

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/276149730>

# Efficient attenuation of 17 $\alpha$ -ethynylestradiol (EE2) and tetracycline using novel hybrid materials: Batch and column reactor studies

Article in RSC Advances · May 2015

DOI: 10.1039/C4RA17197G

CITATIONS

20

READS

146

4 authors, including:



Seung-Mok Lee

Catholic Kwandong University

173 PUBLICATIONS 7,533 CITATIONS

[SEE PROFILE](#)



Diwakar Tiwari

Mizoram University

131 PUBLICATIONS 3,382 CITATIONS

[SEE PROFILE](#)

## PAPER

CrossMark  
click for updatesCite this: *RSC Adv.*, 2015, 5, 46834

## Efficient attenuation of 17 $\alpha$ -ethynylestradiol (EE2) and tetracycline using novel hybrid materials: batch and column reactor studies

Thanhmingliana,<sup>a</sup> Seung Mok Lee,<sup>b</sup> Diwakar Tiwari<sup>\*a</sup> and Shailesh K. Prasad<sup>c</sup>

Hybrid materials were obtained by modifying natural bentonite (B) or locally collected clay (LC) using hexadecyltrimethylammonium bromide (HDTMA) to obtain bentonite-HDTMA (BH) and local clay-HDTMA (LCH), or by simultaneous pillaring with aluminum and modification with HDTMA to obtain BAH and LCAH. The hybrid materials were used for the efficient attenuation of micro-pollutants, 17 $\alpha$ -ethynylestradiol (EE2) and tetracycline (TC), in aqueous solutions under batch and fixed-bed column reactor experiments. Batch data indicated that the uptake of EE2 and TC by the hybrid materials was slightly affected at low and high pH within the pH range of 4.0–10.0. The uptake was not affected by varying the initial sorptive concentration (1.0–10.0 mg L<sup>-1</sup> for EE2 and 1.0–20.0 mg L<sup>-1</sup> for TC) and the background electrolyte (NaCl) concentrations (0.0001–0.1 mol L<sup>-1</sup>). Moreover, the attenuation of EE2 and TC by these hybrid materials was fairly efficient. Within a contact time of 60 min for EE2 and 240 min for TC, an apparent equilibrium between the clay and solution was achieved. Kinetic modeling showed that the data were fitted well to the pseudo-second order (PSO) and fractal-like-pseudo-second order (FL-PSO) kinetic models compared with the pseudo-first order (PFO) model because a low value of the least square sum was obtained for these two models. The fixed-bed column results showed that a high breakthrough volume was obtained for attenuation of EE2 and TC using the hybrid materials. Furthermore, the breakthrough data were fitted well to the Thomas equation; therefore, a very high loading capacity was estimated for EE2 and TC for the hybrid materials. These hybrid materials are useful materials in the remediation of aquatic environments contaminated with these two micro-pollutants.

Received 29th December 2014

Accepted 11th May 2015

DOI: 10.1039/c4ra17197g

[www.rsc.org/advances](http://www.rsc.org/advances)

### 1. Introduction

Clay minerals are composed of fine particles of hydrous aluminosilicates, and develop plasticity when mixed with water. A common characteristic of clay minerals is their layer structure, although they have diverse chemical, mineralogical, and physical characteristics. Clays possess a permanent net negative charge because of isomorphous substitution, which is responsible for the presence of exchangeable cations in the interspace region.<sup>1–3</sup> Therefore, the electrical charge possessed by clay minerals and their microscale porosity makes them suitable as natural sorbing materials for several pollutants in the treatment of contaminated water. Although clay minerals are used widely to decontaminate inorganic pollutants from wastewater, pristine clay minerals possess low sorption capacity for several

hydrophobic and low- or nonpolar organic pollutants owing to the hydrophilic nature of these materials.<sup>4</sup> Moreover, most clays show low settling capacity, limiting their wider practical application in wastewater treatment.<sup>5</sup> The exchange of clay cations with organic cations produces useful hybrid materials for the attenuation of several non-polar organic contaminants (NOC) from aqueous solutions.<sup>6–10</sup> Likewise, hybrid materials obtained by pillaring with poly(hydroxo-metal) cations and simultaneous intercalation of suitable organic cations are particularly suitable for wastewater treatment, because these materials show good affinity for organic impurities, and possess satisfactory settling capacity, allowing easy separation of solid and aqueous components.<sup>3</sup>

The presence of organic micro-pollutants, particularly pharmaceuticals and personal care products (PPCPs) in the aquatic environment is a serious environmental concern because several micro-pollutants are persistent, non-biodegradable and toxic even at low levels. The widespread distribution of PPCPs has been demonstrated by a number of monitoring studies and measurable concentrations of many PPCPs have been found in wastewater, surface water, sediments, groundwater, and even in drinking water.<sup>11–13</sup> PPCPs enter the terrestrial environment through direct runoff and

<sup>a</sup>Department of Chemistry, School of Physical Sciences, Mizoram University, Aizawl-796004, India, +91-389-2330834. E-mail: [diw\\_tiwari@yahoo.com](mailto:diw_tiwari@yahoo.com); Tel: +91-389-2301806

<sup>b</sup>Department of Health and Environment, Catholic Kwandong University, 522 Naegok-dong, Gangneung, Gangwon-do 210-701, Korea

<sup>c</sup>Department of Chemistry, National Institute of Technology, Jamshedpur-831014, India

excretion as unmetabolized drugs or active metabolites and degradation products.<sup>14</sup> Around 70% of pharmaceuticals consumed are excreted in urine as active ingredients or metabolites.<sup>15–17</sup> The normal sewage treatment system cannot eliminate antibiotics completely, which results in the presence of residual antibiotics in effluent.<sup>18</sup>

17 $\alpha$ -ethynylestradiol (EE2) is a synthetic estrogen. It is a derivative of the natural hormone, estradiol (E2). EE2 is used in almost all modern formulations of combined oral contraceptive pills and hormone replacement therapy for treating conditions such as osteoporosis, menstrual disorders, and prostate and breast cancer.<sup>19–21</sup> EE2 is one of the most potent estrogenic chemicals of the known endocrine disruptors.<sup>22</sup> Tetracycline (TC) is a broad-spectrum antibiotic drug commonly prescribed for the treatment of bacterial infections.<sup>23</sup> TC is widely used in aquaculture and the livestock industry<sup>24,25</sup> as a food additive and growth promoter.<sup>26</sup> The consumption of tetracycline for veterinary purposes is higher than for other classes of antibiotics.<sup>27</sup>

Sorptive removal of PPCPs using natural and synthetic materials is a possible method of decontaminating the aquatic environment contaminated with PPCPs. de Rudder *et al.*<sup>28</sup> removed 17 $\alpha$ -ethynylestradiol (EE2) from water in three upstream bioreactors (UBRs), filled with sand, granulated activated carbon (GAC), or MnO<sub>2</sub> granules. The removal of EE2 in the sand, GAC and MnO<sub>2</sub> reactors were 17.3%, 99.8% and 81.7%, respectively. They reported that the removal in the GAC reactor was mainly due to adsorption, whereas the removal in the MnO<sub>2</sub> reactor was possibly through the catalytic properties of MnO<sub>2</sub>. Han *et al.*<sup>20</sup> studied the adsorption of ethynylestradiol (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 for the removal of EE2.<sup>29</sup> The removal percentages using the combined coagulation–adsorption method were similar to those achieved using only an adsorbent. Al-Khateeb *et al.*<sup>30</sup> reported that the adsorption of EE2 on MWCNTs was a pseudo-second-order kinetic process it was exothermic in nature. Adsorption of tetracycline from aqueous solution by graphene oxide (GO) was investigated by Gao *et al.*<sup>31</sup> They reported that tetracycline strongly adsorbed on the GO surface *via* a  $\pi$ – $\pi$  interaction and cation– $\pi$  bonding. Activated carbon with different chemical and textural properties, sludge-derived materials, and the removal by the combined use of microorganisms and activated carbon (bioadsorption) were assessed for the adsorption of three different tetracyclines (TCs) (tetracycline, oxytetracycline, and chlortetracycline).<sup>32</sup> Sludge-derived materials possessed significantly higher removal capacity than the commercial activated carbon sample. Li *et al.*<sup>33</sup> 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

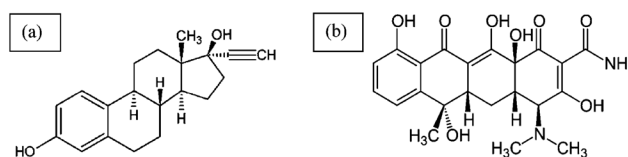
external surfaces *via* cation exchange. TC adsorption was more pH dependent and the sorption capacity was much lower compared with that on swelling clays.

The present study uses porous clay materials, commercial bentonite and locally collected clay (local clay), to obtain the novel hybrid materials, hexadecyltrimethylammonium bromide (HDTMA) or aluminum-pillared HDTMA-modified clay. Organic cations with long-chain alkyl groups (*e.g.*, HDTMA) impart hydrophobic properties to the mineral surface, and these hybrid materials provide a hydrophobic core and organophilic properties, which aids hydrophobic bonding with several organic pollutants.<sup>34</sup> We use the hybrid materials to attenuate the important micro-pollutants, EE2 and TC, in aqueous solutions. Batch reactor experiments are conducted for physico-chemical parametric studies, which provide a plausible mechanism for the interfaces. Similarly, fixed-bed column reactor experiments are conducted to optimize the loading capacity of contaminants under dynamic conditions.

## 2. Materials and methods

### 2.1. Materials

Bentonite was procured from a commercial supplier, and was mined in Bhuj, Gujarat, India. The bentonite clay was used after simple washing with distilled water and drying at 90 °C in an oven for 24 h. Local clay was collected in Phullen, Mizoram, India. Because the local clay contained numerous impurities it was carefully separated using the International Soil Reference and Information Centre (ISRIC) standard procedure, as described elsewhere.<sup>35</sup> The bentonite and local clay samples were crushed in a mortar and sieved to obtain 100 British Standard Sieve (BSS) mesh size particles (0.150 mm). The cation exchange capacity (CEC) of bentonite and local clay powder were then obtained by using standard United States Environmental Protection Agency (US EPA) method 9080.<sup>36</sup> The CEC of bentonite and local clay were 69.35 and 46.38 meq/100 g of clay, respectively. Hexadecyltrimethylammonium bromide (HDTMA), 17 $\alpha$ -ethynylestradiol (EE2) and tetracycline hydrochloride were procured from Sigma-Aldrich, USA. Aluminum(III) chloride was obtained from Merck, India. Sodium chloride (Extrapure) was procured from HiMedia, India. The other chemicals used were of analytical or equivalent grade. The water was purified by using a Millipore water purification system (Milli-Q<sup>+</sup>).



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 standard wet cation exchange process. Hexadecyltrimethylammonium

bromide (HDTMA) was loaded to saturate the clay CEC. HDTMA-modified bentonite and local clay were labeled as BH and LCH samples, respectively. The inorgano-organoclay was prepared by simultaneous pillaring with aluminum and modification with HDTMA to obtain HDTMA-Al-bentonite (BAH) or HDTMA-Al-local clay (LCAH) hybrid materials. A simple wet method was used as described elsewhere.<sup>5,37</sup>

**2.2.2. Characterization and surface morphology of hybrid materials.** The surface morphology of the hybrid materials and the virgin clay was determined from field emission scanning electron microscopy (FE-SEM; S-4700, Hitachi, Japan) images. X-ray diffraction (XRD) data was recorded by using an X-ray diffraction machine (X'Pert PRO MPD, PANalytical, Netherlands) with Cu-K<sub>α</sub> radiation with a wavelength of 1.5418 Å. Fourier transform-infra red (FT-IR) spectroscopy was performed with an FT-IR spectrometer (Bruker, Tensor 27, USA, KBR disk method). The point of zero charge (pH<sub>PZC</sub>) values of bentonite, local clay, BH, LCH, BAH and LCAH were determined by the pH drift method, as described previously.<sup>38</sup>

**2.2.3. Batch reactor experiments.** A stock solution (50 mg L<sup>-1</sup>) of TC was prepared by dissolving an appropriate amount of TC in purified water. The required TC concentration was obtained by successive dilution of stock solution. A stock solution (10 mg L<sup>-1</sup>) of EE2 was prepared by dissolving an appropriate amount of EE2 in purified water at elevated pH with dilute NaOH. The required EE2 concentration was obtained by successive dilution of stock solution and the pH was adjusted with HCl/NaOH. The pH dependence of sorption data was obtained as follows. A series of 5.0 mg L<sup>-1</sup> EE2 or 10.0 mg L<sup>-1</sup> TC solutions (50 mL) was placed in polyethylene bottles and the pH was adjusted by dropwise addition of conc. HCl/NaOH solutions. The clay (0.1 g) was added to 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 ± 1 °C. The prolonged period of 24 h may allow an apparent equilibrium to be achieved between the clay and solution. The bottles were removed from the shaker and the mixture was filtered with a 0.45 μm syringe filter. The filtrate pH was reported as the equilibrium pH. Absorbance of the filtrates was measured with a UV-vis spectrophotometer (UV1, Thermo Electron Corporation, USA). The absorbance was recorded at 280 nm for EE2 and 360 nm for TC. The calibration curve was obtained by using standard EE2 and TC solutions with various concentrations. Results are presented as the percentage of EE2 and TC removed as a function of equilibrium pH. The spectrophotometric determination of EE2 and TC have been performed previously and are described elsewhere.<sup>39,40</sup> The blank EE2 (5.0 mg L<sup>-1</sup>) or TC (10 mg L<sup>-1</sup>) solutions at the appropriate pH were shaken without the hybrid materials in the polyethylene bottles for 24 h. The samples were filtered with a 0.45 μm syringe filter and their absorbance determined at wavelengths of 280 and 360 nm for EE2 and TC, respectively. No decrease in absorbance was observed, which indicated that negligible sorption to the polyethylene bottles occurred.

The concentration dependence study was performed by varying the EE2 concentration from 1.0 to 10.0 mg L<sup>-1</sup> and the TC concentration from 1.0 to 20.0 mg L<sup>-1</sup> at pH 7.0 and 25 ± 1

°C. The adsorption process detailed above was then followed. Results are presented as the percentage removal of EE2 or TC as a function of initial EE2 or TC concentration (mg L<sup>-1</sup>). Time dependent sorption of EE2 and TC by the hybrid materials was obtained at different time intervals. The initial EE2 concentration of 5.0 mg L<sup>-1</sup> and TC concentration of 10.0 mg L<sup>-1</sup> for a clay sample of 2.0 g L<sup>-1</sup> was taken as constant and the sorption experiments were conducted at pH 7.0 and 25 ± 1 °C. Results are reported as percentage removal of EE2 or TC as a function of time (min). The 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<sup>-1</sup> with EE2 and TC solution with initial concentrations 5.0 and 10.0 mg L<sup>-1</sup>, respectively. The solution pH (7.0) and temperature (25 ± 1 °C) was kept constant throughout the experiments. Results are presented as percentage EE2 and TC removed as a function of background electrolyte concentration.

**2.2.4. Fixed-bed column experiments.** Fixed-bed column experiments were conducted with a glass column (1 cm inner diameter) packed with 0.25 g of hybrid materials in the middle of the column. Below and above the hybrid material, 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<sup>-1</sup>) or TC (10.0 mg L<sup>-1</sup>) solution at pH 7.0 was pumped upward from the bottom of the column with a peristaltic pump (KrosFlo Research I Peristaltic Pump, Spectrum Laboratories Inc., California, USA), at a constant flow rate of 1.0 mL min<sup>-1</sup>. Effluent solution was collected by using a fraction collector (Spectra/Chrom CF-2 Fraction Collector, Spectrum Laboratories Inc., California, USA). The collected effluents were filtered with a 0.45 μm syringe filter and the filtrates were then subjected to UV-vis measurements.

Breakthrough data obtained from the fixed-bed column experiments were used to optimize the loading capacity of EE2 or TC on the hybrid material loaded column under dynamic conditions, using the Thomas equation,<sup>41</sup>

$$\frac{C_e}{C_0} = \frac{1}{1 + e^{(K_T(q_0 m - C_0 V))/Q}} \quad (1)$$

where  $C_e$  and  $C_0$  are the concentrations (mg L<sup>-1</sup>) of effluent and influent solutions of EE2 and TC, respectively;  $K_T$  is the Thomas rate constant (L min<sup>-1</sup> mg<sup>-1</sup>);  $q_0$  is the maximum amount (mg g<sup>-1</sup>) of EE2 or TC loaded under the column conditions;  $m$  is the mass (g) of hybrid materials in the column;  $V$  is the throughput volume (L); and  $Q$  is the flow rate (L min<sup>-1</sup>) of EE2 or TC solution. The column data were fitted to a non-linear Thomas equation by using the least squares fitting method to estimate the two unknown parameters,  $K_T$  and  $q_0$ .

## 3. Results and discussion

### 3.1. Characterization of materials

FT-IR data indicated that the hybrid materials, BH, BAH, LCH or LCAH, possess prominent IR stretching bands at 2930 and 2850 cm<sup>-1</sup> arising from -CH<sub>2</sub> asymmetric and symmetric stretching vibrations respectively. This confirmed the introduction of HDTMA in the clay network for all these hybrid materials.

Characteristic peaks in the X-ray diffraction analysis showed that both the clay samples contained quartz, smectite, illite and kaolinite in various proportions. The XRD patterns of the modified clay samples were almost identical to the virgin clay, with slight changes in *d*-values and peak intensities. The FE-SEM images clearly show that the organo-modified bentonite or LC (BH or LCH) had more heterogeneous and disordered surface structures. BAH and LCAH showed a similar disordered structure, although fine particles were observed on the surface that were possibly aggregated or immobilized as aluminum hydroxide or  $\text{Al}_2\text{O}_3$ . Detailed characterization of these hybrid materials has been described previously.<sup>37,42</sup>

### 3.2. Batch reactor experiments

**3.2.1. Effect of pH.** The pH dependent removal of EE2 (pH 4.01 to 10.14) and TC (pH 3.96 to 10.06) by the clays is presented in Fig. 1(a) and (b), respectively. The very high uptake of EE2 was not changed in the pH region of 4.0 to 8.0 by the clays. However, a further increase above pH 8.0 decreased the uptake of EE2. The uptake of EE2 by these clays may be increased by speciation of EE2 and the surface properties of the clays. EE2 has a  $\text{pK}_a$  of 10.4,<sup>43</sup> indicating that EE2 is a neutral molecule up to pH 10.0 and carries a net negative charge above pH 10.4. However, the  $\text{pH}_{\text{PZC}}$  values of the clays were 10.0, 8.2, 6.1, 5.8, 5.1 and 5.1 for B, BH, BAH, LC, LCH and LCAH, respectively. This implies that except bentonite, the other clays possess a net negative charge around pH 7. Therefore, there is unlikely to be electrostatic attraction between the clay surface and EE2. Hence, the possible mechanism of EE2 uptake by these hybrid materials is demonstrated by the fact that the introduction of an organic cation (HDTMA) increases the hydrophobicity and organophilicity of the surface. This enables EE2 to partition at the HDTMA hydrophobic core.<sup>44</sup> However, Al-pillared HDTMA-modified local clay (LCAH) showed slightly less uptake of EE2, possibly because of the screening of HDTMA by small aluminum oxide/hydroxide particles on the clay surface. Furthermore, the removal of EE2 was decreased by increasing the solution pH to 10.0 because partial acidic dissociation of EE2 occurred at this pH. The dissociation caused electrostatic repulsion, reducing the partitioning of the EE2 in the hydrophobic core of the hybrid materials. Previously, hybrid materials obtained by modifying natural sericite with HDTMA and alkyltrimethylbenzylammonium chloride were used in the remediation of wastewaters contaminated with BPA. The increase in pH from 2.0 to 10.0 did not significantly affect the percentage uptake of BPA by the hybrid materials. Furthermore, it was reported that organoclays containing longer chain surfactant molecules were less affected by the solution pH<sup>45</sup> and consistently possessed a high adsorption capacity for BPA even under alkaline conditions.<sup>46</sup> Virgin bentonite and local clay showed an insignificant uptake of EE2 (42% and 36% at pH 6.0 to 8.0 for B and LC respectively), which decreased further at low and high pH. The sorption of EE2 by all these hybrid materials showed a substantially higher percentage uptake (94%) compared with the unmodified clays.

Interestingly, the high attenuation of EE2 was almost independent of the pH up to pH 8.5 (Fig. 1(a)).

TC has different functional groups with  $\text{pK}_{a1}$ ,  $\text{pK}_{a2}$  and  $\text{pK}_{a3}$  values of 3.3, 7.7 and 9.7, respectively.<sup>47</sup> For the unmodified clays, B and LC, very high sorption of TC was achieved at lower pH values (pH 4), it decreased significantly between pH 4.0 and 6.0, remained nearly constant from pH 6.0–8.0, and then it decreased markedly at pH 10.0. These results agree well with other reports, in which TC adsorption was higher at low pH, and this was attributed to the cation exchange mechanism.<sup>33,44</sup> At pH values below 3.3, TC exists as a cation ( $\text{TCH}_3^+$  or  $\text{TCH}_3^{+0}$ ), because of the protonation of the dimethyl-ammonium group. At pH 3.3–7.7, TC exists as a zwitterion ( $\text{TCH}_2^0$  or  $\text{TCH}_2^{0+}$ ), because of the loss of a proton from the phenolic diketone moiety. At pHs greater than 7.7, TC exists as an anion ( $\text{TCH}^-$  or  $\text{TCH}^{+-}$ ), and at pH 9.7, it exists in di-anionic form ( $\text{TC}^{2-}$  or  $\text{TC}^{0-}$ ) through the loss of another proton from the tri-carbonyl system and phenolic diketone moiety.<sup>41</sup> The higher removal at pH 6–8 for TC compared with EE2 for the unmodified clays indicates that the positive part of the TC zwitterions interacted with the clays. Because  $\text{TCH}_2^0$  and  $\text{TCH}^-$  both contain a positively charged group in their structure, the molecules are probably arranged at the surface so that the positively charged group is close to the surface and the negatively charged group is furthest from the surface, which reveals that electrostatic attraction may play an important role in the sorption, not only of  $\text{TCH}_3^+$ , but also of  $\text{TCH}_2^0$  and  $\text{TCH}^-$ .<sup>48</sup>

A slightly lower uptake of TC was observed for the hybrid material at pH 4.0. The uptake gradually increased at pH 6 (99.5%), and then remained nearly constant from pH 6.0 to 9.0. These results clearly indicate that hydrophobic interactions play a prominent role in TC sorption.<sup>49</sup> Above pH 9.0, a slight decrease in the removal of TC by the hybrid materials was observed, owing to the strong electrostatic repulsion. The slightly lower uptake of TC by LCAH may arise from the screening of HDTMA molecule by aluminum oxide/hydroxide particles on the clay surface, restricting the partitioning of TC in the hydrophobic core. Similar results were reported for the uptake of TC by  $\text{MnFe}_2\text{O}_4$ /activated carbon magnetic composite<sup>50</sup> and activated carbons.<sup>32</sup> Zhang *et al.*<sup>51</sup> observed similar behavior in the removal of TC by multi-walled carbon nanotubes (MWCNTs) and proposed that adsorption probably occurred *via* non-electrostatic  $\pi$ - $\pi$  dispersion interactions between bulk  $\pi$  systems on the MWCNT surface and TC molecules containing benzene rings and double bonds, or *via* hydrophobic interactions between MWCNTs and TC.

**3.2.2. Effect of EE2 or TC concentration.** The effect of initial sorptive concentration can be used for estimating the sorption efficiency and capacity. The concentration dependence of removal was studied for initial EE2 concentrations from 1.0 to 10.0  $\text{mg L}^{-1}$  and TC concentrations from 1.0 to 20.0  $\text{mg L}^{-1}$  at pH 7.0. Results for EE2 and TC are presented in Fig. 2(a) and (b), respectively. Increasing the concentration of EE2 or TC did not affect the very high percentage uptake of EE2 and TC. These results also suggest the strong affinity of hybrid materials (BH, BAH and LCH) for EE2 and TC. At lower concentrations, the hybrid materials showed very high removal for TC, whereas the



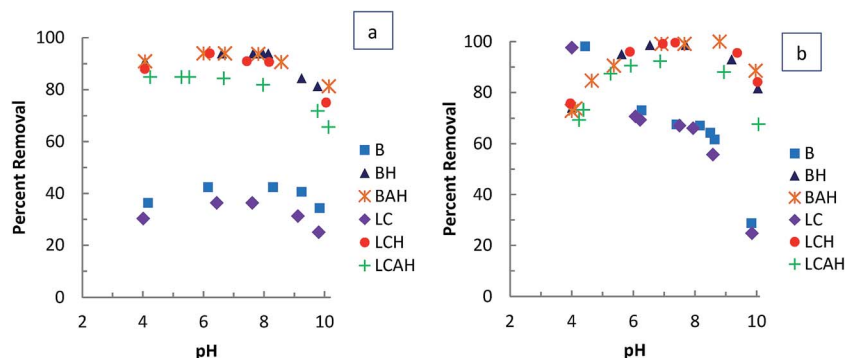


Fig. 1 pH dependence of sorption of (a) EE2 and (b) TC by B, BH, BAH, LC, LCH and LCAH.

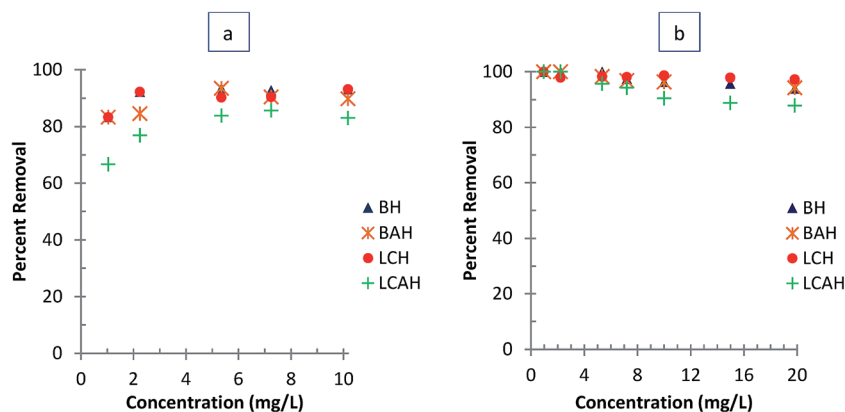


Fig. 2 Effect of concentration of (a) EE2 and (b) TC on the removal by BH, BAH, LCH and LCAH.

percent removal was slightly lower for EE2. A slightly lower removal of EE2 and TC was observed for LCAH. The results were consistent with the pH dependence study.

**3.2.3. Effect of background electrolyte concentration.** The effect of background electrolytes in the sorptive removal of EE2 and TC by the hybrid materials could help to explain the mechanism at solid/solution interfaces.<sup>52,53</sup> Specific sorption is not usually affected by the change in background electrolyte concentrations, whereas electrolyte concentration strongly affects non-specific sorption. Therefore, the sorption of EE2 or TC by BH, BAH, LCH and LCAH was assessed varying the background electrolyte concentrations from 0.0001 to 0.1 mol L<sup>-1</sup> NaCl at an initial EE2 concentration of 5.0 mg L<sup>-1</sup> and TC concentration of 10.0 mg L<sup>-1</sup> at pH 7.0. The percent removal of EE2 and TC was obtained as a function of the background electrolyte (NaCl) concentrations. The results are presented in Fig. 3(a) and (b) for EE2 and TC, respectively. Increasing the background electrolyte concentrations even up to 1000 times did not significantly affect the percentage uptake of either EE2 or TC by the hybrid materials BH, BAH, LCH and LCAH. This indicated the strong affinity of the clays toward EE2 or TC. This implies that the partitioned EE2 or TC was bound strongly by van der Waals forces in the interspace of the hybrid materials. Previously, it was reported that increasing the NaCl concentration from 0 to 320 mM did not significantly change the

adsorption of EE2 from landfill leachate on single-walled carbon nanotubes (SWCNTs).<sup>54</sup> Similarly, Zhang *et al.*<sup>51</sup> studied TC adsorption on multi-walled carbon nanotubes (MWCNT) at two ionic strengths (0.02 and 0.2 mol L<sup>-1</sup> NaCl) and two initial TC concentrations (20.0 and 70.0 mg L<sup>-1</sup>). In the pH range of 2.5 to 9, the ionic strength showed little effect on the sorption of TC on MWCNT.

**3.2.4. Time dependence removal.** The percent removal of EE2 or TC as a function of time was presented in Fig. 4(a) and (b). The materials are efficient in the removal of EE2 and TC from aqueous solutions because within the initial 10–15 min of contact time for EE2 and 60 min for TC, the uptake was very fast, and then it gradually increased until an apparent equilibrium was achieved within 60 min for EE2 and 240 min for TC. This also demonstrates the affinity of these clays for EE2 and TC. However, the uptake of EE2 and TC on LCAH was slower compared with the other hybrid materials.

The time dependence sorption data was then used to perform kinetic modelling. The three different kinetic models, pseudo-first order (PFO),<sup>55</sup> pseudo-second order (PSO)<sup>56</sup> and fractal-like pseudo-second order (FL-PSO)<sup>57</sup> models of its non-linear form (eqn (2)–(4)) were used.

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

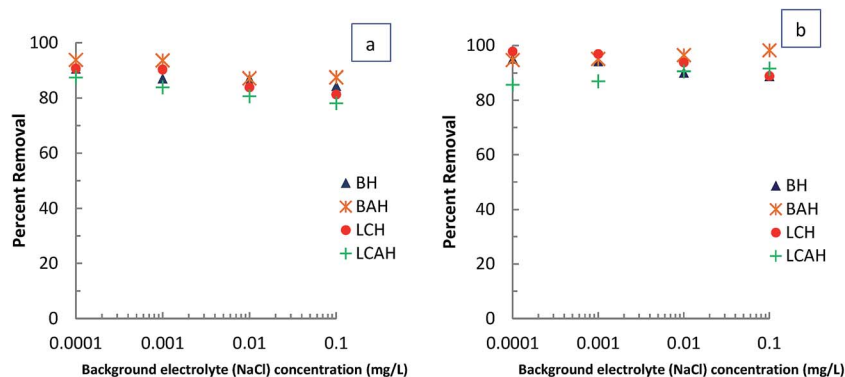


Fig. 3 Effect of background electrolyte (NaCl) concentration on the removal of (a) EE2 and (b) TC by BH, BAH, LCH and LCAH.

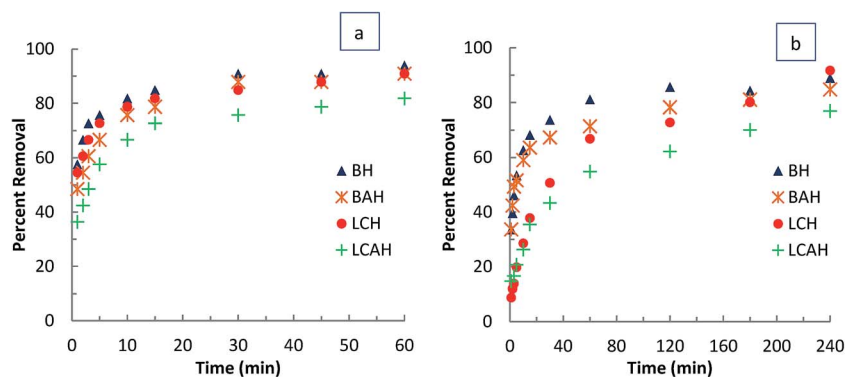


Fig. 4 Time dependence of the adsorption of (a) EE2 and (b) TC by BH, BAH, LCH and LCAH.

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

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

Here,  $q_t$  and  $q_e$  are the amount of EE2 or TC removed at time  $t$  and the removal capacity at equilibrium, respectively.  $k_1$  and  $k_2$  are the pseudo-first and pseudo-second order rate constants, respectively.  $k$  and  $\alpha$  are the rate constant and fractal constant, respectively. A non-linear least squares fitting was performed and the unknown parameters were optimized. The estimated values of the unknown parameters along with the least square sum are shown in Table 1. The simulation data was best fitted by the PSO and FL-PSO kinetic models compared with the PFO model because a low value of the least square sum was obtained for these two models. These results showed that the removal capacity of these hybrid materials was higher for TC compared with EE2. Furthermore, the applicability of the PSO or FL-PSO models shows that the EE2 or TC species were bound to the surface of the hybrid materials with strong forces. Earlier reports indicated that the sorption of divalent metal cations on *Sphagnum* moss peat followed second-order rate laws. Therefore, metal cations were strongly bound by covalent bonds between the peat surface active groups and the divalent metal

ions.<sup>58,59</sup> Similar results were obtained in the sorptive removal of bisphenol A by a hybrid material, made from a natural sericite precursor.<sup>49</sup>

### 3.3. Fixed-bed column reactor experiments

Fixed-bed column experiments were performed to assess the loading capacity of the hybrid materials BH, BAH, LCH and LCAH for EE2 and TC under dynamic conditions. The column experiments were carried out under various column conditions. The breakthrough curves are presented in Fig. 5(a) and (b) for EE2 and TC, respectively. A high breakthrough volume was obtained for EE2 and TC on these clays. A complete breakthrough volume was observed at throughput volumes of 7.68, 6.36, 6.24 and 5.041 L for EE2; and 1.33, 1.09, 1.06 and 0.94 L for TC; for BH, BAH, LCH and LCAH, respectively. The high breakthrough volume indicates the higher removal capacity of EE2 and TC by the modified clays under dynamic conditions. This further shows that the modified clays could be promising sorbing materials for the removal of EE2 and TC.

The non-linear least square fitting was conducted for the breakthrough column data employing the Thomas equation (eqn (1)). The fitting was performed to simulate the two unknown parameters,  $K_T$  and  $q_0$ . The values of the Thomas constants and the least square sum were estimated (Table 2).

Table 1 Kinetic parameters obtained for the sorption of EE2 and TC by hybrid materials by using various kinetic models<sup>a</sup>

Systems	Kinetic models									
	PFO			PSO			FL-PSO			
	$q_e$	$k_1$	$s^2$	$q_e$	$k_2$	$s^2$	$q_e$	$k$	$\alpha$	$s^2$
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

<sup>a</sup>  $s^2$ : least square sum.

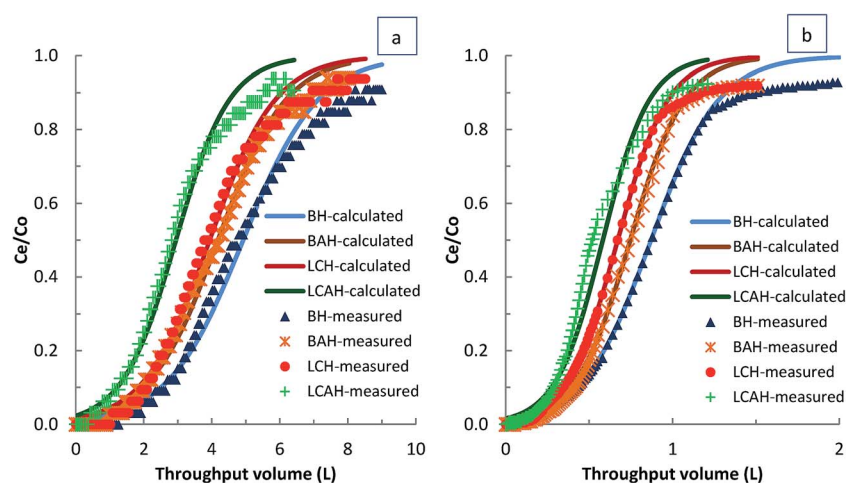


Fig. 5 Breakthrough curves for the removal of (a) EE2 and (b) TC by BH, BAH, LCH and LCAH.

A high loading capacity was achieved for EE2 and TC for these clays under dynamic conditions. BH showed a higher removal capacity for EE2 and TC compared with BAH. Similarly, LCH possessed a higher removal capacity than LCAH. The overall removal capacity was in the order BH > BAH  $\approx$  LCH > LCAH. The removal capacity of BAH and LCH for EE2 and TC was comparable hence, the locally collected clay could be a useful natural material for the efficient, 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 comparable with BH or LCH. Although a slight decrease was observed for BAH and LCAH, these materials showed a good settling capacity, and would be a superior alternative in solid/solution separation and wastewater treatment plants. These results were similar to the findings of the batch reactor experiments. The results were consistent

Table 2 Thomas constants and the least square sum for the removal of EE2 and TC by B, BH, BAH, LC, LCH and LCAH

Materials	EE2			TC		
	Thomas constants			Thomas constants		
	$K_T \times 10^{-4}$ (L min <sup>-1</sup> mg <sup>-1</sup> )	$q_0$ (mg g <sup>-1</sup> )	Least square sum ( $s^2$ )	$K_T \times 10^{-4}$ (L min <sup>-1</sup> mg <sup>-1</sup> )	$q_0$ (mg g <sup>-1</sup> )	Least square sum ( $s^2$ )
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



with previous reports in which the Thomas equation was used to demonstrate the loading capacity of different sorbing materials.<sup>60,61</sup>

## 4. Conclusion

Organo-modified clay and inorgano-organomodified clays were synthesized from natural bentonite and local clay and characterized by IR and XRD. The IR data showed that HDTMA was introduced in the clay network. XRD analysis indicated the presence of quartz, smectite, kaolinite and illite in various proportions in bentonite and local clay. SEM images of the modified clays showed that the structures of HDTMA-modified clay materials were disordered, whereas Al-pillared clays contained fine particles of aluminum hydroxides or Al<sub>2</sub>O<sub>3</sub> aggregated on the clay surface. The clays were used for the remediation of EE2 and TC contaminated waters in batch and column reactor experiments. The batch data implied that the uptake of EE2 and TC by the hybrid materials was slightly affected at low and high pH in the range 4.0–10.0. The uptake was not affected by varying the sorptive concentration (1.0 to 10.0 mg L<sup>-1</sup> for EE2 and 1.0 to 20.0 mg L<sup>-1</sup> for TC) and the background electrolyte concentration (0.0001 to 0.1 mol L<sup>-1</sup> NaCl). Moreover, the attenuation of EE2 and TC by these hybrid materials was efficient; within 60 min of contact time for EE2 and 240 min for TC, an apparent equilibrium between clay and solution was achieved. The fixed-bed column results showed that a high breakthrough volume was obtained for attenuating EE2 and TC using the hybrid materials. Furthermore, the breakthrough data were fitted well to the Thomas equation; therefore, the loading capacity for EE2 was estimated to be 111.979, 97.987, 86.965 and 64.996 mg g<sup>-1</sup> and that for TC was 34.976, 29.963, 26.956 and 23.478 mg g<sup>-1</sup> for BH, BAH, LCH and LCAH, respectively. Hence, these hybrid materials are promising for the remediation of the aquatic environment contaminated with two important micro-pollutants, EE2 and TC.

## Acknowledgements

DT wishes to acknowledge CSIR, New Delhi for the financial support through Research Project (no. 01 (2567)/12/EMR-II). The work is also partly supported by UGC (NERO) financial assistance (no. F.5-22/2013-14/(MRP/NERO)/261).

## References

- 1 *Crystal structure of clay minerals and their X-ray identification*, ed. S. W. Bailey, G. W. Brindley and G. Brown, Mineralogical Society, London, 1980, pp. 1–113.
- 2 J. Konta, *Appl. Clay Sci.*, 1995, **10**, 275–335.
- 3 S. M. Lee and D. Tiwari, *Appl. Clay Sci.*, 2012, **59–60**, 84–102.
- 4 Y. Park, G. A. Ayoko and R. L. Frost, *J. Colloid Interface Sci.*, 2011, **354**, 292–305.
- 5 D. Tiwari and S. M. Lee, *Chem. Eng. J.*, 2012, **204–206**, 23–31.
- 6 Z. Li and R. S. Bowman, *Water Res.*, 2001, **35**, 3771–3776.
- 7 Z. Li, D. Alessi, P. Zhang and R. S. Bowman, *J. Environ. Eng.*, 2002, **128**, 583–587.
- 8 G. R. Alther, *Waste Manag.*, 2002, **22**, 507–513.
- 9 J. Q. Jiang, C. Cooper and S. Ouki, *Chemosphere*, 2002, **47**, 711–716.
- 10 J. Smith, S. Bartlett-Hunt and S. Burns, *J. Hazard. Mater.*, 2003, **96**, 91–97.
- 11 E. Benfenati, D. Barceló, I. Johnson, S. Galassi and K. Levsen, *Trends Anal. Chem.*, 2003, **22**, 757–765.
- 12 S. A. Snyder, P. Westerhoff, Y. Yoon and D. L. Sedlak, *Environ. Eng. Sci.*, 2003, **20**, 449–469.
- 13 M. Petrović, E. Eljarrat, M. J. L. de Alda and D. Barceló, *Anal. Bioanal. Chem.*, 2004, **378**, 549–562.
- 14 J. Niu, S. Ding, L. Zhang, J. Zhao and C. Feng, *Chemosphere*, 2013, **93**, 1–8.
- 15 J. Lienert, T. Buerki and B. I. Escher, *Water Sci. Technol.*, 2007, **56**, 87–96.
- 16 A. Joss, E. Keller, A. Alder, A. Gobel, C. McArdell, T. Ternes and H. Siegrist, *Water Res.*, 2005, **39**, 3139–3152.
- 17 K. A. Landry and T. H. Boyer, *Water Res.*, 2013, **47**, 6432–6444.
- 18 S. Larcher and V. Yargeau, *Environ. Pollut.*, 2013, **173**, 17–22.
- 19 Datapharm, EMC Medicine Guides (UK) – Ethinylestradiol, 2008, <http://www.medicines.org.uk/guides/ethinylestradiol>.
- 20 J. Han, W. Qiu, Z. Cao, J. Hu and W. Gao, *Water Res.*, 2013, **47**, 2273–2284.
- 21 A. Z. Aris, A. S. Shamsuddin and S. M. Praveena, *Environ. Int.*, 2014, **69**, 104–119.
- 22 USFDA, U.S. Food and Drug Administration (USFDA) and National Center for Toxicological Research (NCTR), Endocrine Disruptor Knowledge Base (EDKB), 2012, [http://www.fda.gov/scienceresearch/bioinformaticstools/endocrine\\_disruptorknowledgebase/default.htm](http://www.fda.gov/scienceresearch/bioinformaticstools/endocrine_disruptorknowledgebase/default.htm).
- 23 P. C. Heaton, S. R. Fenwick and D. E. Brewer, *J. Clin. Pharm. Ther.*, 2007, **32**, 483–487.
- 24 S. Yahiat, F. Fourcade, S. Brosillon and A. Amrane, *Int. Biodeterior. Biodegrad.*, 2011, **65**, 997–1003.
- 25 P. Gao, M. Munir and I. Xagorarakis, *Sci. Total Environ.*, 2012, **173**, 421–422.
- 26 W. Yang, Z. Tang, F. Zhou, W. Zhang and L. Song, *Environ. Toxicol. Pharmacol.*, 2013, **35**, 320–324.
- 27 H. Y. Kim, J. Jeon, J. Hollender, S. Yu and S. D. Kim, *J. Hazard. Mater.*, 2014, **279**, 428–435.
- 28 J. de Rudder, T. V. de Wiele, W. Dhooge, F. Comhaire and W. Verstraete, *Water Res.*, 2004, **38**, 184–192.
- 29 L. Joseph, L. K. Boateng, J. R. V. Flora, Y.-G. Park, A. Son, M. Badawy and Y. Yoon, *Sep. Purif. Technol.*, 2013, **107**, 37–47.
- 30 L. A. Al-Khateeb, A. Y. Obaid, N. A. Asiri and M. A. Salam, *J. Ind. Eng. Chem.*, 2014, **20**, 916–924.
- 31 Y. Gao, Y. Li, L. Zhang, H. Huang, J. Hu, S. M. Shah and X. Su, *J. Colloid Interface Sci.*, 2012, **368**, 540–546.
- 32 J. Rivera-Utrilla, C. V. Gómez-Pacheco, M. Sánchez-Polo, J. J. López-Peñalver and R. Ocampo-Pérez, *J. Environ. Manage.*, 2013, **131**, 16–24.
- 33 Z. Li, L. Schulz, C. Ackley and N. Fenske, *J. Colloid Interface Sci.*, 2010, **351**, 254–260.
- 34 S. A. Boyd, S. Shaobai, J.-F. Lee and M. M. Mortland, *Clays Clay Miner.*, 1988, **36**, 125–130.

- 35 ISRIC (International Soil Reference and Information Centre), *Procedures for soil analysis*, ed. L. P. van Reeuwijk, FAO, UN, Wageningen, The Netherlands, 6th edn, 2012, pp. 3.1–3.7, [http://www.isric.org/isric/webdocs/docs/ISRIC\\_TechPap09\\_2002.pdf](http://www.isric.org/isric/webdocs/docs/ISRIC_TechPap09_2002.pdf).
- 36 US EPA (United States Environment Protection Agency), *Method 9080, Cation-Exchange Capacity of Soils (Ammonium Acetate)*, 1986, pp. 1–9.
- 37 Thanhmingliana and D. Tiwari, *Chem. Eng. J.*, 2015, **263**, 364–373.
- 38 P. C. C. Faria, J. J. M. Órfão and M. F. R. Pereira, *Water Res.*, 2004, **38**, 2043–2052.
- 39 Y. Gao, Y. Li, L. Zhang, H. Huang, J. Hu, S. M. Shah and X. Su, *J. Colloid Interface Sci.*, 2012, **368**, 540–546.
- 40 M. Brigante and P. C. Schulz, *J. Hazard. Mater.*, 2011, **192**, 1597–1608.
- 41 H. C. Thomas, *J. Am. Chem. Soc.*, 1944, **66**, 1664–1666.
- 42 S. M. Lee, Lalhmunsiama, Thanhmingliana and D. Tiwari, *Chem. Eng. J.*, 2015, **270**, 496–507.
- 43 X. Yang, R. C. Flowers, H. S. Weinberg and P. C. Singer, *Water Res.*, 2011, **45**, 5218–5228.
- 44 Z. Li and R. S. Bowman, *Environ. Sci. Technol.*, 1997, **31**, 2407–2412.
- 45 Y. Park, G. A. Ayoko, R. Kurdi, E. Horváth, J. Kristóf and R. L. Frost, *J. Colloid Interface Sci.*, 2013, **406**, 196–208.
- 46 S. Zheng, Z. Sun, Y. Park, G. A. Ayoko and R. L. Frost, *Chem. Eng. J.*, 2013, **234**, 416–422.
- 47 P. Kulshrestha, R. F. Giese Jr and D. S. Aga, *Environ. Sci. Technol.*, 2004, **38**, 4097–4105.
- 48 M. E. Parolo, M. C. Savini, J. M. Vallés, M. T. Baschini and M. J. Avena, *Appl. Clay Sci.*, 2008, **40**, 179–186.
- 49 Thanhmingliana, S. M. Lee and D. Tiwari, *RSC Adv.*, 2014, **4**, 43921–43930.
- 50 L. Shao, Z. Ren, G. Zhang and L. Chen, *Mater. Chem. Phys.*, 2012, **135**, 16–24.
- 51 L. Zhang, X. Song, X. Liu, L. Yang, F. Pan and J. Lv, *Chem. Eng. J.*, 2011, **178**, 26–33.
- 52 K. F. Hayes, C. Papelis and J. O. Leckie, *J. Colloid Interface Sci.*, 1988, **125**, 717–726.
- 53 S. M. Lee, Lalhmunsiama and D. Tiwari, *Environ. Sci. Pollut. Res. Int.*, 2014, **21**, 3686–3696.
- 54 L. Joseph, Q. Zaib, I. A. Khan, N. D. Berge, Y.-G. Park, N. B. Saleh and Y. Yoon, *Water Res.*, 2011, **45**, 4056–4068.
- 55 T. Yang, M. L. Chen, L. H. Liu, J. H. Wang and P. K. Dasgupta, *Environ. Sci. Technol.*, 2012, **46**, 2251–2256.
- 56 Y. S. Ho and G. McKay, *Process Saf. Environ. Prot.*, 1998, **76**, 332–340.
- 57 M. Haerifar and S. Azizian, *Chem. Eng. J.*, 2013, **215–216**, 65–71.
- 58 Y. S. Ho, *J. Hazard. Mater.*, 2006, **136**, 681–689.
- 59 Y. S. Ho and G. McKay, *Water Res.*, 2000, **34**, 735–742.
- 60 D. Tiwari, C. Laldawngliana and S. M. Lee, *Environmental Engineering Research*, 2014, **19**, 107–113.
- 61 S. M. Lee, D. Tiwari, K. M. Choi, J. K. Yang, Y. Y. Chang and H. D. Lee, *J. Chem. Eng. Data*, 2009, **54**, 1823–1828.