series of batch experiments under different experimental conditions. The effect of adsorbent amount, initial concentration, and contact time on BPA adsorption into IOCs was determined. Kinetics and adsorption isotherm models involved with the adsorption process were suggested and the adsorption mechanism was proposed. Overall, this work exhibits the potential application of IOCs as effective adsorbents for organic contaminants during environmental remediation and water purification.

2. Experimental

2.1. Materials

Texas Montmorillonite STx-1 (denoted as Ca–Mt) used in this study was supplied by the Clay Minerals Society and was used without further purification. The cation exchange capacity of this montmorillonite is 84.4 meq/100 g. The surfactant selected for this study is octadecyltrimethylammonium bromide (denoted as ODTMA, $C_{21}H_{46}BrN$, FW: 392.50) and bisphenol-A (BPA) were analytical grade and purchased from Sigma–Aldrich.

2.2. Synthesis of IOCs

A summary of the three intercalation methods used to synthesis IOCs along with synthesis of organoclays and Al-pillared clays are presented in Table 2. The detailed synthesis procedures are presented in a previously published paper by Rathnayake et al. [54].

2.3. Characterisation of IOCs

2.3.1. Fourier transform infrared spectroscopy (FTIR)

The infrared spectra were obtained using a Thermo Scientific Nicolet iS50 FTIR Spectrometer with a smart endurance