Adsorptive removal of PPCPs by biomorphic HAP templated from cotton

Bin Huang, Dan Xiong, Tingting Zhao, Huan He and Xuejun Pan

ABSTRACT

Biomorphic nano-hydroxyapatite (HAP) was fabricated by a co-precipitation method using cotton as bio-templates and employed in adsorptive removal of oloxacin (OFL) and triclosan (TCS) that are two representative pharmaceuticals and personal care products (PPCPs). The surface area and porosity, crystal phase, functional group, morphology and micro-structure of the synthesized HAP were characterized by Brunauer–Emmett–Teller isotherm, X-ray powder diffraction, Fourier transform infrared spectroscopy, scanning electron macroscopic and transmission electron microscopy. The effects of initial pH, ionic strength, initial concentration, contact time and temperature on the removal of PPCPs were studied in a batch experiment. The adsorption of OFL and TCS was rapid and almost accomplished within 50 min. Kinetic studies indicated that the adsorption process of OFL and TCS followed the pseudo-first-order and pseudo-second-order models, respectively. The Freundlich isotherm described the OFL adsorption process well but the adsorption of TCS fitted the Langmuir isotherm better. Thermodynamics and isotherm parameters suggested that both OFL and TCS adsorption were feasible and spontaneous. Hydrogen bond and Lewis acid–base reaction may be the dominating adsorption mechanism of OFL and TCS, respectively. Compared to other adsorbents, biomorphic HAP is environmentally friendly and has the advantages of high adsorption capacity, exhibiting potential application for PPCPs removal.

Key words | adsorption, biomorphic, HAP, kinetic studies, PPCPs, removal

INTRODUCTION

Pharmaceuticals and personal care products (PPCPs) comprise all prescription and over-the-counter drugs, diagnostic agents, fungicides, disinfectants, cosmetics, fragrances and UV-filters (Liu & Wong 2013). As an emerging class of environmental pollutants, PPCPs have attracted much public and scientific attention due to their widespread contamination in aquatic environment, sediment, sewage sludge and agricultural lands (Wu et al. 2010; Blair et al. 2013). Even with the low concentration levels (ng/L to mg/L range), PPCPs may pose potential risks to humans and the ecosystem. The removal of PPCPs is therefore of great importance and urgency.

Oloxacin (OFL) is one of the most consumed antibiotics which belongs to the quinolone group, a broad spectrum class of antibiotics that act by the inhibition of the gyrase enzyme. A wide range of antibiotics has been detected in the environment due to incomplete treatment of wastewater treatment plants (WWTPs) and their persistent nature (Le-Minh et al. 2010), and OFL was found to be the dominant contaminant with concentrations up to 24,760 μg·kg⁻¹ in Chinese municipal sewage sludge (Chen et al. 2013). Abuse of antibiotics could cause resistant strains of bacteria surge and diminish effectiveness of human therapeutic drugs.

Triclosan (TCS) is a common broad spectrum antimicrobial due to its ability to inhibit the enoyl-acyl carrier protein reductase for fatty acid synthesis in bacteria. Up to 0.3% and 5% (w/w) of TCS were added to a variety of consumer products such as cosmetic products, deodorants, toothpastes and disinfectants in hospitals or households (Hinther et al. 2011). It has been reported that effluent concentrations of WWTPs range from 10 to 600 ng·L⁻¹, and as high as 2.7 μg·L⁻¹ (Anger et al. 2015). TCS has been proved to be an endocrine disruptor (Waller & Kookana 2009). In addition, polychlorinated phenoxy phenols and triclosan-methyl, which are more persistent and toxic than TCS,
would derive from photo degradation or biodegradation of TCS. (Chen et al. 2011). So, if TCS exists in the environment, it will cause a lot of secondary pollution, and choosing the appropriate method to remove it is an important issue.

Various methods have been employed for the treatment of PPCPs, including biodegradation, ozonation, membrane ultrafiltration, chlorination, coagulation, photo degradation, and adsorption (Yu et al. 2008; Ji et al. 2009). Adsorption techniques have been widely used to remove PPCPs on account of the economical and environmentally friendly advantage. Also, in terms of other treatments, adsorption is flexible and feasible in operation and has no byproduct (Putra et al, 2009).

Hydroxyapatite (Ca10(PO4)6(OH)2, HAP) is an important inorganic material in biology and chemistry, which is available, low cost and nontoxic to human (Zhu et al. 2008). Many investigations focus on the usage of HAP to stabilize a wide variety of metals. Moreover, recent studies suggest that HAP show a good affinity for organic pollutants such as methylene blue, basic yellow 28, pyridine, phenol and blue SBL dye (Malash & El-Khaiary 2010; El Boujaady et al. 2011). Nowadays, the synthesis of materials with bio-template has attracted considerable attention owing to simple, mild, high-yield, and environmentally friendly advantages. This bio-inspired method provides a green synthesis route to obtain advanced functional materials. The performance characteristics of nanomaterial have particular relevance with the shape and structure of the template. To the best of our knowledge, the HAP in cotton morphology has not been synthesized to remove PPCPs from the aqueous solution.

The aim of current study was to investigate and explore the possibility of using HAP in cotton morphology for PPCPs removal. Two typical and representative PPCPs, OFL and TCS, have been chosen as adsorbate by virtue of a quite different physico-chemical property. The effects of adsorbent dose, initial dye concentration, contact time, temperature, pH and ionic strength on OFL and TCS adsorption using HAP in cotton morphology were investigated. Adsorption kinetics, isotherms and thermodynamic parameters were also evaluated and reported.

**MATERIALS AND METHODS**

**Materials**

TCS (97%) was purchased from Sigma-Aldrich (St Louis MO, USA) while OFL (98%) was obtained from Bio Basic Inc. (Japan). The physico-chemical properties of OFL and TCS were shown in Table 1. The compounds were stored at 4 °C in the dark to minimize photolytically induced degradation. Potassium bromide (KBr, 99.9%, optical grade) was supplied by Aladdin Chemistry Co., Ltd (Shanghai, China). Methanol (HPLC grade) was obtained from Merck Co. (Germany). Hydrochloric acid (HCl, GR) was purchased from United Chemical Industry (Chengdu, China). Other reagents used in this work, including Ca(NO3)2·4H2O (Xilong Chemical Co., Ltd), (NH4)2HPO4 (Tianjin Fengchuan Chemical Reagent Co., Ltd), ammonia solution (25–28%, Aladdin), sodium hydroxide (NaOH, Xilong Chemical Co., Ltd), are of analytical grade. Absorbent cotton was obtained from Nanchang Leiyi Medical Apparatus Co., Ltd. Filter membrane (pore size 0.45 μm, diameter 13 mm) was purchased from Tianjin Hengao Technology Development Co., Ltd. Milli-Q water was used throughout.

**Synthesis of biomorphic HAP**

HAP nano-crystalline was synthesized by co-precipitation method utilizing cotton as bio-template. Some cotton was washed several times with Milli-Q water and dried at 50 °C. 2.50 g of the mentioned cotton were sonicated for 30 min in 0.1 mol·L⁻¹ Ca(NO3)2·4H2O, which was adjusted to pH 10.5 using diluted ammonia solution. Then 0.06 mol·L⁻¹ (NH4)2HPO4 (pH = 10.5) was added into the cotton-containing solution at a rate of 15 s per drop under stirring at 85 °C. The reaction was carried out in the pH range of 10

| Table 1 | Physico-chemical properties of OFL and TCS |
| Pollutants | Structures | MW/g·mol⁻¹ | Solubility/mg·L⁻¹ | lgKow | pKₐ/pKₐ² |
| OFL (C₁₈H₂₀FN₃O₄) | 361 | 3,400 | -0.35 | 6.1/8.28 |
| TCS (C₁₂H₇Cl₃O₂) | 289.5 | 10 | 4.76 | 7.8–8.14 |
to 11 and for 7 h. Subsequently, the obtained templated hybrid was rinsed with Milli-Q water several times. Finally, the templated hybrid was dried at 60 °C for 24 h, and sintered at 550 °C for 6 h to achieve the HAP with cotton morphology.

**Characterizations**

The specific surface area and porosity of the yielded products were measured from nitrogen adsorption experiments (Auto-sorb-I, Quantachrome) at 77 K. The specific surface area was estimated using the Brunauer–Emmett–Teller (BET) isotherm, and the pore size distribution was calculated by the method of Barret–Joyner–Halenda. Crystalline phases of the obtained materials were investigated by X-ray powder diffraction (XRD, Rigaku-D/Max 2200) in reflection mode (Cu Kα radiation) at a scanning rate of 5 °/min in the 2θ range of 5–90 °. Functional groups of the as-prepared sample before and after adsorption were analyzed by a Fourier transform infrared spectrometer (FTIR, Varian 640-IR). The spectra were collected in the range of 4,000–400 cm⁻¹ with 16 scans at a resolution of 8 cm⁻¹. Scanning electron macroscopic (SEM, FEI QUANTA200) and transmission electron microscopy (TEM, FEI Tecnai G2 F30) were performed to observe the morphology and structures of the material before and after adsorption. Energy-dispersive X-ray (EDX) analyzer equipped with the TEM was used to determine the elemental composition of the as-obtained sample before and after adsorption.

**Batch adsorption experiments**

Batch adsorption experiments were carried out in a dark area and shaken at 160 rpm. For adsorption experiments at varying pH, the initial OFL and TCS concentration were 40 mg/L and 25 mg/L, respectively, and the pH was adjusted to 2.5–10.5 with either 1 M HCl or 1 M NaOH. The effect of ionic strength on OFL and TCS adsorption was studied in pH 4.5 and pH 2.5 with initial concentrations of 40 and 25 mg/L. The isotherms were determined by a batch equilibration technique at 288 K, 298 K, 308 K and 318 K. A certain amount of as-obtained HAP and solution (20 mL) with different initial concentrations (5–50 mg/L for OFL adsorption and 5–35 mg/L for TCS adsorption) were added to a 50 mL conical flask and shaken for 2 h at pH 4.5 and pH 2.5, respectively. HAP dosage was 1 g/L for OFL adsorption and 0.5 g/L for TCS adsorption. The procedures of kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of phenol were measured. After reaching equilibrium, the suspension was filtered through 0.45 μm membrane, and the filtrate was analyzed by UV–vis spectrophotometer (Shimadzu 2450) at 291 nm for OFL and 278 nm for TCS. Each experiment was duplicated under identical conditions. The removal efficiency and adsorption capacity of HAP was calculated according to the following expressions:

$$q_e = \frac{(C_0 - C_e)V}{m}$$  \hspace{1cm} (1)

$$\text{Removal}\% = \frac{C_0 - C_e}{C_0} \times 100\%$$  \hspace{1cm} (2)

where $C_0$ and $C_e$ were initial and equilibrium concentrations of OFL and TCS (mg/L), respectively, m was the mass of adsorbent (g) and V was volume of the solution (L).

**RESULTS AND DISCUSSION**

**Characterization**

**Surface area and porosity**

The N₂ adsorption–desorption isotherms of synthesized HAP was shown in Figure 1. The isotherms were assigned to style IV defined by IUPAC. Distinct H-3 type hysteresis loops were observed in the range 0.6 P/P₀ to 1.0 P/P₀, indicating the existence of mesopores (2–50 nm) with pore sizes close to the micropore range. In addition, H-3 loops demonstrated the formation of slitlike pores which were caused by aggregates (loose assemblages) of HAP nanoparticles. The pore sizes exhibited narrow bimodal distributions. The most probable aperture appeared at 2–3 nm and
4–5 nm, which were consistent with the small mesopores (2–50 nm) porous structure of HAP mentioned above. The surface area was 158.5 m\(^2\) g\(^{-1}\), pore volume was 0.8625 cm\(^3\) g\(^{-1}\) and average pore diameter was 21.77 nm.

**XRD results**

Figure 2 showed the XRD pattern of the synthesized sample. The crystalline peaks at \(2\theta = 25.9^\circ, 28.9^\circ, 31.8^\circ, 32.9^\circ, 34.1^\circ\) and 49.5 \(^\circ\) confirm the formation of HAP structure (Jiménez-Reyes & Solache-Ríos 2010). No other impurity peak was detected, suggesting the precursor was pure. Meanwhile, the shape of the sharp diffraction peaks indicated that the HAP was well crystallized. Moreover, no peaks corresponding to the crystal carbon were observed, indicating that the templates had been removed after calcinations.

**FTIR analysis**

The obtained FTIR spectra of synthesized HAP before and after adsorption were presented in Figure 3. The sharp band at 3,600 cm\(^{-1}\) was assigned to the stretching vibration of free hydroxyl and the broad peak of associating hydroxyls near 3,441 cm\(^{-1}\) was found in the spectrum. The strong band at 1,039 cm\(^{-1}\) was attributed to the asymmetric stretching vibration of the PO\(_4\) group, while the bands at 605 and 566 cm\(^{-1}\) corresponded to bending modes of P-O. The band at 1,639 cm\(^{-1}\) was caused by ambient humidity. Thus, it can be seen that the features in Figure 3(a) are consistent with hydroxyapatite.

After adsorption of OFL by HAP, the characteristic bands of OFL, such as the stretching vibration of C=O at 1,720 cm\(^{-1}\) and the bending vibration of phenolic hydroxyl group at 1,317 cm\(^{-1}\), was recorded in the spectrum of the adsorptive adduct (Figure 3(b)), while the contraction vibration of N-H at 2,359 cm\(^{-1}\) was ascribed to the hydrogen bonding between OFL and POH of HAP. Likewise, the characteristic bands of TCS, such as the contraction vibration of C-O at 1,064 cm\(^{-1}\) and the bending vibration of -OH at 1,317 cm\(^{-1}\), appeared in the TCS-adsorbed HAP spectrum. Those all indicated that OFL and TCS had been adsorbed to HAP.

**SEM and TEM-EDX analysis**

The morphological characteristics of prepared HAP before and after adsorption were examined by SEM as shown in Figure 4. It was observed that the original fibrous morphology of cotton was found to be replicated by HAP. The biomorphic HAP fibers were long and curly, which retain the cotton morphology. After adsorption of OFL and TCS, the morphology of HAP changed to short, rod-like and blocky. The magnified
SEM images showed that the surface of as-obtained HAP was relatively smooth and uniform while, after adsorption, the surface became rough and heterogeneous.

Further microstructural information and chemical composition of the nano-HAP before and after adsorption was provided by TEM with an EDX accessory in Figure 5. The TEM image showed that the cotton morphology was fabricated by numerous HAP nanoparticles. Single HAP was cylindrical rod-like, with a length of 50–100 nm and a diameter of 10–30 nm. The particles were of homogeneous microstructure and formed a uniform nanomaterial. Pores were observed in interparticle and intragranular. The crystal lattice of HAP can be seen in the high resolution TEM images. There was no significant difference in single nano-HAP after adsorption of OFL and TCS. EDX analysis revealed that, besides the Cu peaks which came from the copper grids, only Ca, P and O peaks appeared in the spectrum of HAP. The peaks corresponding to N, F and Cl were clearly visible on the spectrum of HAP after adsorption, confirming the OFL and TCS adsorption on the HAP, respectively.

**Effect of pH, initial concentration and ionic strength**

The aqueous chemistry and surface charge of the adsorbent are both affected by solution pH. The effect of pH on the adsorption of OFL and TCS by synthesized HAP were presented in Figure 6. The maximum adsorption of OFL was observed at pH 4.5. OFL is an amphoteric substance, which is zwitterionic at $pK_a1 < pK_a2 = 8.28$ (Van Wieren et al. 2012). Below pH 5, the fraction of zwitterionic OFL is very low; virtually all of OFL is cationic. It is known that the pH at zero point charge ($pH_{ZPC}$) of HAP is 6–8, and the surface is positively charged below $pH_{ZPC}$. Because of the electrostatic repulsion and the presence of strong intermolecular interactions (such as hydrogen bond) between OFL and water molecules reported by Peng et al. (2012), the adsorptive removal of OFL was quite inefficient at pH 2.5. Hydrogen ions decrease as pH increases, resulting in stronger OFL-HAP H-bonds than OFL-water H-bonds and high removal efficiency of OFL at pH 4.5, consequently. Above pH 5, both OFL and HAP became more negatively charged and the electrostatic repulsion between OFL and HAP surfaces hindered the adsorption. It is worth noting that Nikolenko and Esajenko declared that adsorption of nitrogen-containing organic compounds onto HAP occurred predominantly through H-bonds rather than interacting with calcium ion (Nikolenko & Esajenko 2005). The claim was further confirmed by the steric constraints and the intramolecular hydrogen bonding between the carboxylic acid and the neighboring keto functional group of OFL (Li et al. 2013).
It is observed that the stronger the acidity of solution is, the higher the adsorbent capacity of TCS will be over the whole pH range. Similar trends have been found by previous studies (Behera et al. 2013). When pH > pKa, the anionic form of TCS is dominant in solution, while when pH < pKa, TCS is nonionized and exits in molecular form. In quite an acidic condition such as pH 2.5, there are mainly POH group and calcium ions on the HAP surface (Nikolenko & Esajenko 2005), and TCS interactions with HAP are expected to be two-fold: hydrogen bonding with POH group and Lewis acid-base interactions involving Ca$^{2+}$. As pH increased, the weaker TCS-HAP interaction and electrostatic repulsion between anionic TCS and negative charged HAP resulted in a decreased amount of sorbed TCS.

The equilibrium data of OFL and TCS adsorption on HAP were obtained to investigate the effect of initial adsorbate concentration on adsorption. As presented in Figure 7, adsorption percentage of OFL and TCS decreased with increase in initial concentration. This can be explained that HAP has a limited number of active sites, which become saturated at a certain adsorbate concentration. However, both the OFL and TCS adsorption capacity increased with increasing of initial
concentration. This may be attributed to stronger driving force to overcome the mass transfer resistance between the aqueous and solid phase with increasing concentration gradient. It is noticed that removal efficiency of OFL is quite low compared to TCS. According to Li et al. (2013), only solute-adsorbent H-bonds that are much stronger than solute-water and water-adsorbent H-bonds can contribute substantially to overall adsorption. Therefore, the strong hydrogen bond between OFL and water leads to relatively low removal efficiency of OFL from aqueous solution by HAP.

The effects of ionic strength on the adsorption of OFL and TCS were displayed in Figure 8. It was found that the increase of NaCl concentration from 0 to 0.8 M resulted in a slight increase in OFL adsorption. This phenomenon was possibly derived from the charge screening effect that can reduce the repulsion between the OFL molecules sorbed on the surface of HAP. Also, due to the very strong interactions between OFL and water molecules, the salting out effect was negligible. Similar trends have been reported by Kushwaha (2015).

Compared to OFL, the adsorption percentage of TCS significantly increased as a function of the ionic strength, both the charge screening effect and the salting out effect were contributed to the adsorption on HAP when ionic strength increased. This phenomenon was also observed by Behera et al. (2010).

AdSORPTION kinetics

Kinetic analysis is required to provide an insight for understanding the adsorption mechanism and figuring out the rate limiting step. OFL and TCS adsorption on HAP are rapid and almost accomplished within 50 min and 40 min, respectively. Different kinetic models, including the pseudo-first-order, pseudo-second-order and intraparticle diffusion models, were applied for the experimental data to describe the adsorption system. The calculated constants

![Figure 6](http://iwaponline.com/wst/article-pdf/74/1/276/460272/wst074010276.pdf)

**Figure 6** | Effect of initial pH on removal percentage of OFL and/or TCS by nano-HAP.

![Figure 7](http://iwaponline.com/wst/article-pdf/74/1/276/460272/wst074010276.pdf)

**Figure 7** | Effect of initial target materials concentrations on adsorption of OFL and/or TCS by nano-HAP.

![Figure 8](http://iwaponline.com/wst/article-pdf/74/1/276/460272/wst074010276.pdf)

**Figure 8** | Effect of ionic strength on the OFL and TCS adsorption.
of the three isotherm equations and $R^2$ values are presented in Table 2.

$$\ln (q_e - q_t) = \ln q_e - k_1 t$$  \hspace{1cm} (3)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^0} + \frac{t}{q_e}$$  \hspace{1cm} (4)

$$q_t = k_{id} t^{0.5} + c$$  \hspace{1cm} (5)

where $q_t$ and $q_e$ are the adsorption capacity (mg·g$^{-1}$) at a certain time $t$ (min) and equilibrium, respectively; $k_1$ (min$^{-1}$) is the pseudo-first-order rate constant; $k_2$ (g·mg$^{-1}$·min$^{-1}$) is the rate constant of the pseudo-second-order equation; $k_{id}$ (mg·g·min$^{-1/2}$) is the intraparticle diffusion rate constant; $C_i$ is the intercept. The value of $C_i$ is related to the thickness of the boundary layer. The larger $C_i$ represents the greater effect of the boundary layer on ion diffusion.

The coefficient of determination ($R^2$) is relatively high, which may be indicative of a good correlation. In addition, $q_e$ cal determined from the model was in accordance with the experimental value, i.e. $q_e$ exp, which indicated that the adsorption of OFL followed the pseudo-first-order model. It was therefore suggested the adsorption of OFL onto HAP was not controlled by a chemisorption process but rather a physical process (Yang et al. 2012).

For TCS adsorption, the relatively high $R^2$ and similarity between the theoretical and the experimental equilibrium adsorption capacities indicated that the pseudo-second-order model fits the experimental data quite well. This implied that chemisorption was the main rate-controlling step of the TCS adsorption process.

As shown in Figure 9, there were three distinct regions in the Weber Morris plots for OFL and TCS adsorption (Venkata Ramana et al. 2013). The first, sharper portion was attributed to rapid external surface adsorption or boundary layer diffusion due to the large surface and active adsorption sites of HAP. The second subdued section was a gradual adsorption stage, where intra-particle diffusion was rate-controlled. The third portion was the final equilibrium stage, when adsorption became very slow and stable. The deviation from the origin of both OFL and TCS plots (C ≠ 0) suggested that the intraparticle diffusion was not the only rate-controlling step in adsorption reaction by HAP. Values of intercept $C$ give an idea of the thickness of the boundary layer: the larger intercept, the greater is the boundary layer effect. It was noticed that the $K_{id}$ value of OFL was less than TCS, suggesting that intraparticle diffusion rate of OFL was slower than TCS, which may be involved with the difference of molecular size between OFL and TCS.

### Adsorption isotherms

In this study, equilibrium adsorption for OFL and TCS onto HAP at 288, 298, 308, 318 K were applied separately to Langmuir and Freundlich isotherms. Table 3 lists the fitting parameters of both isotherm models at different temperatures.

$$\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{c_e}{q_m}$$  \hspace{1cm} (6)

$$R_L = \frac{1}{1 + K_L C_0}$$  \hspace{1cm} (7)

$$lg q_e = lg K_F + \frac{1}{n} lg C_e$$  \hspace{1cm} (8)

where $q_e$ (mg·g$^{-1}$) and $C_e$ (mg·L$^{-1}$) are the solid phase concentration and the liquid phase concentration of adsorbate at equilibrium, respectively; $q_m$ (mg·g$^{-1}$) is the maximum adsorption capacity; $K_L$ (L·mg$^{-1}$) is Langmuir constant; $K_F$ (mg·g$^{-1}$·L$^{-1}$)$^{-1}$ is Freundlich constant and $n$ and $n$ are both the Freundlich constant related to sorption capacity and surface heterogeneity, respectively. $R_L$ is the dimensionless equilibrium parameter of Langmuir isotherm. $C_0$ (mg·L$^{-1}$) is the initial solute concentration.

Langmuir isotherms describe monolayer adsorption with uniform energies and suggest that the adsorption is controlled by chemical interaction (Joseph et al. 2012). The

---

**Table 2** | Kinetics parameters for adsorption of OFL or TCS on nano-HAP

<table>
<thead>
<tr>
<th>Materials</th>
<th>$q_{exp}$/mg·g$^{-1}$</th>
<th>$q_e$/mg·g$^{-1}$</th>
<th>$k_1$/min$^{-1}$</th>
<th>$R^2$</th>
<th>$q_e$/mg·g$^{-1}$</th>
<th>$k_1$/g·mg$^{-1}$·min$^{-1}$</th>
<th>$R^2$</th>
<th>$k_{id}$/mg·g·min$^{-1/2}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCS</td>
<td>43.86</td>
<td>35.60</td>
<td>0.1380</td>
<td>0.9900</td>
<td>44.84</td>
<td>0.0106</td>
<td>0.9993</td>
<td>2.3134</td>
<td>0.9558</td>
</tr>
<tr>
<td>OFL</td>
<td>18.98</td>
<td>18.44</td>
<td>0.1258</td>
<td>0.9993</td>
<td>19.57</td>
<td>0.0176</td>
<td>0.9989</td>
<td>1.3323</td>
<td>0.9634</td>
</tr>
</tbody>
</table>
Freundlich model is an empirical model based on multilayer adsorption on heterogeneous surfaces with the exponential distribution of active sites and energies. It can be seen that OFL adsorption on HAP could be well fitted by Freundlich isotherm in view of the higher values of $R^2$, and Langmuir isotherm can provide a satisfactory fit to the TCS adsorption data on account of the higher $R^2$. As shown in Table 4, the values of $K_L$ increased with the increase in temperature, indicating that increasing temperature induced a higher maximum adsorption capacity of HAP for TCS. As for OFL adsorption, $K_F$ decreased with increase in temperature. The values of $n$ are all greater than 1 (i.e. $1/n$ less than 1), representing the favorable adsorption. The value of $R_L$ indicates the type of adsorption either to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Joseph et al. 2012). Values of $R_L$ were all between 0 and 1, indicating that both OFL and TCS adsorption on HAP were favorable. It was noticed that $R_L$ increased with the increasing temperature, suggesting that the affinity of HAP for OFL decreased with an increase in

![Figure 9](image)

**Table 3** | Isotherms constants for OFL and/or TCS adsorbed on nano-HAP

<table>
<thead>
<tr>
<th>Materials</th>
<th>$T$/ °C</th>
<th>$q_m$/ mg g$^{-1}$</th>
<th>$K_L$/ L mg$^{-1}$</th>
<th>$R_L$</th>
<th>$R^2$</th>
<th>$K_F$/ (mg g$^{-1}$) (L mg$^{-1}$)$^{1/n}$</th>
<th>$1/n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OFL</td>
<td>15</td>
<td>25.25</td>
<td>0.0413</td>
<td>0.82-0.29</td>
<td>0.9485</td>
<td>1.52</td>
<td>0.6525</td>
<td>0.9994</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>26.67</td>
<td>0.0351</td>
<td>0.8-0.345</td>
<td>0.9428</td>
<td>1.27</td>
<td>0.6886</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>28.57</td>
<td>0.0266</td>
<td>0.86-0.39</td>
<td>0.9364</td>
<td>1.06</td>
<td>0.7304</td>
<td>0.9995</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>29.15</td>
<td>0.0225</td>
<td>0.89-0.43</td>
<td>0.903</td>
<td>0.91</td>
<td>0.748</td>
<td>0.9992</td>
</tr>
<tr>
<td>TCS</td>
<td>15</td>
<td>128.20</td>
<td>0.3196</td>
<td>0.36-0.076</td>
<td>0.9991</td>
<td>28.69</td>
<td>0.7455</td>
<td>0.9925</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>129.87</td>
<td>0.3348</td>
<td>0.36-0.073</td>
<td>0.9997</td>
<td>30.24</td>
<td>0.7468</td>
<td>0.9914</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>131.58</td>
<td>0.3423</td>
<td>0.34-0.072</td>
<td>0.9980</td>
<td>31.18</td>
<td>0.7428</td>
<td>0.9928</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>133.33</td>
<td>0.3505</td>
<td>0.33-0.071</td>
<td>0.9947</td>
<td>32.28</td>
<td>0.7478</td>
<td>0.9927</td>
</tr>
</tbody>
</table>

**Table 4** | The adsorption capacity of various sorbents for TCS or OFL

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>Sorbents</th>
<th>qmax (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCS</td>
<td>Waste tire buffings</td>
<td>66.67</td>
</tr>
<tr>
<td></td>
<td>Carbon black</td>
<td>40.00</td>
</tr>
<tr>
<td></td>
<td>Activated carbon</td>
<td>67.11</td>
</tr>
<tr>
<td></td>
<td>Cetylpyridinium chloride coated zeolite</td>
<td>46.95</td>
</tr>
<tr>
<td></td>
<td>Biomorphic HAP</td>
<td>133.33</td>
</tr>
<tr>
<td>OFL</td>
<td>Molecular imprinting polymeric nanospheres</td>
<td>40.98</td>
</tr>
<tr>
<td></td>
<td>Halloysite</td>
<td>44.70</td>
</tr>
<tr>
<td></td>
<td>Croks</td>
<td>37.9</td>
</tr>
<tr>
<td></td>
<td>Biomorphic HAP</td>
<td>29.15</td>
</tr>
</tbody>
</table>
temperature. The contrary trends of $R_L$ for TCS adsorption indicated that increase of temperature did benefit the process.

The maximum adsorption capacity of the prepared HAP for OFL and TCS can be calculated from Langmuir isotherms. Table 4 summarized the comparison of the maximum adsorption capacities of various sorbents for OFL and TCS. It can be seen that the adsorption capacity of the biomorphic HAP for OFL and TCS is comparable, especially for TCS.

### Adsorption thermodynamic study

The effect of temperature on the adsorption of OFL and TCS were investigated in the temperature range of 15–45°C. Thermodynamic parameters, including the standard free energy change ($\Delta G^0$), enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$), were given by the following equations:

\[
\ln C_e = -\ln K_0 + \frac{\Delta H^0}{RT} \tag{9}
\]

\[
\Delta G^0 = -RT \ln K_0 \tag{10}
\]

\[
\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{11}
\]

where $R$ (8.314 J·mol⁻¹·K⁻¹) is the universal gas constant; $T$ (K) is the absolute temperature; $K_0$ is the constant; and $n$ is the Freundlich constant.

The thermodynamic parameters were listed in Table 5. The negative values of $\Delta G^0$ at all temperatures indicate the spontaneous nature of the adsorption of OFL and TCS on the as-obtained HAP. The increase of $\Delta G^0$ with increasing temperature showed the adsorption of OFL was not favorable at higher temperature (Ahmed & Theydan 2015), while for TCS, the increase of temperature made the adsorption more feasible. The negative value of $\Delta H^0$ confirmed the exothermic nature of OFL adsorption which was supported by the decrease of adsorption capacity with increasing temperature. The positive $\Delta H^0$ value showed that the adsorption of TCS by as-prepared HAP was endothermic and is also consistent with the results above. The negative values of $\Delta S^0$ indicated decrease of randomness at the adsorbent/solution interface during the adsorption of OFL onto HAP. The positive $\Delta S^0$ value for TCS adsorption corresponds to an increase of randomness.

### CONCLUSIONS

In this study, the biomorphic HAP with high surface area was prepared by co-precipitation method utilizing cotton as biotemplate, which was confirmed by BET, XRD, FTIR, SEM and TEM characteristics. The rapid and efficient adsorption for OFL and TCS implied the applicability of the as-obtained HAP for adsorptive removal of PPCPs. Adsorption of OFL was found to follow the pseudo-first-order kinetics model while TCS adsorption obeyed the pseudo-second-order kinetics. Intraparticle diffusion was not the sole rate-controlling factor. Freundlich isotherm described the OFL adsorption process well but adsorption of TCS fitted the Langmuir isotherm better. Thermodynamic parameters suggested that both OFL and TCS adsorption were feasible and spontaneous, which in agreement with the isotherm results. The value of $\Delta H^0$ showed the exothermic and endothermic nature of the OFL and TCS adsorption, respectively. Results of kinetics, isotherm and thermodynamics indicated that adsorption of OFL by HAP was a physical process due to the formation of hydrogen bonds, while TCS adsorption was mainly controlled by Lewis acid-base interactions. The mild, green advantage of bio-inspired method and the efficient removal of OFL and TCS by biomorphic HAP

<table>
<thead>
<tr>
<th>Materials</th>
<th>Q(mg/g)</th>
<th>$\Delta H^0$ (kJ/mol)</th>
<th>288 K</th>
<th>298 K</th>
<th>308 K</th>
<th>318 K</th>
<th>$\Delta S^0$(J/mol·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OFL</td>
<td>4.5</td>
<td>-11.96</td>
<td>-28.78</td>
<td>-28.06</td>
<td>-27.44</td>
<td>-26.49</td>
<td></td>
</tr>
<tr>
<td>TCS</td>
<td>15</td>
<td>3.41</td>
<td>22.97</td>
<td>22.56</td>
<td>22.25</td>
<td>21.82</td>
<td>23.79</td>
</tr>
</tbody>
</table>
suggested that the biomorphic HAP in this study has potential application for wastewater treatment.

REFERENCES


