Calcium-alginate/carbon nanotubes/TiO₂ composite beads for removal of bisphenol A

Maria R. Hartono, Ariel Kushmaro, Robert S. Marks and Xiaodong Chen

ABSTRACT

In this study, composite calcium-alginate/carbon nanotubes/TiO₂ beads were prepared and tested for their potential in the removal of bisphenol A (BPA) from aqueous solutions. The removal traits were inspected using a fixed-bed sorption column. By varying parameters such as bed height (15–20 cm), flow rate (2.0–6.0 mL.min⁻¹) and inlet BPA concentration (10–30 mg.L⁻¹) we assessed the removal capacity of these composites. The highest sorption capacity of 5.46 mg.g⁻¹ was achieved at 10 mg.L⁻¹ BPA concentration, 2.0 mL.min⁻¹ flow rate and 20 cm bed height at saturation. Adams-Bohart, Yoon-Nelson and Dose-Response isotherm models were applied to evaluate the performance of the column at different inlet concentrations. The experimental data satisfactorily fit the Dose-Response model with high correlation (r² > 0.97) across the breakthrough curve. Regeneration of the used adsorbent beads were performed by immersion in the desorption solvent followed by light irradiation. It was postulated that inclusion of TiO₂ facilitates the desorbed pollutant degradation from the used adsorbent beads.

Key words | adsorption, bisphenol A, calcium alginate, carbon nanotubes, packed-bed

INTRODUCTION

Rapid industrialization on a global scale has drawn attention to the need for developing new purification technologies for emerging pollutants. Therefore, the development of novel, non-toxic methodologies for purifying water is imperative. It is estimated that a new molecule is isolated or synthesized every 2.6 seconds (Bradley 2009). Bisphenol A (BPA) has been chosen as the model emerging organic pollutant in our study due to its endocrine disruptive nature and widespread use in consumer products (Liao & Kannan 2014).

Carbon nanomaterials are of great interest in filter technologies due to their superior adsorption performance and better re-usability in comparison to conventional activated carbon (Lu et al. 2007). Recent batch studies have reported higher adsorption capacity of BPA by multi-walled carbon nanotubes (MWCNTs) in comparison to single-walled carbon nanotubes (Dehghani et al. 2015). Despite their superior adsorption performance, their toxicity effects are still unclear (Bottini et al. 2006). Therefore, the entrapment of these nanomaterials is essential to limit their leakage into the environment and to enable further practical application as sorbent material in wastewater treatment.

Heterogenous photo catalysts such as titanium dioxide (TiO₂) are capable of oxidation and subsequently degrading organic compound through the photocatalytic oxidation process (Fujishima & Honda 1972). Complete photocatalytic oxidation results in the mineralization of the organic pollutant to CO₂, H₂O, NO₃⁻, PO₄³⁻ and halide ions (Carp et al. 2004). This mineralization capability indicated the possibility of its playing prominent roles in various applications, including removal of noxious organic pollutants in wastewater (Sekler et al. 2004). In wastewater treatment, titanium has been generally applied in suspension form. However, additional processing steps are often required to re-collect the titanium powder after each batch of photocatalytic oxidation reaction.

Myriad studies have focused on the immobilization of sorbent materials to prevent their release into the environment. One of the commonly used materials for this purpose is based on alginate. Alginate is a family of linear biopolymers comprised of 1,4-linked p-D-mannuronic and
a-L-guluronic acid residues (Martensen et al. 1989) which becomes cross-linked in the presence of divalent ions and results in the formation of hydrogels matrixes (Kierstan & Bucke 1977). Our current study focuses on the entrapment of MWCNTs and TiO₂ inside alginate beads to provide a composite sorbent. By integrating adsorption and photocatalytic oxidation in the beads, it will ease the recovery of the used sorbent and decrease facility footprint.

Most of the adsorption studies involving CNTs reported in the literature were performed in a batch system (Lin & Xing 2008). However, wastewater treatment plants operate in continuous mode with limited contact time to reach equilibrium in comparison to batch mode (Low & Lee 1991). It is therefore necessary to assess the capability of sorbent in continuous flow mode to assess their practical application. Although native form of CNTs has been employed recently in a fixed-bed study (Dichiara et al. 2015), studies involving the BPA removal in packed bed columns using hydrogel encapsulated CNTs are still limited (Fugetsu et al. 2004). Besides the increase in mechanical strength and stability achieved through immobilization, it enables to a certain degree to act as a barrier to prevent the leakage of CNTs.

The study is divided into two parts (Figure 1). In the first part, we applied the composite MWCNTs/TiO₂ alginate beads in a laboratory-scale fixed-bed column reactor for treatment of BPA-spiked feed in continuous flow. The effect of important parameters such as flow rates, initial feed concentrations and bed heights on BPA removal were evaluated. Further, dynamic sorption analysis using several sorption models is frequently used in the design of a fixed-bed system, namely Adams-Bohart (Bohart & Adams 1920), Yoon-Nelson (Yoon & Nelson 1984) and Dose-Response models (Yan et al. 2001; Calero et al. 2009; He et al. 2014). Studies were performed on the obtained experimental data to compare the correlation fit between them and the predicted dynamic behaviors of the column sorption. In the second part of this study, the simultaneous regeneration of the spent composite beads and photolytic BPA removal was assessed in a batch reactor.

**MATERIALS AND METHODS**

**Chemicals**

All chemicals used in this study were of analytical grade. BPA (239658), sodium alginate (B25266) and calcium chloride (CaCl₂, C1016) were obtained from Sigma.

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**Figure 1** | Simplified illustration on the pollutant sorption and subsequent regeneration of the spent composite carbon nanotube-TiO₂ hydrogel beads.
Commercial P25 aeroxide titanium dioxide powder was purchased from Aldrich (TiO$_2$, 718467) and multi-walled carbon nanotubes were obtained from Showa-Denko (MWCNTs, VGCF-X). A stock solution of 200 mg L$^{-1}$ of BPA in distilled water was prepared through autoclaving at 121 °C for 50 min. Subsequent dilutions were performed in distilled water.

**Preparation of the sorbent beads**

The preparation of composite carbon nanotube-alginate-TiO$_2$ beads was modified from our previous work (Hartono et al. 2015). In brief: 400 mg of P25 powder and 350 mg of MWCNTs were added into 50 mL of 2.5 wt% sodium alginate solution. The solution mixture was sonicated for 20 min and stirred overnight. The mixture was dripped using a syringe pump into stirred 0.5 M CaCl$_2$ solution for curing. The resulting beads were then washed twice with distilled water to remove the remaining CaCl$_2$ from the surface of the beads and stored in distilled water prior to application. The average diameter of the beads produced was 2.70 ± 0.15 mm with wet weight to dry weight conversion ratio of 0.093 g.g$^{-1}$.

**Column study and modeling**

The column system was constructed using a glass column of 2.5 cm internal diameter and 30 cm length (Biorad, Econo-column 7372532). Flow adapter (Biorad, 7380017) was attached at the bottom of the column and connected to peristaltic pump (Cole Parmer, Masterflex 07528-30). BPA solution of pre-specified concentration (10, 20 and 30 mg L$^{-1}$) was injected into the column at varying flow rates (2.0, 4.0 and 6.0 mL.min$^{-1}$) and bed heights (15, 20 cm) at ambient laboratory temperature (22 °C). The pH for 100 mg L$^{-1}$ BPA solution was estimated to be 6.11, as the pKa of BPA is within 9.6-10.2 (Staples et al. 1998), the pH of BPA solution used in this study was not adjusted. For bed height of 20 cm, porosity of packing was estimated at 0.39 with apparent volume of 98.1 mL and estimated pore volume of 38.2 mL. Thus for flow rate of 2 mL min$^{-1}$, the retention time in the column was around 19 min. Aliquots of 1.5 mL were collected from the outlet at predetermined time for analysis of residual BPA concentration. Operation of the column was stopped when the BPA concentration in the effluent reached saturation point, or at least 90% breakthrough time ($C_e/C_i = 0.90$).

The dynamic performance of the column is generally described using the following parameters:

\[
q_{total} = v \int_{t=0}^{t=ts} (C_i - C_t) \, dt
\]

\[
q_{e,ts} = \frac{q_{total}}{m_{ads}}
\]

\[
V = v \Delta t
\]

\[
m_{total} = V C_i
\]

\[
\text{Removal} \% = \frac{q_{total}}{m_{total}}
\]

where $q_{total}$ (mg) is the total amount of sorbate adsorbed, $m_{total}$ (mg) is the total amount of pollutant injected into the column, $q_{e,ts}$ (mg.g$^{-1}$) represents the sorption capacity of the column up to saturation or total amount of sorbate adsorbed by the column until the end of operation per unit weight of sorbent added, $v$ (L.h$^{-1}$) refers to the volumetric influent flow rate, $m_{ads}$ (g) is the dry weight of the sorbent added into the column while $C_i$ (mg.L$^{-1}$) and $C_t$ (mg.L$^{-1}$) represents the initial inlet concentration and outlet concentration after operation time $t$ (h), respectively, $V$ (L) represents the total volume of the effluent treated. In this study, the calculation of the area under the curve of concentration of BPA removed against time was performed based on trapezoidal rule aided by integration function in OriginPro 8.5 graphing software.

The concentration-time profile in continuous flow column sorption reactor is commonly represented as a breakthrough curve which is defined as the ratio of pollutant concentration at the outlet at time $t$ to inlet concentration ($C_t/C_i$) as a function of time or volume at specified bed height (Aksu & Gönen 2004). The operation time required until the outlet concentration reaches certain breakthrough concentration is defined as breakthrough time (Goel et al. 2005). It is inherently difficult to ascertain the breakthrough curve profile in continuous flow column reactor as the solute concentration dynamically changes across the bed. Moreover, the shape of the breakthrough curve is affected by transport mechanism within the adsorbent and the column (Vázquez et al. 2006). It is, therefore, favorable to predict the shape of the curve under defined operating conditions. To obtain the breakthrough time, mathematical dynamic sorption models were generated in the past to
lesser the amount of time for experiments and repetitions. These models were built upon the probable assumption on the chief mechanism governing the sorption process such as mass transfer, diffusion or surface reaction. Among the available models, the following three models are selected to predict the column performance for BPA removal in our study:

Adams-Bohart model

Adams-Bohart model (Bohart & Adams 1920) has been used in many column sorption studies and generally applicable to interpret the initial part (10–50%) of the breakthrough curve in the presence of one contaminant (Sarin et al. 2006). In this study, the model is applied to predict the BPA removal using experimental data of up to 50% breakthrough time ($C_t/C_i = 0.5$). The formula can be expressed as follows:

$$
\frac{C_t}{C_i} = \frac{e^{k_{AB}C_i t}}{e^{\frac{k_{AB}N_o Z}{u}} - 1 + e^{k_{AB}C_i t}}
$$

(6)

where $k_{AB}$ (L·mg⁻¹·h⁻¹) represents kinetic coefficient, $N_o$ (mg·L⁻¹) is the volumetric sorption capacity, $u$ (cm·min⁻¹) is the linear influent flow rate which can be obtained by dividing volumetric flow rate with the cross section area of the column and $Z$ is the bed height of the column.

Yoon-Nelson model

Another frequently used model in the fixed-bed sorption system is Yoon-Nelson model (Yoon & Nelson 1984) which was originally developed to describe the adsorption of gases on solid sorbents. The equation is described as follows:

$$
\frac{C_t}{C_i} = \frac{1}{1 + e^{k_{YN} \tau}}
$$

(7)

where $k_{YN}$ (h⁻¹) is the Yoon-Nelson rate constant and $\tau$ is the total operation time at $C_t = 0.5 C_i$.

Dose-Response model

Originally used in pharmacological study, this model has been applied in a bio-sorption column study for the removal of heavy metals with good correlation irrespective of the length of operational time (Calero et al. 2009; He et al. 2014). The derived model is represented as follows:

$$
\frac{C_t}{C_i} = 1 - \frac{1}{1 + (\frac{vt}{V_{50\%}})^a}
$$

(8)

where $a$ is the constant of the dose-response model, and $V_{50\%}$ (L) is the total volume of treated effluent when $C_t = 0.5 C_i$.

Instead of using linear interpolation method, here we are using Microsoft Office Excel 2007 Solver Add-ins function to predict the value of important parameters providing highest correlation with the experimental data.

Photolytic BPA degradation in desorption solvent

Sorbent of 2.0 g·L⁻¹ dosages were added into BPA solutions of known concentration in glass container and agitated at 120 rpm in ambient condition. Aliquots of the solution were taken to monitor the putative removal of BPA from the aqueous solution over time. BPA adsorption capacity in batch study was calculated as follows:

$$
q_{e,batch} = \frac{C_i - C_e}{m} \times V
$$

where $q_{e,batch}$ (mg·g⁻¹) represents the adsorption capacity of the composite beads sorbent at equilibrium; $C_e$ (mg·L⁻¹) represents concentration of BPA in the solution at equilibrium and $V$ (L) is the volume of the solution in the batch experiment. To ensure that the adsorption equilibrium was reached, the beads were immersed in the BPA solutions for at least 8 h. Desorption was conducted by immersing the exhausted beads in ethanol for at least 5 h to allow optimum BPA desorption from the beads. The percentage of BPA recovered from the spent beads after solvent regeneration was estimated based on the ratio between total mass of BPA desorbed in the ethanol and mass of BPA adsorbed by the spent beads. Irradiations were conducted afterwards using Xenon light source (Asahi Spectra, Horiba MAX-303) with above 350 nm long-pass filter (Asahi Spectra, ZUL0350). The flow of the adsorption-desorption-irradiation experiment is illustrated in Figure 2.

Characterizations

BPA concentrations were estimated based on the absorbance value measured using either a UV-Vis spectrophotometer (Shimadzu UV3600) at the wavelength of 276 nm or high performance liquid chromatography (HPLC, Agilent 1200). The HPLC was fitted with BC Eclipse plus column (C18,
4.6 × 150 mm, 3.5 μm), 50% acetonitrile was used as mobile phase at flow rate of 1 mL.min⁻¹. 50 μL from each sample was injected to the column for analysis with UV detector set at 280 nm and monitoring time set at 5.0 min for each analysis. BPA was eluted at around 3.8 min mark. For HPLC, all samples and standards were prepared by filtration through 0.2 μm regenerated cellulose syringe filter prior to analysis. HPLC was used in analysis of effluent from column reactor at the beginning of column operation and regeneration experiment due to their superior detection limit. The calibration curve was prepared for both methods against their known standard concentrations.

RESULTS AND DISCUSSION

Effect of flow rate

The effect of flow rate on the removal of BPA in a fixed bed sorption column was studied by subjecting the column with the influent feed flow of 2.0–6.0 mL.min⁻¹ (0.12–0.36 L.h⁻¹) at constant BPA concentration of 10 mg.L⁻¹ and bed height of 20 cm. It was apparent that the BPA sorption was significantly affected by the flow rate. As shown in Figure 3(a), 50% breakthrough times were estimated at 8 h, 1 h and less than 0.5 h for 2.0, 4.0 and 6.0 mL.min⁻¹ flow rates, respectively. In accordance, the exhaustion of the column occurred faster at higher flow rate with 90% breakthrough times estimated at 90 h, 22 h and 6 h for 2.0, 4.0 and 6.0 mL.min⁻¹ flow rates. The sorption capacity of the composite beads decreased from 5.46 mg.g⁻¹ at 2.0 mL.min⁻¹ flow rate to 2.91 mg.g⁻¹ and 2.04 mg.g⁻¹ at 4.0 and 6.0 mL.min⁻¹ flow rates, respectively. It is evident that saturation of the column occurred more rapidly with higher flow rate. At higher flow rate, the rate of mass transfer increases with shorter contact time, leading to faster saturation of the column (Ko et al. 2000) and decreased sorption capacity. Longer contact time with the sorbent is achieved at lower flow rate facilitating higher removal of BPA. The lowest flow rate of 2.0 mL.min⁻¹ was therefore chosen for the next experiments.

Effect of bed height

The influence of bed height or the amount of composite sorbent used on the BPA removal overtime was tested at the heights of 15 cm (5.65 g dry weight) and 20 cm (7.46 g dry weight) at initial influent BPA concentration of 10 mg.L⁻¹ under constant feed flow rate of 2.0 mL.min⁻¹ (0.12 L.h⁻¹) and the results are shown on Figure 3(b). The breakthrough curves suggested that the shorter bed height resulted in reduced BPA removal and rapid exhaustion of column due to shorter contact time with the composite sorbent. Increase in the dosage of the composite beads with higher bed depth resulted in the increase of surface area available as binding sites for attachment of the pollutant (Ahmad & Hameed 2010). In our study, the 90% breakthrough time for 15 cm bed height was reached after only 7.5 h of column operation time in comparison to 90 h for 20 cm bed height. The 90% breakthrough time for 15 cm column was similar to those conducted at 20 cm bed height and higher flow rate. Based on the experimental results, it was apparent that lower feed flow rate and higher bed height are favorable to extend the operation time of the column.

Effect of BPA concentration

The influence of initial BPA concentrations on the performance of the column was assessed by varying inlet concentration from 10 to 30 mg.L⁻¹ at fixed bed height of 20 cm and flow rate of 2.0 mL.min⁻¹. The experimental setting used in this study and calculated sorption parameters are listed in Tables 1 and 2.

For each concentration, the column was run until it reached saturation. It should be noted that the percentage of BPA removal at the start of the column at 10 mg.L⁻¹ initial BPA concentration was only 98% (Cᵢ/Cᵣ = 0.02) which decreased to 90% (Cᵢ/Cᵣ = 0.1) after 1 h of operation. As shown on Figure 3(c), the 50% breakthrough time for 10 mg.L⁻¹, 20 mg.L⁻¹ and 30 mg.L⁻¹ inlet BPA concentrations according to the experimental observations was estimated to be 8 h, 7 h and 5 h, respectively. The 90% breakthrough time was estimated at 90 h, 50 h and 33 h for 10 mg.L⁻¹, 20 mg.L⁻¹ and 30 mg.L⁻¹ inlet BPA concentrations. The adsorption capacity was estimated at 5.46 mg.g⁻¹, 5.20 mg.g⁻¹ and 4.74 mg.g⁻¹ for 10 mg.L⁻¹, 20 mg.L⁻¹ and 30 mg.L⁻¹ inlet BPA
concentrations with similar total adsorbed BPA, \( q_{\text{total}} \), across the different inlet concentrations tested. A steeper slope of breakthrough curve was evident with the increase in inlet concentration, inferring that the concentration gradient affect the saturation time of the column. The decline in the breakthrough time, adsorption capacity and BPA removal percentage of the column may be attributed to the increased diffusion rate due to the enhanced concentration gradient introduced by higher inlet concentration which, subsequently, resulted in the rapid saturation of the available binding sites (Jain et al. 2014). Similar results were observed in another fixed-bed system (Ahmad & Hameed 2010). The fixed bed column adsorption capacity obtained in this study was higher in comparison to a previous fixed-bed study for BPA removal using modified sericite (Thanhmingliana et al. 2017). However, the adsorption capacity in the continuous flow column reactor was lower than its adsorption capacity in a batch reactor (supporting information, available with the online version of this paper). This is expected due to insufficient contact time to reach equilibrium (Hartono et al. 2015).

### Table 1 | Experimental setting in the breakthrough study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column diameter</td>
<td>0.025 m</td>
</tr>
<tr>
<td>Column length</td>
<td>0.20 m</td>
</tr>
<tr>
<td>Adsorbent weight (dry)</td>
<td>7.45 g</td>
</tr>
<tr>
<td>Average beads diameter</td>
<td>( 2.7 \times 10^{-3} ) m</td>
</tr>
<tr>
<td>Inlet flow rate</td>
<td>0.12 L.h(^{-1}) (2.0 mL.min(^{-1}))</td>
</tr>
<tr>
<td>Temperature</td>
<td>ambient (22 °C)</td>
</tr>
</tbody>
</table>

Figure 3 | BPA sorption curves by the column subjected to different (a) flow rates, (b) bed depths, (c) inlet BPA concentrations and (d) predicted concentration-time profile based on sorption models for 10 mg.L\(^{-1}\) inlet BPA concentration.
The Adams-Bohart, Yoon-Nelson and Dose-Response models were then used to predict the concentration-time profile based on the sorption data obtained at 2.0 mL min⁻¹ flow rate and 20 cm bed height at different inlet BPA concentrations.

Adams-Bohart is applicable to model the initial stage of the breakthrough curve when the pollutant concentration in the effluent is less than 0.5 Cᵢ (Sarin et al. 2006). Therefore, in this study, the model is applied to an experimental data set for the initial portion of the breakthrough curve. As shown on Table 2, the Adams-Bohart model could predict with good fit (r² > 0.92) the initial part of the curves under different inlet BPA concentrations. The volumetric sorption capacity Nᵣ increased, from 95.6 (10 mg.L⁻¹ BPA) to 228.1 (30 mg.L⁻¹ BPA), whilst the kinetics constant decreased from 0.026 L.h⁻¹.mg⁻¹ to 0.007 L.h⁻¹.mg⁻¹ with the increase in inlet concentration. This trend is similar with other reported sorption studies involving different adsorption-column systems and inferred that external mass transfer in the initial portion of the curve dominated the system kinetic (Aksu & Gönen 2004). When the whole range of the breakthrough curves was used for modeling (t = 0 until t = tₛ), however, both Adams-Bohart and Yoon-Nelson produced similar breakthrough curves. Indeed, the mathematical expression of the Yoon-Nelson model is equivalent to that of the Adams-Bohart model with Kᵣᵣ ≅ Kᵣ知名度 Cᵢ (supporting information).

The values for rate constant kᵣᵣ and 50% breakthrough time τ obtained from the Yoon-Nelson model are presented in Table 2. Based on the model, it was predicted that the increase in inlet concentrations resulted in the increased rate constant kᵣᵣ and decreased of 50% breakthrough time, which indicated a more rapid saturation of the column with the increase in inlet concentrations. The τ values obtained from the Yoon-Nelson model differed from the experimental observation, with considerable discrepancy predicted for 10 mg.L⁻¹ BPA concentration. As shown in Figure 3(d), Yoon-Nelson model could not satisfactorily reproduce the experimental data at initial operation time. However, the τ values at 20 and 30 mg.L⁻¹ BPA concentrations are similar to experimental observations. As shown on Figure 3(d) and Table 2, the breakthrough curve of the Dose-Response model can be utilized to predict the removal profile of BPA with relatively good correlation (r² > 0.97) with the experimental data. The calculated value of the sorption capacity based on a predicted breakthrough curve produced by a Dose-Response model, qₑₜₛ cal, is similar to the sorption capacity calculated from the experimental data and constant irrespective of the inlet BPA concentrations tested. Similar findings on the relatively good-fit of the Dose-Response model in reproducing a breakthrough curve in a fixed-bed column study, have been reported by other researchers (Calero et al. 2009; He et al. 2014). The correlation coefficients values (r²) obtained from Yoon-Nelson and the Dose-Response models can be considered good-fit (r² > 0.92) to the experimental data set under different inlet BPA concentrations with the best fit produced by Dose-Response model. The Adams-Bohart model is applicable to predict the initial stage of the breakthrough curve of up to 50% breakthrough time.

### Photolytic degradation

The capability of BPA degradation in the desorption solution was tested in a batch study due to the ease of quantification of the amount of BPA sorbed at equilibrium. Figure 4(a) shows the full cycle of adsorption-desorption-photolytic removal of BPA. The initial BPA solution in the desorption flow rate and 20 cm bed height at different inlet BPA concentrations. This resulted in up to 90% BPA recovery. Subsequent

### Table 2 | Parameters of sorption models at different initial BPA concentrations

<table>
<thead>
<tr>
<th>Parameters</th>
<th>BPA concentrations (mg.L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mₑₜₛ (mg)</td>
<td>154 230 205</td>
</tr>
<tr>
<td>qₑₜₛ/removal (%)</td>
<td>40.8/26.5%</td>
</tr>
<tr>
<td>qₑₜₛ (mg.g⁻¹)</td>
<td>5.46 5.20 4.74</td>
</tr>
<tr>
<td>Adams-Bohart model (t₀ₜ₀.₉₅Cᵢ)</td>
<td>Kₐᵣ (L.h⁻¹.mg⁻¹)</td>
</tr>
<tr>
<td>Nᵣ (mg.L⁻¹)</td>
<td>95.6 196.84 228.13</td>
</tr>
<tr>
<td>τ</td>
<td>0.92 0.99 0.98</td>
</tr>
<tr>
<td>Yoon-Nelson model (t₀ₜ₀.₉₅Cᵢ)</td>
<td>kᵣᵣ (h⁻¹)</td>
</tr>
<tr>
<td>τ</td>
<td>25.3 10.5 5.47</td>
</tr>
<tr>
<td>qₑₜₛ (mg)</td>
<td>40.7 37.4 30.1</td>
</tr>
<tr>
<td>r²</td>
<td>0.92 0.97 0.99</td>
</tr>
<tr>
<td>Dose-Response model (t₀ₜ₀.₉₅Cᵢ)</td>
<td>a</td>
</tr>
<tr>
<td>Vₑₜₙ₀% (L)</td>
<td>1.28 0.78 0.52</td>
</tr>
<tr>
<td>qₑₜₛ (mg.g⁻¹)</td>
<td>40.9 40.9 40.9</td>
</tr>
<tr>
<td>τ</td>
<td>4.58 5.48 5.48</td>
</tr>
<tr>
<td>r²</td>
<td>0.99 0.97 0.99</td>
</tr>
</tbody>
</table>

The used beads were then immersed in ethanol solution.

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Irradiation of the solution in the presence of the beads eliminated the BPA remaining after 1.5 h. It is postulated that the inclusion of TiO₂ into the composite beads assisted subsequent BPA degradation through light irradiation of the spent beads in the desorption solution. The re-usability of the beads after five cycles of adsorption-desorption-irradiation is shown in Figure 4(b). Slight variability in adsorption capacity is apparent, but not significant, which concedes the potential for the composite beads to be used in multiple regeneration cycles.

It is worth note that the percentage of BPA removal at the start of the column with a 2.0 mL min⁻¹ flow rate at a 10 mg L⁻¹ initial BPA concentration was only 98% and decreased to 90% after 1 h of operation. Considering that there already exist different types of activated carbon and their derivatives being used for sorption, there are few caveats that can be improved in order to make use of fast adsorption kinetics that MWCNTs possessed in its powder form, while justifying its cost. Higher pollutant removal may be attained by increasing the percentage of MWCNTs embedded in the alginate beads. Attachment of a functional group onto MWCNTs may help improve their dispersion. Alternatively, other porous encapsulation matrix can be pursued to enable entrapment of MWCNTs at a high percentage without sacrificing their structural integrity. Although our result is preliminary, it opens up potential research inquiries which hopefully will surmount our current limitation towards an application of encapsulated nanomaterials for the removal of aromatic organic pollutants.

**CONCLUSION**

In this study, composite carbon nanotube-alginate-TiO₂ hydrogel beads were fabricated and tested for sorption of BPA in a fixed-bed column reactor. BPA removal is affected by the feed flow rate, bed height and initial inlet concentrations. The breakthrough time was extended with higher bed height, lower flow rate and lower inlet pollutant concentration. The sorption capacity of the composite sorbent at 10 mg L⁻¹ inlet BPA concentration, 2.0 mL min⁻¹ flow rate and 20 cm bed height was 5.46 mg g⁻¹. The modeling study shows that the experimental breakthrough curve could be depicted with satisfactory correlation using the Dose-Response model. Photolytic oxidation of BPA desorbed from the beads is possible under irradiation. Thus, the re-generation of the spent adsorbent beads and eventual photolytic degradation of BPA can be achieved simultaneously. The developed composite adsorbent may be beneficial for in-situ remediation where a wastewater treatment facility is not readily available. The polluted water could be injected into the column in-situ and the spent beads are capable of being re-generated, with simultaneous BPA degradation with light irradiation.

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