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Hybrid materials precursor to natural clay in the attenuation of bisphenol A from aqueous solutions

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ABSTRACT

The present study demonstrates the potential use of organo- and inorgano-organo-modified bentonite and locally collected clay to efficiently attenuate bisphenol A (BPA), one of the most important endocrine disrupting chemical) from aqueous solutions. The hybrid materials were obtained by modifying commercial bentonite or locally collected clay with hexadecyltrimethylammonium bromide (HDTMA) to obtain organo-modifed clay samples (named BH or LCH). Aluminum pillared HDTMA modified clay samples were obtained as inorgano-organo-modified clay hybrid materials (named BAH or LCAH). The hybrid materials were characterized using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) methods. Surface morphology of these solids was determined by field emission scanning electron microscope (FE-SEM) images. pH_{PZC} of these solids were obtained by acid and base titrations. These hybrid materials were used as molecular sieve to attenuate BPA from aqueous solutions. Batch reactor studies were conducted for various physico-chemical parameters. The effect of pH, initial BPA concentration, contact time, and background electrolyte concentrations was studied under the batch mode operations. Porous hybrid materials showed substantially higher sorption capacity than virgin clay. Column reactor operations were performed to obtain loading capacity of these solids for BPA under dynamic conditions.

1. Introduction

Clay minerals are hydrous aluminosilicate with very fine particle size [1], usually composed of mixtures of fine grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate, and metal oxides. Clays invariably contain exchangeable cations and anions lying within the interspace of phyllosilicate sheets. The prominent cations and anions are Ca^{2+}, Mg^{2+}, H^+, K^+, NH_4^+, Na^+, and SO_4^{2-}, Cl^-, PO_4^{3-}, NO_3^-, respectively. Energetically, it is possible to exchange these ions with other cations or anions without affecting the basic structure of clay minerals [2]. Moreover, introduction of cationic surfactant molecules within the interspace by exchange process enables a significant increase in basal spacing of clay sheets. The properties of clay minerals could also be changed from highly hydrophilic/lyophobic to increasingly hydrophobic/lipophilic/organophilic. Materials found to be effective in the attenuation of organic pollutants are reported to have low or no-polarity [1,3].

Application of organo-clay to remove several organic pollutants has been reported in literature. Attenuation of pollutants can be enhanced significantly by organo-modified clay due to possible partitioning of pollutant molecules at the hydrophobic core of the clay. The attenuation of organic impurities largely depends on the kind of surfactant used, the quantity of surfactant molecule, modification conditions, and the pH of the solutions [4,5]. A novel organo-zeolite adduct synthesized by sorbing humic acids (HA) onto zeolitic tuff [6] showed that the HA–zeolite adducts possessed significantly high removal capacity for phenol. Sericite modified with HDTMA and AMBA has been employed in the removal of phenol from aqueous solutions [7]. Moreover, organo-clays (i.e., Cloisite-10A, Cloisite-15A, Cloisite-30B and Cloisite-93A) are used efficiently to attenuate organic pollutants viz., p-nitrophenol, phenol, and aniline from aqueous solutions [8]. Akbal investigated sorption of phenol and 4-chlorophenol on pumice modified with the cationic surfactants hexadecyltrimethylammonium bromide (HDTMA) and benzyldimethyltetradecylammonium chloride (BDTDA) [9]. Similarly, montmorillonite modified with cetyltrimethylammonium bromide (CTAB) was found to be effective for sorptive removal of phenol, m-nitrophenol (m-NP), and o-cresol using column experiments [10].

Thousands of anthropogenic chemicals released into the environment are found to be endocrine-disrupting compounds (EDCs) [11]. These are exogenous chemicals or chemical mixtures that impact endocrine system structure or function and cause adverse

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effects [12,13]. Chemicals implicated in endocrine disruption include biocides, industrial compounds, surfactants, and plasticizers including bisphenol A (BPA) [14,15]. Bisphenol A is ubiquitous in the environment for last 80 years because of its presence in a multitude of products, including food and beverage packaging, flame retardants, adhesives, building materials, electronic components, and paper coatings [16,17]. It is released during chemical manufacture, transport, and processing of materials. Post-consumer releases are primarily via effluent discharge from municipal wastewater treatment plants, leaching from landfills, combustion of domestic waste, and natural breakdown of plastics in the environment [18,12]. Tolerable daily intake of BPA is recommended at 25 μg/kg bodyweight/day by the Health Canada and 50 μg/kg body weight/day by the United States of America and the European Food Safety Authority (EFSA) [19,20]. However, EFSA revised tolerable daily intake (TDI) level of BPA to be 5 μg/kg bw/day (0.005 mg/kg/bw/day) recently [21].

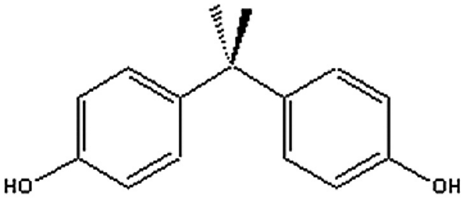
BPA has relatively high concentrations (up to 21 μgL^{-1}) in the rivers and lakes worldwide [18]. Several studies have indicated that BPA at high concentrations causes several adverse effects, especially on reproduction [22]. Studies on the effects of BPA exposure demonstrated many adverse effects on rodents due to high BPA levels, including advanced puberty [23], increased obesity [24], pregnancy complications [25], defects in male and female reproductive organs [26], prostate effects, and increases in malignancies [27]. In mollusk *Mytilusedulis*, spawning induction as well as oocyte and ovarian follicle damage were observed following BPA exposure for 3 weeks at 50 $mg\,L^{-1}$ [28].

Carbon-based hyper cross linked and aminated porous resins are reported to be efficient materials in the removal of BPA and other phenolic compounds [29]. Zeolite synthesized from coal fly ash (ZFA) modified with hexadecyltrimethyl-ammoniumbromide (HDTMA) shows relatively high affinity towards BPA [29]. Fibric peat modified with hexadecyltrimethylammonium bromide (HTAB) is reported to have faster initial BPA sorption with higher removal capacity comparing to unmodified peat over a wide range of concentrations [30]. Organic–inorganic hybrid mesoporous material (Ph-MS) was synthesized by co-condensation of phenyltriethoxysilane and tetraethoxysilane. Ph-MS solid enables the removal of most BPA from aqueous solutions with a faster uptake rate than powder activated carbon (PAC) [31]. Among many common adsorbents, including natural materials and activated carbon, natural clay showed potential as sorbing materials because of its low cost, swelling properties, high surface area, and ion exchange properties [32,33]. Ca-montmorillonite modified with surfactants dodecyltrimethyl ammonium bromide (DDTMA) and hexadecyltrimethyl ammonium bromide (HDTMA) is demonstrated to be effective remediation of water contaminated by BPA [33]. Similarly, polyethersulfone (PES)-organophilic-montmorillonite (OMMT) hybrid particles with various proportions of OMMT are successfully used for the removal of BPA from aqueous solutions [34]. Recently, the hybrid materials precursor to natural clay was obtained and employed in the remediation of diclofenac sodium from aqueous solutions [35]. The present study, further, aims to employ hybrid materials as possible molecular sieve to attenuate the BPA from aqueous solutions under batch and column reactor operations.

2. Methods and materials

2.1. Materials

Bentonite was procured from commercial supplier mined at Bhuj, Gujarat, India. Bentonite clay was used after repeated washings with distilled water and dried at 90 °C in a drying oven. Local clay was collected from the field of Mizoram (India). The clay was separated using standard procedure according to International Soil Reference and Information Centre (ISRIC) available at http://www.isric.org/isric/webdocs/docs/ISRIC_TechPap09_2002.pdf. Clay materials were crushed in mortar and then sieved to obtain 100 British standard sieve (BSS) mesh size particles of 0.150 mm. The bentonite and local clay powder were then subjected to obtain cation exchange capacity (CEC) using standard US EPA (United States Environmental Protection Agency) method 9080 available at http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/9080.pdf. The CEC of bentonite and local clay was found to be 69.35 and 46.38 meq/100 g of clay, respectively. Hexadecyltrimethyl ammonium bromide (HDTMA) and BPA were procured from Sigma-Aldrich, USA. Aluminum(III) chloride was obtained from Merck India. Sodium chloride (extra pure) was obtained from HIMEDIA, India. Other chemicals used were of AR grades. Water was purified using Millipore water purification system (Milli-Q+).



Structure of Bisphenol A

2.2. Methodology

2.2.1. Preparation of HDTMA-modified clay

Bentonite and local clay were modified with hexadecyltrimethylammonium bromide using wet cation exchange process. A total of 20 g of each clay powder was taken separately into 1 L of HDTMA solution with 1.0 CEC of respective clay. The slurry was refluxed for 48 h at 60 °C under constant stirring. The slurry was then filtered. Solid clay was washed with purified water. Excess or free surfactant was removed by Soxhlet extraction. The organo-modified bentonite/or local clay was dried at 90 °C in a drying oven and stored in an airtight polyethylene bottle. The HDTMA-modified bentonite/or local clay were then labelled as BH or LCH samples, respectively.

2.2.2. Preparation of inorgano–organo-modified clay

The bentonite and/or local clay was pillared with aluminum and then modified with organic cations HDTMA to obtain HDTMA-Al-bentonite (BAH) or HDTMA-Al-local clay (LCAH) hybrid materials by simple wet process as detailed elsewhere [35]. Briefly, aluminum(III) pillaring solution was prepared by mixing 100 mL of 0.4 mol/L NaOH and 100 mL of 0.2 mol/L aluminum(III) chloride solutions under vigorous and constant stirring. The solution mixture was then kept 7 days for aging at room temperature. A known amount of HDTMA (equivalent to 1:1CEC of clay) was added into this aluminum solution under stirred conditions. Bentonite and/or LC clay powders (4 g) each in 300 mL of water was taken into a round bottom flask. To this suspension, HDTMA mixed aluminum solution was added and stirred for approximately 5 h at room temperature. The slurry was then kept at room temperature for another 2 days. The hybrid materials of bentonite or local clay were separated carefully and the solid was washed with plenty of distilled water to obtain materials free from halides or any unbound/free HDTMA.