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Efficient use of hybrid materials in the remediation of aquatic environment contaminated with micro-pollutant diclofenac sodium

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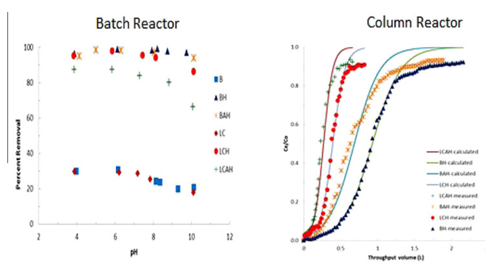
HIGHLIGHTS

- Hybrid materials are obtained using bentonite and locally available clay.
- Materials are characterised by the FT-IR, XRD and SEM analysis.
- Materials are employed in efficient and effective attenuation of diclofenac from aqueous solutions.

GRAPHICAL ABSTRACT



B: Bentonite; BH: HDTMA-B; BAH: HDTMA-Al-B; LC: Local Clay; LCH: HDTMA-LC; and LCAH: HDTMA-Al-LC

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ABSTRACT

The aim of this study is to synthesise indigenously the hybrid materials and their efficient use to treat the wastewater contaminated with one of important micro-pollutant diclofenac. The hybrid materials are obtained modifying the commercial bentonite (B) and locally collected clay (LC) with the hexadecyltrimethylammonium bromide (HDTMA) as to obtain the organo-modified clay samples (BH and LCH). Moreover, the B and LC clay samples are pillared with aluminium and modified with the HDTMA as to obtain inorgano–organo-modified clay hybrid materials (*viz.*, BAH and LCAH solids). The hybrid materials are characterised by the XRD (X-ray diffraction) and FT-IR (Fourier Transform Infra-Red) analytical methods and the surface morphology is obtained by the FE-SEM (Field Emission Scanning Electron Microscope) images of these solids. pH_{PZC} (Point of Zero Charge) of these solids is obtained by acid base titrations. Further, these materials are assessed in the efficient and effective treatment of aquatic environment contaminated with diclofenac sodium under the batch and fixed-bed column reactor operations. Batch data is obtained for various physico-chemical parametric studies *viz.*, the effect of solution pH (3.8–10.0), sorptive concentrations (1.0–20.0 mg/L), and background electrolyte concentrations (0.0001–0.1 mol/L NaCl). The kinetics of the uptake of diclofenac by these solids is conducted using the pseudo-first, pseudo-second and fractal-like-pseudo-second order non-linear rate equations. The rate constants along with the removal capacity are, therefore, estimated. Further, the fixed-bed column reactor operations are performed to obtain the loading capacity of column for diclofenac under the dynamic conditions.

1. Introduction

Clay and minerals are fine particles of hydrous aluminosilicates. Crystal structure of clay and minerals possess layered sheets which are firmly and structurally arranged. Each layer is having two, three or four sheets. The sheets are having tetrahedral (T) $[SiO_4]^{4-}$ or octahedral (O) $[AlO_3(OH)_3]^{6-}$ units. The interiors of these sheets are composed with smaller cations and their apices are occupied by oxygen from which some are bonded with protons (as –OH). This basic structural element is arranged to form a hexagonal network with each sheet [1,2]. Bentonite is natural clay,

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mostly containing the smectite and kaolinite group of clays. The group of smectite is fairly an expanding three-sheet phyllosilicates, where the T:O ratio is 2:1 and the charge of the three-sheet layer (unit cell) is 0.5–1.2 e/uc (negative charge). This charge arises from the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet for Mg^{2+} and Al^{3+} in the octahedral sheet. This possesses no hydroxyl functionality within the interlayer space. Whereas the kaolinite and serpentine group is a typical two-sheet phyllosilicates, where the T:O ratio is 1:1 and the charge of the two-sheet layer (unit cell) is 0 e/uc. Since bentonite contain dominantly the smectite mineral having permanent negative charge which is naturally compensated with the exchangeable cations (i.e., Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}). These exchangeable cations are located within the interlayer space of bentonite sheets [3]. Therefore, bentonite possesses fairly a high cation exchange capacity (CEC), which termed it a good water replaced swelling type mineral. Moreover, because of high specific surface area enables this mineral to show high adsorption/absorption capacity towards several ionic or polar compounds.

Although clay and minerals are natural porous materials and used widely in decontamination of inorganic pollutants from wastewaters [4,5] however; show insignificant applicability in the treatment of several organic pollutants having non- or low-polarity [6]. Moreover, most of the clay materials show less settling capacity hence, limiting its wider practical implication in waste water treatment operations. However, since the clay materials are having exchangeable cations, hence this could be exchanged with the organo cations. Therefore, the modified materials possess an enhanced organophilicity and this, perhaps, be effective in attenuation of several organic pollutants from aqueous solutions. Similarly, the hybrid materials obtained by inorgano–organo-clay shows enhance applicability in waste water treatment since this could not only be effective in the removal of inorganic pollutants but also show fair affinity towards the organic impurities as well. Furthermore, these hybrid materials show achievable settling capacity makes easy for solid/aqueous separation. In a line, silylated pillared bentonite (SPILC) is obtained as inorgano–organo-composite [7]. These materials possess two different sorption sites enabling to remove both organic and inorganic pollutants from aqueous solutions simultaneously. Aluminium pillared sericite is modified with HDTMA and AMBA (alkyldimethylbenzylammonium chloride) surfactants and utilised in the removal of As(III) and As(V) from aqueous solutions even in presence of phenol [6]. Sericite, Na–montmorillonite and zeolite are modified with dimethyltetradecylbenzylammonium chloride, hyamine 1622® and trimethylbenzylammonium chloride organic cations. Further, these organo-modified materials are employed in the attenuation of several non-ionic organic contaminants (NOC) *viz*., benzene, phenol and toluene from aqueous solutions [8]. Previously, sericite was modified with HDTMA and AMBA, which is then employed in the removal of phenol from aqueous solutions [9]. Montmorillonite is pillared with aluminium and modified with the hexadecyl pyridine. The solid is found to be effective and efficient in the removal of phenol from aqueous solutions [10].

The presence of micro-pollutants (in particular, the pharmaceuticals and personal care products) in aquatic environment is received a serious environmental concern during recent past; since several micro-pollutants are persistent at low level, low biodegradability and the toxicity possessed by them. Therefore, these contaminants are known as emerging water pollutants. It is reported that the level of these contaminants increased significantly in the wastewater treatment plant (WWTPs) effluents, surface water, sewage water, ground water or even in the drinking water supply [11–14]. Further, the presence of such residual micro-pollutants in water bodies are found problematic in aquatic ecosystem (e.g., feminisation of fish) and potential concern towards human health (e.g., increasing antibiotic resistance) [15–17]. In addition to the pharmaceutical industries, the human urine and faeces is reported to be additional but significant sources which, elevating the level of pharmaceutical load in the municipal/sewage wastewaters since *Ca* 70% of consumed pharmaceuticals are excreted in human urine as active ingredients and metabolites [17–19]. Diclofenac (2-[-2′,6′-(dichlorophenyl)amino]phenyl acetic acid) is used mostly as its sodium salt. This is a non-steroidal anti-inflammatory drug (NSAID) and prescribed for the treatment of inflammatory and painful diseases of rheumatic, nonrheumatic and antiarthritic origin. It is also recommended to reduce menstrual pain, dysmenorrhea etc. [20,21]. Continued intake of diclofenac, even at low levels, by human shows several adverse biochemical effects e.g., cytotoxicity to liver, kidney and gill cells as well the renal lesions [22–26]. It may also influence the biochemical functions of fish and lead to tissue damage [27]. Further, it is pointed that due to the low solubility, high log K_{ow} value, low dipole moments and negative charges of diclofenac causes easy escape of this chemical from the nano-filtration unit [28]. The unit operations associated with ozonation [29], adsorption on activated carbon [30] and membrane filtration as nano-filtration and reverse osmosis [31,32] are the possible ways that could be employed for the removal of several pharmaceuticals (>99%) [33].

Previously, several materials including activated carbons [33] or advanced materials (Fe^{0} based trimetallics (Pd, Cu and Ni)) [34], anion exchange polymer [19] is demonstrated in the possible attenuation of diclofenac from aqueous wastes. The granular activated carbon in the fixed bed column is found to be effective in the removal of diclofenac from aqueous solution as studied under column reactor operations [35]. The hybrid material precursor to carbon nanotubes and alumina is to be found effective materials in the removal of diclofenac from aqueous solutions [36]. In a line, hexagonal mesoporous silicate (HMS) and amine and mercapto-functionalised HMS derivatives are employed in the sorptive removal of diclofenac. Further, the mechanistic aspects are discussed using several physico-chemical parametric studies [37]. The Isabel grape (*Vitis labrusca* × *Vitis vinifera*) bagasse is employed in the diclofenac removal from aqueous solutions under the batch reactor operations [38]. Therefore, the present investigation aims to exploit the natural bentonite or locally available clay as to obtain the novel hybrid materials using the HDTMA or aluminium pillared HDTMA modified clay. The modified materials possess hydrophobic core, perhaps, provide an efficient partitioning of organic contaminants from aqueous solutions even at low level. The batch reactor operations are conducted at wide range of physico-chemical parametric studies; provides a plausible mechanism involved at solid/solution interfaces along with the fixed-bed column reactor operations performed to optimise the loading capacity of contaminants under the dynamic conditions.

2. Materials and methods

2.1. Materials

Bentonite clay was obtained from commercial supplier. It was mined at Bhuj, Gujarat, India. The bentonite was not separated anymore and used after simple washing with distilled water and dried at 90 °C in a drying oven. However, the local clay was collected from the field of Mizoram. Since this was having several impurities hence, was thoroughly separated using the standard ISRIC (International Soil Reference and Information Centre) method as detailed elsewhere (http://www.isric.org/isric/webdocs/docs/ISRIC_TechPap09_2002.pdf). The bentonite and local clay samples are crushed in mortar and sieved to obtain 100 BSS (British Standard Sieve) mesh size particles (0.150 mm). The bentonite and local clay powder is then subjected for its cation