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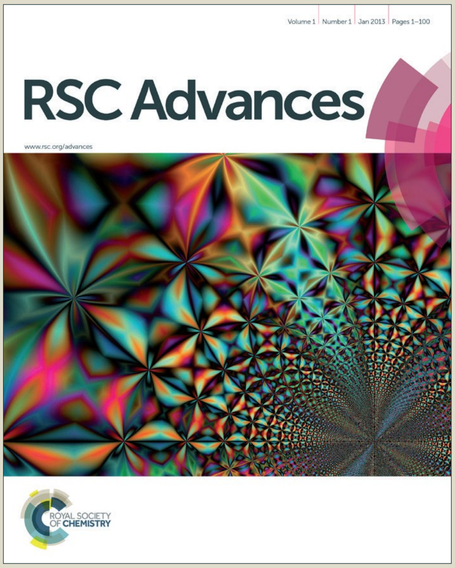

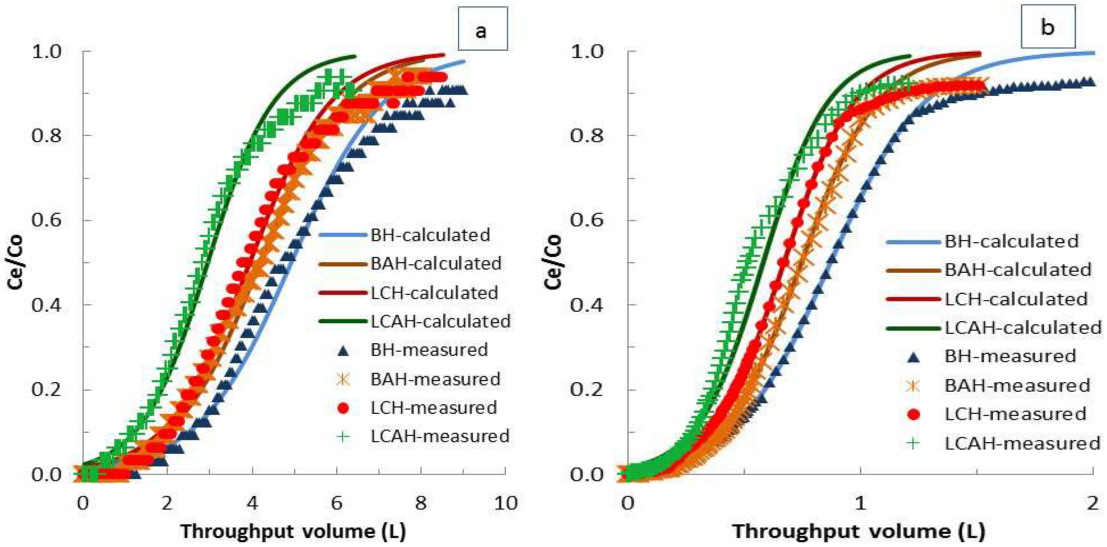

Novel hybrid materials precursor to natural bentonite and locally collected clay partitioned (a) EE2 and (b) tetracycline micro-pollutants effectively from aqueous solutions under column reactor operations

Efficient attenuation of 17α–ethynylestradiol (EE2) and tetracycline using novel hybrid materials: Batch and column reactor studies

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Abstract

Hybrid materials were obtained modifying the natural bentonite (B) or locally collected clay (LC) using hexadecyltrimethylammonium bromide (HDTMA) to obtain the bentonite-HDTMA (BH) and local clay-HDTMA (LCH) or by simultaneous pillaring with aluminium and modification with the HDTMA so as to obtain BAH and LCAH solids. The hybrid materials were employed in the efficient attenuation of micro-pollutants, *viz.*, 17α–ethynylestradiol (EE2) and tetracycline (TC) from aqueous solutions under the batch and fixed-bed column reactor operations. Batch data indicated that the uptake of EE2 and TC by the hybrid materials was slightly affected at low and high pH within the studied pH range of 4.0-10.0. The uptake was insignificantly affected varying the initial sorptive concentration (from 1.0 mg/L to 10.0 mg/L for EE2 and 1.0 mg/L to 20.0 mg/L for TC) and the background electrolyte (NaCl) concentrations from 0.0001 to 0.1 mol/L. Moreover, the attenuation of EE2 and TC by these hybrid materials was fairly efficient as within 60 minutes for EE2 and 240 minutes for TC of contact time, an apparent equilibrium between solid and solution was achieved. Kinetic modeling showed that the data were fitted well to the PSO (Pseudo-Second Order) and FL-PSO (Fractal-Like-Pseudo-Second Order) kinetic models compared to the PFO (Pseudo-First Order) model since reasonably low value of least square sum were obtained for these two models. The fixed-bed column results showed that relatively high breakthrough volume was obtained for attenuation of EE2 and TC using the hybrid materials. Further, the breakthrough data were fitted well to the Thomas equation therefore very high loading capacity was estimated for EE2 and TC by the hybrid materials. The hybrid materials were found to be useful materials in the remediation of aquatic environment contaminated with these two micro-pollutants.

Keywords: *Hybrid materials, surfactant, micro–pollutants, 17α–ethynylestradiol, tetracycline, batch, column, hydrophobic, partitioning.*

1. Introduction

Clay minerals are composed of fine particles of hydrous aluminosilicates, and developed plasticity when mixed with water. A common characteristic of different clay minerals is their layer structure and are having varied chemical, mineralogical or physical characteristics. Clays possess permanent net negative charge because of isomorphous substitution, which is responsible for the presence of exchangeable cations within the interspace region.[1-3] Therefore, the electrical charge possessed by the clay minerals along with the porosity at the micro level makes it viable natural sorbing materials for several pollutants in the treatment of contaminated water. Although clay minerals are used widely to decontaminate the inorganic pollutants from wastewater, however, the pristine clay minerals possesses insignificant sorption capacity towards several hydrophobic and low- or nonpolar organic pollutants due to the hydrophilic nature of these materials.[4] Moreover, most of the clay materials show less settling capacity hence, limiting its wider practical implication in the wastewater treatment operations.[5] However, the exchangeable cations of clay with organo cations makes it useful hybrid materials for the attenuation of several NOC (non-polar organic contaminants) from aqueous solutions.[6-10] Similarly, the hybrid materials obtained by pillaring with poly(hydroxo-metal) cations and simultaneous intercalation of suitable organic cations shows an enhanced applicability in wastewater treatment since this shows fair affinity towards the organic impurities, and possess achievable settling capacity makes easy for solid/aqueous separation.[3]

The presence of organic micro-pollutants, in particular, pharmaceuticals and personal care products (PPCPs) in the aquatic environment received a serious environmental concern during the recent past; since several micro-pollutants are persistent, low biodegradable and toxic even at low levels. The widespread occurrence of PPCPs was demonstrated by a number of monitoring studies and measurable concentrations of many of the PPCPs were found in wastewater, surface water, sediments, groundwater, and even in drinking water.[11-13] PPCPs enter into the terrestrial environment through direct runoff and excretion as unmetabolized drugs or active metabolites and degradation products.[14] It was reported that *Ca (Circa)* 70% of consumed pharmaceuticals were excreted through human urine as active ingredients or metabolites.[15-17] The normal sewage treatment system cannot eliminate antibiotics completely, which results the presence of residual antibiotics in the effluent water.[18]

17α-ethynylestradiol, known as EE2 is one of the synthetic estrogenic compound. It is a derivative of natural hormone estradiol (E2). EE2 is used in almost all modern formulations of combined oral contraceptive pills and hormone replacement therapy for treatment of osteoporosis, menstrual disorders, prostate and breast cancer including other ailments.[19-21] EE2 is identified as one of the most potent estrogenic chemical among all the known endocrine disrupting chemicals.[22] On the other hand tetracycline is a broad-spectrum antibiotic drug widely prescribed in the treatment of bacterial infections.[23] TC is employed in aquaculture and livestock industry as one of typical antibiotic,[24-25] food additives and growth promoters in farming and animal husbandry.[26] The consumption of tetracycline for veterinary purposes is higher than for other classes of antibiotics.[27]

Sorptive removal of PPCPs using different natural and synthetic materials is one of possible ways of decontaminating the aquatic environment contaminated with PPCPs. de Rudder et al.[28] conducted the removal of 17α–ethynylestradiol (EE2) from water in three stream bioreactors (UBRs), filled with, respectively, sand, granulated activated carbon (GAC) and MnO_2 granules. The removal of EE2 in the sand, GAC and MnO_2 reactors were, respectively, 17.3%, 99.8% and 81.7%. They also reported that the removal in the GAC reactor was mainly due to adsorption while the removal in the MnO_2 reactor could be due to its catalytic properties. Han et al.[20] studied the adsorption of ethinylestradiol (EE2) from aqueous solutions using industrial-grade polyamide 612 (PA612) particles. They observed that the adsorption of EE2 on PA612 followed pseudo-second order kinetics and the strong binding affinity between EE2 and PA612 was due to hydrophobic partitioning of EE2 solutes and hydrogen bonding interactions on PA612 amide groups. Combined coagulation-adsorption treatment using single–walled carbon nanotubes (SWCNTs), multiwall carbon nanotubes (MWCNTs), and powdered activated carbon (PAC) was studied in the removal of EE2.[29] The removal percentages using the combined coagulation-adsorption process were similar to those achieved using only adsorbent. Al-Khateeb et al.[30] pointed the adsorption of EE2 on MWCNTs was a pseudo-second-order kinetic process and found exothermic in nature. Adsorption of tetracycline from aqueous solution by graphene oxide (GO) was investigated by Gao et al.,[31] and it was reported that tetracycline strongly deposited on the GO surface via a π–π interaction and cation-π bonding. Activated carbons with different chemical and textural natures, sludge-derived materials, and the removal by the combined use of microorganisms and activated carbon (bioadsorption) were assessed in the adsorption of three different tetracyclines (TCs) (*viz*., tetracycline, oxytetracycline, and chlortetracycline).[32] They observed that sludge-derived materials were possessed significantly higher removal capacity than that of commercial activated carbon sample. Li et al.,[33] investigated the adsorption of tetracycline on kaolinite with pH-dependent surface charges in aqueous solution by batch tests supplemented by FTIR analyses. The adsorption of TC on kaolinite was mainly on the external surfaces via cation exchange. TC adsorption was more pH dependent and the sorption capacity was much lower compared to that on swelling clays.

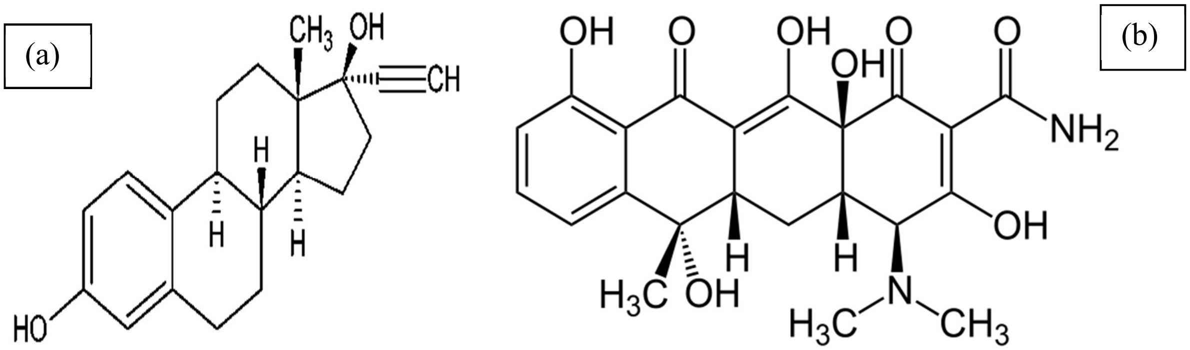
The present study aims to exploit the porous clay materials *viz*., the commercial bentonite and locally collected clay (named local clay) to obtain the novel hybrid materials using the hexadecyltrimethyl ammonium bromide (HDTMA) or the aluminum pillared-HDTMA modified clay materials. It is reported that the organic cations possessed with long-chain alkyl groups (e.g., HDTMA) are particularly able to impart the hydrophobic quality of the mineral surface and such hybrid materials capable to provide hydrophobic core along with organophilic nature which facilitates in hydrophobic bonding with several organic pollutants.[34] The hybrid materials are, then, employed in the attenuation of important micro-pollutants *viz*., EE2 and TC from aqueous solutions. Batch reactor operations are conducted in a wide range of physico-chemical parametric studies which provides to deduce a plausible mechanism occurred at interfaces. Similarly, the fixed-bed column reactor operations conducted to optimize the loading capacity of contaminants under the dynamic conditions.

2. Materials and Methods

2.1. Materials

Bentonite was procured from a commercial supplier which was mined at Bhuj, Gujarat, India. The bentonite clay was not separated anymore and was used after simple washing with distilled water and dried at 90°C in a drying oven for 24 hrs. Local clay was collected from the field of Phullen, Mizoram, India. Since it was having numerous impurities hence, was carefully separated using the ISRIC (International Soil Reference and Information Centre) standard procedure as described elsewhere.[35] The bentonite and local clay samples were crushed in a mortar and sieved to obtain 100 BSS (British Standard Sieve) mesh size particles (0.150 mm).

Bentonite and local clay powder were then subjected to obtain their cation exchange capacity (CEC) using the standard US EPA (United States Environmental Protection Agency) method 9080.[36] The CEC of bentonite and local clay were found to be 69.35 and 46.38 meq/100 g of clay, respectively. Hexadecyltrimethylammonium bromide (HDTMA), 17α–ethynylestradiol (EE2) and tetracycline hydrochloride were procured from Sigma–Aldrich, USA. Aluminium (III) chloride was obtained from the Merck, India. Sodium chloride, Extrapure was procured from the HiMedia, India. The other chemicals used were of analytical or equivalent grade. The water was purified using a Millipore water purification system (Milli–Q+).



Structures of (a) EE2 and (b) tetracycline

2.2 Methodology

2.2.1. Preparation of organoclay and inorgano–organoclay

Bentonite or local clay was organically-modified by the usual wet cation exchange process. Hexadecyltrimethylammonium bromide (HDTMA) was loaded to saturate 100% of the clay CEC. The HDTMA-modified bentonite and local clay were then labeled as BH and LCH samples, respectively. The inorgano–organoclay was prepared by simultaneous pillaring with aluminium and modification with HDTMA to obtain the HDTMA-Al-bentonite (BAH) or HDTMA-Al-local clay (LCAH) hybrid materials. A simple wet method was adopted as described elsewhere.[5,37]

2.2.3. Characterization and surface morphology of hybrid materials

The surface morphology of the hybrid materials along with the virgin clay was obtained taking the FE-SEM (field emission scanning electron microscope) images of these solids using a FE-SEM machine (Model S-4700, Hitachi, Japan). X–ray diffraction (XRD) data was recorded using an X-ray diffraction machine (PANalytical, Netherland; Model X'Pert PRO MPD). Cu-K_α radiations having wavelength 1.5418 Å was used for X-ray diffraction analysis. FT-IR (Fourier Transform-Infra Red) data were collected for these materials using a FT-IR machine (Bruker, Tensor 27, USA by KBR disk method). Similarly, the pH_{PZC} (point of zero charge) of bentonite, local clay, BH, LCH, BAH and LCAH was determined using the pH drift method as described previously.[38]

2.2.5. Batch reactor experiments

A stock solution (50 mg/L) of TC was prepared dissolving an appropriate amount of TC into purified water. The required TC concentration was obtained by successive dilution of stock solution. A stock solution (10 mg/L) of EE2 was prepared; dissolving an appropriate amount of EE2 into purified water at elevated pH with dilute NaOH. Further, the required EE2 concentration was obtained by successive dilution of stock solution and the pH was adjusted with HCl/NaOH. The pH dependence sorption data was obtained as follows: a series of 5.0 mg/L of EE2 or 10.0 mg/L of TC solution (50ml) was taken into polyethylene bottles and the pH was adjusted by drop wise addition of conc. HCl/NaOH solutions. 0.1 g of the solid sample was introduced into these solutions. The bottles were kept in an automatic incubator shaker (Incubator Shaker, TM Weiber, ACMAS Technologies Pvt. Ltd., India) for 24 hours at 25±1°C. The prolonged period, i.e., 24 hours may provide the ability to achieve an apparent equilibrium between the solid/solution interfaces. The bottles were then taken out from the shaker and solution mixture was filtered with 0.45 μm syringe filter and the pH was again checked and reported as equilibrium pH. Absorbance of the filtrates was measured using UV-Visible Spectrophotometer (Model: UV1, Thermo Electron Corporation, USA). The absorbance was recorded at 280 nm for EE2 and 360 nm for TC. Calibration curve was obtained using standard EE2 and TC solutions having varied concentrations. Results were presented as percent EE2 and TC removed as a function of equilibrium pH. The spectrophotometric determination of EE2 and TC were performed previously and described elsewhere.[39-40] The blank EE2 (5.0 mg/L) or TC (10 mg/L) solutions at the studied pH were shaken without the hybrid materials in the polyethylene bottles for the periods of 24 hrs. Further, the samples were filtered using 0.45 μm syringe filter and subjected for the absorbance determination at the wavelength 280 and 360 nm for EE2 and TC, respectively. Results indicated that no decrease in absorbance was obtained which pointed that a negligible sorption was occurred by the polyethylene bottles.

The concentration dependence study was performed varying the EE2 concentrations from 1.0 to 10.0 mg/L and TC concentration from 1.0 to 20.0 mg/L at constant pH~7.0 and at constant temperature 25±1 °C. The adsorption process was followed as detailed above. Results were presented as percent removal of EE2/or TC as a function of initial EE2 or TC concentration (mg/L). Time dependence sorption of EE2 and TC by these hybrid materials was obtained at different time intervals. Initial EE2 concentration 5.0 mg/L and TC concentration 10.0 mg/L at a solid dose of 2.0 g/L was taken as constant and the sorption experiments were conducted at constant pH ~7.0 and temperature 25±1 °C. Results were then reported as percent removal of EE2/or TC as a function of time (min.). Effect of background electrolyte concentration on sorption of EE2/or TC was studied varying the background electrolyte (NaCl) concentration from 0.0001 to 0.1 mol/L with EE2 and TC solution having initial concentrations 5.0 and 10.0 mg/L, respectively. The solution pH (~7.0) and temperature (25±1 °C) was kept constant throughout the experiments. Results were presented as percent EE2 and TC removed as a function of background electrolyte concentration.

2.2.6. Fixed-bed column experiments

Fixed-bed column experiments were conducted using a glass column (1 cm inner diameter) packed with 0.25 g of hybrid materials (kept middle in the column). Below and above to this solid, *Ca (Circa)* 1.0 g of virgin sand particles (14–16 BSS) was placed and the rest of the column was packed with glass beads. EE2 (5.0 mg/L) or TC (10.0 mg/L) solution at pH ~7.0 was pumped upward from the bottom of the column using a peristaltic pump (KrosFlo

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 filtered using 0.45 µm syringe filter and the filtrates were then subjected to UV-Vis Spectrophotometer measurements.

Breakthrough data obtained from the fixed-bed column experiments were further utilized to optimize the loading capacity of EE2 or TC by the hybrid materials loaded column under the dynamic conditions employing the Thomas[41] Eq. (1):

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

where C_e and C_0 are the concentrations (mg/L) of effluent and influent solutions of EE2 and TC, respectively; K_T refer to the Thomas rate constant (L/min/mg); q_0 is the maximum amount (mg/g) of EE2 or TC loaded under the specified column conditions; 'm' is the mass (g) of hybrid materials taken in the column; V is the throughput volume (L); and Q is the flow rate (L/min) of pumped EE2 or TC solution. The column data were fitted to a non-linear Thomas equation using the least square fitting method to estimate two unknown parameters i.e., K_T and q_0.

3. Results and discussion

3.1 Characterization of materials

FT-IR data indicated that the hybrid materials *viz*., BH, BAH, LCH or LCAH possess with prominent IR stretching bands occurring around the wave numbers 2930 cm^{-1} and 2850 cm^{-1} which were considered as –CH_2 asymmetric and symmetric stretching vibrations respectively. This confirmed the introduction of HDTMA within the clay network for all these hybrid materials. Further, from the X-ray diffraction analysis it is noted that both the clay samples contained with the quartz, smectite, illite and kaolinite minerals with varying percent composition as characteristic peaks are assigned in the XRD diffraction pattern. The XRD pattern of the modified clay samples is almost identical to its virgin clay having with slight change in d–values and intensities of the peaks. The FE–SEM images clearly show that the organo-modified bentonite/or LC (i.e., BH or LCH) solids show more heterogeneous and disordered surface structures. Further, the BAH and LCAH solids show similar disordered structure, but possess distinct newly borne fine particles are observed onto the surface, perhaps aluminium is aggregated/immobilized as aluminium hydroxide/or even as Al_2O_3 onto the solid surface. Detailed characterization of these hybrid materials were described previously.[37,42]

3.2. Batch reactor operations

3.2.1. Effect of pH

The pH dependence removal of EE2 (pH 4.01 to 10.14) and TC (pH 3.96 to 10.06) by these solids is presented graphically in figure 1(a) & (b), respectively. It is observed that a very high uptake of EE2 was almost unaffected within the pH region of *Ca* 4.0 to 8.0 by these solids. However, the further increase in pH i.e., beyond the pH 8.0 an apparent decrease in uptake of EE2 was observed. The uptake of EE2 by these solids could be ascribed with the help of speciation of EE2 as well the surface properties of the solids. It is reported that EE2 is having the acid dissociation constant pK_a 10.4.[43] This implies that EE2 molecule exists as a neutral molecule almost up until pH ~10.0 and carries a net negative charge above pH~10.4. On the other hand, the pH_{PZC} value of these solids was found to be 10.0, 8.2, 6.1, 5.8, 5.1 and 5.1 for the samples B, BH, BAH, LC, LCH and LCAH, respectively. This implies that except bentonite solid, other materials possess a net negative charge at and around neutral pH. Therefore, the possibility of electrostatic attraction of EE2 by the solid surface is perhaps not possible. Hence, the possible mechanism of EE2 uptake by these hybrid materials is primarily demonstrated by the fact that the introduction of organic cation (HDTMA) within the clay network caused to enhance the hydrophobicity with enhanced organophilic nature of the surface. This enables EE2 to partition at the introduced hydrophobic core.[44] On the other hand; Al- pillared HDTMA modified local clay (LCAH) show slightly less uptake of EE2, possibly, due to the screening of the introduced HDTMA molecule by the presence of small sized aluminum oxide particles onto the solid surface. Hence, this could reduce the hydrophobic core within the clay network. Further, the removal of EE2 was decreased to some extent increasing the solution pH to 10.0 which was due to the fact that the partial acidic dissociation of EE2 that took place at this pH. This caused for some electrostatic repulsion and hence reduced in partitioning of the EE2 within the hydrophobic core of the hybrid materials. Previously, hybrid materials obtained by modifying the natural sericite with HDTMA and alkyldimethylbenzylammonium chloride were used in the remediation of wastewaters contaminated with BPA. Results indicated that the increase in pH from 2.0 to 10.0 did not significantly affect the percentage uptake of BPA by the hybrid materials. Further, it was reported that the organoclays prepared with longer chain surfactant molecule were less influenced by the solution pH[45] and consistently possessed high adsorption capacity for the BPA even under the alkaline conditions.[46] It was further noted that the virgin bentonite and local clay showed very insignificant uptake of EE2 (*Ca* 42% and 36% at pH 6.0 to 8.0 for B and LC respectively), which was further decreased at low and high pH. The sorption of EE2 by all these hybrid materials, compared to the unmodified clays, show significantly enhanced percent uptake (*Ca* 94 %) of EE2 was obtained, and interesting to note that the high attenuation of EE2 is almost independent of the change in solution pH at least up to the pH 8.5 (*cf*. Figure 1(a)).

TC, with different functional groups, is having pKa_1, pKa_2 and pKa_3 values of 3.3, 7.7 and 9.7, respectively.[47] In the case of TC, for the unmodified clays i.e., B and LC samples, very high sorption is achieved at lower pH values i.e., pH~4 which decreases significantly between pH 4.0 to 6.0 and attains nearly a constant value from pH 6.0-8.0 and then there is a marked decrease at pH ~10.0. These results agree well with the other reports in which TC adsorption was higher at low pH and was attributed to the cation exchange mechanism.[33,44] When solution pH is below 3.3, TC exists as a cation (TCH_3^+ or $TCH_3^{+\,0\,0}$), due to the protonation of dimethyl-ammonium group. At pH between 3.3 and 7.7, TC exists as a zwitterion (TCH_2^0 or $TCH_2^{0\,+\,-}$), due to the loss of a proton from the phenolic diketone moiety. At solution pH greater than 7.7, TC exists as anion (TCH^- or $TCH^{+\,-\,-}$). Further, at pH 9.7 it exists as di-anionic form (TC^{2-} or $TC^{0\,-\,-}$) by the loss of another proton from the tri–carbonyl system and phenolic diketone moiety.[41] The higher removal at medium pH range (6-8) for TC compared to EE2, for the unmodified clays indicates that the positive part of TC zwitterions could interact with the clays. Since both species of TCH_2^0 and TCH^- contain a positively charged group in their structure, it is likely that the molecules are arranged at the surface so that the positively charged group is located very close to the surface, leading the negatively charged one(s) as far as possible from the surface, which reveals that electrostatic attraction may play an important role in the sorption of not only TCH_3^+ but also TCH_2^0 and TCH^- species.[48]

At very low pH (i.e., pH 4.0) a slightly lower uptake of TC was registered with the hybrid material which was gradually increased at pH 6 (*Ca* 99.5%), and then remained nearly constant from *Ca* pH 6.0 to 9.0. Therefore, these results clearly indicate that the hydrophobic interaction play a prominent role in the TC sorption.[49] Further, beyond pH 9.0 a slight decrease in the removal of TC was seen by these hybrid materials which were due to the strong electrostatic repulsion. Slightly lower uptake of TC by LCAH was, perhaps, due to the screening of the HDTMA molecule in presence of aluminum oxide particles onto the clay surface which restricts partly the partitioning of TC within the hydrophobic core. Similar results were found for the uptake of TC by $MnFe_2O_4$/activated carbon magnetic composite[50] and activated carbons.[32] With similar observation on the removal of TC by multi–walled carbon nanotubes (MWCNT), Zhang et al.[51] indicated that the adsorption mechanism was probably the non-electrostatic π–π dispersion interaction between bulk π systems on MWCNT surface and TC molecules contained both benzene rings and double bonds or hydrophobic interaction between MWCNT and TC.

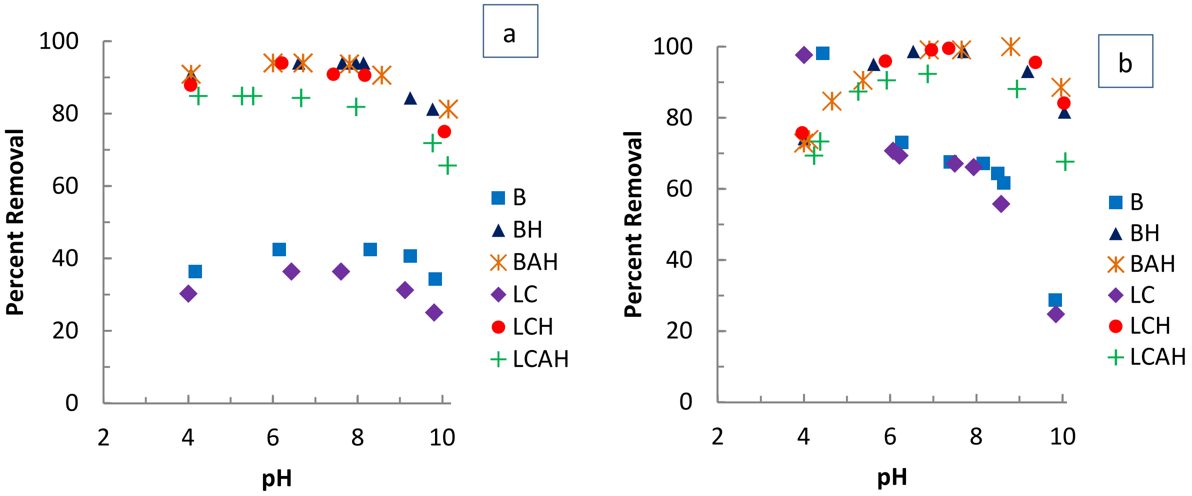


Figure 1. pH dependence sorption of (a) EE2 and (b) TC by B, BH, BAH, LC, LCH and LCAH solids.

3.2.2. Effect of EE2 or TC concentration

Studying the effect of initial sorptive concentration is one of the effective factors for estimating the sorption efficiency/capacity. The concentration dependence removal was studied for the initial EE2 concentrations from 1.0 mg/L to 10.0 mg/L and TC concentrations from 1.0

mg/L to 20.0 mg/L at constant pH 7.0. Results were presented graphically in figure 2(a) and 2(b) for EE2 and TC, respectively. The figure revealed that increasing the concentration of EE2 or TC, a very high percent uptake of EE2 and TC, was not significantly affected. These results again pointed a strong affinity of hybrid materials (BH, BAH and LCH) towards the attenuation of EE2 and TC. At lower concentrations the solids show very high removal for TC whereas the percent removal was slightly lower for EE2. A slightly less removal of EE2 and TC is observed using the LCAH solid. The results were in consistent with the pH dependence study.

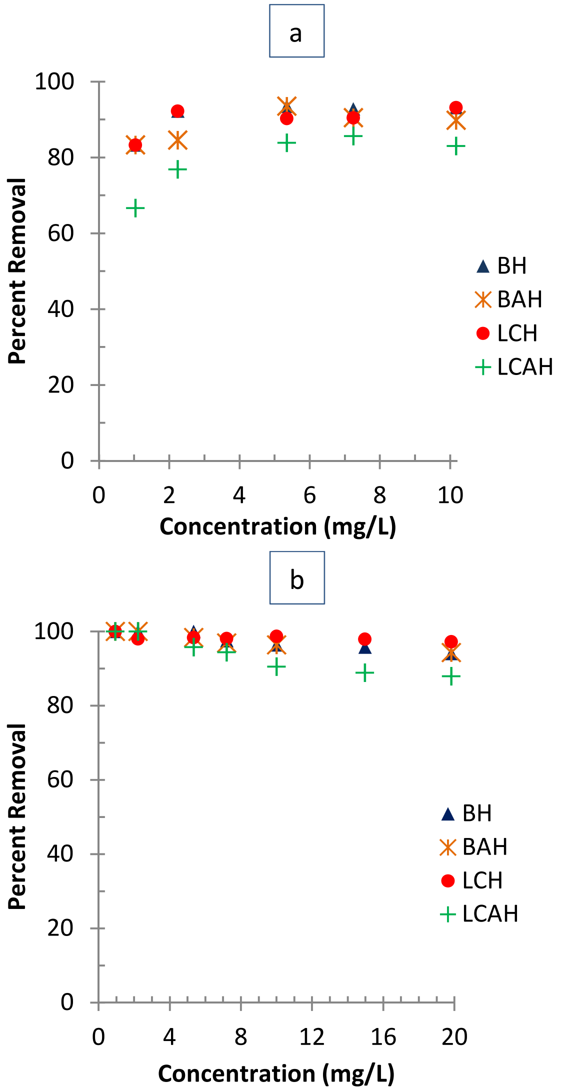


Figure 2. Effect of concentration of (a) EE2 and (b) TC on the removal by BH, BAH, LCH and LCAH solids.

3.2.3. Effect of background electrolyte concentration

Effect of background electrolytes in the sorptive removal of EE2 and TC by the hybrid materials could help to explain the mechanism involved at solid/solution interfaces.[52-53] The specific sorption is usually not much influenced by the change in background electrolyte concentrations; whereas the non-specific sorption is greatly influenced by the change in background electrolyte concentrations. Therefore, the sorption of EE2 or TC by BH, BAH, LCH and LCAH was assessed varying the background electrolyte concentrations from 0.0001 mol/L to 0.1 mol/L NaCl at an initial EE2 concentration 5.0 mg/L and TC concentration of 10.0 mg/L at constant pH 7.0. The percent removal of EE2 and TC was obtained as a function of background electrolyte (NaCl) concentrations. The results were presented graphically in figure 3(a) and (b) for the EE2 and TC, respectively. Results showed that increasing the background electrolyte concentrations even up to 1000 times could not significantly affect the percent uptake of either EE2 or TC by the hybrid materials i.e., BH, BAH, LCH and LCAH. This indicated the strong affinity of solids towards EE2 or TC. Again, this implies that the partitioned EE2 or TC was bound with relatively stronger van der Waals forces which retain firmly the EE2 or TC molecule onto or within the interspace of hybrid materials. Previously, it was reported that the increased in the NaCl concentration from 0 to 320 mM did not significantly change the adsorption of EE2 from landfill leachate onto single–walled carbon nanotubes (SWCNTs).[54] Similarly, Zhang et al.[51] studied TC adsorption onto multi-walled carbon nanotubes (MWCNT) under two ionic strengths (0.02 and 0.2 mol/L NaCl) and two initial TC concentrations (20.0 and 70.0 mg/L). They indicated that in the experimental pH range (*Ca* 2.5 to 9) the ionic strength showed insignificant impact on the sorption of TC onto MWCNT.

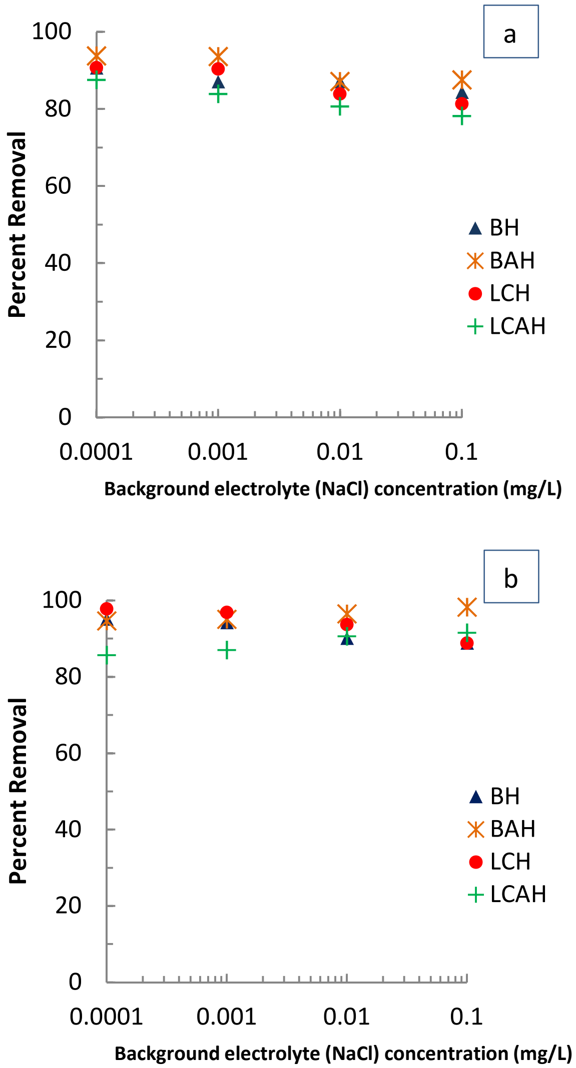


Figure 3. Effect of background electrolyte (NaCl) concentration on the removal of (a) EE2 and (b) TC by BH, BAH, LCH and LCAH solids.

3.2.1. Time dependence removal

The percent of EE2 or TC removed as a function of time was presented graphically in figure 7(a) & (b). It is evident from the figure that the materials are efficient in the removal of EE2 and TC from aqueous solutions since within initial 10-15 mins of contact for EE2 and ~60 mins of contact for TC, the uptake was very fast which was then gradually increased and an apparent equilibrium was achieved within *Ca* 60 mins for EE2 and *Ca* 240 mins for TC. This again reaffirms the affinity of these solids towards EE2 and TC. However, it is observed that the uptake of EE2 and TC onto the LCAH solid show comparatively slower uptake compared to the other hybrid materials.

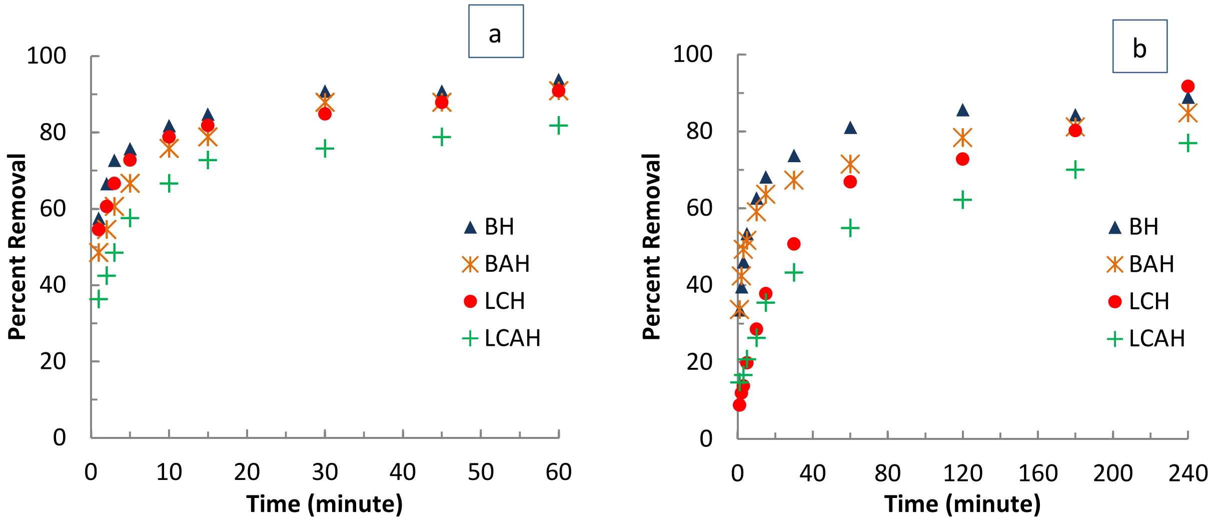


Figure 4. Time dependence of the adsorption of (a) EE2 and (b) TC by BH, BAH, LCH and LCAH solids.

The time dependence sorption data is then utilized to perform the kinetic modelling. The three different kinetic models *viz.*, pseudo-first order (PFO),[55] pseudo-second order (PSO)[56] and fractal- like pseudo-second order (FL-PSO)[57] models to its non-linear form (equations 2, 3 and 4) were utilized:

$$q_t = q_e(1 - \exp(-k_1 t)) \qquad \ldots(2)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \qquad \ldots(3)$$

$$q_t = \frac{k q_e^2 t^{\alpha}}{1 + k q_e t^{\alpha}} \qquad \ldots(4)$$

where q_t and q_e are the amount of EE2/or TC removed at time ‘t’ and removal capacity at equilibrium, respectively. k_1 and k_2 are the pseudo-first and pseudo-second order rate constants, respectively. Similarly, the constants k and α are referred to the rate constant and fractal constant, respectively. A non-linear least square fitting was performed and the unknown parameters were optimized. The estimated values of the unknown parameters along with the least square sum were then returned in table 1. Table 1 indicated that the simulation data was best fitted to the PSO and FL-PSO kinetic models compared to the PFO model since reasonably a low value of least square sum was obtained for these two models. These results showed that the removal capacity of these hybrid materials were higher for the TC compared to the EE2. Further, a fair applicability of the PSO or FL-PSO models points that the EE2/or TC species were bound onto the surface of these hybrid material with strong forces. Earlier, reports indicated that the sorption of divalent metal cations onto the *sphagnum moss* peat followed the second-order rate laws. Therefore, it was concluded that metal cations were bound with strong chemical forces that occurred between the peat surface active groups and divalent metal ions forming covalent bonds with valence forces sharing or the exchange of electrons.[58-59] Similar results were obtained in the sorptive removal of bisphenol A by the some of the hybrid materials precursor to the natural sericite.[49]

Table 1. Kinetic parameters obtained for the sorption of EE2 and TC by hybrid materials using various kinetic models

Systems	Kinetic Models									
	PFO			PSO			FL-PSO			
	q_e	k_1	s^2	q_e	k_2	s^2	q_e	k	α	s^2
BH-EE2	2.340	0.990	0.160	2.515	0.654	0.031	2.940	0.438	0.488	0.004
BAH-EE2	2.203	0.671	0.276	2.411	0.415	0.083	4.038	0.126	0.340	0.003
LCH-EE2	2.230	0.906	0.167	2.399	0.625	0.030	2.751	0.453	0.533	0.004
LCAH-EE2	2.002	0.463	0.164	2.221	0.292	0.045	2.673	0.217	0.611	0.013
BH-TC	3.868	0.289	1.699	4.127	0.100	0.481	4.691	0.108	0.571	0.035
BAH-TC	3.533	0.390	1.766	3.769	0.146	0.656	4.810	0.120	0.410	0.064
LCH-TC	3.940	0.039	0.882	4.506	0.010	0.350	5.534	0.013	0.712	0.143
LCAH-TC	3.296	0.046	1.192	3.700	0.016	0.608	7.395	0.011	0.457	0.088

s^2 : Least Square Sum

3.3. Fixed-bed column reactor operations

Fixed-bed column operations were performed to assess the loading capacity of the hybrid materials BH, BAH, LCH and LCAH for EE2 and TC under the dynamic conditions. The column experiments were carried out keeping with the stated column conditions. The breakthrough curves were obtained and presented graphically in figures 5(a) and (b) for EE2 and TC, respectively. Figures revealed that relatively high breakthrough volume was obtained for EE2 and TC by these solids. A complete breakthrough volume was achieved at the throughput volume of 7.68 L, 6.36 L, 6.24 L and 5.041 L for EE2; and 1.33 L, 1.09 L, 1.06 L and 0.94 L for TC; respectively for the BH, BAH, LCH and LCAH solids. The relatively high value of breakthrough volume indicates the higher removal capacity of EE2 and TC by the modified solids under the dynamic conditions. This further shows that the modified solids could be potential and promising sorbing materials for the removal of EE2 and TC.

Further, the non-linear least square fitting was conducted with the breakthrough column data employing the Thomas equation (Equation 1). The fitting was performed to simulate the two unknown parameters, i.e., K_T and q_0. The values of Thomas constants along with the least square sum were estimated and returned in Table 2. Results indicated that a high loading capacity was achieved for EE2 and TC by these solids under the dynamic conditions. Relatively, BH showed higher removal capacity for EE2 and TC compared to the BAH solid. Similarly, LCH solid possessed relatively higher removal capacity than LCAH solid. Overall removal capacity followed the trend: BH, BAH, LCH and LCAH. It is further noted that the removal capacity of BAH and LCH both for EE2 and TC was found to be comparable hence, the locally collected clay could be a useful natural material to be exploited in the efficient and effective remediation of wastewater contaminated with the micro-pollutants EE2 and TC. Moreover, the removal capacity of BAH or LCAH for EE2 and TC was quite comparable with the materials BH or LCH. Although a slight decrease was observed by the BAH and LCAH solids however, these materials were showed good settling capacity hence, will be a superior alternative in solid/solution separation and wastewater treatment plant implications. These results were similar to the findings of batch reactor experiments. Also, the results were in a line of other reports in which the Thomas equation was utilized to demonstrate the loading capacity of different sorbing materials.[60-61]

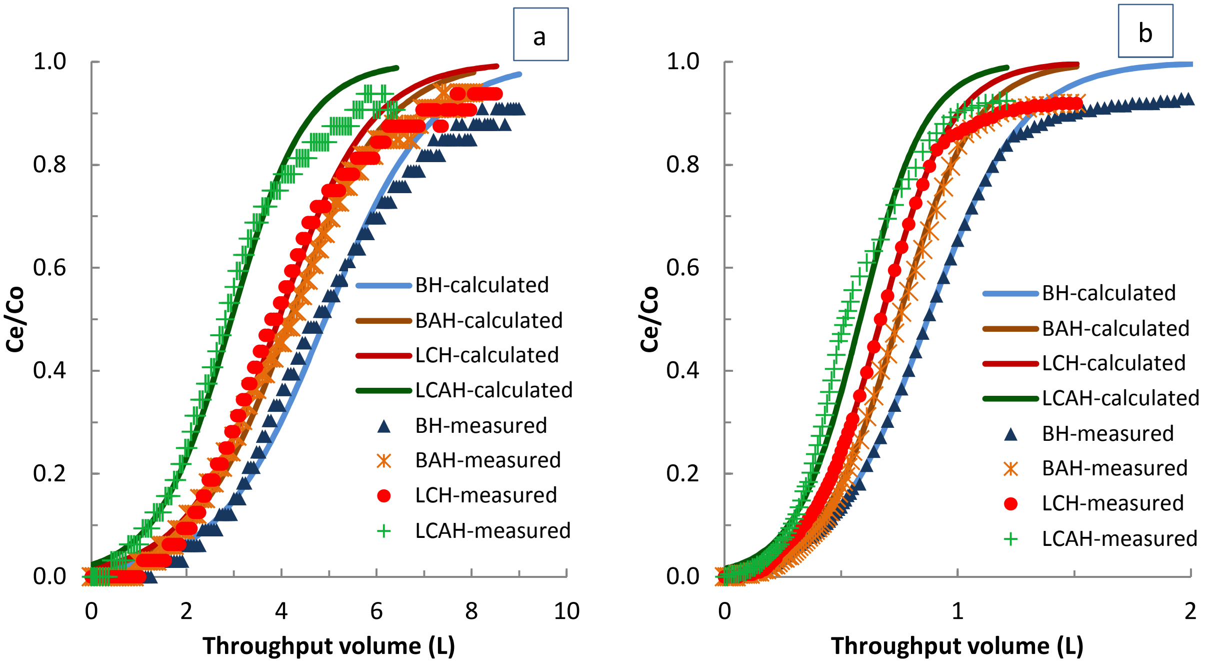


Figure 5. Breakthrough curves for the removal of (a) EE2 and (b) TC by BH, BAH, LCH and LCAH solids.

Table 2. Thomas constants (along with the least square sum) estimated for the removal of EE2 and TC by B, BH, BAH, LC, LCH and LCAH.

	EE2			**TC**		
	Thomas constants		Least square sum (s^2)	Thomas constants		Least square sum (s^2)
Materials	$K_T x10^{-4}$ (L/min/mg)	q_0 (mg/g)		$K_T x10^{-4}$ (L/min/mg)	q_0 (mg/g)	
BH	1.59	111.979	10.0	4.89	34.976	12.0
BAH	1.70	97.987	11.0	6.09	29.963	12.0
LCH	1.88	86.965	11.0	6.59	26.956	12.0
LCAH	2.30	64.996	10.0	7.09	23.478	11.0

4. Conclusion

The organo-modified clay and inorgano-organo-modified clay materials, precursor to the natural bentonite and local clay was synthesized and characterized by the IR and XRD analysis. The IR data showed that the HDTMA was well introduced within the clay network. The XRD analysis enabled the presence of quartz, smectite, kaolinite and illite (having varied percentage) with these two clay samples i.e., bentonite and local clay. SEM images of the modified solids showed the disordered structures of HDTMA modified clay materials whereas Al pillared solids showed that additional fine particles of aluminium hydroxides or Al_2O_3 were aggregated onto the clay surface. Further, the materials were utilized for the remediation of EE2 and TC contaminated waters under the batch and column reactor operations. The batch data implied that the uptake of EE2 and TC by the hybrid materials was slightly affected at low and high pH within the studied pH range 4.0 -10.0. The uptake was insignificantly affected varying the sorptive concentration (from 1.0 mg/L to 10.0 mg/L for EE2 and 1.0 mg/L to 20.0 mg/L for TC) and the background electrolyte concentration (0.0001 to 0.1 mol/L NaCl). Moreover, the attenuation of EE2 and TC by these hybrid materials was fairly efficient as within 60 mins for EE2 and 240 mins for TC of contact time, an apparent equilibrium between solid and solution was achieved. The fixed-bed column results showed that relatively high breakthrough volume was obtained for attenuation of EE2 and TC using the hybrid materials. Further, the breakthrough data were fitted well to the Thomas equation therefore the loading capacity of EE2 was estimated to be 111.979, 97.987, 86.965 and 64.996 mg/g and for TC 34.976, 29.963, 26.956 and 23.478 mg/g for the solids BH, BAH, LCH and LCAH, respectively. Hence the novel hybrids materials were found to be useful in the remediation of aquatic environment contaminated with two important micro-pollutants *viz.*, EE2 and TC.

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