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Removal of emerging micropollutants from water using hybrid material precursor to natural sericite clay

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The occurrence of a wide range of micropollutants in natural aquatic environment has been reported in different parts of the world. These compounds are harmful for the aquatic life and human beings. Diclofenac and clofibric acid are the two common toxic micropollutants due to very large production and high consumption by humans. The present communication addresses the removal of diclofenac and clofibric acid from aqueous solutions using the hybrid material obtained by incorporating 3-aminopropyltriethoxysilane (APTES) onto the activated sericite clay. Initially, sericte clay was treated for activation and further modified with organosilane to obtain hybrid material. The materials were characterized using SEM, BET surface area, XRD, and FT-IR analyses. SEM and BET surface area analyses showed that the textural property of sericite clay was greatly changed after activation and the surface area was immensely increased from 3.65 to 62.92 m^2/g. The organosilane was anchored on the activated clay and confirmed with FTIR analysis. Batch adsorption experiments showed that the diclofenac and clofibric acid removal is maximum at pH 6.0 to 7.0 and the adsorption of these two micropollutants were observed to be very fast and the time dependent adsorption data were best fitted to pseudo-second order kinetic model. The maximum adsorption capacity of diclofenac and clofibric acid using APTES-sericite hybrid material was found to be 1.868 and 1.749 mg/g, respectively. Furthermore, the loading capacities of the column packed with APTES-sericite hybrid material were found to be 0.789 and 1.095 mg/g. Therefore, this study indicated that the APTES-sericite hybrid material must be an useful material for the effective removal of diclofenac and clofibric acid from aqueous waste.

Keywords: Hybrid material, Mesopore, Micropollutants, Organosilane, Sericite

The presence of a wide range of emerging micropollutants, such as pharmaceuticals and hormones (PPHs), preservatives from personal care products (PCPs), pesticides, etc. in the aquatic environment and wastewater treatment plant (WWTP) effluents have been reported in different parts of the world[1]. These compounds are harmful for the aquatic environment and/or humans. Among the common micropollutants, the EDCs or the pharmaceuticals are the major concerns due to their adverse effects towards humans and even in wildlife[2]. Diclofenac is a non-steroidal anti-inflammatory drug (NSAID) with analgesic, anti-inflammatory, and antipyretic properties. It is commercially available in various formulations including the tablet form. The global consumption of diclofenac is estimated to be approximately 940 tons per year. The majority of diclofenac (~65%) consumed by humans is excreted through urine, mainly as unmetabolized active ingredients or metabolites after entero hepatic circulation[3,4]. Due to poor biodegradability and its limited sorption properties onto activated sludge, only about 30% is removed in conventional sewage treatment plants (STPs). Therefore, diclofenac sodium is frequently detected in STP−effluent and surface water even up to 4.7 and 1.2 μg/L, respectively[3,5]. Also, it has been reported that diclofenac is present in rivers, groundwater, hospital effluents, and drinking water at the order of ng/L[6]. Diclofenac is reported to affect renal and gastrointestinal tissues in several vertebrate taxa and it is fatal to vultures. When the birds eat the carcasses of the animals treated with diclofenac, they experience acute kidney failure and die within days[7]. Moreover, it is reported that diclofenac interferes with the biochemical functions of fish and leads to tissue damage even at environmentally relevant concentrations[8]. For all these reasons, diclofenacis one of the most important emerging pollutants in terms of ecotoxicity and persistence in the

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environment. Clofibric acid is the active metabolite of blood lipid regulators. It has drawn more attention from environmental scientists due to the large consumption of blood lipid regulators. It is also one of the most frequently found reported drugs in sewage effluents, ground, surface and even drinking waters all over the world. Clofibric acid is non-biodegradable, highly mobile, and persistent in the environment with a half-life of 21 years[9].

The existing wastewater treatment plants (WWTPs) are not specifically designed to eliminate micropollutants and many of these micropollutants are able to bypasses wastewater treatment processes due to large influx and persistency. Moreover, unlike other pollutants, there is no proper guideline to discharge these emerging pollutants. Therefore, it is necessary to initiate additional treatment technologies to remove the remaining micropollutants from WWTP effluents[10]. Various techniques such as membrane separation, reverse osmosis, precipitation, electroplating, evaporation, ion exchange, coagulation, and some biological processes were applied for the treatment of various micropollutants. Organosilane grafting has been demonstrated to be an efficient method for functionalizing clay, as the formation of covalent bonding between the clay minerals and the organosilane results in stable immobilization of organic moieties and prevents their leaching into the surrounding environment. Therefore, sericite is activated thermally followed by acid treatment in a view to increase the specific surface area of sericite, and thereby, to provide a suitable surface for the introduction of organosilane. The activated sericite was further functionalized by 3-aminopropyltriethoxysilane (APTES), and the surface-functionalized activated sericite was utilized for the effective removal of diclofenac and clofibric acid from aqueous solutions under batch and column reactor system.

Materials and Methods

Materials

The Sericite clay was obtained from the Kangwon province, Korea. The sericite was crushed and sieved using a mechanical sieve to obtain a fine powder having a size of 0.075-0.053 mm. Diclofenac sodium and Clofibric acid were obtained from Duksan Pure Chemicals Co. Ltd., Korea, and (3-aminopropyl) triethoxysilane (APTES) were supplied by Sigma Aldrich Co., USA. All other chemicals used were analytical grade and the de-ionized water used for all the experiments.

Activation of sericite clay

The fine powder sericite was annealed at 800°C for 4 h and then further activated using 3.0 mol/L HCl at 100°C for 1 h with constant stirring. The activated clay was separated and washed several times with distilled water to remove excess acid. Dried at 80°C in a hot air oven and stored in a plastic bottle for further use. This sample is named as activated sericite.

Preparation of hybrid material

15 mL of APTES was taken into a mixture of 150 mL ethanol and 50 mL distilled water. Into this solution, 15 g of AS was dispersed and it was refluxed at 80°C with continuous stirring for 7 h. The solid material was taken out and completely dried at 60°C. In order to remove residual silanes, the dried material was thoroughly washed with a mixture of water and ethanol using a Soxhlet extractor for 24 h. Finally, the slurry was washed with distilled water, and completely dried in a hot air oven at 70°C. The material is named as the APTES-sericite hybrid material or the hybrid material in this paper.

Characterization

The SEM (scanning electron microscope) image by FE-SEM (Model: SU-70, Hitachi, Japan). The specific surface area of the samples was analyzed using a Protech Korea BET surface area analyzer (Model ASAP 2020). Moreover, the X-ray diffraction (XRD) data were collected with an X-ray diffraction instrument (PANalytical, Netherland; Model X'Pert PRO MPD), and the functional groups present in the solid samples were identified using Fourier transform-infrared spectrometry (FT-IR) with the KBR disk method (Bruker, Tensor 27, USA).

pHpzc Determination of the Solids

The point of zero charge (pHpzc) of the hybrid material was evaluated by following the known method[11].

Batch adsorption studies

Batch experiments were carried out to study the effects of pH, initial concentration of pollutants, and contact time by APTES-sericite hybrid material. The pH of the solutions were adjusted by adding 1.0 M HCl or 1.0 M NaOH for all the experiments. For pH dependent studies, 50 mL of the aqueous solution containing diclofenac/clofibric acid was taken in polyethylene bottles. After pH adjustment, 0.1 g of the adsorbent (*i.e.*, APTES-sericite hybrid) was added and then equilibrated using an automatic shaker (KUKJE, Shaking Incubator, Korea, model 36-SIN-125) for 12 h at 25±1°C. The solution was centrifuged and then filtered using 0.45 μM syringe filter. The final pollutant concentration was measured using a UV-visible spectrophotometer (Model: Humas HS 3300). The results are presented as the percentage of pollutants removed. The time dependence removals of these two micropollutants were also carried out at various intervals of time within 30 min. The initial concentration of diclofenac and clofibric acid were 5.2 and 3.1 mg/L, respectively. A constant dose of solid adsorbent (*i.e.*, 2.0 g/L) was introduced and kept at a constant pH 6.5 and temperature 25°C. The results obtained were given as the amount of pollutants removed (mg/g) as a function of time (min). Further, the time dependence data collected were utilized to deduce the kinetic studies to obtain the rate constant and the uptake capacity of APTES-sericite hybrid material to remove these two micropollutants. The equilibrium state sorption data at various concentrations of diclofenac and clofibric acid were collected with the initial concentration ranged from 3.4 to 32.2 mg/L and 2.5 to 30.4 mg/L for diclofenac and clofibric acid, respectively at a constant pH of 6.5 at 25°C. The adsorbent dose is 2.0 g/L and the adsorption process was the same as above. The isotherm studies were performed by equilibrium modelling studies using the Langmuir and Freundlich adsorption isotherms.

Fixed-bed column adsorption studies

Further, the efficiency of APTES-sericite hybrid material for the removal of diclofenac and clofibric acid was assessed in fixed-bed column experiments. The column experiments were performed with a glass column having 1 cm inner diameter. 0.50 g of the synthesized hybrid material was packed at the middle of the column using glass beads. The concentration of diclofenac and clofibric acid in the aqueous solutions were 2.5 and 2.2 mg/L, respectively. The solution was pumped upward from the bottom of the column at a constant flow rate of 1.0 mL/min using Acuflow Series II, High-Pressure liquid chromatograph, and the effluent samples were then collected using Spectra/Chrom CF-2 fraction collector. The collected samples were filtered using 0.45 μm filter and the final concentration of diclofenac and clofibricacid were measured using a UV-visible spectrophotometer (Model: Humas HS 3300).

Results and discussion

Characterization

The SEM images obtained for the pristine sericite displayed a compact but layered structure (Fig. 1A) and the clay structure was completely changed after activation[12]. As shown in Figure 1B, the activated sericite clay have porous structures and the incorporation of organosilane did not cause significant changes in its textural properties of the activated clay (Fig. 1C). The specific surface areas of the materials are measured using BET surface area analyser and the nitrogen adsorption-desorption isotherm obtained for sericite, activated sericite, and hybrid material are shown in (Fig. 2).

All the three samples showed a type IV isotherm with a characteristic hysteresis loop (H3 type) which confirms the existence of mesopores in the materials[13,14]. The BET surface area analyses showed that the specific surface area of pristine sericite clay was relatively small and found to be 3.65 m^2/g only. After activation, the surface area tremendously increased and obtained to be 62.92 m^2/g. The surface area of the activated sericite was slightly decreased after the incorporation of organosilane; therefore, the specific surface area of the hybrid material was observed to be 59.63 m^2/g. Moreover, the activation caused significant increases in

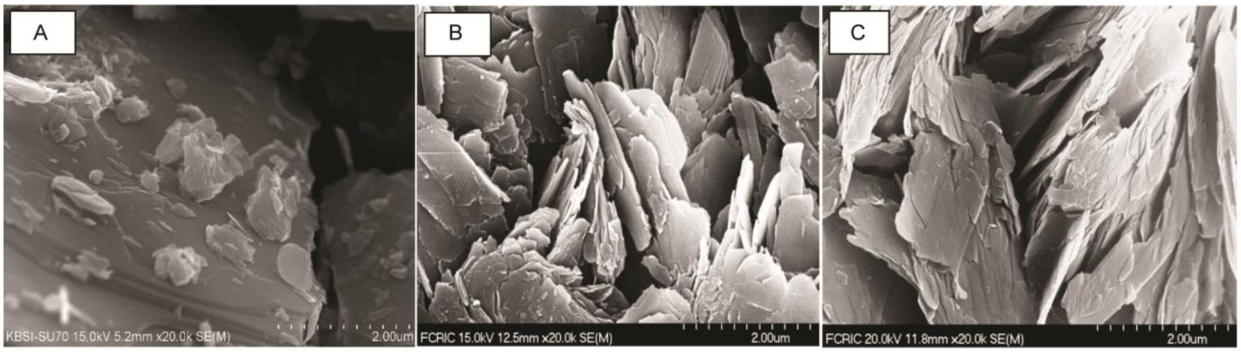

Fig. 1 — SEM micrograph obtained for (A) pristine sericite clay; (B) activated sericite; and (C) hybrid clay

the pore size and pore volume of sericite clay. The pore size increased from 2.45 to 7.89 nm whereas the pore volume was found to be increased from 0.019 to 0.112 cm^3/g. Figure 2 showed that the isotherm obtained for activated sericite and hybrid material is almost same; therefore, there were no significant differences in the pore size and the pore volume for the activated sericite and the hybrid material. The structural changes in layered clay due to activation as obtained by XRD analysis was described in our previous report[15]. The diffraction peak corresponding to the basal spacing of the 001 plane in pristine sericite clay was obtained at 2θ values of 8.81 and it was shifted towards a lower angle after activation and the peak was obtained at 8.63. This XRD data again confirms that the activation caused a significant increase in interlayer space of sericite clay and consequently increases the specific surface area[16]. Further expansion of the interlayer was not observed after the incorporation of organosilane onto activated sericite. Furthermore, the successful incorporation of APTES onto the surface hydroxyl groups of activated sericite was confirmed with the help of FT-IR analysis and discussed in the previous report[15]. It was observed that the peak corresponding to -OH stretching obtained at 3440 cm^{-1} in the activated sericite clay was found to decrease considerably or even disappeared after the incorporation of APTES. This finding demonstrated the successful grafting of APTES onto the surface hydroxyl groups of activated clay[17,18].

Batch reactor operations

Effect of solution pH

The effects of solution pH on the removal of diclofenac and clofibric acid were studied between pH 2.0 to 10.0 and the percentage removal of these micropollutants at different pH is shown in (Fig. 3). In a highly acidic solution, the percentage removal of diclofenac and clofibric acid using APTES-sericite hybrid material was relatively low and increases with increasing the solution pH. The maximum removal was attained at pH 6.0 and then again the percentage removal decreases for these two micropollutants as the basicity of the solution increases. The influence of solution pH on the removal of diclofenac and clofibric acid could be explained with the help of the speciation of these two micropollutants and the charge carried by the hybrid materials at various pH. The point of zero charge (pHpzc) of the APTES-sericite hybrid material was found to be pH 7.8. Therefore, the hybrid solid possessed a net positive charge below pH 7.8 and the surface becomes negatively charge above this pH. On the other hand, the speciation studies of diclofenac in aqueous solutions showed that diclofenac carries a negative charge above pH 4.1 and it is neutral or carries no charge below pH 4.1[19]. Similarly, clofibric acid remains undissociated at highly acidic medium, and at around pH 3.6, approximately 50% are dissociated and beyond pH 5.0 the negatively charge species represents more than 99%[20]. Therefore, the removal efficiency of these two micropollutants using APTES-sericite hybrid material were relatively lower at the highly acidic solution and then it increases with increasing the solution pH and then attained maximum removal at ~pH 6.0 to 7.0. At higher pH, the repulsive forces between the negatively charged species of diclofenac/clofibric acid and the negatively charge surface of the hybrid materials caused

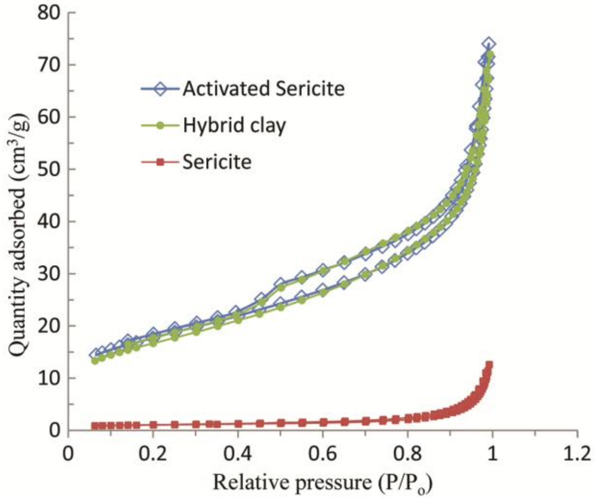

Fig. 2 — Nitrogen adsorption-desorption isotherm obtained for pristine sericite clay, activated sericite, and APTES-sericite hybrid

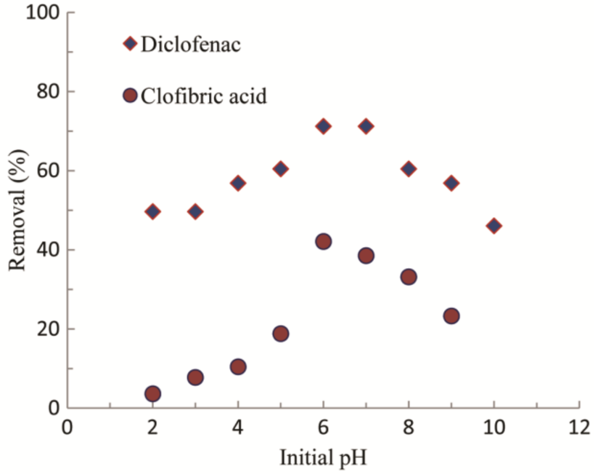

Fig. 3 — Effect of pH in the removal dicofenac (conc: ~2.0 mg/L) and Clofibric acid (conc : ~7.0 mg/L) using hybrid material. (dose of material: 2 g/L)

significant decrease in the percentage removal of these micropollutants. Similar removal behaviour was observed on the adsorption removal of diclofenac and clofibric acid using MIEX resin[21] and the removal of diclofenac using the Al-pillared alkyldimethylbenzyl ammonium chloride (AMBA) modified sericite clay and Al-pillared hexadecyltrimethyl ammonium bromide (HDTMA) modified sericite clay[22].

Effect of contact time

The effect of contact time on the removal of diclofenac and clofibric acid were performed and the results obtained are shown in (Fig. 4A & B). The removals of these two micropollutants were very fast, and the equilibrium sorption was achieved within a short period of contact time. The apparent equilibrium of adsorption for diclofenac and clofibric acid were found to be 15 and 20 min, respectively. The rapid removal of these pollutants indicated that the active sites present on the hybrid material surfaces were readily available to adsorb diclofenac and clofibric acid from aqueous solution[23,24].

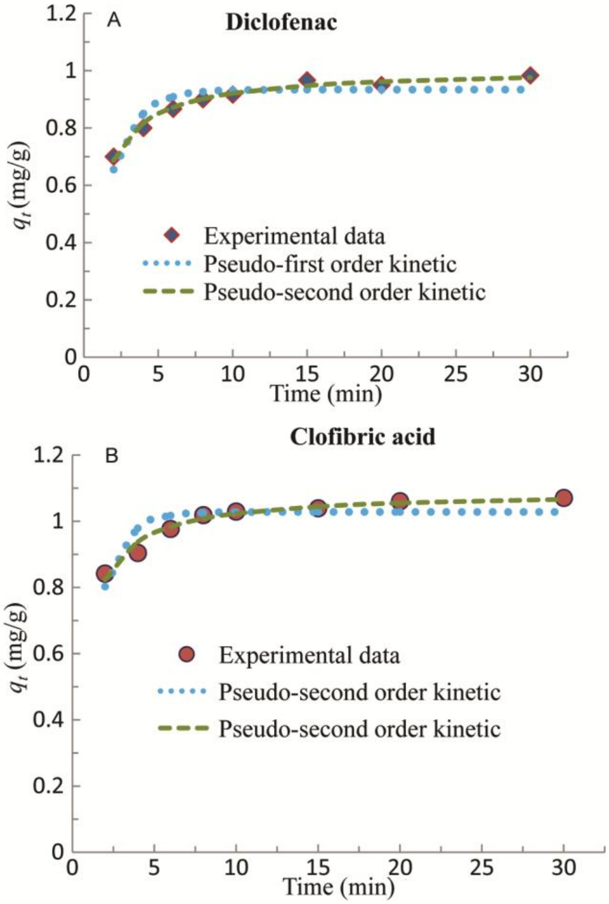

Fig. 4 — (A) Time dependent removal of diclofenac using hybrid material (Concentration: 5.2 mg/L; pH: 6.5; dose: 2g/L); and (B) Time dependent removal of Clofibric acid using hybrid material (Concentration: 3.1 mg/L; pH: 6.5; dose: 2g/L)

Pseudo-first-order (Eq. 4) and pseudo-second-order (Eq. 5) kinetic models in their non-linear form were exploited to clarify the sorption kinetics of diclofenac and clofibric acid onto hybrid material and the equations were taken as[25].

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \qquad \dots (1)$$

$$q_t = q_e \frac{q_e k_2 t}{1+q_e k_2 t} \qquad \dots (2)$$

In Eq. (1) and (2), $q_e$is the uptake capacity (mg/g) of the pollutants and q_t(mg/g) is the amount of diclofenac/clofibric acid adsorbed at time *t*. The k_1 (1/min) and k_2(g/mg/min) are the adsorption rate constant of pseudo-first order and pseudo-second order, respectively. The time dependence data modelled with the non-linear plot of pseudo-first order and pseudo-second order kinetic models are shown in (Fig. 4A & B) and the unknown parameters such as the uptake capacity (q_e) and the rate constant (k_1 and k_2) were evaluated (Table 1). The time-dependent adsorption data collected in the removal of diclofenac and clofibric acid are well fitted to pseudo-first order kinetic model and pseudo-second order kinetic model. However, the kinetic data have shown the best fitting to pseudo-second order kinetic model for both micropollutants. The suitability of a pseudo-second order kinetic model infers that there are chemical forces involved at the solid/solution interface in the removal ofdiclofenac/clofibric acid using sericite based hybrid material[26].

Effect of initial concentration

Batch experiments were carried out varying the initial concentration of diclofenac and clofibric acid between 3 to 32.0 mg/L and 2 to 30 mg/L, respectively at constant pH 6.5. An enhanced percentage of adsorption using the synthesized hybrid material was observed at low level concentration and gradually decreased with increasing initial concentration for both micropollutants. Relatively lower percentage of removals was achieved at higher initial concentrations. The equilibrium adsorption data were plotted between the percentage removal and initial concentration of diclofenac/clofibric acid and shown in (Fig. 5). The amount of diclofenac removed was estimated and it was increased from 0.96 to 1.85 mg/g while increasing the initial concentrations from 3 to 32.0 mg/L. Similarly, the amount of clofibric acid removed was

Table 1 — Rate constants (k_1 and k_2), uptake capacity (q_e) and s^2 values obtained from pseudo-first order and pseudo-second order kinetic model

Sample	Pseudo-First order model			Pseudo second order model		
	k_1 (1/min)	q_e (mg/g)	s^2	k_2 (g/mg.min)	q_e (mg/g)	s^2
Diclofenac	0.603	0.934	0.011	1.069	1.006	0.001
Clofibric acid	0.758	1.028	0.012	1.419	1.089	0.002

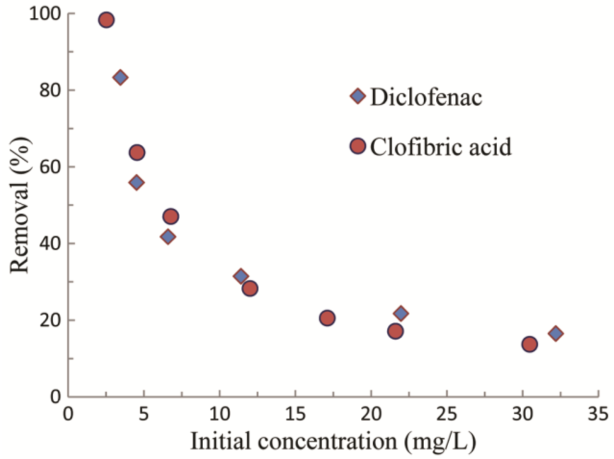

Fig. 5 — Percentage removal of diclofenac and Clofibric acid at various concentrations using hybrid material (pH: 6.5; dose: 2 g/L)

found to be 1.24 to 2.10 mg/g while increasing the initial concentration from 2 to 30 mg/L. The relatively higher amount of micropollutants was removed at higher initial concentrations since the stronger driving force was provided by higher concentration of sorptive solution to overcome the mass transfer barrier at the aqueous and the solid interface[27].

The equilibrium adsorption data collected at different concentrations of diclofenac and clofibric acid were fitted to Langmuir and Freundlich adsorption isotherms. The Langmuir adsorption isotherm equation (Eq. 3) was taken in its non-linear form as:

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \qquad \dots (3)$$

where q_e is the amount of pollutants removed per unit weight of adsorbent (mg/g) at equilibrium; C_e the equilibrium bulk concentration (mg/L); q_m the Langmuir monolayer adsorption capacity, *i.e.*, the amount of solute required to occupy all the available sites in unit mass of solid sample (mg/g) and K_L is the Langmuir constant (L/g)[28,29]. Freundlich adsorption isotherm equation was taken as (Eq. 4):

$$q_e = K_F C_e^{\frac{1}{n}} \qquad \dots (4)$$

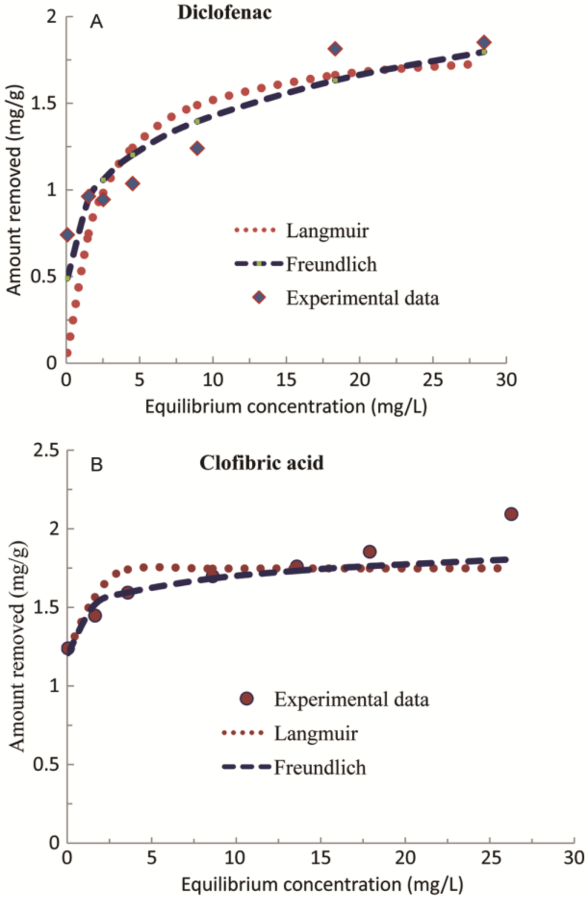

Fig. 6 — (A) Plots of Langmuir and Freundlich adsorption isotherm for the removal of diclofenac from aqueous solutions using hybrid material; and (B) Plots of Langmuir and Freundlich adsorption isotherm for the removal of Clofibric acid from aqueous solutions using hybrid material

where q_e is the amount of micro-pollutant removed (mg/g) and C_e is the micro-pollutant concentration (mg/L) at equilibrium. K_F and *1/n* are the Freundlich constants referring to adsorption capacity and adsorption intensity, respectively[30,31]. The Langmuir and Freundlich adsorption isotherms were plotted for the removal of diclofenac and clofibric acid using the synthesized hybrid material and shown in (Fig. 6A & B). The equilibrium adsorption data obtained for the removal of diclofenac and clofibric acid using clay based hybrid material showed better fitted to

Table 2 — Langmuir and Freundlich constant along with the least square sum obtained for the removal of diclofenac and Clofibric acid using hybrid material.

Sample	Langmuir isotherm			Freundlich isotherm		
	q_o (mg/g)	K_L (L/g)	s^2	$1/n$	K_F (mg/g)	s^2
Diclofenac	1.868	0.440	0.654	0.218	0.864	0.163
Clofibric acid	1.749	55.70	0.168	0.062	1.472	0.007

Freundlich adsorption isotherm rather than Langmuir adsorption isotherm. The Langmuir monolayer adsorption capacity (q_m) of the two micropollutants, Langmuir constant (K_L), Freundlich constants (K_F and $1/n$) along with the least square sum are given in (Table 2). The calculated Langmuir monolayer adsorption capacity of diclofenac using APTES-sericite hybrid material (*i.e.*, 1.868 mg/g) is comparable to the adsorption capacity obtained for two hybrid materials, *i.e.*, Al-pillared alkyldimethylbenzyl ammonium chloride (AMBA) modified sericite (0.845 mg/g) and Al-pillared hexadecyltrimethyl ammonium bromide (HDTMA) modified sericite (2.295 mg/g). The higher values of Freundlich constants(K_F) obtained for both micropollutants confirmed an enhanced affinity of the synthesized hybrid material towards these pollutants. Moreover, the fractional values of Freundlich constant inferred the heterogeneous surface possessed by the hybrid material with an exponential distribution of active sites on the material surface[32].

Fixed bed column adsorption studies

The fixed bed column experiments were conducted for the removal of diclofenac and clofibric acid using APTES-sericite hybrid material and the breakthrough data obtained were shown in (Fig. 7). The breakthrough appeared at the throughput volume of 0.5 and 0.10 L for diclofenac and clofibric acid, respectively. The breakthrough data obtained for both micropollutants are further utilized for evaluation of the loading capacity of the column packed with APTES-sericite hybrid material using the non-linear Thomas equation (Eq. 5)[33].

$$\frac{C_e}{C_o}=\frac{1}{1+e^{(K_T(q_o m-C_o V))/Q}} \quad \text{.... (5)}$$

where C_e is the concentration of diclofenac/clofibric acid in the effluent (mg/L); C_o is concentrationsof diclofenac/clofibric acid in the feed (mg/L); $K_T$representsthe Thomas rate constant (L/min/mg); q_o is the maximum amount of diclofenac/clofibric acid loaded (mg/g) under the specified column conditions;

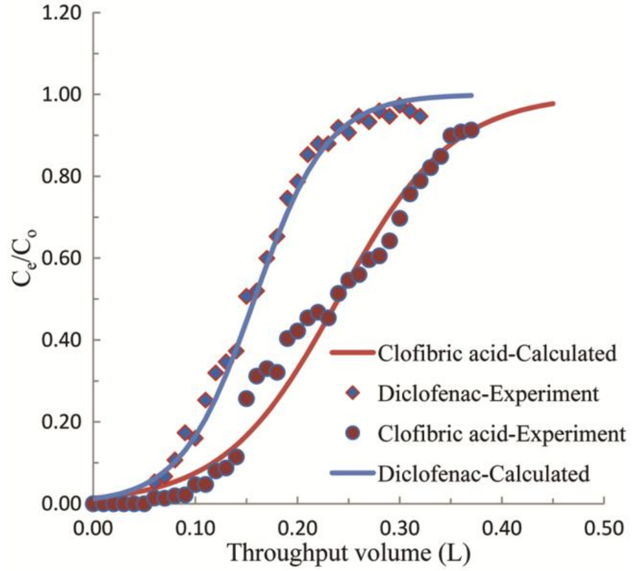

Fig. 7 — Removal of diclofenac and Clofibric acid using hybrid material in fixed bed column reactor ([diclofenac]=2.5 mg/L; [Clofibric acid]= 2.27; pH: 6.5; dose : 0.5 g)

m the mass of adsorbent packed inside the column (g); V the throughput volume (L); and Q the flow rate of the solution (L/min). The non-linear fitting graphs (Fig. 7) showed that the column data collected were fitted well to non-linear Thomas equation and relatively low value of least square sum, *i.e.*, 3.9×10^{-3} for diclofenac and $6.4 \times 10^{-2}$for clofibric acid indicated a good fit of the experimental data with the theoretically calculated data. The loading capacities of diclofenac and clofibric acid into the column packed with APTES-sericite hybrid material were found to be 0.789 mg/g and 1.095 mg/g, respectively. Further, Thomas rate constants (K_T) were found to be 1.12×10^{-2} and 7.90×10^{-3}L/min/mg for diclofenac and clofibric acid, respectively. Fixed bed column experiments showed that the column packed with APTES-sericite hybrid material possessed significant removal capacity for diclofenac and clofibric acid even under the dynamic conditions and suggest the possible application of this hybrid material in the treatment of waste waters contaminated with micropollutants particularly diclofenac and clofibric acid[34].

Conclusion

Naturally occurring sericite clay was activated with heat treatment followed by acid activation. SEM and BET surface area analyses showed that sericite clay become more porous after activation and the surface area was immensely increased from 3.65 to 62.92 m^2/g. The activated sericite was further modified with 3-aminopropyl-triethoxysilane (APTES) to obtain hybrid material. The successful incorporation of organosilane onto the activated sericite was confirmed with FTIR analysis. Batch adsorption experiments showed that the percentage removal of diclofenac and clofibric acid were relatively low at acidic and basic solution; and the maximum removal was attained at pH 6.0 to 7.0. The adsorption was observed to be very fast and the time dependent adsorption data were best fitted to pseudo-second-order kinetic model. The maximum adsorption capacity of diclofenac and clofibric acid using APTES-sericite hybrid material was found to be 1.868 and 1.749 mg/g, respectively. The equilibrium adsorption data were well fitted to Freundlich adsorption isotherm rather than Langmuir adsorption isotherm. Furthermore, the loading capacities of the column packed with APTES-sericite hybrid material were found to be 0.789 mg/g and 1.095 mg/g. Therefore, this study indicated that the APTES-sericite hybrid material could be employed as an efficient and cost-effective adsorbent for the removal of diclofenac and clofibric acid from aqueous waste.

Conflict of interest

All authors declare no conflict of interest.

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