



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 (Fe⁰ 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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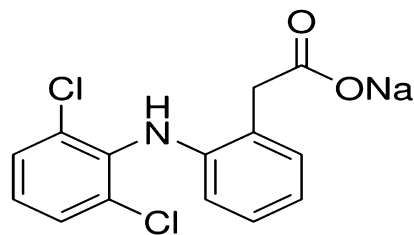
were employed in sorptive removal of diclofenac. Further, the mechanistic aspects were discussed using several physico-chemical parametric studies [27]. The Isabel grape (*Vitis labrusca* × *Vitis vinifera*) bagasse was employed in the diclofenac removal from aqueous solutions under the batch reactor 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-organo-composite [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® 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-organo-sericite

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_{α} 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_{PZC} and BET measurements

The pH_{PZC} (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

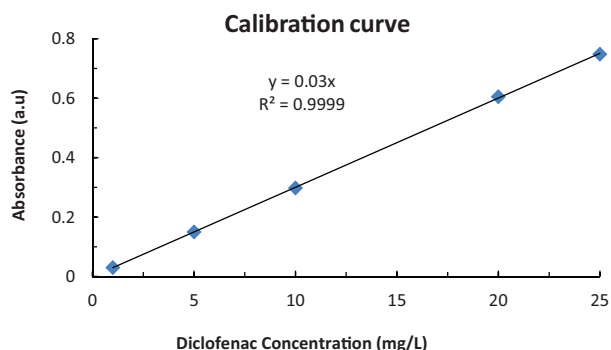


Fig. 1. Calibration curve for diclofenac sodium obtained at 276 nm of wavelength.

solutions. 0.2 g of AHS/or AAS was introduced with these solutions. The bottles were kept in an automatic incubator shaker (Incubator Shaker, TM Weiber, ACMAS Technologies Pvt. Ltd., India) for 24 h at $25 \pm 1^\circ\text{C}$. The prolonged period of shaking i.e., 24 h may enable to achieve an apparent equilibrium between solid/solution interfaces. These bottles were then taken out from the shaker and filtered with $0.45\ \mu\text{m}$ syringe filter and the pH was again checked and reported as equilibrium pH. The filtrates were then subjected to its bulk diclofenac concentration using UV–vis spectrophotometer (Model: UV1, Thermo Electron Corporation, USA). The absorbance was recorded at 276 nm. The calibration curve is obtained with the standard diclofenac solutions having the concentrations of 1.0, 5.0, 10.0, 20.0 and 25.0 mg/L (cf. Fig. 1).

The diclofenac concentration dependence study was performed varying diclofenac sodium concentration from 1.0 to 20.0 mg/L at constant pH ~ 7.10 and at constant temperature $25 \pm 1^\circ\text{C}$. The adsorption process was conducted similarly as detailed above. Results were presented as percent removal of diclofenac as a function of initial diclofenac concentration (mg/L). The sorption data was further utilized to demonstrate the equilibrium state modeling studies using the Freundlich and Langmuir adsorption isotherms as discussed elsewhere [34,42].

Effect of background electrolyte concentrations dependence sorption was studied varying the background electrolyte concentration from 0.0001 to 0.1 mol/L NaCl in diclofenac solution (5 mg/L). The solution pH (~ 7.10) and temperature ($25 \pm 1^\circ\text{C}$) was kept constant throughout the experiments. Results were presented as percent removal of diclofenac with the variation of background electrolyte concentrations.

Time dependence sorption of diclofenac by these materials was obtained at different time intervals. The initial diclofenac concentration 5.0 mg/L with solid dose 5.0 g/L was taken as constant and the sorption experiments are conducted at constant pH ~ 7.10 at $25 \pm 1^\circ\text{C}$. Results were then reported as percent removal of diclofenac as a function of time (min).

Column experiments

Column experiments were conducted using a glass column (1 cm inner diameter) packed with 0.5 g of AAS/or AHS solids (placed in the middle of column); below and above this, ca. 1.5 g of virgin sand particles were placed (14–16 BSS) and then the column was packed with glass beads. Diclofenac sodium solution ca. 5.0 mg/L at pH 7.10 was pumped upward from the bottom of column using peristaltic pump (Kros Flo Research I Peristaltic Pump, Spectrum Laboratories Inc., California, USA), at a constant flow rate of 1.0 mL/min. Effluent solution was collected using a fraction collector (Spectra/Chrom CF-2 Fraction Collector, Spectrum Laboratories Inc., California, USA). The collected effluents were then filtered using $0.45\ \mu\text{m}$ syringe filter and the total bulk

diclofenac concentration was measured using UV–vis spectrophotometer.

The breakthrough data was then utilized to optimize the loading capacity of diclofenac by AAS/or AHS under the dynamic conditions employing the Thomas Eq. (1) [43]:

$$\frac{C_e}{C_0} = \frac{1}{1 + e^{(K_T(q_0m - C_0V))/Q}} \quad (1)$$

where C_e and C_0 is the concentration of effluent and influent solution of diclofenac (mg/L), respectively; K_T refer to the Thomas rate constant (L/min/mg); q_0 is the maximum amount of diclofenac loaded (mg/g) under the specified column conditions; 'm' is the mass of hybrid materials taken in column (g); V is the throughput volume (L); and Q is flow rate of pumped diclofenac solution (L/min). The column data is fitted to a non-linear Thomas equation using the least square fitting method to estimate two unknown variables i.e., K_T and q_0 .

Results and discussion

Characterization of solids

The surface morphology of sericite, AAS and AHS was obtained taking the SEM images of these solids and published elsewhere [44]. Sericite refers to natural fine-grained muscovite having chemical formula of muscovite $\text{KSi}_3\text{Al}_3\text{O}_{10}(\text{OH})_2$. The layer charge density is close to $\leq 2\ \text{e/uc}$ (unit cell) and unit cell containing 2:1 T:O phyllosilicate layers (where 'T': octahedral $[\text{SiO}_4]^{4-}$ and 'O': tetrahedral $[\text{AlO}_3(\text{OH})_3]^{6-}$) [44,45]. Relatively high unit charge causes strong electrostatic attractions. This enables the phyllosilicate layers to hold more tightly with the available cations lying within the interspace. This makes muscovite a non-swollen mineral in water with low cation exchange capacity. The SEM image of sericite shows a compact and layered structure. No micro- or meso-pores are visible on sericite surface. However, AAS and AHS materials show heterogeneous and disordered surface structure. Moreover, the interspace of sericite is, possibly, propped-up to a little extent in presence of aluminum and organic cations HDTMA/or AMBA. It is evident that few micro pores are visible at the surface. It is assumed that aluminum is making a bond with the available oxygen at the apices of phyllosilicate sheet and further the inorganic cations (K or Mg) are replaced by exchangeable organic cations within the interspace of sericite [31,34]. Previously it was observed that the elevated temperature caused to dehydroxylation of the octahedral hydroxyls of sericite and hence facilitated in incorporation of Li ions as to form the '–OLi' bond within the interspace [45].

The characterization of these solids is conducted by the IR and XRD analytical tools. The FT-IR and XRD spectra of sericite, AAS and AHS are presented elsewhere and again reproduced as Fig. S2 and S3, respectively [44]. The FT-IR results indicate that aluminum and organic cations are introduced within the interspace of sericite network and firmly as to obtain the inorgano–organo-modified sericite hybrid materials. On the other hand XRD data shows characteristic diffractions for sericite [34,36]. Moreover, the AAS shows a positive difference in d values, indicating that the interspace is propped up to a little extent. However, the AHS solid show no significant difference in d-values indicating that the interspace is not propped up to a measurable extent.

The pH_{PZC} is found to be 6.89, 6.20 and 6.30, respectively, for the sericite, AAS and AHS samples also reported elsewhere [34]. The BET specific surface area is obtained and found to be 2.06, 0.93 and $1.71\ \text{m}^2/\text{g}$, respectively, for sericite, AAS and AHS hybrid materials.

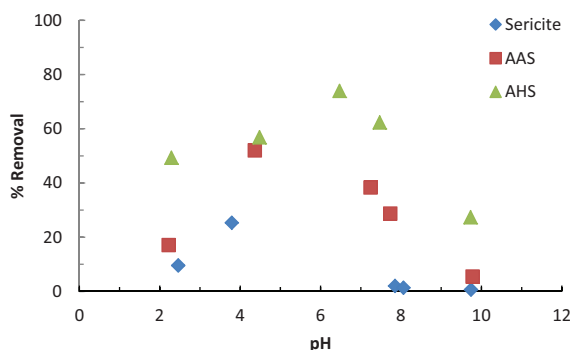


Fig. 2. Effect of pH in the removal of diclofenac by sericite, AHS and AAS solids.

Effect of pH

The pH dependence sorption data is an important physico-chemical parameter enabling to deduce mechanism occurring at solid solution interface. Therefore, the pH dependence sorption of diclofenac sodium is conducted varying the solution pH from pH ~2.0 to 10.0. The percent uptake of diclofenac as a function of pH is represented in Fig. 2. The figure clearly demonstrates that at lower pH values i.e., pH ~2.5 a very low uptake of diclofenac is occurred. However, with gradual increase in pH upto pH ~7.0 a maximum diclofenac is sorbed which further decreases to its minimum value at pH ca. 10.

These results are explained with the charge carried by solid surfaces and also the speciation of diclofenac sodium in aqueous solutions. It is observed that the pH_{PZC} of these solids are found to be 6.89, 6.20 and 6.30, respectively, for the sericite, AAS and AHS solids [34]. Therefore, the solid carries a net positive charge below this pH and becomes negatively charged beyond this pH values according to the following equation:



On the other hand diclofenac is having low dipole moment and acid dissociation constant value pK_a : 4.21 [46]. This implies that diclofenac carries negative charge beyond pH 4.2. Therefore, beyond pH 4.2 a sharp increase in the uptake of diclofenac is observed, perhaps, with a strong electrostatic attraction since the surface carries net positive charge. Additionally, a hydrophobic and p-p bonding interactions may also contribute in the sorption of diclofenac onto these solids [26,47]. However, at very low pH values i.e., around pH 2.5 the surface carries net positive charge whereas the adsorbing species carries no net charge hence refraining in sorption of diclofenac by these solids. Moreover, diclofenac is not a strong organophilic compound; therefore, apparently a less percent uptake is obtained at this low pH values. On the other hand, beyond pH 6.89, 6.30 and 6.20, respectively, for sericite, AHS and AAS the surface becomes negatively charged and the diclofenac is also carrying net negative charge therefore; apparently a strong repulsion between them causes significant decrease in percent uptake of diclofenac by these solids. Similar results are reported previously for the sorption of As(III) and As(V) by the AA and AH solids [34]. Other studies conducted for diclofenac removal shows similar findings using variety of solids viz., molecularly imprinted polymer microspheres [1], carbon nanotubes/alumina hybrid [26], functionalized silica-based porous materials [27] etc.

Further, it is interesting to note that a significant increase in percent removal of diclofenac is occurred with the inorgano-organomodified sericite, i.e., AHS and AAS comparing to the virgin sericite. These results, therefore, demonstrate that aluminum

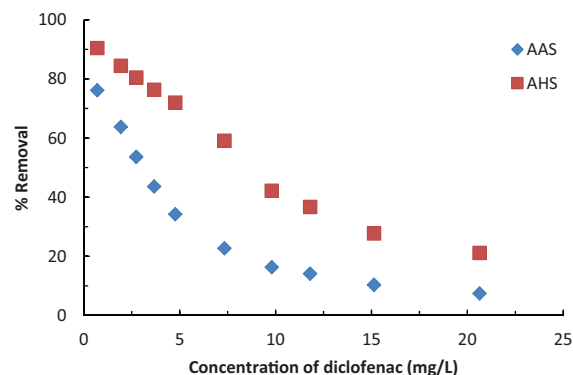


Fig. 3. Effect of sorptive concentration in the removal of diclofenac by the AHS and AAS solids.

along with HDTMA/AMBA takes part in the sorption of diclofenac in the sericite. Furthermore, the HDTMA-modified sericite possesses somewhat higher sorption capacity, at almost all studied pH, comparing to the AMBA modified sericite. This is due to the fact that HDTMA is an aliphatic organic cation whereas AMBA is an aromatic cation ring. The aliphatic chain compounds are lying flat forming a stable monolayer within the interspace of sericite whereas aromatic compounds are less stable in such structural arrangement. Similar results are reported previously in the sorption of As(III) and As(V) from the organo-modified sericite [44] or even aluminum-HDTMA/or AMBA modified sericite [34].

Concentration dependence studies

The concentration dependence sorption of diclofenac by AAS and AHS materials are obtained varying the diclofenac concentration from ca. 1.0 mg/L to 20.0 mg/L at pH 7.10 and at $25 \pm 1^\circ\text{C}$. Results are then presented graphically in Fig. 3. This figure clearly demonstrates that increasing the initial diclofenac concentration from 0.70 mg/L to 20.63 mg/L causes in decrease of diclofenac percent removal from 76.19% to 7.43% (for AAS); from 90.49% to 21.16% (for AHS), respectively. Similar findings are reported previously for the sorption of metal cations onto the sericite [38] or by granular activated carbon derived from coconut shell [48].

Equilibrium state modeling

The equilibrium state sorption data is further employed to the non-linear fitting of Langmuir and Freundlich adsorption isotherm equations:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (3)$$

$$q_e = K_F C_e^{1/n} \quad (4)$$

where q_e and C_e represent, respectively, the amount of diclofenac adsorbed and bulk diclofenac concentration at equilibrium. q_m and K_a are the Langmuir constants indicating the maximum monolayer capacity of solid and strength or affinity of solid toward the sorbing species diclofenac, respectively. On the other hand, the K_F and $1/n$ represent the Freundlich constants; referring to the maximum sorption capacity and adsorption intensity, respectively.

The non-linear fitting of equilibrium state sorption data is presented graphically in Figs. 4 and 5, respectively, for Langmuir and Freundlich adsorption isotherms. The least square fitting is conducted to optimize the two unknown parameters viz., ' q_m ' and ' K_a ' for Langmuir isotherm and ' K_F ' and ' $1/n$ ' for Freundlich

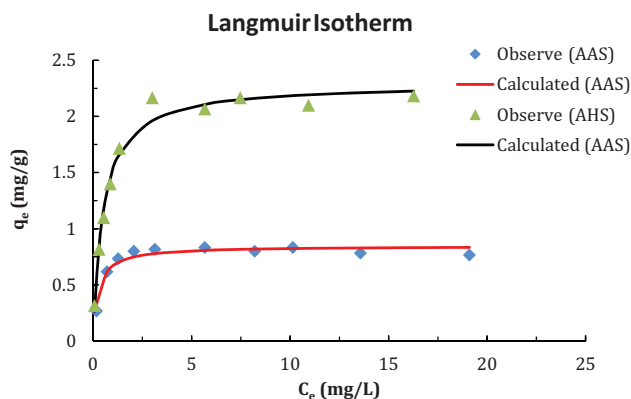


Fig. 4. Langmuir adsorption isotherm fitting in the adsorption of diclofenac by AAS and AHS solids.

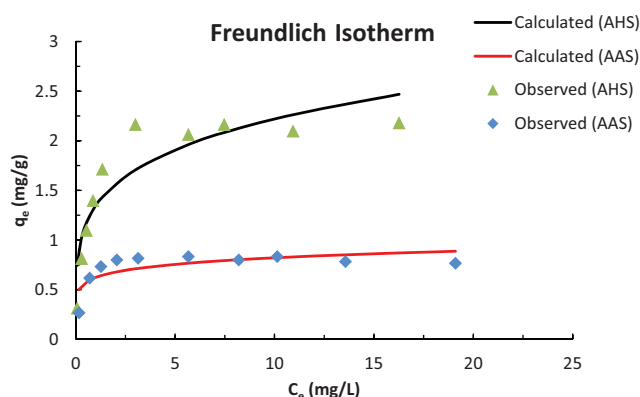
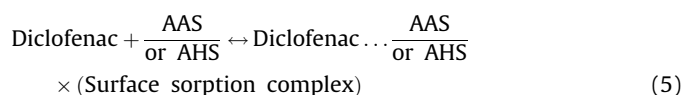


Fig. 5. Freundlich adsorption isotherm fitting in the adsorption of diclofenac by AAS and AHS solids.

adsorption isotherms. The data is reasonably fitted well to the Langmuir and Freundlich adsorption isotherms. However, comparatively, the Langmuir isotherm is better fitted than the Freundlich adsorption isotherm. The unknown parameters are estimated for both the isotherms. The Langmuir constants q_m , K_a and least square sum are found to be 0.845 mg/g, 3.724 L/g and 0.016 (for AAS); 2.295 mg/g, 1.954 L/g and 0.068 (for AHS), respectively. The results indicate that AAS and AHS possess relatively higher monolayer capacity for diclofenac. Further, it is reported that q_m intends to relate the heat of sorption; higher the value of q_m possess higher the heat of sorption and hence forming a stronger bonds [49]. Moreover, the applicability of Langmuir adsorption isotherm indicates that the surface active sites are distributed evenly onto the solid surface. Similar, results are also reported previously for the granular carbon nanotubes/alumina hybrid adsorbent in the removal of diclofenac sodium and carbamazepine from aqueous solutions [26]. On the other hand the Langmuir constant K_a determines equilibrium constant of the sorption process of diclofenac by solid surface [50] as in the following equation:



Similarly, the Freundlich constants K_F , $1/n$ and least square sum are also computed and found to be 0.623 mg/g, 0.120 and 0.113 (for AAS); 1.344 mg/g, 0.218 and 0.664 (for AHS), respectively. A marked difference occurred in the removal capacity of diclofenac

by these hybrid materials as estimated by the two different models is, perhaps, due to the different basic assumptions utilized by the two different isotherms. The applicability of Freundlich adsorption isotherm points toward the sorbing species are forming strong chemical bonds with the surface functional groups and likely to be interacted laterally [28,38,51]. Further, the sorption intensity i.e., '1/n' values are found to be less than unity ($0 < 1/n < 1$) infers to heterogeneous surface structure of solid with an exponential distribution of active sites [38,52].

Effect of background electrolyte concentrations

Effect of background electrolytes in the sorption of diclofenac by the AAS and AHS could enable to explain the mechanism involved at solid/solution interfaces [53]. The specific sorption is not affected with the change in background electrolyte concentrations; whereas the non-specific adsorption is greatly influenced with the change in background electrolyte concentrations. Therefore, the sorption of diclofenac by AAS and AHS is assessed varying the background electrolyte concentrations i.e., NaCl from 0.0001 mol/L to 0.1 mol/L at an initial diclofenac concentration of 5.0 mg/L and at constant pH 7.10. The percent removal of diclofenac is presented as a function of background electrolyte concentrations and presented graphically in Fig. 6. Quantitatively, increasing the background electrolyte concentrations from 0.0001 to 0.1 mol/L NaCl is caused to decrease the uptake of diclofenac, respectively, from 35.26 to 26.92% (for AAS i.e., 8.34% decrease); from 62.18 to 45.51% (for AHS i.e., 16.67% decrease), respectively. These results indicate that 1000 times increase in background electrolyte concentration (NaCl) causes an insignificant decrease of diclofenac removal by the AAS and AHS solids. Therefore, it infers that diclofenac is predominantly adsorbed specifically onto these solids and forming an 'inner-sphere' complex at the solid surface. Previously, it is reported that As(V) is adsorbed specifically onto $\gamma\text{-Al}_2\text{O}_3$ within the pH region 3.0 to 9.2; whereas As(III) is not adsorbed specifically within the pH region 4.5 to 9.0 [54,55]. Similarly, the anion exchange polymer resin showed the uptake of diclofenac is not significantly affected in presence of citrate or phosphate from aqueous solutions [8].

Kinetic studies

Further, the time dependence removal of diclofenac by AAS and AHS solids is obtained as collecting the sorption data at wide range of time intervals i.e., from 5 min to 180 min. The initial concentration of diclofenac is taken as 5.0 mg/L and the sorption is performed at constant pH 7.10. The percent removal of diclofenac as a function of time is presented graphically in

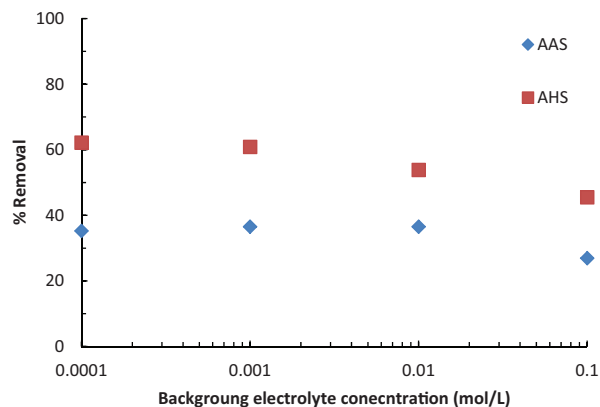


Fig. 6. Effect of background electrolyte concentration in the removal of diclofenac by AAS and AHS solids.

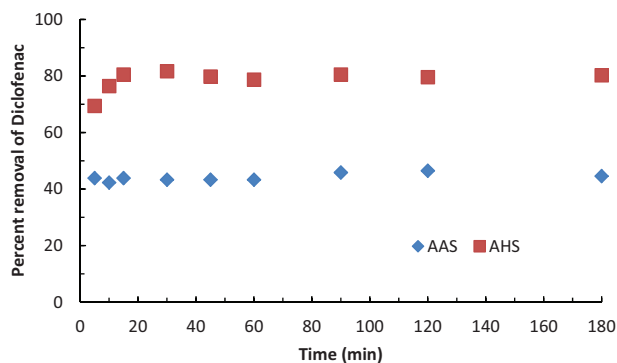


Fig. 7. Time dependence sorption of diclofenac by the AHS and AAS solids.

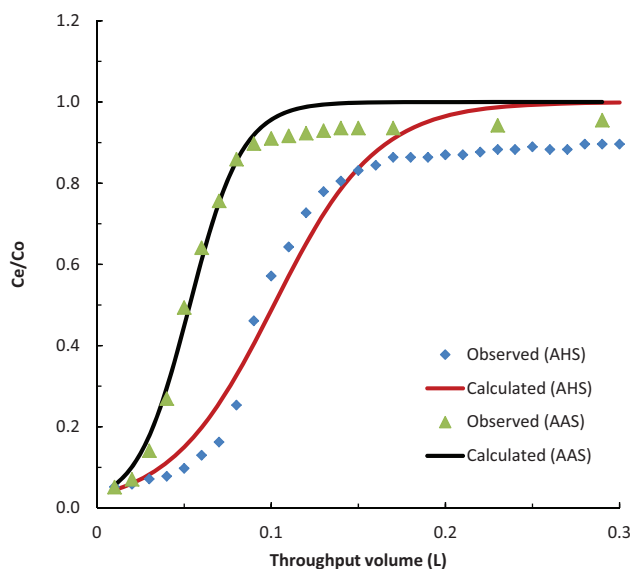


Fig. 8. Breakthrough curves in the removal of diclofenac from aqueous solutions using AAS and AHS packed column.

Fig. 7. It is evident from the figure that diclofenac is aggregated quickly onto the solid surface and an apparent equilibrium is achieved between the solid solution interfaces within ca. 5–10 min of contact. Since the uptake process is relatively fast which restricted to further demonstrate the kinetic modeling or to determine the rate constant of uptake process. The rapid and fast aggregation of diclofenac onto the solid surface of AAS and AHS hybrid materials further indicated the higher affinity of these solids toward the diclofenac. Similar fast attenuation of diclofenac sodium was obtained by different hybrid materials precursor to the natural bentonite [56].

Column experiments

Further, the column experiments are performed to assess the removal behavior of AAS and AHS materials for diclofenac under the dynamic conditions. The column conditions are maintained as stated previously. The breakthrough curves are presented graphically in Fig. 8. Closure scrutiny of this figure revealed that relatively a high breakthrough volume was obtained for diclofenac by AAS and AHS solids. A complete breakthrough volume was obtained at 0.11 L and 0.17 L, respectively for the AAS and AHS solids. Relatively high breakthrough volume obtained for diclofenac clearly indicated strong affinity of these solids toward diclofenac under the fixed bed column conditions [57,58]. It was reported previously that a fixed-bed process is having an additional

Table 1

Thomas constants estimated in the removal of diclofenac by AAS and AHS solids.

Systems	Thomas constants		Least square sum (s^2)
	q_0	K_T	
DF-AAS	0.561	1.25×10^{-2}	3.8×10^{-2}
DF-AHS	1.056	6.48×10^{-3}	1.8×10^{-1}

advantage of continuous contact of sorbing species with solid surface which may result in better exhaustion capacity than batch reactor operation [59].

Further, non-linear least square fitting is performed using the breakthrough column data. The fitting is conducted to simulate with two unknown constants i.e., K_T and q_0 (cf. Fig. 8). The values of Thomas constants along with least square sum are returned in Table 1. The data indicated that relatively a high loading capacity was achieved for diclofenac by AAS and AHS under the dynamic conditions. This inferred useful practical applicability of these solids in the decontamination of diclofenac from aqueous solutions. These results are similar to the findings of batch reactor experiments. Also results are in a line to other reports in which the Thomas equation is utilized to demonstrate the loading capacity of different sorbents [38,60] or the RDX, TNT and Cd(II) using the buffalo weed biochar-alginate beads packed column [61]. The removal capacity obtained with the column reactor operations found to be less comparing to the corresponding batch experiments is, perhaps, because of insufficient time of contact given to sorbing species diclofenac to the solid surface [38].

Conclusions

Al-pillared HDTMA/or AMBA modified sericite is synthesized and characterized by the IR and XRD analysis. The surface morphology of these solids is discussed with the SEM images. Sericite possess a compact layered structure however, the hybrid materials AHS and AAS show a heterogeneous structure composed with micro pores onto the solid surface. Further, these hybrid materials are utilized in the remediation of diclofenac sodium from aqueous solutions under the batch and column reactor operations. The batch studies enable that decrease in concentration of diclofenac (20.0 to 1.0 mg/L) favors greatly the percent removal of diclofenac by AAS and AHS. The pH dependence data shows that the pH region 5–7 favors greatly the uptake of diclofenac. Further, the equilibrium state sorption data is fitted reasonably well to the Langmuir adsorption isotherm hence, the estimated Langmuir monolayer capacity for diclofenac is found to be 0.845 mg/g and 2.295 mg/g, respectively, for AAS and AHS solids. Moreover, the change in background electrolyte concentrations (0.0001 to 0.1 mol/L NaCl) is not affecting significantly the percent removal of diclofenac which points the specific sorption of diclofenac onto the solid surface and likely to form an ‘inner sphere’ complexes at the surface of AAS or AHS. The kinetic data shows that the uptake of diclofenac is completed within 5 min of contact and an apparent saturation between solid/solution is obtained within the contact of 5 min. Further, fixed-bed column experiments indicate that relatively a high loading capacity is obtained for the diclofenac using the AAS or AHS packed columns. The hybrid materials AAS and AHS are therefore found to be efficient and useful materials in the attenuation of diclofenac from aqueous solutions.

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