



## Hybrid materials in the removal of diclofenac sodium from aqueous solutions: Batch and column studies



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### ABSTRACT

Hybrid materials (AAS (Al-AMBA-sericite and AHS (Al-HDTMA-sericite)) was obtained and materials are characterized by XRD, SEM and IR analytical techniques. Hybrid materials were assessed for efficient removal of diclofenac from aqueous solutions. Increasing the diclofenac concentration (1.0 to 20.0 mg/L) and pH 2 to 7 favored greatly the removal of diclofenac by AAS and AHS. Background electrolyte concentrations from 0.0001 to 0.1 mol/L NaCl, insignificantly affected percent removal of diclofenac. The breakthrough results were fitted well to the Thomas equation and hence, loading capacity of diclofenac was found to be 0.561 and 1.056 mg/g for AAS and AHS, respectively.

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### Introduction

The contamination of aquatic environment by micro-pollutants, particularly, the hormones, pharmaceuticals and personal care products is a serious environmental concern during recent past; because of their persistency, low biodegradability and toxicity. It was reported that the level of these pollutants was increased significantly in the wastewater treatment plants (WWTPs) effluents, surface water, sewage water, ground water or even the drinking water [1–5]. In addition to the pharmaceutical industries, the human urine and feces is reported to be additional important and significant sources of increasing the pharmaceutical load in the municipal/sewage wastewaters since ca. 70% of consumed pharmaceuticals are excreted in human urine as active ingredients and metabolites [6–8]. Diclofenac (2-[-2',6'-(dichlorophenyl)amino]phenyl acetic acid), used mostly as its sodium salt is a non-steroidal anti-inflammatory drug (NSAID) widely used in treatment of inflammatory and painful diseases of rheumatic, nonrheumatic and antiarthritic origin. It is recommended to reduce menstrual pain, dysmenorrhea etc. An annual consumption of diclofenac is ca. 940 t globally with a recommended dose of 100 mg/day [9,10].

The continued intake of diclofenac even, at low level, by human shows several adverse biochemical effects e.g., cytotoxicity to liver, kidney and gill cells as well the renal lesions even at a concentration of 1 µg/L [11–15]. It may also influence the biochemical functions of fish and lead to tissue damage [16]. Since the WWTPs are inappropriate to degrade/remove diclofenac or its metabolites from aqueous solutions hence, advanced treatment methods is a need of present day. The low solubility, high log  $K_{ow}$  values, low dipole moments and negative charges makes high rejection values for diclofenac in the nano-filtration unit [17]. The unit operations associated with ozonation [18], adsorption on activated carbon [19] and membrane filtration as nano-filtration and reverse osmosis [20,21] are some of possible ways which could be employed in the removal of several pharmaceuticals (>99%) [22]. Several materials including activated carbons [22] or advanced materials (Fe<sup>0</sup> based trimetallics (Pd, Cu and Ni)) [23], anion exchange polymer [8] were employed in the removal of diclofenac from aqueous wastes. The granular activated carbon in the fixed bed column was found to be effective in the diclofenac removal studied under column reactor operations [24]. Similarly, the ozone oxidation in presence of activated carbon was found an efficient way of removing the diclofenac from aqueous solutions [25]. The re-generable hybrid carbon nanotubes/alumina was used in effective removal of diclofenac from aqueous solutions [26]. In a line, hexagonal mesoporous silicate (HMS) and amine and mercapto-functionalized HMS derivatives

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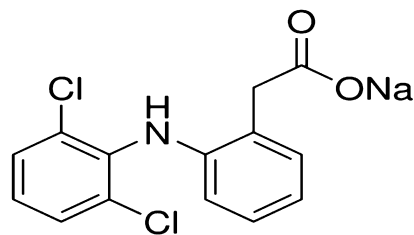
were employed in sorptive removal of diclofenac. Further, the mechanistic aspects were discussed using several physico-chemical parametric studies [27]. The Isabel grape (*Vitis labrusca* × *Vitis vinifera*) bagasse was employed in the diclofenac removal from aqueous solutions under the batch reactor operations [28].

Clay and minerals are natural porous materials, employed widely in decontamination of inorganic pollutants from wastewaters [29] however; show insignificant applicability in treatment of organic pollutants. These materials possess low settling properties hence, limiting its practical implication in such purposes. However, the organo-modified clays are found to be more organophilic and perhaps effective in organic pollutants attenuation [30]. Similarly, the hybrid materials obtained by inorganic- and organic-modification possess enhanced applicability as it could not only be effective in the removal of inorganic pollutants but also show fair affinity toward organic impurities simultaneously from aqueous wastes. Additionally, the hybrid materials show achievable settling capacity which offers an easy separation. In a line, silylated pillared bentonite (SPILC) was obtained as inorgano-organocomposite [31]. These materials possess two different sorption sites enabling to remove both organic and inorganic pollutants from aqueous solutions simultaneously [32,33]. Similarly, aluminum pillared sericite was modified with HDTMA and AMBA and utilized in the removal of As(III) and As(V) from aqueous solutions even in presence of phenol [34]. Exfoliated sericite-polyamide 6 nano-composite was obtained and the mechanical properties of solids were discussed elsewhere [35]. Sericite, Na-montmorillonite and zeolite were modified with dimethyltetradecylbenzyl ammonium chloride, hyamine 1622<sup>®</sup> and trimethylbenzyl ammonium chloride organic cations. Further, these organo-modified materials were employed in the attenuation of several non-ionic organic contaminants (NOC) viz., benzene, phenol and toluene from aqueous solutions [36]. Previously, sericite was modified with HDTMA and AMBA, which was then employed in the removal of phenol from aqueous solutions [37]. The present communication relates the use of aluminum pillared HDTMA/or AMBA modified sericite hybrid materials in the remediation of diclofenac sodium contaminated waters. The natural abundance of sericite could, perhaps, enable the materials more cost effective and environmentally benign.

## Materials and methods

### Materials

Natural mica based clay sericite was obtained from the Keumnam deposit, Samcheok, Korea. The sericite was crushed and sieved to obtain 200–300 BSS (British Standard Sieve) mesh size particles. This powder was washed with purified water and dried at 90 °C in a drying oven. Cation exchange capacity (CEC) of this sericite sample was obtained using standard US EPA method 9080 (<http://www.epa.gov/osw/hazard/test.methods/sw846/pdfs/9080.pdf>) and was found to be 8.85 meq/100 g of sericite. Sericite was contained with several metal oxides mainly as silicon and aluminum oxides listed elsewhere [38]. Hexadecyltrimethyl ammonium bromide (HDTMA) was procured from Sigma-Aldrich, USA whereas alkyldimethylbenzyl ammonium chloride (AMBA) 50% solution, and aluminum(III) chloride were obtained from Junsei Chemical Co. Ltd., Japan. Diclofenac sodium salt was procured from Sigma-Aldrich, USA (Structure given below). Sodium chloride, Extrapure was obtained from HIMEDIA, India. The other chemicals used were of Analytical or equivalent grades. Deionized water was further purified (18 MΩ cm) using a Millipore water purification system (Milli-Q+).



Structure of diclofenac sodium

### Methodology

#### Preparation of inorgano-organosericite

Sericite was pillared with aluminum and then modified with organic cations viz., HDTMA or AMBA as to obtain the HDTMA-Al-sericite (AHS) or AMBA-Al-sericite (AAS) materials. A simple wet synthesis is followed as described elsewhere [34]. In brief, aluminum solution was prepared by mixing 100 mL of 0.4 mol/L NaOH and 100 mL of 0.2 mol/L aluminum chloride solutions under vigorous and constant stirring and this solution mixture was kept 7 days for aging at room temperature. To this aluminum solution, a known amount of HDTMA/or AMBA (the HDTMA/or AMBA was introduced equivalent to 1:1 CEC of sericite) under stirred conditions. Sericite powder (4 g) in 300 mL of water was then taken in a round bottom flask. To this solution mixture, HDTMA/or AMBA mixed aluminum solution was introduced and stirred for ca. 5 h at room temperature. The slurry was then kept at room temperature for another 2 days. The modified sericite slurry was separated carefully and the solid was washed with plenty of purified water as to free it from the halides. These solids were then dried at 50 °C in a drying oven and grounded gently in mortar. The powders were kept in an airtight polyethylene bottles for further investigations.

#### Characterization and surface morphology of hybrid materials

Surface morphology of AAS and AHS along with the unmodified sericite was obtained by taking the SEM (scanning electron microscopic) images using the scanning electron microscope (Model FE-SEM SU-70, Hitachi, Japan). X-ray diffraction (XRD) data was recorded using the X-ray diffraction machine (PANalytical, Netherland; Model X'Pert PRO MPD). The Cu  $K_{\alpha}$  radiation having wavelength 1.5418 Å is used. FT-IR data was obtained for these materials using FT-IR machine (Bruker, Tensor 27, USA by KBR disk method).

#### pH<sub>PZC</sub> and BET measurements

The pH<sub>PZC</sub> (point of zero charge) of sericite, AHS and AAS was obtained using the known method as described previously [34, 39–41]. Similarly, the specific surface area of these solids was obtained using the BET Analyzer Macsorb HM machine (Model-1201) Japan.

#### Batch reactor experiments

Stock solution of diclofenac sodium (50 mg/L) was prepared by dissolving accurate and appropriate amount of diclofenac sodium salt in purified water. The solubility was greatly enhanced with the sonication of solution for 5 min. Further, the required diclofenac concentration was obtained by successive dilution of stock solution 5.0 mg/L of diclofenac solution (100 mL) was taken in polyethylene bottles and the pH was adjusted by drop-wise addition of concentrated HCl/NaOH

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